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Fundamentals, Processes, and Applications

Edited by

Rafael Luque and James G. Speight

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Gasification and synthetic liquid fuel production: an overview

1

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1.1 Introduction

Gasification is a process that converts organic (carbonaceous) feedstocks into carbon monoxide, carbon dioxide, and hydrogen by reacting the feedstock at high temperatures (>700 °C, 1290 °F), without combustion, with a controlled amount of oxygen and/or steam (Lee, Speight, & Loyalka, 2007; Speight, 2008, 2013). The resulting gas mixture (*synthesis gas*, or *syngas*) is itself a fuel. The power derived from carbonaceous feedstocks and gasification, followed by the combustion of the product gas (es), is considered to be a source of renewable energy if derived gaseous products are generated from a source (e.g., biomass) other than a fossil fuel (Speight, 2008).

The advantage of gasification is that the use of synthesis gas (syngas) is potentially more efficient as compared to direct combustion of the original fuel because it can be (1) combusted at higher temperatures, (2) used in fuel cells, (3) used to produce methanol and hydrogen, and (4) converted via the Fischer–Tropsch (FT) process into a range of synthesis liquid fuels suitable for use in gasoline engines or diesel engines. The gasification process can also utilize carbonaceous feedstocks that would otherwise have been discarded (e.g., biodegradable waste).

In addition, the high-temperature process causes corrosive ash elements, including metal chlorides and potassium salts, that allow clean gas production from otherwise problematic fuels.

Coal has been the primary feedstock for gasification units for many decades. However, due to the concern of environmental pollutants and the potential shortage of coal in some areas (except the United States), there is a movement to use materials other than coal feedstocks for gasification processes. Nevertheless, coal still prevails and will continue to prevail for at least several decades into the future, if not well into the next century (Speight, 2013).

Coal gasification plants are cleaner with respect to standard pulverized coal combustion facilities, producing fewer sulfur and nitrogen by-products, which contribute to smog and acid rain. For this reason, gasification is an appealing way to utilize relatively inexpensive and expansive coal reserves, while reducing the environmental impact. Indeed, the increasing mounting interest in coal gasification technology reflects a convergence of two changes in the electricity-generation marketplace: (1) the maturity of gasification technology and (2) the extremely low emissions from integrated gasification combined cycle (IGCC) plants, especially air emissions, and the potential for lower cost control of greenhouse gases than other coal-based systems.

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Fluctuations in the costs associated with natural gas-based power, which is viewed as a major competitor to coal-based power, can also play a role.

Furthermore, gasification permits the utilization of various feedstocks (coal, biomass, petroleum residues, and other carbonaceous wastes) to their fullest potential. Thus, power developers would be well advised to consider gasification as a means of converting coal to gas.

Liquid fuels, including gasoline, diesel, naphtha, and jet fuel, are usually processed via the refining of crude oil (Speight, 2014). Due to the direct distillation, crude oil is the best-suited raw material for liquid fuel production. However, with fluctuating and rising prices of petroleum, coal-to-liquids and biomass-to-liquids processes are starting to be considered as alternative routes for liquid fuels production. Both feedstocks are converted to syngas (a mixture of carbon monoxide and hydrogen), which is subsequently converted into a mixture of liquid products by FT processes. The liquid fuel obtained after FT synthesis is eventually upgraded using known petroleum refinery technologies to produce gasoline, naphtha, diesel fuel, and jet fuel (Chadeesingh, 2011; Dry, 1976; Speight, 2014).

1.2 Gasification processes

Gasification processes are segregated according to bed types, which differ in their ability to accept (and use) caking coals. They are generally divided into four categories based on reactor (bed) configuration: (1) fixed bed, (2) fluidized bed, (3) entrained bed, and (4) molten salt.

In a fixed-bed process, the coal is supported by a grate. Combustion gases (steam, air, oxygen, etc.) pass through the supported coal where the produced hot gases then exit from the top of the reactor. Heat is supplied internally or from an outside source, but caking coals cannot be used in an unmodified fixed-bed reactor.

The fluidized-bed system uses finely sized coal particles and the bed exhibits liquid-like characteristics when a gas flows upward through the bed. Gas flowing through the coal produces turbulent lifting and separation of particles, which results in an expanded bed having a greater coal surface area to promote the chemical reaction. However, such systems have a limited ability to handle caking coals.

An entrained-bed system uses finely sized coal particles blown into the gas steam prior to entry into the reactor, and combustion occurs with the coal particles suspended in the gas phase. The entrained system is suitable for both caking and noncaking coals.

The fourth and final category of the gasification process is the molten salt system. It employs a bath of molten salt to convert coal (Cover, Schreiner, & Skaperdas, 1973; Howard-Smith & Werner, 1976; Speight, 2013, and references cited therein).

The aim of underground (or *in situ*) gasification of coal is the conversion into combustible gases by combustion of a coal seam in the presence of air and oxygen, or oxygen and steam. Thus, seams that were once considered to be inaccessible, unworkable, or uneconomical to mine could be put to use. In addition, strip mining and the accompanying environmental impacts – the problems of spoil banks, acid mine drainage, and the problems associated with use of high-ash coal – are minimized or even eliminated.

The principles of underground gasification are very similar to those involved in the above-ground gasification of coal. The concept involves the drilling and subsequent linking of two boreholes so that gas will pass between the two (King & Magee, 1979). Combustion is then initiated at the bottom of one borehole (injection well) and is maintained by the continuous injection of air. In the initial reaction zone (combustion zone), carbon dioxide is generated by the reaction of oxygen (air) with the coal:

$$[C]_{coal} + O_2 \rightarrow CO_2$$

The carbon dioxide reacts with coal (partially devolatilized) further along the seam (reduction zone) to produce carbon monoxide:

$$[C]_{coal} + CO_2 \rightarrow 2CO$$

In addition, at the high temperatures that can frequently occur, moisture injected with oxygen or even moisture inherent in the seam may also react with the coal to produce carbon monoxide and hydrogen:

$$[C]_{coal} + H_2O \rightarrow CO + H_2$$

The gas product varies in character and composition but usually falls into the low-heat (low Btu) category ranging from 125 to 175 Btu/ft^3 (King & Magee, 1979).

1.3 Gasification feedstocks

Gasification processes can accept a variety of feedstocks but the reactor must be selected on the basis of feedstock properties and behavior in the process.

1.3.1 Coal

Coal is a fossil fuel formed in swamp ecosystems where plant remains were saved from oxidization and biodegradation by water and mud. Coal is a combustible organic sedimentary rock (composed primarily of carbon, hydrogen, and oxygen, as well as other minor elements including sulfur) formed from ancient vegetation and consolidated between other rock strata to form coal seams. The harder forms can be regarded as organic metamorphic rocks (e.g., anthracite coal) because of a higher degree of maturation.

Coal is the largest single source of fuel for generating electricity worldwide, as well as the largest source of carbon dioxide emissions, which have been implicated as the primary cause of global warming. Coal is found as successive layers, or seams, sandwiched between strata of sandstone and shale and extracted from the ground by coal mining – either underground coal seams (underground mining) or by open-pit mining (surface mining).

There is an adequate supply of coal; at current rates of recovery and consumption, the world global coal reserves have been variously estimated to have a reserves/production ratio of at least 155 years. However, as with all estimates of resource longevity, coal longevity is subject to the assumed rate of consumption remaining at the current rate of consumption and, moreover, to technological developments that dictate the rate at which the coal can be mined. But most importantly, coal is a fossil fuel and an *unclean* energy source that will only add to global warming. In fact, the next time electricity is advertised as a clean energy source, consider the means by which the majority of electricity is produced – almost 50% of the electricity generated in the United States derives from coal (EIA, 2007; Speight, 2013).

There are different forms or *types* of coal (Speight, 2013). Variations in the nature of the source material, as well as local or regional variations in the coalification processes cause the vegetal matter to evolve differently. Various classification systems thus exist to define the different types of coal. The coal precursors are transformed over time (as geological processes increase their effect over time) into:

1. Lignite – Also referred to as brown coal, this is the lowest rank of coal and used almost exclusively as fuel for steam-electric power generation. Jet is a compact form of lignite that is sometimes polished and has been used as an ornamental stone since the Iron Age.
2. Sub-bituminous coal – The properties of this type of coal range from those of lignite to those of bituminous coal and is used primarily as fuel for steam-electric power generation.
3. Bituminous coal – This dense coal, usually black but sometimes dark brown, often with well-defined bands of brittle and dull material, is used primarily as fuel in steam-electric power generation, with substantial quantities also used for heat and power applications in manufacturing and to make coke.
4. Anthracite – This harder, glossy, black coal is used primarily for residential and commercial space heating; it is the highest-ranking coal.

Chemically, coal is a hydrogen-deficient hydrocarbon with an atomic hydrogen-to-carbon ratio near 0.8, as compared to petroleum hydrocarbons, which have an atomic hydrogen-to-carbon ratio approximately equal to two, and methane (CH_4) that has an atomic carbon-to-hydrogen ratio equal to four. For this reason, any process used to convert coal to alternative fuels must add hydrogen or redistribute the hydrogen in the original coal to generate hydrogen-rich products and coke (Speight, 2013).

The chemical composition of the coal is defined in terms of its proximate and ultimate (elemental) analyses (Speight, 2013). The parameters of proximate analysis are moisture, volatile matter, ash, and fixed carbon. Elemental or ultimate analysis encompasses the quantitative determination of carbon, hydrogen, nitrogen, sulfur, and oxygen within the coal. Additionally, specific physical and mechanical properties of coal and particular carbonization properties are also determined.

Carbon monoxide and hydrogen are produced by the gasification of coal in which a mixture of gases is produced. In addition to carbon monoxide and hydrogen, methane and other hydrocarbons are also produced depending on conditions. Gasification may be accomplished either *in situ* or in processing plants. *In situ* gasification is accomplished by controlled, incomplete burning of a coal bed underground while adding air and steam. The gases are withdrawn and may be burned to produce heat and generate electricity, or are utilized as syngas in indirect liquefaction as well as for the production of chemicals.

Producing diesel and other fuels from coal can be performed through the conversion of coal to syngas, a combination of carbon monoxide, hydrogen, carbon dioxide, and methane. Syngas is subsequently reacted through FT synthesis processes to produce hydrocarbons that can be refined into liquid fuels. By increasing the quantity of high-quality fuels from coal (while reducing costs), research into this process could help mitigate the dependence on ever-increasingly expensive and depleting stocks of petroleum.

Although coal is an abundant natural resource, its combustion or gasification produces both toxic pollutants and greenhouse gases. By developing adsorbents to capture the pollutants (mercury, sulfur, arsenic, and other harmful gases), scientists are striving not only to reduce the quantity of emitted gases but also to maximize the thermal efficiency of the clean-up.

Gasification thus offers one of the most clean and versatile ways to convert the energy contained in coal into electricity, hydrogen, and other sources of power. Turning coal into syngas isn't a new concept; in fact, the basic technology dates back to World War II.

1.3.2 Biomass

Biomass can be considered as any renewable feedstock that, in principle, is *carbon neutral*. (While the plant is growing, it uses the sun's energy to absorb the same amount of carbon from the atmosphere as it releases into the atmosphere.)

Raw materials that can be used to produce biomass-derived fuels are widely available; they come from a large number of different sources and in numerous forms (Rajvanshi, 1986). The basic sources of biomass include (1) wood, including bark, logs, sawdust, wood chips, wood pellets, and briquettes; (2) high-yield energy crops, such as wheat, grown specifically for energy applications; (3) agricultural crops and residues (e.g., straw); and (4) industrial waste, such as wood pulp or paper pulp. For processing, a simple form of biomass, such as untreated and unfinished wood, may be converted into a number of physical forms, including pellets and wood chips, for use in biomass boilers and stoves.

Biomass includes a wide range of materials that produce a variety of products that are dependent on the feedstock (Balat, 2011; Demirbaş, 2011; Ramroop Singh, 2011; Speight, 2011a). In addition, the heat content of the different types of biomass widely varies and has to be taken into consideration when designing any conversion process (Jenkins & Ebeling, 1985).

Thermal conversion processes use heat as the dominant mechanism to convert biomass into another chemical form. The basic alternatives of combustion – torrefaction, pyrolysis, and gasification – are separated principally by the extent to which the chemical reactions involved are allowed to proceed (mainly controlled by the availability of oxygen and conversion temperature) (Speight, 2011a).

Energy created by burning biomass (fuelwood), also known as dendrothermal energy, is particularly suited for countries where fuelwood grows more rapidly (e.g., tropical countries). A number of other less common, more experimental or proprietary thermal processes may offer benefits, including hydrothermal upgrading and hydroprocessing. Some have been developed to be compatible with high-moisture content biomass (e.g., aqueous slurries) and allow them to be converted into more convenient forms.

Some of the applications of thermal conversion are combined heat and power and cofiring. In a typical dedicated biomass power plant, efficiencies range from 7% to 27%. In contrast, biomass cofiring with coal typically occurs at efficiencies close to those of coal combustors (30–40%) (Baxter, 2005; Liu, Larson, Williams, Kreutz, & Guo, 2011).

Many forms of biomass contain a high percentage of moisture (along with carbohydrates and sugars) and mineral constituents, both of which can influence the economics and viability of a gasification process. The presence of high levels of moisture in biomass reduces the temperature inside the gasifier, which then reduces the efficiency of the gasifier. Many biomass gasification technologies therefore require dried biomass to reduce the moisture content prior to feeding into the gasifier. In addition, biomass can come in a range of sizes. In many biomass gasification systems, biomass must be processed to a uniform size or shape to be fed into the gasifier at a consistent rate as well as to maximize gasification efficiency.

Biomass such as wood pellets, yard and crop waste, and “energy crops,” including switchgrass and waste from pulp and paper mills, can also be employed to produce bioethanol and synthetic diesel. Biomass is first gasified to produce syngas and then subsequently converted via catalytic processes to the aforementioned downstream products. Biomass can also be used to produce electricity – either blended with traditional feedstocks, such as coal, or by itself.

Most biomass gasification systems use air instead of oxygen for gasification reactions (which is typically used in large-scale industrial and power gasification plants). Gasifiers that use oxygen require an air separation unit (ASU) to provide the gaseous/liquid oxygen; this is usually not cost-effective at the smaller scales used in biomass gasification plants. Air-blown gasifiers utilize oxygen from air for gasification processes.

In general, biomass gasification plants are comparatively smaller than those of typical coal or petroleum coke plants used in the power, chemical, fertilizer, and refining industries. As such, they are less expensive to build and have a smaller environmental footprint. Whereas a large industrial gasification plant may take up 150 acres of land and process 2500–15,000 tons per day of feedstock (e.g., coal or petroleum coke), smaller biomass plants typically process 25–200 tons of feedstock per day and take up less than 10 acres.

Finally, although biomass may seem to some observers to be the answer to the global climate change issue, advantages and disadvantages of biomass as feedstock must be considered carefully:

> *Advantages*: (1) theoretically inexhaustible fuel source; (2) minimal environmental impact when direct combustion of plant mass is not used to generate energy (i.e., fermentation, pyrolysis, etc., are used instead); (3) alcohols and other fuels produced by biomass are efficient, viable, and relatively clean-burning; and (4) available on a worldwide basis.
>
> *Disadvantages*: (1) could contribute a great deal to global climate change and particulate pollution if combusted directly; (2) remains an expensive source of energy, both in terms of producing biomass and the technological conversion to alcohols or other fuels; and (3) life cycle assessments should be taken into account to address energy inputs and outputs but there is most likely a net loss of energy when operated on a small scale (as energy must be put in to grow the plant mass).

Also, while taking the issues of global climate change into account, it must be remembered that the Earth is in an interglacial period when warming will take place. The extent of this warming is not known – no one was around to measure the temperature change in the last interglacial period – and by the same token the contribution of anthropological sources to global climate change cannot be measure accurately.

1.3.3 Petroleum residues

Gasification is the only technology that makes possible a zero residue target for refineries. All other conversion technologies (including thermal cracking, catalytic cracking, cooking, deasphalting, hydroprocessing, etc.) can only reduce the bottom volume, with the complication that the residue qualities generally get worse with the degree of conversion (Speight, 2014).

The flexibility of gasification allows the handling of any type of refinery residue, including petroleum coke, tank bottoms, and refinery sludge. Gasification makes available a range of value-added products, including electricity, steam, hydrogen, and various chemicals based on syngas chemistry: methanol, ammonia, MTBE, TAME, acetic acid, and formaldehyde (Speight, 2008; Chapter 7). The environmental performance of gasification is unmatched. No other technology processing low-value refinery residues can come close to the emission levels achievable with gasification (Speight, 2014).

Gasification is also a method for converting petroleum coke and other refinery nonvolatile waste streams (often referred to as *refinery residuals* and include but are not limited to atmospheric residuum, vacuum residuum, visbreaker tar, and deasphalter pitch) into power, steam, and hydrogen for use in the production of cleaner transportation fuels. The main requirement for a gasification feedstock (including coal and biomass) is that it contains both hydrogen and carbon (Table 1.1).

The typical gasification system incorporated into a refinery consists of several process units, including feed preparation, the gasifier itself, an ASU, syngas cleanup, sulfur recovery unit (SRU), and downstream process options depending on target

Table 1.1 Types of refinery feedstocks available for gasification on-site

Ultimate analysis	Units	Vacuum Residue	Visbreaker tar	Asphalt	Petcoke
C	w/w	84.9%	86.1%	85.1%	88.6%
H	w/w	10.4%	10.4%	9.1%	2.8%
N[a]	w/w	0.5%	0.6%	0.7%	1.1%
S[a]	w/w	4.2%	2.4%	5.1%	7.3%
O	w/w		0.5%		0.0%
Ash	w/w	0.0%		0.1%	0.2%
Total	w/w	100.0%	100.0%	100.0%	100.0%
H_2/C ratio	mol/mol	0.727	0.720	0.640	0.188
Density specific	60°/60°	1.028	1.008	1.070	0.863
API gravity	°API	6.2	8.88	0.8	–
Heating values					
HHV (dry)	M Btu/lb	17.72	18.6	17.28	14.85
LHV (dry)	M Btu/lb	16.77	17.6	16.45	14.48

http://www.netl.doe.gov/technologies/coalpower/gasification/gasifipedia/7-advantages/7-3-4_refinery.html.

[a] Nitrogen and sulfur contents vary widely.

Source: National Energy Technology Laboratory, United States Department of Energy, Washington, DC.

products. Figure 1.1 shows a typical arrangement of these process units in addition to the optional downstream processes for producing power through cogeneration, hydrogen, FT, or methanol synthesis.

The benefits of the addition of a gasification system in a refinery to process petroleum coke or other residuals include (1) production of power, steam, oxygen, and nitrogen for refinery use or sale; (2) the source of syngas for hydrogen to be used in refinery operations as well as for the production of light refinery products through FT synthesis; (3) increased efficiency of power generation, improved air emissions, and reduced waste stream versus combustion of petroleum coke or residues or incineration; (4) no off-site transportation or storage for petroleum coke or residuals; and (5) the potential to dispose of waste streams including hazardous materials.

Gasification can provide high-purity hydrogen for a variety of uses within the refinery (Speight, 2014). Hydrogen is used in refineries to remove sulfur, nitrogen, and other impurities from intermediate to finished product streams and in hydrocracking operations for the conversion of heavy distillates and oils into light products, naphtha, kerosene, and diesel fuel. Hydrocracking and severe hydrotreating require hydrogen that is at least 99% (v/v), whereas less severe hydrotreating can work with gas streams containing 90% (v/v) pure hydrogen.

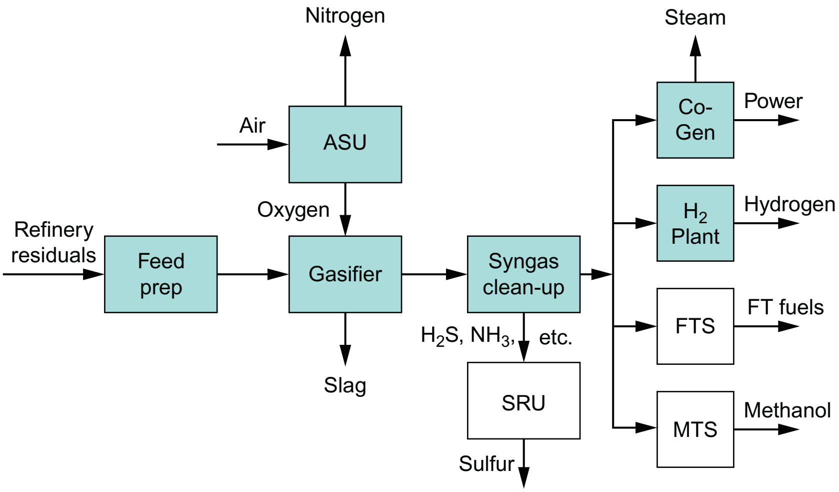

Figure 1.1 Gasification as might be employed on-site in a refinery. ASU, air separation unit to generate enriched oxygen supply; SRU, sulfur recovery unit; FTS, Fischer–Tropsch synthesis; MTS, methanol synthesis.
National Energy Technology Laboratory, United States Department of Energy, Washington, DC, http://www.netl.doe.gov/technologies/coalpower/gasification/gasifipedia/7-advantages/7-3-4_refinery.html.

Electric power and high-pressure steam can be generated via gasification of petroleum coke and residuals to drive mostly small and intermittent loads such as compressors, blowers, and pumps. Steam can also be used for process heating, steam tracing, partial pressure reduction in fractionation systems, and stripping low-boiling components to stabilize process streams.

Carbon soot is produced during gasification, which ends up in the quench water. The soot is transferred to the feedstock by contacting, in sequence, the quench water blowdown with naphtha, and then the naphtha-soot slurry with a fraction of the feed. The soot mixed with the feed is finally recycled into the gasifier, thus achieving 100% conversion of carbon to gas.

1.3.4 Black liquor

Black liquor is the spent liquor from the Kraft process in which pulpwood is converted into paper pulp by removing lignin and hemicellulose constituents as well as other extractable materials from wood to free the cellulose fibers. The equivalent spent cooking liquor in the sulfite process is usually called *brown liquor*, but the terms *red liquor*, *thick liquor*, and *sulfite liquor* are also used. Approximately seven units of black liquor are produced in the manufacture of one unit of pulp (Biermann, 1993).

Black liquor is comprised of an aqueous solution of lignin residues, hemicellulose, the inorganic chemical used in the process, and 15% (w/w) solids of which 10% (w/w) are inorganic and 5% (w/w) are organic. Typically, the organic constituents in black liquor are 40–45% (w/w) soaps, 35–45% (w/w) lignin, and 10–15% (w/w) other (miscellaneous) organic materials.

The organic constituents in the black liquor are made up of water/alkali soluble degradation components from the wood. Lignin is partially degraded to shorter fragments with sulfur contents of about 1–2% (w/w) and sodium content at approximately 6% (w/w) of the dry solids. Cellulose (and hemicellulose) is degraded to aliphatic carboxylic acid soaps and hemicellulose fragments. The extractable constituents yield *tall oil soap* and crude turpentine. The tall oil soap may contain up to 20% (w/w) sodium. Residual lignin components currently serve hydrolytic or pyrolytic conversion or combustion. Alternatively, hemicellulose constituents may also be used in fermentation processes.

Gasification of black liquor has the potential to achieve higher overall energy efficiency, as compared to those of conventional recovery boilers, while generating an energy-rich syngas. The syngas can then be burned in a gas turbine combined cycle system (BLGCC – black liquor gasification combined cycle – similar to *IGCC*) to produce electricity, or the syngas can be converted through catalytic processes into chemicals or fuels, such as methanol, dimethyl ether, FT hydrocarbons, and diesel fuel.

1.4 Gasification for power generation

1.4.1 General aspects

The gasification of coal, biomass, petroleum, or any carbonaceous residues is generally aimed at feedstock conversion to gaseous products. In fact, gasification offers one of the most versatile methods (with a reduced environmental impact with respect to combustion) to convert carbonaceous feedstocks into electricity, hydrogen, and other valuable energy products.

Depending on the previously described type of gasifier (e.g., air-blown, enriched oxygen-blown) and the operating conditions, gasification can be used to produce a fuel gas that is suitable for several applications.

Gasification for generating electric power enables the use of a common technology in modern gas-fired power plants (combined cycle) to recover more of the energy released by burning the fuel. The use of these two types of turbines in the combined cycle system involves (1) a combustion turbine and (2) a steam turbine. The increased efficiency of the combined cycle for electrical power generation results in a 50% (v/v) decrease in carbon dioxide emissions compared to conventional coal plants. Gasification units could be modified to further reduce their climate-change impact, because a large part of the carbon dioxide generated can be separated from the other product gas *before* combustion. For example, carbon dioxide can be separated or sequestered from gaseous by-products by using absorbents (e.g., MOFs) to prevent its release to the atmosphere.

Gasification has also been considered for many years as an alternative to combustion of solid or liquid fuels. Compared to solid or high-viscosity liquid fuels, gaseous mixtures are simpler to clean. Cleaned gases can be used in internal combustion-based power plants that would suffer from severe fouling or corrosion if solid or low-quality liquid fuels were burned inside them.

In fact, the hot syngas produced by gasification of carbonaceous feedstocks can then be processed to remove sulfur compounds, mercury, and particulate matter, prior to its use as fuel in a combustion turbine generator to produce electricity. The heat in the exhaust gases from the combustion turbine is recovered to generate additional steam. This steam, along with the steam produced by the gasification process, drives a steam turbine generator to produce additional electricity. In the past decade, the primary application of gasification to power production has become more common due to the demand for high efficiency and low environmental impact.

As anticipated, the quality of the gas generated in a system is influenced by feedstock characteristics and gasifier configuration, as well as the amount of air, oxygen, or steam introduced into the system. The output and quality of the gas produced is determined by the equilibrium established when the heat of oxidation (combustion) balances the heat of vaporization and volatilization plus the sensible heat (temperature rise) of the exhaust gases. The quality of the outlet gas (Btu/ft^3) is determined by the amount of volatile gases, such as hydrogen, carbon monoxide, water, carbon dioxide, and methane, in the gas stream. With some feedstocks, the higher the amounts of volatile produced in the early stages of the process, the higher the heat content of the product gas. In some cases, the highest gas quality may be produced at lower temperatures. However, char oxidation reaction is suppressed when the temperature is too low, and the overall heat content of the product gas is diminished.

Gasification agents are normally air, oxygen-enriched air, or oxygen. Steam is sometimes added to control for temperature, to enhance heating value, or to allow the use of external heat (allothermal gasification). The major chemical reactions break and oxidize hydrocarbons to produce a product gas containing carbon monoxide, carbon dioxide, hydrogen, and water. Other important components include hydrogen sulfide, various compounds of sulfur and carbon, ammonia, light hydrocarbons, and heavy hydrocarbons (tars).

Depending on the employed gasifier technology and operating conditions, significant quantities of water, carbon dioxide, and methane can be present in the product gas, as well as a number of minor and trace components. Under reducing conditions in the gasifier, most of the feedstock sulfur converts to hydrogen sulfide (H_2S), but 3–10% converts to carbonyl sulfide. Organically bound nitrogen in the coal feedstock is generally converted to gaseous nitrogen (N_2), but some ammonia (NH_3) and a small amount of hydrogen cyanide (HCN) are also formed. Any chlorine in the coal is converted to hydrogen chloride (HCl), with some chlorine present in the particulate matter (fly ash). Trace elements, such as mercury and arsenic, are released during gasification and partition among the different phases (e.g., fly ash, bottom ash, slag, and product gas).

1.4.2 Cogasification of coal with biomass and waste

Pyrolysis and gasification of fossil fuels, biomass materials, and waste have been used for many years to convert organic solids and liquids into useful gaseous, liquid, and cleaner solid fuels (Brar, Singh, Wang, & Kumar, 2012; Speight, 2011a).

1.4.2.1 Biomass

Coal gasification is an established technology (Hotchkiss, 2003; Ishi, 1982; Speight, 2013). Comparatively, biomass gasification has been the focus of research in recent years for the purpose of estimating efficiency and performance of the gasification process using various types of biomass such as sugarcane residue (Gabra, Pettersson, Backman, & Kjellström, 2001), rice hulls (Boateng, Walawender, Fan, & Chee, 1992), pine sawdust (Lv *et al*., 2004), almond shells (Rapagnà, Kiennemann, & Foscolo, 2000; Rapagnà & Latif, 1997), wheat straw (Ergudenler & Ghaly, 1993), food waste (Ko, Lee, Kim, Lee, & Chun, 2001), and wood biomass (Bhattacharya, Siddique, & Pham, 1999; Chen, Sjöström, & Bjornbom, 1992; Hanaoka, Inoue, Uno, Ogi, & Minowa, 2005; Pakdel & Roy, 1991). Recently, cogasification of various biomass and coal mixtures has attracted a great deal of interest from the scientific community. Feedstock combinations, including Japanese cedar wood and coal (Kumabe, Hanaoka, Fujimoto, Minowa, & Sakanishi, 2007), coal and saw dust (Vélez, Chejne, Valdés, Emery, & Londoño, 2009), coal and pine chips (Pan, Velo, Roca, Manyà, & Puigjaner, 2000), coal and silver birch wood (Collot, Zhuo, Dugwell, & Kandiyoti, 1999), and coal and birch wood (Brage, Yu, Chen, & Sjöström, 2000) have been reported in gasification practices. Cogasification of coal and biomass has some synergy – the process not only produces a low carbon footprint on the environment, but it also improves the H_2/CO ratio in the produced gas, which is required for liquid fuel synthesis (Kumabe *et al*., 2007; Sjöström, Chen, Yu, Brage, & Rosén, 1999). In addition, the inorganic matter present in biomass catalyzes the gasification of coal. However, cogasification processes require custom fittings and optimized processes for the coal and region-specific wood residues.

Although cogasification of coal and biomass is advantageous from a chemical viewpoint, some practical problems are present on upstream, gasification, and downstream processes. On the upstream side, the particle size of the coal and biomass is required to be uniform for optimum gasification. In addition, moisture content and pretreatment (torrefaction) are very important during upstream processing.

Upstream processing is influential from a material handling point of view, but the choice of gasifier operation parameters (temperature, gasifying agent, and catalysts) dictate the product gas composition and quality. Biomass decomposition occurs at a lower temperature than coal, and therefore different reactors compatible to the feedstock mixture are required (Brar *et al*., 2012). Furthermore, feedstock and gasifier type, along with operating parameters, not only decide product gas composition but also dictate the amount of impurities to be handled downstream.

Downstream processes need to be modified if coal is cogasified with biomass. Heavy metal and impurities, such as sulfur and mercury, present in coal can make syngas difficult to use and unhealthy for the environment. Alkali present in biomass can also cause corrosion problems and high temperatures in downstream pipes. An alternative option to downstream gas cleaning would be to process coal to remove mercury and sulfur prior to its feeding into the gasifier.

However, first and foremost, coal and biomass require drying and size reduction before they can be fed into a gasifier. Size reduction is needed to obtain appropriate particle sizes; however, drying is required to achieve moisture content suitable for gasification operations. In addition, biomass densification may be conducted to prepare pellets and improve density and material flow in the feeder areas.

It is recommended that biomass moisture content should be less than 15% (w/w) prior to gasification. High-moisture content reduces the temperature achieved in the gasification zone, thus resulting in incomplete gasification. Forest residues or wood has a fiber saturation point at 30–31% moisture content (dry basis) (Brar *et al.*, 2012). Compressive and shear strength of the wood increases with decreased moisture content below the fiber saturation point. In such a situation, water is removed from the cell wall leading to its shrinkage. The long-chain molecule constituents of the cell wall move closer to each other and bind more tightly. A high level of moisture, usually injected in the form of steam in the gasification zone, favors formation of a water-gas shift reaction that increases hydrogen concentration in the resulting gas.

The torrefaction process is a thermal treatment of biomass in the absence of oxygen, usually at 250–300 °C to drive off moisture, decompose hemicellulose completely, and partially decompose cellulose (Speight, 2011a). Torrefied biomass has reactive and unstable cellulose molecules with broken hydrogen bonds. Not only does it retain 79–95% of feedstock energy, but it also produces a more reactive feedstock with lower atomic hydrogen–carbon and oxygen–carbon ratios compared to the original biomass. Torrefaction results in higher yields of hydrogen and carbon monoxide in the gasification process.

Finally, the presence of mineral matter in the coal-biomass feedstock is not appropriate for fluidized-bed gasification. The low melting point of ash present in woody biomass leads to agglomeration that causes defluidization of the ash, sintering, and deposition, as well as corrosion of the gasifier construction metal bed (Vélez *et al.*, 2009). Biomass containing alkali oxides and salts are likely to produce clinkering/slagging problems from ash formation (McKendry, 2002). Thus, it is imperative to be aware of the melting of biomass ash, its chemistry within the gasification bed (no bed, silica/sand, or calcium bed), and the fate of alkali metals when using fluidized-bed gasifiers.

Most small to medium-sized biomass/waste gasifiers are air blown, operate at atmospheric pressure, and range in temperatures from 800 to 100 °C (1470–2190 °F). They face very different challenges from large gasification plants – such as the use of small-scale air separation plant should oxygen gasification be preferred or application of pressurized operation, which eases gas cleaning, may not be practical.

Biomass fuel producers, coal producers, and, to a lesser extent, waste companies are enthusiastic about supplying cogasification power plants and realize the benefits of cogasification with alternate fuels (Lee & Shah, 2013; Speight, 2008, 2011a, 2013). The benefits of a cogasification technology involving coal and biomass include the use of a reliable coal supply with gate-fee waste and biomass, which allows the economies of scale from a larger plant to be supplied just with waste and biomass. In addition, the technology offers a future option of hydrogen production and fuel development in refineries. In fact, oil refineries and petrochemical plants are opportunities for gasifiers when the hydrogen is particularly valuable (Speight, 2011b, 2014).

1.4.2.2 Waste

Waste may be municipal solid waste which had minimal presorting, or refuse-derived fuel with significant pretreatment, usually mechanical screening and shredding. Other more specific waste sources (excluding hazardous waste) and possibly including petroleum coke, may provide niche opportunities for coutilization.

The traditional waste-to-energy plant, based on mass-burn combustion on an inclined grate, has a low public acceptability despite the very low emissions achieved over the last decade with modern flue gas clean-up equipment. This has led to difficulty in obtaining planning permissions to construct much-needed new waste-to-energy plants. After a great deal of debate, various governments have allowed options for advanced waste conversion technologies (gasification, pyrolysis, and anaerobic digestion), but will give credit only to the proportion of electricity generated from nonfossil waste.

Coutilization of waste and biomass with coal may provide economies of scale that help achieve the identified policy objectives at an affordable cost. In some countries, governments propose cogasification processes as being well suited for community-sized developments, suggesting that waste should be dealt with in smaller plants serving towns and cities, rather than moved to large, central plants, thus satisfying the so-called proximity principal.

In fact, neither biomass nor wastes are currently produced or naturally gathered at sites in sufficient quantities to fuel a modern large and efficient power plant. Disruption, transport issues, fuel use, and public opinion all act against gathering hundreds of megawatts (MWe) at a single location. Biomass or waste-fired power plants are therefore inherently limited in size and hence in efficiency (labor costs per unit electricity produced) and in other economies of scale. The production rates of municipal refuse follow reasonably predictable patterns over time periods of a few years. Recent experience with the very limited current biomass-for-energy harvesting has shown unpredictable variations in harvesting capability with long periods of zero production over large areas during wet weather.

The situation is very different for coal. Coal is generally mined or imported, and thus large quantities are available from a single source or a number of closely located sources, and supply has been reliable and predictable. However, the economics of new coal-fired power plants of any technology or size have not encouraged any new coal-fired power plant in the gas-generation market.

The potential unreliability of biomass, longer-term changes in refuse, and the size limitation of a power plant using only waste and/or biomass can be overcome by combining biomass, refuse, and coal. Users would benefit from a premium electricity price for electricity from biomass and the gate fee associated with waste. If the power plant is gasification-based, rather than direct-combustion-based, further benefits may be available. These include a premium price for the electricity from waste, a range of technologies available for the gas-to-electricity part of the process, gas cleaning prior to the main combustion stage instead of after combustion, and an improved public image, which is currently generally better for gasification as compared to combustion. These considerations lead to current studies of cogasification of wastes/biomass with coal (Speight, 2008).

For large-scale power generation (>50 MWe), the gasification field is dominated by plants based on the pressurized, oxygen-blown, entrained flow or fixed-bed gasification of fossil fuels. Entrained gasifier operational experience to date has largely been with well-controlled fuel feedstocks with short-term trial work at low cogasification ratios and with easily handled fuels.

Use of waste materials as cogasification feedstocks may attract significant disposal credits. Cleaner biomass materials are renewable fuels and may attract premium prices for the electricity generated. Availability of sufficient fuel locally for an economic plant size is often a major issue, as is the reliability of the fuel supply. Use of more predictably available coal alongside these fuels overcomes some of these difficulties and risks. Coal could be regarded as the "flywheel" that keeps the plant running when the fuels producing the better revenue streams are not available in sufficient quantities.

Coal characteristics are very different in younger hydrocarbon fuels such as biomass and waste. Hydrogen-to-carbon ratios are higher for younger fuels, as is the oxygen content. This means that reactivity is also quite different under gasification conditions. Gas-cleaning issues can also be dissimilar, given that sulfur is a major concern for coal gasification and chlorine compounds and tars are more important for waste and biomass gasification. There are no current proposals for adjacent gasifiers and gas-cleaning systems, one handling biomass or waste and one handling coal, alongside each other and feeding the same power production equipment. However, there are some advantages to such a design, as compared with mixing fuels in the same gasifier and gas-cleaning systems.

Electricity production or combined electricity and heat production remain the most likely area for the application of gasification or cogasification. The lowest investment cost per unit of electricity generated is the use of the gas in an existing large power station. This has been done in several large utility boilers, often with the gas fired alongside the main fuel. This option allows a comparatively small thermal output of gas to be used with the same efficiency as the main fuel in the boiler as a large, efficient steam turbine can be used. It is anticipated that addition of gas from a biomass or wood gasifier into the natural gas feed to a gas turbine could be technically possible, but there will be concerns as to the balance of commercial risks to a large power plant and the benefits of using the gas from the gasifier. The use of fuel cells with gasifiers is frequently discussed but the current cost of fuel cells is such that their use for mainstream electricity generation is uneconomic.

Furthermore, the disposal of municipal and industrial waste has become an important problem because the traditional means of disposal – landfill – are much less environmentally acceptable than previously. Much stricter regulation of these disposal methods will make the economics of waste processing for resource recovery much more favorable.

One method of processing waste streams is to convert the energy value of the combustible waste into a fuel. One type of fuel attainable from waste is a low-heating value gas, usually 100–150 Btus per standard cubic foot (scf), which can be used to generate process steam or to generate electricity (Gay, Barclay, Grantham, & Yosim, 1980). Coprocessing such waste with coal is also an option (Speight, 2008).

In summary, coal may be cogasified with waste or biomass for environmental, technical, or commercial reasons. It allows larger, more efficient plants than those sized for grown biomass or arising waste within a reasonable transport distance; specific operating costs are likely to be lower and fuel supply security is assured.

Cogasification technology varies, usually being site specific and dependent on high feedstock. At the largest scale, the plant may include the well-proven fixed-bed and entrained flow gasification processes. At smaller scales, emphasis is placed on technologies that appear closest to commercial operation. Pyrolysis and other advanced thermal conversion processes are included where power generation is practical using the on-site feedstock produced. However, the needs to be addressed are (1) core fuel handling and gasification/pyrolysis technologies, (2) fuel gas clean-up, and (3) conversion of fuel gas to electric power (Ricketts, Hotchkiss, Livingston, & Hall, 2002).

1.5 Gasification for synthetic fuel production

The gasification of coal or a derivative (i.e., char produced from coal) is the conversion of coal (by any one of a variety of processes) to produce gaseous products that are combustible as well as a wide range of chemical products (Figure 1.2). With the rapid increase in the use of coal from the fifteenth century onward (Nef, 1957; Taylor & Singer, 1957), it is not surprising that the concept of using coal to produce a flammable gas, especially the use of the water and hot coal (Van Heek & Muhlen, 1991), became commonplace (Elton, 1958).

In fact, the production of gas from coal has been a vastly expanding area of coal technology, leading to numerous research and development programs. As a result, the

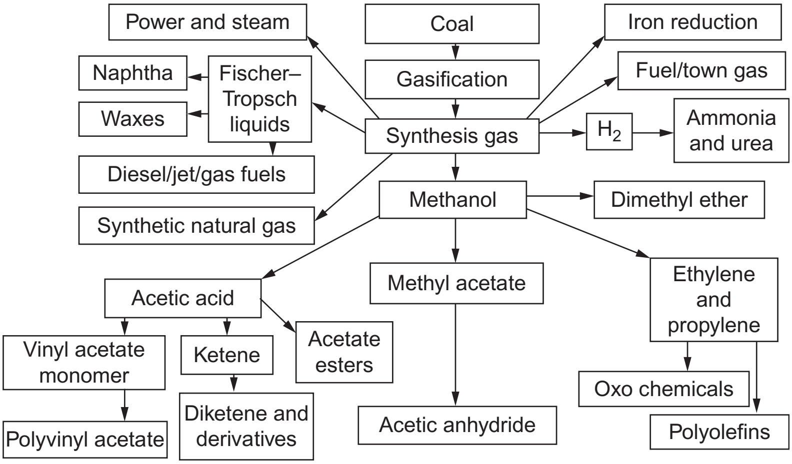

Figure 1.2 Potential products from coal gasification.
Lynn Schloesser, L. (2006). Gasification incentives. In: *Workshop on gasification technologies*. June 28–29. Ramkota, Bismarck, North Dakota.

characteristics of rank, mineral matter, particle size, and reaction conditions are all recognized as having a bearing on the outcome of the process – not only in terms of gas yields but also gas properties (Massey, 1974; Van Heek & Muhlen, 1991). The products from the gasification of coal may be of low-, medium-, or high-heat content (high Btu) as dictated by the process as well as by the ultimate use for the gas (Figure 1.2) (Anderson & Tillman, 1979; Argonne National Laboratory, 1990; Baker & Rodriguez, 1990; Bodle & Huebler, 1981; Cavagnaro, 1980; Fryer & Speight, 1976; Lahaye & Ehrburger, 1991; Mahajan & Walker, 1978; Matsukata, Kikuchi, & Morita, 1992; Probstein & Hicks, 1990; Speight, 2013, and references cited therein).

1.5.1 Gaseous products

The products of gasification are different insofar as the gas composition varies with the system employed (Speight, 2013). It is emphasized that the gas product must first be freed from any pollutants such as particulate matter and sulfur compounds before further use, particularly when the intended use is a water–gas shift or methanation (Cusumano, Dalla Betta, & Levy, 1978; Probstein & Hicks, 1990).

1.5.1.1 Synthesis gas

Synthesis gas (*syngas*) is a mixture mainly of hydrogen and carbon monoxide that is comparable in its combustion efficiency to natural gas (Speight, 2008; Chapter 7). This reduces the emissions of sulfur, nitrogen oxides, and mercury, resulting in a much cleaner fuel (Lee *et al.*, 2007; Nordstrand, Duong, & Miller, 2008; Sondreal, Benson, & Pavlish, 2006; Sondreal, Benson, Pavlish, & Ralston, 2004; Wang *et al.*, 2008; Yang, Xua, Fan, Bland, & Judkins, 2007). The resulting hydrogen gas can be used for electricity generation or as a transport fuel. The gasification process also facilitates capture of carbon dioxide emissions from the combustion effluent. (A discussion about carbon capture and storage will be presented later.)

Although syngas can be used as a stand-alone fuel, its energy density is approximately half that of natural gas and is therefore mostly suited for the production of transportation fuels and other chemical products. Syngas is mainly used as an intermediary building block for the final production (synthesis) of various fuels such as synthetic natural gas, methanol, and synthetic petroleum fuel (dimethyl ether – synthesized gasoline and diesel fuel) (Chadeesingh, 2011; Speight, 2013).

The use of syngas offers the opportunity to furnish a broad range of environmentally clean fuels and chemicals, and there has been steady growth in the traditional uses of this fuel. Almost all hydrogen gas is manufactured from synthesis gas; not surprisingly, there has been an increase in the demand for this basic chemical. In fact, the major use of syngas is in the manufacture of hydrogen for a growing number of purposes, especially in petroleum refineries (Speight, 2014). Methanol not only remains the second largest consumer of synthesis gas, but has shown remarkable growth as part of the methyl ethers used as octane enhancers in automotive fuels.

The FT synthesis remains the third largest consumer of syngas, mostly for transportation fuels but also as a growing feedstock source for the manufacture of chemicals, including polymers. The hydroformylation of olefins (the Oxo reaction), a completely chemical use of syngas, is the fourth largest use of carbon monoxide and hydrogen mixtures. A direct application of syngas as fuel (and eventually also for chemicals) that promises to increase is its use for IGCC units for the generation of electricity (and also chemicals) from coal, petroleum coke, or heavy residuals. Finally, synthesis gas is the principal source of carbon monoxide, which is used in an expanding list of carbonylation reactions, which are of major industrial interest.

1.5.1.2 Low-heat content (low-Btu) gas

During the production of coal gas by oxidation with air, the oxygen is not separated from the air and, as a result, the gas product invariably has a low-heat content (150–300 Btu/ft^3). Low-heat content gas is also the usual product of *in situ* gasification of coal (Speight, 2013), which is essentially used as a method for obtaining energy from coal without the necessity of mining the coal, especially if the coal cannot be mined or if mining is uneconomical.

Several important chemical reactions and a host of side reactions are involved in the manufacture of low-heat content gas under the high temperature conditions employed (Balat, 2011; Speight, 2013). Low-heat content gas contains several components, four of which are always major components present at levels of at least several percent; a fifth component, methane, is marginally a major component.

The nitrogen content of low-heat content gas ranges from somewhat less than 33% (v/v) to slightly more than 50% (v/v) and cannot be removed by any reasonable means; the presence of nitrogen at these levels makes the product gas *low-heat content* by definition. The nitrogen also strongly limits the applicability of the gas to chemical synthesis. Two other noncombustible components – water (H_2O) and carbon dioxide (CO) – further lower the heating value of the gas; water can be removed by condensation and carbon dioxide by relatively straightforward chemical means.

The two major combustible components are hydrogen and carbon monoxide; the H_2/CO ratio varies from approximately 2:3 to about 3:2. Methane may also make an appreciable contribution to the heat content of the gas. Of the minor components, hydrogen sulfide is the most significant; in fact, the amount produced is proportional to the sulfur content of the feed coal. Any hydrogen sulfide present must be removed by one or more of several procedures (Mokhatab, Poe, & Speight, 2006; Speight, 2007).

Low-heat content gas is of interest to industry as a fuel gas or occasionally as a raw material from which ammonia, methanol, and other compounds may be synthesized.

1.5.1.3 Medium-heat content (medium-Btu) gas

Medium-heat content gas has a heating value in the range 300–550 Btu/ft^3 and the composition is much like that of low-heat content gas, except that there is virtually no nitrogen. The primary combustible gases in medium-heat content gas are hydrogen and carbon monoxide (Kasem, 1979). Medium-heat content gas is considerably more versatile than low-heat content gas; like low-heat content gas, medium-heat content gas may be used directly as a fuel to raise steam, or used through a combined power cycle to drive a gas turbine, with the hot exhaust gases employed to raise steam. But medium-heat content gas is especially amenable to synthesize methane (by methanation), higher hydrocarbons (by FT synthesis), methanol, and a variety of synthetic chemicals.

The reactions used to produce medium-heat content gas are the same as those employed for low-heat content gas synthesis. The major difference is the application of a nitrogen barrier (such as the use of pure oxygen) to keep diluent nitrogen out of the system.

In medium-heat content gas, the H_2/CO ratio varies from 2:3 C to 3:1 and the increased heating value correlates with higher methane and hydrogen contents as well as with lower carbon dioxide contents. Furthermore, the very nature of the gasification process used to produce the medium-heat content gas has a marked effect on the ease of subsequent processing. For example, the CO_2-acceptor product is quite amenable to use for methane production because it has (1) the desired H_2/CO ratio just exceeding 3:1, (2) an initially high methane content, and (3) relatively low water and carbon dioxide contents. Other gases may require appreciable shift reaction and removal of large quantities of water and carbon dioxide prior to methanation.

1.5.1.4 High-heat content (high-Btu) gas

High-heat content gas is essentially pure methane and is often referred to as *synthetic natural gas* or *substitute natural gas* (*SNG*) (Kasem, 1979; c.f. Speight, 1990, 2013). However, to qualify as SNG, a product must contain at least 95% methane, giving an energy content (heat content) of synthetic natural gas on the order of 980–1080 Btu/ft^3.

The commonly accepted approach to the synthesis of high-heat content gas is the catalytic reaction of hydrogen and carbon monoxide:

$$3H_2 + CO \rightarrow CH_4 + H_2O$$

To avoid catalyst poisoning, the feed gases for this reaction must be quite pure; therefore, impurities in the product are rare. The large quantities of water produced are removed by condensation and recirculated as very pure water through the gasification system. The hydrogen is usually present in slight excess to ensure that the toxic carbon monoxide is reacted; this small quantity of hydrogen will lower the heat content to a small degree.

The carbon monoxide/hydrogen reaction is somewhat inefficient as a means of producing methane because the reaction liberates large quantities of heat. In addition, the methanation catalyst is troublesome and prone to poisoning by sulfur compounds and the decomposition of metals can destroy the catalyst. Hydrogasification may be thus employed to minimize the need for methanation:

$$[C]_{coal} + 2H_2 \rightarrow CH_4$$

The product of hydrogasification is far from pure methane, and additional methanation is required after hydrogen sulfide and other impurities are removed.

1.5.2 Liquid fuels

The production of liquid fuels from coal via gasification is often referred to as the *indirect liquefaction* of coal (Speight, 2013). In these processes, coal is not converted directly into liquid products but involves a two-stage conversion operation in which coal is first converted (by reaction with steam and oxygen) to produce a gaseous mixture that is composed primarily of carbon monoxide and hydrogen (synthesis gas). The gas stream is subsequently purified (to remove sulfur, nitrogen, and any particulate matter) after which it is catalytically converted to a mixture of liquid hydrocarbon products.

The synthesis of hydrocarbons from carbon monoxide and hydrogen (the FT synthesis) is a procedure for the indirect liquefaction of coal and other carbonaceous feedstocks (Anderson, 1984; Batchelder, 1962; Dry, 1976; Speight, 2011a,b; Storch, Golumbic, & Anderson, 1951). This process is the only coal liquefaction scheme currently in use on a relatively large commercial scale; South Africa is currently using the FT process on a commercial scale in their Sasol complex.

Thus, coal is converted to gaseous products at temperatures in excess of 800 °C (1470 °F), and at moderate pressures, to produce syngas:

$$[C]_{coal} + H_2O \rightarrow CO + H_2$$

The gasification may be attained by means of any one of several processes or even by gasification of coal in place (underground, or *in situ*, gasification of coal).

In practice, the FT reaction is carried out at temperatures of 200–350 °C (390–660 °F) and at pressures of 75–4000 psi. The hydrogen/carbon monoxide ratio is typically on the order of 2/2:1 or 2/5:1. As up to three volumes of hydrogen may be required to achieve the next stage of the liquids production, the synthesis gas must then be converted by means of the water–gas shift reaction to the desired level of hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2$$

After this, the gaseous mix is purified and converted to a wide variety of hydrocarbons:

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

These reactions result primarily in low- and medium-boiling aliphatic compounds suitable for gasoline and diesel fuel.

1.6 Future trends

The future depends very much on the effect of coal gasification processes on the surrounding environment. It is these environmental effects and issues that will direct the success of gasification.

Clean coal technologies (CCTs) are a new generation of advanced coal utilization processes that are designed to enhance both the efficiency and the environmental acceptability of coal extraction, preparation, and use. These technologies reduce emissions, reduce waste, and increase the amount of energy gained from coal. The goal of the program is to foster development of the most promising CCTs such as improved methods of cleaning coal, fluidized-bed combustion, IGCC, furnace sorbent injection, and advanced flue-gas desulfurization.

In fact, there is a distinct possibility that within the foreseeable future the gasification process will increase in popularity in petroleum refineries – some refineries may even be known as gasification refineries (Speight, 2011b). A gasification refinery, such as the Sasol refinery in South Africa (Couvaras, 1997), would produce synthesis gas (from the carbonaceous feedstock) from which liquid fuels would be manufactured using the FT synthesis technology.

In fact, gasification to produce synthesis gas can proceed from any carbonaceous material, including biomass. Inorganic components of the feedstock, such as metals and minerals, are trapped in an inert and environmentally safe form as char, which may have use as a fertilizer. Biomass gasification is therefore one of the most technically and economically convincing energy possibilities for a potentially carbon neutral economy.

The manufacture of gas mixtures of carbon monoxide and hydrogen has been an important part of chemical technology for about a century. Originally, such mixtures were obtained by the reaction of steam with incandescent coke and were known as *water gas*. Eventually, steam-reforming processes, in which steam is reacted with natural gas (methane) or petroleum naphtha over a nickel catalyst, found wide application for the production of synthesis gas.

A modified version of steam reforming known as autothermal reforming, which is a combination of partial oxidation near the reactor inlet with conventional steam reforming further along the reactor, improves the overall reactor efficiency and increases the flexibility of the process. Partial oxidation processes using oxygen instead of steam also found wide application for the manufacture of synthesis gas, with the special feature that low-value feedstocks, such as heavy petroleum residues, could be used. In recent years, catalytic partial oxidation employing very short reaction times (milliseconds) at high temperatures (850–1000 °C) is providing still another approach to synthesis gas manufacture (Hickman & Schmidt, 1993).

In a gasifier, the carbonaceous material undergoes several different processes: (1) pyrolysis of carbonaceous fuels, (2) combustion, and (3) gasification of the remaining char. The process is highly dependent on the properties of the carbonaceous material and determines the structure and composition of the char, which will then undergo gasification reactions.

As petroleum supplies decrease, the desirability of producing gas from other carbonaceous feedstocks will increase, especially in those areas where natural gas is in short supply. It is also anticipated that costs of natural gas will increase, allowing coal gasification to compete as an economically viable process. Research in progress on a laboratory and pilot-plant scale should lead to the invention of new process technology by the end of the century, thus accelerating the industrial use of coal gasification.

The conversion of the gaseous products of gasification processes to synthesis gas – a mixture of hydrogen (H_2) and carbon monoxide (CO), in a ratio appropriate to the application – needs additional steps after purification. The product gases (carbon monoxide, carbon dioxide, hydrogen, methane, and nitrogen) can be used as fuels or as raw materials for chemical or fertilizer manufacture.

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Types of gasifier for synthetic liquid fuel production: design and technology

2

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2.1 Introduction

The gasification of any carbonaceous feedstock is the conversion of the feedstock by any one of a variety of processes to combustible gases (Calemma & Radović, 1991; Fryer & Speight, 1976; Garcia & Radović, 1986; Kristiansen, 1996; Radović & Walker, 1984; Radović, Walker, & Jenkins, 1983; Speight, 2008). In fact, gasification offers one of the most versatile methods (with a lesser environmental impact than combustion) to convert carbonaceous feedstocks, such as coal, petroleum residua, biomass, and industrial waste (Butterman & Castaldi, 2008; Jangsawang, Klimanek, & Gupta, 2006; Senneca, 2007; Speight, 2008, 2013, 2014), into electricity, hydrogen, and other valuable energy products. Gasification may be one of the most flexible technologies to produce clean burning as the chemical building block for a wide range of products.

Moreover, gasification is one of the critical technologies that enable hydrogen production from carbonaceous feedstocks (Lee, Speight, & Loyalka, 2007; Speight, 2008, 2011, 2013, 2014). Gasifiers produce synthesis gas (syngas) that has multiple applications and can be used for hydrogen production, electricity generation, and chemical plants. Integrated gasification combined cycle (IGCC) plants utilize the syngas in a combined cycle power plant (gas turbine and steam turbine) to produce electricity (Speight, 2013).

There has been a general tendency to classify gasification processes by virtue of the heat content of the gas that is produced; it is also possible to classify gasification processes according to the type of reactor vessel and whether or not the system reacts under pressure. However, for the purposes of this text, gasification processes are segregated according to the bed types, which differ in their ability to accept (and convert) various types of feedstock (Collot, 2002).

Although there are many successful commercial coal gasifiers, the basic form and concept details on the design and operation for the commercial coal gasifiers are closely guarded as proprietary information. In fact, the production of gas from carbonaceous feedstocks has been an expanding area of technology. As a result, several types of gasification reactors have arisen. Table 2.1 will show the commonly known processes for gasification reactors (Speight, 2013).

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Table 2.1 Categories of gasification processes

Fixed-Bed Processes	Foster Wheeler stoic process Lurgi process Wellman Galusha process Woodall-Duckham process
Fluidized-Bed Processes	Agglomerating Burner process Carbon Dioxide Acceptor process Coalcon process COED/COGAS process Exxon catalytic gasification process Hydrane process Hygas process Pressurized fluid-bed process Synthane process U-gas process Winkler process
Entrained-Bed Processes	Bi-gas process Combustion engineering process Koppers-Totzek process Texaco process
Molten Salt Processes	Atgas process Pullman-Kellogg process Rockgas process Rummel single-shaft process

2.2 Gasifier types

Several types of fuels are available for gasification and include coal, petroleum residuals, wood, and wood waste (branches, twigs, roots, bark, wood shavings, and sawdust) as well as a multitude of agricultural residues (maize cobs, coconut shells, coconut husks, cereal straws, rice husks, etc.) and peat. Because the fuels vary greatly in their chemical, physical, and morphological properties, they make different demands on the method of gasification and consequently require different reactor design and/or gasification technology. It is for this reason that, during more than a century of gasification experience, a large number of different gasifiers has been developed and marketed, all types geared toward handling the specific properties of a typical fuel or range of fuels. The universal gasifier that is able to handle all or most fuels or fuel types does not exist, and may not exist in the foreseeable future.

In fact, compared to a typical fossil fuel, the complex ligno-cellulosic structure of biomass is more difficult to gasify. The nature of the mineral impurities in conjunction with the presence of various inorganic species, as well as sulfur- and nitrogen-containing compounds, adversely impacts the benign thermal processing of the oxygenated hydrocarbon structure of the biomass. In contrast to combustion of biomass feedstocks in which fuel-bound nitrogen and sulfur are converted to NOx and SOx, steam gasification involves thermal treatment under a reducing atmosphere resulting in fuel-bound nitrogen release as molecular nitrogen and fuel-bound sulfur conversion to hydrogen sulfide, that is, more easily removed by means of adsorption beds (Mokhatab *et al*., 2006; Speight, 2009, 2013). Unlike combustion, the gasification process is more energy intensive. Careful engineering of the process reactor is necessary if the result is to produce rather than consume a significant amount of energy or power as a result of the thermal treatment.

Four types of gasifier configurations are currently available for commercial use: (1) the fixed-bed gasifier, which is subdivided into the countercurrent fixed-bed gasifier and the co-current fixed-bed gasifier, (2) the fluid-bed gasifier, (3) the entrained-flow gasifier, and (4) the processes involving the use of molten salt(s) or molten metal(s) (Speight, 2011, 2013). All systems show relative advantages and disadvantages with respect to fuel type, application, and simplicity of operation, and for this reason each will have its own technical and/or economic advantages in a particular set of circumstances.

However, each type of gasifier may be designed to operate either at atmospheric pressure or at high pressure. In the latter type of operation, the hydrogasification process is optimized and the quality of the product gas (in terms of heat, or Btu, content) is improved. In addition, the reactor size may be reduced and the need to pressurize the gas before it is introduced into a pipeline is eliminated (if a high-heat content gas is to be the ultimate product). High-pressure systems may have problems associated with the introduction of the feedstock into the reactor. Furthermore, low pressure or atmospheric pressure gasification reactors are frequently designed with an accompanying fuel gas compressor after the synthesis gas clean-up processes.

Each type of gasifier will operate satisfactorily with respect to stability, gas quality, efficiency, and pressure losses within only certain ranges of the fuel properties of which the most important are (1) energy content, (2) moisture content, (3) volatile matter production, (4) mineral matter content – ash forming propensity, (5) ash chemical composition and reactivity, (6) feedstock reactivity, (7) feedstock size and size distribution, (8) bulk density of the feedstock, and (9) feedstock propensity for char formation. Before choosing a gasifier for any individual fuel, it is important to ensure that the fuel meets the requirements of the gasifier or that it can be treated to meet these requirements.

2.2.1 Fixed-bed gasifiers

In a fixed-bed process, the feedstock is supported by a grate. Combustion gases (such as steam, air, and oxygen) pass through the supported feedstock where the produced hot gases exit from the top of the reactor. Heat is supplied internally or from an outside source, but some carbonaceous feedstocks (such as caking coal) cannot be used in an unmodified fixed-bed reactor.

The *descending-bed-of-solids system* is often referred to as a *moving* or *fixed bed* or, on occasion, a *countercurrent descending-bed reactor*. In the gasifier, the feedstock (approximately 1/8-1 in., 3-25 mm, diameter) is laid down at the top of a vessel, while reactant gases are introduced at the bottom of the vessel and flow at relatively low velocity upward through the interstices between the coal lumps. As the feedstock descends, it is reacted first by devolatilization using the sensible heat from the rising gas, then hydrogenated by the hydrogen in the reactant gas, and finally burned to an ash. Therefore, the reactions are carried out in a countercurrent fashion.

Thus, the *countercurrent fixed-bed gasifier* (*updraft gasifier*, *counterflow gasifier*) consists of a fixed bed of carbonaceous fuel through which the gasification agent (steam, oxygen, and/or air) flows in a countercurrent configuration. The ash is either removed dry or as a slag. The slagging gasifiers require a higher ratio of steam and oxygen to carbon in order to reach temperatures higher than the ash fusion temperature. The nature of the gasifier means that the fuel must have high mechanical strength and must be non-caking so that it will form a permeable bed, although recent developments have reduced these restrictions to some extent. The throughput for this type of gasifier is relatively low but thermal efficiency is high as the gas exit temperatures are relatively low, but as a result, production of methane and tar is significant at typical operation temperatures.

The main advantage of this gasifier is the effective heat exchange in the reactor. Previously, high-temperature syngas led out of the gasifier, drying the biomass material as it moves down the reactor. By that heat exchange that takes place, the raw syngas is cooled significantly on its way through the bulk filling. Syngas temperature at its exit from the reactor is about 250 °C (480 °F); in downdraft gasifiers, it is approximately 800 °C, or 1470 °F. Given that synthesis gas is exploited in order to dry the incoming feedstock, the system sensitivity to feedstock moisture content is less than that in other gasification reactors. On the other hand, the countercurrent flow of feedstock and syngas results in higher tar content (10-20% w/w) in the raw synthesis gas. Other advantages of updraft gasification include (1) simple, low-cost process; (2) able to handle feedstocks (such as biomass) with a high moisture and high inorganic content (such as municipal solid waste, MSW); and (3) proven technology.

The *co-current fixed-bed* (*downdraft*) gasifier is similar to the countercurrent gasifier, but the gasification agent gas flows in co-current configuration with the fuel (downward, hence the name *downdraft gasifier*). Heat needs to be added to the upper part of the bed, either by combusting small amounts of the fuel or from external heat sources. The produced gas leaves the gasifier at a high temperature, and most of this heat is often transferred to the gasification agent added in the top of the bed, resulting in energy efficiency almost equivalent to that of the countercurrent gasifier. In this configuration, any produced tar must pass through a hot bed of char, thereby removing much of the tar from the product slate.

Due to the fact that the gaseous products from the pyrolysis step pass through the oxidation zone, the tar compounds concentration in the raw synthesis gas is less than that of updraft gasifiers. These gasifiers are easier to control but are more sensitive to the quality of the feedstock. For example, in the case of biomass feedstocks, updraft gasifiers can process biomass with moisture content up to 50% w/w, but in downdraft gasification a moisture content range between 10% and 25% is required.

The advantages of downdraft gasification are (1) up to 99.9% of the tar formed is consumed, requiring minimal or no tar clean-up; (2) minerals remain with the char/ash, reducing the need for a cyclone; and (3) it is a proven, simple, and low-cost process. However, the disadvantages of downdraft gasification are (1) the feed should be dried to a low moisture content (<20% w/w moisture); (2) the synthesis gas exiting the reactor is at a high temperature, requiring a secondary heat recovery system; and (3) 4-7% of the carbon remains unconverted.

Cross-draft gasification reactors, which operate well on dry air blast and dry fuel, do have advantages over updraft gasification reactors and downdraft gasifiers. But the disadvantages – such as high exit gas temperature, poor carbon dioxide reduction, and high gas velocity, which are the consequences of the design – outweigh the advantages.

Unlike downdraft and updraft gasifiers, the ash bin, fire, and reduction zone in cross-draft gasifiers are separated. This design characteristic limits the type of fuel for operation to low mineral matter fuels such as wood, charcoal, and coke. The load-following ability of the cross-draft gasifier is quite good due to concentrated partial zones that operate at temperatures up to 2000 °C (3600 °F). The relatively higher temperature in cross-draft gasification reactors has an effect on gas composition, resulting in high carbon monoxide content and low hydrogen and methane content when dry fuel such as charcoal is used.

2.2.2 Fluid-bed gasifiers

In the *fluidized bed gasifier* (*fluid bed gasifier*), the fuel is fluidized in oxygen (or air) and steam and the ash is removed dry or as heavy agglomerates. The temperatures are relatively low in dry ash gasifiers, so the fuel must be highly reactive. Feedstock throughput is higher than for the fixed bed, but not as high as for the entrained-flow gasifier. The conversion efficiency is low and a recycle operation or subsequent combustion of solids is necessary to increase conversion. Fluidized-bed gasifiers are most useful for fuels that form highly corrosive ash (such as biomass) that would damage the walls of slagging gasifiers.

The fluidized-bed system uses finely sized feedstock particles and the bed exhibits liquid-like characteristics (in the form of fluid flow) when a gas flows upward through the bed. Gas flowing through the feedstock produces turbulent lifting and separation of particles, which result in an expanded bed having a greater feedstock surface area to promote the chemical reaction.

The fluidized-bed system requires the feedstock to be finely ground, and the reactant gases are introduced through a perforated deck near the bottom of the vessel. The volume rate of gas flow is such that its velocity is sufficient to suspend the solids but not high enough to blow them out of the top of the vessel. The result is an active boiling bed of solids having very intimate contact with the upward-flowing gas, which gives a very uniform temperature distribution. The solid flows rapidly and repeatedly from bottom to top and back again, whereas the gas flows rather uniformly upward. The reactor is said to be completely back-mixed and no countercurrent flow is possible. If a degree of countercurrent flow is desired, two or more fluid-bed stages are placed one above the other. Reaction rates are faster than in the moving bed because of the intimate contact between gas and solids and the increased solids surface area due to the smaller particle size.

Compared with the fixed-bed gasifiers, the sequence of reactor processes (drying, pyrolysis, oxidation, and reduction) is not obvious at a certain point of the gasifier because the processes take place in the entire reactor, thus resulting to a more homogeneous type of reaction. This means that more constant and lower temperatures exist inside the reactor, where no *hot spots* are observed. Due to the lower operating temperatures, ash does not melt and it is more easily removed from the reactor. In addition, sulfur-containing and chlorine-containing constituents of the feedstock can be absorbed in the inert bed material, thus eliminating the fouling hazard and reducing the maintenance costs. Another significant difference is that fluidized-bed gasifiers are much less to biomass quality than fixed-bed systems, and they can even operate with mixed biomass feedstock.

One critical advantage of a fluidized bed gasification system (as opposed to downdraft or fixed-bed system) is the use of multiple feedstocks without experiencing downtime (Capareda, 2011). Another important characteristic of the fluidized-bed system is the ability to operate at various throughputs without having to use a larger diameter unit. This is accomplished by changing the appropriate bed material. By using a larger bed material, a higher air flow rate is required for fluidization and thus more biomass may need to be fed at higher rates to maintain the same fuel-to-air ratio as before. The reactor freeboard must then be high enough so that bed materials are not blown out of the system. Also, a fluidized-bed gasification reactor is designed to be accompanied by a cyclone downstream of the gasifier to capture the larger particles that are entrained out of the reactor as a result of the fluidity of the bed and the velocity of the gas rising though the bed. These particles are recycled back into the reactor but, overall, the residence time of coal particles in a fluidized-bed gasifier is shorter than that of a moving-bed gasifier.

Uniform-bed formation in a fluid-bed reactor is very important for efficient bed utilization and consistent operation during gasification of the feedstock. In order to enhance the mixing and uniformity of a bubbling fluid bed, the feedstock is fed to the bed at multiple feed points around the circumference of the reactor vessel. In addition, the fluidization medium – whether air, oxygen, steam, or some combination of these substances – should be uniform in composition and should be introduced in multiple locations.

Finally, depending on the inflow speed, the fluidized-bed gasifier can be characterized either as a *bubbling fluidized-bed system* or as a *circulating fluidized-bed system*. The circulating fluidized-bed system corresponds to higher velocity of the gasification medium.

A *bubbling fluid-bed* design is generally more sensitive to bed utilization. The size of the feedstock particles greatly affects the rate of gasification and the ability of the biomass to migrate to the center of the bed in a bubbling fluid-bed design. With small particles, the gasification is very quick, and unburned material might not make it to the center of the bed, resulting in oxygen slip and a void center in the bubbling fluid-bed reactor. If all or a majority of the feedstock quickly gasifies, there will be insufficient char to maintain a uniform bed. For this reason, more detail is required in designing the in-feed system with the proper number of in-feed points and controlling and/or monitoring the size particle distribution of the feedstock material. A bubbling fluid bed will generally require additional feed points that must be balanced for larger particle sizes.

The advantages of the bubbling fluidized-bed gasifier are (1) it yields a uniform product gas; (2) it exhibits a nearly uniform temperature distribution throughout the reactor; (3) it is able to accept a wide range of fuel particle sizes, including fines; (4) it provides high rates of heat transfer between inert material, fuel, and gas; and (5) a high conversion is possible with low tar and unconverted carbon. The disadvantages of bubbling fluidized-bed gasification are that a large bubble size may result in gas bypass through the bed.

A circulating fluid-bed design, on the other hand, operates at a higher velocity and incorporates recycling of the char and bed material, resulting in complete mixing regardless of feedstock size. Generally, the circulating fluid-bed designs are more flexible but are still limited by the amount of very fine material that they can process.

The advantages of the circulating fluidized-bed gasifier are (1) it is suitable for rapid reactions, (2) high heat transport rates are possible due to high heat capacity of bed material, and (3) high conversion rates are possible with low tar and unconverted carbon. The disadvantages of the circulating fluidized-bed gasifier are (1) temperature gradients occur in the direction of solid flow, (2) the size of fuel particles determine minimum transport velocity (high velocities may result in equipment erosion, and (3) heat exchange is less efficient than in the bubbling fluidized-bed system.

A novel reactor design that is particularly appropraite for biomass is the *indirectly heated gasification* technology that utilizes a bed of hot particles (sand), which is fluidized-using steam. Solids (sand and char) are separated from the syngas via a cyclone and then transported to a second fluidized-bed reactor. The second bed is air blown and acts as a char combustor, generating a flue-gas exhaust stream and a stream of hot particles. The hot (sand) particles are separated from the flue gas and recirculated to the gasifier to provide the heat required for pyrolysis. This approach results in a product gas that is practically nitrogen free and has a heating value of approximately 400 Btu/ft^3 (Turn, 1999).

Another novel design is the new fluidized bed gasifier with increased gas-solid interaction combining two circulating fluidized-bed reactors (Schmid, Pfeifer, Kitzler, Pröll, & Hofbauer, 2011). The aim of the design is to generate a nitrogen-free product gas with low tar content and low fines (particulate matter) content. The system accomplishes this by division into an air/combustion and a fuel/gasification reactor – the two reactors are interconnected via loop seals to assure the global circulation of bed material.

The fuel/gasification reactor is a circulating fluidized bed but with the special characteristic of almost countercurrent flow conditions for gas phase and solids. The gas velocity and the geometrical properties in the fuel/gasification reactor are chosen in such a way that entrainment of coarse particles is low at the top. Due to the dispersed downward movement of the solids, volatile products are not produced in the upper part of the fuel reactor and the issues related to insufficient gas phase conversion and high tar content are avoided.

Finally, the design of a fluidized-bed gasification reactor is extremely important (for all of the reasons given earlier) because both the axial and radial transport of solids within the bed influence gas-solid contact, the thermal gradient, and the heat transfer coefficient. Segregation in a fluidized bed is affected by the particle density, shape, size, superficial gas velocity, mixture composition, and bed aspect ratio (the ratio of the static bed height divided by the dynamic or expanded bed height). Variations in the size, shape, and density of the fuel particles can cause severe mixing problems that result in changes in temperature gradients within the reactor, increase tar formation and agglomeration, and decrease the conversion efficiency (Bilbao, Lezaun, Menendez, & Abanades, 1988; Cranfield, 1978). Effective mixing of fuels of various sizes is needed to maintain uniform temperature, and a good mix depends on the relative concentrations of the solids in the bed and the velocity of the gas (Bilbao *et al.*, 1988; Ghaly, Al-Taweel, Hamdullahpur, & Ugwu, 1989).

2.2.3 Entrained-bed gasifier

An entrained-bed system (entrained flow system) uses finely sized feedstock particles blown into the gas steam prior to entry into the reactor. Combustion occurs with the feedstock particles suspended in the gas phase.

In the *entrained-flow gasifier* (*entrained-bed gasifier*) a dry pulverized solid, an atomized liquid fuel, or a fuel slurry is gasified with oxygen (or, much less frequently, air) in co-current flow and the gasification reactions take place in a dense cloud of very fine particles. The high temperatures and pressures also mean that a higher throughput can be achieved; however, thermal efficiency is somewhat lower because, with existing technology, the gas must be cooled before it can be cleaned. The high temperatures also mean that tar and methane are not present in the product gas; however, the oxygen requirement is higher than for the other types of gasifiers.

The entrained-flow reactor requires a smaller particle size of the feedstock than the fluid-bed gasifier so that the feedstock can be conveyed pneumatically by the reactant gases. Velocity of the mixture must be about 20 ft/s (6.1 m/s) or higher, depending on the fineness of the feedstock. In this case, there is little or no mixing of the solids and gases, except when the gas initially meets the solids. Furthermore, apart from higher temperature, entrained-flow gasification usually takes place at elevated pressure (pressurized entrained-flow gasifiers), reaching operating pressures even up to 40 and 50 bars. The existence of such high temperatures and pressures requires a more sophisticated reactor design and construction materials.

The design of an entrained-flow reactor gives a residence time of the feedstock in the reaction zone to be on the order of seconds, or tens of seconds. This short residence time requires that entrained-flow gasifiers operate at high temperatures to achieve high carbon conversion. Consequently, most entrained-flow gasifiers are designed to use oxygen rather than air, as well as operate above the slagging temperature of the feedstock mineral matter.

All entrained-flow gasifiers are designed to remove the major part of the ash as a slag, because the operating temperature is well above the ash fusion temperature. A smaller fraction of the ash is produced either as a very fine dry fly ash or as black-colored fly ash slurry. Some fuels, in particular certain types of biomass, can form slag that is corrosive for ceramic inner walls that serve to protect the gasifier outer wall. However, some entrained-bed type of gasifiers do not possess a ceramic inner wall but have an inner water- or steam-cooled wall covered with partially solidified slag. For fuel that produces ash with a high ash fusion temperature, limestone can be mixed with the fuel prior to gasification in order to lower the ash fusion temperature. Typically, the fuel particles must be smaller than for other types of gasifier; in fact, the fuel must be pulverized.

2.2.4 Molten salt gasifier

The molten salt gasifier (molten metal gasifier), as the name implies, uses a molten medium of an inorganic salt (or molten metal) to generate the heat to decompose the feedstock into products. There are numerous applications of the molten bath gasification.

A number of different designs have evolved through various stages of development, but the basic concept is that instead of using a formed gasifying chamber where the reactions occur in suspension, the feedstocks are gasified in a molten bath of salt or metal. This type of design allows for more complete processing of the feedstock as well as greater variety of feedstocks to be efficiently processed in the same gasifier.

In molten bath gasifiers, crushed feedstock, steam air, and/or oxygen are injected into a bath of molten salt, iron, or feedstock ash. The feedstock appears to dissolve in the melt where the volatiles crack and are converted into carbon monoxide and hydrogen. The feedstock's carbon reacts with oxygen and steam to produce carbon monoxide and hydrogen. Unreacted carbon and mineral ash float on the surface from which they are discharged.

High temperatures (approximately 900 °C, 1650 °F and above, depending on the nature of the melt) are required to maintain the bath molten. Such temperature levels favor high reaction rates and throughputs, and low residence times. Consequently, tar and volatile oil products are not produced in any great quantity, if at all. Gasification may be enhanced by the catalytic properties of the melt used. Molten salts, which are generally less corrosive and have lower melting points than molten metals, can strongly catalyze the steam-coal reaction and lead to very high conversion efficiencies.

In the process, the carbonaceous feedstock devolatilizes with some thermal cracking of the volatile constituents, leaving the fixed carbon and sulfur to dissolve in the molten salt (such as an iron salt) whereupon carbon is oxidized to carbon monoxide by oxygen introduced through lances placed at a shallow depth in the bath. The sulfur migrates from the molten salt to the slag layer where it reacts with lime to produce calcium sulfide.

The product gas, which leaves the gasifier at about 1425 °C (2600 °F), is cooled, compressed, and fed to a shift converter where a portion of the carbon monoxide is reacted with steam to attain a carbon monoxide to hydrogen ratio of 1:3. The carbon dioxide, that is, produced is removed and the gas is again cooled and enters a methanator where carbon monoxide and hydrogen react to form methane. Excess water is removed from the methane-rich product and, depending on the type of feedstock used and the extent of purification required, the final gas product may have a heat content of 920 Btu/ft^3.

As another example, the Pullman-Kellogg process involves contacting feedstock with a melt of an inorganic salt such as sodium carbonate to convert the feedstock. In the process, air is bubbled into the bottom of the gasifier through multiple inlet nozzles and the feedstock (typically sized to 1/4 in.; 6 mm) is fed beneath the surface of the molten salt bath using a central feed tube whereupon natural circulation and agitation of the melt disperses the material. The main gasification reaction is a partial oxidation reaction and any volatile matter from the feedstock reacts to produce a fuel gas free of oils, tars, and ammonia. A water-gas shift equilibrium exists above the melt and, accordingly, in the reducing environment, carbon dioxide and water concentrations are minimal.

In practice, the molten salt design allows for some of the catalysis process to take place within the gasifier instead of downstream. For example, if the reactor or process design allows the hydrogen and carbon monoxide to be produced in separate distinct streams, the need for post-process separation prior to catalyzing into synthetic fuels will be eliminated.

The molten salt/metal design also allows for a greater variety of co-products to be produced on site. All gasification methods allow for co-production of various chemicals and gases, but the molten metal process adds various metals, such as vanadium and nickel as well as a variety of trace elements, to the mix. Most gasifier feedstocks contain trace metals that can then be extracted in the molten metal process, instead of being disposed of as slag. Also, the design and operation of molten metal reactors is such that the use of a fluxing material, such as lime or limestone, is required. When combined with the silica ash that is generated through normal gasification, the slag produced and removed from the molten metal reactor can be used directly as cement or formed into bricks for construction materials.

2.3 Products of gasification

Gasification agents are typically air, oxygen-enriched air, or oxygen. The products of the combustion or gasification oxidation reaction change significantly as the oxygen-to-fuel ratio changes from combustion to gasification conditions (Table 2.2), which are dependent on gasifier design and operation.

The mixture under gasifying conditions is fuel-rich and there is not enough oxygen to effect complete conversion of the feedstock, in terms of gas quality. As a result, the feedstock carbon reacts to produce carbon instead of carbon dioxide and the feedstock

Table 2.2 **Comparison of products from combustion and gasification processes**

	Combustion	Gasification
Carbon	CO_2	CO
Hydrogen	H_2O	H_2
Nitrogen	NO, NO_2	HCN, NH_3, or N_2
Sulfur	SO_2 or SO_3	H_2S or COS
Water	H_2O	H_2

hydrogen is converted to hydrogen rather than to water. Thus, the quantity and quality of the gas generated in a gasification reactor is influenced not only by the feedstock characteristics but also predominantly by the gasifier type and configuration, as well as by the amount of air, oxygen, or steam introduced into the system, which is also influence by the gasifier configuration.

At the same time, the fate of the nitrogen and sulfur in the fuel is also dictated by oxygen availability (i.e., the configuration of the gasification reactor). The nitrogen and sulfur in a gasification process has important and environmental consequences. Instead of being converted to the respective oxides, the fuel-bound nitrogen is predominantly converted to molecular nitrogen (N2) and hydrogen cyanide (HCN) while the sulfur in the fuel produces hydrogen cyanide (HCN) and carbonyl sulfide (COS).

Steam is sometimes added for temperature control, heating value enhancement, or the use of external heat (*allothermal gasification*). The major chemical reactions break and oxidize hydrocarbons to give a product gas of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), and water (H_2O). Other important components include hydrogen sulfide (H_2S), various compounds of sulfur and carbon, ammonia, low molecular weight hydrocarbons, and tar.

As a very general rule of thumb, optimum gas yields and gas quality are obtained at operating temperatures of approximately 595-650 °C (1100-1200 °F). A gaseous product with a higher heat content (Btu/ft.^{3}) can be obtained at lower system temperatures, but the overall yield of gas (determined as the fuel-to-gas ratio) is reduced by the unburned portion of the feedstock, which usually appears as char.

2.3.1 Gases

The products from gasification may be of low, medium, or high heat content (high Btu) as dictated by the process as well as by the ultimate use for the gas (Speight, 2008, 2011, 2013).

Product gases from fixed-bed versus fluidized-bed gasifier configurations vary significantly. Fixed-bed gasifiers are relatively easy to design and operate and are best suited for small- to medium-scale applications with thermal requirements of up to several megawatts thermal (MWt). For large-scale applications, fixed-bed gasifiers may encounter problems with bridging of the feedstock (especially in the case of biomass feedstocks) and non-uniform bed temperatures. Bridging leads to uneven gas flow, whereas non-uniform bed temperature may lead to hot spots, ash formation, and slagging. Large-scale applications are also susceptible to temperature variations throughout the gasifier because of poor mixing in the reaction zone.

Pressurized gasification systems lend themselves to economical syngas production; they can also be more flexible in production turndown depending on the reactor design. Typically, this is the case for both a pressurized bubbling reactor and a circulating fluidized-bed reactor, whereas the flexibility of an atmospheric fluidized-bed reactor is typically limited to narrower pressure and production ranges. Both designs are well suited for pressurized syngas production. Pressurized designs require more costly reactors, but the downstream equipment (such as gas clean-up equipment, heat exchangers, synthesis gas reactors) will consist of fewer and less expensive components (Worley & Yale, 2012).

In the process, the feedstock undergoes three processes during the conversation to synthesis gas (syngas) – the first two processes, pyrolysis and combustion, occur very rapidly. In pyrolysis, char is produced as the feedstock heats up and volatile products are released. In the combustion process, the volatile products and some of the char reacts with oxygen to produce secondary products (primarily carbon dioxide and carbon monoxide) and the heat required for subsequent gasification reactions. Finally, the char reacts with steam to produce hydrogen (H_2) and carbon monoxide (CO).

Combustion:

$$2C_{\text{feedstock}} + O_2 \rightarrow 2CO + H_2O$$

Gasification:

$$C_{\text{feedstock}} + H_2O \rightarrow H_2 + CO$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

At the gasifier temperature, the ash and other feedstock mineral matter liquefies and exits at the bottom of the gasifier as slag, a sand-like inert material that can be sold as a co-product to other industries (e.g., road building). The synthesis gas exits the gasifier at pressure and high temperature and must be cooled prior to the cleaning stage. Full-quench cooling, by which the synthesis gas is cooled by the direct injection of water, is more appropriate for hydrogen production. The procedure provides the steam necessary to facilitate the water-gas shift reaction, in which carbon monoxide is converted to hydrogen and carbon dioxide in the presence of a catalyst:

Water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

This reaction maximizes the hydrogen content of the synthesis gas, which consists primarily of hydrogen and carbon dioxide at this stage. The synthesis gas is then scrubbed of particulate matter, and sulfur is removed via physical absorption

(Chadeesingh, 2011; Speight, 2008, 2013). The carbon dioxide is captured by physical absorption or a membrane and either vented or sequestered.

Given that the synthesis gas is at high pressure and has a high concentration of carbon dioxide, a physical solvent can be used to capture carbon dioxide (Speight, 2008, 2013). The carbon dioxide is desorbed from the solvent by pressure reduction, and the solvent is recycled into the system.

2.3.2 Other gaseous products

There is a series of products that are called by older (even archaic) names that should also be mentioned here as clarification.

Producer gas is a low Btu gas typically obtained from a coal gasifier (fixed-bed) when air is introduced into the fuel bed instead of oxygen. The composition of the producer gas is approximately 28% v/v carbon monoxide, 55% v/v nitrogen, 12% v/v hydrogen, and 5% v/v methane with some carbon dioxide.

Water gas is a medium Btu gas that is produced by the introduction of steam into the hot fuel bed of the gasifier. The composition of the gas is approximately 50% v/v hydrogen and 40% v/v carbon monoxide, with small amounts of nitrogen and carbon dioxide.

Town gas is a medium Btu gas that is produced in the coke ovens and has the approximate composition of 55% v/v hydrogen, 27% v/v methane, 6% v/v carbon monoxide, 10% v/v nitrogen, and 2% v/v carbon dioxide. Carbon monoxide can be removed from the gas by catalytic treatment with steam to produce carbon dioxide and hydrogen.

Synthetic natural gas (SNG) is methane obtained from the reaction of carbon monoxide or carbon with hydrogen. Depending on the methane concentration, the heating value can be in the range of high-Btu gases.

2.3.3 Tar

Another key contribution to an efficient gasifier operation is the need for a tar reformer. Tar reforming occurs when water vapor in the incoming synthesis gas is heated to a sufficient temperature to cause steam reforming in the gas conditioning reactor, converting condensable hydrocarbons (tars) to non-condensable lower molecular weight molecules. The residence time in the conditioning reactor is sufficient to also allow a water-gas shift reaction to occur and generate increased amounts of hydrogen in the synthesis gas.

Thus, tar reforming technologies, which can be thermally driven and/or catalytically driven, are utilized to break down or decompose tar products and high-boiling hydrocarbon products into hydrogen and carbon monoxide. This reaction increases the hydrogen/carbon monoxide ratio of the syngas and reduces or eliminates tar condensation in downstream process equipment. Thermal tar reformer designs are typically fluid-bed or fixed-bed type. Catalytic tar reformers are filled with heated loose catalyst material or catalyst block material and can be fixed- or fluid-bed designs.

Typically, the tar reformer is a refractory-lined steel vessel equipped with catalyst blocks, which may contain a noble metal or a nickel-enhanced material. Synthesis gas is routed to the top of the vessel and flows down through the catalyst blocks. Oxygen and steam are added to the tar reformer at several locations along the flow path to enhance the syngas composition and achieve optimum performance in the reformer. The tar reformer utilizes a catalyst to decompose tars and heavy hydrocarbons into hydrogen and carbon monoxide. Without this decomposition, the tars and heavy hydrocarbons in the synthesis gas will condense as the synthesis gas is cooled in the downstream process equipment. In addition, the tar reformer increases the hydrogen/carbon monoxide ratio for optimal conversion. The syngas is routed from the tar reformer to downstream heat recovery and gas clean-up unit operations.

2.4 Reactor design: chemical aspects

Generally, gasification involves two distinct stages that are both feedstock and reactor dependent: (1) devolatilization to produce a semi-char at which point, the rate of devolatilization has passed a maximum the semi-char is converted to char by elimination of hydrogen followed by (2) gasification of the char, which is specific to the reactor and the conditions of the reaction.

2.4.1 Feedstock devolatilization

In a gasifier, the carbonaceous feedstock is exposed to high temperatures generated from the partial oxidation of the carbon. The devolatilization (or pyrolysis) process commences at approximately 200-300 °C (390-570 °F), depending on the nature and properties of the feedstock. Volatiles are released, and a carbonaceous residue (char) is produced, resulting in up to 70% weight loss for many feedstocks. The process determines the structure and composition of the char, which will then undergo gasification reactions.

More specifically, as the feedstock particle is heated, any residual moisture (assuming that the feedstock has been pre-dried) is driven off. After all the moisture contained in the feedstock particle(s) has evaporated, the particles undergo devolatilization. The devolatilization and discharge of volatiles generates a range of products varying from carbon monoxide and methane to high molecular weight hydrocarbons comprising paraffin/olefin hydrocarbons, aromatic hydrocarbons, heavy oil, and tar, which are also feedstock dependent. As these products pass from the devolatilization (pyrolsis) zone, further thermal reactions will occur, and gasification of the volatile products will commence.

At temperatures above 500 °C (930 °F). the conversion of the feedstock to char and mineral matter ash is completed. The gasification of char particles occurs after the devolatilization process has finished (Silaen & Wang, 2008). For gas generation, the char provides the necessary energy to promote further heating. Typically, the char is contacted with air or oxygen and steam to generate the product gases.

For some feedstocks, carbon conversion is believed to be independent of the devolatilization rate and less sensible to feedstock particle size. However, it is sensitive to the heterogeneous char-oxygen, char-CO^2, and char-steam reaction kinetics (Chen, Horio, & Kojima, 2000).

2.4.2 Char gasification

The gasification process occurs as the char reacts with gases such as carbon dioxide and steam to produce carbon monoxide and hydrogen. Also, corrosive ash elements such as chloride and potassium may be refined out by the gasification process, allowing the high-temperature combustion of the gas from otherwise problematic feedstocks.

Although the initial gasification stage is completed in seconds, or even less at elevated temperature, the subsequent gasification of the char produced at the initial gasification stage is much slower, requiring minutes or hours to obtain significant conversion under practical conditions. Reactor designs for commercial gasifiers are largely dependent on the reactivity of the char, which in turn depends on nature of feedstock. The reactivity of char also depends on parameters of the thermal process required to produce the char from the original feedstock. The rate of gasification of the char decreases as the process temperature increases due to the decrease in active surface area of char. Therefore, a change of char preparation temperature may change the chemical nature of char, which in turn may change the gasification. The reactivity of char may be influenced by catalytic effect of mineral matter in the char.

Heat and mass transfer processes in fixed- or moving-bed gasifiers are affected by complex solids flow and chemical reactions. Moving-bed gasifiers are countercurrent flow reactors in which the feedstock enters at the top of the reactor, and oxygen (air) enters at the bottom of the reactor. Because of the countercurrent flow arrangement of the reactor, the heat of reaction from the gasification reactions serves to pre-heat the coal before it enters the gasification reaction zone. Consequently, the temperature of the synthesis gas exiting the gasifier is significantly lower than the temperature needed for complete conversion of the feedstock. However, coarsely crushed feedstock may settle while undergoing (1) thermal drying, (2) pyrolysis-devolatilization, (3) gasification, and (4) reduction. In addition, the particles change in diameter, shape, and porosity – non-ideal behavior may result from bridges, gas bubbles, and channeling, and a variable void fraction may also change heat and mass transfer characteristics.

Although there is a considerable overlap of the processes, each can be assumed to occupy a separate zone where fundamentally different chemical and thermal reactions take place. The gasification technology package consists of a fuel and ash handling system, gasification system – reactor, gas cooling, and cleaning system. There are also auxiliary systems – namely, the water treatment plant to meet the requirements of industry and pollution control board. The prime mover for power generation consists of either a diesel engine or a spark-ignited engine coupled to an alternator. In the case of thermal system, the end-use device is a standard industrial burner.

2.4.3 Chemistry

The major difference between combustion and gasification from the point of view of the chemistry involved is that combustion takes place under oxidizing conditions, whereas gasification occurs under reducing conditions. In the gasification process, the feedstock (in the presence of steam and oxygen at high temperature and moderate pressure) is converted to a mixture of product gases. The chemistry of the gasification of various feedstocks can be conveniently (and simply) represented by the following reactions:

$$C_{feedstock} + O_2 \rightarrow CO_2 \tag{1}$$

$$C_{feedstock} + \tfrac{1}{2} O_2 \rightarrow CO \tag{2}$$

$$C_{feedstock} + H_2O \rightarrow H_2 + CO \tag{3}$$

$$C_{feedstock} + CO_2 \leftrightarrow 2CO \tag{4}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{5}$$

$$C_{feedstock} + 2H_2 \rightarrow CH_4 \tag{6}$$

Reactions (1) and (2) are exothermic oxidation reactions and provide most of the energy required by the endothermic gasification reactions (3) and (4). The oxidation reactions occur very rapidly, completely consuming all the oxygen present in the gasifier, so that most of the gasifier operates under reducing conditions. Reaction (5) is the water-gas shift reaction, when water (steam) is converted to hydrogen. This reaction is used to alter the hydrogen/carbon monoxide ratio when synthesis gas is the desired product, such as for use in Fischer-Tropsch processes. Reaction (6) is favored by high pressure and low temperature and is mainly important in low-temperature gasification systems. Methane formation is an exothermic reaction that does not consume oxygen and, therefore, increases the efficiency of the gasification process and the final heat content of the product gas. Overall, approximately 70% of the heating value of the product gas is associated with the carbon monoxide and hydrogen, but this can be higher depending on the gasifier type (Chadeesingh, 2011).

Many other reactions, besides those presented here also occur. In the initial stages of gasification, the rising temperature of the feedstock initiates devolatilization of the feedstock and the breaking of weaker chemical bonds to yield tar, oil, volatile species, and hydrocarbon gases. These products generally react further to form hydrogen, carbon monoxide, and carbon dioxide. The fixed carbon that remains after devolatilization reacts with oxygen, steam, carbon dioxide, and hydrogen.

Depending on the gasifier technology employed and the operating conditions, significant quantities of water, carbon dioxide, and methane can be present in the product gas, as well as a number of minor and trace components. Under the reducing conditions in the gasifier, most of the sulfur in the fuel sulfur is converted to hydrogen sulfide (H_2S) as well as to smaller yields of carbonyl sulfide (COS). Organically bound nitrogen in the feedstock is generally (but not always) converted to gaseous nitrogen (N_2) – some ammonia (NH_3) and a small amount of hydrogen cyanide (HCN) are also formed. Any chlorine in the feedstock (such as coal) is converted to hydrogen chloride (HCl) with some chlorine present in the particulate matter (fly ash). Trace elements, such as mercury and arsenic, are released during gasification and partition among the different phases, such as fly ash, bottom ash, slag, and product gas.

2.5 Reactor design: physical aspects

Fuels for gasification reactors differ significantly in chemical properties, physical properties, and morphological properties; therefore they require different reactor design and operation. It is for this reason that, during more than a century of gasification experience, a large number of different gasifiers has been developed – each reactor designed to accommodate the specific properties of a typical fuel or range of fuels. In short, the gasification reactor that is designed to accommodate all (or most) types of fuels does not exist.

However, before choosing a gasifier for any individual fuel, it is important to ensure that the fuel meets the requirements of the gasifier or that it can be treated to meet these requirements. Practical tests are needed if the fuel has not previously been successfully gasified. In other words, the fuel must match the gasifier and the gasifier must match the fuel.

2.5.1 Influence of feedstock quality

There is an influence of physical process parameters and the effect of feedstock type on gasification. For example, the reactivity of coal generally decreases with increase in rank (from lignite to subbituminous coal to bituminous coal anthracite). Furthermore, the smaller the particle size, the more contact area between the coal and the reaction gases, leading to a more rapid reaction. For medium-rank coal and a low-rank coal, reactivity increases with an increase in pore volume and surface area, but for coal having a carbon content greater than 85% w/w, these factors have no effect on reactivity. In fact, in high-rank coal, pore sizes are so small that the reaction is diffusion controlled.

Other feedstocks (such as petroleum residual and biomass) are so variable that gasification behavior and products vary over a wide range. The volatile matter produced during the thermal reactions varies widely and the ease with which tar products are formed as part of the gaseous products makes gas clean-up more difficult.

The mineral matter content of the feedstock also has an impact on the composition of the produced syngas. Gasifiers may be designed to remove the produced ash in solid or liquid (slag) form. In fluidized- or fixed-bed gasifiers, the ash is typically removed as a solid, which limits operational temperatures in the gasifier to well below the ash melting point. In other designs, particularly slagging gasifiers, the operational temperatures are designed to be above the ash melting temperature. The selection of the most appropriate gasifier is often dependent on the melting temperature and/or the softening temperature of the ash and the feedstock that is to be used at the facility.

High-moisture content of the feedstock lowers internal gasifier temperatures through evaporation and the endothermic reaction of steam and char. Usually, a limit is set on the moisture content of feedstock supplied to the gasifier, which can be met by drying operations if necessary. For a typical fixed-bed gasifier and moderate carbon content and mineral matter content of the feedstock, the moisture limit may be on the order of 35% w/w. Fluidized-bed and entrained-bed gasifiers have a lower tolerance for moisture, limiting the moisture content to approximately 5-10% w/w of the feedstock. Oxygen supplied to the gasifiers must be increased with added mineral matter content (ash production) or moisture content in the feedstock.

Depending on the type of feedstock being processed and the analysis of the gas product desired, pressure also plays a role in product definition (Speight, 2011, 2013). In fact, some (or all) of the following processing steps will be required: (1) pre-treatment of the feedstock; (2) primary gasification; (3) secondary gasification of the carbonaceous residue – char – from the primary gasifier; (4) removal of carbon dioxide, hydrogen sulfide, and other acid gases; (5) shift conversion for adjustment of the carbon monoxide/hydrogen ratio to the desired ratio; and (6) catalytic methanation of the carbon monoxide/hydrogen mixture to form methane. If high- heat content (high-Btu) gas is desired, all of these processing steps are required because gasifiers do not yield methane in the concentrations required (Speight, 2008, 2011, 2013).

Thus, the reactivity of the feedstock is an important factor in determining the design of the reactor because feedstock reactivity, which determines the rate of reduction of carbon dioxide to carbon monoxide in the reactor, influences reactor design insofar as it dictates the height needed in the reduction zone.

In addition, certain operational design characteristics of the reactor system (load following response, restarting after temporary shutdown) are affected by the reactivity of the char produced in the reactor. There is also a relationship between feedstock reactivity and the number of active places on the char surface, these being influenced by the morphological characteristics as well as the geological age of the fuel. The grain size and the porosity of the char produced in the reduction zone influence the surface available for reduction as well as the rate of the reduction reactions that are facilitated by reactor design.

2.5.2 Mixed feedstocks

Both fixed-bed and fluidized-bed gasifiers have been used in co-gasification of coal and biomass – and these include a downdraft fixed-bed gasifier (Kumabe, Hanaoka, Fujimoto, Minowa, & Sakanishi, 2007; Speight, 2011). However, operational problems when a fluidized-bed gasifier was employed included (1) defluidization of the fluidized-bed gasifier due to agglomeration of low melting point ash present in the biomass and (2) clogging of the downstream pipes due to excessive tar accumulation (Pan, Velo, Roca, Manyà, & Puigjaner, 2000; Vélez *et al.*, 2009). In addition, co-gasification and co-pyrolysis of birch wood and coal in an updraft fixed-bed gasifier as well as in a fluidized-bed gasifier has yielded overhead products with 4.0-6.0% w/w tar content, whereas the fixed-bed reactor gave tar yields on the order of 25-26% w/w for co-gasification of coal and silver birch wood mixtures (1:1 w/w ratio) at 1000 °C (1830 °F) (Collot, Zhuo, Dugwell, & Kandiyoti, 1999).

From the perspective of the efficient operation of the reactor, the presence of mineral matter has a deleterious effect on fluidized-bed reactors. The low melting point of ash formed from the mineral matter present in woody biomass can lead to agglomeration. Such agglomeration influences the efficiency of the fluidization – the ash can cause sintering, deposition, and corrosion of the gasifier construction metal. In addition, biomass containing alkali oxides and salts can cause clinkering/slagging problems (McKendry, 2002).

2.5.3 Mineral matter content and ash production

Finally, gasification reactors are very susceptible to ash production and properties. Ash can cause a variety of problems, particularly in up or downdraft gasifiers. Slagging or clinker formation in the reactor, caused by melting and agglomeration of ashes, at best will greatly add to the difficulty of gasifier operation. If no special measures are taken, slagging can lead to excessive tar formation and/or complete blocking of the reactor. A worst-case scenario is the possibility of air channeling, which can lead to a risk of explosion, especially in updraft gasifiers.

Whether slagging does or does not occur depends on the ash content of the fuel, the melting characteristics of the ash, and the temperature pattern allowed by gasifier design. In the fuel bed, local high temperatures in voids in the oxidation zone, caused by bridging in the bed, may cause slagging even when using fuels with a high ash melting temperature.

Generally, slagging is not observed with fuels having mineral matter ash contents less than below 5-6% w/w. Severe slagging can be expected for fuels having mineral matter contents in excess of 12% w/w. For fuels with mineral matter contents between 6% and 12%, the slagging behavior depends to a large extent on the mineral matter composition – reflected in the ash melting temperature, which is influenced by the presence of trace elements giving rise to the formation of low melting point eutectic mixtures.

Updraft and downdraft gasification reactors are able to operate with slagging fuels if they are specially modified (continuously moving grates and/or external pyrolysis gas combustion). Cross-draft gasification reactors, which work at temperatures on the order of 1500 °C (2700 °F) and higher, need special safeguards with respect to the mineral matter content of the fuel. Fluidized bed reactors, because of their inherent capacity to control the operating temperature, suffer less from ash melting and fusion problems.

2.5.4 Heat release

The gasification reactor must be configured to accommodate the energy balance of the chemical reactions. During the gasification process, most of the energy bound up in the fuel is not released as heat. In fact, the fraction of the feedstock's chemical energy, or heating value, that remains in the product gases (especially the synthesis gas) is an important measure of the efficiency of a gasification process (which is dependent on the reactor configuration); it is known as the *cold gas efficiency*. Most commercial-scale gasification reactors have a cold gas efficiency on the order of 65-80%, or even higher.

Thus, it is important for the reactor to limit the amount of heat that is transferred out of the zone where the gasification reactions are occurring. If not, the temperature within the gasification zone could be too low to allow the reactions to proceed. As an example, a minimum temperature on the order of 1000 °C (1830 °F) is typically needed to gasify coal. As a result, a gasification reactor is typically refractory lined with no water cooling to ensure as little heat loss as possible. Gasification reactors also typically operate at elevated pressure (often as high as 900 psia), which allows them to have very compact construction with minimum surface area and minimal heat loss.

2.5.5 Other design options

In addition to being designed and selected for feedstock type, another design option for the gasification reactor involves the method for cooling the synthesis gas produced by the gasifier.

Regardless of the type of gasifier, the exiting synthesis gas must be cooled down to approximately 100 °C (212 °F) in order to utilize conventional acid gas removal technology. This can be accomplished either by passing the syngas through a series of heat exchangers that recover the sensible heat for use (for example, in the stem cycle of an IGCC unit) or by directly contacting the synthesis gas with relatively cool water (a *quench* operation). The quench operation results in some of the quench water being vaporized and mixed with the synthesis gas. The quenched syngas is saturated with water and must pass through a series of condensing heat exchanges that remove the moisture from the synthesis gas (so it can be recycled to the quench zone).

Quench designs have a negative impact on the heating rate of related equipment (such as the IGCC unit) because the sensible heat of the high temperature synthesis gas is converted to low-level process heat rather than high-pressure steam. However, quench designs have much lower capital costs and can be justified when low-cost feedstock (such as biomass or waste) is available. Quench designs also have an advantage if carbon dioxide capture is desired. The saturated synthesis gas exiting a quench section has near the optimum water/carbon monoxide ratio as the feedstock to a water-gas shift reactor that will convert the carbon monoxide to carbon dioxide. Non-quench designs that require carbon dioxide capture need to add steam to the syngas before it is sent to a water-gas shift reactor.

2.6 Gasification mechanism

Gasification involves the thermal decomposition of the feedstock and the reaction of the feedstock carbon and other pyrolysis products with oxygen, water, and fuel gases such as methane (Speight, 2013).

The presence of oxygen, hydrogen, water vapor, carbon oxides, and other compounds in the reaction atmosphere during pyrolysis may either support or inhibit numerous reactions with the feedstock and with the products evolved. The distribution of weight and chemical composition of the products are also influenced by the prevailing conditions (i.e., temperature, heating rate, pressure, residence time, etc.) and, last but not least, the nature of the feedstock (Speight, 2011, 2013, 2014).

If air is used for combustion, the product gas will have a heat content of approximately 150-300 Btu/ft^3 (depending on reactor design, process design characteristics, and the feedstock) and will contain undesirable constituents such as carbon dioxide, hydrogen sulfide, and nitrogen. The use of pure oxygen, although expensive, results in a product gas having a heat content of 300-400 Btu/ft^3 with carbon dioxide and hydrogen sulfide as by-products, both of which can be removed from low-heat content or medium-heat content gas by any of several available processes (Mokhatab *et al.*, 2006; Speight, 2007).

If a high-heat content (high-Btu) gas (900-1000 Btu/ft^3) is required, efforts must be made to increase the methane content of the gas. The reactions that generate methane are all exothermic and have negative values, but the reaction rates are relatively slow and catalysts may therefore be necessary to accelerate the reactions to acceptable commercial rates. Indeed, the overall reactivity of feedstock and char may be subject to catalytic effects. It is also possible that the mineral constituents of the feedstock may modify the reactivity by a direct catalytic effect (Speight, 2013).

Gasification of char in a carbon dioxide atmosphere can be divided into two stages: (1) pyrolysis (i.e., removal of moisture content and devolatilization which is comparatively at lower temperature) and (2) char gasification by different oxygen/carbon dioxide mixtures at high temperature. The combination of pyrolysis and gasification processes can be both a unique and a fruitful technique, as it can save the prior use of gasifying medium and the production of fresh char simultaneously in one process. Also, the increase of heating rate causes a decrease in activation energy value (Irfan, 2009).

2.6.1 Primary gasification

Primary gasification involves thermal decomposition of the feedstock by way of various chemical processes (Table 2.3) and many schemes involve pressures ranging from atmospheric to 1000 psi. Air or oxygen may be admitted to support combustion to provide the necessary heat. The product is usually a low-heat content gas (low-Btu gas) ranging from a carbon monoxide/hydrogen mixture to mixtures containing varying amounts of carbon monoxide, carbon dioxide, hydrogen, water, methane, hydrogen sulfide, nitrogen, and typical products of thermal decomposition such as tar, hydrocarbon species, and other chemical species.

A solid char product may also be produced, and may represent the bulk of the weight of the original feedstock. This type of feedstock being processed determines (to a large extent) the amount of char produced and the analysis of the gas product.

Table 2.3 **Coal gasification reactions**

$2C + O_2 \rightarrow 2CO$

$C + O_2 \rightarrow CO_2$

$C + CO_2 \rightarrow 2CO$

$CO + H_2O \rightarrow CO_2 + H_2$ (shift reaction)

$C + H_2O \rightarrow CO + H_2$ (water gas reaction)

$C + 2\,H_2 \rightarrow CH_4$

$2\,H_2 + O_2 \rightarrow 2\,H_2O$

$CO + 2\,H_2 \rightarrow CH_3OH$

$CO + 3\,H_2 \rightarrow CH_4 + H_2O$ (methanation reaction)

$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$

$C + 2\,H_2O \rightarrow 2\,H_2 + CO_2$

$2\,C + H_2 \rightarrow C_2H_2$

$CH_4 + 2\,H_2O \rightarrow CO_2 + 4\,H_2$

2.6.2 Secondary gasification

Secondary gasification usually involves the gasification of char from the primary gasifier. This is usually done by reaction of the hot char with water vapor to produce carbon monoxide and hydrogen:

$$C_{\mathrm{char}} + H_2O \rightarrow CO + H_2$$

2.6.3 Shift conversion

The gaseous product from a gasifier generally contains large amounts of carbon monoxide and hydrogen, plus lesser amounts of other gases. Carbon monoxide and hydrogen (if they are present in the mole ratio of 1:3) can be reacted in the presence of a catalyst to produce methane. However, some adjustment to the ideal (1:3) is usually required. To accomplish this, all or part of the stream is treated according to the water-gas shift (shift conversion) reaction. This involves reacting carbon monoxide with steam to produce a carbon dioxide and hydrogen whereby the desired 1:3 mole ratio of carbon monoxide to hydrogen may be obtained.

$$CO + H_2O \rightarrow CO_2 + H_2$$

2.6.4 Hydrogasification

Not all high-heat content (high-Btu) gasification technologies depend entirely on catalytic methanation. In fact, a number of gasification processes use hydrogasification – that is, the direct addition of hydrogen to the feedstock (in most cases, coal) under pressure to form methane (Anthony & Howard, 1976).

$$C_{char} + 2H_2 \rightarrow CH_4$$

The hydrogen-rich gas for hydrogasification can be manufactured from steam by using the char that leaves the hydrogasifier. Appreciable quantities of methane are formed directly in the primary gasifier and the heat released by methane formation is at a sufficiently high temperature to be used in the steam-carbon reaction to produce hydrogen so that less oxygen is used to produce heat. Hence, less heat is lost in the low-temperature methanation step, thereby leading to higher overall process efficiency.

2.6.5 Catalytic gasification

Catalysts are commonly used in the chemical and petroleum industries to increase reaction rates, sometimes making certain previously unachievable products possible (Hsu & Robinson, 2006; Speight, 2002, 2014). Acids, through donated protons (H^+), are common reaction catalysts, especially in the organic chemical industries. It is not surprising that catalysts can be used to enhance the reactions involved in gasification, as the use of appropriate catalysts not only reduces reaction temperature but also improves the gasification rates.

In addition, thermodynamic constraints of the gasification process that limit the thermal efficiency are not inherent; rather, they are the result of design decisions based on available technology, as well as the kinetic properties of available catalysts. The latter limits the yield of methane to that obtainable at global equilibrium over carbon in the presence of carbon monoxide and hydrogen. The equilibrium composition is shown to be independent of the thermodynamic properties of the char or feedstock. These limitations give non-isothermal two-stage processes significant thermodynamic advantages. The results of the analysis suggest directions for modifying present processes to obtain higher thermal efficiencies. The two-stage process scheme would have significant advantages over present technologies and should be applicable to a wide range of catalytic and non-catalytic processes (McKee, 1981; Shinnar, Fortuna, & Shapira, 1982).

Alkali metal salts of weak acids – such as potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), potassium sulfide (K_2S), and sodium sulfide (Na_2S) – can catalyze the carbon-steam gasification reaction. Catalyst amounts on the order of 10-20% w/w K_2CO_3 will lower the temperature required for gasification of bituminous coal from approximately 925 °C (1695 °F) to 700 °C (1090 °F) and then the catalyst can be introduced to the gasifier impregnated on coal or char.

Ruthenium-containing catalysts are used primarily in the production of ammonia. It has been shown that ruthenium catalysts provide 5-10 times higher reactivity rates than other catalysts. However, ruthenium quickly becomes inactive due to its necessary supporting material, such as activated carbon, which is used to achieve effective reactivity. But during the process, the carbon is consumed, thereby reducing the effect of the ruthenium catalyst.

Catalysts can also be used to favor or suppress the formation of certain components in the gaseous product. For example, in the production of synthesis gas (mixtures of hydrogen and carbon monoxide), methane is also produced in small amounts. Catalytic gasification can be used to either promote methane formation or suppress it.

Disadvantages of catalytic gasification include increased cost of materials for the catalyst itself (often rare metals), as well as diminishing catalyst performance over time. Catalysts can be recycled, but their performance tends to diminish with age or by poisoning. The relative difficulty in reclaiming and recycling the catalyst can also be a disadvantage. For example, the potassium carbonate catalyst can be recovered from spent char with a simple water wash, but some catalysts may not be so accommodating. In addition to age, catalysts can also be diminished by poisoning. On the other hand, many catalysts are sensitive to particular chemical species that bond with the catalyst or alter it in such a way that it no longer functions. Sulfur, for example, can poison several types of catalysts, including palladium and platinum.

2.6.6 Plasma gasification

Plasma is a high-temperature, highly ionized (electrically charged) gas capable of conducting electrical current. Plasma technology has a long history of development and has evolved into a valuable tool for engineers and scientists who need to use very high temperatures for new process applications (Messerle & Ustimenko, 2007). Human-made plasma is formed by passing an electrical discharge through a gas such as air or oxygen (O_2). The interaction of the gas with the electric arc dissociates the gas into electrons and ions, and causes its temperature to increase significantly, often (in theory) exceeding 6000 °C (10,830°F).

Serious efforts have been made, with some success, to apply plasma gasification technology and to treat industrial and MSW over the last two decades. It is believed that the technology can be used as a gasification reactor, thereby allowing (1) greater feedstock flexibility enabling a variety of fuels such as coal, biomass, and MSW to be used as fuel without the need for pulverizing; (2) air blowing and thus not requiring an oxygen plant; (3) high conversion (>99%) of carbonaceous matter to synthesis gas; (4) the absence of tar in the synthesis; (5) production of high heating value synthesis gas suitable use in a combustion turbine operation; (6) production of little or no char, ash, or residual carbon; (7) production of a glassy slag with beneficial value; (8) high thermal efficiency; and (9) low carbon dioxide emissions.

In the process, the gasifier is heated by a plasma torch system located near the bottom of the reactor vessel. In the gasifier, the feedstock is charged into a vertical reactor vessel (refractory-lined or water-cooled) at atmospheric pressure. A superheated blast of air, which may be enriched with oxygen, is provided to the bottom of the gasifier, at the stoichiometric amount required for gasification. The amount of air fed is such that the superficial velocity of the upward flowing gas is low, and that the pulverized feedstock can be fed directly into the reactor. Additional air and/or steam can be provided at different levels of the gasifier to assist with pyrolysis and gasification. The temperature of the syngas leaving the top of the gasifier is maintained above 1000 °C (1,830 °F). At this temperature, tar formation is eliminated.

Gasification takes place at very high temperatures, driven by the plasma torch system, which is located at the bottom of the gasifier vessel. The high operating temperatures break down the feedstock and/or all hazardous and toxic components into their respective elemental constituents. They then dramatically increase the kinetics of the various reactions occurring in the gasification zone, converting all organic materials into hydrogen (H_2) and carbon monoxide (CO). Any residual materials from inorganic constituents of the feedstock (including heavy metals) will be melted and produced as a vitrified slag that is highly resistant to leaching.

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Preparation of feedstocks for gasification for synthetic liquid fuel production

3

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3.1 Introduction

Effective utilization of various energy resources is currently a worldwide issue worthy of investigation. Coal, petroleum, and natural gas are the main fossil-based feedstocks for energy production and are responsible for about three-quarters of the world's primary energy consumption, each corresponding to 33%, 24%, and 19%, respectively (Stocker, 2008). With increasing focus on global warming, CO_2 emission, secure energy supply, and less consumption of fossil-based fuels, use of renewable energy resources is essential. In addition to these resources, some of the end-of-life products such as MSW and biosolids could be effectively used for gasification. The so-called black liquor (BL) obtained as a waste product of the paper industry serves as an example that could be gasified. Additional sources of lignin are the sugar industry, where the fermentable sugars are converted into ethanol, and lignin is left over as residue. Today, most of this lignin is burnt, but it could be utilized by various other processes to produce electrical energy or various hydrocarbons. It is essential to move the world market dependence away from fossil-based energy resources to renewable alternatives, such as biomass, to make an important contribution toward the establishment of favorable conditions for climate and a sustainable economy (Ragauskas *et al.*, 2006). Lignocellulosic biomass is composed of cellulose, hemicellulose, lignin, and other inorganic materials. Third-generation algal biofuel has a by-product cell mass that can be referred to as de-fatted algae.

There are numerous methods by which all these materials can be converted to various types of electrical/chemical energies. All the processes that occur in high temperature, high/low pressure, and in the presence or absence of catalysts come under the umbrella of thermo-chemical/catalytic methods of conversion. There are various types of processes such as combustion, gasification, pyrolysis, liquefaction, and carbonization under the thermo-chemical methods of conversion. Gasification takes place at high temperature in the presence of an oxidizing agent (also called a gasifying agent). Heat is supplied to the gasifier either directly or indirectly to reach the gasification temperature of 600–1000 °C. Oxidizing agents typically used are air, steam, nitrogen, carbon dioxide, oxygen, and a combination of these. In the presence of an oxidizing agent at high temperature, the large polymeric molecules of biomass

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decompose into lighter molecules and eventually to permanent gases (CO, H_2, CH_4, and lighter hydrocarbons), ash, char, tar, and minor contaminants. Char and tar are the result of incomplete conversion of biomass (Kumar, Jones, & Hanna, 2009). This process produces a low- to medium-Btu gas (4–10 MJ/m^3) that can be used to run gas-powered devices for heat generation as well as internal combustion engines, gas turbines, and fuel cells. The gas derived from this process may contain up to 90% of the energy of the initial feedstock.

Gasification can be carried out using any carbonaceous material; currently, coal is the major substance used as feedstock. The biomass gasification process would be carbon neutral because it will not have a net affect on the existing greenhouse gas concentrations. The pre-treatment process for any feedstock constitutes the steps that must be imposed on the raw material in preparation for the use in a gasification reactor. Raw material typically requires an initial drying before pulverization and screening to the desired size (http://agronomyday.cropsci.illinois.edu/2010/tours/c3chips/). The pre-treatment process is an essential step to avoid any damage to the gasifier and to produce high-quality gas as a product.

There are several complexities in the process of feedstock pre-treatment for gasification due to the presence of non-convertible (inorganic) materials, which further increases when renewable resources are used. The preparation of both the categories (fossil and renewable based) of feedstocks is distinct and varies with the type of gasifier to be used in the next step. When low-density feedstocks are used, their logistics becomes difficult and uneconomical if certain handling processes are not applied. Hence, such feedstocks have to be densified into pellets, or briquettes, to ensure efficient and safe transportation.

All the preceding requirements and processes will be discussed in detail in the following sections. The various characteristics and properties of feedstocks such as coal, petroleum residue, BL, biomass, and MSWs are mentioned under the various sections that follow.

3.2 Feedstock types, properties, and characterization

There are various kinds of feedstocks under the two categories for gasification. The fossil-based feedstocks are coal and petroleum residue. The renewable feedstocks are the lignocellulosic biomass, MSW, biosolids, and BL.

Coal is a complex chemical latticework of carbon, hydrogen, and dozens of trace elements (Franco & Diaz, 2009). *Coal preparation or cleaning* is the removal of mineral matter from as-mined coal to produce clean coal. The primary purpose is to increase the quality and heating value (Btu/lb) of coal by lowering the level of sulfur and mineral constituents (ash). In the case of most eastern bituminous coals, roughly one-half to two-thirds of the sulfur exists in a form that can be liberated by crushing and separated by mechanical processing. Western coals typically contain much lower levels of sulfur, have lower heating values (LHVs), and are not readily amenable to physical cleaning methods for sulfur reduction. All coals contain mineral matter that can also be removed through physical cleaning. Coal preparation as currently practiced in the coal industry involves four generic steps: characterization, liberation, separation, and disposition. During *characterization,* the composition of the different-sized raw coal particles is identified. The composition of the raw coal and the required clean coal specifications dictate the type of equipment that must be used to remove the mineral matter. Crushing liberates mineral matter, and complete *liberation* can be achieved by reducing the mined coal to very fine sizes as particles containing both coal and mineral matter, called *middlings,* are produced during crushing. *Separation* involves partitioning the individual particles into their appropriate-sized groupings – coarse, intermediate, and fine fractions – and separating the mineral matter particles from the coal particles within each size fraction. Separation techniques for larger-sized raw coal particles generally depend on the relative density difference between the organic coal and inorganic mineral matter particles. In the case of fine raw coal particles, difference in the surface properties of the particles in water is utilized. *Disposition* is the dewatering and storage of the cleaned coal and the disposal of the mineral matter. Entrained-solid gasifiers are insensitive to most coal properties so long as the coal can be pulverized to about 80% below 200 mesh (44 μm) size (Longwell, Rubint, & Wilso, 1995).

Petroleum coke is the final by-product during the refining process in delay-coke equipment. With a continuous increase in the worldwide supply of heavy crude oil and the installation of more petroleum deep conversion process units, the output of petroleum coke is steadily increasing (Gary & Handwerk, 2001; Wang, Anthony, & Abanades, 2004). Gasification reactivity of petroleum coke is improved by adding coal liquefaction residue (CLR) as a catalyst (Zhou, Fang, & Cheng, 2006). There are plenty of alkali and alkaline earth metallic (AAEM) species and iron oxygen in the CLR. They are effective catalysts for combustion and gasification of carbonaceous materials (Liu, Zhou, Hu, Dai, & Wang, 2011). *Petroleum residues* refer to the heavy fractions generated in petroleum refining, including atmosphere residue, vacuum residue, and de-oiled asphalt. The newly exploited heavy crudes, such as natural bitumen and shale oil, also have properties similar to such petroleum residues. Thus, the terminology of heavy oil or heavy residue can also be used to indicate all such heavy petroleum oils (Zhang *et al*., 2012).

BL, a major waste from chemical pulp and paper production, contains, on a dry basis, about 40% of inorganic compounds and 60% of organic compounds (Naqvi, Yan, & Dahlquist, 2010; Sricharoenchaikul, 2009). The organic compounds are composed mainly of degraded lignin (alkali lignin), and the inorganic compounds are mostly recyclable pulping chemicals (alkali salts) (Pettersson & Harvey, 2010; Sánchez *et al*., 2004).

The degree of pre-treatment of biomass feedstock is dependent on the gasification technology used. High mineral matter could make gasification impossible. Fuel with moisture content above about 30% makes ignition difficult and reduces the calorific value (CV) of the product gas due to the need to evaporate the additional moisture before combustion/gasification can occur. High-moisture content reduces the temperature achieved in the oxidation zone, resulting in the incomplete cracking of the hydrocarbons released from the pyrolysis zone. Increased levels of moisture and the presence of CO produce H_2 by the water–gas shift reaction, and in turn the increased H_2 content of the gas, produces more CH_4 by direct hydrogenation. The gain in H_2 and CH_4 of the product gas does not compensate for the loss of energy due to the reduced CO content of the gas, thereby producing a product gas with lower CV.

The oxidation temperature is often above the melting point of the biomass ash, leading to clinkering/slagging problems in the hearth and subsequent feed blockages. Clinker is a problem for ash contents above 5%, especially if the ash is high in alkali oxides and salts that produce eutectic mixtures with low melting points. The gasifier has to be designed to destruct tars as well as the heavy hydrocarbons released during the pyrolysis stage of the gasification process. The particle size of the feedstock material depends on the hearth dimensions but is typically 10–20% of the hearth diameter. Larger particles could form bridges that would prevent the feed from moving down, whereas smaller particles would tend to clog the available air void, leading to a high pressure drop and subsequent shutdown of the gasifier (McKendry, 2002).

MSW composition does not always remain the same. It varies from site to site regionally as well as varies depending on developing or developed countries. The segregated waste is easier to be gasified than the non-segregated waste due to the presence of non-convertible matter, glass, water, and metals.

3.3 Feedstock suitability and utilization challenges

There are various challenges for gasification depending on the feedstock used. The feedstock has to be made suitable by employing a variety of techniques for gasification. Some of the critical issues are explained in this section.

The mechanical properties and the moisture content of the feedstock mainly govern the type and scope of pre-treatment such as storage, conveyance, crushing, drying, and feeding systems. The chemical analysis, the content of volatile matter, and the CV, which are interrelated in a certain manner, are decisive for the selection of the gasification process and its conditions. Gasification is comprised of two successive steps when, during pyrolysis, volatile matter is released and the remaining char, essentially consisting of fixed carbon and ash, is partially oxidized. Consequently, not only are the properties of the used feedstock important for the gasification process but also the behavior of the char. This especially applies to the reactivity normally attributed to the char. The *coalification index* (also termed *rank*) is an indication of the natural age of a fossil fuel. As the coalification index rises, the carbon content and the CV increase, whereas the oxygen content, in particular, and the portion of volatile matter decrease.

Wood has a coalific index of 0–0.18, a net CV of 17.5–20 MJ/Kg (moisture- and ash-free, MAF, basis), and a volatile matter 80–90 wt.% (MAF). Municipal waste has a coalific index of 0.03, net CV of 17 MJ/Kg (MAF) and volatile matter 85 wt.% (MAF). Peat has a coalific index of 0.18–0.36, a net CV of 22 MJ/Kg (MAF), and a volatile matter 61–73 wt.% (MAF). Brown coal has a coalific index of 0.45–0.48, a net CV of 25–27 MJ/Kg (MAF), and a volatile matter of 45–55 wt.% (MAF). Lignite has a coalific index of 0.52, a net CV of 28 MJ/Kg (MAF), and volatile matter of 40–50 wt.% (MAF). Sub-bituminous coal has a coalific index of 0.58–0.59, a net CV of 28.5–31.5 MJ/Kg (MAF), and a volatile matter of 30–35 wt.% (MAF). Bituminous coal (medium volatile) has a coalific index of 0.63, a net CV of 31 MJ/Kg (MAF), and a volatile matter of 25–30 wt.% (MAF). Anthracite has a net CV of 31–32 MJ/Kg (MAF) and volatile matter of 2–14 wt.% (MAF). Heavy residues have a coalific index of 0.32–0.65, a net CV of 35–38 MJ/Kg (MAF), and volatile matter of >40 wt.% (MAF). All these factors (ash content and properties, sulfur, and chloride) must be taken into account when selecting and designing the process from both the technical and economic aspects. Intended utilization of the gas obtained and required gas treatment steps must be taken into consideration (Keller, 1990).

It is important to understand the properties and thermal behavior of feedstock to design a suitable gasifier. The properties of fuel that influence gasification are energy content, moisture content, particle size and distribution, form of the fuel, bulk density of the fuel, volatile matter content, ash content and composition, and reactivity of the fuel. Energy content of fuel is mostly obtained in an adiabatic, constant volume bomb calorimeter. The values obtained are higher heating values, which include the heat of condensation from water formed in the combustion of fuel and may be reported on moisture and ash basis. Fuel with higher energy content are preferred for gasification, and most biomass feedstocks (wood, straw) have heating value in the range of 10–16 MJ/kg, whereas liquid fuel (diesel, gasoline) has a higher heating value. Moisture content of the fuel is usually referred to inherent moisture plus surface moisture. Generally, a weight less than 15% is desirable for trouble-free and economical operation of the gasifier. In general, a wood gasifier works well on wood blocks and wood chips ranging from 80 × 40 × 40 mm to 10 × 5 × 5 mm. For a charcoal gasifier, charcoal with size ranging from 10 × 10 × 10 mm to 30 × 30 × 30 mm is quite suitable.

Bulk density is defined as the weight per unit volume of loosely tipped fuel; it varies significantly with moisture content and particle size of fuel. Volume occupied by stored fuel depends on the bulk density of fuel and the manner in which fuel is piled. Bulk density has considerable impact on gas quality, as it influences the fuel residence time in the fire box, fuel velocity, and gas flow rate. The form in which fuel is fed to a gasifier has an economical impact on gasification. Cupers and Pelletisers densify all kinds of biomass and municipal waste into "energy cubes." These cubes are available in cylindrical or cubic form and have a high density of 600–1000 kg/m^3. The specific volumetric content of cubes is much higher than the raw material from which they are made. Volatile matter and inherently bound water in the fuel are given up in the pyrolysis zone at the temperatures of 100–150 °C, forming a vapor consisting of water, tar, oils, and gases. Fuel with high volatile matter content produces more tar, causing problems to the internal combustion engine. Volatile matters in the fuel determine the design of the gasifier for removal of tar. Compared to other biomass materials (crop residue: 63–80%; wood: 72–78%; peat: 70%; coal: up to 40%), charcoal contains the least percentage of volatile matter (3–30%). The mineral content of fuel that remains in oxidized form after combustion of the fuel is called *ash* and also contains some unburned fuel. Ash content and ash composition have an impact on the smooth running of the gasifier. Melting and agglomeration of ashes in the reactor causes slagging and clinker formation. If no measures are taken, slagging or clinker formation leads to excessive tar formation or complete blocking of the reactor, and in general, no slagging occurs with fuel having ash content below 5%.

Wood chips contain 0.1% ash, whereas rice husk contains a high amount of ash (16–23%). Reactivity determines the rate of reduction of carbon dioxide to carbon monoxide in the gasifier and depends on the type of fuel. There is relationship between reactivity and the number of active places on the char surfaces. Reactivity of the char surface can be improved through various processes, including stream treatment (activated carbon) or treatment with lime and sodium carbonate. A number of elements act as catalysts that influence the gasification process, and small quantities of potassium, sodium, and zinc can have a large influence on reactivity of the fuel (http://cturare.tripod.com/fue.htm).

Li and colleages have carried out various studies to explain the char reactivity during gasification. It has been observed that the information about char reactivity is important for the effective utilization of coal, especially low-rank coals, in the low-temperature gasification processes (Li, Tay, Kajitan, & Zhang, 2013). The reactivity of Victorian brown coal char is affected by a few factors (Li, 2007). Victorian brown coal contained inherent alkali and AAEM species (Hayashi & Li, 2004). When the AAEM species are retained in the char during pyrolysis, they could act as catalysts for the gasification of char. Therefore, the concentration of the AAEM species in the coal/char has a direct influence on the char reactivity (Wu, Hayashi, Chiba, Takarada, & Li, 2004; Wu, Li, Hayashi, Chiba, & Li, 2005). Dispersion of the AAEM species in the char matrix also plays an important role in terms of char reactivity. This is because a catalyst could be active only for gasification if it is on the char (pore) surface and accessible to the gasifying agents (Li, 2007). The char structure could also affect the char reactivity, and these factors also influence each other. When the concentrations of large aromatic ring systems in char are increased, the dispersion of sodium in char appears to deteriorate to affect the char gasification reactivity (Li & Li, 2006).

Any coal can be gasified if properly pre-treated. High-moisture coals, for example, may require drying and some caking coals may require partial oxidation to simplify gasifier operation. Other pre-treatment operations include crushing, sizing, and briquetting of fines for feed to fixed-bed gasifiers. The coal feed is pulverized for fluid or entrained-bed gasifiers. Coal pre-treatment generally consists of coal pulverizing and drying. The dissolution of coal is best affected if the coal is dry and finely ground. The heater used to dry coal is typically coal fired, but it may also combust low-BTU-value product streams or may use waste heat from other sources (http://www.epa.gov/ttnchie1/ap42/ch11/final/c11s11.pdf). The chemical reactivity of the coal is potentially very important for underground coal gasification. The reported intrinsic reactivities of low-rank coals differ by up to four orders of magnitude when extrapolated to typical gasifier operating temperatures (Perkins & Sahajwalla, 2006). The intrinsic reactivity of coal has a big impact on the distributions in the gasifier and on the final product gas. In particular, high reactivity favors the production of methane via the char-H_2 reaction. Because this reaction is exothermic, the increased reactivity for this reaction can lead to big changes in the final product gas CV (Bhutto, Bazmi, & Zahedi, 2013). The heavy petroleum residues have the characteristics of high boiling point, high Conradson carbon residue, and high content of heavy metals (i.e., Ni and V), sulfur, and nitrogen (Zhang *et al.*, 2012).

The performances of a waste-to-energy gasification-based process are necessarily affected by the specific properties of the MSW. The most important properties for gasification are elemental composition, LHV, ash content (and composition), moisture content, volatile matter content, other contaminants (such as N, S, Cl, alkalis, heavy metals, etc.), and bulk density and size (C-Tech, 2003; Heermann, Schwager, & Whiting, 2001; Zevenhoven-Onderwater, Backman, Skifvars, & Hupa, 2001). Some of these properties are so crucial that most current gasification technologies generally utilize pre-processed waste or refuse-derived fuel rather than the waste as it is. The pre-treatment adequately limits the highly heterogeneous nature of the waste and reduces its size as well as its ash and moisture content. Moreover, the composition of waste (in particular its heating value) and that of its ash (which in some cases could provide a catalytic action) could prompt an investigation regarding the possibility of using a co-gasification process – in other words, to feed into the gasifier a mixture of different fuels because the possible synergy between their products and intermediates could lead to maximizing the process performance, to reducing the carbon losses (in both particulate and tar fractions), and to increasing the energy content of syngas (Arena, 2012; Mastellone, Zaccariello, & Arena, 2010; Pinto, Lopes, André, Gulyurtlu, & Cabrita, 2007, 2008).

The advantage of the direct melting system process is that no pre-treatment of MSW is required, which differs from other gasification technologies such as a fluidized-bed gasifier. MSW is directly charged into a gasification and melting furnace from the top with coke and limestone, which function as a reducing agent and a viscosity regulator, respectively (Tanigaki, Manako, & Osada, 2012).

A fixed-bed gasifier is attractive for relatively large and dense fuels (wood chips or densified biomass/waste material) for small-scale application. Its main advantages are high ash content, feedstock acceptability, and high carbon conversion efficiency. However, several disadvantages – such as hot spots and channeling are possible in the fixed-bed as well as limited ability to handle fines – have to be considered. An updraft gasifier is more suitable for air as a gasifying agent due to LHV product gas with high levels of tars and a relative small feed rate. A downdraft gasifier favors the relatively dry biomass as feed, although the product gas has relatively low tar. Cross-flow is more suitable for feed such as charcoal with poor reactivity and low content of tar or ash because the temperature is around 2000 °C in the combustion zone. A fluidized-bed gasifier has high throughput capability and great fuel flexibility to handle low-density feedstocks such as undensified crop residues or sawdust. Cylindrical bubbling fluidized-bed systems are generally operated for industrial application at the current stage, which requires a narrow particle size distribution (PSD) for obtaining a better fluidization of particles within the bed. Unfortunately, biomass feed used in the gasification process is generally crushed by a mill, thereby exhibiting a wide PSD in nature. As a result, the small particles tend to be entrained out of the gasifier, while the large particles still remain above the distributor when operational gas velocity is fixed. This results in poor fluidization and unstable operation (Zhang *et al.*, 2013). Biomass has volatile matter of 80–90% by weight and forms a very reactive char, which enables effective gasification in a fluidized bed at a moderate temperature. The ash-melting behavior of these feedstocks therefore is not critical. Moreover, the ash content of this group of feedstocks is usually very low (Keller, 1990).

3.4 Preparation techniques for onward processing

Preparation techniques are very much essential in the case of solid feedstocks for gasification. The onward processing steps depend on the individual feedstocks as well. Coal only needs to be pulverized, but biomass has be dried, powdered, and also compacted owing to its low bulk density. It also depends on the end-products to be formed from the process such as electrical energy or chemical energy in the form of hydrocarbons. In the planning of biorefineries and production of liquid biofuels for transport via synthesis gas route, several biomass materials, such as wood, forest residues, bark, straw, energy crops, peat, and agricultural residues, are used. In addition to conversion, the pre-treatment of feedstocks is important, including transfer, storage, chipping, crushing, and drying, and there are many different techniques with variable cost structures (Fagernäs, Brammer, Wilén, Lauer, & Verhoeff, 2010).

3.4.1 Crushing, separation, and drying

The preparation steps depend on the feedstock and the type of reactor used in the next step. In all cases, drying is the most challenging step. Important issues in drying are energy efficiency, emissions, heat integration, and dryer performance. In syngas production the feedstocks must be dried to below the 30 wt.% moisture content, preferably to about 15 wt.%, and in pyrolysis to below 10 wt.%. Biomass usually has moisture content on delivery to the plant in the range 30–60 wt.%, depending on type, location, time of harvest, and period of storage after harvest. Particle size requirements are dictated largely by the bioenergy process, but the biomass at the point of delivery to the drying process is likely to be in large particulate form (e.g., chips or chunks with a large dimension in the range 10–80 mm). Rotary dryers may accept large and variable particle size fuels, but flash and belt dryers usually require crushing of the fuel to a particle size below 10 mm. The material will have a bulk density in the range 50–400 kg/m^3, depending on type and moisture content. Bulk material usually has moderate flow properties, but readily permits thorough circulation of the drying medium.

During the microwave heating process, energy transfer occurs through the interaction of molecules or atoms. Compared with conventional heating methods, more uniform temperature distribution can be achieved and the undesired secondary reactions may be avoided. As a result, better control of the process and more desired products will be obtained (Yu, Ruan, Deng, Chen, & Lin, 2006). More importantly, because heat is transformed by microwave energy within feedstock internally, the large-sized materials, such as wood block and stalk bale, can be processed. Consequently, a large quantity of electricity consumed for grinding and shredding could be saved.

Evaporative drying processes require heat exchange, by convection or conduction. Possible sources of heat for drying within a bioenergy plant are hot furnace, engine or gas turbine exhaust gases, high-pressure steam from a steam or combined cycle plant, warm air from an air-cooled condenser in a steam or combined cycle plant, and steam from a dedicated combustion of surplus biomass, or diverted product gas, char, or bio-oil. Drying can be a stand-alone process or integrated with other plants.

The dryers for biofuels can be classified according to the drying medium (e.g., flue-gas dryers and superheated steam dryers), or to the heat exchange used (conductive/convective or indirect/direct dryers, respectively). The most common types of flue-gas dryers are rotary and flash dryers. The commercial scale steam dryer types are tubular dryer, fluidized-bed dryers, and pneumatic conveying dryers (Fagernäs *et al.*, 2010).

The two most common devices for comminuting biomass to sizes appropriate for gasification are knife chippers and hammermills. *Chippers* are high-speed rotary devices, operating at speeds up to 1800 rpm, and are better suited for comminuting wood. *Hammermills* are also rotary devices where biomass is crushed by large metal hammers rather than being cut by blades as in chippers. Hammermills are suited to process wood as well as herbaceous energy crops such as switchgrass. Tub grinders are becoming a viable alternative to chippers and traditional hammermills, particularly for the sizing of forestry residues. *Tub grinders* are small, mobile hammermills, often designed as pull-behind units for agricultural uses or mounted on tractor-trailers for larger waste-removal uses. Tub grinders consist of a rotating tub, which feeds material into a hammermill. The mill discharges the comminuted material onto a conveyor that exits via the tub grinder (Cummer & Brown, 2002).

In order to ensure that feedstocks have been properly sized, screens may be used. Screens may be used at the inlet of comminution equipment to divert undersized material, whereas screens at the exit recirculate large pieces that require further size reduction. Other methods of ensuring proper size are by flotation and air classification, using buoyancy and pneumatic principles, respectively, to separate the different sizes (Cummer & Brown, 2002).

In the case of coal as feedstock, the pulverization is the most important step. Depending on the gasifier to be used at the next stage, the size of coal particles is decided. It is necessary to make sure that the size is uniform to avoid any hot spots.

3.4.2 Compaction, pelletizing, and briquetting

During the processing and transport of biomass, technical and economic problems mainly related to the large volume of biomass result in high transport costs and increased requirements for storage space. High water content causes biological degradation as well as the freezing of fuel, which brings some obstacles in the transport system. In addition, differences in water content create problems in finding the optimal operation and management of energy facilities. All these problems could be partially minimized by the densification of the material, which provides more uniform fuel properties. The transportation costs depend on the feedstock densification level and represent between 13% and 28% of the production price of bioenergy (Badger & Fransham, 2006; Cundiff & Grisso, 2008; Vinterback, 2004). Feedstock in pellet, briquette, cube, and veneer form can be easily conveyed, allowing control over energy release. In addition, compression and pelletization represent elementary processes in the production of the “uniform” and “advanced uniform” feedstock form, which is aimed at the reduction of supply chain costs and improve supply efficiencies (Hess, Wright, & Kenney, 2007; Tumuluru, Wright, Hess, & Kenney, 2011).

In biomass feedstock rheology, densification comprises a complex interaction among pressure-induced forces, feedstock forms, physical properties, chemical composition, and moisture content (Adapa, Schoenau, Tabil, Sokhansanj, & Singh, 2007; Carone, Pantaleo, & Pellerano, 2011; Han, Collins, Newman, & Dougherty, 2006; Kaliyan & Morey, 2009). The main objectives in feedstock rheological compression research are measurement of energy consumption and the influence of feedstock properties and binding agents on force-deformation behavior. Biomass densification could be either (1) low-level compression, with the objective to contain the material with wiring, netting, or a container by increasing the density to a level that does not require decompression for subsequent treatment or (2) high-level compression with the objective to produce a self-contained material by increasing the density to a level that may require decompression for subsequent treatment. Low-level compression is mainly used for bulk format or bale compression with a string or net wrapper, bag, container, or trailer equipment to hold the post-densification biomass (Dooley, Lanning, Lanning, & Fridley, 2008). High-level compression is mainly used for pellets, briquettes, cubes, and veneer. Energy consumption of biomass densification plays an essential role in studying the efficiency of feedstock supply-conversion systems (Miao, Grift, Hansen, & Ting, 2012).

Densification causes an increase in the bulk density from 80 to 150 kg/m^3 for straw and 200 kg/m^3 for sawdust up to 600–700 kg/m^3 after the densification, although it is possible to achieve even higher values. This reduces transport costs, reduces the need for very large storage spaces, and simplifies the handling of the fuel.

The main disadvantage of densification is the relatively high cost of input energy, which is needed for the production of pellets and briquettes. This also increases the price of the output product, that is, in the form of briquettes or pellets. CV, water content, and chemical composition are approximately same for both, but the density and strength is usually higher for pellets. Pellets are four to five times longer than their diameter (ranging between about 6 and 12 mm), whereas briquettes have a diameter of 80–90 mm, or dimensions of 150 × 70 × 60 mm in the case of prisms (http://www.coach-bioenergy.eu/en/cbe-offers-services/technology-descriptions-and-tools/technologies/231-pab.html).

There are two approaches to briquetting and both require the loose biomass to be ground to a coarse powder similar to sawdust. Briquetting is a way to make use of biomass residues that would otherwise go to waste, and replace the use of wood and charcoal (often produced unsustainably) as well as fossil fuels, thus cutting greenhouse gas emissions. Briquettes are easier to store and use for cooking than wood because they are uniform in size and composition. They are much cleaner to handle than charcoal or coal, and they produce less local air pollution.

There are some concerns about using field waste for briquettes, because it is sometimes also valuable as a soil improver. However, residues such as sawdust and rice husk have limited agricultural use and can be a fire hazard, as can pine needles. High-pressure briquetting requires electricity or mechanical power. The energy input depends on the biomass used and the quality of the briquette produced, but it is typically between 40 and 60 kWh/tonne, or only 3–9% of the heat produced by the briquettes. Also, extra heat may be needed to dry the biomass, but this can usually be provided by burning below-specification briquettes. High-pressure briquetting uses a power-driven press to raise the pressure of dry, powdered biomass to about 1500 bar (150 MPa). This compression heats the biomass to a temperature of about 120 °C, which melts the lignin in the woody material. The press forces the hot material through a die at a controlled rate. As the pressure decreases, the lignin cools and re-solidifies, binding the biomass powder into uniform, solid briquettes.

The three main types of briquetting machine are the piston press, the screw press, and the pellet mill. The piston press uses an oscillating piston to compress the biomass, and produces cylindrical briquettes, 50–100 mm in diameter. The screw press uses a tapered screw, and produces longer, hollow briquettes. The pellet mill compresses the biomass between rollers and makes smaller cylindrical pellets (similar to animal feed pellets) 6–12 mm in diameter.

The dies and moving components in the machines are made from hardened steel because they are abraded by the biomass at the high pressures used. Lower pressures can be used if the die is heated, but this requires additional energy for heating. High-pressure briquetting machines are produced in a wide range of sizes.

Low-pressure briquetting can be used for materials with a low amount of lignin, such as paper and charcoal dust. In this process, the powdered biomass is mixed into a paste, using water and a binder such as starch or clay. A briquetting press is used to push the paste into a mold or through an extruder, or it can simply be shaped by hand. The briquettes are left to dry so that the binder sets and holds the biomass powder together. Low-pressure briquetting machines are often hand operated using a lever that drives a piston to compress the paste (http://www.ashden.org/briquettes).

Compaction is a common term for densifying the feedstock. The choice of pelletization or briquetting depends on the feedstock used and the type of gasifier to be used at the next stage.

3.5 Advantages and limitations of feedstocks for gasification

The various processes described in the preceding sections and the various feedstocks that can be gasified have their own advantages and limitations. The feedstock and, in turn, the kind of preparation steps to be used for a particular type of gasifier is dependent on various factors. The process, economics, and the end-product requirement generally dictate the selection of the steps involved. Some of the challenges in the processes are mentioned here, along with their solutions wherever possible.

During chipping, care must be taken to remove any metal that may be mixed with the wood, as this can severely damage the knives; however, this problem is usually limited to waste wood residues and is not a large concern for dedicated feedstocks. The mobility of these grinders also allows on-site grinding, potentially reducing transportation costs of the feedstock. It is conceivable to envision a system of on-site tub-grinding at dedicated-feedstock wood farms, allowing further sizing to be performed with larger hammermills located within biomass power plants (Cummer & Brown, 2002).

Biological activity may cause slow self-heating in stock piles of wet biomass. Smoldering lumps of biomass constitute a significant ignition source to a violent dust explosion. Spontaneous ignition is another risk factor when handling or storing thermally dried fuels. Proper cooling of the biomass after drying is important to avoid self-ignition problems in intermediate storage bins (Fagernäs *et al.*, 2010; Wilén *et al.*, 1999).

Drying to low-moisture contents is problematic and has not been optimized for biomass conversion processes. The organic emissions during drying can be categorized into volatile organic compounds and condensable compounds. In addition, there are particulate emissions. At low-drying temperatures (under 100 °C) the compounds emitted consist mainly of monoterpenes and sesquiterpenes.

A dryer fire or explosion can arise from ignition of a dust cloud if substantial amounts of fines are present, or from ignition of combustible gases released from the drying material. Both causes of ignition require the presence of sufficient oxygen and either a sufficiently high temperature or some other source of ignition. Under conditions found in most dryers, the risk of fire or explosion becomes significant if the drying medium has an oxygen concentration over approximately 10% (vol.) (Fagernäs *et al.*, 2010).

If a low-oxygen environment can be guaranteed, much higher inlet temperatures may be used, provided material temperatures do not become excessive; prevention of accidental air in-leakage can be difficult and expensive. The user is cautioned to maintain a sufficiently inert atmosphere in the dryer during operation and especially during startup and shutdown. A high-drying temperature creates a risk of spark development and carbon monoxide release through slow pyrolysis and smoldering. Evolution of combustible gases induces a risk of a gas explosion, which may trigger a chain of dust explosions. Proper ventilation and maintaining the inert atmosphere is required before restart. Carbon monoxide together with dust creates a risk of hybrid explosion, which is very violent. With carbon monoxide present in the atmosphere, the safe oxygen level is decreased substantially. The oxygen level has to be kept below 8%. During startup and shutdown of the drying processes, temporary high-oxygen content has to be considered as a risk factor. In superheated steam drying, the guaranteed absence of air and oxygen eliminates fire and explosion risks (Fagernäs *et al.*, 2010; van Deventer, 2004).

Dust emissions from coal storage, handling, and crushing/sizing can be controlled with available techniques. Controlling air emissions from coal drying, briquetting, and partial oxidation processes is more difficult because of the volatile organics and possible trace metals liberated as the coal is heated. The coal gasification process itself appears to be the most serious potential source of air emissions. The feeding of coal and the withdrawal of ash release emissions of coal or ash dust and organic and inorganic gases are potentially toxic and carcinogenic. Because of their reduced production of tars and condensable organics, slagging gasifiers pose less severe emission problems at the coal inlet and ash outlet. Emissions from coal preparation include coal dust from the many handling operations and combustion products from the drying operation. The most significant pollutant from these operations is the coal dust from crushing, screening, and drying activities. Wetting down the surface of the coal, enclosing the operations, and venting effluents to a scrubber or fabric filter are effective means of particulate control (http://www.epa.gov/ttnchie1/ap42/ch11/final/c11s11.pdf). In spite of the several limitations, it must be acknowledged that gasification is the only process that completely utilizes the carbon to produce value-added hydrocarbons.

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Sustainability assessment of gasification processes for synthetic liquid fuel production: economic, environmental, and policy issues

4

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4.1 Introduction

The emerging awareness in energy security over the last decade has contributed to recent international research in alternative energy resources. Biofuels, in particular second-generation biofuels (from non-food sources), draw the attention of developed and developing countries for their use – mainly for transportation applications. Many urban centers, for example, are converting their environment with smart technology to promote ecological mobility with the specific aim of decreasing carbon emissions. Similarly, rural landscapes are gradually benefiting from biofuels production techniques that are used in sustainable agricultural practices. These techniques also contribute to sustain the economy of marginal areas with the creation of employment opportunities and agricultural demand for feedstock conversion (Hazell & Pachauri, 2006). This picture is nonetheless without limitations. First-generation biofuels cause several negative effects. Most feedstock is obtained from energy crops using available land needed for food purposes, which can cause dramatic repercussions in terms of inflationary distortions particularly relevant in developing countries. Given the urgency of these effects at a global scale, most biofuels research is turning its attention to second-generation biofuels (also known as advanced biofuels). Advanced biofuels are mainly produced from lignocellulosic feedstock (biomass) and are attractive because they are less water and land intensive than first-generation biofuels.

The international political, commercial, and scientific community expects second-generation biofuels to have great potential in terms of energy content, cost reductions, and increased yield and productivity as more experience in research and development (R&D) is gained. Second-generation biofuels are likely to contribute most to the expansion of a sustainable transport sector worldwide and to reduce greenhouse gases (GHGs).

Despite the preceding interests in advanced biofuels, significant progress still needs to be done in order to commercialize large-scale plants (Cherubini *et al.*, 2011; IEA, 2011). To this end, considerable investments are taking place to improve technology for the conversion of lignocellulosic feedstock.

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Life cycle assessment (LCA) and economic assessment are needed to study the economic and environmental viability of advanced biofuels. The (LCA) becomes instrumental to interpreting the results of technology conversion, input combination, product, by- and co-product achievement, and carbon reduction. The economic assessment, on the other hand, aims at evaluating cost-efficient solutions (i.e., cost minimization, economic sustainability, and performance) among different alternatives for the implementation of technologies in each phase of the biofuels life cycle. The degree of accuracy of LCA and economic assessment reports and interpretations for second-generation biofuels will deeply affect the route from R&D to commercialization of biofuel feedstock and products on a local as well as global scale. The extent and rate at which the limitations of future generation biofuels can be greatly overcome depend, to a certain extent, on consistency of LCA and economic assessment studies.

The chapter is organized as follows. Section 4.2 analyzes the main environmental and energy issues (e.g., energy security) related to LCA techniques in biofuels production. Section 4.3 discusses economic potentials and limitations of various types of liquid biofuels, in particular biodiesel, bioethanol, and algae fuels. The section will also discuss economic alternatives for biogas fuels. Section 4.4 draws some policy implications emerging from the analysis provided in the previous parts.

4.2 Environmental and energy issues

The recurring theme that has driven the scientific and policy community to replace conventional fossil fuels with biosynthetic fuels is the beneficial emission reduction of GHGs and their contribution to achieving the goals of the international environmental and energy policy agenda. The aim of this section is to illustrate an overview of LCAs and energy issues that contribute to the environmental aspect of biofuels use.

4.2.1 LCA of biofuels

As mentioned earlier, LCA is performed to assess environmental viability of various processes. The assessment consists of standardized methods that are internationally accepted (ISO 14040 and 14044) to evaluate the needs and modification of current technologies with new ones, so that the entire process of a given commodity reflects the main environmental implications. According to McKone *et al.* (2011), an LCA develops over four steps: (1) definition of the aims and objectives of the analysis; (2) collection of data for energy, emission, and waste inventories; (3) assessment of the impacts; and (4) computation of sensitivity analysis, interpretation, and discussion of results with important indications for the policymaker.

In a more detailed perspective, Davis, Anderson-Teixera, and Delucia (2008) asserts that LCA generally starts by defining a system boundary and an inventory that vary with the scope of the analysis. The system boundary defines the spatial and temporal trajectories within which the analysis of the processes takes shape. A typical system boundary for biofuels could be the available land for energy crops (the spatial dimension), the fertilizer used, and the products or by-products obtained (starting point and end-points of the boundary). What is “inside” the system boundary is mainly the technology used in the production process. Therefore, the spatial dimension, the technology, the input, and the output all produce energy flows and wastes (i.e., carbon and other emissions) that are accounted for in specific inventories (i.e., GHG balances). It is also important to define the functional unit that records LCA data. Energy requirements are typically expressed in megajoules (MJ), whereas the net carbon sequestration requirement in GHG balances is expressed in megagrams of carbon dioxide equivalent (Mg CO_2eq or Mg CO_2e).

The current LCAs of biofuels literature (Cherubini *et al*., 2009; Cherubini *et al*., 2011; Quintero, Montoya, Sánchez, Giraldo, & Cardona, 2008) addresses the environmental assessment issue under various points. First, there is the need to understand which biofuel contributes the most to emission reductions. Also, LCA techniques applied in transportation studies recognize that biodiesel and bioethanol have a significant impact in GHG emission reductions (Kim & Dale, 2005). Several studies consider bioethanol from sugarcane to be more efficient in GHG emission reductions than biodiesel (Kim & Dale, 2008; Xiao, Shen, Zhang, & Gu, 2009). However, other studies point out the severe effect in land use change (e.g., deforestation) from forests to sugarcane plantations for bioethanol purposes. The IPCC (2006) assesses a reduction in carbon storage of up to 120 t C/ha in above-ground vegetation pools.

Other studies (Cherubini & Strømman, 2011) point out negative environmental effects in bioenergy crop production in addition to water and soil pollution due to the use of fertilizers and pesticides. First, the release of these substances in agricultural soils would provide an increase in nitrogen (N) and phosphorous (P) levels, which counterbalance the positive effect of bioenergy crops production for GHG emission reductions. Furthermore, the effect of other non-carbon pollutants such as nitrogen dioxide (N_2O) results an important variable to consider in LCA for biofuel studies. Nitrogen dioxide evolves from fertilizers and its impact on GHG emission balances may be greater than that of carbon dioxide. Based on IPCC estimates (2006), Cherubini and Strømman (2011) argue that the potential effect of N_2O emissions could be “298 times greater than CO_2” (page 443). Due to the frequency of fertilizer rates, the impact would be significantly higher in annual biofuel crops than in perennial bioenergy crops. Quantification of N_2O impacts in LCA studies generally refers to fractions of fertilizers releasing nitrogen and is based on default values determined by the IPCC (2006). Also, contrasting evidence is produced for the contribution of methane (CH_4) emissions in LCA for biofuel studies. Generally, energy crops may provide a reduction in oxidation processes of soils and therefore increase emission values in GHG balances. However, this increase would be accounted for small changes in total life cycle of GHG emissions for biofuels in transportation studies (Delucchi, 2005).

Second, agricultural crop residues may affect life cycle and GHG balances for biofuels production. Crop residues can be used as animal feed or as fertilizer to increase the productivity of soils. Current LCA studies (Lal, 2005; Spatari, Bagley, & MacLean, 2010; Spatari, Zhang, & MacLean, 2005, Wilhelm, Johnson, Hatfield, Voorhees, & Linden, 2004) argue that agricultural crop residues are influential in terms of N_2O and N emissions and changes in soil organic carbon (SOC).

Third, the feedstock employed for biofuel production affects differences in GHG balances as well as land use availability and management. Hamelinck *et al.* (2008) argue on the effects on GHG balances of direct and indirect land use. *Direct land use changes* refer to changes in the use of agricultural land with corresponding direct impacts occurring on emissions, land, and agricultural productions. *Indirect land use changes* (ILUC) refer to the spatial dimension of the impacts occurring on other lands due to the displacement effect of previous agricultural land management and practices. Major environmental effects on GHG balances due to *direct land use changes* refer to changes in carbon stocks. Changing crop production may generate positive or negative effects in terms of carbon stocks (C). Converting forest land for agricultural purposes would cause a decrease in carbon emissions. Converting set-aside lands for energy (e.g., switchgrass used as biomass feedstock, Franck, Berdahl, Hanson, Liebig, & Johnson, 2004) or alternative purposes (i.e., crops, grass, Gebhart, Johnson, Mayeux, & Polley, 1994) would contribute to an increase in C (Cherubini *et al.*, 2009). Generally, carbon can be stored above and below vegetation ground, litter, soil, and dead wood. Changing land use would contribute to changing the equilibrium reached in carbon storage from actual pools; this is, an important aspect because the higher the SOC (i.e., the carbon that can be absorbed in the soil), the little is its relevance in GHG emission balances. According to the nature of the change (direct vs. ILUC), different effects could be accounted for in GHG savings for biofuel crops.

LCA studies of greenhouse gas emissions due to direct land use changes are relatively recent and most are related to biofuels production. The IPCC (2006) provides estimate values for direct land use conversion in GHG balances. Table 4.1 illustrates an example of C sequestration in direct land use that can be divided by 20 years (the default value applied by the IPCC for plantation lifetime) to determine CO_2 emissions.

Computations for CO_2 emissions due to ILUC would be more complex to obtain, although studies (Fargione, Hill, Tilman, Polasky, & Hawthorne, 2008; Fritsche,

Table 4.1 **Carbon sequestration for direct land use change (Soil C stock change in t C/Ha)**

	To						
From	**Wheat**	**Sugar beet**	**Sugar-cane**	**Maize**	**Palm Oil**	**Rapeseed**	**Soy-bean**
Set-aside	−9	−9	n.a.	−9	n.a.	−9	−9
Temperate grassland	−9	−9	n.a.	−9	n.a.	−9	n.a.
Temperate forest	−13	−13	n.a.	−13	n.a.	−13	n.a.
Tropical grassland	n.a.	n.a.	n.a.	n.a.	−2	n.a.	n.a.
Tropical moist rain forest	n.a.	n.a.	−31	n.a.	−4	n.a.	−31

Source: IPCC, 2006 and Hamelinck *et al.*, 2008.

2010) claim it to be more influential in GHG balances than in direct land use changes. Table 4.2 shows life cycle GHG emissions due to the displacement effect in land use change. Values reported refer to minimum (25%), medium (50%), and maximum (75%) life cycle GHG emissions in the occurrence of displacement effects.

Another important aspect to consider is the carbon neutrality over the life cycle of dedicated energy crops for biomass production. Carbon neutrality concerns releasing net zero carbon emissions in the atmosphere because these are captured by dedicated plants during their growth stage. However, GHG emissions may emerge during the production process of the bioenergy life cycle, such as harvesting the feedstock using external fossil fuels, handling the biomass, and handling transportation operations. A final issue to consider is the generation of co-products replacing conventional products for further environmental benefits in LCA for the biofuels chain. Environmental impacts can be assessed in terms of mass or energy content or by defining certain system boundaries in which the economic value of the co-product and/or the technology used for meeting the needs of the plant energy is set.

4.2.2 Impacts on energy

Main implications on energy can be grouped into three broad categories: (1) energy balances, (2) efficient biomass use, and (3) net savings of fossil fuels and GHG per hectare (Ha) of land used for energy crop.

A consistent part of LCAs for biofuels should include energy requirements computed through energy balances (Davis *et al.*, 2008). Energy balances are a tool indicating the supply and use of energy showing input/output sources, energy processes,

Table 4.2 **Life cycle GHG emissions (including indirect land use change)**

	Life cycle GHG emissions[a] (g CO_2eq/MJ)		
Biofuel route, country location	**Minimum**	**Medium**	**Maximum**
Rapeseed to FAME[b], EU	117	188	260
Palm oil to FAME[b], Indonesia	45	64	84
Soyoil to FAME[b], Brazil	51	76	101
Sugarcane to EtOH, Brazil	36	42	48
Maize to EtOH, USA	72	101	129
Wheat to EtOH, EU	77	110	144
SRC[c] to BtL[d], EU	42	75	109
SRC[c] to BtL[d], Brazil (tropical)	17	25	34
SRC[c] to BtL[d], Brazil (Savannah)	25	42	59
Conventional gasoline		87-90	
Conventional diesel		85-90	

Source: Cherubini *et al.* (2009).

[a] Including cultivation, processing, by-products and indirect land use change.

[b] Fatty acid methyl ester.

[c] Short rotation crop.

[d] Biomass to liquid.

and conversions. The final goal of energy balances for bioenergy systems is to show proper indicators of energy performance describing which production chain is more efficient than others, according to the crop, fertilizer use, irrigation techniques and water requirements, feedstock and energy processes (including the use of non-renewable energy), conversion procedures, and efficient energy pathways (Cherubini *et al.*, 2011; Davis *et al.*, 2008). Table 4.3 illustrates main indicators from energy balances for biofuels (e.g., in the transportation sector) indicating the ratio of non-renewables inputs versus energy outputs ($E_{\text{non-ren-in/Eout}}$) and the cumulative energy requirement (CER, expressed in MJ/Km) obtained by adding fossil fuels (FER, expressed in MJ/Km) and renewable energy requirements (RER, expressed in MJ/Km).

The second column in Table 4.3 shows the ratio of non-renewables inputs versus energy outputs ($E_{\text{non-ren-in/Eout}}$) and indicates how much fossil fuel is needed to obtain one unit output of energy from biofuels in the bioenergy process. The third column shows the total energy requirements in bioenergy processes, which is given by the sum of the fourth and fifth columns. In bioenergy systems, FER have a positive (though small) value due to the use of fossil fuels in processing bioenergy sources. Biofuels from ethanol from sugarcane provide high renewable energy values (compared to other energy sources) obtained by biomass residues during the processing phase. On the other hand, biodiesel from oils (rapeseed, soy, and sunflowers) requires high amounts of fossil inputs (compared to other energy sources) due to the use of machines in the cultivation stage and further chemical and combustion processes

Table 4.3 Energy balance indicators for biofuels in the transportation sector

Transportation fuel	$E_{\text{non-ren-in/Eout}}$	**Cumulative ER (CER) (MJ/Km)**	**Fossil (FER) (MJ/Km)**	**Renewable ER (RER) (MJ/Km)**
Bioethanol from sugarcane	0.15-0.25	12-13	0.2-0.3	11.8-12.8
Bioethanol from other crops (corn, sugar beet, wheat)	0.50-0.85	3.5-5-5	0.7-1.5	2.8-4
Biogas	0.15-0.40	3.5-4.5	0.3-1	3.0-4.0
Biodiesel (rapeseed, soy, sunflower)	0.40-0.70	3.5-4.5	0.8-1.8	2.5-3.3
FT-diesel from biomass[a]	0.15-0.40	4.4-4.8	0.1-0.2	4.2-4.6
Bioethanol from lignocellulose[a]	0.15-0.45	6.1-9.3	0.1-0.8	6.0-8.5
Gasoline	1.20	1.7-2.4	1.7-2.4	<0.001
Diesel	1.20	1.3-1.9	1.3-1.9	<0.001
Natural gas	1.05-1.20	2.5-2.8	2.5-2.8	<0.001

[a] Technology under development

Source: Cherubini *et al.* (2009)

(i.e., fermentation, transesterification) involving additional energy needs. These values would be consistent with other studies (Cherubini *et al*., 2011; IPCC, 2006).

A broader picture of energy requirements and efficacy of a biofuel/bioenergy system pathway is pertained by the identification/quantification of GHGs per unit of energy output consumed. Table 4.4 shows the amount of GHGs emitted in the transportation sector by using renewable sources (the table also contains values for non-renewable sources).

Table 4.4 should be read with caution because other factors such as other non-carbon pollutants or transport modes (including engines efficiency per kilometer) may affect GHG estimates. For bioethanol from other crops, generation of GHGs is also affected by the agricultural phase and other processes that may vary across biofuels.

A further important aspect relevant to the energy impact analysis is the amount of fossil energy and GHG savings per Ha of land use. Table 4.5 illustrates how much fossil fuel and GHG emissions are saved for 1 Ha of land used to produce one unit of biofuel. Bioethanol from sugarcane produces the largest amount of energy saving (120-200 GJ saved/Ha), and savings in terms of GHG emissions (10-16 t CO_2eq saved/Ha).

Finally, given the relative importance of biomass sources to current biofuels in global market competition, a comparison between these sources would ensure the best selection across bioenergy system applications. Current LCA studies (Cherubini *et al*., 2009; Searcy & Flynn, 2008) make an attempt to analyze biomass use as biofuels in power energy systems for electricity generation (e.g., combined heat and power (CHP)).

Generally, electricity production from biomass provides larger amounts of GHG emission savings compared to conventional first-generation biofuels; similarly, the displacement effect of electricity from fossil fuels (e.g., coal) in bioelectricity markets makes GHG savings more evident when electricity is produced with natural gas (Greene, 2004). Searcy and Flynn (2008) also argue that electricity produced via agricultural residues through gasification processes reveals to be more appealing in terms of GHG savings. These would be in the range of three times higher than the savings

Table 4.4 GHG emissions balance for biofuels

Energy product: transportation fuels	GHG emissions (g CO_2eq/Km)
Bioethanol from sugarcane	50-75
Bioethanol from other crops (corn, sugar beet, wheat)	100-195
Biogas	25-100
Biodiesel (rapeseed, soy, sunflower)	80-100
FT-diesel from biomass[a]	15-55
Bioethanol from lignocellulose[a]	25-50
Gasoline[b]	210-220
Diesel[c]	185-220
Natural gas	155-185

[a] Technology under development.
[b] GHG from combustion already included: 75.92 g CO2-eq./MJ (consumption: 2.45 MJ/km).
[c] GHG from combustion already included: 75.34 g CO2-eq./MJ (consumption: 2.45 MJ/km).
Source: Cherubini *et al*. (2009)

Table 4.5 Fossil fuels and GHG savings per Ha of land used

Energy product: transportation Fuels[a]	Energy saved (GJ saved/ha)	GHG saved (t CO_2eq saved/ha)
Bioethanol from sugarcane	120-200	10-16
Bioethanol from other crops (corn, sugar beet, wheat)	15-150	0.5-11
Biogas	30-70	1.5-4.5
Biodiesel (rapeseed, soy, sunflower)	15-65	0.5-4
FT-diesel from biomass[b]	110-160	8-12
Bioethanol from lignocellulose[b]	25-95	2-7

[a] The savings are related to gasoline (for bioethanol), diesel (for biodiesel).
[b] Technologies under development.
Source: Cherubini *et al*. (2009)

obtained with bioethanol and FT-diesel. Finally, when considering GHG savings per Ha of land, biomass used for heating purposes reveals larger outcomes than biofuels (Kaltschmitt, Reinhardt, & Stelzer, 1997).

4.3 Economic assessment of synthetic liquid and gaseous biofuels

First-generation biofuels are obtained from sugar conversion processes (i.e., fermentation), such as starch and vegetable oils of conventional arable energy crops – for example, wheat, corn, or sugarcane. Second-generation biofuels are instead the result of biomass transformation techniques that use the carbon cycle mainly from lignocellulosic biomass, woody crops, and agricultural residues or waste, including wastewater. Gasification techniques are mainly used in second-generation biofuels and can be listed as follows: thermochemical processes, pyrolysis, supercritical processes (for transesterification), and gasification processes. This section provides a brief discussion on the economic drivers (e.g., feedstock, capital costs, and prices) for gasification processes to obtain synthetic biofuels. In particular, the section gives an overview of the economic assessment for both liquid (e.g., advanced biodiesel, bioethanol, and algae fuels) and gaseous biofuels (e.g., syngas and synthetic natural gas (SNG)).

4.3.1 Biodiesel

4.3.1.1 Feedstock options and land use

Sun, Sun, and Tomkinson (2004) argue that global lignocellulosic material is about 85×10^9 t/year; and, as for biodiesel, lignocellulosic residuals are still under progress in the demonstration phase. Major ligno-cellulosic feedstock are summarized in Table 4.6.

Table 4.6 Lignocellulosic feedstock for biodiesel

Food crops	Energy crops	Forest residues	Industrial process residues
Rice straw	Cardoon	Tree residues	Rice
Wheat	Giant reed	Twigs	husk
Sugarcane tops	Salix	Leaves	bran
Maize stalks millet	Jute stalks	Bark	Sugarcane bagasse
Groundnut stalks	Willow	Roots	Coconuts
Corn straw	Poplar	Wood processing	Shells
Soybean residues	Eucalyptus	Sawmill off cuts	Husks
Residues	Miscanthus	Sawdust	Maize
from vegetables	Reed canary	Recycle wood	Cob
from pulses	grass	From building	Husks
	Switch grass	demolition	Groundnut husks
	Hemp	Pallets	
		Packing crates	

Source: Yousuf (2012).

As shown in Table 4.6, land for lignocellulosic feedstock is mainly used for energy crops, food crops, industrial processes, and forest residues. Lignocellulosic feedstock from land used for nutritional purposes would largely neglect the possibility to satisfy dietary needs with particular repercussions in developing countries and rural/marginal areas where the effect of food prices is larger than that of other countries due to the high marginal propensity to consume households' income for food purchases (FAO, 2008). To overcome this problem, most lignocellulosic feedstock comes from food crop residues where residues are collected at a later stage or soon after the harvest of primary food crops. In most cases, this second-step collection causes SOC to improve the concentration of nutrients in the soils, providing an increase in soil productivity and crop yield over time (Al-muyeed & Shadullah, 2010). However, although this is true for warm climatic regions, the opposite takes place in those regions with particular cold winters. In this latter case, crop residues collection provides soils to impoverish with consequent decreases in soil productivity and crop yields (USDA, 2006). Land use becomes unsustainable. Dedicated energy crops, on the other hand, show higher soil and nutrients productivity and higher yield crops than lignocellulosic feedstock from food crops. Therefore, there is a high expectation that these crops are considered in future productions for advanced biodiesel. To this end, famers should be encouraged to cultivate energy crops, although current economic crises prevents them from doing so. KPMG (2012) argues that most EU countries are cutting their subsidies for renewable energy purposes. It would be advisable for farmers to get other financial sources through, for example, transfers from the energy sector in addition to those actually received from central governments.

Forest residues in Table 4.6 refers to tree residues, residues from wood processing, and residues from recycling wood such as pallets or packing crates. These types of residues are considered to have high potential in future biodiesel production for avoiding competition with land use for nutritional purposes. Similar reasons can be advocated for lignocellulosic feedstock from industrial processes (e.g., mainly rice, maize, and coconuts processes), which provide relatively inexpensive collection costs in addition to the high sugar content of these residues that can be used for fermentation purposes.

A relatively important matter concerning biodiesel is water use. This issue received wide attention in first-generation production practices (FAO, 2008), but in the case of second-generation biodiesel this is still debated because water use can vary according to the type of feedstock used in the production process. Rowe, Street, and Taylor (2009) argue that water use is of no concern in the case of agricultural and forest residues, yet it affects the production (mostly) of energy crops due to a combination effect of longer roots and water transpiration rates than conventional or other crops. Finally, Jeswani and Azapagic (2012) argue that water use is rarely used in LCA due to a lack of available data for conventional crops and some of the lignocellulosic feedstock; nonetheless, some attempts have been made in terms of computing water footprint assessment (Jeswani & Azapagic, 2011).

4.3.1.2 Feedstock, capital, and other costs

This sub-section illustrates the feedstock, capital, and other costs for advanced biodiesel. The latest report by Asian-Pacific Economic Cooperation (APEC) (2010) shows relevant information on the economic and technology assumptions for various biofuels. In particular, the "economics" refers to the costs of production of a given biodiesel. In describing the main costs for advanced biodiesel, the attention will shift on biodiesel obtained from selected enzymatic feedstock from non-edible plant oils (i.e., jatropha and castor beans), waste oils, and oleaginous microorganisms. Economic assessment of biodiesel from algae is described in Section 4.3.3.

Table 4.7 shows the main costs for producing biodiesel in Malaysia over a 10-year period. Values are expressed per $/gallon and $/liter and refer to a plant in Sabah that

Table 4.7 **Economic costs of biodiesel production from jatropha**

Type of costs	$/Gallon	$/Liter
Feedstock	1.86	0.49
Capital Cost/Interest	0.33	0.09
Chemicals/Enzymes	0.18	0.05
Co-product Credits	−0.04	−0.01
Energy/Utility	0.03	0.01
Operations/Maintenance	0.14	0.04
Total	2.50	0.66

Source: APEC (2010).

produces 106 million liters/year (28 gallons/year of biodiesel), using palm and jatropha oil as main feedstocks, and that consumes $0.65 kWh of electricity, $0.77 MJ of natural gas, and obtains glycerine as a main by-product from its production. Feedstock costs of jatropha oil have a notable incidence in total costs ($0.49/L), followed by capital costs ($0.09/L), the costs for using necessary enzymes/chemical processes ($0.05/L), the costs of operation ($0.04/L).

Castor bean is one of the largest non-edible seeds. It is cultivated in China, Brazil, Russian Federation, Thailand, Ethiopia, and the Philippines. India, the largest producer, contributes about 60% of the world's demand (http://finance.indiamart.com/markets/commodity/castor_oil.html).

The National Program of Biodiesel Production and Use (PNPB) in Brazil states that vegetable oils used as raw materials for biodiesel production account for 75-85% of the total biodiesel production worldwide. Oliveira, Araujo, Rosa, Barata, and La Rovere (2008) assessed an economic evaluation of biodiesel from various raw materials in which castor beans accounted for 2.209 Brazilian Real/Liter for operating and maintenance (O&M) costs and 0.076 Brazilian Real/Liter for investment costs. The obtained yearly biodiesel production is approximately 58 million liters.

With reference to enzymatic feedstock (including non-edible plants), the study of Hama and Kondo (2013) illustrates relevant economic information. For a biodiesel production plant of small (8000 t/year) and large (200,000 ton/year) scale, the cost of feedstock ranges between 70% and 95% of total costs. Enzyme costs and O&M costs are 762.71 euros/kg-enzyme and 114,000 euros/year respectively, regardless of plant size.

4.3.2 Bioethanol

4.3.2.1 Feedstock options and land use

Pitkanen, Aristidou, Salusjarvi, Ruohonen, and Penttila (2003) disagree over the potential of lignocellulosic feedstock in supporting future sustainable production of liquid fuels in transportation systems. In supporting this assertion, Kim and Dale (2004) point out that 73.9 Teragrams (Tg) dry crop residues would be needed to produce 49.1 GL (Gigalitres)/year of bioethanol globablly, increasing actual production by 16 times. Furthermore, Prasad, Singh, Jain, and Joshi (2007), in discussing the role of bioethanol in the international market, assess that this could replace 353 GL of gasoline, almost one-third of actual worldwide gasoline consumption.

Most ethanol feedstock options rely on the use of grass residues, residues from arable land originating from primary crops (i.e., straw, maize, cotton stalks, oil seed crops, etc.), agricultural by-products (i.e., sugarcane, bagasse, barley hull, rice husks, etc.), forest residues (i.e., sawdust, forest thinning, wood residues), and dedicated energy crops (i.e., mischantus, switchgrass, etc.) (von Blottnitz & Curran, 2007). Table 4.8 illustrates feedstock options based on residues from arable land.

Table 4.8 Composition of arable crops for bioethanol production

Biomass	Residues/ crop ratio	DM (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Carbohydrates (%)	Ethanol (L Kg^{-1} DM)
Barley	1.2	81.0	-	-	9.0	70.0	0.31
Maize (stover)	1	78.5	45	35	15-19	58.3	0.29
Oats	1.3	90.1	-	-	13.7	59.1	0.26
Rice	1.4	88.0	40	18	5.5-7.1	49.3	0.28
Sorghum	1.3	88.0	-	-	15.0	61.0	0.27
Wheat	1.3	90.1	33-40	20-25	16-20	54.0	0.29
Bagasse	0.6	71.0			14.5	67.1	0.28

Source: Singh *et al*. (2010).

4.3.2.2 Feedstock, capital, and other costs

Due to the lack of adequate historical data for second-generation bioethanol production (the market is still in its infancy), most economic costs are based on simulated computations and modeling. Roy, Tokuyasu, Orisaka, Nakamura, & Shiina (2012) assessed a life cycle study to analyze the potential for bioethanol production from rice straw in Japan. The study considered a plant capacity of 15,000 m^3/year and an average transportation distance of 33-36 km from production to waste. Bioethanol was obtained through a fermentation and distillation process using enzyme and yeast. Estimated fixed costs – including depreciation, labor, maintenance, and interests – amounted to 33,800 ¥/m^3 (about 246,000 Euros/m^3) (exchange rate: 1 euro = 137.281) JPY (November 25, 2013). Littlewood, Murphy, and Wang (2013) argued on the economic feasibility of producing bioethanol from wheat straw in the UK. Considering a plant life of 30 years, the cost of wheat straw amounts to 45.7 £/t (around 56 euros/t) (exchange rate: 1 euro = 0.8362) GPB (November 25, 2013), with annual maintenance costs of 3% of total capital costs. The process employing the lowest minimum ethanol selling price (MESP) is wet oxidation with a cost of 0.347 £/L. The authors also argued that feedstock and enzyme costs contribute the most to shape total costs. The ranges are 36-56% and 18-43% of MESP for feedstock and enzyme costs, respectively. The authors also highlighted the strategic importance of policy support to lower feedstock costs. Sensitivity analysis offers a scenario of £35/t for wheat straw to enhance competitiveness with conventional fuels prices.

The work of Sanchez-Segado *et al.* (2012) examined the possibility to process bioethanol from carob pods (Ceratonia siliqua) in Spain. In the base case scenario, the plant process was assumed to operate 330 days/year, use 68,000 t/year of carob and 15,053 tones/year of ethanol, and produce 28.15 GWh/year of electricity. The prices of carob pod and ethanol were fixed at 0.17 euro/kg and 0.55/L, respectively; while the electricity credit amounted to 0.04 euro/kWh. The authors showed that a variation of the feedstock price (e.g., lower than 0.188 euro/kg) and a plant capacity greater than just about 45,000 tones/year would allow the whole process to be profitable and competitive compared to conventional fuels.

Wang, Sharifzadeh, Templer, and Murphy (2013) analyzed the economic feasibility of bioethanol from waste papers in the UK. In particular, the authors set up two base cases: the first one dealt with bioethanol from waste paper and the second one referred to bioethanol obtained from two pre-treatment processes such as dilute acid (for office paper) and oxidative lime (for newspaper). The model considered a plant using 2000 dry tone waste paper/day. The cost of waste paper was, on average, £44/t; and pre-treatment costs for sulphuric acid and lime amounted to £34.65/t and £71.94/t, respectively. Sensitivity analysis considered varying main cost parameters (total capital costs, feedstock costs, enzyme costs) within a range of ±30-50% and revealed that the MESP would be highly sensitive to variations in the process parameters such as solids loading and fermentation. These latter would reduce the MESP by 25% and 6% respectively, indicating a viable economic potential with petrol prices.

4.3.3 Algae fuels

Over the last years, emerging R&D has been looking into new ways to produce second-generation biofuels contributing both to the decrease of GHG emissions and to the possibility of leaving available lands for nutritional purposes only. For these reasons, microalgae have been receiving worldwide attention. The photosynthetic microorganisms are able to grow and live in extreme conditions and to reproduce fast. Microalgae can grow in terrestrial as well as aquatic environments. Richmond (2004) estimated the existence of more than 50,000 species and argued that just more than half are known to scientists.

Why use microalgae for biofuel purposes? The existing literature (Chisti, 2007; Li, Horsman, Wu, Lan, & Dubois-Calero, 2008) describes the advantages of microalgae used as feedstock for biodiesel production and for other purposes such as wastewater treatment removal, organic fertilizer after oil extraction in biomass processes (Wang, Li, Wu, & Lan, 2008), biochemical compounds in many industrial applications (Li *et al*., 2008), and several other potential applications for commercial purposes (Raja, Hemaiswarya, Kumar, Sridhar, & Rengasamy, 2008).

Despite recent events of peaked oil prices and financial market distortions, the interest in R&D for microalgae biodiesel has been increasing as well as the creation of a niche market for this type of feedstock (Torrey, 2008). Research has concentrated in finding ways to increase algae reproduction rates and identify species with high levels of productivity and lipid content (Rodolfi *et al*., 2009); further developments are also in search of optimal processes for oil extraction and cost reduction. In terms of extraction costs, De Lucia and Datta (2012), based on a study by Trostle (2008), argue that the average extraction costs (expressed in 2009 dollars) present the following figures: (1) productivity of 100 mt/ha/year; (2) lipid concentration of 35% by weight; (3) biodiesel yield of 10,421 gallons/ha; (4) capital costs of $112,400/ha; and (5) operating costs of $39,000/ha.

Biodiesel from microalgae is also attractive due to a series of other applications and products deriving from the microalgae production chain (De Lucia & Datta, 2012). Carbon dioxide recycling can be profitable and cost effective (Takeshita, 2011). The interesting work by Takeshita (2011) on worldwide competitiveness scenarios of algae diesel also shows relevant techno-economic values of extraction costs obtained via transesterification processes. Table 4.9 summarizes these findings.

Furthermore, Delrue *et al*. (2012) assessed a model of biodiesel production from microalgae for a plant in southeastern France, covering 333.3 ha of raceways (30 cm depth). The main technology assumed in their model was a hybrid photo-bio-reactor (PBR), with a capital cost in the range of 625-1875 euros/m^3. The biomass productivity in raceways ranges between 20 and 30 g/m^2/day; however, with the use of a PBR, it is assumed to be 1.25 kg/m^3/day according to the computations of Davis *et al*. (2008). An economic evaluation of this type of biodiesel from microalgae plant is shown in Table 4.10.

Despite the potential positive effects of algae fuels, uncertainties still exist in computing adequate figures for economic analysis. These uncertainties are mainly due to

Table 4.9 Extraction costs of biodiesel from algae through transesterification processes

Techno-economic parameters	**Unit**	**Value**	
		2010	**2050**
Capital costs	US$$_{2000}$/GJ of biodiesel	43.4	22.5
Operational costs	US$$_{2000}$/GJ of biodiesel	9.6	4.8
Process electricity demand[a]	kWh/GJ of biodiesel	−135.0	−56.9
Microalgae biodiesel yield	GJ of biodiesel/ha/yr	294-490	1029-1715

[a] Anaerobic digestion of microalgae residues is used to supply process electricity. Negative values indicate a net output of electricity, part of which is used to meet the process electricity demand for microalgal production.

Source: Takeshita (2011).

Table 4.10 Economic evaluation of biodiesel production with PBR technology

Parameter	**Method of calculations**
Capital Cost	***Various estimation methods and actual prices from manufacturers***
Cost of utilities	Actual prices of electricity, natural gas, nutrients, solvents, chemicals and utilities
Labour cost	$\text{Labour cost} = 10^6 \left(\frac{\text{Capital cost}}{10^6 \times 500}\right)^{0.2}$
Other costs	0.9% of the capital cost
Operating Cost	***Sum of the cost of utilities, the labour cost and the other costs***
General maintenance and storage costs	35% of the capital cost
Engineering cost	15% of the capital cost
Spare parts cost	15% of the capital cost
License fees	Fixed at 0.5 M€
Fixed Capital	*Sum of the capital cost, the general maintenance and storage costs, the engineering cost, the spare parts and the license fees*
Initial expenses	2% of the capital cost
Process start-up cost	25% of the operating cost
Additional Expenses	***Sum of initial expenses and process start-up cost***
Depreciable Capital	***Sum of the fixed capital and the additional expenses***
Annuities	20 years
Discount rate	8%/yr
Maintenance cost	4% of the capital cost per year
Taxes and insurances	2% of the capital cost per year
Business expenses	1% of capital cost per year
Fixed cost	***Sum of the pay-off, the return on investment, the maintenance cost, the taxes and insurances and the business expenses***
Total Operating Cost	***Sum of the operating cost and the fixed cost*** ***Can be converted in €/L of biodiesel***

Source: Delrue *et al*. (2012).

the presence of a niche market for harvesting and processing algae fuels, market price instabilities due to current economic crises, and adequate estimation of biomass yield. The cost of harvesting is complex. The correct selection of optimal microalgae nutritional components is essential in deciding which harvesting technique should be adopted. Concerns of actual market prices are mainly due to current biodiesel policies establishing blending contents. Finally, adequate policies can only be put into practice nationally or internationally depending on how fast R&D moves to the commercialization stage.

4.3.4 Biogas fuels

This section deals with economic assessment of biogas fuels from biomass. In particular, it briefly underlines the role of gasification in biomass transformation processes and provides an indication of an impact assessment of biogas (e.g., syngas and SNG), a processed hydrogen from biomass obtained in biomass-to-liquid (i.e.. Fischer-Tropsch) and SNG technologies (i.e., extension to existing CHP steam plants).

4.3.4.1 The role of gasification

Gasification is an important part of the transformation process from feedstock to biogas fuels. During gasification, the feedstock is transformed at high temperatures via thermal energy, which can be provided either directly (e.g., endogenously using the combustion of the carbon content within the feedstock) or indirectly through a conductor. Further sub-processes (e.g., drying, pyrolitic decomposition, oxidation, and reduction) take place to obtain hydrogen or synthetic gas. These then undergo a cleaning process to obtain syngas. Syngas is a by-product, an intermediate of production, through which synthesis technologies (i.e., Fischer-Tropsch, Dimethyether) are transformed into liquid forms to obtain bioliquid fuels.

4.3.4.2 Economic assessment of syngas

Trippe, Fröhling, Schultmann, Stahl, & Henrich (2011) argued that given the early stage of technological investments in second-generation biofuel production, data availability and comparability on cost effectiveness of gasification processes is almost non-existent. Generally, an economic assessment is based on the definition of mass and energy balances. These determine the necessary system boundaries, the main energy input assumptions, the heat coefficients and parameters, and the primary chemical components for which a gasification process should be investigated. Tables 4.11 and 4.12 show the percentages of capital investments and maintenance costs for a 1000 MW capacity biomass plant (Trippe *et al.*, 2011). Table 4.12, in particular, shows that gasifier and other appliances constitute a larger share in total maintenance costs (5% compared to other costs).

Table 4.11 **Shares of capital costs in biomass production with gasification processes**

Percentage of investment for main equipment components	
Direct investments	%
Investment for installed main equipment components	100
Instrumentation and controls	24
Piping	46
Electrical systems	8
Buildings	12
Yard improvements	7
Service facilities	48
Total direct investment	245
Indirect investments	%
Engineering and supervision	22
Construction expenses	28
Legal expenses	3
Contractor's fee	15
Contingency	30
Total indirect investment	98
Fixed Capital Investment (FCI)	343

Source: Adapted from Trippe *et al.* (2011).

Table 4.12 **Shares of maintenance costs in biomass production with gasification processes**

Functional unit	**Mantainance costs as % of fixed capital investments (%)**
Slurry handling and feed	2
Optional coal handling and feed preparation	2
Air separation unit (cyrogenic)	5
Cooling and quench water system	5
Optional steam gasification equipment	5
Gasifier	5
Wet raw syngas treatment	5
Slag recovery and handling	2

Source: Adapted from Trippe *et al.* (2011).

4.3.4.3 Economic assessment of SNG

Heyne and Harvey (2013) defined an energy system framework to compare alternative market scenario hypotheses of processes for the production of SNG from biomass. In particular, the authors estimated the investment opportunities (i.e., opportunity costs to reach the annual break-even point) in extending an existing CHP plant (assuming that the plant is fully operative for 5000 h/year) to SNG production. To do this, the authors relied on market policy scenarios (low and high cuts in emissions due to current policies) based on the World Energy Outlook of the IEA (2011). Table 4.13 summarizes the energy market scenarios and Figure 4.1 shows relevant investment opportunity results for the scenarios illustrated in Table 4.13.

Results from simulation analysis in Figure 4.1 show that the opportunity costs to invest in SNG technologies from existing CHP plants are unlikely to take place, given

Table 4.13 Energy market scenarios for SNG production

Scenario	**Unit**	**Scenario 1 (Low)**	**Scenario 2 (Low)**	**Scenario 3 (High)**	**Scenario 4 (High)**
Fossil fuel price level (input)[a]					
Crude oil	€2005/MWh$_{LHV}$	40	40	55	55
Natural gas	€2005/MWh$_{LHV}$	22	22	28.5	28.5
Coal	€2005/MWh$_{LHV}$	6.5	6.5	10	10
CO_2 charge (input)	€2005/MWh$_{LHV}$	27	85	27	85
End user prices and policy instruments					
Wood fuel (forest residue)	€2005/MWh$_{LHV}$	24	44	28	48
Electricity (incl. CO_2 charge)	€2005/MWh$_{el}$	51	67	58	77
Natural gas (incl. CO_2 charge)	€2005/MWh$_{LHV}$	32	45	39	51
Reference electricity production technology		Coal	Coal, CCS	Coal	Coal, CCS
District heating[b]	€2005/MWh$_{q}$	51	71	53	72
Renewable electricity support (input)	€2005/MWh$_{el}$	20	20	20	20
CO_2 emissions					
Electricity	Kg CO_2/MWh$_{el}$	679	129	679	129
Biomass	Kg CO_2/ MWh$_{LHV}$	336	336	336	336
Natural gas	Kg CO_2/ MWh$_{LHV}$	202/217	202/217	202/217	202/217
District heating	Kg CO_2/MWh$_{q}$	156	387	156	387

[a] Further information in Heyne and Harvey (2013).
[b] Average value for Europe.
Source: Heyne and Harvey (2013).

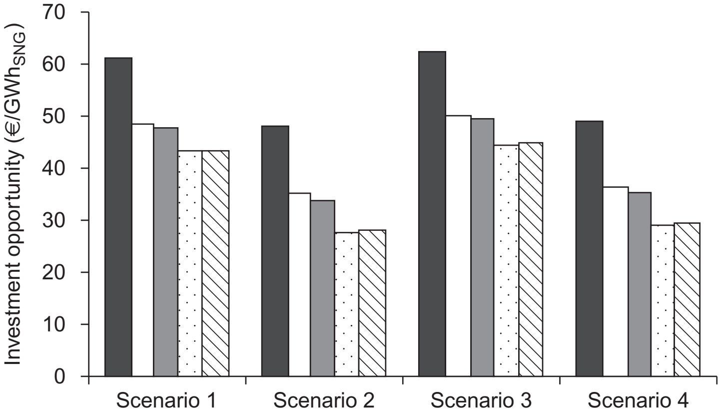

Figure 4.1 Investment opportunities for SNG production. Notes: Black, stand-alone combined heat and power existing plant; White, steam drying with balancing integration technology; Grey, steam drying with maximum integration technology; Dotted, low-temperature air drying with balancing integration technology; Dashed, low-temperature air drying with maximum integration technology.
Source: Heyne & Harvey, 2013

that the difference between the "old" and "new" technology is relatively small to reach the break-even point (Heyne & Harvey, 2013). Biofuel support policies for enhancing the production and commercialization of second-generation biofuels become essential to convert niche markets in competitive markets.

4.4 The role of sustainability assessment in supporting international biofuel policies

The emerging need for energy security and prevention of environmental disasters has pushed governments to adopt support policies in favor of renewable energy sources (De Lucia & Datta, 2012; Escobar *et al.*, 2009). In the European Union, the Renewable Energy Directive (Directive 2009/28/EC), also known as the "20-20-20" strategy, sets the objective of reaching a further 20% reduction of GHG emissions (in addition to the commitments of the Kyoto Protocol) with 20% use of renewable energy by the year 2020. For biofuels, this would require saving at least 35% of GHGs from fossil fuel during the period from 2013 until 2020, up to almost 60% around the end of the post-Kyoto period. In terms of blending mandates for automotive fuel consumption the 20-20-20 strategy includes a 10% target by the year 2020. Other countries – such as China, India, and South Africa – have followed the example of the European Union or the United States setting sustainability policies in support of increasing demand in biofuel products (De Lucia & Datta, 2012).

In the United States, the Energy Independence and Security Act of 2005, subsequently modified in 2007 (EPA, 2007), set a target of 36 billion gallon of renewable fuels for road transport by the year 2022. To reach this target, about 58% of renewable energy would come from lignocellulosic feedstock and other biofuels of second generation. According to the Renewable Fuel Standard program (EPA, 2007), the use of wood feedstock would require up to 60.6 billion/L/year to ensure a reduction of 100 million tones of CO_2/year by 2022 (IEA, 2010).

It is clear that advanced biofuels would require more sophisticated processing equipment (i.e., for feedstock production and conversion), investments in R&D and demonstration works, and reduction of capital and unit costs of production to accomplish the promising benefits to society and to ensure their contribution to the achievement of policy and environmental targets. Sustainability assessment plays an essential role in support of policymakers' strategies. From a societal point of view, distorted information would negatively affect pricing and tax policies and provide bad repercussions on farmers' behaviors. Most of second-generation biofuel markets are considered niche markets and therefore are still in infancy in their structure.

Sustainability assessments achieve more information on processing feedstock and respond to the many alternatives and options posed by the markets. Many feedstock combinations include mixed output products, for example, and necessitate a detailed allocation of benefits, costs, and impacts among products, by-products, and residues of the production (McKone *et al.*, 2011). It is also important that sustainability assessment studies disclose information to reveal non-market values that otherwise would remain unknown in competitive markets. This is of particular relevance in developing countries where second-generation biofuels have the great potential to be produced and processed over the next years (Demirbas, 2008). Generally, small-scale farmers as well as big companies rely on market prices (other than public incentives) from energy crops or the lands on which these are cultivated. In the case when energy crops or land prices are estimated because a proper market does not yet exist, producers and investors would be unlikely to invest and benefit from lignocellulosic feedstock and preserve available lands for nutritional purposes. Sustainability assessment approaches become essential to determine the best option to accurately combine glucose through cellulose hydrolysis processes and obtain reduction in total costs, fermentation processes, and increases in energy content.

One of the prominent second-generation biofuel types that could potentially be produced at large scale over the next years are those known as *biomass-to-liquid* (BTL) fuels. Germany could reach almost 4 million tons of BTL production over the next years (Spielmann, Dones, Bauer, & Tuchschmid, 2007) with a corresponding 10% BTL market share in Europe by the end of 2015 (Swain, Das, & Naik, 2011). This will greatly contribute to the achievements of the 20-20-20 EU energy strategy. Major drawbacks for BTL production are mainly high investment costs, lack of adequate infrastructures and logistics to create opportunities to meet demand and supply, and low energy content of woody biomass. Sustainability assessment is advocated to overcome these problems by better understanding the processes for catalytic conversion of lignocellulosic feedstock into liquid oils and the possibility to guarantee a large-scale production of BTL.

Biorefinery could be seen as a viable solution for large-scale BTL and other lignocellulosic feedstock productions. The biorefinery concept is gradually taking place in current markets and research due its complementarity with existing industries. The development of biorefineries over the next decade, in particular in developing countries owning large supply of biomass, can create employment opportunities and sustain the quality of life in suburban and rural areas (Cherubini *et al.*, 2009; De Lucia & Datta, 2012). Cherubini *et al.* (2009) emphasized the importance of life cycle analysis for biorefineries, but very few LCA studies currently exist in the literature. Preliminary approaches to LCA for biorefineries based on lignocellulosic biomass indicate that these could save up to 60% of GHG emissions (Cherubini & Jungmeier, 2008).

The issue of job creation from biofuel plants is somewhat controversial. van der Horst and Vermeylen (2011) argue that the switch to energy crops may not result in net gains for small farmers or for new employees in rural/marginal areas. There is little or no access to financial credit services to rural communities that would allow the possibility of capital accumulation and investments for existing land conversion into energy crops. Furthermore, the volatility of prices for food commodities or energy inputs (as it has been seen over the last years) will discourage farmers from switching their lands into alternative crops rather than nutritional ones.

How can sustainability assessment help deal with the land issue and address adequate policy intervention? ILUC effects have received considerable attention over the last years in current research (Cherubini *et al.*, 2011; Fritsche, 2010; McKone *et al.*, 2011; European Commission, 2012). ILUC from biomass production could potentially affect deforestation or induce displacement effects of land already used for food purposes. Furthermore, the issue for advanced biofuels to use marginal lands is also contentious. How does one achieve optimal availability of marginal lands? What are the alterations in SOC? How much nutrient and water content would be needed to cultivate biomass energy crops in marginal lands such that biofuel production is efficient and sustainable over time? These questions remain unanswered due to lack of data availability and empirical applications. LCAs of biofuels, through increasing the number of indicators and indices and providing a more detailed interpretation of results and inventories (Cherubini *et al.*, 2011), may be a viable option to address the preceding questions by looking at biofuels and agriculture as a synergic system that can offer successful bi- or multidirectional relationships with the policymaker. Computation of ILUC effects in LCA would provide the possibility to establish adequate land use policies in the light of current climate change economic instruments such as the clean development mechanism (CDM). The CDM implies the possibility for a developed country to invest in carbon-free projects in developing countries to counterbalance CO_2 deficits. There still exists a small number of CDM projects for biofuels approved by the executive board of the United Nations (UNFCCC, 2013). LCA inventories, which account for ILUC and adequate economic assessment, may turn out to be strategic tools for the approval of further CDMs in advanced biofuels.

4.5 Conclusions

This chapter aimed at presenting a discussion on important economic, environmental, and policy aspects of sustainability assessment for second-generation biofuels. The limited potentials of first-generation biofuels to reduce greenhouse gas emissions, the increasing competition for land for food versus energy crops, and the current economic crises that have provided general discomfort to agents' expectations have accompanied a sense of urgency to find new solutions and new investment opportunities to follow sustainable development paths. One of these opportunities rely on the enhancement of second-generation biofuels,which are less intensive in land and input requirements, thus providing a more favorable vision of GHG reductions. This vision would not find its way without consistent and proper techno-economic analysis throughout the entire life of a biofuel chain. Evaluating the potentials and limitations of sustainability assessment for biofuels (e.g., biodiesel, ethanol, algae fuels, and biogas) has been the main objective of the chapter.

Important potentials for advanced biodiesel and algae biodiesel derive from an accurate study on the feedstock used in production processes and their costs. Second-generation biofuels feedstock consist primarily of lignocellulosic residues from crops, forests, and wastes. In terms of feedstock costs, it has been observed that non-edible plant oils, waste oils, and oleaginous microorganisms have a great potential for advanced biodiesel production. Furthermore, considerable research exists on biodiesel production from microalgae. These present important possibilities in terms of reproductive rates, energy contents, and yield increases.

The use of bioethanol on a global scale could replace 353 GL of gasoline, almost one-third of actual worldwide gasoline consumption. Sustainability assessment varies according to the feedstock used, and the economic assessment of costs is generally limited by the lack of historical and actual data on cellulosic biomass markets. In conducting sustainability assessment for bioethanol, one should consider the following main criteria: availability of biomass residues, land composition, costs to plant, costs to harvest, and transportation costs. As for forest residues, costs also include logging methods (e.g., short versus tree length). Also major costs are attributable to transportation, still considered high for second-generation biomass from forest residues. The correct definition of these costs will also be influenced by variations in energy fluxes and GHG emissions. These,in turn, are affected by employing adequate process techniques. Capital costs and chemical process costs represent major costs in second-generation bioethanol production (i.e., in the case of switchgrass feedstock).

This chapter also compared biodiesel, biofuels, and algae fuels against the economic assessment of biogas fuels from biomass. Gasification assumes an important role in transforming feedstock to biogas fuels because, according to the technology used in the process, important effects would occur in terms of energy requirements and GHG balances. In addition, support policies for enhancing the production and commercialization of second-generation biofuels are essential to convert niche markets in competitive markets.

Also, this chapter underlined the interlinked relationships between sustainability assessment and policy repercussions. Generally, sustainability assessment supports the decision maker in implementing adequate policies. Distorted information would negatively affect pricing and tax policies and have negative repercussions on farmers' behaviors. Sustainability assessment achieves more information on processing feedstock and responds to the many alternatives and options posed by markets. It is also important that sustainability assessment reveals information on non-market values in order for farmers to have the opportunity to invest in second-generation biofuels.

The issue of job creation from biofuels seems controversial. The switch to energy crops may not produce net gains for small farmers because of the limited credit access that these people have in rural areas. Policymakers need to consider carefully which goals to pursue in providing support to different biofuels. Funding will provide an essential support policy to boost opportunity investments in developing countries.

The chapter also discussed the links between the environment and LCAs and the impact of LCA on energy. In particular, life cycle analysis provides computations and data for GHG balances that show the amount of GHG releases from a given technology employed in the production process.

Main impacts of LCA on energy can generally be defined considering energy balances, efficient biomass use, net savings of fossil fuels, and GHG per Ha of land used for energy crops. Also, energy balances for bioenergy systems show proper indicators of energy performance describing which production chain is more efficient than others, according to crop and fertilizer use, irrigation techniques and water requirements, feedstock, and energy processes. Finally, given the relative importance of biomass sources to current biofuels in global market competition, a comparison between these sources would ensure the best selection across bioenergy system applications.

4.6 Future trends

What are the main challenges that sustainability assessment on biofuels should meet in the coming decades? Current literature suggests both technical and socioeconomic visions. For the first one, LCA studies should take into account more indirect effects from land use change. This is because biomass production for biofuels could have negative repercussions on deforestation rates and the carbon content in soils. The magnitude that these changes have on climate change still remains a debated issue. In particular, an LCA study should quantify what levels of nutrients are needed to produce biofuels in a sustainable way; how water constraints and climatic variability influence farmers' choices in their management practices; and how changes in dietary needs would affect land use for biofuel production. Also, LCA for biorefineries should be addressed, given the importance that the biorefinery concept will achieve over in the future. Further research should also address the question of how indirect land use impacts biofuels production. In particular, an assessment of the temporal dimension of indirect effects has not been investigated yet as well as concerns over biodiversity loss and standardization of GHG emissions. A step toward this direction has been made by the Land Use, Land Use Change and Forestry (LULUFC), which has seen its definitions set during the COP 7 (Conference of Parties) of the Kyoto Protocol in 2001 (Marrakesh Accords). The UNFCCC Secretariat has provided parties with the implementation of an inventory that covers GHG emissions and removals from forest, cropland, and grazing land management. To date, legislation setting accounting rules is still in progress, although in 2012, the European Union set a Proposal for a Decision on Accounting rules and actions. Inclusion of these rules in LCA would certainly benefit the quantification and valuation of biofuels processes.

Finally, under a socioeconomic point of view, sustainability assessment seemscontroversial. van der Horst and Vermeylen (2011) contrast the positive view that biofuels production creates employment opportunities. The real question would seem to be: At what cost? Many indigenous people living in Latin American communities have suffered from price increases of food commodities, land conversion practices for energy crops, and rainforest cuts. A standard method to evaluate these external effects does not yet exist. Current environmental economic practices invoke the principle of nonmarket valuation for resources and commodities having no market. The social impacts mentioned previously would certainly affect the value of lands, and these would reflect changes of feedstock and land prices. However, considering the technical skills required to conduct a sustainability assessment, the incorporation of all these uncovered social and environmental effects would require more interdisciplinary analysis across subjects, methods, and scientists.

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Gasification reaction kinetics for synthetic liquid fuel production

5

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5.1 Introduction

Essentially the gasification of coal or coal char is the conversion of coal by any one of a variety of chemical processes to produce combustible gases (Higman & Van der Burgt, 2008; Speight, 2008, 2013a). With the rapid increase in the use of coal from the fifteenth century onward, it is not surprising that coal was used to produce a flammable gas for domestic heating, industrial heating, and power generation. The use of water and hot coal especially became commonplace in the nineteenth and twentieth centuries (Speight, 2013a, 2013b).

Coal gasification includes a series of reaction steps that convert coal (composed of carbon, hydrogen, and oxygen as well as impurities such as sulfur-containing and nitrogen-containing moieties and metallic constituents) into *synthesis gas* (*syngas*, $CO + H_2$) and hydrocarbons. This conversion is generally accomplished by introducing a gasifying agent (air, oxygen, and/or steam) into a reactor vessel containing coal feedstock where the temperature, pressure, and flow pattern (moving bed, fluidized, or entrained bed) are controlled. However, there are gases other than carbon monoxide and hydrogen. The proportions of the resultant product gases – such as carbon dioxide (CO_2), methane (CH_4), water vapor (H_2O), hydrogen sulfide (H_2S), and sulfur dioxide (SO_2), but including carbon monoxide (CO) and hydrogen (H_2) – depends on the type of coal and its composition, the gasifying agent (or gasifying medium), and the thermodynamics and chemistry of the gasification reactions as controlled by the process operating parameters (Shabbar & Janajreh, 2013; Singh, Weil, & Babu, 1980; Speight, 2013a, 2013b).

The kinetic rates and extents of conversion for the several chemical reactions that are a part of the gasification process are variable and are typically functions of (1) temperature, (2) pressure, (3) reactor and configuration, (4) gas composition, and (5) the nature – chemical composition and properties – of the coal being gasified (Johnson, 1979; Müller, von Zedtwitz, Wokaun & Steinfeld, 2003; Penner, 1987; Slavinskaya, Petrea, & Riedel, 2009; Speight, 2013a, 2013b).

Generally, the reaction rate (i.e., the rate of coal conversion) is higher at higher temperatures, whereas reaction equilibrium may be favored at either higher or lower temperatures, depending on the specific type of gasification reaction. The effect of pressure on the rate also depends on the specific reaction. Thermodynamically, some

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gasification reactions such as carbon-hydrogen reaction producing methane are favored at high pressures (>1030 psi) and relatively lower temperatures (760-930 °C; 1400-1705 °F), whereas low pressures and high temperatures favor the production of synthesis gas (i.e., carbon monoxide and hydrogen) via steam or carbon dioxide gasification reaction.

Because of the overall complexity of the gasification process, it necessary to present a description of the chemistry of the gasification reactions. It is the purpose of this chapter to present descriptions of the various reactions involved in (coal) gasification as well as the various thermodynamic aspects of these reactions that dictate the process parameters used to produce the various gases.

5.2 General chemistry of gasification

Chemically, coal gasification involves the thermal decomposition of coal and the reaction of the coal carbon and other pyrolysis products with oxygen, water, and fuel gases such as methane (Table 5.1). In fact, coal gasification is often considered to involve two distinct chemical stages: (1) devolatilization of the coal to produced volatile matter and char followed by (2) char gasification, which is complex and specific to the conditions of the reaction. Both processes contribute to the complex kinetics of the gasification process (Sundaresan & Amundson, 1978).

Thus, in the initial stages of coal gasification, the rising temperature of the feedstock initiates devolatilization and the breaking of weaker chemical bonds to yield volatile tar, volatile oil, phenol derivatives, and hydrocarbon gases. These products generally react further in the gaseous phase to form hydrogen, carbon monoxide, and carbon dioxide. The char (fixed carbon) that remains after devolatilization reacts

Table 5.1 Coal gasification reactions

$2C + O_2 \longrightarrow 2CO$
$C + O_2 \longrightarrow CO_2$
$C + CO_2 \longrightarrow 2CO$
$CO + H_2O \longrightarrow CO_2 + H_2$ (shift reaction)
$C + H_2O \longrightarrow CO + H_2$ (water gas reaction)
$C + 2H_2 \longrightarrow CH_4$
$2H_2 + O_2 \longrightarrow 2H_2O$
$CO + 2H_2 \longrightarrow CH_3OH$
$CO + 3H_2 \longrightarrow CH_4 + H_2O$ (methanation reaction)
$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$
$C + 2H_2O \longrightarrow 2H_2 + CO_2$
$2C + H_2 \longrightarrow C_2H_2$
$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$

with oxygen, steam, carbon dioxide, and hydrogen. Overall, the chemistry of coal gasification is conveniently (and simply) represented by the following reaction:

$$C + O_2 \rightarrow CO_2 \quad \Delta H_r = -393.4\,\text{MJ/kmol} \tag{1}$$

$$C + ½O_2 \rightarrow CO \quad \Delta H_r = -111.4\,\text{MJ/kmol} \tag{2}$$

$$C + H_2O \rightarrow H_2 + CO \quad \Delta H_r = 130.5\,\text{MJ/kmol} \tag{3}$$

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H_r = 170.7\,\text{MJ/kmol} \tag{4}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H_r = -40.2\,\text{MJ/kmol} \tag{5}$$

$$C + 2H_2 \rightarrow CH_4 \quad \Delta H_r = -74.7\,\text{MJ/kmol} \tag{6}$$

The designation C represents carbon in the original coal as well as carbon in the char formed by devolatilization of the coal. Reactions (1) and (2) are exothermic oxidation reactions and provide most of the energy required by the endothermic gasification reactions (3) and (4). The oxidation reactions occur very rapidly, completely consuming all of the oxygen present in the gasifier, so that most of the gasifier operates under reducing conditions. Reaction (5) is the water-gas shift reaction, in which water (steam) is converted to hydrogen. This reaction is used to alter the hydrogen/carbon monoxide ratio when synthesis gas is the desired product, such as for use in Fischer-Tropsch processes. Reaction (6) is favored by high pressure and low temperature and is therefore mainly important in lower temperature gasification systems. Methane formation is an exothermic reaction that does not consume oxygen and therefore increases the efficiency of the gasification process and the final heat content of the product gas. Overall, approximately 70% of the heating value of the gas product is associated with the carbon monoxide and hydrogen but this varies depending on the gasifier type and the process parameters (Chadeesingh, 2011).

Basically, the direction of the gasification process is subject to the constraints of thermodynamic equilibrium and variable reaction kinetics. The combustion reactions (reaction of coal or char with oxygen) essentially go to completion. The thermodynamic equilibrium of the rest of the gasification reactions are relatively well defined and collectively have a major influence on thermal efficiency of the process as well as on the gas composition. Thus, thermodynamic data are useful for estimating key design parameters for a gasification process, such as (1) calculating the relative amounts of oxygen and/or steam required per unit of coal feedstock, (2) estimating the composition of the produced synthesis gas, and (3) optimizing process efficiency at various operating conditions.

Other deductions concerning gasification process design and operations can also be derived from the thermodynamic understanding of its reactions. Examples include (1) production of synthesis gas with low methane content at high temperature, which requires an amount of steam in excess of the stoichiometric requirement; (2) gasification at high temperature, which increases oxygen consumption and decreases the overall process efficiency; and (3) production of synthesis gas with a high methane content, which requires operation at low temperature (approximately 700 °C, 1290 °F) but the methanation reaction kinetics will be poor without the presence of a catalyst.

Relative to the thermodynamic understanding of the gasification process, the kinetic behavior is much more complex. In fact, very little reliable global kinetic information on coal gasification reactions exists, partly because it is highly dependent on (1) the process conditions and (2) the chemical nature of the coal feed, which varies significantly with respect to composition, mineral impurities, and reactivity. In addition, physical characteristics of the coal (or char) also play a role in phenomena such boundary layer diffusion, pore diffusion, and ash layer diffusion, which also influence the kinetic picture. Furthermore, certain impurities are known to have catalytic activity on some of the gasification reactions, which can have further influence on the kinetic imprint of the gasification reactions.

5.2.1 Devolatilization

Devolatilization occurs rapidly as the coal is heated above 400 °C (750 °F). During this period, the coal structure is altered, producing solid char, tars, condensable liquids, and low molecular weight gases. Furthermore, the products of the devolatilization stage in an inert gas atmosphere are very different from those in an atmosphere containing hydrogen at elevated pressure. In a hydrogen atmosphere at elevated pressure, additional yields of methane or other low molecular weight gaseous hydrocarbon can result during the initial coal gasification stage from reactions such as (1) direct hydrogenation of coal or semi-char because of active intermediate formed in coal structure after coal pyrolysis, and (2) the hydrogenation of other gaseous hydrocarbons, oils, tars, and carbon oxides. Again, the kinetic picture for such reactions is complex due to the varying composition of the volatile products which, in turn, are related to the character of the coal feedstock and the process parameters, including the reactor type.

5.2.2 Char gasification

After the rate of devolatilization has passed, another reaction becomes important. In this reaction, the semi-char is converted to char (sometimes erroneously referred to as *stable char*) primarily through the evolution of hydrogen. Thus, the gasification process occurs as the char reacts with gases such as carbon dioxide and steam to produce carbon monoxide and hydrogen. The resulting gas (producer gas or synthesis gas) may be more efficiently converted to electricity than is typically possible by direct combustion of the. Also, corrosive ash elements such as chloride and potassium may be refined by the gasification process, allowing high temperature combustion of the gas from otherwise problematic coal feedstocks (Speight, 2013a, 2013b).

Oxidation and gasification reactions consume the char, and the oxidation and the gasification kinetic rates follow Arrhenius-type dependence on temperature; the kinetic parameters are coal-rank-specific and there is no true global relationship to describe the kinetics of coal (char) gasification. The complexity of the reactions makes the reaction initiation and the subsequent rates subject to many factors, any one of which can influence the kinetic aspects of the reaction.

Although the initial gasification stage (devolatilization) is completed in seconds or even less at elevated temperature, the subsequent gasification of the coal char produced at the initial coal-gasification stage is much slower, requiring minutes or hours to obtain significant conversion under practical conditions. Reactor designs for commercial gasifiers are largely dependent on the reactivity of the coal char and also on the gasification medium rate (Johnson, 1979; Penner, 1987; Sha, 2005). Thus, the distribution and chemical composition of the products are also influenced by the prevailing conditions (i.e., temperature, heating rate, pressure, residence time, etc.) and, last but not least, the nature of the feedstock. Also, the presence of oxygen, hydrogen, water vapor, carbon oxides, and other compounds in the reaction atmosphere during pyrolysis may either support or inhibit numerous reactions with coal and with the products evolved.

The reactivity of char produced in the pyrolysis step depends on the nature of parent coal. It increases with oxygen content of parent coal but decreases with carbon content. In general, char produced from low-rank coal is more reactive than char produced from high-rank coal. The reactivity of char from low-rank coal may be influenced by catalytic effect of mineral matter in char. In addition, as the carbon content of coal increases, the reactive functional groups present in coal decrease and the coal substance becomes more aromatic and cross-linked in nature (Speight, 2013a). Therefore, char obtained from high-rank coal contains a lesser number of functional groups and a higher proportion of aromatic and cross-linked structures, which reduce reactivity. The reactivity of char also depends on the thermal treatment it receives during formation from the parent coal. The gasification rate of char decreases as the char preparation temperature increases due to the decrease in active surface areas of char. Thus, a change of char preparation temperature may change the chemical nature of char, which, in turn, may change the gasification rate.

Typically, char has a higher surface area compared to the surface area of the parent coal. The surface area changes as char undergoes gasification, increasing the surface area with carbon conversion, reaching maximum, and then decreasing. These changes, in turn, affect gasification rates. In general, reactivity increases with the increase in surface area. The initial increase in surface area appears to be caused by clean-up and widening of pores. The decrease in surface area at high carbon conversion may be due to coalescence of pores, which ultimately leads to collapse of the pore structure.

Furthermore, char reactivity is also influenced by the catalytic effect of mineral matter in char. The reactivity of lignite char, which had been initially treated with acid to remove mineral constituents, was much lower than the corresponding reactivity exhibited by untreated char. However, this phenomenon has not been observed with char from bituminous and sub-bituminous coal (Speight, 2013a, 2013b, and references cited therein). The behavior of the lignite char may be the result of the catalytic effect of sodium or calcium combined with carboxyl functional groups in the organic structure of the lignite. Given that the concentration of carboxyl functional groups decreases significantly with increasing coal rank, this catalytic effect would predominate in lignite and would decrease rapidly with increasing coal rank.

Heat transfer and mass transfer processes in fixed or moving bed gasifiers are affected by complex solids flow and chemical reactions. Coarsely crushed coal settles while undergoing heating, drying, devolatilization, gasification, and combustion. Coal particles change in diameter, shape, and porosity – non-ideal behavior may result from coal bridges, gas bubbles, and channel, and a variable void fraction may also change heat and mass transfer characteristics.

An important issue is the significance of the pyrolysis temperature as a major factor in the thermal history, and consequently in the thermodynamics of the coal chars. However, the thermal history of a char should also depend on the rate of temperature rise to the pyrolysis temperature and on the length of time the char is kept at the pyrolysis temperature (soak time), which might be expected to reduce the residual entropy of the char by employing a longer soak time.

5.2.3 Products

If air is used for combustion, the product gas will have a heat content on the order of 150-300 Btu/ft^3 depending on process design characteristics and will contain undesirable constituents such as carbon dioxide, hydrogen sulfide, and nitrogen. The use of pure oxygen results in a product gas having a heat content of 300-400 Btu/ft^3 with carbon dioxide and hydrogen sulfide as by-products, both of which can be removed from low-heat content or medium-heat content – low-Btu or medium-Btu gas (Table 5.2) – by any of several available processes (Mokhatab, Poe, & Speight, 2006; Speight, 2013a, 2014).

If high-heat content (high-Btu) gas (900-1000 Btu/ft^3) is required, efforts must be made to increase the methane content of the gas. The reactions that generate methane are all exothermic and have negative values, but the reaction rates are relatively slow, and catalysts may therefore be necessary to accelerate the reactions to acceptable commercial rates. Indeed, it is also possible that the mineral constituents of coal and char may modify the reactivity by a direct catalytic mechanism. The presence of oxygen, hydrogen, water vapor, carbon oxides, and other compounds in the reaction

Table 5.2 **Coal gasification products**

Product	Characteristics
Low-Btu gas (150-300 Btu/scf)	Around 50% nitrogen with smaller quantities of combustible H_2 and CO, CO_2 and trace gases, such as methane
Medium-Btu gas (300-550 Btu/scf)	Predominantly CO and H_2, with some incombustible gases and sometimes methane
High-Btu gas (980-1080 Btu/scf)	Almost pure methane

atmosphere during pyrolysis may either support or inhibit numerous reactions with coal and with the products evolved.

5.3 Process chemistry

5.3.1 General aspects

In a gasifier, the coal particle is exposed to high temperatures generated from the partial oxidation of the carbon. As the particle is heated, any residual moisture (assuming that the coal has been pre-fired) is driven off, and further heating of the particle begins to drive off the volatile gases. Discharge of the volatile products will generate a wide spectrum of hydrocarbons ranging from carbon monoxide and methane to long-chain hydrocarbons comprising tars, creosote, and heavy oil. The complexity of the products will also affect the progress and rate of the reaction, as each product is produced by a different chemical process at a different rate. At a temperature above 500 °C (930 °F), the conversion of the coal to char, and ash and char, is completed. In most of the early gasification processes, this was the desired by-product, but for gas generation, the char provides the necessary energy to effect further heating. Typically, the char is contacted with air or oxygen and steam to generate the product gases.

Furthermore, with an increase in heating rate, coal particles are heated more rapidly and are burned in a higher temperature region, but the increase in heating rate has almost no substantial effect on the mechanism. Also, the increase in the heating rate causes a decrease in the activation energy value. Activation energy values were calculated by various well-known methods at different fractions from 90% to 15% of the original coal within the temperature range of about 400-600 °C (750-1110 °F), and the Coats-Redfern approach showed the highest value of activation energy, whereas the Freeman-Carroll method showed the least value of activation energy for every fraction of converted coal (Irfan, 2009).

The most notable effects in the physical chemistry of coal gasification are those effects due to coal character, and often those effects relate to the maceral type and maceral content (Speight, 2013a, 2013b). With regard to the maceral content, differences have been noted between the different maceral groups, with inertinite being the most reactive (Huang *et al.*, 1991). In more general terms of the character of the coal, gasification technologies generally require some initial processing of the coal feedstock with the type and degree of pretreatment being a function of the process and/or the type of coal. For example, the Lurgi process will accept lump coal (1 in., 25 mm, to 28 mesh), but it must be non-caking coal with the fines removed. Caking or agglomerating coals tend to form a plastic mass in the bottom of a gasifier and subsequently plugs up the system, thereby markedly reducing process efficiency. Thus, some attempt to reduce caking tendencies is necessary and can involve preliminary partial oxidation of the coal, thus destroying the caking properties.

Another factor, often presented as a general rule of thumb, is that optimum gas yields and gas quality are obtained at operating temperatures of approximately 595-650 °C (1100-1200 °F). A gaseous product with a higher heat content (Btu/ft^3)

can be obtained at lower system temperatures but the overall yield of gas (determined as the fuel-to-gas ratio) is reduced by the unburned char fraction.

With some coal feedstocks, the higher the amounts of volatile produced in the early stages of the process, the higher the heat content of the product gas. In some cases, the highest gas quality may be produced at the lowest temperatures, but when the temperature is too low, char oxidation reaction is suppressed and the overall heat content of the product gas is diminished. All such events serve to complicate the reaction rate and make derivative of a global kinetic relationship applicable to all types of coal subject to serious question and doubt.

Depending on the type of coal being processed and the analysis of the gas product desired, pressure also plays a role in product definition. In fact, some (or all) of the following processing steps will be required: (1) pretreatment of the coal (if caking is a problem); (2) primary gasification of the coal; (3) secondary gasification of the carbonaceous residue from the primary gasifier; (4) removal of carbon dioxide, hydrogen sulfide, and other acid gases; (5) shift conversion for adjustment of the carbon monoxide/hydrogen mole ratio to the desired ratio; and (6) catalytic methanation of the carbon monoxide/hydrogen mixture to form methane. If high-heat content (high-Btu) gas is desired, all of these processing steps are required because coal gasifiers do not yield methane in the concentrations.

5.3.2 Pretreatment

Some coals display caking, or agglomerating, characteristics when heated. These coals are usually not amenable to treatment by gasification processes employing fluidized-bed or moving-bed reactors; in fact, caked coal is difficult to handle in fixed-bed reactors. The pre treatment involves a mild oxidation treatment that destroys the caking characteristics of coals and usually consists of low-temperature heating of the coal in the presence of air or oxygen.

5.3.3 Primary gasification

Primary gasification involves thermal decomposition of the raw coal via various chemical processes. Many schemes involve pressures ranging from atmospheric pressure to high pressure (14.7-1000 psi). Air or oxygen may be admitted to support combustion to provide the necessary heat. The product is usually a low-Btu gas (low-heat content gas) ranging from a carbon monoxide/hydrogen mixture to mixtures containing varying amounts of carbon monoxide, carbon dioxide, hydrogen, water, methane, hydrogen sulfide, nitrogen, and typical products of thermal decomposition such as tar (themselves being complex mixtures), hydrocarbon oils, and phenol derivatives (Speight, 2013a, 2013b).

The solid char product is produced that may represent the bulk of the weight of the original coal. This type of coal being processed determines (to a large extent) the amount of char produced and the composition of the gas product.

5.3.4 Secondary gasification

Secondary gasification usually involves the gasification of char from the primary gasification step. This is usually achieved by reaction of the hot char with water vapor (steam gasification) to produce carbon monoxide and hydrogen:

$$[C]_{char} + H_2O \rightarrow CO + H_2$$

The reaction requires heat input (endothermic) in order to proceed in its forward direction. Usually, an excess amount of steam is also needed to promote the reaction. However, excess steam used in this reaction has an adverse effect on the thermal efficiency of the process. Therefore, this reaction is typically combined with other gasification reactions in practical applications. The hydrogen-carbon monoxide ratio of the syngas product depends on the synthesis chemistry as well as process engineering.

The mechanism of this reaction section is based on the reaction between carbon and gaseous reactants, not for the reactions between coal and gaseous reactants. Hence the equations may oversimpifly the actual chemistry of the steam gasification reaction. Even though carbon is the dominant atomic species present in coal, coal is more reactive than pure carbon. The presence of various reactive organic functional groups and the availability of catalytic activity via naturally occurring mineral ingredients can enhance the relative reactivity of coal – anthracite – which has the highest carbon content among all ranks of coal (Speight, 2013a) and is most difficult to gasify or liquefy.

Alkali metal salts are known to catalyze the steam gasification reaction of carbonaceous materials, including coal. The process is based on the concept that alkali metal salts (such as potassium carbonate, sodium carbonate, potassium sulfide, sodium sulfide, and the like) will catalyze the steam gasification of coal. The order of catalytic activity of alkali metals on coal gasification reaction is:

$$\text{Cesium}(\text{Cs}) > \text{rubidium}(\text{Rb}) > \text{potassium}(\text{K}) > \text{sodium}(\text{Na}) > \text{lithium}(\text{Li})$$

Catalyst amounts on the order of 10-20% w/w potassium carbonate will lower bituminous coal gasifier temperatures from 925 °C (1695 °F) to 700 °C (1090 °F) and then the catalyst can be introduced to the gasifier impregnated on coal or char.

In addition, tests with potassium carbonate showed that this material also acts as a catalyst for the methanation reaction. In addition, the use of catalysts can reduce the amount of tar formed in the process (Cusumano, Dalla Betta, & Levy, 1978; McKee, 1981; Shinnar, Fortuna, & Shapira, 1982). In the case of catalytic steam gasification of coal, carbon deposition reaction may affect catalyst life by fouling the catalyst active sites. This carbon deposition reaction is more likely to take place whenever the steam concentration is low.

Ruthenium-containing catalysts are used primarily in the production of ammonia. It has been shown that ruthenium catalysts provide 5-10 times higher reactivity rates than other catalysts. But ruthenium quickly becomes inactive due to its necessary supporting material, such as activated carbon, which is used to achieve effective reactivity. However, during the process, the carbon is consumed, thereby reducing the effect of the ruthenium catalyst.

Catalysts can also be used to favor or suppress the formation of certain components in the gaseous product by changing the chemistry of the reaction, the rate of reaction, and the thermodynamic balance of the reaction. For example, in the production of synthesis gas (mixtures of hydrogen and carbon monoxide), methane is also produced in small amounts. Catalytic gasification can be used to either promote methane formation or suppress it.

5.3.5 Carbon dioxide gasification

The reaction of coal with carbon dioxide produces carbon monoxide (*Boudouard reaction*), and, like the steam-gasification reaction, is also an endothermic reaction:

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

The reverse reaction results in carbon deposition (carbon fouling) on many surfaces, including the catalysts and results in catalyst deactivation.

This gasification reaction is thermodynamically favored at high temperatures (>680 °C, >1255 °F), which is also quite similar to the steam gasification. If carried out alone, the reaction requires high temperature (for fast reaction) and high pressure (for higher reactant concentrations) for significant conversion. But as a separate reaction, a variety of factors come into play: (1) low conversion, (2) slow kinetic rate, and (3) low thermal efficiency.

Also, the rate of the carbon dioxide gasification of coal is different from the rate of the carbon dioxide gasification of carbon. Generally, the carbon-carbon dioxide reaction follows a reaction order based on the partial pressure of the carbon dioxide that is approximately 1.0 (or lower), whereas the coal-carbon dioxide reaction follows a reaction order based on the partial pressure of the carbon dioxide that is 1.0 (or higher). The observed higher reaction order for the coal reaction is also based on the relative reactivity of the coal in the gasification system.

5.3.6 Water gas shift reaction

The water gas shift reaction (shift conversion) is necessary because the gaseous product from a gasifier generally contains large amounts of carbon monoxide and hydrogen, plus lesser amounts of other gases. Carbon monoxide and hydrogen (if they are present in the mole ratio of 1:3) can be reacted in the presence of a catalyst to produce methane. However, some adjustment to the ideal (1:3) is usually required. To accomplish this, all or part of the stream is treated according to the water-gas shift (shift conversion) reaction. This involves reacting carbon monoxide with steam to produce a carbon dioxide and hydrogen whereby the desired 1:3 mol ratio of carbon monoxide to hydrogen may be obtained:

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

Even though the water-gas shift reaction is not classified as one of the principal gasification reactions, it cannot be omitted in the analysis of chemical reaction systems that involve synthesis gas. Among all reactions involving syngas, this reaction equilibrium is least sensitive to the temperature variation – the equilibrium constant is least dependent on the temperature. Therefore, the reaction equilibrium can be reversed in a variety of practical process conditions over a wide range of temperature.

The water-gas shift reaction in its forward direction is mildly exothermic. Although all the participating chemical species are in gaseous form, the reaction is believed to be heterogeneous insofar as the chemistry occurs at the surface of the coal and the reaction is actually catalyzed by carbon surfaces. In addition, the reaction can also take place homogeneously as well as heterogeneously. A general understanding of the water-gas shift reaction is difficult to achieve; even the published kinetic rate information is not immediately useful or applicable to a practical reactor situation.

Synthesis gas from a gasifier contains a variety of gaseous species other than carbon monoxide and hydrogen. Typically, they include carbon dioxide, methane, and water (steam). Depending on the objective of the ensuing process, the composition of syngas may need to be preferentially readjusted. If the objective of the gasification process is to obtain a high yield of methane, it would be preferred to have the molar ratio of hydrogen to carbon monoxide at 3:1:

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$$

On the other hand, if the objective of generating syngas is the synthesis of methanol via a vapor-phase low-pressure process, the stoichiometrically consistent ratio between hydrogen and carbon monoxide would be 2:1. In such cases, the stoichiometrically consistent synthesis gas mixture is often referred to as *balanced gas*, whereas a synthesis gas composition that is substantially deviated from the principal reaction's stoichiometry is called *unbalanced gas*. If the objective of synthesis gas production is to obtain a high yield of hydrogen, it would be advantageous to increase the ratio of hydrogen to carbon monoxide by further converting carbon monoxide (and water) into hydrogen (and carbon dioxide) via the water-gas shift reaction.

The water-gas shift reaction is one of the major reactions in the steam gasification process, where both water and carbon monoxide are present in ample amounts. Although the four chemical species involved in the water-gas shift reaction are gaseous compounds at the reaction stage of most gas processing, the water-gas shift reaction, in the case of steam gasification of coal, predominantly takes place on the solid surface of coal (heterogeneous reaction). If the product synthesis gas from a gasifier needs to be reconditioned by the water-gas shift reaction, this reaction can be catalyzed by a variety of metallic catalysts.

Choice of specific kinds of catalysts has always depended on the desired outcome, the prevailing temperature conditions, composition of gas mixture, and process economics. Typical catalysts used for the reaction include catalysts containing iron, copper, zinc, nickel, chromium, and molybdenum.

5.3.7 Methanation

Several exothermic reactions may occur simultaneously within a methanation unit. A variety of metals have been used as catalysts for the methanation reaction; the most common, and to some extent the most effective methanation catalysts, appear to be nickel and ruthenium, with nickel being the most widely (Cusumano *et al.*, 1978):

$$\text{Ruthenium(Ru)} > \text{nickel(Ni)} > \text{cobalt(Co)} > \text{iron(Fe)} > \text{molybdenum(Mo)}$$

Nearly all the commercially available catalysts used for this process are very susceptible to sulfur poisoning, so efforts must be taken to remove all hydrogen sulfide (H_2S) before the catalytic reaction starts. It is necessary to reduce the sulfur concentration in the feed gas to less than 0.5 ppm v/v in order to maintain adequate catalyst activity for a long period of time.

The synthesis gas must be desulfurized before the methanation step because sulfur compounds will rapidly deactivate (poison) the catalysts. A problem may arise when the concentration of carbon monoxide is excessive in the stream to be methanated. Large amounts of heat must be removed from the system to prevent high temperatures and deactivation of the catalyst by sintering as well as the deposition of carbon. To eliminate this problem, temperatures should be maintained below 400 °C (750 °F).

The methanation reaction is used to increase the methane content of the product gas, as needed for the production of high-Btu gas.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

$$2CO \rightarrow C + CO_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Among these, the most dominant chemical reaction leading to methane is the first one. Therefore, if methanation is carried out over a catalyst with a synthesis gas mixture of hydrogen and carbon monoxide, the desired hydrogen-carbon monoxide ratio of the feed synthesis gas is around 3:1. The large amount of water (vapor) produced is removed by condensation and recirculated as process water or steam. During this process, most of the exothermic heat due to the methanation reaction is also recovered through a variety of energy integration processes.

Whereas all the reactions listed here are quite strongly exothermic except the forward water-gas shift reaction, which is mildly exothermic, the heat release depends largely on the amount of carbon monoxide present in the feed synthesis gas. For each 1% v/v carbon monoxide in the feed synthesis gas, an adiabatic reaction will experience a 60 °C (108 °F) temperature rise, which may be termed as *adiabatic temperature rise*.

5.3.8 Hydrogasification

Hydrogasification is the gasification of coal in the presence of an atmosphere of hydrogen under pressure (Anthony & Howard, 1976). Thus, not all high-heat content (high-Btu) gasification technologies depend entirely on catalytic methanation. In fact, a number of gasification processes use hydrogasification – that is, the direct addition of hydrogen to coal under pressure to form methane:

$$[C]_{coal} + H_2 \rightarrow CH_4$$

The hydrogen-rich gas for hydrogasification can be manufactured from steam by using the char that leaves the hydrogasifier. Appreciable quantities of methane are formed directly in the primary gasifier, and the heat released by methane formation is at a sufficiently high temperature to be used in the steam-carbon reaction to produce hydrogen so that less oxygen is used to produce heat for the steam-carbon reaction. Hence, less heat is lost in the low-temperature methanation step, thereby leading to higher overall process efficiency.

The hydrogasification reaction is exothermic and is thermodynamically favored at low temperatures ($<670\,°C$, $<1240\,°F$), unlike the endothermic steam gasification and carbon dioxide gasification reactions. However, at low temperatures, the reaction rate is inevitably too slow. Therefore, a high temperature is always required for kinetic reasons, which, in turn, requires high pressure of hydrogen, which is also preferred from equilibrium considerations. This reaction can be catalyzed by salts such as potassium carbonate (K_2CO_3), nickel chloride ($NiCl_2$), iron chloride ($FeCl_2$), and iron sulfate ($FeSO_4$). However, use of a catalyst in coal gasification suffers from difficulty in recovering and reusing the catalyst and the potential for the spent catalyst becoming an environmental issue.

In a hydrogen atmosphere at elevated pressure, additional yields of methane or other low molecular weight hydrocarbons can result during the initial coal gasification stage from direct hydrogenation of coal or semi-char because of the active intermediate formed in coal structure after coal pyrolysis. The direct hydrogenation can also increase the amount of coal carbon that is gasified as well as the hydrogenation of gaseous hydrocarbons, oil, and tar.

The kinetics of the rapid-rate reaction between gaseous hydrogen and the active intermediate depends on hydrogen partial pressure (P_{H2}). Greatly increased gaseous hydrocarbons produced during the initial coal gasification stage are extremely important in processes to convert coal into methane (SNG, synthetic natural gas).

5.4 Conclusions

Relative to the chemical and thermodynamic understanding of the gasification process and data derived from thermodynamic studies (Shabbar & Janajreh, 2013; Van der Burgt, 2008), the kinetic behavior of coal feedstocks is more complex.

The chemistry of coal gasification is quite complex and, only for discussion purposes, can the chemistry be viewed as consisting of a few major reactions that can progress to different extents depending on the gasification conditions (such as temperature and pressure) and the feedstock used. Combustion reactions take place in a gasification process, but, in comparison with conventional combustion, which uses a stoichiometric excess of oxidant, gasification typically uses one-fifth to one-third of the theoretical oxidant. This only partially oxidizes the carbon feedstock. As a *partial oxidation* process, the major combustible products of gasification are carbon monoxide (CO) and hydrogen, with only a minor portion of the carbon completely oxidized to carbon dioxide (CO_2). The heat produced by the partial oxidation provides most of the energy required to drive the endothermic gasification reactions.

Furthermore, while the basic thermodynamic cycles pertinent to coal gasification have long been established, novel combination and the use of alternative fluids to water/steam offer the prospect of higher process efficiency through use of thermodynamic studies.

Finally, very little reliable kinetic information on coal gasification reactions exists, partly because it is highly dependent on the process conditions *and* the nature of the coal feedstock. The coal feedstock can vary significantly with respect to composition, mineral impurities, and reactivity, as well as the potential for certain impurities to exhibit catalytic activity on some of the gasification reactions. Indeed, in spite of the efforts of many researchers, kinetic data are far from able to be applied to gasification of coal or char in various processes. All such parameters serve to complicate the reaction rate and make derivative of a global kinetic relationship applicable to all types of coal subject to serious question and doubt.

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Gasification processes for syngas and hydrogen production

6

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6.1 Introduction

Gasification processes are used to convert a carbon-containing (carbonaceous) material into a synthesis gas (syngas), which is a combustible gas mixture that typically contains carbon monoxide, hydrogen, nitrogen, carbon dioxide, and methane. The impure synthesis gas has a relatively low calorific value, ranging from 100 to 300 Btu/ft^3. The gasification process can accommodate a wide variety of gaseous, liquid, and solid feedstocks and it has been widely used in commercial applications for the production of fuels and chemicals (Chapters 1 and 10). Conventional fuels such as coal and petroleum, as well as low- or negative-value materials and wastes such as petroleum coke, refinery residue, refinery waste, municipal sewage sludge, biomass, hydrocarbon contaminated soils, and chlorinated hydrocarbon by-products have all been used successfully in gasification operations (Speight, 2008, 2013a, 2013b). In addition, syngas is used as a source of hydrogen or as an intermediate in producing a variety of hydrocarbon products by means of the Fischer-Tropsch synthesis (FTS) (Table 6.1) (Chadeesingh, 2011). In fact, gasification to produce synthesis gas can proceed from any carbonaceous material, including biomass and waste.

The synthesis of hydrocarbons from the hydrogenation of carbon monoxide was discovered in 1902 by Sabatier and Sanderens, who produced methane by passing carbon monoxide and hydrogen over nickel, iron, and cobalt catalysts. At about the same time, the first commercial hydrogen from syngas produced from steam methane reforming was commercialized. Haber and Bosch discovered the synthesis of ammonia from hydrogen and nitrogen in 1910 and the first industrial ammonia synthesis plant was commissioned in 1913. The production of liquid hydrocarbons and oxygenates from syngas conversion over iron catalysts was discovered in 1923 by Fischer and Tropsch. Variations on this synthesis pathway were soon to follow for the selective production of methanol, mixed alcohols, and iso-hydrocarbon products. Another outgrowth of FTS was the hydroformylation of olefins discovered in 1938.

In principle, synthesis gas can be produced from any hydrocarbon feedstock, which include natural gas, naphtha, residual oil, petroleum coke, coal, biomass, and municipal or industrial waste (Chapter 1). The product gas stream is subsequently purified (to remove sulfur, nitrogen, and any particulate matter) after which it is catalytically converted to a mixture of liquid hydrocarbon products. In addition, synthesis gas may also be used to produce a variety of products, including ammonia, and methanol.

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Table 6.1 **General carbon ranges and common names of hydrocarbons produced from synthesis gas by the Fischer-Tropsch process**

Carbon number range	Common name
C1-C2	SNG (Synthetic Natural Gas)
C3-C4	LPG (Liquefied Petroleum Gas)
C5-C7	Light petroleum
C8-C10	Heavy Petroleum
C11-C17	Middle distillate – kerosene, diesel
C18-C30	Soft wax
C31-C60	Hard wax

Of all of the carbonaceous materials used as feedstocks for gasification process, coal represents the most widely used feedstocks and, accordingly, the feedstock about which most is known. In fact, gasification of coal has been a commercially available proven technology (Speight, 2013a, 2013b) (Chapters 1 and 10). The modern gasification processes have evolved from three first-generation process technologies: (1) Lurgi fixed-bed reactor, (2) high-temperature Winkler fluidized-bed reactor, and (3) Koppers-Totzek entrained-flow reactor. In each case steam/air/oxygen are passed through heated coal, which may either be a fixed bed, fluidized bed or entrained in the gas. Exit gas temperatures from the reactor are 500 °C (930 °F), 900 to 1100 °C (1650 to 2010 °F), and 1300 to 1600 °C (2370 to 2910 °F), respectively. In addition to the steam/air/oxygen mixture being used as the feed gases, steam/oxygen mixtures can also be used in which membrane technology and a compressed oxygen-containing gas is employed.

However, the choice of technology for synthesis gas production also depends on the scale of the synthesis operation. Syngas production from solid fuels can require an even greater capital investment with the addition of feedstock handling and more complex syngas purification operations. The greatest impact on improving gas-to-liquids plant economics is to decrease capital costs associated with syngas production and improve thermal efficiency through better heat integration and utilization. Improved thermal efficiency can be obtained by combining the gas-to-liquids plant with a power generation plant to take advantage of the availability of low-pressure steam.

This chapter presents the means by which synthesis gas and hydrogen are produced from carbonaceous feedstocks.

6.2 Synthesis gas production

Both nonrenewable and renewable energy sources are important for production of synthesis gas and hydrogen. As energy carriers, hydrogen and synthesis can be produced from catalytic processing of various hydrocarbon fuels, alcohol fuels, and a variety of biofuels and biomass feedstocks.

In most cases, synthesis gas is produced from coal (gasification, carbonization), natural gas, and light hydrocarbons such as propane gas (steam reforming, partial oxidation, autothermal reforming, plasma reforming); petroleum fractions (dehydrocyclization and aromatization, oxidative steam reforming, pyrolytic decomposition); biomass (gasification, steam reforming, biologic conversion); and water (electrolysis, photo-catalytic conversion, chemical and catalytic conversion) (Liu, Song, & Subramani, 2010; Speight, 2008, 2011a, 2013a, 2013b, 2014; Wesenberg & Svendsen, 2007). The relative competitiveness of different options depends on the economics of the given processes, which, in turn, depend on many factors such as the (1) suitability and availability of the feedstock, (2) efficiency of the catalysis, (3) scale of production, (4) required hydrogen purity, and (5) economics of feedstock production and the processing steps.

Current commercial processes for synthesis gas and hydrogen production largely depend on fossil fuels both as the source of hydrogen and as the source of energy for the production processing. Fossil fuels are nonrenewable energy resources, but they provide a more economical path to hydrogen production in the near term (next three decades) and perhaps they will continue to play an important role in the midterm (up to 50 years from now) (Speight, 2011b). Alternative processes need to be developed that do not depend on fossil hydrocarbon resources for either the hydrogen source or the energy source, and these processes need to be economical, environmentally friendly, and competitive. Efficient separation of the hydrogen from the gaseous products is also a major issue that must be addressed. In this respect, pressure swing adsorption (PSA) is used in current industrial practice. Furthermore, several types of membranes are being developed that would, when incorporated into the separation process, enable more efficient gas separation (Ho & Sirkar, 1992).

The process for producing syngas involves three individual components: (1) synthesis gas generation, (2) waste heat recovery, and (3) gas processing (Speight, 2013a, 2013b, 2014). Within each of the three listed systems are several options. Synthesis gas can be generated to yield a range of compositions ranging from high-purity hydrogen to high-purity carbon monoxide. Two major routes can be utilized for high-purity gas production: (1) pressure swing adsorption and (2) utilization of a cold box, where separation is achieved by distillation at low temperatures. In fact, both processes can also be used in combination as well. Unfortunately, both processes require high capital expenditure. However, to address these concerns, research and development is ongoing and successes can be measured by the demonstration and commercialization of technologies such as permeable membrane for the generation of high-purity hydrogen, which in itself can be used to adjust the H_2/CO ratio of the synthesis gas produced.

6.2.1 Steam-methane reforming

Steam-methane reforming is the benchmark process that has been employed over a period of several decades for hydrogen production. The process involves reforming natural gas in a continuous catalytic process in which the major reaction is the formation of carbon monoxide and hydrogen from methane and steam:

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H_{298K} = +97{,}400\,\text{Btu/lb}$$

Higher molecular weight feedstocks can also be reformed to hydrogen:

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2$$

That is,

$$C_nH_m + nH_2O \rightarrow nCO + (0.5m + n)H_2$$

In the actual process, the feedstock is first desulfurized by passage through activated carbon, which may be preceded by caustic and water washes. The desulfurized material is then mixed with steam and passed over a nickel-based catalyst (730 to 845 °C, 1350 to 1550 °F and 400 psi. Effluent gases are cooled by the addition of steam or condensate to about 370 °C (700 °F), at which point carbon monoxide reacts with steam in the presence of iron oxide in a shift converter to produce carbon dioxide and hydrogen:

$$CO + H_2O = CO_2 + H_2$$

The carbon dioxide is removed by amine washing; the hydrogen is usually a high-purity (>99%) material.

Steam reforming of natural gas (sometimes referred to as *steam-methane reforming*, SMR) is the part of the gas-refining process where the natural gas is converted to syngas, which is further used in the synthesis to methanol or Fischer-Tropsch products. Hydrogen-rich synthesis gas can also be used directly for hydrogen enrichment. The technology for steam reforming is of great interest because this part of the process represents a substantial portion of the investment costs. The reforming section costs about 60 to 80% of the total cost of the entire gas-refining plant. Improvements and cost savings in the reforming section will therefore become very noticeable in the total plant cost.

Steam reforming is an exothermic reaction that is carried out by passing a preheated mixture comprising methane (sometimes substituted by natural gas having high methane content) and steam through catalyst-filled tubes. The products of the process are a mixture of hydrogen, carbon monoxide, and carbon dioxide. To maximize the conversion of the methane feed, primary and secondary reformers are often used – the *primary reformer* elicits a 90 to 92% v/v conversion of methane. Here, the hydrocarbon feed is partially reacted with steam at 900 °C (1650 °F) at 220 to 500 psi over a nickel-alumina catalyst to produce a synthesis gas in which the hydrogen/carbon monoxide (H_2/CO) ratio is on the order of 3:1. Any unconverted methane is reacted with oxygen at the top of a *secondary autothermal reformer,* which contains a nickel catalyst in the lower region of the vessel.

In autothermal (or secondary) reformers, the oxidation of methane supplies the necessary energy and carries out either simultaneously or in advance of the reforming reaction (Brandmair, Find, & Lercher, 2003; Ehwald, Kürschner, Smejkal, & Lieske, 2003; Nagaoka, Jentys, & Lecher, 2003). The equilibrium of the methane steam reaction and the water-gas shift reaction determines the conditions for optimum hydrogen yields. The optimum conditions for hydrogen production require high temperature at the exit of the reforming reactor (800 to 900 °C; 1470 to 1650 °F); high excess of steam (molar steam-to-carbon ratio of 2.5 to 3); and relatively low pressures (below 450 psi). Most commercial plants employ supported nickel catalysts for the process.

One way of overcoming the thermodynamic limitation of steam reforming is to remove either hydrogen or carbon dioxide as it is produced, hence shifting the thermodynamic equilibrium toward the product side. The concept for sorption-enhanced methane steam reforming is based on *in situ* removal of carbon dioxide by a sorbent such as calcium oxide (CaO).

$$CaO + CO_2 \rightarrow CaCO_3$$

Sorption enhancement enables lower reaction temperatures, which may reduce catalyst coking and sintering, while enabling use of less expensive reactor wall materials. In addition, heat release by the exothermic carbonation reaction supplies most of the heat required by the endothermic reforming reactions. However, energy is required to regenerate the sorbent to its oxide form by the energy-intensive calcination reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

Use of a sorbent requires either that there be parallel reactors operated alternatively and out of phase in reforming and sorbent regeneration modes, or that sorbent be continuously transferred between the reformer/carbonator and regenerator/calciner (Balasubramanian, Ortiz, Kaytakoglu, & Harrison, 1999; Hufton, Mayorga, & Sircar, 1999).

Synthesis gas produced from natural gas (or coal or other carbonaceous feedstocks) is the building block in the synthesis of ammonia, methanol, Fischer-Tropsch (FT) fuels, hydrogen for hydrocracking at oil refineries, Oxo-alcohols, and other fine chemicals. The gas composition varies with the intended use of the syngas; ammonia production requires a molar H2/N2 ratio of 3, and for hydrogen production, the H2 content should be as high as possible. Because of the active shift reaction, both carbon monoxide and carbon dioxide are reactants in the methanol synthesis and in high temperature FTS. The syngas composition is therefore specified by a stoichiometric number [SN = (H2 – CO2)/(CO + CO2)] which should be close to 2. On the other hand, only carbon monoxide is a reactant for the low-temperature FTS, and the synthesis gas should have a H2/CO ratio close to 2. These different syngas compositions are achieved by using different types of reactor technology and by varying the amount of added steam and possibly oxygen or air, which is discussed later. The synthesis gas composition is also dependent on the feed gas composition and on the outlet temperature and pressure of the reforming reactor (Chadeesingh, 2011).

The higher molecular weight hydrocarbons that are also constituents of natural gas (Speight, 2007, 2014) are converted to methane in an adiabatic pre-reformer upstream of the steam reformer. In the pre-reformer, all higher hydrocarbons (C_{2+}) are converted into a mixture of methane, hydrogen, and carbon oxides:

$$CnHm + nH_2O \rightarrow nCO + (n + m/2)H_2$$

$$3H_2 + CO \leftrightarrow CH_4 + H_2O$$

$$CO + H_2O \leftrightarrow H_2 + CO_2$$

The pre-reforming process utilizes an adiabatic fixed-bed reactor with highly active nickel catalysts. The reactions take place at temperatures of approximately 350 to 550 °C (650 to 1020 °F), which makes it possible to preheat the steam reformer feed to higher temperatures without getting problems with olefin formation from the higher hydrocarbons. Olefins are unwanted in the steam reformer feed because they generally cause coking of the catalyst pellets at high temperatures. Preheating of the steam reformer feed is of great advantage because the reformer unit can be scaled down to a minimum size (Aasberg-Petersen *et al*., 2001; Aasberg-Petersen, Christensen, Stub Nielsen, & Dybkjær, 2002; Hagh, 2004).

The reactions are catalyzed by pellets coated with nickel and are highly endothermic overall. Effective heat transport to the reactor tubes and further into the center of the catalytic fixed bed is therefore a very important aspect during design and operation of steam reformers. The reactions take place in several tubular fixed-bed reactors of low diameter-to-height ratio to ensure efficient heat transport in radial direction. The process conditions are typically 300 to 600 psi bar with inlet temperature of 300 to 650 °C (570 to 1200 °F) and outlet temperature of 700 to 950 °C (1290 to 1740 °F). There is often an approach to equilibrium of about 5 to 20 °C, which means that the outlet temperature is slightly higher than the equilibrium temperature calculated from the actual outlet composition (Rostrup-Nielsen, Christiansen, & Bak Hansen, 1988).

In a pre-reformer, whisker carbon can be formed either from methane or higher molecular weight hydrocarbons. The lower limit of the H_2O/C ratio depends on a number of factors, including the feed gas composition, the operating temperature, and the choice of catalyst. In a pre-reformer operating at low H_2O/C-ratio, the risk of carbon formation from methane is most pronounced in the reaction zone where the temperature is highest. Carbon formation from higher molecular weight hydrocarbons can take place only in the first part of the reactor with the highest concentrations of C2+compounds.

In addition, two water-gas shift (WGS) reactors are used downstream of the secondary reformer to adjust the H_2/CO ratio, depending on the end use of the steam reformed products. The first of the two shift reactors utilize an iron-based catalyst that is heated to approximately 400 °C (750 °F), whereas the second shift reactor operates at approximately 200 °C (390 °F) and contains a copper-based catalyst.

The deposition of carbon on the catalyst (coking) can be an acute problem with the use of Ni-based catalysts in the primary reformer (Alstrup, 1988; Rostrup-Nielsen, 1984, 1993). The *carbon deposition reactions* occur in parallel with the reforming reactions and are undesirable, as they cause poisoning of the surface of the catalyst pellets. This leads to lower catalyst activity and the need for more frequent catalyst reloading. The coking reactions are the CO reduction, methane cracking, and Boudouard reaction, given by the respective equilibrium reactions:

$$CO + H_2 + H_2O \rightarrow C + H_2O$$

$$CH_4 \leftrightarrow C + 2H_2$$

$$2CO \leftrightarrow C + CO_2$$

Thus, low steam excess can lead to critical conditions causing coke formation – equilibrium calculations of the coking reactions can be a useful tool for predicting the danger for catalyst poisoning but the reaction kinetics may nevertheless be so slow that coking is no concern. A complete analysis should therefore also involve kinetic calculations, which will be feedstock-dependent expressions for these reactions.

Traditionally, steam reformers have been run with a steam/carbon ratio of 2 to 4 to ensure low coking potential. It is desirable to reduce this ratio for methanol and FTS purposes because it will give great cost savings in form of smaller reformer units with higher methane conversion. Technical developments such as new noble metal catalysts and the use of pre-reformers are continually decreasing the feasible team/carbon ratio.

A successful technique is to use a steam/carbon ratio in the feed gas that does not allow the formation of carbon, but the process has a lower efficiency. Another approach is to use sulfur passivation, which led to the development of the SPARG process (Rostrup-Nielsen, 1984, 2006; Udengaard, Hansen, Hanson, & Stal, 1992). This technique utilizes the principle that the reaction leading to the deposition of carbon requires a larger number of adjacent nickel atoms on the catalyst surface than does steam reforming. A third method is to use Group VIII metals (such as platinum) that do not form carbides.

The most common reactor concept for steam reforming of natural gas is the fired steam reformer. Natural gas and the tail gas from the synthesis loop are burned in a firebox where several reactor tubes are placed in rows with a number of 40 to 400 tubes. The reactor tubes are about 33 to 40 feet with diameters of about 4 to 5 inches. The reactions for conversion of natural gas to synthesis gas take place over the catalytic beds in the reactor tubes. The burners can be located in different places: on the roof, on the floor, on leveled terraces on the walls, or on the walls (side-fired heating).

The top-fired steam reformer must be operated carefully because the tube wall temperature and heat flux show a peak in the upper part of the reformer. The bottom-fired reformers achieve a stable heat flux profile along the tube length, which causes high tube skin temperatures at the reactor outlet. The terrace wall-fired reformer is a modification of the bottom fired reformer and has some smaller problem with high metal temperatures. The side-fired reformer has the most effective design and is also the most flexible reformer, both in design and in operation (Dybkjær, 1995).

This configuration has the highest total heat flux possible combined with the lowest heat flux where the tube skin temperature is at its highest. In this type of reformer, it is possible to combine a low steam-to-carbon ratio with a high outlet temperature. The most critical operation parameter is the maximum temperature difference over the tube wall, not the maximum heat flux (Aasberg-Petersen *et al.*, 2001).

6.2.2 Autothermal reforming

Autothermal reforming (ATR) uses oxygen and carbon dioxide or steam in a reaction with methane to form synthesis. The reaction takes place in a single chamber where the methane is partially oxidized. The reaction is exothermic due to the oxidation. The main difference between autothermal reforming and steam-methane reforming is that steam-methane reforming does not use or require oxygen. The advantage of autothermal reforming is that H_2/CO can be varied, which is particularly useful for producing certain second-generation biofuels such as dimethyl ether synthesis, which requires a 1:1 H_2/CO ratio.

The process was developed in the 1950s and is used in commercial applications to provide syngas for ammonia and methanol synthesis. In the case of ammonia production, where high H_2/CO ratios are needed, the process is operated at high steam/carbon ratios. In the case of methanol synthesis, the required H_2/CO ratio is provided by manipulating the carbon dioxide recycle. In fact, development and optimization of this technology has led to cost-effective operation at very low steam/carbon feed ratios to produce CO-rich syngas, for example, which is preferred in FTS. These are the advantages of using the autothermal reactor: (1) the reactor is compact in design and therefore has a smaller footprint; (2) it has flexibility in its operation, with short startup periods and fast load changes; and (3) it is a soot-free operation. In addition, the reactor offers a better economic profile.

In the process, an organic feedstock (such as natural gas) and steam (there may also be low amounts of carbon dioxide in the feed) are mixed directly with oxygen and air in the reformer. The reformer itself comprises a refractory-lined vessel that contains the catalyst, together with an injector located at the top of the vessel. Partial oxidation reactions occur in the combustion zone of the reactor and the gaseous mixture then flows through a catalyst bed where the actual reforming reactions occur. Heat generated in the combustion zone from partial oxidation reactions is utilized in the reforming zone, so that in the ideal case, it is possible that the process can be in complete heat balance.

The autothermal reforming reactor consists of three zones: (1) the burner, where the feed streams are mixed in a turbulent diffusion flame; (2) the combustion zone, where partial oxidation reactions produce a mixture of carbon monoxide and hydrogen; and (3) the catalytic zone, where the gases leaving the combustion zone attain thermodynamic equilibrium. Key elements in the reactor are the burner and the catalyst bed – the burner provides mixing of the feed streams and the natural gas is converted in a turbulent diffusion flame:

$$CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$$

When carbon dioxide is present in the feed, the H_2/CO ratio produced is on the order of 1:1, but when the process employs steam, the H_2/CO ratio produced is 2.5:1.

$$2CH_4 + O_2 + CO_2 \rightarrow 3H_2 + 3CO + H_2O$$

$$4CH_4 + O_2 + 2H_2O \rightarrow 10H_2 + 4CO$$

The risk of soot formation in an ATR reactor depends on a number of parameters, including feed gas composition, temperature, pressure, and especially burner design. Soot precursors may be formed in the combustion chamber during operation, so it is essential that the design of the burner, catalyst, and reactor is such that the precursors are destroyed by the catalyst bed to avoid soot formation.

Many observers consider the combination of adiabatic pre-reforming and autothermal reforming at low H_2O/C ratios to be the preferred layout for production of synthesis gas for large gas-to-liquids plants.

6.2.3 Combined reforming

Combined reforming incorporates the combination of both steam reforming and autothermal reforming. In such a configuration, the hydrocarbon (e.g., natural gas) is first only partially converted, under mild conditions, to syngas in a relatively small steam reformer (Wang, Stagg-Williams, Noronha, Mattos, & Passos, 2004). The off-gases from the steam reformer are then sent to an oxygen-fired secondary reactor, such as an autothermal reactor, where the unreacted methane is converted to syngas by partial oxidation followed by steam reforming.

Another configuration requires that the hydrocarbon feed be split into two streams that are then fed in parallel, to a steam-reforming reactor and an autothermal reactor (gas-heated reforming). This process is an alternative to the fired steam reformer and has been commercially proven. There is also interest for the gas-heated steam reformer in relation to the FTS of hydrocarbons and methanol production.

6.2.4 Partial oxidation

Partial oxidation is the process in which the feed fuel, such as methane or a suitable hydrocarbonaceous fuel, reacts exothermically in the presence of a small amount of air (Vernon, Green, Cheetham, & Ashcroft, 1990; Rostrup-Nielsen, 2002; Zhu, Zhao, & Deng, 2004). Because incomplete combustion occurs, a gas containing hydrogen and carbon monoxide is produced. The hydrogen can be used to extend the lean limit of diesel, for instance, which indicates a higher efficiency of the fuel and lower pollutants emissions.

Partial oxidation (POX, P_{OX}) reactions occur when a substoichiometric hydrocarbon-air mixture is partially combusted in a reformer:

$$C_nH_m + (2n+m)/2O_2 \rightarrow nCO + (m/2)H_2O$$

Thus, for coal or any carbonaceous feedstocks the reaction can be represented simply as (understanding the in reality the reaction is extremely complex):

$$[CH]_{coal} + O_2 \rightarrow CO + H_2$$

In the process, the feedstock is partially burned in a simple pre-combustion chamber in the presence of a small amount of air and converted into carbon monoxide and hydrogen. Because partial oxidation is an exothermic reaction, some of the heat of combustion is released. The released energy is converted into heat, which brings the temperature of the gas to approximately 870 °C (1600 °F). The temperature of the gas needs to be lowered before entering the combustion engine. Otherwise, the density of the gas is too low to have a good volumetric efficiency. The resulting gas can be burned in a gas engine.

A thermal partial oxidation reactor is similar to the autothermal reactor with the main difference being no catalyst is used. In the process, the feedstock, which may include steam, is mixed directly with oxygen by an injector that is located near the top of the reaction vessel. Both partial oxidation as well as reforming reactions occur in the combustion zone below the burner.

The principal advantage of the partial oxidation process is the ability of the system to accommodate almost any carbonaceous feedstock, which can comprise very high molecular-weight organic constituents such as petroleum residual and petroleum coke (Gunardson & Abrardo, 1999; Speight, 2014). Additionally, because the emission of nitrogen oxides (NOx) and sulfur oxides (SOx) are minimal, partial oxidation does not leave a large environmental footprint.

On the other hand, very high temperatures, approximately 1300 °C (2370 °F), are required to achieve near complete reaction. This necessitates the consumption of some of the hydrogen and a greater than stoichiometric consumption of oxygen (i.e., oxygen-rich conditions).

Partial oxidation cannot be used for gasifying gasoline, diesel, methanol, or ethanol, because of the decrease in energy content of the fuel. However, the hydrogen-rich gas (hence, the preference for this type of process in the petroleum industry) that is produced by partial oxidation may be used to enrich other fuels. For the production of hydrogen, partial oxidation is often used in combination with steam reforming, using the heat of the partial oxidation for the endothermic steam reforming. However, given that steam reforming can be accomplished by using the energy from the exhaust gases coming out of the combustion engine, there is no need to partially oxidize the fuel first. Doing so would result in loss of the heating value of the fuel, and thus an overall energy loss for the process.

A possible means of improving the efficiency of syngas production is by use of the *catalytic partial oxidation* (CPOX, CP_{OX}) technology, which has the potential to offer several advantages over steam reforming and thermal particle oxidation, particularly higher energy efficiency (Enger, Lødeng, & Holmen, 2008). The reaction is not endothermic – as is the case with steam reforming – but slightly exothermic. Furthermore, an H_2/CO ratio of close to 2.0 (i.e., the ideal ratio for the Fischer-Tropsch and methanol synthesis) is produced by this technology, which can occur by either of two routes: direct or indirect.

The *indirect route* comprises total combustion of methane to carbon dioxide and water, followed by steam reforming and the water-gas shift reaction in which equilibrium conversions can be greater than 90% at ambient pressure. However, in order for an industrial process for this technology to be economically viable, an operating pressure in excess of 300 psi would be required. Unfortunately, at high pressures, equilibrium conversions are lower and, because of the exothermic combustion step, process control is more difficult and there is the potential for temperature runaways.

The *direct route* occurs by a mechanism involving only surface reaction on the catalyst:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$$

Compared with conventional synthesis gas production methods, the *direct route* would drastically reduce the amount of catalyst used, making it possible to use compact reactors.

6.2.5 Membrane reactors

An innovative technology for combining air separation and natural gas reforming processes is using membrane technology, which has the potential to reduce the cost of syngas generation and hydrocarbon products (Carolan, Chen, & Rynders, 2002; Khassin, 2005). The technology (oxygen transport membranes) can combine five unit operations currently in use: (1) oxygen separation, (2) oxygen compression, (3) partial oxidation, (4) steam methane reforming, and (5) heat exchange. The technology incorporates the use of catalytic components with the membrane to accelerate the reforming reactions.

A patented a two-step process for synthesis gas generation has been developed (Nataraj, Moore, & Russek, 2000) that can be utilized to generate synthesis gas from several feedstocks, including natural gas, associated gas (from crude oil production), light hydrocarbon gases from refineries, and medium-weight hydrocarbon fractions such as naphtha. The first stage comprises conventional steam reforming with partial conversion to synthesis gas and is followed by complete conversion in an ion transport ceramic membrane (ITM) reactor. This combination resolves any issues associated with steam reforming for feedstocks with hydrocarbons higher in molecular weight than methane, because the higher molecular weight hydrocarbons tend to crack and degrade both the catalyst and membrane.

By shifting the equilibrium in the steam reforming process through removal of hydrogen from the reaction zone, membrane reactors can also be used to increase the equilibrium-limited methane conversion. Using Pd-Ag alloy membrane reactors. methane conversion can reach as close to 100 % (Shu, Grandjean, & Kaliaguine, 1995).

6.3 Hydrogen production

Throughout the previous section there has been, of necessity, frequent reference to the production of hydrogen as an integral part of the production of carbon monoxide, because the two gases make up the mixture known as synthesis gas. Hydrogen is indeed an important commodity in the refining industry because of its use in hydrotreating processes, such as desulfurization, and in hydroconversion processes, such as hydrocracking. Part of the hydrogen is produced during reforming processes but that source, once sufficient, is now insufficient for the hydrogen needs of a modern refinery (Ancheyta & Speight, 2007; Speight, 2000; Speight, 2014; Speight & Ozum, 2002). In addition, optimum hydrogen purity at the reactor inlet extends catalyst life by maintaining desulphurization kinetics at lower operating temperatures and reducing carbon laydown. Typical purity increases resulting from hydrogen purification equipment and/or increased hydrogen sulfide removal, as well as tuning hydrogen circulation and purge rates, may extend catalyst life up to about 25%. Indeed, as hydrogen use has become more widespread in refineries, hydrogen production has moved from the status of a high-tech specialty operation to an integral feature of most refineries (Raissi, 2001; Vauk *et al.*, 2008).

The gasification of residue and coke to produce hydrogen and/or power may increase in use in refineries over the next two decades (Speight, 2011b), but several other processes are available for the production of the additi onal hydrogen that is necessary for the various heavy feedstock hydroprocessing sequences (Speight, 2014). This section presents a general description of these processes. These gasification processes, which are often referred to the *garbage disposal units* of the refinery, have not been described earlier.

6.3.1 Heavy residue gasification and combined cycle power generation

Heavy residues are gasified and the produced gas is purified to fuel gas that is free of contaminants (Gross & Wolff, 2000). As an example, solvent deasphalter residuum (*deasphalter bottoms*) is gasified by partial oxidation method under pressure of about 570 psi and at a temperature between 1300 and 1500 °C (2370 °F and 2730 °F). The high temperature generates gas stream flows into a waste heat boiler, in which the hot gas is cooled and high pressure saturated steam is generated. The gas from the waste heat boiler is then heat exchanged with the fuel gas and flows to the carbon scrubber, where unreacted carbon particles are removed from the generated gas by water scrubbing.

The gas from the carbon scrubber is further cooled by the fuel gas and boiler feed water and led into the sulfur compound removal section, where hydrogen sulfide (H_2S) and carbonyl sulfide (COS) are removed from the gas to obtain clean fuel gas. This clean fuel gas is heated with the hot gas generated in the gasifier and finally supplied to the gas turbine at a temperature of 250 to 300 °C (480 to 570 °F).

In order to decrease the nitrogen oxide (NO_x) content in the flue gas, two methods can be applied. The first method is the injection of water into the gas turbine combustor. The second method is to selectively reduce the nitrogen oxide content by injecting ammonia gas in the presence of de-NO_x catalyst that is packed in a proper position of the heat recovery steam generator. The latter is more effective that the former to lower the nitrogen oxide emissions to the air.

6.3.2 Hybrid gasification process

In the hybrid gasification process, a coal/residual oil slurry is injected into the gasifier where it is pyrolyzed in the upper part of the reactor to produce gas and chars. The chars produced are then partially oxidized to ash. The ash is removed continuously from the bottom of the reactor.

In this process, coal and vacuum residue are mixed together into slurry to produce clean fuel gas. The slurry fed into the pressurized gasifier is thermally cracked at a temperature of 850 to 950 °C (1560 to 1740 °F) and is converted into gas, tar, and char. The mixture of oxygen and steam in the lower zone of the gasifier converts the char to gaseous products. The gas leaving the gasifier is quenched to a temperature of 450 °C (840 °F) in the fluidized-bed heat exchanger, and is then scrubbed to remove tar, dust, and steam at around 200 °C (390 °F).

Ash is discharged from the gasifier and indirectly cooled with steam and then discharged into the ash hopper. It is burned with an incinerator to produce process steam. Coke deposited on the silica sand is removed in the incinerator.

6.3.3 Hydrocarbon gasification

The gasification of hydrocarbons to produce hydrogen is a continuous, noncatalytic process that involves partial oxidation of the hydrocarbon and one of several processes that are used for gasification of carbonaceous fuels to gaseous products (Breault, 2010).

In the process, air or oxygen, with steam or carbon dioxide, is used as the oxidant at 1095 to 1480 °C (2000 to 2700 °F). Any carbon produced (2 to 3% w/w of the feedstock) during the process is removed as a slurry in a carbon separator and pelletized for use either as a fuel or as raw material for carbon-based products.

6.3.4 Hypro process

Due to its abundance and high H/C ratio (highest among all hydrocarbons), methane is an obvious source for hydrogen. The steam reforming of methane represents the current trend for hydrogen production (Hypro process). Other popular methods of hydrogen production include autothermal reforming and partial oxidation. However, if hydrogen is the desire product, all these processes involve the formation of large amounts of unwanted carbon monoxide and carbon dioxide (COx) as a by-product.

Hydrogen production routes, which do not require complex COx removal procedures, are therefore desired for production of high-purity hydrogen. Thus, there is much interest in the catalytic decomposition of natural gas, whose major constituent is methane, for production of hydrogen. Given that only hydrogen and carbon are formed in the decomposition process, the separation of products is not an issue. The other main advantage is the simplicity of the methane decomposition process as compared to conventional methods. For example, the high- and low-temperature water-gas shift reactions and carbon dioxide removal step (involved in the conventional methods) are completely eliminated. Catalyst regeneration is extremely important for the practical application of the clean hydrogen production process.

The hypro process is a continuous catalytic method for hydrogen manufacture from natural gas or from refinery effluent gases, especially the decomposition of methane to hydrogen and carbon (Choudhary & Goodman, 2006; Choudhary, Sivadinarayana, & Goodman, 2003):

$$\mathrm{CH_4 \rightarrow C + 2H_2}$$

Hydrogen is recovered by phase separation to yield hydrogen of about 93% purity, and the principal contaminant is methane.

6.3.5 Pyrolysis processes

There has been recent interest in the use of pyrolysis processes to produce hydrogen. Specifically, the interest has focused on the pyrolysis of methane (natural gas) and hydrogen sulfide.

Natural gas is readily available and offers a relatively rich stream of methane with lower amounts of ethane, propane, and butane also present. The thermocatalytic decompositon of natural gas hydrocarbons (c.f., hypro process) offers an alternate method for the production of hydrogen (Dahl & Weimer, 2001; Uemura, Ohe, Ohzuno, & Hatate, 1999; Weimer *et al*., 2000):

$$\mathrm{C}_n\mathrm{H}_m \rightarrow n\mathrm{C} + (m/2)\mathrm{H_2}$$

The production of hydrogen by direct decomposition of hydrogen sulfide has also been proposed (Clark & Wassink, 1990; Donini, 1996; Luinstra, 1996; Zaman & Chakma, 1995). Hydrogen sulfide decomposition is a highly endothermic process, and equilibrium yields are poor (Clark, Dowling, Hyne, & Moon, 1995). At temperatures less than 1500 °C (2730 °F), the thermodynamic equilibrium is unfavorable toward hydrogen formation. However, in the presence of catalysts such as platinum-cobalt at 1000 °C (1830 °F), disulfides of molybdenum (Mo) or tungsten (W) at 800 °C (1470 °F) (Kotera, Todo, & Fukuda, 1976), or other transition metal sulfides supported on alumina at 500 to 800 °C (930 to 1470 °F), decomposition of hydrogen sulfide proceeds. In the temperature range of about 800 to 1500 °C (1470 to 2730 °F), thermolysis of hydrogen sulfide can be treated simply:

$$\mathrm{H_2S \rightarrow H_2} + 1/xS_x \quad \Delta\mathrm{H_{298K}} = +34{,}300\,\mathrm{Btu/lb}$$

where $x = 2$. Outside this temperature range, multiple equilibria may be present, depending on temperature, pressure, and relative abundance of hydrogen and sulfur (Clark & Wassink, 1990).

In addition, the steam-iron process is an established process, which was used for the production of hydrogen from cokes at the beginning of the twentieth century. However, the process could not compete with the later-developed steam reforming of methane, and so the process fell into disuse. The renewed interest in the development of the steam-iron process is mainly focused on the use of renewable energy sources, like biomass. In this thesis, the production of hydrogen by the steam-iron process from pyrolysis oil is studied. Pyrolysis oil, obtained from the pyrolysis of biomass, is used to facilitate transportation and to simplify gasification and combustion processes, before being processed to hydrogen. The benefit of the steam-iron process compared to other thermo-chemical routes of biomass is that hydrogen can be produced in a two-step redox cycle, without the need of any purification steps (such as pressure-swing adsorption) (Bleeker, 2009; Bleeker, Kersten, & Veringa, 2007).

6.3.6 Shell gasification process

The Shell gasification process (*partial oxidation process*) is a flexible process for generating syngas, principally hydrogen and carbon monoxide, for the ultimate production of high-purity, high-pressure hydrogen, ammonia, methanol, fuel gas, and town gas, or for reducing gas by reaction of gaseous or liquid hydrocarbons with oxygen, air, or oxygen-enriched air. Traditionally, petroleum residues have been sold as marine bunker fuel or used on-site as furnace fuel. However, with changing legislation, refineries are under pressure to reduce both their emissions and the sulfur content of their products. In addition, the market for fuel oil is shrinking. The Shell gasification process can be combined with other upgrading and treating technologies to convert a wide range of low-value residue into syngas.

The most important step in converting heavy residue into industrial gas is the partial oxidation of the oil using oxygen with the addition of steam. The gasification process takes place in an empty, refractory-lined reactor at temperatures of about 1400 °C (2550 °F) and pressures between 29 and 1140 psi. The chemical reactions in the gasification reactor proceed without catalyst to produce gas that contains carbon amounting to some 0.5 to 2% by weight, based on the feedstock. The carbon is removed from the gas with water, extracted in most cases with feed oil from the water, and returned to the feed oil. The high reformed gas temperature is utilized in a waste heat boiler for generating steam. The steam is generated at 850 to 1565 psi. Some of this steam is used as process steam and for oxygen and oil preheating. The surplus steam is used for energy production and heating purposes.

6.3.7 Steam-naphtha reforming

Liquid feedstocks, either liquefied petroleum gas or naphtha, can also provide backup feed for the steam-methane reformer, if there is a risk of natural gas curtailments (Breault, 2010; Rostrup-Nielsen & Christiansen, 2011). The feed-handling system needs to include a surge drum, feed pump, a vaporizer (usually steam-heated) followed by further heating before desulfurization. The sulfur in liquid feedstocks occurs as mercaptans, thiophene derivatives, or higher boiling compounds. These compounds are stable and will not be removed by zinc oxide, therefore a hydrogenation unit will be required. In addition, as with refinery gas, olefins must also be hydrogenated if they are present.

Thus, steam-naphtha reforming is a continuous process for the production of hydrogen from liquid hydrocarbons. In fact, it is similar to steam-methane reforming, which is one of several possible processes for the production of hydrogen from low-boiling hydrocarbons other than ethane (Brandmair *et al*., 2003; Find, Nagaoka, & Lercher, 2003; Muradov, 1998; Murata, Ushijima, & Fujita, 1997). A variety of naphtha-types in the gasoline boiling range may be employed, including feeds containing up to 35% aromatics. Thus, following pre-treatment to remove sulfur compounds, the feedstock is mixed with steam and taken to the reforming furnace (675 to 815 °C, 1250 to 1500 °F, 300 psi, where hydrogen is produced.

6.3.8 Texaco gasification (partial oxidation) process

The Texaco gasification (partial oxidation) process is a partial oxidation gasification process for generating synthesis gas (Breault, 2010). The characteristic of the process is to inject feedstock together with carbon dioxide, steam, or water into the gasifier. Therefore, solvent deasphalted residue or petroleum coke rejected from any coking method can be used as feedstock for this gasification process. The produced gas from this gasification process can be used for the production of high-purity, high-pressurized hydrogen, ammonia, and methanol. The heat recovered from the high-temperature gas is used for the generation of steam in the waste heat boiler. Alternatively the less expensive quench-type configuration is preferred when high-pressure steam is not needed or when a high degree of shift is needed in the downstream carbon monoxide converter.

In the process, the feedstock, together with the feedstock carbon slurry recovered in the carbon recovery section, is pressurized to a given pressure, mixed with high-pressure steam, and then blown into the gas generator through the burner together with oxygen.

The gasification reaction is a partial oxidation of hydrocarbons to carbon monoxide and hydrogen:

$$C_xH_{2y} + x/2O_2 \rightarrow xCO + yH_2$$

$$C_xH_{2y} + xH_2O \rightarrow xCO + (x + y)H_2$$

The gasification reaction is instantly completed, thus producing gas mainly consisting of H_2 and CO ($H_2 + CO = >90\%$). The high-temperature gas leaving the reaction chamber of the gas generator enters the quenching chamber linked to the bottom of the gas generator and is quenched to 200 to 260 °C (390 to 500 °F) with water.

6.3.9 Recovery from fuel gas

Recovering of hydrogen from refinery fuel gas can help refineries satisfy high hydrogen demand. Cryogenic separation is typically viewed as being the most thermodynamically efficient separation technology. The basic configuration for hydrogen recovery from refinery gases involves a two-stage partial condensation process, with post purification via pressure swing adsorption (Dragomir *et al.*, 2010). The major steps in this process involve first compressing and pre-treating the crude refinery gas stream before chilling to an intermediate temperature (–60 to –120°F). This partially condensed stream is then separated in a flash-drum after which the liquid stream is expanded through a Joule-Thompson valve to generate refrigeration and then is fed to the wash column. Optionally, the wash column can be replaced by a simple flash drum.

A crude liquefied petroleum gas (LPG) stream is collected at the bottom of the column, and a methane-rich vapor is obtained at the top. The methane-rich vapor is sent to compression and then to fuel. The vapor from the flash drum is further cooled in a second heat exchanger before being fed to a second flash drum where it produces a hydrogen-rich stream and a methane-rich liquid. The liquid is expanded in a Joule-Thomson valve to generate refrigeration, and then is sent for further cooling. Next, the hydrogen-rich gas is sent to the pressure swing adsorption unit for further purification. The tail gas from this unit is compressed and returned to fuel, together with the methane-rich gas.

6.4 Gasification products: composition and quality

The composition of the products from gasification processes is varied insofar as the gas composition varies with the type of feedstock and the gasification system employed (Chapters 1, 2, and 10). Furthermore, the quality of gaseous product(s) must be improved by removal of any pollutants such as particulate matter and sulfur compounds before further use, particularly when the intended use is a water-gas shift or methanation (Speight, 2007, 2008, 2013a, 2013b).

Generally, products from gasification processes can range from (1) high-purity hydrogen, (2) high-purity carbon monoxide, (3) high-purity carbon dioxide, and (4) a range of H_2/CO mixtures (Chapter 10). In fact, the H_2/CO ratio can be selected at will and the appropriate process scheme chosen, in part, by the product composition required. At one end of the scale, (i.e., if hydrogen is the desired product), the H_2/CO ratio can approach infinity by converting (*shifting*) all of the carbon monoxide to CO_2. By contrast, on the other end, the ratio cannot be adjusted to zero because hydrogen and water are always produced.

Low-Btu gas (low-heat content gas) is the product when the oxygen is not separated from the air and, as a result, the gas product invariably has a low-heat content (150 to 300 Btu/ft^3). In *medium-Btu gas* (medium-heat content gas), the heating value is in the range 300 to 550 Btu/ft^3 and the composition is much like that of low-heat content gas, except that there is virtually no nitrogen and the H_2/CO ratio varies from 2:3 to approximately 3:1 and the increased heating value correlates with higher methane and hydrogen contents as well as with lower carbon dioxide content. *High-Btu gas* (high-heat content gas) is essentially pure methane and often referred to as synthetic natural gas or substitute natural gas. However, to qualify as substitute natural gas, a product must contain at least 95% methane; the energy content of synthetic natural gas is 980 to 1080 Btu/ft^3. The commonly accepted approach to the synthesis of high-heat content gas is the catalytic reaction of hydrogen and carbon monoxide.

Hydrogen is also produced during gasification of carbonaceous feedstocks. Although several gasifier types exist (Chapter 2), entrained-flow gasifiers are considered most appropriate for producing both hydrogen and electricity from coal. This is because they operate at temperatures high enough (approximately 1500 °C, 2730 °F) to enable high carbon conversion and prevent downstream fouling from tars and other residuals.

There is also a series of products that are called by older (even archaic) names that evolved from older coal gasification technologies and warrant mention: (1) producer gas, (2) water gas, (3) town gas, and (4) synthetic natural gas. These products are typically low-to-medium Btu gases (Chapter 10).

6.4.1 Purification

The processes that have been developed for gas cleaning (Mokhatab, Poe, & Speight, 2006; Speight, 2007, 2008) vary from a simple once-through wash operation to complex multistep systems with options for recycle of the gases (Mokhatab *et al.*, 2006). In some cases, process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form.

In more general terms, gas cleaning is divided into removal of particulate impurities and removal of gaseous impurities. For the purposes of this chapter, the latter operation includes the removal of hydrogen sulfide, carbon dioxide, sulfur dioxide, and products that are not related to synthesis gas and hydrogen production. However, there is also need for subdivision of these two categories as dictated by needs and process capabilities: (1) coarse cleaning whereby substantial amounts of unwanted impurities are removed in the simplest, most convenient, manner; (2) fine cleaning for the removal of residual impurities to a degree sufficient for the majority of normal chemical plant operations, such as catalysis or preparation of normal commercial products, or cleaning to a degree sufficient to discharge an effluent gas to atmosphere through a chimney; and (3) ultra-fine cleaning where the extra step (as well as the extra expense) is justified by the nature of the subsequent operations or the need to produce a particularly pure product.

Contrary to the general belief of some scientists and engineers, all gas-cleaning systems are *not* alike, and having a good understanding of the type of gaseous effluents from coal-based processes is necessary to implementing the appropriate solution. The design of a gas-cleaning system must always take into account the operation of the upstream installations, because every process will have a specific set of requirements. In some cases, the application of a dry dusting removal unit may not be possible and thus requires a special process design of the wet gas-cleaning plant. Thus, the gas-cleaning process must always be of optimal design – one for both the upstream and downstream processes.

Gas processing, although generally simple in chemical and/or physical principles, is often confusing because of the frequent changes in terminology and, often, lack of cross-referencing (Mokhatab *et al.*, 2006; Speight, 2007, 2008, 2013a, 2014). Although gas processing employs different process types, there is always overlap between the various concepts. And, with the variety of possible constituents and process operating conditions, a universal purification system cannot be specified for economic application in all cases.

Nevertheless, the first step in gas cleaning is usually a device to remove large particles of carryover (entrained) material coal and other solid materials (Mokhatab *et al.*, 2006; Speight, 2007, 2008). This is followed by cooling, quenching, or washing to condense tars and oils and to remove dust and water-soluble materials from the gas stream. Water washing is desirable for simplicity in gas cleaning; however, the purification of this water is not simple.

Clean-up steps and their sequence can be affected by the type of gas produced and its end use (Mokhatab *et al.*, 2006; Speight, 2007, 2008). The minimum requirement in this respect would be the application of low-heat value (low-Btu) gas produced from low-sulfur anthracite coal as a fuel gas. The gas may pass directly from the gasifier to the burners and, in this case, the burners are the clean-up system. Many variations on this theme are possible; also, the order of the cleanup stages may be varied.

The selection of a particular process-type for gas cleaning is not simple. Several factors have to be considered, not the least of which is the constitution of the gas stream that requires treatment. Indeed, process selectivity indicates the preference with which the process will remove one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only (Mokhatab *et al.*, 2006; Speight, 2007, 2014).

Gas cleaning by absorption by a liquid or adsorption by use of a solid sorbent is one of the most widely applied operations in the chemical and process industries (Mokhatab *et al.*, 2006; Speight, 2007). Some processes have the potential for sorbent regeneration, but in a few cases, the process is applied in a nonregenerative manner. The interaction between sorbate and sorbent may either be physical in nature or consist of physical sorption followed by chemical reaction. Other gas stream treatments use the principle of chemical conversion of the contaminants with the production of "harmless" (noncontaminant) products or to substances that can be removed much more readily than the impurities from which they are derived (Mokhatab *et al.*, 2006; Speight, 2007, 2008).

Any gases, such as hydrogen sulfide and/or carbon dioxide, that are the products of coal processing can be removed by application of an amine washing procedure.

$$2RNH_2 + H_2S \rightarrow (RNH_3)_2S$$

$$(RNH_3)_2S + H_2S \rightarrow 2RNH_3HS$$

$$2RNH_2 + CO_2 + H_2O \rightarrow (RNH_3)_2CO_3$$

$$(RNH_3)_2CO_3 + H_2O \rightarrow 2RNH_3HCO_3$$

There are also *solvent extraction* methods for producing low-sulfur and low-mineral matter coal, but hydrotreatment of the coal extract is also required. In these methods, the organic material is extracted from the inorganic material in coal. A study has indicated that solvent-refined coal will probably not penetrate the power generation industry on a large scale for several years to come.

In addition to hydrogen sulfide and carbon dioxide, gas streams may contain other contaminants such as sulfur dioxide, mercaptans, and carbonyl sulfide. The presence of these impurities may eliminate some of the sweetening processes because some processes will remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases, yet they are capable of removing the acid gas impurities to very low levels when the acid gases are there in low-to-medium concentrations in the gas stream.

Many different methods have been developed for carbon dioxide and hydrogen sulfide removal, some of which are briefly discussed here. Concentrates of hydrogen sulfide obtained as by-products of gas desulfurization are often converted by partial oxidation to elemental sulfur (Claus process) (Mokhatab *et al*., 2006; Speight, 2007, 2013a, 2014).

Pressure swing adsorption units use beds of solid adsorbent to separate impurities from hydrogen streams leading to high-purity, high-pressure hydrogen and a low-pressure tail gas stream containing the impurities and some of the hydrogen. The beds are then regenerated by depressuring and purging. Part of the hydrogen (up to 20% v/v) may be lost in the tail gas.

Pressure swing adsorption is generally the purification method of choice for steam reforming units because of its production of high-purity hydrogen. It is also used for purification of refinery off-gases, where it competes with membrane systems.

Many hydrogen plants that formerly used a *wet scrubbing* process for hydrogen purification are now using the *pressure swing adsorption* (PSA) for purification (Speight, 2007, 2014). The pressure swing adsorption process is a cyclic process that uses beds of solid adsorbent to remove impurities from the gas and generally produces higher-purity hydrogen (99.9% v/v purity compared to less than 97% v/v purity). The purified hydrogen passes through the adsorbent beds with only a tiny fraction absorbed, and the beds are regenerated by depressurization followed by purging at low pressure.

When the beds are depressurized, a waste gas (or *tail gas*) stream is produced and consists of the impurities from the feed (carbon monoxide, carbon dioxide, methane, and nitrogen) plus some hydrogen. This stream is burned in the reformer as fuel and reformer operating conditions in a pressure swing adsorption plant are set so that the tail gas provides no more than about 85% v/v of the reformer fuel. This gives good burner control because the tail gas is more difficult to burn than regular fuel gas and the high content of carbon monoxide can interfere with the stability of the flame.

As the reformer operating temperature is increased, the reforming equilibrium shifts, resulting in more hydrogen and less methane in the reformer outlet and hence less methane in the tail gas.

Membrane systems separate gases by taking advantage of the difference in rates of diffusion through membranes (Brüschke, 1995, 2003). Gases that diffuse faster (including hydrogen) become the permeate stream and are available at low pressure, whereas the slower-diffusing gases become the nonpermeate and leave the unit at a pressure close to the pressure of the feedstock at the entry point. Membrane systems contain no moving parts or switch valves and have potentially very high reliability. The major threat is from components in the gas (such as aromatics) that attack the membranes, or from liquids, which plug them.

Membranes are fabricated in relatively small modules; for larger capacity, more modules are added. Cost is therefore virtually linear with capacity, making them more competitive at lower capacities. The design of membrane systems involves a tradeoff between pressure drop (or diffusion rate) and surface area, as well as between product purity and recovery. As the surface area is increased, the recovery of fast components increases; however, more of the slow components are recovered, which lowers the purity.

Cryogenic separation units operate by cooling the gas and condensing some, or all, of the constituents for the gas stream. Depending on the product purity required, separation may involve flashing or distillation. Cryogenic units offer the advantage of being able to separate a variety of products from a single-feed stream. One specific example is the separation of light olefins from a hydrogen stream.

Hydrogen recovery is in the range of 95% v/v, with purity above 98% v/v obtainable. In addition to the general description of the purification processes presented earlier, four of the major process techniques for achieving this level of purity are:

(i) *Cryogenics plus methanation*, which utilizes a cryogenic process whereby carbon monoxide is liquefied in a number of steps until hydrogen with a purity of on the order of 98% is produced. The condensed carbon monoxide, which would contain methane, is then distilled to produce pure carbon monoxide and a mixture of carbon monoxide and methane. The hydrogen stream is taken to a *shift converter* where the remaining carbon monoxide is converted to carbon dioxide and hydrogen. The carbon dioxide is removed and any further carbon monoxide or carbon dioxide can be removed by methanation. The resulting hydrogen stream typically has purity on the order of 99.7% v/v.

(ii) *Cryogenics plus pressure swing adsorption (PSA)*, which utilizes the similar sequential liquefaction of carbon monoxide until hydrogen having 98% purity is obtained. Again, the carbon monoxide stream can be further distilled to remove methane until it is essentially pure. The hydrogen stream is then allowed to go through multiple *pressure swing adsorption* cycles until the hydrogen purity is as high as 99.999% v/v.

(iii) *Methane-wash cryogenic process* utilizes the principle of carbon monoxide absorption in a liquid methane stream so that the hydrogen stream produced contains only low levels (on the order of parts per million) of carbon monoxide but about 5 to 8% v/v methane. Hence, the hydrogen stream may have purity on the order of only 95% v/v. However, the liquid carbon monoxide/methane stream can be distilled to produce a pure carbon monoxide stream and a carbon monoxide/methane stream, which can be used as fuel.

(iv) *COsorb process* utilizes copper ions (cuprous aluminum chloride, $CuAlCl_4$) in toluene to form a chemical complex with the carbon monoxide to separate it from hydrogen, nitrogen, carbon dioxide, and methane. This process can capture about 96% of the available carbon monoxide to produce a stream of greater than 99% purity. On the other hand, water, hydrogen sulfide, and other trace chemicals can poison the copper catalyst and must be removed prior to the reactor.

Although the efficiency of cryogenic separation decreases with a content of low carbon monoxide in the feed, the COsorb process is able to process gas streams with low carbon monoxide content much more efficiently.

6.4.2 Oil-water separation

The typical oil-water separation process occurs in a device designed to separate gross amounts of oil and suspended solids from the effluents of petroleum and gas processing. The most common type of separator is the API separator, which is a gravity separation device designed by using the specific gravity difference between the oil and water (depending on the pressure, the gas remains in the volatile state) while the oil and water separate from stream as liquids (Mokhatab *et al*., 2006; Speight, 2007). Based on that design criterion, any suspended solids settle to the bottom of the separator as a sediment layer, the oil will rise to the top of the separator, and the wastewater will be the middle layer between the oil on the top and the solids on the bottom.

Typically, the oil layer is skimmed off and subsequently reprocessed or disposed of, and the bottom sediment layer is removed by a chain and flight scraper (or similar device) and a sludge pump. The water layer is sent to further treatment consisting usually of a dissolved air flotation unit for further removal of any residual oil and then to some type of biological treatment unit for removal of undesirable dissolved chemical compounds.

Parallel plate separators are similar to API separators but include tilted parallel plate assemblies, and the underside of each parallel plate provides more surface for suspended oil droplets to coalesce into larger globules. Any sediment slides down the topside of each parallel plate. Such separators still depend on the specific gravity between the suspended oil and the water. However, the parallel plates enhance the degree of oil-water separation. The result is that a parallel plate separator requires significantly less space than a conventional API separator to achieve the same degree of separation.

6.5 Advantages and limitations

In the early days of the petroleum industry, the delayed coking unit was considered as the *garbage can* of the refinery in which any high-boiling petroleum-based feedstock (typically not much good for anything else) could be converted to distillates. For some time, gasifiers were considered in the same light, but that was not always the case. Advantages were obvious and disadvantages were not always obvious but they were not insurmountable. This section relates to the advantages and limitations of the gasification process that should be taken into consideration for efficient operation of a gasification plant – all relate to the production of the two major products (carbon monoxide and hydrogen) being given consideration here.

Gasification enables the capture – in an environmentally beneficial manner – of the value present in a variety of low-grade carbonaceous, wastes, or biomass. Without gasification, these materials would have to be disposed of by an alternate route that could potentially damage the environment and, equally important, ignore or discard a valuable source of energy. Although traditional feedstocks included coal and petroleum coke in large-scale industrial plants, there is an increasing use of municipal solid waste, industrial waste, and biomass in smaller-scale plants, converting that material to energy.

In fact, the increasing costs of conventional waste management and disposal options, and the desire, in most developed countries, to divert an increasing proportion of mixed organic waste materials from landfill disposal, for environmental reasons, will render the investment in energy from waste projects increasingly attractive. Indeed, gasification also offers more scope for recovering products from waste than incineration. When waste is burnt in an incinerator, the only practical product is energy, whereas the gases, oils, and solid char from pyrolysis and gasification not only can be used as a fuel but they may also be purified and used as a feedstock for petrochemicals and other applications. Rather than producing only ash, many processes also produce a stable granulate, which can be more easily and safely utilized. In addition, some processes are targeted at producing specific recyclables such as metal alloys and carbon black. From waste gasification, in particular, it is feasible to produce hydrogen, which many see as an increasingly valuable resource.

Most new projects for the recovery of energy from various carbonaceous feedstocks (including wastes such as municipal waste materials) will involve the installation of new purpose-designed incineration plant with heat recovery and power generation. However, advanced thermal processes for municipal solid waste that are based on pyrolysis or gasification processes are also being introduced. These processes offer significant environmental and other attractions and will likely have an increasing role to play, but the rate of increase of use is difficult to predict.

Despite the benefits of using coal as a gasification feedstock, there are several environmental challenges, including significant air quality, climate change, and mining impacts. However, coal gasification technologies have been demonstrated that provide order-of-magnitude reductions in criteria pollutant emissions and, when coupled with carbon capture and sequestration (CCS), the potential for significant reductions in carbon dioxide emissions. Therefore, although coal is a finite nonrenewable resource, coal-derived hydrogen with carbon capture and storage can increase domestic energy independence, provide near-term carbon dioxide and criteria pollutant reduction benefits, and facilitate the transition to a more sustainable hydrogen-based transportation system. Carbon capture and storage is one of the critical enabling technologies that could lead to coal-based hydrogen production for use as a transportation fuel. However, there are other risks to the environment that need to be addressed.

Although not a limiting factor of the process, many forms of biomass contain a high percentage of moisture (along with carbohydrates and sugars) and mineral constituents – both of which can influence the economics and viability of a gasification process. The presence of high levels of moisture in the biomass reduces the temperature inside the gasifier, which then reduces the efficiency of the gasifier. Therefore, many biomass gasification technologies require that the biomass be dried to reduce the moisture content prior to feeding into the gasifier. In addition, biomass can come in a range of sizes. In many biomass gasification systems, the biomass must be processed to a uniform size or shape to feed into the gasifier at a consistent rate and to ensure that as much of the biomass is gasified as possible.

Furthermore, the presence of mineral matter in the coal-biomass feedstock is not appropriate for fluidized-bed gasification. The low melting point of ash present in woody biomass leads to agglomeration, which causes defluidization of the ash as well as sintering, deposition, and corrosion of the gasifier construction metal bed (Vélez *et al.*, 2009). Biomass containing alkali oxides and salts with the propensity of produce yield higher than 5% w/w ash causes clinkering/slagging problems (McKendry, 2002). Thus, it is imperative to be aware of the melting of biomass ash, its chemistry within the gasification bed (no bed, silica/sand, or calcium bed), and the fate of alkali metals when using fluidized-bed gasifiers.

Furthermore, the disposal of municipal and industrial wastes has become an important problem because the traditional means of disposal – landfill – has become environmentally much less acceptable than previously. New, much stricter regulations of these disposal methods will make the economics of waste processing for resource recovery much more favorable. One method of processing waste streams is to convert the energy value of the combustible waste into a fuel. One type of fuel attainable from wastes is a low-heating value gas, usually 100 to 150 Btu/ft^3, which can be used to generate process steam or to generate electricity. Co-processing such waste with coal is also an option (Speight, 2008).

One of the major disadvantages of gasification plants in general, irrespective of the feedstock, is the environmental impact that has drawn increasing concern. Attention is not only focused on controlling pollutants such as sulfur dioxide (SO_2), oxides of nitrogen (NOx), and particulates (PM) but also for controlling the emission of carbon dioxide (CO2). There is an increasing need to reduce the emissions of carbon dioxide to the atmosphere to alleviate the global warming effect. It induces significant challenges to generate electricity efficiently together with near-zero carbon dioxide emissions.

In the process, carbon dioxide, hydrogen, and other coal by-products are captured so they can be used for useful purposes. Evolving technologies are also making coal at existing plants cleaner – refined coal technologies remove many of the impurities contained in existing coal. New techniques are helping remove mercury and harmful gases while unlocking more energy potential.

In co-gasification of coal with other feedstocks or with a mixture of feedstocks (coal may be excluded), the technology varies and is usually site specific with high dependence on the feedstock (Brar, Singh, Wang, & Kumar, 2012). At the largest scale, the plant may include the well-proven fixed-bed and entrained-flow gasification processes. At smaller scales, emphasis is placed on technologies that appear closest to commercial operation. Pyrolysis and other advanced thermal conversion processes are included where power generation is practical, using the on-site feedstock produced (Chapter 1).

A major advantage of the gasification process is that it lends itself to the installation of a gasification refinery that would have, as the centerpiece, gasification technology or at least as a section of a conventional petroleum refinery (Speight, 2011b). The refinery would produce syngas (from the carbonaceous feedstock) from which liquid fuels would be manufactured using the FTS technology.

The manufacture of gas mixtures of carbon monoxide and hydrogen has been an important part of chemical technology for approximately 100 years. Originally, such mixtures were obtained by the reaction of steam with incandescent coke and were known as *water gas*. Eventually, steam reforming processes, in which steam is reacted with natural gas (methane) or petroleum naphtha over a nickel catalyst, found wide application for the production of synthesis gas.

As petroleum supplies decrease, the desirability of producing gas from other carbonaceous feedstocks will increase, especially in those areas where natural gas is in short supply. It is also anticipated that costs of natural gas will increase, allowing coal gasification to compete as an economically viable process. Research in progress on a laboratory and pilot-plant scale should lead to the invention of new process technology by the end of the 21st Century, thus accelerating the industrial use of coal gasification.

The conversion of the gaseous products of gasification processes to synthesis gas, a mixture of hydrogen (H_2) and carbon monoxide (CO), in a ratio appropriate to the application, needs additional steps, after purification. The product gases – carbon monoxide, carbon dioxide, hydrogen, methane, and nitrogen – can be used as fuels or as raw materials for chemical or fertilizer manufacture.

Finally, the gas from any gasification process is inherently toxic because of essential components such as carbon monoxide and unwanted components. However, this inherent toxicity is not the reason for gas cleaning because the gas should never be released to the atmosphere directly.

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Synthetic liquid fuel production from gasification

7

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7.1 Introduction

The varying prices of crude oil, the politics of crude oil, and other variable economic factors have led to a strong interest in the production of liquid fuels from coal, natural gas, and biomass (Hu, Yu, & Lu, 2012; Speight, 2008, 2011a, 2011b). The technology to produce fuels from such sources is varied, but a tried and true technology involves the so-called *indirect* process in which the feedstock is first converted to gases (particularly synthesis gas) from which liquid products are generated by the Fischer-Tropsch (FT) process (Kreutz, Larson, Liu, & Williams, 2008).

Current conditions almost reprise the era of the 1970s when energy security concerns generated by oil embargoes stimulated federal spending in synthetic fuels. Despite considerable investment, federal support in many countries was withdrawn after supply concerns eased in the 1980s. The currently favored approach to producing synthetic fuels – the Fischer-Tropsch process – used synthesis gas (mixtures of carbon monoxide and hydrogen from the gasification of carbonaceous materials (fossil fuels or organically derived feedstocks) (Gary, Handwerk, & Kaiser, 2007; Hsu & Robinson, 2006; Speight, 2008, 2013a, 2013b, 2014; Speight & Ozum, 2002).

Many countries have attempted to capitalize on the gasification-with-Fischer-Tropsch method but the up-and-down prices of petroleum – especially when petroleum process are lower – tend to discourage such efforts on the basis of poor economic return. Nevertheless, several private ventures in the United States and throughout the world are now studying the feasibility of constructing FT synthetic fuel plants based on petroleum residue, coal, natural gas, and biomass. It is required that governments make the decision to support such efforts rather than react at a time when the occasion has passed and fuel shortages are endemic. Perhaps this is too much to ask – that a government will use foresight instead of hindsight, which is always 20-20.

The Fischer-Tropsch process is well suited to producing naphtha, which is the precursor to gasoline, as well as middle-distillate range fuels such as diesel fuel and jet fuel. The diesel produced is superior to conventionally refined diesel in terms of higher cetane number and low sulfur content. Overall, middle distillate fuels represent roughly a quarter of many refinery operations, which are typically driven by the demand for gasoline. In order for a synthetic fuels industry (whether coal, natural gas, or biomass based) to begin rivaling or even supplanting conventional petroleum refining, a major shift in political outlook would have to occur.

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In addition, recent energy legislation promotes research on capturing and storing greenhouse gas emissions and improving vehicle fuel efficiency, among other goals. Fisher-Tropsch fuels present the paradox of high-carbon emissions associated with production versus lower-carbon emissions associated with their use.

Hence, as crude oil production decreases and its price increases, the Fischer-Tropsch technology, which enables the production of synthetic hydrocarbons from carbonaceous feedstocks, is becoming an increasingly attractive technology in the energy mix. In fact, coupled with this is the fact that FT products are ultra-clean fuels in that they contain no aromatics, no sulfur compounds, and no nitrogen compounds. In essence, compared to petroleum-derived gasoline and diesel fuel, the analogous product produced by the Fischer-Tropsch process will burn to produce considerably less polynuclear aromatic hydrocarbons (PNAs), and no sulfur oxides (SOx) and no nitrogen oxides (NOx). With global pressures to reduce greenhouse gas emissions intensifying, legislative frameworks in Europe and the United States have already been put in place to force producers of liquid transportation fuels to comply with stricter emission standards. The impact of such legislation is that dilution of petroleum-derived fuels with the cleaner FT-derived fuels is becoming an increasingly important way to achieve environmental compliance. Thus, it is not surprising that FT technology now occupies a visible place in the energy mix required for sustainable global development.

This section will provide the reader with a broad perspective of thermal decompositon pyrolysis technology as it relates to converting a variety of feedstocks substrates (tar sand bitumen, coal, oil shale, and biomass are used as the examples) to distillate products for the reader to compare with gasification technologies and Fischer-Tropsch technologies that are the focus of this book. Thus, this chapter provides a general description of the FT technology and the production and upgrading of synthetic crude oil (Figure 7.1). In addition, recent developments in thermal technology for synthetic fuel production are also presented and, for comparison, the chapter also provides presentation of the means by which non–Fischer-Tropsch synthetic crude oil is converted to specification-grade fuels.

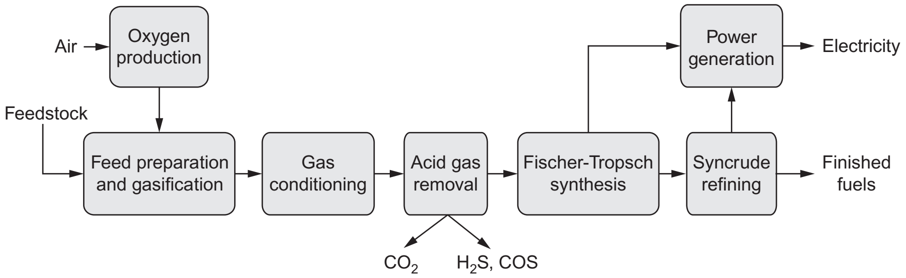

Figure 7.1 General Aspects of the Gasification Process to Produce Synthetic Crude Oil by the Fischer-Tropsch Process.

7.2 Fischer-Tropsch synthesis

The Fischer-Tropsch process is well known and has been commercially demonstrated internationally and in pilot plant demonstration in many countries (Chadeesingh, 2011). As an abundant resource in many non-oil–producing countries, coal has long been exploited as a solid fossil fuel. As oil and natural gas supplanted coal throughout the last two centuries, technologies developed to convert coal into other fuels. Proponents of expanding the use of the FT process argue that the United States and many other countries could alleviate its dependence on imported petroleum and strained refinery capacity by converting non-petroleum feedstocks to transportation fuels.

Fischer-Tropsch synthesis, particularly the coal-based process, poses several challenges: (1) the process is criticized as inefficient and costly; (2) carbon dioxide – a greenhouse gas associated with global climate change – is a by-product of the process; (3) the use of coal and natural gas as Fischer-Tropsch feedstocks would compete with electric power generation; (4) the fuels produced, primarily diesel fuel and jet fuel, would not substitute widely for the preferred transportation fuel – gasoline; and (5) the use of biomass as feedstock would compete with cellulosic ethanol production, as it is now envisioned. Each of these items is part reality and part mythology that can be overcome by judicious planning to silence (if that is possible) the nay-sayers.

The FT process is not new. For more than 75 years, synthesis gas which, in addition to carbon monoxide and hydrogen, may also contain water, carbon dioxide, nitrogen (when air is used as the gasification oxidant), and methane, has been produced on a commercial scale.

7.2.1 Fischer-Tropsch liquids

In principle, synthesis gas (primarily consisting of carbon monoxide and hydrogen) can be produced from any carbonaceous feedstock, including natural gas, naphtha, residual oil, petroleum coke, coal, and biomass, all leading to a host of reactions and products (Wender, 1996). Today's economic considerations dictate that the current production of liquid fuels from syngas translates into the use of coal or natural gas as the hydrocarbon source with the economics of the use of other feedstocks continuing to improve. Nevertheless, the synthesis gas production operation in a gas-to-liquids plant amounts to greater than half of the capital cost of the plant (Spath & Dayton, 2003). The choice of technology for syngas production also depends on the scale of the synthesis operation. Improving the economics of a feedstock-to-liquids plant is through (1) decreasing capital costs associated with synthesis gas production and (2) improving the thermal efficiency with better heat integration and utilization. Improved thermal efficiency can be obtained by combining the gas-to-liquids plant with a power generation plant to take advantage of the availability of low-pressure steam.

Two main characteristics of Fischer-Tropsch synthesis are the unavoidable production of a wide range of hydrocarbon products (olefins, paraffins, and oxygenated products) and the liberation of a large amount of heat from the highly exothermic synthesis reactions. Product distributions are influenced by (1) temperature, (2) feed gas composition (H_2/CO), (3) pressure, (4) catalyst type, and (5) catalyst composition. Fischer-Tropsch products are produced in four main steps: synthesis gas generation, gas purification, Fischer-Tropsch synthesis, and product upgrading. Depending on the types and quantities of FT products desired, either low (200 to 240 °C, 390 to 465 °F) or high temperature (300-350 °C, 570 to 660 °F) synthesis is used with either an iron (Fe) or cobalt catalyst (Co).

The process for producing synthesis gas can be described as comprising three components (see Figure 7.1): (1) synthesis gas generation, (2) waste heat recovery, and (3) gas processing. Within each of these three listed systems are several options. For example, synthesis gas can be generated to yield a range of compositions ranging from high-purity hydrogen to high-purity carbon monoxide. Two major routes can be utilized for high purity gas production: (1) pressure swing adsorption and (2) utilization of a cold box, where separation is achieved by distillation at low temperatures. In fact, both processes can also be used in combination as well. Unfortunately, both processes require high capital expenditure. However, to address these concerns, research and development is ongoing. Successes can be measured by the demonstration and commercialization of technologies such as permeable membrane for the generation of high-purity hydrogen, which in itself can be used to adjust the H_2/CO ratio of the synthesis gas produced.

Essentially, the Fischer-Tropsch synthesis is the formation of straight-chain hydrocarbons and relies on the potential for carbon monoxide to exchange oxygen with hydrogen in the presence of a catalyst (Chadeesingh, 2011). The carbonaceous feedstock is gasified in the presence of a calculated amount of oxygen (or air) to produce carbon monoxide and hydrogen. At the same time steam reacts with the carbonaceous feedstock to produce water gas, coal is burned to produce the carbon monoxide, and steam reacting with hot coal disassociates to produce hydrogen. Other gases are also produced by-products:

$$C_{coal} + O2 \rightarrow CO + H_2 + H_2O + CO_2 + CH_4$$

$$C_{coal} + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Then:

$$2H_2 + CO \rightarrow H(CH_2)_nH + H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$2CO + H_2 \rightarrow H(CH_2)_nH + CO_2$$

Unfortunately, these simple equations must suffice but they are not a true representation of the complexity of the gasification process followed by the FT synthesis. A key issue is the composition of the hydrocarbon product [$H(CH_2)_nH$], which will vary depending on (1) the configuration of the reactor, (2) the process parameter, and (3) the catalyst.

Catalysts used for the FT reaction are generally based on iron and cobalt (Khodakov, Chu, & Fongarland, 2007). Ruthenium is an active catalyst for Fischer-Tropsch but it is not economically feasible due to its high cost and insufficient reserves worldwide. Iron has been the traditional catalyst of choice for the FT reaction. It is reactive as well as the most economical catalyst for synthesis of clean fuel from the synthesis gas mixture. Compared to cobalt, iron tends to produce more olefins and also catalyzes the water-gas shift reaction. An iron-based catalyst is usually employed in high-temperature operations (300 to 350 °C, 570 to 660 °F) (Steynberg, Espinoza, Jager, & Vosloo, 1999).

Cobalt, which has higher activity for the Fischer-Tropsch reaction, is more expensive than iron. The low-temperature (200 to 240 °C; 390 to 465 °F) Fischer-Tropsch process usually employs cobalt-based catalysts due to their stability and high hydrocarbon productivity. Catalyst supports that have been utilized include silica (SiO_2), alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), magnesia (MgO), carbon, and molecular sieves. Catalyst support, metal, and catalyst preparation contribute to the cost of Fischer-Tropsch catalyst, which represents a significant part of the overall cost for the Fischer-Tropsch technology. Various types of reactors have been installed in the FT industry, such as fixed-bed reactors, multitubular reactors, adiabatic fixed-bed reactors, slurry reactors, fluidized-bed reactors, and circulating fluid-bed reactor systems (Chadeesingh, 2011; Steynberg *et al*., 1999). Given that the Fischer-Tropsch reaction is highly exothermic, temperature control and heat removal constitute the two most important design factors for the Fischer-Tropsch reactors (Hu *et al*., 2012).

7.2.2 Upgrading Fischer-Tropsch liquids

Typically, the Fischer Tropsch process produces four streams: (1) low molecular weight gases in the raw Fischer-Tropsch product (unconverted syngas and C1–C4 gases), which are separated from the liquid fraction in a hydrocarbon recovery step; (2) naphtha – light and heavy; (3) middle distillate; and (4) wax – soft and hard. All of these are co-produced as synthetic crude oil (Table 7.1) (Chadeesingh, 2011).

Table 7.1 **Range of products from the Fischer-Tropsch process**

Product	Carbon number
SNG (Synthetic Natural Gas)	C1-C2
LPG (Liquefied Petroleum Gas)	C3-C4
Light naphtha	C5-C7
Heavy naphtha	C8-C10
Middle distillate	C11-C20
Soft Wax	C21-C30
Hard Wax	C31-C60

Fractions 2-4 form the basis of the synthetic crude oil, which is distilled to produce separate streams, and each fraction is then processed through a series of refining steps suitable to the boiling range of the fraction (Speight, 2014).

Product upgrading processes for the synthetic fuel directly originate from the refining industry and are highly optimized using appropriate catalysts (De Klerk, 2011; De Klerk & Furimsky, 2010). Thus, the naphtha stream is first hydrotreated, resulting in the production of hydrogen-saturated liquids (primarily paraffins), a portion of which are converted by isomerization from normal paraffins to iso-paraffins to boost the octane value. Another fraction of the hydrotreated naphtha is catalytically reformed to provide some aromatic content to (and further boost the octane value of) the final gasoline blending stock. The middle distillate stream is also hydrotreated, resulting directly in a finished diesel blending stock. The wax fraction is hydrocracked into a finished distillate stream, and the naphtha streams that augment the hydrotreated naphtha streams are sent for isomerization and for catalytic cracking. In some scenarios, any unconverted wax is recycled to extinction within the hydroprocessing section (Collins, Joep, Freide, & Nay, 2006).

Generally, the Fischer-Tropsch synthesis is well suited to produce synthetic naphtha and diesel fuel because FT products are free from sulfur, nitrogen, and metals (such as nickel and vanadium), and the levels of naphthenes and aromatics are very low. In fact, the Fischer-Tropsch liquids (*synthetic crude oil*) can be refined into end-products in current refineries or integrated refining units. The synthetic crude oil is sulfur-free, nitrogen-free, and contains little or no aromatic constituents. Possible products from the synthetic crude oil include liquefied petroleum gas, gasoline, diesel fuel, jet fuel, and kerosene. These products are fully compatible with the comparable petroleum based products and fit into the current distribution network. Furthermore, Fischer-Tropsch products are very well suited for use as vehicle fuels from an environmental point. Future market demands will determine the product emphasis.

Finally, the product distribution of hydrocarbons formed during the Fischer–Tropsch process follows an Anderson–Schulz–Flory distribution, which can be expressed as:

$$W_n/n = (1-\alpha)^2\alpha^{n-1}$$

Where W_n is the weight fraction of hydrocarbons containing n carbon atoms, and α is the chain growth probability or the probability that a molecule will continue reacting to form a longer chain, which is dependent on the catalyst type and the process parameters.

In addition, a value of α close to unity increases production of long-chain hydrocarbons – typically waxes, which are solid at room temperature. Therefore, for production of liquid transportation fuels it will be necessary to thermally decompose (crack) these waxes. There are suggestions that the use of zeolite catalysts (or other catalysts with fixed-sized pores) can restrict the formation of hydrocarbons longer than some characteristic size (usually $n < 10$).

7.2.2.1 Gasoline production

From synthesis gas, the FT process produces a wide range of hydrocarbon products:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$$

The alkanes, or saturated hydrocarbons ($C_nH_{(2n+2)}$), tend to be normal, or straight-chain isomers. The mean value of n is determined by catalyst, process conditions, and residence time, which are usually selected to maximize formation of alkanes in the range $C_5 - C_{21}$. –. The lower boiling fraction ($C_5 - C_{12}$), is separated as naphtha, which may be further refined into gasoline (which typically contains aromatic and branched hydrocarbon fractions).

High-temperature circulating fluidized-bed reactors (Synthol reactors) have been developed for gasoline and light olefin production, and these reactors operate at 350 °C (660 °F) and up to 400 psi. The combined gas feed (fresh and recycled) enters at the bottom of the reactor and entrains catalyst that is flowing down the standpipe and through the slide valve. The high gas velocity carries the entrained catalyst into the reaction zone where heat is removed through heat exchangers. Product gases and catalyst are then transported into a large-diameter catalyst hopper where the catalyst settles out and the product gases exit through a cyclone. These Synthol reactors have been successfully used for many years; however, they do have limitations: They are physically very complex reactors that involve circulation of large amounts of catalyst that leads to considerable erosion in particular regions of the reactor.

The higher boiling fraction ($C_8 - C_{21}$), being straight-chain hydrocarbons, is suitable for direct blending into the diesel fuel pool. Higher molecular weight alkanes (waxes) may also be formed but are usually undesirable. One inescapable aspect of Fischer-Tropsch chemistry is that more water will be produced than hydrocarbons (by mass). This produced water must be considered an undesirable sink for expensive and valuable hydrogen and also an unwanted waste stream.

The naphtha fraction, which is not generally marketable, must be shipped to a refinery for further processing into gasoline blending stock. It is advisable to have a commercial Fischer-Tropsch plant associated with a refinery complexes. In fact, the composition of the naphtha gasoline fraction [$H(CH_2)_nH$, where $n =$ approximately 5 to 12] is an issue. The FT synthesis produces primarily straight-chain paraffins, thus any gasoline produced is low in octane rating (<85).

The naphtha fraction contains components that are equivalent to the petroleum counterparts produced in a typical refinery. Alkylate, produced from reacting C_3, C_4, and C_5 olefins with isobutane, is the highest octane component in the gasoline. Isomerate is produced from isomerizing normal pentane and hexane. It has a moderate octane rating but is relatively volatile. The reformate, on the other hand, has a high octane rating but contains undesirable aromatic components. All of the gasoline-blending components have zero sulfur and olefins, which is of considerable benefit when manufacturing specification-grade and environmentally mandated fuels.

Modern automobile gasoline as sold to the consumer ranges in octane from 87 to 93, which is achieved by blending various petroleum streams distillates, reforming gasoline-range hydrocarbons, and ethanol or other additives increase the octane-number (Gary *et al.*, 2007; Hsu & Robinson, 2006; Speight, 2014; Speight & Ozum, 2002). Branched paraffin series like iso-octane cannot be directly produced in Fischer-Tropsch synthesis. Consequently, when Fisher-Tropsch synthesis has been used to produce gasoline, it has been blended with conventionally refined petroleum to achieve the desired octane number.

On the other hand, the methanol-to-gasoline (MTG) process developed by Mobil Oil Corporation involves the conversion of methanol to hydrocarbons over zeolite catalysts and offers a better-quality naphtha-gasoline (Hindman, 2013).

Methanol synthesis also enjoys a long history, actually preceding the Fischer-Tropsch process. In 1923, BASF first synthesized methanol on an industrial scale, also from coal-produced synthesis gas:

$$H_2 + CO - CH_3OH$$

The methanol-to-gasoline process occurs in two steps. First, crude methanol (containing 17% v/v water) is super-heated to 300 °C (570 °F) and partially dehydrated over an alumina catalyst at 400 psi to yield an equilibrium mixture of methanol, dimethyl ether, and water (75% of the methanol is converted). Second, this effluent is then mixed with heated recycled synthesis gas and introduced into a reactor containing ZSM-5 zeolite catalyst at 350 to 365 °C (660 to 690 °F) and 280 to 340 psi to produce hydrocarbons (44%) and water (56%) (Spath & Dayton, 2003). The overall process usually contains multiple gasoline conversion reactors in parallel because the zeolites have to be regenerated frequently to burn off the coke formed during the reaction. The reactors are then cycled so that individual reactors can be regenerated without stopping the process (Kam, Schreiner, & Yurchak, 1984). The process reactions may be summarized simply as:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

$$CH_3OCH_3 \rightarrow C_2 - C_5\,\text{olefins}$$

$$C_2 - C_5\text{ olefins} \rightarrow \text{paraffins, cycloparaffins, aromatics}$$

The selectivity to gasoline range hydrocarbons is greater than 85%, with the remainder of the product being primarily low-boiling hydrocarbons (such as LPG constituents) (Wender, 1996). Approximately 40% of the gasoline produced from the process is aromatic hydrocarbons with the following distribution: 4% v/v benzene, 26% v/v toluene, 2% v/v ethylbenzene, 43% v/v mixed xylenes, 14% v/v trimethyl-substituted benzenes, plus 12% v/v other aromatics (Wender, 1996). The shape selectivity of the zeolite catalyst results in a relatively high durene (1,2,4,5-tetramethylbenzene) concentration, which is 3 to 5% of the gasoline produced (MacDougall, 1991).

7.2.2.2 Diesel production

The Fischer-Tropsch synthesis is well suited to producing middle-distillate range fuels such as diesel fuel and jet fuel. The diesel produced is superior to conventionally refined diesel in terms of higher cetane number and low sulfur content. Thus, the Fischer-Tropsch process is more amenable to the production of diesel fuel [$H(CH_2)_nH$, where n = approximately 7 to 24] and the various types of jet fuel [$H(CH_2)_nH$, where n = approximately 5 to 18].

Diesel produced from conventional upgrading of Fischer-Tropsch synthetic fuel consists of hydrotreated straight-run distillate blended with distillate from wax hydrocracking. Like the naphtha/gasoline, FT diesel has rather unique properties relative to petroleum-derived diesels: It it is sulfur free, almost completely paraffinic, and typically has an acceptable-to-high cetane rating.

The standard for diesel fuel rates the ease of which autoignition occurs during compression in the engine cylinder, thus eliminating the need for a spark plug. The number 100 was assigned to cetane (*n*-hexadecane, $C_{16}H_{34}$) to represent a straight-chain hydrocarbon in the paraffin series. This is the hydrocarbon type and molecular weight that the Fischer-Tropsch synthesis is best suited to produce. Diesel fuel cetane numbers range from 40 to 45, and as high as 55 in Europe, where high-speed diesel engines are prevalent in light-duty passenger vehicles.

Recent efforts to improve the Fischer-Tropsch process tend to focus on increasing selectivity for the diesel fraction and minimizing the naphtha fraction. With certain modifications and modest post-processing, the Fischer-Tropsch process can currently claim selectivity for the diesel fraction with the distribution of the hydrocarbon fraction as diesel (kerosene) 75% v/v, naphtha (gasoline) 20% v/v, and LPG 5% v/v (Lewis, 2013).

7.3 Sabatier-Senderens process

The synthesis of hydrocarbons from hydrogenation of carbon monoxide was discovered in 1902 by Sabatier and Senderens who produced methane by passing carbon monoxide and hydrogen over nickel-, iron-, and cobalt-containing catalysts. At about the same time, the first commercial hydrogen from synthesis gas produced from steam methane reforming was commercialized. The production of liquid hydrocarbons and oxygenates from synthesis gas conversion over iron catalysts was discovered in 1923 by Fischer and Tropsch. Variations on this synthesis pathway were soon to follow for the selective production of methanol and mixed alcohols. Another outgrowth of Fischer-Tropsch Synthesis (FTS) was the hydroformylation of olefins discovered in 1938.

The Sabatier reaction (Sabatier-Senderens process) involves the reaction of hydrogen with carbon dioxide at elevated temperatures (optimal 300 to 400 °C, 570 to 750 °F) and pressures in the presence of a nickel-based catalysts to produce methane and water:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Ruthenium on alumina (Al_2O_3) has been shown to be a more (aluminum oxide) makes a more efficient catalyst. The reaction is exothermic and some initial energy/heat has to be added to start the reaction.

Interest in the Sabatier reaction has increased recently because of growing concerns about global climate change and the reaction/process represents a means to reduce emissions of carbon dioxide. Considerable efforts are currently underway to develop practical and affordable ways to capture carbon dioxide from major point sources, such as gasification plants, and dispose of this carbon dioxide by means of geologic sequestration.

Common applications of the Sabatier reaction include scrubbing traces of carbon dioxide from hydrogen-containing gas. Thus, there is the potential of using the process to reduce the emissions of carbon dioxide from sources such as power plants and gasification plants. The increased urgency in addressing greenhouse gas emissions warrants further investigation of the application of carbon dioxide recycling from power plant emissions and gasification plant emissions by the Sabatier reaction.

When used in the gasification industry, this reaction will take place in a specifically designed reactor in the presence of an efficient catalyst. The flue gas containing the carbon dioxide will have to be cooled by a heat exchanger to reach the optimum reaction temperature. The water formed during the combustion of methane and the Sabatier reaction will be removed from the stream coming from the methanation reactor. This water will be used to cool the flue gas and the methanation reactor. After recovering this heat, the water will be sent to the water splitter where the generated hydrogen will be mixed with the flue gas from the reactor before it enters the methanation reactor. The methane generated will be mixed with any required make-up natural gas needed to operate the process at the desired capacity.

It will not be necessary to isolate and compress the carbon dioxide. The reaction between the carbon dioxide and hydrogen will take place in the gaseous phase and the amount of methane produced will depend on the amount of hydrogen produced by the splitting of water (Brooks, Hu, Zhu, & Kee, 2007; Du *et al*., 2007; Fujita, Nakamura, Doi, & Takezawa, 1993; Görke *et al*, 2005; Takenaka, Shimizu, & Otsuka, 2004; Zhilyaeva, Volnina, Kukuna, & Frolov, 2002). A high conversion (98% v/v) of carbon dioxide to methane has been achieved at a space velocity of more than 15,000 h^{-1} and at a temperature of 350 °C (660 °F).

7.3.1 Methanol production

The first idea of using synthesis gas for producing methanol was found by Paul Sabatier in 1905. Eight years later, the first synthesis patent was given to the Badische Anilin und Soda Fabrik (BASF) (Cheng & Kung, 1994). The synthesis process developed by BASF operates at a temperature between 300 and 400 °C and a pressure between 100 and 250 bar over sulfur-resistant zinc oxide-chromia ($ZnO\text{-}Cr2O_3$) catalyst. Ten years later, the first commercial methanol synthesis plant was built. For many years this was the only technique to produce methanol, but it was not energy-efficient. In this exothermic process, synthesis gas is converted into methanol:

$$CO + 2H_2 \rightarrow CH_3OH$$

In 1927, methanol was produced for the first time by using carbon dioxide instead of carbon monoxide and hydrogen, both obtained as fermentation gases:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

In the same year, DuPont improved the BASF process with a more efficient zinc/copper catalyst. Both processes, with coal as a feedstock, continued to produce methanol up to 1940, when natural gas became abundant From this time on, the only reforming of natural gas was used to produce methanol, because natural gas as a feedstock was economical and more beneficial (Lee, 1990). The first real breakthrough for energy-efficient production of methanol was in 1966 by Imperial Chemical Industries (ICI, now Synetix), which developed a CU/ZnO/Al_2O_3 catalyst (Weissermel, 2003). This process operates at relatively low pressures (700 to 1500 psi) and lower temperatures (250 to 300 °C, 480 to 570 °F). The first time in this process, only 10 to 15% v/v of the new inlet gases convert into methanol and water; the rest remains unreacted. To achieve high conversion rates, and therefore a higher energy efficiency, ICI developed a process in which the unreacted gases were recycled and put back into the catalyst of the reactor. Another improvement was that the inlet gases and the recycled gases were preheated by a heat exchanger before they were inserted into the reactor vessel. The exothermic heat that was generated by the conversion process was recovered in the reactor vessel and used to pre-heat the feed water from the boiler. This new process of methanol synthesis was the end of the inefficient methanol production techniques developed by BASF and DuPont (Lee, 1990). A few years later, the Lurgi low-pressure process was developed; overall, it uses the same type of catalyst. The difference with the ICI process is that the temperature of the inlet gases are regulated by boiling water in the reactor instead of pre-heating the synthesis gas outside the reactor vessel.

In 2006, 60% of the commercial methanol was produced by the process of ICI and 27% by the Lurgi process (Olah, Goeppert, & Surya Prakash, 2003). The rest was generally produced by the Kellog process or in laboratories. According to the patents of the Icelandic company CRI, it is using the Lurgi methanol processes with hydrogen and carbon dioxide as feedstock. Hydrogen is produced by the electrolysis of water, and carbon dioxide is recovered from a geothermal power plant located in Svartsengi, Iceland. These two streams are compressed to approximately 50 bars and a temperature around 225 °C (435 °F). After the reactor vessel, a mixture of unreacted hydrogen, carbon dioxide, methanol, and water (by-product) flows through a heat exchanger to preheat the inlet gases. After that, this mixture flows to a pre-heater for the distillation system and then methanol is condensed in a condenser.

7.3.2 Dimethyl ether production

The synthesis of dimethyl ether (DME) from the syngas process can be carried out in the liquid phase at moderate temperature and pressure, 250 °C (480 °F) and 1000 psi. This single-stage process involves dual catalysts slurried in a liquid oil medium. The bi-functional catalyst consists of a mixture of methanol synthesis catalyst

($Cu/ZnO/Al_2O_3$) and methanol dehydration catalyst (γ-Al_2O_3). The process is represented by chemical equations that might belie the true more complex character of the process:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

The single-stage, liquid-phase process reduces the chemical equilibrium limitation that could be encountered in methanol synthesis from synthesis gas, especially in the areas of catalyst activity, per-pass conversion, and reactor productivity.

The single-stage process offers considerable advantages over the conventional vapor-phase synthesis of methanol in the areas of heat transfer, exothermic character, and selectivity toward methanol. However, this process suffers from the drawback that the methanol synthesis reaction is a thermodynamically governed equilibrium reaction and the concentration of methanol in the liquid phase in the vicinity of the catalytic sites is quite high due to its low solubility. Thus, the productivity of the liquid-phase methanol synthesis as well as the conversion of synthesis gas could be limited by the chemical equilibrium barrier caused by high local methanol concentration in the liquid phase. One of the routes to alleviate this limitation is the *in situ* dehydration of methanol into dimethyl ether, which significantly improves the methanol reactor productivity. Two functionally different yet compatible catalysts are used in this dual catalytic mode of operation.

This single-step, liquid-phase synthesis of dimethyl ether from synthesis gas is extremely significant from both scientific and commercial perspectives. Several key advantages of this process over methanol synthesis include higher methanol reactor productivity, higher synthesis gas conversion, and lesser dual catalyst deactivation and crystal growth.

Furthermore, a process that can convert dimethyl ether to gasoline-range hydrocarbons or to lower olefins over zeolite catalysts has been developed (Lee, Gogate, Fullerton, & Kulik, 1995). When coupled with a single-stage process for the synthesis of dimethyl ether, this process offers a ready route to gasoline-range hydrocarbons:

$$CH_3OCH_3 \rightarrow C_2 - C_4 \text{olefins} \rightarrow \text{Aromatics} + \text{Paraffins}$$

Selectivity toward light olefins can be enhanced by using low acidity catalysts (high SiO_2/Al_2O_3 ratio) and optimum operating conditions such as temperature, partial pressure, and space velocity of dimethyl ether. Zeolite catalysts (such as ZSM-5) have pores and channels of molecular dimensions that impose spatial constraints on reactants/products of the reaction. Shape selectivity is an important property in terms of product distribution as well as the catalyst activity. Zeolites exhibit product shape selectivity, which involves the limitation of diffusion of some of the hydrocarbon products out of the pores, thereby enabling a tailored product spectrum. Another important aspect of the process is the transition state shape selectivity that offers constraints toward the formation of transition states based on molecular size and orientation – the formation of high molecular weight and sterically-bulky molecular products (especially coke precursors that deactivate the catalyst) is hindered.

7.4 Thermal, catalytic, and hydrocracking processes

Thermal decomposition (pyrolysis) is practiced in a variety of processes to convert various feedstocks to liquid products, often referred to as synthetic crude oil and higher-value products (Ringer, Putsche, & Scahill, 2006; Speight, 2008, 2011b, 2013a, 2014). As such, this technology (in the form of coking technologies) has played a basic role in many refineries to expand the suite of product options available from petroleum and other feedstocks.

The intent of this section is to provide the reader with a broad perspective of thermal decompositon pyrolysis technology as it relates to converting a variety of feedstocks (tar sand bitumen, coal, oil shale, and biomass are used as the examples) substrates to distillate products for the reader to compare with the gasification and Fischer-Tropsch technologies that are the focus of this book.

Synthetic fuels are typically formed from the processes that involve either thermal cracking or catalytic cracking, or hydrocracking of fossil fuels and biomass. Once formed, the fuel product must be hydrotreated (or otherwise improved) to remove non-hydrocarbon by-products that would otherwise render the products unsuitable for sale as specification-grade fuels. In addition, synthetic fuels vary considerably in composition and properties – these being dependent on the source of the synthetic fuels and the process(es) by which they were produced.

Gaseous fuels are considered elsewhere as well as in earlier chapter of this book. In the current context, the term *solid fuel* refers to various types of solid material that is used as fuel to produce energy and provide heating, usually released through combustion of the fuel. Coke, the most common coal-based solid fuel, is a solid carbonaceous residue derived from low-ash, low-sulfur bituminous coal from which the volatile constituents are driven off by baking in an oven without oxygen at temperatures as high as 1,000 °C (1,832 °F) so that the fixed carbon and residual ash are fused together. Like gaseous fuels, solid fuels are not considered here but are described in detail elsewhere (Speight, 2008, 2011b, 2013a, 2013b, 2014).

In terms of refining products produced from fossil fuels such as coal and oil shale, the refinery (although appearing to be a relatively facile system) is actually a complex integrated series of operations that ultimately results in the production of high-value, salable materials from low-value feedstocks (Speight, 2014). Processes involving the use of a variety of complex and expensive catalysts are also a necessary part of any refinery. Such processes will play an important role in the processing of the products from non-petroleum fossil fuels and biomass (Speight, 2008).

For example, in the catalytic cracking process, the objective is to produce gasoline, heating oil, and the like from a heavier feedstock such as gas oil by means of an aluminosilicate base catalyst. However, the reactions that occur are varied and, especially with the heavier or more aromatic feedstocks, there is the inevitable deposition of carbon (coke) on the catalyst and the accompanying decrease in catalyst activity. In addition, hydrocracking is a process that accomplishes the same goals as catalytic cracking but the presence of hydrogen often allows much better control of the reaction and therefore results in a better distribution of products. The hydrocracker is operated at elevated pressures (several thousand psi in the case of the heavier feedstocks) and employs a bifunctional catalyst that has sites capable of promoting the hydrogenation reactions as well as the cracking reactions.

Thus, although current refinery technology may suffice to a point for the production of saleable products from refining of petroleum, there are many aspects of the operation that may need some modification when the products from the liquid products from other fossil fuels are added as refinery feedstocks. Such modification may dictate the creation and evolution of a completely new refining technology.

7.4.1 Tar sand bitumen

Tar sand bitumen (called *oil sand bitumen* in Canada) is a viscous non-mobile carbonaceous material that typically is less than 10° API depending on the deposit; its viscosity is very high. Conventional crude oils may have a viscosity of several poise (at 40 °C, 105 °F), but the tar sand bitumen has a viscosity of the order of 50,000 to 1,000,000 centipoises or more at deposit (formation) temperatures (approximately 0 to 10 °C, 32 to 50 °F depending on the season). This offers a formidable, but not insurmountable, obstacle to bitumen recovery.

The major commercial operations for the recovery of bitumen are located in the north-eastern region of the Province of Alberta (Canada). Once recovered by mining or *in situ* techniques (Speight, 2009), tar sand bitumen offers a source of liquid fuels.

7.4.1.1 Conversion to liquids

After recovery, the bitumen is transported to a limited scope refinery that typically involves application of one of two coking processes that have been applied to the production of liquids from Athabasca bitumen. *Delayed coking* is practiced at the Suncor (formerly Great Canadian Oil Sands) plant, whereas Syncrude employs a *fluid coking process* that produces less coke than the delayed coking in exchange for more liquids and gases. In each case, the bitumen is converted to distillate, coke, and low-boiling gases. The coke fraction and product gases can be used for plant fuel. The distillate (raw synthetic crude oil, raw syncrude) is a partially upgraded material and is a suitable feed for hydrodesulfurization to produce a low-sulfur synthetic crude oil as a saleable product.

7.4.1.2 Upgrading tar sand liquids

Sulfur is distributed throughout the boiling range of the delayed coker distillate, as with distillates from direct coking. Nitrogen is more heavily concentrated in the higher boiling fractions but is present in most of the distillate fractions. Raw coker naphtha contains significant quantities of olefins and di-olefins that must be saturated by downstream hydrotreating. The gas oil has a high aromatic content typical of coker gas oils.

Catalytic hydrotreating is used for secondary upgrading to remove impurities and enhance the quality of the final synthetic crude oil product. In a typical catalytic hydrotreating unit, the feedstock is mixed with hydrogen, preheated in a fired heater and then charged under high pressure to a fixed-bed catalytic reactor. Hydrotreating converts sulfur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia. Sour gases from the hydrotreater(s) are treated for use as plant fuel. A further option is that hydrocracking may also be employed at this stage to improve product yields and quality.

Thus, the primary liquid product (synthetic crude oil) is, of necessity, hydrotreated (*secondary upgrading*) to remove sulfur and nitrogen (as hydrogen sulphide and ammonia, respectively) and to hydrogenate the unsaturated sites exposed by the conversion process. It may be necessary to employ separate hydrotreaters for the lower-, medium-, and high-boiling distillates. For example, the higher-boiling distillates fractions require higher hydrogen partial pressures and higher operating temperatures to achieve the desired degree of sulfur and nitrogen removal. Commercial applications have therefore been based on the separate treatment of two or three distillate fractions at the appropriate severity to achieve the required product quality and process efficiency.

The synthetic crude oil is a blend of naphtha, middles distillate, and gas oil range materials, with no residuum (1050 °F+, 565 °C+material). Canadian synthetic crude oil first became available in 1967 when Suncor started to market a blend produced by hydrotreating the naphtha, distillate, and gas oil generated in a delayed coking unit. The light, sweet synthetic crude currently marketed by Suncor is called *Suncor oil sands blend A* (OSA). Syncrude Canada Ltd. started production in 1978, marketing a fully hydrotreated blend utilizing fluidized-bed coking technology as the primary upgrading step. This product is referred to as *Syncrude sweet blend* (SSB).

7.4.2 Coal

Coal is a fossil fuel formed as an organic sediment in swamp ecosystems where plant remains were saved by water and mud from oxidization and biodegradation. It occurs worldwide as a combustible black or brownish-black organic rock and is composed primarily of carbon along with assorted other elements, including sulfur. Coal is extracted from the ground by either underground mining or open-pit mining (surface mining) (Speight, 2008, 2013a, 2013b).

7.4.2.1 Conversion to liquids

The production of liquid fuels from coal is not new. It has received considerable attention because the concept does represent alternate pathways to liquid fuels (Speight, 2008, and references cited therein). In fact, the concept is often cited as a viable option for alleviating projected shortages of liquid fuels as well as offering some measure of energy independence for those countries with vast resources of coal who are also net importers of crude oil.

There are inherent technological advantages with the conversion of coal to liquid products because *coal liquefaction* can produce clean liquid fuels that can be sold as transportation fuels such as gasoline and diesel. The three principal routes by which liquid fuels can be produced from solid coal are (1) direct conversion to liquids by thermal cracking, (2) hydrocracking the coal, and (3) indirect conversion to liquids using the Fischer-Tropsch technology. The third route involves gasification of coal to mixtures of carbon monoxide and hydrogen (synthesis gas) followed by application of the Fischer-Tropsch process in which the syngas is converted to hydrocarbons under catalytic conditions of temperature and pressure. This section will focus on the conversion of coal to liquids by direct liquefaction technologies.

The direct liquefaction of coal by the Bergius process (liquefaction by hydrogenation) is also available. In the process, coal is finely ground and mixed with heavy oil recycled from the process. Catalyst is typically added to the mixture and the mixture is pumped into a reactor. The reaction occurs at between 400 to 500 °C and 20 to 70 MPa hydrogen pressure. The reaction produces heavy oil, middle oil, gasoline, and gas:

$$n\mathrm{C}_{\mathrm{coal}} + (n+1)\mathrm{H}_2 \rightarrow \mathrm{C}n\mathrm{H}_{2n+2}$$

A number of catalysts have been developed over the years, including catalysts containing tungsten, molybdenum, tin, or nickel.

Another process to manufacture liquid hydrocarbons from coal is low-temperature carbonization (LTC) (referred to as the Karrick process). Coal is coked at temperatures between 450 and 700 °C (840 and 1290 °F) compared to 800 to 1000 °C (1830 °F) for metallurgical coke. The lower temperatures optimize the production of coal tar that is richer in lighter hydrocarbons than high-temperature coal tar. The coal tar is then further processed into fuels. Several other direct liquefaction processes have been developed over the last four decades with varying degrees of success (Speight, 2013a).

The thermal decomposition of coal on a commercial scale is often more commonly referred to as carbonization and is more usually achieved by the use of temperatures up to 1500 °C (2730 °F). The degradation of the coal is quite severe at these temperatures and produces (in addition to the desired coke) substantial amounts of gaseous products. However, carbonization is essentially a process for the production of a carbonaceous residue by thermal decomposition (with simultaneous removal of distillate) of organic substances.

$$[C]_{\mathrm{organic\,carbon}} \rightarrow [C]_{\mathrm{coke/char/carbon}} + \mathrm{liquids} + \mathrm{gases}$$

The process is a complex sequence of events that can be described in terms of several important physicochemical changes, such as the tendency of the coal to soften and flow when heated (plastic properties or the relationship to carbon-type in the coal). In fact, some coals become quite fluid at temperatures on the order of 400 to 500 °C (750 to 930 °F), and there is a considerable variation in the degree of the temperature of maximum plasticity, as well as the plasticity temperature range for various types of coal. The yields of tar and low molecular weight liquids are, to some extent, variable but are greatly dependent on the process parameters, especially temperature, as well as the type of coal.

7.4.2.2 Upgrading coal liquids

Liquid products from coal are generally different from those produced by petroleum refining, particularly as they can contain substantial amounts of phenols. In fact and in spite of the interest in coal liquefaction processes that emerged during the 1970s and the 1980s, petroleum prices always remained sufficiently low to ensure that the initiation of a synthetic fuels industry based on non-petroleum sources would not become a commercial reality.

The different fractions are not suitable for immediate use as a fuel but must be sent to a refinery for further processing to yield a synthetic fuel or a fuel blending stock of the desired quality. It has been reported that as much as 97% of the coal carbon can be converted to synthetic fuel, but this greatly depends on the coal type, the reactor configuration, and the process parameters.

Typically, the liquids need to be hydrotreated, and the manner by which hydrogenation can occur varies from process to process and may even occur as part of the process by the use of a hydrogen atmosphere and a solvent capable of donating hydrogen to the system and the type of catalyst employed (Speight, 2013a, 2014). Nevertheless, in the more general sense, at some stage of the operation, the liquid products need to be stabilized (i.e., freed from unsaturated materials as well as nitrogen, oxygen, and sulfur species) by what may be simply referred to as a hydrotreating operation.

For the most part, current concepts for refining the products of coal liquefaction processes rely on the already existing petroleum refineries, although it must be recognized that the acidity (i.e., phenol content) of the coal liquids and the potential incompatibility of the coal liquids with conventional petroleum (or even heavy oil) feedstocks may pose severe problems within the refinery system. Thus, the first essential step in refining coal liquids is severe catalytic hydrogenation to remove most of the nitrogen, sulfur, and oxygen and to convert at least part of the high-boiling material to lower-boiling distillates that might be further refined. This is analogous to the hydrodesulfurization of heavy oils using a preliminary cracking technique so that after product separation (by distillation) the most suitable choice of process conditions can be made (Ancheyta & Speight, 2007; Speight, 2000).

However, a major limiting factor in refining coal liquids is due to the high aromatics content and to the condensed nature of many of the aromatic ring systems (Speight, 2013a). Thus, to produce liquid fuels of the types currently in demand, each condensed aromatic ring would have to be hydrogenated (saturated) and cracked to produce the lower-boiling distillate material. The hydrogen demand for such conversions and the effect of these polynuclear aromatic systems (especially those which contain nitrogen and other heteroatoms) systems on catalysts is a very worthy hurdle to overcome! Nevertheless, it is a hurdle that can be surpassed, and by a variety of process conditions.

7.4.3 Oil shale

Just like the term *oil sand* (*tar sand* in the United States), the term *oil shale* is a misnomer, as the mineral does not contain oil nor is it always *shale* (Speight, 2008). The organic material is chiefly *kerogen* and the *shale* is usually a relatively hard rock called *marl*. Properly processed, kerogen can be converted into a substance somewhat similar to petroleum, which is often better than the lowest grade of oil produced from conventional oil reservoirs but of lower quality than conventional light oil.

7.4.3.1 Conversion to liquids

Retorting at high temperature (approximately 500 °C, 930 °F) is the process of heating oil shale in order to recover the organic material, predominantly as a liquid (*shale oil*). A *retort* is simply a vessel (a rock formation for *in situ* retorting or a manufacture reactor of surface retorting) in which the oil shale is heated so that the product gases and vapors can escape to a collector.

Retorting involves the destructive distillation (pyrolysis) of oil shale in the absence of oxygen. At temperatures above 500 °C, 930 °F, pyrolisis thermally decomposes or breaks down (cracks) the kerogen (the organic constituent of oil shale) to release the hydrocarbons and then cracks the hydrocarbons into lower-weight hydrocarbon molecules.

The active devolatilization of oil shale begins at about 350 to 400 °C, with the peak rate of oil evolution at about 425 °C, and with devolatilization essentially complete in the range of 470 to 500 °C (Speight, 2008). At temperatures of approximately 500 °C (930 °F), mineral matter, consisting mainly of calcium, magnesium and calcium carbonates, begins to decompose, yielding carbon dioxide as the principal product. The properties of crude shale oil are dependent on the retorting temperature, but more importantly on the temperature-time history because of the secondary reactions accompanying the evolution of the liquid and gaseous products. The produced shale oil is dark brown, is odoriferous, and tends toward waxy oil.

Oil derived from shale has been referred to as a *synthetic crude oil* and thus is closely associated with synthetic fuel production. However, the process of retorting shale oil bears more similarities to conventional refining processes, such as the delayed coking process, than to synthetic fuel processes. For the purpose of this chapter, the term *oil-shale distillate* is used to refer to middle-distillate range hydrocarbons produced by retorting oil shale. Disposal of spent shale is also a problem that must be solved in economic fashion for the large-scale development of oil shale to proceed. Retorted shale contains carbon as a kind of char, representing more than half of the original carbon values in the shale. The char is potentially pyrophoric and can burn if dumped into the open air while hot. The heating process results in a solid that occupies more volume than the fresh shale because of the problems of packing random particles.

A preferred method for thermally treating oil shale involves using a moving bed reactor followed by a fractionation step to divide the wide boiling-range crude oil produced from the shale oil into two separate fractions. The lighter fraction is hydrotreated for the removal of residual metals, sulfur, and nitrogen, whereas the heavier fraction is cracked in a second fixed bed reactor normally operated under high-severity conditions.

Also, the fluidized-bed hydroretort process eliminates the retorting stage of conventional shale upgrading, by directly subjecting crushed oil shale to a hydroretorting treatment in an upflow fluidized-bed reactor, such as that used for the hydrocracking of heavy petroleum residues. This process is a *single-stage retorting and upgrading* process. Therefore, the process involves (1) crushing oil shale; (2) mixing the crushed oil shale with a hydrocarbon liquid to provide a pumpable slurry; (3) introducing the slurry along with a hydrogen-containing gas into an upflow, fluidized-bed reactor at a superficial fluid velocity sufficient to move the mixture upwardly through the reactor; (4) hydroretorting the oil shale; (5) removing the reaction mixture from the reactor; and (6) separating the reactor effluent into several components.

7.4.3.2 Upgrading refining shale oil

Shale retorting processes produce oil with almost no heavy residual (high-boiling) fraction. With upgrading, shale oil is a light boiling premium product more valuable than most crude oils. However, the properties of shale oil vary as a function of the production (retorting) process. Fine mineral matter carried over from the retorting process and the high viscosity and instability of shale oil produced by present retorting processes have necessitated upgrading of the shale oil before transport to a refinery.

Shale oil contains a wide variety of hydrocarbon compounds, but it also has high nitrogen content compared to a nitrogen content of 0.2 to 0.3 wt. % for a typical petroleum. In addition, shale oil also has a high olefin and di-olefin content. It is the presence of these olefins and diolefins, in conjunction with high nitrogen content, that gives shale oil the characteristic difficulty in refining and the tendency to form insoluble sediment. Crude shale oil also contains appreciable amounts of arsenic, iron, and nickel that interfere with refining.

To improve the qualities of crude shale oil, upgrading, or partial refining, may be carried out using different options, after removal of the inorganic fines. Hydrotreating is the option of choice to produce a stable product that is comparable to benchmark crude oils. In terms of refining and catalyst activity, the nitrogen content of shale oil is a disadvantage. But, in terms of the use of shale oil residue as a modifier for asphalt, the nitrogen content is beneficial, as nitrogen species can enhance binding with the inorganic aggregate. If not removed, the arsenic and iron in shale oil would poison and foul the supported catalysts used in hydrotreating.

Blending refined shale oil products with corresponding crude oil products, and using shale oil fractions obtained from a very mildly hydrogen treated shale oil, yields kerosene and diesel fuel of satisfactory properties. Hydroprocessing shale oil products, either alone or in a blend with the corresponding crude oil fractions, is therefore necessary. The severity of the hydroprocessing has to be adjusted according to the particular properties of the feed and the required level of the stability of the product.

Gasoline from shale oil usually contains a high percentage of aromatic and naphthenic compounds that are not affected by the various treatment processes. The olefin content, although reduced in most cases by refining processes, will still remain significant. It is assumed that di-olefins and the higher unsaturated constituents will be removed from the gasoline product by appropriate treatment processes. The same should be true, although to a lesser extent, for nitrogen- and sulfur-containing constituents.

The sulfur content of raw shale oil gasoline may be rather high due to the high sulfur content of the shale oil itself and the frequently even distribution of the sulfur compounds in the various shale oil fractions. Not only the concentration but also the type of the sulfur compounds are important when studying the effect on gum formation tendency of the gasoline containing them.

Catalytic hydrodesulfurization processes are not a good solution for the removal of sulfur constituents from gasoline when high proportions of unsaturated constituents are present. A significant amount of the hydrogen would be used for hydrogenation of the unsaturated components. However, when hydrogenation of the unsaturated hydrocarbons is desirable, catalytic hydrogenation processes would be effective.

The naphtha fraction (the gasoline precursor fraction) derived from shale oil contains varying amounts of oxygen compounds. The presence of oxygen in a product, in which free radicals form easily, is a cause for concern. Free hydroxyl radicals are generated and the polymerization chain reaction is quickly brought to its propagation stage. Unless effective means are provided for the termination of the polymerization process, the propagation stage may well lead to an uncontrollable generation of oxygen bearing free radicals leading to gum and other polymeric products.

Diesel fuel derived from oil shale is also subject to the degree of unsaturation, the effect of di-olefins, the effect of aromatics, and the effect of nitrogen and sulfur compounds. In addition, jet fuel produced from shale oil would have to be subjected to suitable refining treatments and special processes. The resulting product must be identical in its properties to corresponding products obtained from conventional crude oil. This can be achieved by subjecting the shale oil product to a severe catalytic hydrogenation process with a subsequent addition of additives to ensure resistance to oxidation.

Thus, like coal liquids, shale oil is different to conventional crude oils, and several refining technologies have been developed to deal with this. The primary problems identified in the past were arsenic, nitrogen, and the waxy nature of the raw synthetic crude oil. Nitrogen and wax problems were solved using hydroprocessing approaches, essentially classical hydrocracking and the production of high-quality lube stocks, which require that waxy materials be removed or isomerized. However, the arsenic problem remains.

In general, oil-shale distillates have a much higher concentration of high boiling-point compounds that would favor production of middle-distillates (such as diesel and jet fuels) rather than naphtha. Oil-shale distillates also have a higher content of olefins, oxygen, and nitrogen than crude oil, as well as higher pour points and viscosities. Above-ground retorting processes tended to yield a lower API gravity oil than the *in situ* processes (a 25° API gravity was the highest produced). Additional processing equivalent to hydrocracking would be required to convert oil-shale distillates to a lighter range hydrocarbon (gasoline). Removal of sulfur and nitrogen would, however, require hydrotreating.

Arsenic removed from the shale oil by hydrotreating remains on the catalyst, generating a material that is a carcinogen, an acute poison, and a chronic poison. The catalyst must be removed and replaced when its capacity to hold arsenic is reached.

7.4.4 Biomass

Biomass refers to (1) energy crops grown specifically to be used as fuel, such as fast-growing trees or switch grass; (2) agricultural residues and by-products, such as straw, sugarane fiber, and rice hulls; and (3) residues from forestry, construction, and other wood-processing industries (Speight, 2008, 2011b).

In fact, biomass is a term used to describe any material of recent biological origin, including plant materials such as trees, grasses, agricultural crops, and even animal manure. Other biomass components, which are generally present in minor amounts, include triglycerides, sterols, alkaloids, resins, terpenes, terpenoids, and waxes. This includes everything from *primary sources* of crops and residues harvested/collected directly from the land, to *secondary sources* such as sawmill residuals, to *tertiary sources* of post-consumer residuals that often end up in landfills.

Biomass feedstocks and fuels exhibit a wide range of physical, chemical, and agricultural/process engineering properties. Thus, biomass forms a carbonaceous feedstock that offers a ready path to synthetic fuels, albeit of different types because of the varying nature of biomass.

7.4.4.1 Conversion to liquids

Biomass (other than by fermentation to alcohol fuels) is typically converted to liquids by fast pyrolysis – a process in which organic materials are rapidly heated to 450 to 600 °C (840 to 1110 °F) in the absence of air. Under these conditions, organic vapors, pyrolysis gases, and charcoal are produced – the vapors are condensed to bio-oil. Depending on the biomass feedstock, a 50 to 70% w/w yield of liquid can be expected. However, fast pyrolysis is a non-equilibrium process and bio-oil properties are a function of temperature, pressure, residence time, reactor configuration, and quench method.

In fast pyrolysis, biomass decomposes quickly to generate mostly vapors and aerosols and some charcoal and gas. After cooling and condensation, a dark brown homogeneous mobile liquid is formed that has a heating value about half that of conventional fuel oil. In a particular example, biomass particles are fed near the bottom of the fluidized-bed reactor (analogous to a fluid-bed catalytic cracking unit (Speight, 2008, 2011b, 2014) together with an excess flow of hot heat carrier material such as sand. The pyrolysis reactor is integrated in a circulating sand system composed of a riser, a fluidized-bed char combustor, the pyrolysis reactor, and a down-comer. The bio-oil is treated (typically in a cyclone) to remove particulate matter before entering the condenser, in which the volatile products are quenched by recirculated bio-oil. Any char that is produced is burned with air to provide the heat required for the pyrolysis process, and non-condensable pyrolysis gases are combusted to generate additional steam as well as heat for drying the biomass feedstock.

However, due to the presence of oxygenated constituents, bio-oil is polar and does not mix readily with hydrocarbons. The degradation products from the biomass constituents include organic acids – such as formic acid (HCO_2H) and acetic acid (CH_3CO_2H) – that give the oil a low pH and hydrophilic character. Typically, hydrophilic bio-oils have water content on the order of 15 to 35% w/w, and phase separation does occur when the water content is higher than about 30 to 45% w/w.

7.4.4.2 *Upgrading bio-oil*

The high acidity and chemical instability of bio-oils impose severe limitations on the extent to which they might be processed in a refinery. One way to address this is by treating the bio-oil with a low-cost alcohol (e.g., methanol, ethanol, or butanol) in the presence of an acid catalyst, converting the carboxyl and carbonyl groups to esters and acetals or ketals, respectively. As esterification and acetylation reactions are equilibrium reactions, increasing concentrations of esters, acetals, and water will tend to shift equilibrium back toward the original reactants. A solution to this problem is to remove the reaction products as they are formed by azeotropic water removal or reactive distillation (Moens, Black, Myers, & Czernik, 2009).

Pyrolysis oils from biomass pyrolysis are free-flowing liquids, usually dark brown in color, often with an odor of smoke. Liquid yields and properties depend on biomass type, temperature, hot vapor residence time, char separation, and mineral matter content of the biomass feedstock. The last two factors have a catalytic effect on vapor cracking (Bertero, de la Puente, & Sedran, 2012; Bridgwater, 2012; Lédé *et al.*, 2007; Zheng & Wei, 2011).

However, high oxygen content, storage instability, particulate matter, and corrosiveness contribute to downstream upgrading difficulties for bio-oil. In fact, the most important properties affecting bio-oil fuel quality are incompatibility with conventional fuels from the high oxygen content of the bio-oil, high solids content, high viscosity, and chemical instability. Mitigating these effects involves understanding or achieving (1) reduced oxygen content; (2) effective particulate matter removal; (3) sulfur, nitrogen, and other contaminant species distribution among the gas, liquid, and char; and (4) reduction of corrosion potential. Furthermore, bio-oils can be emulsified with conventional fuel with the aid of surfactants. The main drawback of this approach is the cost of surfactants, the high energy required for emulsion and the significantly higher levels of corrosion/erosion in engine applications (Baglioni *et al.*, 2003).

Hydrotreating removes oxygen as well as nitrogen and sulfur. It can also saturate olefins and aromatics, and will completely deoxygenate phenolic constituents depending on the severity of the operation. In fact, upgrading fast pyrolysis oil to stable hydrocarbon oil occurs in two steps. The first reactor step uses mild hydrotreating conditions to remove some of the oxygen and prevent secondary reactions (such as polymerization) that lead to catalyst deactivation. The second reactor operates at greater severity than the first; it uses higher temperatures and/or lower space velocities to achieve low levels of oxygen ($<1\%$ w/w).

The process is typically high pressure and moderate temperature (up to 400 °C, 750 °F) and produces a naphtha-like product that requires orthodox refining to derive conventional transport fuel. Typical catalysts are sulfided CoMo or NiMo supported on alumina or aluminosilicates. Ketones and aldehydes can be hydrogenated to alcohols under mild conditions over Raney nickel catalyst. In the presence of the reduced Mo-10 Ni/γ-alumina,hydrotreatment as well as the esterification have happened in the bio-oil during the upgrading process. The optimal conditions for hydroprocessing of bio-oil are quite different from those for petroleum-derived products. A two-step hydroprocessing scheme comprising a mild stabilization step and a more intensive upgrading step are necessary.

Catalytic cracking accomplishes deoxygenating through simultaneous dehydration, decarboxylation, and decarbonylation reactions occurring in the presence of zeolite catalysts. Bio-oils are generally best upgraded by HZSM-5 or ZSM-5, as these zeolite catalysts promote high yields of liquid products and propylene (Alonso, Bond, & Dumesic, 2010). There is also an increasing interest in improving the quality of bio-oils by integrated catalytic pyrolysis – pyrolysis of biomass in the presence of ZSM-5 to produce naphtha and kerosene, heating oil, and renewable chemicals, including benzene, toluene, and xylenes, has been claimed (Williams & Nugranad, 2000).

7.5 Product quality

The quality of synthetic crude oil is difficult to describe and has several different meanings because quality depends largely on the source of the synthetic fuel. Furthermore, the composition of the synthetic fuel also plays a major role in define quality. Acceptable quality in one scenario might be unacceptable quality in another scenario.

More generally, the term *synthetic crude* has come to mean a blend of naphtha, distillate, and gas oil range materials, but there are no residues (1050 °F+, 565 °C+material). Typically, synthetic crude oil from various sources can contain contaminants that often prevent the synthesis crude being sold directly as a fuel. Additional refining (usually hydrotreating for *purification* or *contaminant removal*) is required to convert the synthetic crude oil to specification-grade products.

The distillate products from the thermal decompositon of fossil fuels and biomass are greatly dependent on the fossil fuel/biomass and the process. On the other hand, the products from the gasification/Fischer-Tropsch process are free of contaminants such as nitrogen, oxygen, sulfur, and metals. In addition, it is important that the Fischer-Tropsch naphtha show a workable octane number that can be upgraded by the use of blending and additives. However, the naphtha fraction, the diesel fraction, and the higher-boiling fractions may require hydrotreating before blending into saleable product streams. A possible alternate product is the stable hydrocarbon synthetic crude oil, which could be sold as a fuel oil substitute.

The primary characteristic that distinguishes one synthetic fuel from another stems from (1) the type of feedstock and (2) the physical processes needed to convert the raw feedstock to a specification-grade fuel that meets air pollution regulations. In general, the higher-quality raw fuels (such as Fischer-Tropsch liquids) are worth more because they typically decrease refining and environmental costs. The reduction in production costs may more than offset higher delivered prices for the better fuel. Hence, the cost of generating a synthetic fuel is a function of the quality of the feedstock as well as the price of the commodity.

However, the choice will vary depending on the country in which the synthetic fuel is produced and the available resource to refine the raw fuel into a specification-grade fuel. In fact, a protocol (or protocols) is needed for the acceptance of synthetic fuels from a variety of feedstocks; each protocol may have to be feedstock specific. Generally, the synthetic fuel must meet the desired requirements of a purchaser or regulation and the producer of the synthetic fuel must demonstrate that the fuel has defined properties and characteristics that fall within the range of experience with conventional, petroleum-derived fuel.

7.6 Conclusions

As energy demands continue to increase, so does concern over the future availability of conventional fuels. There is a growing need to find alternative fuel options, such as synthetic fuels. Conventional transport fuels are products of crude oil refining, but synthetic fuels can be produced from various fossil fuels and biomass. In fact, synthetic fuels derived from various sources are already available and the supplies are due to increase over the next few years.

Furthermore, many countries could eliminate the need for crude oil by using a combination of coal, natural gas, oil shale, non-food crops to make synthetic fuel, as well as waste carbonaceous materials. Synthetic fuels would be an easy fit for the transportation system because they could be used directly in automobile engines and are almost identical to fuels refined from crude oil. That sets them apart from currently available biofuels, such as ethanol, which have to be mixed with gas or require special engines.

A realistic approach would call for a gradual implementation of synthetic fuel technology, and it would take 30 to 40 years for the United States to fully adopt synthetic fuel production in a way that it could supplement petroleum supplies (Speight, 2008, 2011a, 2011b). The economics of synthetic fuel production is often quoted favorably and unfavorably, but more realistically and even including the capital costs, synthetic fuels can still approach profitability depending on the feedstock and the processes required. It would take decisions by typically indecisive governments to support country-wide synthetic fuels industries when those same politicians might have to inform their constituents that gasoline/diesel process will increase. It is the perennial question: *What is a country willing to pay for energy independence*?

Over the years, the original Fischer-Tropsch method has been tweaked and improved to increase efficiency and acceptability (Table 7.2). The hydrocarbon product mixture leaving the Fischer-Tropsch reactor is frequently referred to as *synthetic*

Table 7.2 **Benefits of Fischer-Tropsch synthetic fuels**

- Composition:
    - Sulfur-free:
    - Low aromatics content
    - Odorless
    - Colorless
- Local emissions:
    - Allow significant reduction of regulated and non-regulated vehicle pollutant emissions (NOx, SOx, PM, VOC, CO, CO_2)
    - CO_2 separation during synthesis gas production makes capture feasible.
- Diversification of energy supply:
    - Contributes to petroleum substitution
    - Diversification and security of energy supply
- Distribution infrastructure:
    - Can be used in existing fuel infrastructure
- Compatibility with existing engines:
    - Can be used in existing automobile and diesel engines
    - Produces ultra-low sulfur, high-cetane diesel
    - Produces low-octane gasoline that can be improved
- Potential for future engines:
    - Enable the development of new generation of internal combustion engine technologies
    - Lead to improved engine efficiency
    - Further reduction of vehicle pollutant emissions
- Impact on bio-sphere:
    - Readily biodegradable
    - Non-toxic
    - Not harmful to aquatic organisms

crude oil. This already illustrates that the standard product upgrading techniques that are used in refineries are also suitable for the upgrading of the Fischer-Tropsch wax (Marano, 2007).

Thus, advantages of producing fuels by means of gasification followed by the Fischer-Tropsch process include (1) Fischer-Tropsch–based fuels are compatible with current diesel- and gasoline-powered vehicles and fuel distribution infrastructure – these fuels do not require new or modified pipelines, storage tanks, or retail station pumps; (2) there is reduced reliance on imported petroleum and increase energy security; and (3) little or no particulate emissions exist because Fischer-Tropsch fuels have no sulfur and aromatics content, and there are fewer hydrocarbon and carbon monoxide emissions (Table 7.2) (Chadeesingh, 2011; Speight, 2008, 2013a).

In fact, in many ways, synthetic fuels from Fischer-Tropsch liquids are cleaner than fuels produced thermally from fossil fuel and biomass. The heavy metal and sulfur contaminants of fossil fuels can be captured in the synthetic plants before the fuel is shipped out. Fischer-Tropsch fuels also can be used in gasoline and diesel engines with no (or little) need for modifications. These fuels do not have to compete with conventional petroleum-based fuels but can act as a valuable less environmentally objectionable blend stock that would allow carbon reduction with the fleet of cars currently on the road.

However, it must never be forgotten that the production of synthetic fuel from the Fischer-Tropsch process alone has a head-start insofar as the process commences with a *clean* (non-contaminated) feedstock – the gases have to be free of contaminants or the catalysts will be contaminated and rendered inefficient – to produce the clean (sulfur-free, nitrogen-free, metals-free) synthetic fuel.

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Assessing fuels for gasification: analytical and quality control techniques for coal

8

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8.1 Introduction

The effect of various coal properties such as mineral matter, moisture, fixed carbon, and calorific value can impact the gasification process. Thus, the data obtained from coal analyses are valuable for an accurate determination of process viability and efficiency (Speight, 2013a, 2013b). Much work, and the formation of various national standards associations, has led to the development of methods for coal evaluation. For example, the American Society for Testing and Materials (ASTM) has carried out uninterrupted work in this field for many years (Table 8.1), while investigations on the development of the standardization of methods for coal evaluation has occurred in all of the major coal-producing countries.

The most important properties of coal in relation to the gasification process are (1) coal type; (2) proximate analysis – determination of moisture, ash, volatile matter, and fixed carbon; (3) ultimate or elementary analysis – determination of the elemental composition of the coal; (4) calorific value or heat content; (5) caking properties – for bituminous coals only; and (6) grindability – to determine the ease of pulverization of the coal.

In addition, coal properties that affect those parts of the gasification process that are in direct contact with the coal handling when the coal is conveyed from the stockpile to pulverizing mills are (1) specific energy, which determines the quantity of coal required for a given plant output; (2) surface moisture, which affects flow characteristics; (3) size distribution and especially proportion of fine material, which affects surface moisture; and (4) the nature of the mineral matter, especially clay minerals, which affects flow characteristics.

In addition to the ASTM, other organizations for development and standardization of analytical methods operate on a national level; examples are the British Standards Organization (BS) and the German Standards Organization (DIN). Furthermore, the increased trade between various coal-producing countries that followed World War II meant that cross-referencing of the already accepted standards was a necessity and the mandate for such work fell to the International Standards Organization (ISO), located in Geneva, Switzerland. Membership in the ISO is allocated to participating (and observer) countries.

It is appropriate that in any discussion of the particular methods used to evaluate coal for coal products, reference should be made to the relevant test. Accordingly, the

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Table 8.1 **Procedures and purposes for coal testing using the standard test methods of the American Society for Testing and Materials (ASTM)**

Procedure	Outcome
Calorific value	Potential for energy production
Classification of coal by rank	Estimate of coal behavior in mining, preparation, and utilization
Coal ash	Amount of ash produced at a given temperature
Equilibrium moisture	Moisture-holding capacity of coal (natural bed moisture)
Forms of sulfur	Form of sulfur – organic sulfur, inorganic sulfur (pyrite, sulfate)
Major and minor elements	Identification of major and minor (trace) elements
Proximate analysis	Amount moisture, volatile matter, ash, and fixed carbon
Maceral analysis	Types and amounts of macerals in coal
Total moisture	Inherent water and any other water present
Trace elements	Identification of trace elements
Ultimate analysis	Amount carbon, hydrogen, nitrogen, oxygen, sulfur, and ash
Volatile matter	Products evolved as gases or vapors

necessary ASTM test numbers have been included as well as those, where known, of the test numbers from the standards organizations of other countries. As a part of the multifaceted program of coal evaluation, new methods are continually being developed and the already accepted methods may need regular modification to increase the *accuracy* of the method as well as the *precision* of the results (Speight, 2005, 2013a, 2013b).

Finally, there are two methods of analysis: ultimate analysis and proximate analysis. The *ultimate analysis* determines all coal component elements, solid or gaseous; the *proximate analysis* determines only the fixed carbon, volatile matter yield, moisture content, and ash yield as percentages of the original coal. The proximate and ultimate analyses of coal provide important information regarding the overall characteristic of a particular coal. Ultimate analysis includes elemental analysis of coal and has been used to assess the thermal characteristics and to estimate the maximum emission of sulfur and nitrogen oxides. The detailed description of these analyses can be found in a number of references (Gupta, 2007; Raask, 1985; Sharkey & McCartney, 1981; Speight, 2005; Speight, 2013a, 2013b).

Accordingly, this chapter presents the various analytical methods that can be applied to determining the composition of coal. By analogy with the petroleum industry (Speight, 2014), some gasification plants may carry out a full analysis of every new batch of feedstock (coal) received at the plant, whereas other companies may perform a partial analysis of the feedstock to determine specific properties that have a stronger influence on the behavior of the coal during the gasification process.

8.2 Sampling

Optimization of coal behavior in gasifiers is a function of the many variable constituents of coal. Thus, it is not surprising, perhaps it is even anticipated, that sampling is conducted to determine efficiency, heat inputs, and operating needs. Thus, coal sampling is an important part of the process control in a coal preparation plant. Most analyses of coal for both standard and research purposes are conducted on carefully collected samples (representative sample) of whole coal. On the other hand, a *grab sample* is a one-time sample of the coal at a point in the process stream, and tends not to be very representative. A *routine sample* is taken at a set frequency, either over a period of time or per shipment.

After a gross sample has been taken, it is crushed and then quartered to obtain a net sample that is then sent to an independent laboratory for testing, where the results will be shared with the buyer as well as the supplier. In many cases, the buyer may request a repeat analysis or a second analysis by another laboratory to assure the quality of the data. Continuous measurement of ash, moisture, heat content (Btu/lb), sulfur iron, calcium sodium, and other elemental constituents of the coal are reported.

Furthermore, recognition of the issues involved in obtaining representative samples of coal has resulted in the designation of methods that dictate the correct manner for the sampling of coal (ASTM D346; ASTM D2013; ASTM D2234; ISO 1988; ISO 2309). However, it is possible by use of these methods to reduce an extremely large consignment (that may be of the order of several thousand pounds) to a representative sample that can be employed (with confidence that it is a representative sample) as a laboratory test sample.

8.3 Proximate analysis

The proximate analysis of coal indicates the percentage by weight of the fixed carbon, volatile matter, mineral matter (determined as mineral ash), and moisture content in coal. The amounts of fixed carbon and volatile matter directly contribute to the heating value of coal. Fixed carbon acts as a main heat generator during burning. High volatile matter content indicates easy ignition and devolatilization of the coal. The ash-producing propensity of coal is important in the design of the grate, gasifier volume, pollution control equipment, and ash handling system.

The proximate analysis of coal consists of a group of tests that have been used widely as the basis for coal characterization in connection with coal utilization (ASTM D3172). In reality, we are speaking of the determination of moisture content, volatile matter content, ash yield, and (by difference) fixed carbon yield – in contrast to the ultimate analysis of coal that provides the elemental composition (Figure 8.1).

The variables are measured in percent by weight (% w/w) and are calculated on several different bases: (1) AR – as-received basis, which is the most widely used basis in industrial applications and puts all variables into consideration and uses the total weight as the basis of measurement; (2) AD – air-dried basis, which neglects the

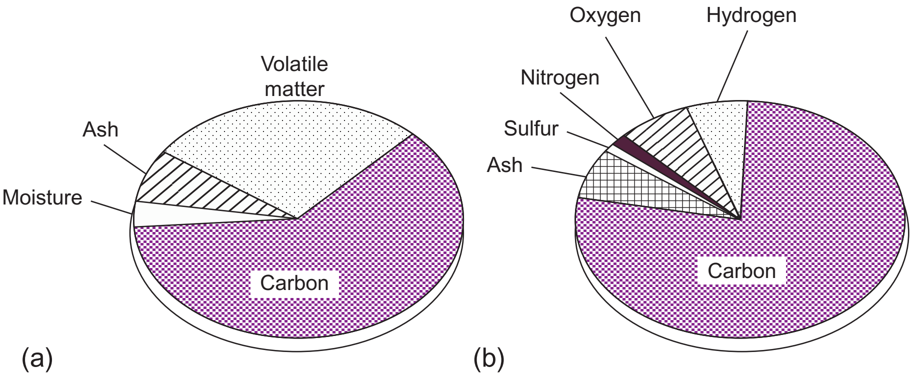

Figure 8.1 Data types obtained from (a) proximate analysis and (b) ultimate analysis (Speight, 2005, 2008, 2013a, 2013b).

presence of moistures other than inherent moisture; (3) DB – dry-basis, which omits all moisture, including surface moisture, inherent moisture, and other moistures; (4) DAF – dry, ash-free basis, which omits all moisture and mineral matter (determined as mineral ash) constituents in coal; and (5) DMMF – dry, mineral-matter-free, which omits the presence of moisture and mineral matter in coal, such as quartz, pyrite, calcite, and clay.

8.3.1 Moisture content

Moisture in coal is an important property (ASTM D1412; ASTM D2961; ASTM D3173; ASTM D3302) – more important than often recognized by the non-industrial coal theorists. Moisture that exists in coal (on the order of 0.5-15% w/w) must be transported, handled, and stored before gasification. Given that the moisture replaces organic volatiles, it (1) decreases the heat content of the coal; (2) increases heat loss, due to evaporation and superheating of vapor; and (3) aids radiation heat transfer. Furthermore, the higher the amount of moisture in coal, the greater the potential for the generation of heat leading to spontaneous ignition and spontaneous combustion (Speight, 2013a). The most dangerous scenario for spontaneous combustion is when wet and dry coals are combined in a stockpile – the interface between wet and dry coal becomes a heat exchanger. If coal is either completely wet or completely dry, the risk is substantially reduced. In general, the moisture content of coal increases with decreasing rank.

8.3.2 Volatile matter

Generally, the original raw coal does *not* contain much natural volatile matter. The volatile matter in coal refers to the components of coal, except for moisture, which are liberated at high temperature in the absence of air (i.e., during pyrolysis or during the initial stages of thermal treatment). The volatile matter obtained during the initial heating stage influences commencement of the gasification process coal, which consists mainly of gases such as hydrogen, carbon monoxide, methane, higher molecular weight hydrocarbons, volatile oil, volatile tar, as well as carbon dioxide and steam. Any coal that can generate substantial amounts of volatile matter can ignite easily, which is a significant factor for coal selected as a feedstock in a coal gasification system.

Just like the moisture content, volatile matter (ASTM D3175; ISO 562) depends on coal rank and ranges from <5% for anthracites to >50% w/w for sub-bituminous and lignite. There are large variations in gas content within a single coal at a single location. The gases in coal are located in pores and are retained on the surface of the pores by adsorption forces.

As for all standard test methods, the volatile matter of coal is determined under rigidly controlled standards. In Australian and British standard test methods, the procedure involves heating the coal sample to 900 ± 5 °C (1650 ± 10 °F) for 7 min in a cylindrical silica crucible in a muffle furnace. The standard test method of analysis involves heating coal to 950 ± 25 °C (1740 ± 45 °F) in a vertical platinum crucible (ASTM D3175; ISO 1350). The composition of the volatile matter evolved from coal is substantially different for the different ranks of coal.

8.3.3 Ash

Coal *does not* contain ash but does contain ash-forming mineral constituents (Speight, 2005, 2013a, 2013b). Ash is further classified into (1) fly ash and (2) bottom ash. *Fly ash* is the fine particle that rises with the flue gases during gasification (and combustion), whereas *bottom ash* is the ash that does not rise. The quantity of fly ash generated during gasification and combustion processes is also dependent on the rank of the coal.

The presence of inorganic matter (mineral materials) in coal reduces the heating value of the coal. The mineral matter may also contribute to the volatile matter in coal by virtue of the loss of water from the clay minerals, the loss of carbon dioxide from the carbonate minerals, the loss of sulfur from pyrite (FeS_2), and the generation of hydrogen chloride from chloride minerals. The most commonly found minerals in coal are clay minerals, quartz minerals, sulfide minerals, and carbonate minerals.

Clay minerals, such as montmorillonite, may or may not break down (dissociate) into its constituent parts when coal is heated. If it does dissociate, then, after cooling, it may recombine with other elements or minerals to form mineral deposits on the inside surfaces of furnaces and boilers (*slagging* or *fouling*). This produces barriers to heat exchange in the affected equipment, which can substantially reduce its efficiency and require costly repairs. Illite, however, with its simpler composition, does not cause such problems under normal furnace operating conditions.

The mineral matter content of coal, and hence the yield of ash during gasification (usually on the order of 5-40% w/w), can lead to slagging, fouling, and corrosion. *Slagging* is the deposition of fly ash (ash that does not descend to the bottom of the gasifier) on both heat transfer surfaces and refractory surfaces. *Fouling* includes deposition of ash and volatiles as well as sulfidation reactions of ash. Fouling results in loss of heat transfer efficiency and blockage of the gas flow path. *Corrosion* results in thinning of metals walls with the potential for leaks and equipment shutdown.

Determination of the mineral matter content (as the yield of mineral ash) is necessary because it directly affects process efficiency (ASTM D3174; ISO 1171). Several formulae have been proposed for calculating the amount of mineral matter originally in the coal by using the data from ashing techniques as the basis of the calculations. Of these formulae, two have survived and have been used regularly to assess the proportion of mineral matter in coal: the Parr formula and the King-Mavies-Crossley formula.

In the Parr formula, the mineral matter content of coal is derived from the expression:

$$\%\,\mathrm{w/w\,mineral\,matter} = 1.08\mathrm{A} + 0.55\mathrm{S}$$

where A is the weight percent of ash produced in the test method and S is the total sulfur in the coal.

The King-Mavies-Crossley formula is a more complex formula:

$$\begin{aligned}\%\,\mathrm{w/w\,mineral\,matter} = {} & 1.09\mathrm{A} + 0.5\mathrm{S_{pyr}} + 0.8\mathrm{CO_2} - 1.1\mathrm{SO_{3(in\,ash)}} + \mathrm{SO_{3(in\,coal)}} \\ & + 0.5\mathrm{Cl}\end{aligned}$$

where A = the weight percent yield of ash, S_{pyr} = the percentage of pyritic sulfur in the coal, CO_2 = the percentage of mineral (non-organic) carbon dioxide in the coal, $SO_{3(\mathrm{in\ ash})}$ = the percentage of sulfur trioxide in the ash, $SO_{3(\mathrm{in\ coal})}$ = the percentage of sulfur trioxide in the coal, and Cl = the percentage of chlorine in the coal.

8.3.4 Fixed carbon

The *fixed carbon content* (more correctly, the *fixed carbon yield* or *carbonaceous residue yield*) (FC) of the coal can be related to the anticipated yield of char produced during the devolatilization process (Chapter 5). It is the carbon found in the material that remains after volatile materials are driven off. Thus:

$$\mathrm{FC} = 100 - (\%\mathrm{H_2O} + \%\mathrm{VM} + \%\mathrm{Ash})$$

The value for the fixed carbon content of coal differs from the ultimate carbon content of the coal because some carbon is lost in hydrocarbons in the volatile matter.

In the determination of fixed carbon (ASTM 3172; ISO 1350), the cover from the crucible used in the volatile matter last test is removed and the crucible is heated over the Bunsen burner until all the carbon is burned. The residue is weighed, and the difference in weight from the previous weighing is the fixed carbon.

8.4 Calorific value

The calorific or heating value of a coal is a direct indication of the energy content and therefore is probably the most important property for determining the usefulness of coal in the context of a coal gasification plant (Speight, 2013a, 2013b). It is the amount of energy that a given quantity of coal will produce when burned. It is used in determining the rank of coals and in determining the maximum theoretical fuel energy available for the production of steam. Calorific value is also used to determine the quantity of fuel that must be handled, pulverized, and fired in the boiler.

The calorific value is determined in a bomb calorimeter either by a static (isothermal) (ASTM D3286; ISO 1928) or by an adiabatic method (ASTM D2015; ISO 1928). The computed value for the calorific value of coal is usually expressed in British thermal units per pound, kilocalories per kilogram, or kilojoules per kilogram (1.8 Btu/lb = 1.0 kcal/kgm = 4.187 kJ/kgm).

The experimental conditions require an initial oxygen pressure of 300-600 psi and a final temperature in the range 20-35 °C (68-95 °F) with the products in the form of ash, water, carbon dioxide, sulfur dioxide, and nitrogen. Thus, once the gross calorific value (GCV) has been determined, the net calorific value (NCV) (i.e., the net heat of combustion) is calculated from the GCV (at 20 °C; 68 °F) by deducting 1030 Btu/lb (2.4 × 103 kJ/kg) to allow for the heat of vaporization of the water. The deduction is not actually equal to the heat of vaporization of water (1055 Btu/lb) because the calculation is to reduce the data from a gross value at constant volume to a net value at constant pressure. Thus, the differences between the GCV) and the NCV are given by:

$$\mathrm{NCV(Btu/lb)} = \mathrm{GCV} - (1030 \times \text{total hydrogen} \times 9)/100.$$

In either form of measurement, the calorific value is reported as GCV, with a correction made if NCV is of interest (ASTM D121; AST M D2015; ASTM D3286; ASTM D5865; ISO 1928).

If a coal does not have a measured heat content (calorific value), it is possible to make a close estimation of the calorific value (CV) by means of various formulae, the most popular of which are (Selvig, 1945):

The Dulong formula

$$\mathrm{CV} = 144.4(\%\mathrm{C}) + 610.2(\%\mathrm{H}) - 65.9(\%\mathrm{O}) - 0.39(\%\mathrm{O})$$

The Dulong-Berthelot formula:

$$\mathrm{CV} = 81{,}370 + 345[\%\mathrm{H} - (\%\mathrm{O} + \%\mathrm{N} - 1)/8] + 22.2(\%\mathrm{S})$$

The respective carbon, hydrogen, nitrogen, oxygen, and organic sulfur contents of the coal are %C, %H, %N, %O, and %S, all of which are calculated to a dry, ash-free basis. In both cases, the calculated values are in close agreement with the experimental calorific values.

Finally, and in order to remove any potential confusion, the chemical energy in coal is often stated as either the lower heating value (LHV) or the higher-heating value (HHV) with units such as Btu/lb or MJ/kg or Btu/lb (1 MJ/kg is approximately equal to 430 Btu/lb). The HHV considers the heat released upon condensation of water vapor (latent heat/heat of vaporization/condensation), whereas the LHV excludes this factor.

8.5 Ultimate analysis

The objective of ultimate analysis (ASTM D5373; ASTM D4239) is to determine the constituents of coal in the form of the proportions of the chemical elements. Thus, the ultimate analysis (Figure 8.1) (ASTM D3176) determines the amount of carbon (C), hydrogen (H), oxygen (O), sulfur (S) – as well as the forms of sulfur (ASTM D2492, ISO 157) and other elements within the coal sample (Speight, 2005, 2013a, 2013b). The amount of carbon includes that present in the organic coal substance as well as that originally present as mineral carbonates. Similarly, the amount of hydrogen includes that of the organic coal substance and the hydrogen present in the form of moisture and the water of constitution of the silicate minerals.

Thus, for coal gasification systems, ultimate analysis is used (along with the heating value of the coal) to estimate gasifier performance criteria such as (1) coal feed rate, (2) air requirements, and (3) sulfur emissions (Speight, 2005, 2013a, 2013b).

Chlorine also occurs in coal and is believed to be a factor not only in fouling problems but also in corrosion problems (Canfield, Ibarra, & McCoy, 1979; Slack, 1981). The occurrence of chlorine in coal leads to the formation of hydrogen chloride, and the condensation of water containing hydrogen chloride (hydrochloric acid) on the cooler parts of equipment can lead to severe corrosion of the metal surfaces. The chlorine content of coal is usually low and occurs predominantly as sodium, potassium, and calcium chlorides, with magnesium and iron chlorides present in some coal types.

The generally accepted fouling classification of coal, according to total chlorine content (ASTM D2361; ASTM D4208; ISO 352; ISO 587) is as follows:

Chlorine % w/w	***Fouling* type**
<0.2	Low
0.2-0.3	Medium
0.3-0.5	High
>0.5	Severe

Mercury, which occurs in coal (Speight, 2005, 2013a, 2013b; Tewalt, Bragg, & Finkelman, 2001; Wang *et al.*, 2010), has been identified as a very dangerous environmental contaminant, largely by reason of the process of concentration in the food chain.

The test for mercury (ASTM D3684) consists of burning the sample in an oxygen bomb with diluted nitric acid and determination of the mercury by flameless cold vapor atomic absorption. Because of the different chemistry of mercury species, the fate of mercury in gasifier emissions is variable and requires treatment according to the mercury species present (Cao *et al.*, 2008a, 2008b; Lee, Serre, Zhao, Lee, & Hastings, 2008; Lee *et al.*, 2006; Meij, Vredendregt, & Winkel, 2002; Park, Seo, Lee, & Lee, 2008; Pavlish *et al.*, 2003; Srivastava, Hutson, Martin, Princiotta, & Staudt, 2006).

Trace elements that occur in coal are often included as part of the ultimate analysis (ASTM D6349; ASTM D6357). All coals contain small concentrations of trace elements, although there mode of occurrence and distribution vary from coal to coal and are present in coal in both organic and inorganic forms, and most of these elements are found simultaneously in both forms (Speight, 2013a, 2013b, and references cited therein). The trace elements are released into the atmosphere during coal gasification as particulate matter. Studies have revealed the distributions and concentrations of trace elements in organic and inorganic components of coal impacts the quality of coal gasification by-products.

8.6 Physical properties

The physical properties of coal, such as color, specific gravity, and hardness, vary considerably (Table 8.2) (Speight, 2005, 2013a, 2013b). At first consideration, there may appear to be little, if any, relationship between the physical, mechanical, and chemical behavior of coal, but in fact the converse is true. For example, the pore size of coal (which is truly a physical property) is a major factor in determining the chemical reactivity of coal. Also, chemical effects that result in the swelling and caking of coal(s) have a substantial impact on the means by which coal should be handled either prior to or during coal gasification.

Table 8.2 Physical, mechanical, and thermal properties of coal of relevance to gasification

		Comments
Physical properties	Density	True density
	Porosity and surface area	Nature of pore structure
	Surface area	Surface characteristics
Mechanical properties	Strength	Ability to withstand external forces
	Hardness index	Measurement of scratch hardness
	Friability	Ability to withstand degradation during handling
	Grindability	Energy needed to pulverize or grind coal
Thermal properties	Heat capacity	Indication of energy content
	Thermal conductivity	Rate of heat transfer through unit area
	Plastic properties	Changes of coal on or during heating
	Agglutinating properties	Changes of coal on or during heating
	Agglomerating index	Determination of nature of residue after heating
	Free-swelling index	Increase in volume when coal is heated

8.6.1 Density

Density is an important aspect of reactor engineering. It indicates the reactor size and throughput for gasification processes. With the free-swelling index (FSI), the density is also used to estimate the volume of the char produced during the devolatilization process.

The term *coal density* therefore carries several different connotations. A distinction must be made among bulk densities, which are determined by the average particle (or lump) size, size distribution, and packing density of the coal, because these affect handling, transportation, and storage.

The *true density* (ASTM D167) is usually determined by displacement of a fluid. Because of the porous nature of coal and physicochemical interactions, the observed density data vary with the particular fluids employed (Agrawal, 1959; Mahajan & Walker, 1978).

The *apparent density* of coal is determined by immersing a weighed sample of coal in a liquid followed by the accurate measurement of the liquid that is displaced. For this procedure, the liquid should (1) wet the surface of the coal, (2) not absorb strongly to the coal surface, (3) not cause swelling, and (4) penetrate the pores of the coal. Incidentally, the lower the rank of the coal, the greater is the "wettability" with water. On the other hand, the higher the rank, the greater the "wettability" with (coal) tar or the non-volatile pitch.

The *bulk density* (ASTM D291) is not an intrinsic property of coal and varies depending on how the coal is handled. Bulk density is the mass of many particles of coal divided by the total volume occupied by the particles. The total volume includes particle volume, interparticle void volume, and internal pore volume. This variable composition allows the density of coal to be expressed in terms of the cubic foot weight of crushed coal, which varies with particle size of the coal and packing in a container.

8.6.2 Porosity and surface area

Coal is a porous material, thus the porosity and surface area of coal (Mahajan & Walker, 1978) have a large influence on coal behavior during gasification because the reactivity of coal increases as the porosity and surface area of the coal increases. Porosity dictates the rate at which volatile matter can diffuse out of the coal (in the gasifier) and the rate at which oxygen or other gasification agents can interact with the coal.

As already noted with respect to coal density, the porosity of coal decreases with carbon content, reaching a minimum at coal containing ~89% carbon followed by a marked increase in porosity. There are also differences in the pore size that make up the porosity of coal. For example, macropores are usually predominant in the lower carbon (rank) coals, whereas higher carbon (rank) coals contain predominantly micropores. Thus, pore volume can be calculated from the relationship:

$$V_{\mathrm{p}} = 1/\rho_{\mathrm{Hg}} - 1\rho_{\mathrm{He}}$$

In this equation, ρ_{Hg} is the mercury density, and ρ_{He} is the helium density; both decrease with carbon content. In addition, the surface area of coal varies over the range of 10-200 m^2/g and also tends to decrease with the carbon content of the coal. The porosity of coal is calculated from the relationship:

$$\rho = 100\rho_{Hg}\left(1/\rho_{Hg} - 1\rho_{He}\right)$$

By determining the apparent density of coal in fluids of different, but known, dimensions, it is possible to calculate the pore size (pore volume) distribution. The open pore volume (*V*), (i.e., the pore volume accessible to a particular fluid) can be calculated from the relationship:

$$V = \left(1\rho_{Hg} - 1\rho_{a}\right)$$

where ρ_a is the apparent density in the fluid.

The size distribution of the pores within the coal can be determined by immersing the coal in mercury and progressively increasing the pressure. Surface tension effects prevent the mercury from entering the pores with a diameter smaller than a given value d for any particular pressure P such that

$$P = 4\sigma.\cos\theta/d$$

In this equation, σ is the surface tension and θ is the angle of contact (Van Krevelen, 1957). However, the total pore volume accounted for by this method is substantially less than that derived from the helium density, thereby giving rise to the concept that coal contains two pore systems: (1) a macropore system accessible to mercury under pressure and (2) a micropore system that is inaccessible to mercury but accessible to helium.

8.7 Mechanical properties

In contrast to the proximate analysis, the ultimate analysis (Chapter 5) and certain physical properties (discussed earlier), the mechanical properties of coal (Table 8.2) should be of consideration in predicting coal behavior during mining, handling, and preparation in the context of use in a gasification plant.

8.7.1 Strength

There are different methods for estimating coal strength and hardness: compressive strength, fracture toughness, and grindability, all of which show a trend relative to rank, type, and grade of the coal. The measurement of coal strength is affected by the size of the test specimen, the orientation of stress relative to banding, and the confining pressure of the test (Hobbs, 1964; Medhurst & Brown, 1998; Zipf & Bieniawski, 1988).

Thus, the strength of a bituminous coal specimen is influenced also by its lateral dimension, the smaller specimens showing greater strength than the larger, which can be attributed to the presence in the larger specimen of fracture planes or cleats. In fact, it is the smaller samples that present a more accurate indication of the strength of the coal. The variation of strength with rank of coals has been noted and a plot of strength against volatile matter shows the customary minimum to be 20-25% dry, ash-free volatile matter for compression both perpendicular and parallel to the bedding plane (Speight, 2013a).

The only standard test method that is available is actually a test method for determining coke reactivity and coke strength after reaction (ASTM D5341). This test method describes the equipment and techniques used for determining lump coke reactivity in carbon dioxide (CO_2) gas at elevated temperatures and its strength after reaction in carbon dioxide gas by tumbling in a cylindrical chamber.

8.7.2 Hardness

Although the resistance of coal to abrasion may have little apparent commercial significance, the abrasiveness of coal is, on the other hand, a factor of considerable importance when coal is used in a gasifier. The wear of grinding elements due to the abrasive action of coal results in maintenance charges that constitute one of the major items in the cost of grinding coal for use as pulverized fuel. Moreover, as coals vary widely in abrasiveness, this factor must be considered when coals are selected for plants that employ pulverized coal (Speight, 2005, 2013a).

The abrasiveness of coal may be determined more by the nature of its associated impurities than by the nature of the coal substance. For example, pyrite is 20 times harder than coal, and the individual grains of sandstone, another common impurity in coal are hard and abrasive.

8.7.3 Friability

Friability is of interest primarily because friable coals yield smaller proportions of the coarse sizes, which may (depending on use) be more desirable. There may also be an increased amount of surface in the friable coals. This surface allows more rapid oxidation; hence conditions are more favorable for spontaneous ignition leading to loss in coking quality in coking coals, and other changes that accompany oxidation.

The tumbler test for measuring coal friability (ASTM D441) employs a cylindrical porcelain jar mill (7.25 in., 18.4 cm in size) fitted with three lifters that assist in tumbling the coal. A 1000-g sample of coal sized between 1.5 and 1.05-in. square-hole screens is tumbled in the mill (without grinding medium) for 1 h at 40 rpm. The coal is then removed and screened on square-hole sieves with openings of 1.05, 0.742, 0.525, 0.371, 0.0369, and 0.0117 in.

A drop shatter test is also used for determining the friability of coal (ASTM D440), which is similar to the standard method used as a shatter test for coke (ASTM D3038).

In this method, a 50-lb sample of 2- to 3-in. pieces of coal is dropped twice from a drop-bottom box onto a steel plate 6 ft below the box. The materials shattered by the two drops are then screened over round-hole screens with 3.0 in. (76.2 mm), 2.0 in. (50.8 mm), 1.5 in. (38.1 mm), 1.0 in. (25.4 mm). 0.75 in. (19.05 mm) and 0.5 in. (12.7 mm) openings and the average particle size is determined.

8.7.4 Grindability

The grindability of coal (i.e., the ease with which coal may be ground fine enough for use as pulverized fuel) is a composite physical property embracing other specific properties such as hardness, strength, tenacity, and fracture. Several methods of estimating relative grindability utilize a porcelain jar mill in which each coal may be ground for, say, 400 revolutions and the amount of new surface is estimated from screen analyses of the feed and of the ground product. Coals are then rated in grindability by comparing the amount of new surface found in the test with that obtained for a standard coal.

A particularly important mechanical test designed to provide a measure of the ease of pulverization of a coal in comparison with other standard reference coals is the Hardgrove grindability index (HGI). Grindability changes with coal rank; that is, coals of very low and very high rank are more difficult to grind than middle-rank coking coals. The test for grindability (ASTM D409; ISO 5074) utilizes a ball-and-ring-type mill in which a 50-g sample of closely sized coal is ground for 60 revolutions after which the ground product is screened through a 200-mesh sieve.

The results are converted into the equivalent HGI. The HGI numbers indicate easy-to-grind coals. There is an approximate relationship between volatile matter yield and grindability in the low-volatile, medium-volatile, and high-volatile bituminous coals. Among these, the low-volatile coals exhibit the highest values for the HGI, often in excess of 100. The high-volatile bituminous coals range in the HGI from ~54 to 56 and as low as 36 to 39. Soft, easily fractured coals generally exhibit relatively high grindability index (GI) values. There are two standard test methods for measuring friability (ASTM D440: the drop shatter test, and ASTM D441: the tumbler test, D441) that should be used where a more accurate estimation of friability is required.

8.8 Thermal properties

The thermal properties of coal (Table 8.2) present an indication of the behavior of coal during thermal processes, and they are required for the design of equipment that is to be employed for gasification. For example, especially as it pertains to gasification, when a sample of powdered coal is heated out of contact with air, it loses occluded gases consisting of methane, ethane, nitrogen, and carbon dioxide (there may be other gases) at temperatures below 100 °C (212 °F); moisture is evolved between 100 and 150 °C (212 and 300 °F). The initial temperature of decomposition of bituminous coals is 200-300 °C (390 and 570 °F), whereas active decomposition starts at 300-375 °C (570 and 705 °F) for these coals. Pyrogenic water, primary tar, and gases evolve during the primary devolatilization (at 300-550 °C; 570-1000 °F), whereas gases (mainly hydrogen) are evolved during the secondary devolatilization at around 700 °C (1290 °F).

The dynamic features of the devolatilization process include phenomena such as particle softening, bubbling, swelling, evolution of volatiles, and contracting. Furthermore, while the coal undergoes decomposition on heating, the residue becomes richer in carbon content. In the case of caking coals, the residue passes through a plastic state in the range 300-350 °C (570-660 °F) and to 500-550 °C (930-100 °F). The fluidity of the plastic mass initially increases, attains a maximum and then decreases to zero. If coke is heated further, significant changes take place around 2000 °C (3630 °F) and graphite-like product is the result. Non-caking coals are not amenable to graphitization.

The porosity of coal decreases on heating and attains a minimum in the plastic state. After resolidification, porosity again rises considerably – the porosity of coke is 40% or above. This property ensures smooth burning of coke in furnaces. Because of the simultaneous formation of the plastic state and volatile products of thermal decomposition, the carbonaceous residue exhibits an initial contraction and decreases in porosity followed by swelling, dilation, and rise in porosity.

8.8.1 Heat capacity

The *heat capacity* of coal is the heat required to raise the temperature of one unit weight of a substance 1° and the ratio of the heat capacity of one substance to the heat capacity of water at 15 °C (60 °F) in the specific heat. The heat capacity of coal can be measured by standard calorimetric methods for mixtures (e.g., see ASTM C351).

The units for heat capacity are Btu per pound per degree Fahrenheit (Btu/lb/°F) or calories per gram per degree centigrade (cal/gm/°C), but the specific heat is the ratio of two heat capacities and is therefore dimensionless. The heat capacity of water is 1.0 Btu/lb/°F ($=4.2 \times 103$ J/kg/°K); thus, the heat capacity of any material will always be numerically equal to the specific heat. Consequently, there is a tendency to use the terms *heat capacity* and *specific heat* synonymously.

From the data for various coals, it has been possible to derive a formula that indicates the relationship between the specific heat and the elemental analysis of coal (mmf basis):

$$C_p = 0.189\mathrm{C} + 0.874\mathrm{H} + 0.491\mathrm{N} + 0.3600 + 0.215\mathrm{S}$$

C, H, N, O, and S are the respective amounts (% w/w) of the elements in the coal.

8.8.2 Thermal conductivity

Thermal conductivity is the rate of transfer of heat by conduction through a unit area across a unit thickness for a unit difference in temperature:

$$Q = kA(t_2 - t_1)/d$$

where Q = heat, expressed as kcal/sec cm °C or as Btu/ft h °F (1 Btu/ft h °F = 1.7 J/s m °K), A = area, $t_2 - t_1$ = temperature differential for the distance (d), and k = thermal conductivity (Carslaw & Jaeger, 1959). However, the banding and bedding planes in coal (Speight, 2013a) can complicate the matter to such an extent that it is difficult, if not almost impossible, to determine a single value for the thermal conductivity of a particular coal. Nevertheless, it has been possible to draw relevant conclusions from the data.

8.8.3 Plastic and agglutinating properties

Plastic and agglutinating properties, as well as phenomena such as the agglomerating index, give indications of how coal will behave in a gasification reactor. For example, when coal is heated, it passes through a transient stage called a plastic state (caking). If a particular coal does not pass through a plastic state, it is called sintered mass (non-coking). Although the plastic properties of coal are more definitive in terms of the production of metallurgical coke from coal blends, such properties can also influence coal gasification and whether or not the stickiness or fluidity of the coal will influence coal behavior in a gasifier as used on a coal-fired power plant (Speight, 2013a, 2013b).

All coals undergo chemical changes when heated, but there are certain types of coal that also exhibit physical changes when subjected to the influence of heat. These particular types of coals are generally known as *caking coals*, whereas the remaining coals are referred to as *non-caking coals*.

Caking coals pass through a series of physical changes during the heating process insofar as they soften, melt, fuse, swell, and resolidify within a specific temperature range. This temperature has been called the “plastic range” of coal and thus the physical changes that occur within this range have been termed the *plastic properties* (*plasticity*) of coal. On the other hand, when non-caking coal (non-plastic coal) is heated, the residue is pulverent and non-coherent. Furthermore, caking coals produce residues that are coherent and have varying degrees of friability and swelling. In the plastic range, caking coal particles have a tendency to form agglomerates (cakes) and may even adhere to surfaces of process equipment, thereby giving rise to reactor plugging problems. Thus, the plastic properties of coal are an important means of projecting and predicting how coal will behave under various process conditions as well as assisting in the selection of process equipment.

The Gieseler test is a standard test method (ASTM D2639) that attempts to measure the actual extent of the plasticity of fluidity. The Gieseler test is used to characterize coals with regard to thermo-plasticity and is an important method used for coal blending for commercial coke manufacture. The maximum fluidity determined by the Gieseler is very sensitive to weathering (oxidation) of the coal.

8.8.4 Agglomerating index

The *agglomerating index* is a grading index based on the nature of the residue from a one-gram sample of coal when heated at 950 °C (1740 °F) in the volatile matter determination (ASTM D3175).

The agglomerating index has been adopted as a requisite physical property to differentiate semi-anthracite from low-C volatile bituminous coal and also high-volatile C bituminous coal from sub-bituminous coal (Speight, 2013a, 2013b). From the standpoint of the caking action of coal in a gasifier, the agglomerating index has some interest. For example, coals having indexes NAa or NAb, such as anthracite or semi-anthracite, certainly do not give any problems from caking, whereas those coals having a Cg index are, in fact, the high-caking coals.

The agglomerating (or agglutinating) tendency of coal may also be determined by the Roga test (ISO 335). The Roga index (calculated from the abrasion properties when a mixture of a specific coal and anthracite is heated) is used as an indicator of the agglomerating tendencies of coal.

8.8.5 Free-swelling index

The FSI of coal is a measure of the increase in volume of a coal when it is heated (without restriction) under prescribed conditions (ASTM D720; ISO 335). The ISO test (ISO 335) and the Roga test measure mechanical strength rather than size profiles of coke buttons; another ISO test (ISO 501) gives a crucible swelling number of coal.

The nature of the volume increase is associated with the plastic properties of coal. As might be anticipated, coals that do not exhibit plastic properties when heated do not exhibit free swelling. Although this relationship between free swelling and plastic properties may be quite complex, it is presumed that when the coal is in a plastic (or semi-fluid) condition, the gas bubbles formed as a part of the thermal decomposition process within the fluid material cause the swelling phenomenon. This, in turn, is influenced by the thickness of the bubble walls, the fluidity of the coal, and the interfacial tension between the fluid material and the solid particles that are presumed to be present under the test conditions.

The test for the FSI of coal requires that several 1-g samples of coal be heated to 820 °C (1508 °F) within a specified time to produce buttons of coke. The shape, or profile, of the buttons determines the FSI of the coal (BSI, 2011). Anthracites do not usually fuse or exhibit a FSI, whereas the FSI of bituminous coals will increase as the rank increases from the high-volatile C bituminous coal to the low-volatile bituminous coal.

Other effects which can influence the FSI of coal include the weathering (oxidation) of the coal. Hence, it is advisable to test coal as soon as possible after collection and preparation. There is also evidence that the size of the sample can influence the outcome of the free-swelling test; an excess of fine (100 mesh) coal in a sample has reputedly been responsible for excessive swelling to the extent that the FSI numbers can be up to two numbers higher than is the true case.

8.8.6 Ash fusion temperature

The behavior of the coal ash residue at high temperature is a critical factor in selecting coals for gasification. Coal that has ash that fuses into a hard glassy slag (*clinker*) is usually unsatisfactory in gasifiers, but gasification equipment can be designed to handle the clinker, generally by removing it as a molten liquid.

Ash fusion temperatures are determined by viewing a molded specimen of the coal ash through an observation window in a high-temperature furnace (ASTM D1857). The ash, in the form of a cone, pyramid, or cube, is heated steadily past 1000 °C (1832°°F) to as high a temperature as possible, preferably 1600°°C (2910°°F).

The fusibility of ash is important in understanding the process of slagging and fouling in a gasifier. Ash fusion temperatures give an indication of the softening and melting behavior of fuel ash and therefore an estimation of the variability in fusibility characteristics among different coals. Ash fusion temperatures are also able to provide an indication of the progressive melting of coal ash to slag.

However, despite the shortcomings, fusion temperatures are valuable guides to the high-temperature behavior of the fuel inorganic material. The ash fusion temperature has been correlated with the mineral and chemical composition of coal ash (Vassilev, Kitano, Takeda, & Tsurue, 1995).

8.9 Real-time analysis for quality control

8.9.1 Method evolution

Real-time analysis of coal, once considered difficult because of the nature of the solid heterogeneous nature of coal, is now the wave of the future. Real-time analysis affords immediate knowledge of any unanticipated, unknown, and unmonitored changes in coal quality. Coal has a varying composition and its properties vary considerably from coal type to coal type and even from sample to sample within a coal seam. For decades, reliable property data could be obtained only by application of a series of standard test methods (Speight, 2005, 2013a, 2013b; Zimmerman, 1979), provided that the standard sampling methods are adhered to strictly. However, the operator of the gasification process may need to change equipment parameters to prevent loss of efficiency. An informed decision based on real-time data can change an outcome based on guesswork while analytical data are produced by the standard time-consuming methods.

To be profitable and sustainable the coal industry needs to achieve (1) greater energy efficiency, (2) improved use of coal in existing plants, (3) improved product quality and safety margins, and (4) reduced waste material and pollution levels. To do this improved control systems across the full range of industry applications, from mining to processing and use, are needed. These systems rely heavily on the availability of suitable on-line process instrumentation to provide the data and feedback necessary for implementation.

In the past, measurement of coal properties has involved (and still does involve) manual sampling followed by sample preparation (drying, mixing, crushing, and dividing) and off-line laboratory analysis. However, this procedure is often too slow for control purposes. By contrast, on-line analysis can provide rapid and accurate measurement in real time, opening up new possibilities for improved process control. On-line analysis can also lead to a reduction in the cost of sampling and analysis, and a reduced reliance on sampling equipment. As a result, there has been a rapid increase in the industrial application of on-line analysis instrumentation over the past few decades (Snider, 2004; Woodward, Empey, & Evans, 2003). Although it is not the purpose of this section to promote any one particular method, it is the purpose of this section to outline the methods that are available or under further development for real-time analysis of coal.

A current method for on-line analysis of coal ore is prompt gamma neutron activation analysis. With this technique, the sample is irradiated with a continuous neutron beam. The neutrons are absorbed by each of the elements within the sample, which then emit gamma rays at characteristic energies. The gamma rays are then directed toward a gamma ray spectrometer where the peaks are identified. The energies where the peaks are found signify the constituent elements within the sample, and the magnitudes of the peaks reveal the concentrations of each component. The response time for measurements is on the order of 1 min (Gaft, Nagli, Fasaki, Kompitsas, & Wilsch, 2007; Gozani, 1985; Romero *et al.*, 2010). This analysis tool can be installed on a conveyor belt to continuously analyze coal samples. The biggest drawback is the requirement of maintaining a nuclear isotope source to provide the neutrons and maintaining a safe environment for employees.

A pulsed laser technique that is promising for many real-time applications in coal gasification operations is light-induced breakdown spectroscopy (LIBS). All elements radiate characteristic frequencies of light when excited to high enough temperatures. LIBS exploits this by focusing an energetic laser pulse into the sample to be investigated. For solid targets, the laser pulse ablates a small amount of material from the target surface. The ablated material is heated to high enough temperatures to ionize and form localized plasma from the target constituents. Immediately following the plasma formation, a continuum of light frequencies is radiated from the plasma. Shortly after this phase, the plasma begins to cool and the characteristic emission lines from the target's constituent elements become visible. This light is collected and analyzed with a spectrometer to reveal the chemical makeup of the target (Cremers & Radziemski, 2006; Gaft *et al.*, 2007; Gaft *et al.*, 2008).

On-line analysis of coal ore at mines allows process engineers to determine the proper direction to take in mining operations. Coal compositions can vary with mine location and depth. Prompt analysis of compositions reveals whether chosen mining directions are maintaining steady quality or are moving toward unfavorable composition (Yin, Zhang, Dong, Ma, & Jia, 2009).

8.10 Advantages and limitations

Knowledge of coal properties is an important aspect of coal characterization and has been used as a means of determining the suitability of coal for commercial use for decades, perhaps even centuries. Therefore coal properties must always be borne in mind when consideration is being given to the suitability of coal for use in a gasifier that converts the chemical energy in the coal to thermal as well as gaseous products.

Analytical data for a variety of coal properties were necessary to assess gasifier performance. In addition, ash disposal, leachate containment, and ultimate rehabilitation are also cost items for coal-fired power plants. The coal properties affecting ash disposal are (1) coal reactivity, which influences the residual carbon in ash where fly ash is sold to the cement industry; this level of carbon in ash must be less than prescribed limits (usually ~5% w/w) but if the carbon in ash is above this limit, then disposal by other means will be required, at increased cost; (2) mineral matter content, which will affect the quality of ash to be disposed; and (3) trace element levels and leaching to the environment, which may lead to breaching of environmental regulations.

Utilities are governed by statutory regulations as to the maximum allowable discharge of gaseous pollutants, nitrogen oxides (NO_x), and sulfur oxides (SO_x). Flue-gas treating plants (Speight, 2013a, 2013b, 2014) for removing nitrogen oxides and/or sulfur oxides may need to be incorporated into the power plant during the design and construction phase, and these will have a large impact on both capital and operation and maintenance costs.

The determination of all the preceding properties can be determined in the analytical laboratory. But correlations of coal quality with gasifier impacts are impossible and the lack of knowledge of coal variability leads to questions related to the reliability of the analytical data as it relates to the *current* feedstock for the gasifier. However, the issue is not the accuracy and precision of the analysis but the time required to produce the data. This is where real-time analysis can be a good fit and even complement the original laboratory data. The original data serve as the base for which to work. Real-time analysis serves as a spot-check on the changing properties (quality) of the coal. In fact, the potential benefits of real-time analysis include (1) tracking the impact of coal quality, (2) immediate feedback for gasifier adjustments, and (3) plant diagnostics.

In terms of tracking the impact of coal quality, real-time analysis allows faster troubleshooting, more accurate heat rate reporting, and safer usage of opportunity fuels such as coal blends. In terms of gasifier adjustments, real-time analysis can provide continuous analysis at the receiving point and at the shipping point. In addition, real-time analysis also provides improved maintenance predictions and plant diagnostics. However, issues related to on-line analyzer reliability were foremost in the minds of coal utilization operators.

The new on-line analyzer designs offer more reliable performance and can provide coal parameters on an hourly basis. In addition, the elimination of coal sampling by utilizing a through-belt design has improved analyzer availability. The sampling system, once needed to feed coal to the analyzer, can now be eliminated and the major sources of analyzer downtime have been eliminated.

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Coal gasification processes for synthetic liquid fuel production

9

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9.1 Introduction

The chemical conversion of coal to gaseous products was first used to produce gas for lighting and heat in the United Kingdom more than 200 years ago. The gasification of coal or a derivative (i.e., char produced from coal) is, essentially, the conversion of coal (by any one of a variety of processes) to produce combustible gases (Calemma & Radović, 1991; Fryer & Speight, 1976; Garcia & Radović, 1986; Kristiansen, 1996; Radović & Walker, 1984; Radović, Walker, & Jenkins, 1983; Speight, 2008). With the rapid increase in the use of coal from the fifteenth century onward (Nef, 1957; Taylor & Singer, 1957), it is not surprising that the concept of using coal to produce a flammable gas became commonplace (Elton, 1958).

Depending on the type of gasifier (e.g., air-blown, enriched oxygen-blown) and the operating conditions (Chapter 2), gasification can be used to produce a fuel gas that is suitable for several applications. Coal gasification for electric power generation enables the use of a technology common in modern gas-fired power plants – the use of *combined cycle* technology to recover more of the energy released by burning the fuel.

As a very general rule of thumb, optimum gas yields and gas quality are obtained at operating temperatures of ~595-650 °C (1100-1200 °F). A gaseous product with a higher heat content (Btu/ft.^{3}) can be obtained at lower system temperatures but the overall yield of gas (determined as the *fuel-to-gas ratio*) is reduced by the unburned char fraction.

9.2 Coal types and properties

The influence of physical process parameters and the effect of coal type on coal conversion is an important part of any process where coal is used as a feedstock, especially with respect to coal combustion and coal gasification (Speight, 2013a,2013b). The reactivity of coal generally decreases with increase in rank (from lignite to subbituminous coal to bituminous coal anthracite). Furthermore, the smaller the particle size, the more contact area between the coal and the reaction gases, thereby causing faster reaction. For medium-rank coal and low-rank coal, reactivity increases with an increase in pore volume and surface area, but these factors have no effect on reactivity for coals having carbon content >85% w/w. In fact, in high rank coals, pore sizes are so small that the reaction is diffusion controlled.

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The volatile matter produced by the coal during thermal reactions varies widely for the four main coal ranks and is low for high rank coals (such as anthracite) and higher for increasingly low rank coals (such as lignite) (Speight, 2013a,2013b). The more reactive coals produce higher yields of gas and volatile products as well as lower yields of char. Thus, for high-rank coals, the utilization of char within the gasifier is much more of an issue than with lower-rank coal. However, the ease with which they are gasified leads to high levels of tar in the gaseous products, which makes gas clean-up more difficult.

The mineral matter content of the coal does not have much impact on the composition of the gas product. Gasifiers may be designed to remove the produced ash in solid or liquid (slag) form (Chapter 2). In fluidized- or fixed-bed gasifiers, the ash is typically removed as a solid, which limits operational temperatures in the gasifier to well below the ash melting point. In other designs, particularly slagging gasifiers, the operational temperatures are designed to be above the ash-melting temperature. The selection of the most appropriate gasifier is often dependent on the melting temperature and/or the softening temperature of the ash and the type of coal that is to be used at the facility.

In fact, coal that displays caking, or agglomerating, characteristics when heated (Speight, 2013a) are not usually amenable to use as feedstock for gasification processes that employ fluidized-bed or moving-bed reactors; in fact, caking coal is difficult to handle in fixed-bed reactors. Pretreatment of the caking coal by a mild oxidation process (typically consisting of low-temperature heating of the coal in the presence of air or oxygen) destroys the caking characteristics of the coal.

High-moisture content of the feedstock lowers internal gasifier temperatures through evaporation and the endothermic reaction of steam and char. Usually, a limit is set on the moisture content of coal supplied to the gasifier, which can be met by coal-drying operations if necessary. For a typical fixed-bed gasifier and moderate rank and ash content of the coal, this moisture limit in the coal is on the order of 35% w/w. Fluidized-bed and entrained-bed gasifiers have a lower tolerance for moisture, limiting the moisture content to ~5-10% w/w of the coal feedstock. Oxygen supplied to the gasifiers must be increased with an increase in mineral matter content (ash production) or moisture content in the coal.

With regard to the maceral content, differences have been noted between the different maceral groups with inertinite being the most reactive. In more general terms of the character of the coal, gasification technologies generally require some initial processing of the coal feedstock with the type and degree of pre-treatment a function of the process and/or the type of coal. For example, the Lurgi process will accept *lump* coal (1 inch [25 mm] to 28 mesh), but it must be non-caking coal with the fines removed. The caking, agglomerating coals tend to form a plastic mass in the bottom of a gasifier and subsequently plug up the system, thereby markedly reducing process efficiency.

With some coal feedstocks, the higher the amounts of volatile matter produced in the early stages of the gasification process, the higher the heat content of the product gas. In some cases, the highest gas quality may be produced at the lowest temperatures, but when the temperature is too low, char oxidation reaction is suppressed and the overall heat content of the product gas is diminished.

Coals of the western United States tend to have lower heating values, lower sulfur contents, and higher moisture content relative to bituminous coals from the eastern United States. The efficiency loss associated with high moisture and ash content coals is more significant for slurry-feed gasifiers. Consequently, dry-feed gasifiers, such as the Shell gasifier, may be more appropriate for low-quality coals. There is also the possibility that western coals can be combined with petroleum coke in order to increase the heating value and decrease the moisture content of the gasification feedstock.

9.3 Gas products

The products from the gasification of coal may be of low-, medium-, or high-heat content (high-Btu) as dictated by the process as well as by the ultimate use for the gas (Chapter 1) (Anderson & Tillman, 1979; Argonne, 1990; Baker & Rodriguez, 1990; Bodle & Huebler, 1981; Cavagnaro, 1980; Fryer & Speight, 1976; Lahaye & Ehrburger, 1991; Mahajan & Walker, 1978; Matsukata, Kikuchi, & Morita, 1992; Probstein & Hicks, 1990). Furthermore, variation in coal quality has an impact on the heating value of the product gas as well as the conditions in the gasifier (i.e., temperature, heating rate, pressure, and residence time) (Speight, 2013a,2013b).

The gasification process involves two distinct stages: (1) *coal devolatilization* followed by (2) *char gasification*, which is specific to the conditions of the reaction. Both stages have an effect on the yield and quality of the product gas.

Depending on the type of coal being processed and the analysis of the gas product desired, pressure also plays a role in product definition (Speight, 2013a). In fact, some (or all) of the following processing steps will be required: (1) pre-treatment of the coal (if caking is a problem); (2) primary gasification of the coal; (3) secondary gasification of the carbonaceous residue from the primary gasifier; (4) removal of carbon dioxide, hydrogen sulfide, and other acid gases; (5) shift conversion for adjustment of the carbon monoxide/hydrogen mole ratio to the desired ratio; and (6) catalytic methanation of the carbon monoxide/hydrogen mixture to form methane. If high-heat content (high-Btu) gas is desired, all of these processing steps are required because coal gasifiers do not yield methane in the concentrations required (Cusumano, Dalla Betta, & Levy, 1978; Mills, 1969).

9.3.1 Coal devolatilization

Devolatilization occurs when the coal is heated above 400 °C (750 °F). During this period, the coal structure is altered, producing solid char, tars, condensable liquids, and light gases. The devolatilization products formed in an inert gas atmosphere are very different from those in an atmosphere containing hydrogen at elevated pressure. After devolatilization, char then gasifies at a lower rate. The specific reactions that take place during this second stage depend on the gasification medium.

After the rate of devolatilization has passed a maximum, another reaction occurs in which the semi-char is converted to char primarily through the evolution of hydrogen.

In a hydrogen atmosphere at elevated pressure, additional yields of methane or other low molecular weight gaseous hydrocarbon can result during the initial coal gasification stage from reactions such as (1) direct hydrogenation of coal or semi-char because of active intermediate formed in coal structure after coal pyrolysis, and (2) the hydrogenation of other gaseous hydrocarbons, oils, tars, and carbon oxides.

9.3.2 Char gasification

Char gasification occurs as the char reacts with gases such as carbon dioxide (CO_2) and steam (H_2O) to produce carbon monoxide (CO) and hydrogen (H_2):

$$2C + CO_2 + H_2O \rightarrow 3CO + H_2$$

The resulting gas (producer gas or synthesis gas) may be more efficiently converted to electricity than is typically possible by direct combustion of coal. Also, corrosive ash elements such as chloride and potassium may be refined out by the gasification process, allowing high temperature combustion of the gas from otherwise problematic coal feedstocks.

Although the devolatilization reaction is completed in short order (typically in seconds) at elevated temperatures, the subsequent gasification of the char is much slower, requiring minutes or hours to obtain significant conversion under practical conditions. In fact, reactor design for commercial gasification processes is largely dependent on the reactivity of the char.

The reactivity of char produced in the pyrolysis step depends on the nature of the parent coal; it increases with oxygen content of the parent coal but decreases with carbon content. In general, char produced from low-rank coal is more reactive than char produced from high-rank coal. The reactivity of char from low-rank coal may be influenced by catalytic effect of mineral matter in char. In addition, as the carbon content of coal increases, the reactive functional groups present in coal decrease and the coal substance becomes more aromatic and cross-linked in nature (Speight, 2013a). Therefore, char obtained from high-rank coal contains a lesser number of functional groups and a higher proportion of aromatic and cross-linked structures, which reduce reactivity. The rate of gasification of the char decreases as the process temperature increases due to the decrease in active surface area of char. So, a change of char preparation temperature may change the chemical nature of char, which in turn may change the gasification rate (Johnson, 1979; Penner, 1987; Speight, 2013a).

9.3.3 Gasification chemistry

Coal gasification occurs under reducing conditions – coal (in the presence of steam and oxygen at high temperature and moderate pressure) is converted to a mixture of product gases. The chemistry of coal gasification is but can be conveniently (and simply) represented by the following reactions:

$$C + O_2 \rightarrow CO_2 \quad \Delta Hr = -393.4 MJ/kmol \qquad (9.1)$$

$$C + ½O_2 \rightarrow CO \quad \Delta Hr = -111.4\,MJ/kmol \tag{9.2}$$

$$C + H_2O \rightarrow H_2 + CO \quad \Delta Hr = 130.5\,MJ/kmol \tag{9.3}$$

$$C + CO_2 \leftrightarrow 2CO \quad \Delta Hr = 170.7\,MJ/kmol \tag{9.4}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta Hr = -40.2\,MJ/kmol \tag{9.5}$$

$$C + 2H_2 \rightarrow CH_4 \quad \Delta Hr = -74.7\,MJ/kmol \tag{9.6}$$

Reactions (9.1) and (9.2) are exothermic oxidation reactions and provide most of the energy required by the endothermic gasification reactions (9.3) and (9.4). The oxidation reactions occur very rapidly, completely consuming all of the oxygen present in the gasifier, so that most of the gasifier operates under reducing conditions. Reaction (9.5) is the water-gas shift reaction, where water (steam) is converted to hydrogen. This reaction is used to alter the hydrogen/carbon monoxide ratio when synthesis gas is the desired product, such as for use in Fischer-Tropsch processes. Reaction (9.6) is favored by high pressure and low temperature and is therefore important mainly in lower temperature gasification systems. Methane formation is an exothermic reaction that does not consume oxygen and so it increases the efficiency of the gasification process and the final heat content of the product gas. Overall, ~70% of the heating value of the product gas is associated with the carbon monoxide and hydrogen, but this can be higher depending on the gasifier type (Chapter 2; Chadeesingh, 2011).

Depending on the gasifier technology employed and the operating conditions (Chapter 2), significant quantities of water, carbon dioxide, and methane can be present in the product gas, as well as a number of minor and trace components. Under the reducing conditions in the gasifier, most of the organically bound sulfur in the coal feedstock is converted to hydrogen sulfide (H_2S), but a small amount (3-10% w/w) is converted to carbonyl sulfide (COS). Organically bound nitrogen in the coal feedstock is generally converted to gaseous nitrogen (N_2), but small amounts of ammonia (NH_3) and hydrogen cyanide (HCN) are also formed. Any chlorine in the coal (which typically originates from tine in the coal seam) is converted to hydrogen chloride (HCl) with some chlorine present in the particulate matter (fly ash). Trace elements, such as mercury and arsenic, are released during gasification and partition among the different phases, such as fly ash, bottom ash, slag, and product gas.

9.3.4 Other process options

9.3.4.1 Hydrogasification

Not all high-heat content (high-Btu) gasification technologies depend entirely on catalytic methanation. In fact, a number of gasification processes use hydrogasification – that is, the direct addition of hydrogen to coal under pressure to form methane (Anthony & Howard, 1976).

$$C_{char} + 2H_2 \rightarrow CH_4$$

The hydrogen-rich gas for hydrogasification can be manufactured from steam by using the char that leaves the hydrogasifier. Appreciable quantities of methane are formed directly in the primary gasifier and the heat released by methane formation is at a sufficiently high temperature to be used in the steam-carbon reaction to produce hydrogen, which then requires less oxygen to produce heat for the steam-carbon reaction.

9.3.4.2 Catalytic gasification

Catalysts are commonly used in the chemical and petroleum industries to increase reaction rates, sometimes making certain previously unachievable products possible (Hsu & Robinson, 2006; Speight, 2002, 2007). Use of appropriate catalysts not only reduces reaction temperature but it also improves the gasification rates. In addition, catalysts also reduce tar formation (McKee, 1981; Shinnar, Fortuna, & Shapira, 1982). Catalysts can also be used to favor or suppress the formation of certain components in the gaseous product. For example, in the production of synthesis gas (mixtures of hydrogen and carbon monoxide), methane is also produced in small amounts. Catalytic gasification can be used either to promote or to suppress methane formation.

Alkali metal salts of weak acids, such as potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), potassium sulfide (K_2S), and sodium sulfide (Na_2S) can catalyze steam gasification of coal. Catalyst amounts on the order of 10-20% w/w potassium carbonate (K_2CO_3) will lower bituminous coal gasifier temperatures from 925 °C (1695 °F) to 700 °C (1090 °F), and the catalyst can be introduced to the gasifier impregnated on coal or char.

Ruthenium-containing catalysts are used primarily in the production of ammonia. It has been shown that ruthenium catalysts provide 5 to 10 times higher reactivity rates than other catalysts. However, ruthenium quickly becomes inactive due to its necessary supporting material, such as activated carbon, which is used to achieve effective reactivity. However, during the process, the carbon is consumed, thereby reducing the effect of the ruthenium catalyst.

Disadvantages of catalytic gasification include increased materials costs for the catalyst itself (often rare metals), as well as diminishing catalyst performance over time. Catalysts can be recycled, but their performance tends to diminish with age or by poisoning. The relative difficulty in reclaiming and recycling the catalyst can also be a disadvantage. For example, the potassium carbonate catalyst can be recovered from spent char with a simple water wash, but some catalysts may not be so accommodating. In addition to age, catalysts can also be diminished by poisoning. On the other hand, many catalysts are sensitive to particular chemical species that bond with the catalyst or alter it in such a way that it no longer functions. Sulfur, for example, can poison several types of catalysts, including palladium and platinum.

9.3.4.3 Plasma gasification

Plasma is a high-temperature, highly ionized (electrically charged) gas capable of conducting electrical current. Plasma technology has a long history of development and has evolved into a valuable tool for engineers and scientists who need to use very high temperatures for new process applications (Kalinenko *et al.*, 1993; Messerle & Ustimenko, 2007). Human-made plasma is formed by passing an electrical discharge through a gas such as air or oxygen (O_2). The interaction of the gas with the electric arc dissociates the gas into electrons and ions, and causes its temperature to increase significantly, often (in theory) exceeding 6000 °C (10,830 °F).

Plasma technology has the following potential benefits over a typical coal gasification plant: (1) greater feedstock flexibility enabling coal, coal fines, mining waste, lignite, and other opportunity fuels (such as biomass and municipal solid waste) to be used as fuel without the need for pulverizing; (2) air blown and thus an oxygen plant is not required; (3) high conversion (>99%) of carbonaceous matter to synthesis gas; (3) absence of tar in the synthesis; (4) capable of producing high-heating value synthesis gas suitable for use in a combustion turbine operation; (5) no char, ash, or residual carbon; (6) only producing a glassy slag with beneficial value; (7) high thermal efficiency; and (8) low carbon dioxide emissions.

In the process, the gasifier is heated by a *plasma torch* system located near the bottom of the gasifier. The coal feedstock is charged into the vertical gasifier (refractory-lined or water-cooled) at atmospheric pressure. A superheated blast of air, which may be enriched with oxygen, is provided to the bottom of the gasifier, at the stoichiometric amount required for gasification. The amount of air fed is such that the superficial velocity of the upward flowing gas is low, and the pulverized feedstock can be fed directly into the reactor. Additional air and/or steam can be provided at different levels of the gasifier to assist with pyrolysis and gasification. The temperature of the syngas leaving the top of the gasifier is maintained above 1000 °C (1830 °F). At this temperature, tar formation is eliminated.

9.3.5 Process optimization

The output and quality of the gas produced is determined by the equilibrium established when the heat of oxidation (combustion) balances the heat of vaporization and volatilization plus the sensible heat (temperature rise) of the exhaust gases. The quality of the outlet gas (BTU/$ft.^3$) is determined by the amount of volatile gases (such as hydrogen, carbon monoxide, water, carbon dioxide, and methane) in the gas stream.

In a gasifier, the coal particle is exposed to high temperatures generated from the partial oxidation of the carbon. As the particle is heated, any residual moisture (assuming that the coal has been pre-fired) is driven off and further heating of the particle begins to drive off the volatile gases. Discharge of these volatiles will generate a wide spectrum of hydrocarbons ranging from carbon monoxide and methane to long-chain hydrocarbons comprising tars, creosote, and heavy oil. At temperatures above 500 °C (930 °F), the conversion of the coal to char and ash is completed. In most of the early gasification processes, this was the desired by-product, but for gas generation the char provides the necessary energy to effect further heating. Typically, the char is contacted with air or oxygen and steam to generate the product gases.

Gasification of coal/char in a carbon dioxide atmosphere can be divided into two stages. The first stage is due to pyrolysis (removal of moisture content and devolatilization), which is comparatively at lower temperature and the second stage is char gasification by different oxygen/carbon dioxide mixtures at high temperature. In nitrogen and carbon dioxide environments from room temperature to 1000 °C (1830 °F), the mass loss rate of coal pyrolysis in nitrogen is lower than that of carbon dioxide due to the difference in properties of the bulk gases. The gasification process of pulverized coal in the oxygen/carbon dioxide environment is almost the same as compared with that in oxygen/nitrogen at the same oxygen concentration, but this effect is little bit delayed at high temperature. This may be due to the lower rate of diffusion of oxygen through carbon dioxide and the higher specific heat capacity of carbon dioxide. However, with the increase of oxygen concentration, the mass loss rate of coal also increases and hence it shortens the burnout time of coal. The optimum value oxygen/carbon dioxide ratio for the reaction of oxygen with the functional group present in the coal sample was found to be about 8%.

The combination of pyrolysis and gasification process can be the unique and fruitful technique, as it can save the prior use of gasifying medium and the production of fresh char simultaneously in one process. With the increase of heating rate, coal particles are faster heated in a short period of time and burned in a higher temperature region, but the increase in heating rate has almost no substantial effect on the combustion mechanism of coal. The increase of heating rate causes a decrease in activation energy value (Irfan, 2009).

9.4 Products and product quality

The products of coal gasification are varied insofar as the gas composition varies with the type of coal and the gasification system employed. Furthermore, the quality of gaseous product(s) must be improved by removal of any pollutants such as particulate matter and sulfur compounds before further use, particularly when the intended use is a water-gas shift or methanation (Cusumano *et al*., 1978; Probstein & Hicks, 1990; Speight, 2013a,2013b).

9.4.1 Low Btu gas

Low Btu gas (low-heat content gas) is the product when the oxygen is not separated from the air and, as a result, the gas product invariably has a low-heat content (150-300 Btu/ft^3). Several important chemical reactions (Table 9.1), and a host of side reactions, are involved in the manufacture of low-heat content gas under the high temperature conditions employed. Low Btu gas (low-heat content gas) contains several components (Table 9.2). In medium-heat content gas, the H_2/CO ratio varies from 2:3 to ~3:1, and the increased heating value correlates with higher methane and hydrogen content, as well as with lower carbon dioxide content.

The nitrogen content of low-heat content gas ranges from somewhat less than 33% v/v to slightly more than 50% v/v and cannot be removed by any reasonable means, which limits the applicability of the gas to chemical synthesis. Two other

Table 9.1 Coal gasification reactions

$2C + O_2 \longrightarrow 2CO$
$C + O_2 \longrightarrow CO_2$
$C + CO_2 \longrightarrow 2CO$
$CO + H_2O \longrightarrow CO_2 + H_2$ (shift reaction)
$C + H_2O \longrightarrow CO + H_2$ (water-gas reaction)
$C + 2H_2 \longrightarrow CH_4$
$2H_2 + O_2 \longrightarrow 2H_2O$
$CO + 2H_2 \longrightarrow CH_3OH$
$CO + 3H_2 \longrightarrow CH_4 + H_2O$ (methanation reaction)
$CO_2 + 4\ H_2 \longrightarrow CH_4 + 2H_2O$
$C + 2H_2O \longrightarrow 2H_2 + CO_2$
$2C + H_2 \longrightarrow C_2H_2$
$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$

Table 9.2 Coal gasification products

Product	Characteristics
Low-Btu gas (150-300 Btu/scf)	Around 50% nitrogen, with smaller quantities of combustible H_2 and CO, CO; and trace gases, such as methane
Medium-Btu gas (300-550 Btu/scf)	Predominantly CO and H_2, with some incombustible gases and sometimes methane
High-Btu gas (980-1080 Btu/scf)	Almost pure methane

noncombustible components, water and carbon dioxide, further lower the heating value of the gas. Water can be removed by condensation, and carbon dioxide by relatively straightforward chemical means.

The two major combustible components are hydrogen and carbon monoxide; the hydrogen/carbon monoxide ratio varies from ~2:3 to about 3:2. Methane may also make an appreciable contribution to the heat content of the gas. Of the minor components, hydrogen sulfide is the most significant and the amount produced is, in fact, proportional to the sulfur content of the feed coal. Any hydrogen sulfide present must be removed by one, or more, of several available on-stream commercial processes (Speight, 2007, 2013a, 2014).

9.4.2 Medium Btu gas

Medium Btu gas (medium-heat content gas) has a heating value in the range 300-550 Btu/ft^3, and the composition is much like that of low-heat content gas, except that there is virtually no nitrogen. The primary combustible gases in medium-heat content gas are hydrogen and carbon monoxide (Kasem, 1979).

Medium-heat content gas is considerably more versatile than low-heat content gas; as with low-heat content gas, medium-heat content gas may be used directly as a fuel to raise steam, or used through a combined power cycle to drive a gas turbine, with the hot exhaust gases employed to raise steam. Medium-heat content gas, however, is especially amenable to synthesizing methane by methanation, higher hydrocarbons by Fischer-Tropsch synthesis, methanol, and a variety of synthetic chemicals (Chadeesingh, 2011; Davis and Occelli, 2010).

The reactions used to produce medium-heat content gas are the same as those employed for low-heat content gas synthesis, with the major difference being the application of a nitrogen barrier, such as the use of pure oxygen, to keep diluent nitrogen out of the system.

9.4.3 High Btu gas

High Btu gas (high-heat content gas) is essentially pure methane and often referred to as synthetic natural gas (SNG) (Kasem, 1979; Speight, 1990, 2013a). However, to qualify as a synthetic natural gas, a product must contain at least 95% methane, and the energy content of synthetic natural gas is 980-1080 Btu/ft^3. The commonly accepted approach to the synthesis of high-heat content gas is the catalytic reaction of hydrogen and carbon monoxide.

$$3H_2 + CO \rightarrow CH_4 + H_2O$$

During this process, the hydrogen is usually present in slight excess to ensure that the toxic carbon monoxide is reacted; this small quantity of hydrogen will lower the heat content to a small degree.

The carbon monoxide/hydrogen reaction is somewhat inefficient as a means of producing methane because the reaction liberates large quantities of heat. In addition, the methanation catalyst is troublesome and prone to poisoning by sulfur compounds, and the decomposition of metals can destroy the catalyst. Thus, hydrogasification may be employed to minimize the need for methanation.

$$C_{coal} + 2H_2 \rightarrow CH_4$$

The product of hydrogasification is *not* pure methane. Additional methanation is required after hydrogen sulfide and other impurities are removed.

9.4.4 Methane

Several exothermic reactions may occur simultaneously within a methanation unit (Seglin, 1975). A variety of metals have been used as catalysts for the methanation reaction, and the most common, and to some extent the most effective, methanation catalysts appear to be nickel and ruthenium, with nickel being the most widely used (Cusumano *et al*., 1978; Seglin, 1975; Tucci & Thompson, 1979; Watson, 1980). The synthesis gas must be desulfurized before the methanation step, because sulfur compounds will rapidly deactivate (poison) the catalysts (Cusumano *et al*., 1978). A problem may arise when the concentration of carbon monoxide is excessive in the stream to be methanated. Large amounts of heat must be removed from the system to prevent high temperatures and deactivation of the catalyst by sintering as well as the deposition of carbon (Cusumano *et al*., 1978). So, to eliminate carbon deposition, process temperatures should be maintained below 400°C (750 °F).

9.4.5 Hydrogen

Hydrogen is also produced by coal gasification (Johnson, Yang, & Ogden, 2007). Although several gasifier types exist (Chapter 2), entrained-flow gasifiers are considered most appropriate for producing both hydrogen and electricity from coal. This is because they operate at temperatures high enough (~1500 °C, 2730 °F) to enable high carbon conversion and prevent downstream fouling from tars and other residuals.

In the process, the coal undergoes three processes in its conversation to synthesis gas. The first two processes, pyrolysis and combustion, occur very rapidly. In pyrolysis, char is produced as the coal heats up and the volatiles are released. In the combustion process, the volatile products and some of the char react with oxygen to produce various products (primarily carbon dioxide and carbon monoxide) and the heat required for subsequent gasification reactions. Finally, in the third process – gasification – the coal char reacts with steam to produce hydrogen (H_2) and carbon monoxide (CO).

$$2C_{coal} + O_2 \rightarrow 2CO + H_2O$$

$$C_{coal} + H_2O \rightarrow H_2 + CO$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

The resulting syngas is ~63% v/v carbon monoxide, 34% v/v hydrogen, and 3% v/v carbon dioxide. At the gasifier temperature, the ash and other coal mineral matter liquefy and exit at the bottom of the gasifier as slag, a sand-like inert material that can be sold as a co-product to other industries (such as the road-building industry). The synthesis gas exits the gasifier at high pressure and high temperature and must be cooled prior to the syngas cleaning stage.

Although processes that use the high temperature to raise high-pressure steam are more efficient for electricity production (Speight, 2013b), full-quench cooling, by which the synthesis gas is cooled by the direct injection of water, is more appropriate for hydrogen production and provides the necessary steam to facilitate the catalytic water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Unlike pulverized coal combustion plants in which expensive emissions control technologies are required to scrub contaminants from large volumes of flue gas, smaller and less expensive emissions control technologies are appropriate for coal gasification plants because the clean-up occurs in the syngas. The synthesis gas is at high pressure and contains contaminants at high partial pressures, which facilitates gas cleaning.

As with other processes, the characteristics of the coal feedstock (e.g., heating value and ash, moisture, and sulfur content) have a substantial impact on plant efficiency and emissions. As a result, the cost of producing hydrogen from coal gasification can vary substantially, depending on the proximity to appropriate coal types.

9.4.6 Other products

There is a series of products that are called by older (even archaic) names that should also be mentioned here for clarification: (1) producer gas, (2) water gas, (3) town gas, and (4) synthetic natural gas.

Producer gas is a low-Btu gas obtained from a coal gasifier (fixed-bed) when air instead of oxygen is introduced into the fuel bed. The composition of the producer gas is ~28% v/v carbon monoxide, 55% v/v nitrogen, 12% v/v hydrogen, and 5% v/v methane with some carbon dioxide.

Water gas is a medium-Btu gas that is produced by the introduction of steam into the hot fuel bed of the gasifier. The composition of the gas is ~50% v/v hydrogen and 40% v/v carbon monoxide with small amounts of nitrogen and carbon dioxide.

Town gas is a medium-Btu gas that is produced in the coke ovens and has the following approximate composition: 55% v/v hydrogen, 27% v/v methane, 6% v/v carbon monoxide, 10% v/v nitrogen, and 2% v/v carbon dioxide. Carbon monoxide can be removed from the gas by catalytic treatment with steam to produce carbon dioxide and hydrogen.

Synthetic natural gas (SNG) is methane obtained from the reaction of carbon monoxide or carbon with hydrogen. Depending on the methane concentration, the heating value can be in the range of high-Btu gases.

9.5 Production of chemicals

The coal carbonization industry was established initially as a means of producing coke, but a secondary industry emerged (in fact, became necessary) to deal with the secondary or by-products (namely, gas, ammonia liquor, crude benzole, and tar) produced during carbonization (Table 9.3; Speight, 2013a).

9.5.1 Coal tar chemicals

Coal tar is a black or dark brown liquid or a high-viscosity semi-solid that is one of the by-products formed when coal is carbonized. Coal tars are complex and variable mixtures of polycyclic aromatic hydrocarbons (PAHs), phenols, and heterocyclic compounds. Because of its flammable composition, coal tar is often used for fire boilers in order to create heat. They must be heated before any heavy oil flows easily.

Table 9.3 Products (% w/w) from coal carbonization

Product	Low Temperature	High Temperature
Gas	5.0	20.0
Liquor	15.0	2.0
Light oils	2.0	0.5
Tar	10.0	4.0
Coke	70.0	75.0

Source: Speight, 2013a.

By comparison, coal tar creosote is a distillation product of coal tar and consists of aromatic hydrocarbons, anthracene, naphthalene, and phenanthrene derivatives. At least 75% of the coal tar creosote mixture is PAHs. Unlike the coal tars and coal tar creosotes, coal tar pitch is a residue produced during the distillation of coal tar. The pitch is a shiny, dark brown to black residue that contains PAHs and their methyl and poly-methyl derivatives, as well as heteronuclear aromatic compounds.

Primary distillation of crude tar produces pitch (residue) and several distillate fractions, the amounts and boiling ranges of which are influenced by the nature of the crude tar (which depends on the coal feedstock) and the processing conditions. For example, in the case of the tar from continuous vertical retorts, the objective is to concentrate the tar acids (phenol derivatives, cresol derivatives, and xylenol derivatives) into carbolic oil fractions. On the other hand, the objective with coke oven tar is to concentrate the naphthalene and anthracene components into naphthalene oil and anthracene oil, respectively.

The first step in refining benzole is steam distillation, which is employed to remove compounds boiling below benzene. To obtain pure products, the benzole can be distilled to yield a fraction containing benzene, toluene, and xylene(s). Benzene is used in the manufacture of numerous products, including nylon, gammexane, polystyrene, phenol, nitrobenzene, and aniline. On the other hand, toluene is a starting material in the preparation of saccharin, trinitrotoluene, and polyurethane foams. The xylenes present in the light oil are not always separated into the individual pure isomers because xylene mixtures can be marketed as specialty solvents. Higher boiling fractions of the distillate from the tar contain pyridine bases, naphtha, and coumarone resins. Other tar bases occur in the higher boiling range and these are mainly quinoline, iso-quinoline, and quinaldine.

Pyridine has long been used as a solvent in the production of rubber chemicals and textile water-repellant agents, and in the synthesis of drugs. The derivatives 2-benzylpyridine and 2-aminopyridine are used in the preparation of antihistamines. Another market for pyridine is in the manufacture of the non-persistent herbicides *diquat* and *paraquat*. Alpha-picoline (2-picoline; 2-methylpryridine) is used for the production of 2-vinylpyridine, which, when co-polymerized with butadiene and styrene, produces a used as a latex adhesive that is used in the manufacture of car tires. Other uses are in the preparation of 2-beta-methoxyethylpyridine (known as Promintic, an anthelmintic for cattle) and in the synthesis of a 2-picoline quaternary compound (Amprolium), which is used against coccidiosis in young poultry. Beta-picoline (3-picoline; 3-methylpryridine) can be oxidized to nicotinic acid, which, with the amide form (nicotinamide), belongs to the vitamin B complex; both products are widely used to fortify human and animal diets. Gama-picoline (4-picoline; 4-methylpyridine) is an intermediate in the manufacture of isonicotinic acid hydrazide (Isoniazide), which is a tuberculostatic drug. And 2,6-Lutidine (2,6-dimethylpyridine) can be converted to dipicolinic acid, which is used as a stabilizer for hydrogen peroxide and peracetic acid.

Solvent naphtha and heavy naphtha are the mixtures obtained when the 150-200 °C (300-390 °F) fraction, after removal of tar acids and tar bases, is fractionated. These naphtha fractions are used as solvents.

The tar-acid-free and tar-base-free coke-oven naphtha can be fractionated to give a narrow-boiling fraction (170-185 °C; 340-365 °F) containing coumarone and indene. This is treated with strong sulfuric acid to remove unsaturated components and is then washed and re-distilled. The concentrate is heated with a catalyst (such as a boron fluoride/phenol complex) to polymerize the indene and part of the coumarone. Unreacted oil is distilled off and the resins obtained vary from pale amber to dark brown in color. They are used in the production of flooring tiles and in paints and polishes.

Naphthalene and several tar acids are the important products extracted from volatile oils from coal tar. It is necessary to first extract the phenolic compounds from the oils and then to process the phenol-depleted oils for naphthalene recovery.

Tar acids are produced by extraction of the oils with aqueous caustic soda at a temperature sufficient to prevent naphthalene from crystallizing. The phenols react with the sodium hydroxide to give the corresponding sodium salts an aqueous extract known variously as crude sodium phenate, sodium phenolate, sodium carbolate, or sodium cresylate. The extract is separated from the phenol-free oils that are then taken for naphthalene recovery.

Naphthalene is probably the most abundant component in high-temperature coal tars. The primary fractionation of the crude tar concentrates the naphthalene into oils which, in the case of coke-oven tar, contain the majority (75-90% w/w) of the total naphthalene. After separation, naphthalene can be oxidized to produce phthalic anhydride, which is used in the manufacture of alkyd and glyptal resins and plasticizers for polyvinyl chloride and other plastics.

The main chemical extracted on the commercial scale from the higher-boiling oils (b.p. 250 °C, 480 °F) is crude anthracene. The majority of the crude anthracene is used in the manufacture of dyes after purification and oxidation to anthraquinone.

Creosote is the residual distillate oils obtained when the valuable components, such as naphthalene, anthracene, tar acids, and tar bases, have been removed from the corresponding fractions. Creosote is a brownish-black/yellowish-dark green oily liquid with a characteristic sharp odor, obtained by the fractional distillation of crude coal tars. The approximate distillation range is 200-400 °C (390-750 °F). The chemical composition of creosotes is influenced by the origin of the coal and also by the nature of the distilling process. As a result, the creosote components are rarely consistent in their type and concentration.

As a corollary to this section where the emphasis has been on the production of bulk chemicals from coal, a tendency-to-be-forgotten item must also be included. That is the mineral ash from coal processes. Coal minerals are a very important part of the coal matrix; it offers the potential for the recovery of valuable inorganic materials (Speight, 2013a). However, there is another aspect of the mineral content of coal that must be addressed, and it relates to the use of the ash as materials for roadbed stabilization, landfill cover, cementing (due to the content of pozzolanic materials), and wall construction.

9.5.2 Fischer-Tropsch chemicals

Fischer-Tropsch chemicals are those chemicals produced by conversion of the synthesis gas mixture (carbon monoxide, CO, and hydrogen, H_2) to higher molecular weight liquid fuels and other chemicals (Chadeesingh, 2011; Penner, 1987; Speight, 2013a). In principle, syngas can be produced from any hydrocarbon feedstock. These include natural gas, naphtha, residual oil, petroleum coke, coal, and biomass.

The synthesis of hydrocarbons from carbon monoxide and hydrogen (the Fischer-Tropsch synthesis) is a procedure for the indirect liquefaction of coal (Anderson, 1984; Dry & Erasmus, 1987). This process is the only coal liquefaction scheme currently in use on a relatively large commercial scale. South Africa is currently using the Fischer-Tropsch process on a commercial scale in their SASOL (South Africa) complex, although Germany produced roughly 156 million barrels of synthetic petroleum annually using the Fischer-Tropsch process during the Second World War.

9.5.2.1 Fischer-Tropsch process

In the Fischer-Tropsch process, coal is converted to gaseous products at temperatures in excess of 800 °C (1470 °F), and at moderate pressures, to produce synthesis gas.

$$C + H_2O \rightarrow CO + H_2$$

In practice, the FT reaction is generally carried out at temperatures in the range 200-350 °C (390-660 °F) and at pressures of 75-4000 psi; the hydrogen/carbon monoxide ratio is usually at ca. 2.2:1 or 2.5:1. Because up to three volumes of hydrogen may be required to achieve the next stage of the liquids production, the synthesis gas must then be converted by means of the water-gas shift reaction to the desired level of hydrogen after which the gaseous mix is purified (acid gas removal, etc.) and converted to a wide variety of hydrocarbons.

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$CO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + H_2O$$

These reactions result primarily in low- and medium-boiling aliphatic compounds; present commercial objectives are focused on the conditions that result in the production of n-hydrocarbons as well as olefins and oxygenated materials (Speight, 2013a).

9.5.2.2 Fischer-Tropsch catalysts

Catalysts play a major role in syngas conversion reactions. For hydrocarbon and synthesis of higher molecular weight alcohols, dissociation of carbon monoxide is a necessary reaction condition. For methanol synthesis, the carbon monoxide molecule remains intact. Hydrogen has two roles in catalytic syngas synthesis reactions. In addition to being a reactant needed for hydrogenation of carbon monoxide, it is commonly used to reduce the metalized synthesis catalysts and activate the metal surface. A variety of catalysts can be used for the Fischer-Tropsch process, but the most common are the transition metals cobalt, iron, and ruthenium. Nickel can also be used, but it tends to favor methane formation (*methanation*).

Cobalt-based catalysts are highly active, although iron may be more suitable for low-hydrogen-content synthesis gases such as those derived from coal due to its promotion of the water-gas-shift reaction. In addition to the active metal, the catalysts typically contain a number of promoters, such as potassium and copper.

Group 1 alkali metals (including potassium) are poisons for cobalt catalysts but are promoters for iron catalysts. Catalysts are supported on high-surface-area binders/supports such as silica, alumina, and zeolites (Spath & Dayton, 2003). Cobalt catalysts are more active for FT synthesis when the feedstock is natural gas. Natural gas has a high hydrogen to carbon ratio, so the water-gas shift is not needed for cobalt catalysts. Iron catalysts are preferred for lower-quality feedstocks such as coal or biomass. Unlike the other metals used for this process (Co, Ni, Ru), which remain in the metallic state during synthesis, iron catalysts tend to form a number of phases, including various oxides and carbides during the reaction. Control of these phase transformations can be important in maintaining catalytic activity and preventing breakdown of the catalyst particles.

Fischer-Tropsch catalysts are sensitive to poisoning by sulfur-containing compounds. The sensitivity of the catalyst to sulfur is greater for cobalt-based catalysts than for their iron counterparts. Promoters also have an important influence on activity. Alkali metal oxides and copper are common promoters, but the formulation depends on the primary metal, iron versus cobalt (Spath & Dayton, 2003). Alkali oxides on cobalt catalysts generally cause activity to drop severely, even with very low alkali loadings. C_{5+} and carbon dioxide selectivity increase, wherease methane and C_2 to C_4 selectivity decrease. In addition, the olefin to paraffin ratio increases.

9.5.2.3 Product distribution

The product distribution of hydrocarbons formed during the Fischer-Tropsch process follows an Anderson-Schulz-Flory distribution (Spath & Dayton, 2003):

$$W_n/n = (1-\alpha)^2\alpha^{n-1}$$

where W_n = the weight fraction of hydrocarbon molecules containing n carbon atoms, and α = the chain growth probability or the probability that a molecule will continue reacting to form a longer chain. In general, α is largely determined by the catalyst and the specific process conditions.

According to the preceding equation, methane will always be the largest single product; however, by increasing α close to one, the total amount of methane formed can be minimized compared to the sum of all of the various long-chained products. Therefore, for production of liquid transportation fuels it may be necessary to crack the Fischer-Tropsch longer chain products.

It has been proposed that zeolites or other catalyst substrates with fixed-sized pores can restrict the formation of hydrocarbons longer than some characteristic size (usually $n < 10$). This would tend to drive the reaction to minimum methane formation without producing the waxy products.

9.6 Advantages and limitations

The production of gas from coal has been a vastly expanding area of coal technology for power generation. In reality, it is another form of coal-fired power generation in which coal is used as the feedstock to produce the hot gases to drive the turbines. As with combustion processes, coal characteristics such as rank, mineral matter, particle size, and reaction conditions are all recognized as having a bearing on the outcome of the gasification process – not only in terms of gas yields but also on gas properties (Hanson, Patrick, & Walker, 2002; Massey, 1974).

Coal gasification technology offers the poly-generation co-production of electric power, liquid fuels, chemicals, hydrogen, and from the syngas generated from gasification. Chemical gasification plants based on entrained flow, and more specifically on moving-bed technologies, are currently operating all over the world, with the biggest plants located in South Africa (SASOL) (Speight, 2008, 2013a). In addition, gasification is an important step of the indirect liquefaction of coal for production of liquid fuels (Speight, 2008, 2013a). Another advantage is the ability of the gasifier technology to accommodate feedstock other than coal either separately or as a blend with coal (Speight, 2013a,2013b).

One of the major environmental advantages of coal gasification is the opportunity to remove impurities such as sulfur. Mercury, and soot before burning the fuel, using readily available chemical engineering processes. In addition, the ash produced is in a vitreous or glass-like state that can be recycled as concrete aggregate – unlike pulverized coal combustion plants that generate ash that must be landfilled, potentially contaminating groundwater.

The increased efficiency of the “combined cycle” for electrical power generation results in a 50% decrease in emissions of carbon dioxide compared to conventional coal plants. To develop economical methods of carbon sequestration, which is the removal of carbon dioxide from combustion by-products to prevent its release to the atmosphere, coal gasification units could be modified to further reduce their climate change impact because a large part of the carbon dioxide generated can be separated from the synthesis gas before combustion.

However, coal gasification, while providing a route to deriving energy from coal which facilitates the removal of ash and sulfur, has two major disadvantages: (1) the process consumes large quantities of water, especially significant in arid western states where some of the largest coal reserves are located, and (2) the process is less efficient than direct combustion. Some reactors provide limited optimization of either process efficiency or water consumption. Performance optimization is both application- and site-specific, and the choice of a coal gasification system depends to a large extent on the requirements and locations of the end-use markets.

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Heavy hydrocarbon gasification for synthetic fuel production

10

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10.1 Introduction

Heavy feedstocks (*hydrocarbonaceous materials*, *residua*, *process residues*, *process bottoms*) are nonvolatile materials that are not truly hydrocarbons insofar as they contain elements other than carbon and hydrogen. As with other gasification processes, the gasification of heavy feedstocks involves the complete thermal decomposition of the feedstock into gaseous products (Speight, 2014; Wolff & Vliegenthart, 2011). The term *heavy hydrocarbons* is often applied to residua, but it is, in fact, an incorrect term because the residua are not composed of true hydrocarbons – the so-called *hydrocarbons* in residua contain elements other than carbon and hydrogen.

Typically, gasification of heavy feedstocks is carried out at high temperature (>1000 °C, >1830 °F), producing synthesis gas (*syngas*), some carbon black, and ash as major products, and the amount of ash depends on the amount of mineral matter in the feedstock. The integrated gasification combined cycle (IGCC) is an alternative process for residua conversion and is a known and used technology within the refining industry for (1) hydrogen production, (2) fuel gas production, and (3) power generation, which, when coupled with efficient gas-cleaning methods, has a minimal effect on the environment (low SO_x and NO_x) (Speight, 2013c, 2013d; Wolff, 2007).

The ability of the gasification process to handle heavy crude oil, tar sand bitumen, or any refinery bottom streams enhances the economic potential of most refineries and oil fields (Goldhammer *et al.*, 2008). Upgrading heavy crude oil – either in the oil field at the source or residua in the refinery – is (and will continue to be) an increasingly prevalent means of extracting maximum value from each barrel of oil produced (Speight, 2011a, 2014). Upgrading can convert marginal heavy crude oil into light, higher value crude, and can convert heavy, sour refinery bottoms into valuable transportation fuels. On the other hand, most upgrading techniques leave behind an even heavier residue and the costs deposition of such a by-product may approach the value of the production of liquid fuels and other saleable products. In short, the gasification of residua, petroleum coke, or other heavy feedstocks to generate synthesis gas produces a clean fuel for firing in a gas turbine. Gasification (1) is a well-established technology, (2) has broad flexibility of feedstocks and operation, and (3) is the most environmentally friendly route for handling these feedstocks for power production.

Within the refinery, residuum coking and solvent deasphalting have been used for several decades to upgrade bottoms streams to intermediate products that may be processed to produce transportation fuels (Gary, Handwerk, & Kaiser, 2007;

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Hsu & Robinson, 2006; Speight, 2011a, 2014; Speight & Ozum, 2002). The installation of a gasifier in a refinery is a realistic option for the conversion of heavy feedstocks leading to the production of added value. In fact, the flexicoking process uses a gasifier as an integral part of the system to convert excess coke to fuel gas (Gary *et al.*, 2007; Gray & Tomlinson, 2000; Hsu & Robinson, 2006; Speight, 2011a, 2014; Speight & Ozum, 2002; Sutikno & Turini, 2012). Thus, by integrating the gasifier as a fully functional process option with gasification, important synergies may be realized and include: (1) increased crude and fuel flexibility, (2) enhanced profitability through reduced capital and operating cost, (3) lower environmental emissions, and (4) increased reliability and efficiency of utilities. Indeed, the integration between bottoms processing units and gasification can serve as a springboard for other economically enhancing integration. The integration of gasification with new or existing hydroprocessing and power generation units presents some unique synergies that will enhance the efficiency of a refinery.

The production of high-quality fuels will result in a higher demand for related hydrogen and conversion technologies. Furthermore, the trend towards low-sulfur fuels and changes in the product mix of refineries will affect technology choice and needs. For example, the current desulfurization and conversion technologies use relatively large amounts of hydrogen, which is an energy intensive product, and increased hydrogen consumption will lead to increased energy use and operation expenses, unless more efficient technologies for hydrogen production are developed.

The demand for high-value petroleum products will maximize production of transportation fuels at the expense of both residua and light gases. Hydroprocessing of residua will be widespread rather than appearing in selected refineries. At the same time, hydrotreated residua will be the common feedstocks for fluid catalytic cracking units. Also, additional conversion capacity will be necessary to process increasingly heavier crudes and meet a reduced demand for residua.

Thus, the gasification of such feedstocks to produce hydrogen, power, or both will be an attractive option for refiners (Campbell, 1997; Dickenson, Biasca, Schulman, & Johnson, 1997; Fleshman, 1997; Gross & Wolff, 2000; Speight, 2011a). The premise that the gasification section of a refinery will be the *garbage can* for deasphalter residues, high-sulfur coke, and other refinery wastes is worthy of consideration.

10.2 Heavy feedstocks

Heavy feedstocks are materials such as petroleum residua, heavy oils, tar sand bitumen, and petroleum coke that have low volatility. In fact many such materials have no volatility. However, for the purposes of this chapter, non-volatile products from other sources, such as coal and oil shale, are not included. Furthermore, it is preferable to use the term *heavy feedstocks* (or *hydrocarbonaceous materials*) because the presence of elements other than carbon and hydrogen in these materials means that they are not true hydrocarbons. Thus, the term hydrocarbonaceous materials includes (1) petroleum residua, (2) heavy oil, (3) extra heavy oil, (4) tar sand bitumen, and (5) other feedstocks such as petroleum coke, all of which can be used as feedstocks for the gasification process (Table 10.1, Figure 10.1) (Gary *et al.*, 2007; Hsu & Robinson, 2006; Speight, 2011a, 2014; Speight & Ozum, 2002).

10.2.1 Petroleum residua

A petroleum *resid* (*residuum*, *pl. resids*, *residua*) is the non-volatile residue obtained from petroleum after non-destructive distillation has removed all the volatile constituents of the feedstock. The temperature of the distillation unit is usually maintained below 350 °C (660 °F) because the rate of thermal decomposition of petroleum constituents is minimal below this temperature, and the rate of thermal decomposition of petroleum constituents is substantial above 350 °C (660 °F). This is not always the case, however, as residence time in the hot zone is also a factor.

Resids are black, viscous materials and are obtained by distillation of a crude oil under atmospheric pressure (atmospheric residuum) or under reduced pressure (vacuum residuum). They may be liquid at room temperature (generally atmospheric

Table 10.1 **Analysis of various refinery feedstocks for gasification**

	Units	Vacuum residue	Visbreaker tar	Asphalt	Petcoke
Ultimate analysis					
C	wt/wt	84.9%	86.1%	85.1%	88.6%
H	wt/wt	10.4%	10.4%	9.1%	2.8%
N[a]	wt/wt	0.5%	0.6%	0.7%	1.1%
S[a]	wt/wt	4.2%	2.4%	5.1%	7.3%
O	wt/wt		0.5%		0.0%
Ash	wt/wt	0.0%		0.1%	0.2%
Total	wt/wt	100.0%	100.0%	100.0%	100.0%
H_2C ratio	mol/mol	0.727	0.720	0.640	0.188
Density					
Specific gravity	60°/60°	1.028	1.008	1.070	0.883
API gravity	°API	6.2	8.88	0.8	-
Heating values					
HHV (dry)	M Btu/lb	17.72	18.6	17.28	14.85
LHV (dry)	M Btu/lb	16.77	17.6	16.45	14.48

[a] Nitrogen and sulfur contents vary widely.

Source: National Energy Technology Laboratory. http://www.netl.doe.gov/technologies/coalpower/gasification/gasifipedia/refinery.html.

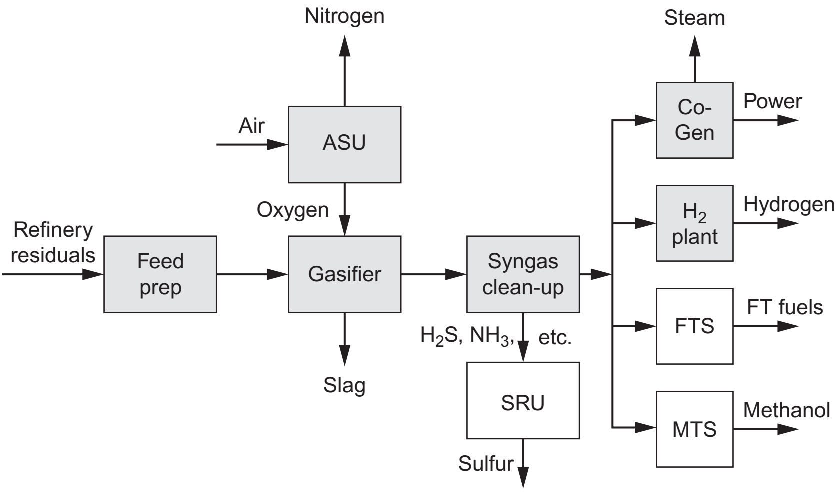

Figure 10.1 Schematic of a refinery gasification operation. ASU, air separation unit to generate enriched oxygen supply; SRU, sulfur recovery unit; FTS, Fischer-Tropsch synthesis; MTS, methanol synthesis.

Source: National Energy Technology Laboratory, United States Department of Energy, Washington, DC. http://www.netl.doe.gov/technologies/coalpower/gasification/gasifipedia/7-advantages/7-3-4_refinery.html.

residua) or almost solid (generally vacuum residua) depending upon the nature of the crude oil. When a residuum is obtained from crude oil and thermal decomposition has commenced, many in the industry incorrectly refer to this product as *pitch* (Speight, 2014). The differences between parent petroleum and the residua are due to the relative amounts of various constituents present, which are removed or remain by virtue of their relative volatility.

The chemical composition of a residuum from is complex. Physical methods of fractionation usually indicate high proportions of asphaltene constituents and resins, even in amounts up to 50% (or higher) of the residuum (Gary *et al.*, 2007; Hsu & Robinson, 2006; Speight, 2011a, 2014; Speight & Ozum, 2002). In addition, the presence of ash-forming metallic constituents, including such organometallic compounds, as those of vanadium and nickel, as well as other metal constituents, is also a distinguishing feature of residua and the non-volatile feedstocks. Furthermore, the deeper the *cut* into the crude oil, the greater the concentration of sulfur and metals in the residuum and, as a result, the greater the deterioration in physical properties of the residuum (Gary *et al.*, 2007; Hsu & Robinson, 2006; Speight, 2011a, 2014; Speight & Ozum, 2002).

10.2.2 Heavy oil

When crude petroleum can be pumped from a reservoir as a free-flowing dark to light colored liquid, it is often referred to as *conventional petroleum*. Heavy oil is a type of petroleum that is different from the conventional petroleum insofar as it is more difficult to recover from the reservoir. Heavy oil has a much higher viscosity and lower

American Petroleum Institute (API) gravity than conventional petroleum, and primary recovery of heavy oil requires thermal stimulation of the reservoir (Speight, 2008, 2009, 2013a, 2013b, 2014).

The definition of heavy oil is commonly (but incorrectly) based on the API gravity or viscosity. In fact, for many years, petroleum and heavy oil were very generally defined in terms of physical properties, despite a lack of scientific foundation. For example, heavy oils were considered to be those crude oils that had gravity somewhat <20° API, with the heavy oils falling into the API gravity range 10-15°. For example, Cold Lake heavy crude oil has an API gravity equal to 12°, and extra heavy oils, such as tar sand bitumen, usually have an API gravity in the range 5-10° (Athabasca bitumen = 8° API). Residua would vary depending upon the temperature at which distillation was terminated, but usually, vacuum residua are in the range 2-8° API (Ancheyta & Speight, 2007; Speight, 2000; Speight, 2014; Speight & Ozum, 2002).

10.2.3 Extra heavy oil

Extra heavy oil is also a material that suffers from the use of arbitrary nomenclature. Extra heavy oil occurs in the solid or near-solid state and generally has mobility under reservoir conditions, possibly due to the temperature of the reservoir or deposit rather than the ambient properties of the material. In fact, the term *extra heavy oil* is a recently evolved term (related to viscosity) of little scientific meaning and often initiates confusion, as it is incorrectly used to refer to tar sand bitumen. While this type of oil may resemble tar sand bitumen and does not flow easily, extra heavy oil is generally recognized as having mobility in the reservoir compared to tar sand bitumen, which is typically incapable of mobility (free flow) under reservoir conditions. For example, the tar sand bitumen located in Alberta, Canada, is not mobile in the deposit and requires extreme methods of recovery to recover the bitumen, while much of the extra heavy oil located in the Orinoco belt of Venezuela requires recovery methods that are less extreme because of the mobility of the material in the reservoir (Speight, 2009, 2013a, 2013b, 2014).

10.2.4 Tar sand bitumen

Also, on occasion, referred to as *native asphalt* and *extra heavy oil*, bitumen is a naturally occurring material that is found in tar sand deposits, such as the oil sand deposits in Canada, where the permeability is low and passage of fluids through the deposit can only be achieved by prior application of fracturing techniques. Tar sand bitumen is a high-boiling material with little, if any, material boiling below 350 °C (660 °F), and the properties of this substance may resemble those of an atmospheric residuum. However, to get beyond the use of one or two properties to define tar sand bitumen, *tar sands* have been defined in the United States (FE-76-4) more correctly and from a functional aspect as:

> *···the several rock types that contain an extremely viscous hydrocarbon which is not recoverable in its natural state by conventional oil well production methods including currently used enhanced recovery techniques. The hydrocarbon-bearing rocks are variously known as bitumen-rocks oil, impregnated rocks, oil sands, and rock asphalt.*

Furthermore, the recovery of the bitumen depends to a large degree on the collective composition of the material, and generally, the bitumen found in tar sand deposits is an extremely viscous material that is immobile under reservoir conditions and cannot be recovered through a well by the application of secondary or enhanced recovery techniques (Speight, 2013a, 2013b, 2014). However, the term tar sand is actually a misnomer; more correctly, the name *tar* is usually applied to the heavy product remaining after the destructive distillation of coal or other organic matter (Speight, 2013c).

The bitumen in tar sand formations requires a high degree of thermal stimulation for recovery to the extent that some thermal decomposition may have to be induced. Current recovery operations of bitumen in tar sand formations involve the use of a mining technique, and non-mining techniques are continually being developed (Speight, 2009, 2013a, 2013b, 2014).

It is incorrect to refer to native bituminous materials as *tar* or *pitch*. Although the word tar is descriptive of the black, heavy bituminous material, those in the industry should avoid its use with respect to natural materials and to restrict the meaning to the volatile or near-volatile products produced in the destructive distillation of organic substances such as coal (Speight, 2013c). Thus, alternative names, such as *bituminous sand* or *oil sand*, are gradually finding usage, with the former name being more technically correct. The term *oil sand* is also used in the same way as the term *tar sand*, and these terms are used interchangeably throughout this text.

10.2.5 Other feedstocks

Other gasification feedstocks are variable and will depend upon the location of the refinery into which the gasifier has been integrated. Such feedstocks may arise from fossil fuel and from non-fossil fuel sources (Speight, 2008, 2011a, 2011b).

10.2.5.1 Petroleum coke

Another noteworthy feedstock for the gasification processes is petroleum coke, which is the residue left by the destructive distillation of petroleum residua (Gray & Tomlinson, 2000; Patel, 1982; Speight, 2008, 2014). Petroleum coke formed in catalytic cracking operations is usually non-recoverable, as it is often employed as fuel for the process. The composition of petroleum coke also varies with the source of the crude oil, but in general, large amounts of high-molecular-weight complex hydrocarbons, which are rich in carbon but correspondingly poor in hydrogen, make up a high proportion of the coke. The solubility of petroleum coke in carbon disulfide has been reported to be as high as 50-80% w/w, but this is in fact a misnomer, since the coke is the insoluble, honeycomb material that is the end product of thermal processes.

Delayed coking can produce three physical structures of coke: (1) shot coke, (2) sponge coke, or (3) needle coke.

Shot coke is an abnormal type of coke resembling small balls. Due to mechanisms not well understood, the coke from some coker feedstocks forms small, tight, non-attached clusters that look like pellets, marbles, or ball bearings. Shot coke is usually a very hard coke with a low Hardgrove grindability index (Speight, 2013a, 2013b, 2013c, 2013d, 2014). Such coke is less desirable to end users because of difficulties in handling and grinding. It is believed that feedstocks high in asphaltene constituents and with low API favor shot coke formation. Blending aromatic materials with the feedstock, increasing the recycle ratio, or both reduces the yield of shot coke. Fluidization in the coke drums may cause the formation of shot coke. Occasionally, the smaller *shot coke* may agglomerate into ostrich egg sized pieces. While shot coke may look like it is entirely made up of shot, most shot coke is not 100% shot.

Sponge coke is the common type of coke produced by delayed coking units (Gary *et al*., 2007; Hsu & Robinson, 2006; Speight, 2011a, 2014; Speight & Ozum, 2002). It is in a form that resembles a sponge and has been called honeycombed. Sponge coke, which is mostly used for anode-grade, is dull and black, with a porous, amorphous structure.

Needle coke (*acicular coke*) is a special quality coke produced from aromatic feedstocks. Needle coke is silver-gray, with a crystalline broken needle structure, and it is believed to be chemically produced through the crosslinking of condensed aromatic hydrocarbons during coking reactions. It has a crystalline structure with more unidirectional pores and is used in the production of electrodes for the steel and aluminum industries, making it particularly valuable because the electrodes must be replaced regularly.

Petroleum coke is employed for a number of purposes, but its chief use (subject to composition and properties) is in the manufacture of carbon electrodes for aluminum refining. As these electrodes require a high-purity carbon that is low in ash and sulfur free, the volatile matter must be removed by calcining. In addition to its use as a metallurgical reducing agent, petroleum coke is employed in the manufacture of carbon brushes, silicon carbide abrasives, and structural carbon (e.g., pipes and Rashig rings), as well as calcium carbide manufacture from which acetylene is produced:

$$\text{Coke} \rightarrow \text{CaC}_2$$

$$\text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{HC} \equiv \text{CH}$$

Coke that is unsuitable for any of the above applications is used either as a fuel for the refinery or as a source of synthesis gas and hydrogen. In either case the presence of nitrogen, oxygen, sulfur, and metals in the coke feedstock requires that the gaseous products be subject to thorough gas-cleaning methods (Speight, 2014).

10.2.5.2 Solvent deasphalter bottoms

The deasphalting unit (deasphalter) is a unit in a petroleum refinery for bitumen upgrading that separates an asphalt-like product from petroleum, heavy oil, or bitumen. The deasphalter unit is usually placed after the vacuum distillation tower, where, by the use of a low-boiling liquid hydrocarbon solvent, such as propane or butane under pressure, the insoluble asphalt-like product (*deasphalter bottoms*) is separated from the feedstock. The other output from the deasphalter is deasphalted oil.

The solvent deasphalting process has been employed for more than six decades to separate high molecular weight fractions of crude oil boiling beyond the range of economical commercial distillation. The earliest commercial applications of solvent deasphalting used liquid propane as the solvent to extract high quality lubricating oil bright stock from vacuum residue. The process has been extended to the preparation of catalytic cracking feeds, hydrocracking feeds, hydrodesulfurization feedstocks, and asphalts. The latter product (asphalt, also called *deasphalter bottoms*) is used for road asphalt manufacture, refinery fuel, or gasification feedstock for hydrogen production.

In fact, the combination of ROSE solvent deasphalting and gasification has been commercially proven at the ERG Petroli refinery (Bernetti, De Franchis, Moretta, & Shah, 2000). The combination is very synergistic and offers a number of advantages, including a low-cost gasifier feedstock that enhances refinery economics. The process then converts low-value feedstock to high-value products such as power, steam, hydrogen, and chemical feedstock. The process also improves the economics of the refinery by eliminating or reducing the production of low-value fuel oil and maximizing the production of transportation fuel.

10.3 Synthesis gas production

Heavy feedstocks are gasified, and the produced gas is purified into clean fuel gas (Gross & Wolff, 2000), for example:

$$\text{Residuum} \rightarrow CO + CO_2 + H_2 + SO_x + NO_x + \text{particulate matter} \rightarrow \underset{\text{Synthesis gas}}{CO + H_2}$$

As an example, solvent deasphalter residuum is gasified using the partial oxidation (POX) method under a pressure of about 570 psi and at a temperature between 1300 and 1500 °C (2370 and 2730 °F) (Bernetti *et al.*, 2000). The high-temperature-generated gas flows into a waste heat boiler, in which the hot gas is cooled and high-pressure-saturated steam is generated. The gas from the waste heat boiler is then heat-exchanged with the fuel gas and flows to the carbon scrubber, where particulate matter is removed from the generated gas by water scrubbing. The fuel gas and boiler feed water further cool the gas from the carbon scrubber before it enters the sulfur compound removal section, where hydrogen sulfide (H_2S) and carbonyl sulfide (COS) are removed from the gas to obtain clean fuel gas. Hydrogen sulfide and carbonyl sulfide are not always present, however, and their presence is dependent upon the operational parameters of the gasification process. If the gas is designated as fuel gas, the clean gas is heated with the hot gas generated in the gasifier and finally supplied to the gas turbine at a temperature of 250-300 °C (480-570 °F).

The exhaust gas from the gas turbine, which has a temperature of about 550-600 °C (1020-1110 °F), flows into the heat recovery steam generator consisting of five heat exchange elements. The first element is a superheater in which the combined stream of the high-pressure-saturated steam generated in the waste heat boiler and in the second element (high-pressure steam evaporator) is super-heated. The third element is an economizer. The fourth element is a low-pressure steam evaporator, and the fifth element is a de-aerator heater. The off-gas from heat recovery steam generator, with a temperature of about 130 °C, is then emitted into the air via a stack.

Two methods can be applied to decrease the nitrogen oxide (NO_x) content in the flue gas. The first method is the injection of water into the gas turbine combustor. The second method is to selectively reduce the nitrogen oxide content by injecting ammonia gas in the presence of a de-NO_x catalyst that is packed in a proper position of the steam generator. The latter is more effective that the former to lower the nitrogen oxide emissions to the air.

The process for producing synthesis gas typically has three components: (1) synthesis gas generation, (2) waste heat recovery, and (3) gas processing. Within each of these components, there are several options. For example, synthesis gas can be generated to yield a range of compositions ranging from high-purity hydrogen to high-purity carbon monoxide. Three major routes can be utilized for high purity gas production: (1) pressure-swing adsorption, (2) utilization of a cryogenic procedure, where separation is achieved using low temperatures, and (3) permeable membrane technology, which is increasingly common (Speight, 2007, 2014).

10.3.1 POX technology

POX is the most commonly used process for the gasification of heavy oils and other refinery residues, although virtually all mixtures are suitable feedstocks, regardless of volatility (Liebner, 2000). However, aside from special applications, gasification is a *bottom-of-the-barrel process* that converts feedstocks containing sulfur and nitrogen to a clean synthesis gas consisting mainly of hydrogen and carbon monoxide. In fact, gasification is replacing direct combustion due to environmental regulations, since ash removal and flue gas clean-up are more difficult and expensive than synthesis gas cleaning at elevated pressures.

The main advantages derived from the application of gasification in a refinery are: (1) the capability of processing low-quality, highly viscous, and heavy feedstocks, as well as emulsions (tank sludge), slurries (coke) and other liquid wastes in quench gasifiers; (2) the capability of processing high-sulfur feedstocks because of the almost complete removal of sulfur compounds in the gas treating unit downstream of the gasifier; (3) the possibility of producing hydrogen for the various conversion and upgrading processes of the refinery, with increased production of gas oil, which is a desirable product or feedstock for other refinery units; and (4) the many outlets for synthesis gas, such as hydrogen for the refinery or for export, electricity via the IGCC process, and the production of chemicals such as ammonia, methanol, acetic acid, and oxo-alcohols.

POX or POx reactions occur when a sub-stoichiometric fuel-air mixture is partially combusted in a reformer. The general reaction equation without a catalyst, called *thermal partial oxidation* (TPOX or TPOx), can be represented as:

$$C_nH_m + (2n+m)/2O_2 \rightarrow nCO + (m/2)H_2O$$

The variable composition of the gasifier feedstocks prevents exact stoichiometric reactions. To produce an equation for such a reaction would only serve to mislead any potential kinetic studies.

A TPOX reactor is similar to the autothermal reactor (ATR), with the main difference being no catalyst is used. The feedstock, which may include steam, is mixed directly with oxygen by an injector that is located near the top of the reaction vessel. Both POX and reforming reactions occur in the combustion zone below the burner.

The principal advantage of the POX process is the ability of the process to accommodate a variety of feedstocks. These feedstocks can include high molecular-weight organic feedstocks, such as petroleum coke (Gunardson & Abrardo, 1999). Additionally, since emissions of nitrogen oxides (NO_x) and sulfur oxides (SO_x) are minimal, the technology can be considered to be environmentally acceptable. On the other hand, very high temperatures, ~1300 °C (2370 °F), are required to achieve a near complete reaction. This high reaction temperature necessitates the consumption of some of the hydrogen and a greater than stoichiometric consumption of oxygen.

10.3.1.1 Shell gasification process

The *Shell gasification process* (a POX process) is a flexible process for generating synthesis gas, principally hydrogen and carbon monoxide, for the ultimate production of high-purity, high-pressure hydrogen, ammonia, methanol, fuel gas, town gas, or reducing gas. This process uses a reaction of gaseous or liquid hydrocarbons with oxygen, air, or oxygen-enriched air, and the most important step in converting heavy feedstocks into industrial gas is the POX of the oil using oxygen with the addition of steam. The gasification process takes place in a refractory-lined reactor at temperatures of around 1400 °C (2550 °F) and pressures between 30 and 1140 psi. The chemical reactions in the gasification reactor proceed without a catalyst to produce a gas containing carbon at 0.5-2% w/w by weight, depending on the feedstock. The carbon is removed from the gas with water, extracted in most cases with feed oil from the water, and returned to the feed oil. The high reformed gas temperature is utilized in a waste heat boiler for generating steam. The steam is generated at 850-1565 psi, and some of it is used as process steam and for oxygen and oil preheating.

10.3.1.2 Texaco process

The *Texaco gasification process* (a POX gasification process) generates synthetic gas, principally hydrogen and carbon monoxide. The process is characterized by the injection of feedstock, as well as carbon dioxide, steam or water, into the gasifier. Therefore, this gasification process can use feedstocks such as residua, solvent deasphalted residua, or petroleum coke produced by any coking process. The product gas from the Texaco process can be used for the production of high-purity, high-pressure hydrogen, ammonia, and methanol. The heat recovered from the high temperature gas is also used for the generation of steam in the waste heat boiler. Alternatively, the less expensive quench type configuration is preferred when high-pressure steam is not needed or when a high degree of shift is needed in the downstream carbon monoxide converter.

In the POX process, the gasification reaction is a POX of hydrocarbons to carbon monoxide and hydrogen and can be represented in simple chemical terms:

$$C_xH_{2y} + x/2O_2 \rightarrow xCO + yH_2$$

$$C_xH_{2y} + xH_2O \rightarrow xCO + (x+y)H_2$$

The gasification reaction is instantly completed, thus producing gas mainly consisting of carbon monoxide and hydrogen, and upon leaving the reaction chamber of the gas generator, the high temperature gas enters a quenching chamber usually linked to the bottom of the gas generator, where it is quenched with water to 200-260 °C (390-500 °F).

10.3.1.3 Phillips process

In the *Phillips process*, petroleum coke is mixed with water to make a pumpable slurry that is then fed into a two-stage gasifier. The slurry reacts readily with the oxygen in the first stage of the gasifier to form hydrogen, carbon monoxide, carbon dioxide, and methane. The high temperature in the first-stage ensures the conversion of all feedstock materials and traps inorganic materials, such as ash and metals, in a glassy matrix resembling coarse sand. This sand-like material (slag) is inert and has an array of uses in the construction industry.

The hot synthesis gas from the horizontal first stage enters the vertical, second stage of the gasifier, where additional slurry is added to increase the energy content of the gas. This two-stage design increases efficiencies, particularly for low reactivity fuels such as petroleum coke. Hot synthesis gas is then cooled in a heat recovery system, producing high-pressure steam in a fire tube boiler.

The dry system improves efficiency over wet systems by removing more particulates, and thus avoiding black-water problems that lead to equipment wear, and it minimizes water consumption and wastewater generation. Sulfur in the synthesis gas is recovered and converted to elemental sulfur, which can be sold in agricultural and other markets. Maximizing sulfur recovery at over 99% of that found in the feedstock, the process recycles all unconverted gases from the tail gas of the sulfur recovery unit to the second stage of the gasifier.

The clean synthesis gas can be further processed, shifting the synthesis gas equilibrium for additional hydrogen production. The required hydrogen purity standards are achieved through a standard pressure-swing adsorption design. The downstream hydrogen production process units also facilitate the capture of carbon dioxide, which can then be compressed and used for enhanced oil recovery or other beneficial uses, or placed in geologic storage. Steam production is achieved through heat recovery steam generators, as needed, for power or steam export to the host facility.

10.3.2 Catalytic partial oxidation

Catalytic partial oxidation (CPOX or CPOx) technology offers possible means of improving the efficiency of synthesis gas production from heavy feedstocks. This technology has several advantages over steam reforming, especially the higher energy efficiency. In fact, the reaction is exothermic rather than endothermic, as is the case with steam reforming. Furthermore, a carbon monoxide-hydrogen ratio (CO/H_2) ratio approximately equal to 2.0, which is the ideal ratio for the Fischer-Tropsch process and methanol synthesis, is produced by this technology.

10.3.3 Steam reforming

While not truly the subject of this chapter, *steam reforming*, which is sometimes referred to as *steam-methane reforming* (SMR), deserves some consideration because of the production of synthesis gas. The steam reforming process involves passing a preheated mixture essentially composed of methane and steam through catalyst-filled tubes. As the reaction is endothermic, heat must be provided in order to effect the conversion, and the heat is provided by burners located adjacent to the tubes. The product of the process is a mixture of hydrogen, carbon monoxide, and carbon dioxide.

In order to maximize the conversion of the methane feed, both a primary and secondary reformer are generally utilized. A *primary reformer* is used to effect 90-92% conversion of methane. Here, the hydrocarbon feed partially reacts with steam over a nickel-alumina catalyst to produce a synthesis gas with an H_2/CO ratio of ~3:1. This partial reaction occurs in a fired tube furnace at 900 °C (1650 °F) and at a pressure of 220-450 psi. The unconverted methane is reacted with oxygen at the top of a *secondary autothermal reformer*, which contains a nickel catalyst in the lower region of the vessel.

The deposition of carbon can be an acute problem with the use of nickel-based catalysts in the primary reformer (Alstrup, 1988; Rostrup-Neilsen, 1984, 1993). Considerable research has been done with the aim of finding approaches to prevent carbon formation. A successful technique is to use a steam/carbon ratio in the feed gas that does not allow the formation of carbon. However, this method results in lowering the efficiency of the process. Another approach utilizes sulfur passivation, which led to the development of the SPARG process (Rostrup-Neilsen, 1984; Udengaard, Bak-Hansen, Hanson, & Stal, 1992). The SPARG process utilizes the principle that the reaction leading to the deposition of carbon requires a larger number of adjacent surface Ni atoms than does steam reforming. When a fraction of the surface atoms are covered by sulfur, the deposition of carbon is thus more greatly inhibited than it is in steam reforming reactions. A third approach is to use Group VIII metals that do not form carbides, such as platinum (Pt). However, due to the high cost of such metals, using them is not as economical as using nickel.

A major challenge in steam reforming development is its energy intensive nature due to the high endothermic character of the reactions. Thus, the development tends to focus on seeking higher energy efficiency. Improvements in catalysts and metallurgy require adaption to lower steam/carbon ratios and higher heat flux.

10.3.4 Autothermal reforming

In the *autothermal reforming process* (ATR process), the organic feedstock, steam, and sometimes carbon dioxide are mixed directly with oxygen and air in the reformer. The reformer itself comprises a refractory-lined vessel that contains the catalyst, together with an injector located at the top of the vessel. This type of reformer consists of three zones: (1) the burner in which the feedstock streams are mixed in a turbulent diffusion flame, (2) the combustion zone in which POX reactions produce a mixture of carbon monoxide and hydrogen, and (3) the catalytic zone in which the gases leaving the combustion zone reach thermodynamic equilibrium.

POX reactions occur in a region of the reactor referred to as the combustion zone. The mixture formed in this zone then flows through a catalyst bed where the actual reforming reactions occur. Heat generated in the combustion zone as the result of the POX reactions is utilized in the reforming zone, so that, in the ideal case, the ATR process can exhibit excellent heat balance. In addition, the process offers comparatively flexible operation, including short startup periods and fast load changes, as well as the potential for soot-free operation depending on the feedstock used.

10.3.5 Combined reforming

Combined reforming incorporates the combination of both steam reforming and autothermal reforming. In such a configuration, the feedstock is only partially converted under mild conditions in the first stage to synthesis gas in a relatively small steam reformer. The off-gas from the steam reformer is then sent to an oxygen-fired secondary reactor, the autothermal reforming reactor, where any hydrocarbons in the gas stream are converted to synthesis gas by POX followed by steam reforming. Another configuration requires the feedstock to be split into two streams that are then fed, in parallel, to the steam reforming and autothermal reactors.

10.4 Output products

Synthesis gas processes can produce a range of gases, including carbon monoxide and hydrogen mixtures, high-purity hydrogen, high-purity carbon monoxide, and high-purity carbon dioxide.

If hydrogen is the desired product for refinery operations (Speight, 2014; Sutikno & Turini, 2012; Wolff, 2007), the carbon monoxide-hydrogen ratio can approach infinity by conversion of all of the carbon monoxide to carbon dioxide. By contrast, on the other end, the ratio cannot be adjusted to zero (i.e., 100% v/v hydrogen) because water is always produced with the hydrogen. In fact, a general rule of thumb exists in terms of the hydrogen and carbon monoxide produced by the different gasification processes:

Gasification process	H_2/CO ratio
Steam reforming	3.0-5.0
Steam reforming plus oxygen secondary reforming	2.5-4.0
Autothermal reforming (ATR)	1.6-2.65
Partial oxidation (POX)	1.6-1.9

However, in practice, the options are not limited to the ranges shown. Rather, even greater hydrogen-carbon monoxide ratios can be observed if adjustments are made to the process, such as steam adjustment or the inclusion of a shift converter to effect near-equilibrium water-gas-shift conversion.

10.4.1 Gas purification and quality

Purities in excess of 99.5% v/v of either hydrogen or carbon monoxide produced from synthesis gas can be achieved if required by the refinery. Four of the major process technologies available are:

1. *Cryogenics plus methanation*: This method utilizes a cryogenic process whereby carbon monoxide is liquefied in one or more steps to produce hydrogen with a purity of on the order of 98% v/v. The condensed carbon monoxide, which often contains methane, is distilled to produce a stream of pure carbon monoxide and a mixed stream of carbon monoxide and methane. The mixed carbon monoxide and methane stream can be used as fuel. The hydrogen stream is routed to a shift converter where any remaining carbon monoxide is converted to carbon dioxide and hydrogen. The carbon dioxide is removed, and any further carbon monoxide or carbon dioxide can be removed by methanation. The resulting hydrogen stream can have purity as high as 99.7% v/v.
2. *Cryogenics plus pressure-swing adsorption*: This method also uses the sequential liquefaction of carbon monoxide to produce hydrogen with a purity of ~98% v/v. Again, the carbon monoxide stream can be distilled to remove methane, until it is essentially pure. Depending on the hydrogen purity required, the hydrogen stream is then processed through multiple swings of pressure-swing adsorption cycles until the hydrogen purity is as high as 99.999% v/v.
3. *Methane-wash cryogenic process*: In this method, liquid carbon monoxide is absorbed into a liquid methane stream so that the resulting hydrogen stream contains ppm levels of carbon monoxide and ~5-8% v/v methane. As a result, the purity of the hydrogen stream produced by this process is limited to ~95% v/v. The liquid carbon monoxide-/methane stream can be distilled to produce pure carbon monoxide, as well as a carbon monoxide-methane stream that can be used as fuel gas.
4. *COsorb process*: This method utilizes copper ions (cuprous aluminum chloride, $CuAlCl_4$) in toluene to form a chemical complex with the carbon monoxide, thereby separating it from the product gas steam. This process can capture ~96% v/v of the carbon monoxide to produce a carbon monoxide stream having purity >99% v/v. However, water, hydrogen sulfide, and other trace constituents that can poison the copper catalyst must be removed prior to

introduction of the product gas into the reactor. Furthermore, a hydrogen stream of only up to 97% v/v purity is obtained. However, while the efficiency of cryogenic separation decreases with a decrease in the carbon monoxide content of the feedstock gas, the COsorb process is a more efficient process for treating feedstock gas with low carbon monoxide content.

10.4.2 Process optimization

Process optimization includes the development of technologies to facilitate cost-effective gasification of all hydrocarbonaceous feedstocks produced by a refinery, as well as coal and biomass. Thus, the use of high-pressure feed systems and the development of technologies for co-feeding mixtures to high-pressure gasifiers are necessary options. In addition, attention must be given to the use of the refinery gasifier to process waste, reduce the refinery footprint, and produce marketable products.

10.5 Conclusion and future trends

One of the most compelling challenges of the twenty-first century is finding a way to meet national and global energy needs. Petroleum refineries can help meet this challenge, while generating more economic value by adopting a gasification process. There may always be competition for gasification in the processes that convert the heavy feedstocks into added-value products, such as liquid fuels, however.

Accordingly, adding a gasification system to a refinery offers clear benefits (Speight, 2011a), such as (1) the production of power, steam, oxygen, and nitrogen for refinery use or sale (Refineries have typically converted resids and waste or residue into asphalt or bitumen, products from which they may derive very little economic value. Gasification technology, on the other hand, converts this waste into valuable commodities, such as power, steam, oxygen, hydrogen and nitrogen, which are used in everyday refinery operations.); (2) increased efficiency of power generation, improved air emissions, and reduced waste stream versus combustion of petroleum coke or residua or incineration; and (3) the potential to provide high-purity hydrogen used in a variety of refinery operations, such as the removal of impurities though and hydrotreating and hydrocracking processes.

10.5.1 Other uses of residua

The residua (heavy feedstocks, bottoms, hydrocarbonaceous feedstocks) can be routed to other conversion units or blended to heavy industrial fuel, asphalt, or a combination of both. The heavy feedstocks typically have a relatively low economic value, and often they are of lower value than the original crude oil. Thus, most refineries convert or upgrade the low-value heavy feedstocks into more valuable low-boiling products, such as gasoline, jet fuel, and diesel fuel.

Thus upgrading heavy feedstocks creates a need for additional bottom-of-the-barrel processing, both for expansion and for yield improvement. Traditionally, this would automatically call for the addition of atmospheric distillation and/or vacuum distillation units as a starting point. However, there are alternative processing schemes for processing the vacuum or atmospheric residues in order to maximize the value of the heavier crude oils.

10.5.2 Gasification in the future refinery

Hydrogen management has become a priority for current and future refinery operations as consumption continues to rise for greater hydrotreating processes, as well as the processing of heavier and higher sulfur crude oils. In many cases, the hydrogen network is limiting refinery throughput and operating margins. The current main source for hydrogen is the SMR of refinery off-gases and natural gas, an inefficient and cost-incurring process.

As refineries continue to evolve (Furimsky, 1999; Speight, 2011a), the panacea (rather than the Pandora's box) for a variety of feedstocks could well be the *gasification refinery* (Figure 10.1), which is capable of supplying the traditional refined products, while meeting much more severe specifications, and the use of petrochemical intermediates such as olefins, aromatics, hydrogen, and methanol (Figure 10.2) (Breault, 2010; Penrose, Wallace, Kasbaum, Anderson, & Preston, 1999; Phillips & Liu, 2002; Speight, 2011a, 2011b). Furthermore, in addition to the production of synthesis gas, the IGCC) can be used to raise power from feedstocks such as vacuum residua and cracked residua, and a major benefit of IGCC is that power can be produced with the lowest sulfur oxide (SO_x) and nitrogen oxide (NO_x) emissions of any liquid or solid feed power generation technology.

In fact, the future of the petroleum refining industry will primarily depend on processes for the production of improved quality products. Thus, the refinery of the future will have a gasification section devoted to the conversion of coal and biomass to

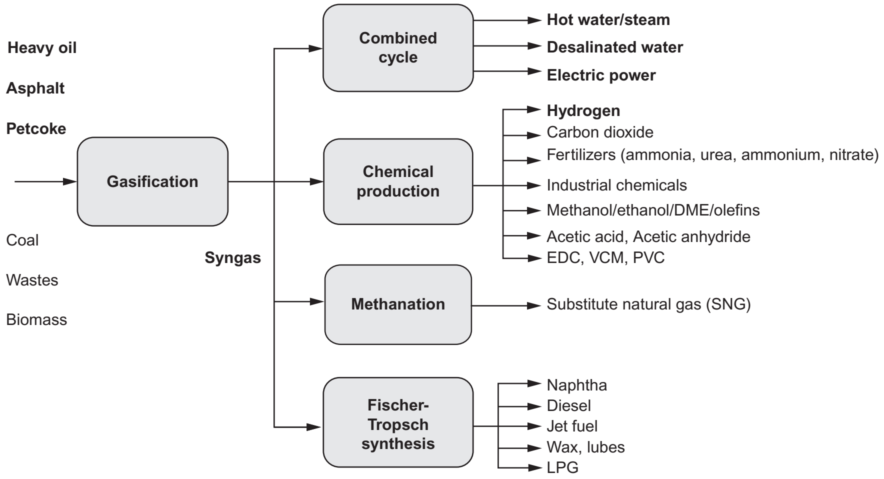

Figure 10.2 Potential feedstocks and products from a refinery gasification process. *Source*: US government work.

Fischer-Tropsch hydrocarbons, perhaps even with rich oil shale added to the gasifier feedstock. Many refineries already have gasification capabilities, but over the next two to three decades, the trend will increase to the point where nearly all refineries recognize the need to construct a gasification section to handle residua and a variety of other feedstocks. Biomass, liquids from coal, and liquids from oil shale will increase in importance, and such feedstocks will likely be sent to refineries or processed at a remote location and then blended with refinery stocks. Above all, though, such feedstock must be compatible with refinery feedstocks and not cause fouling, which can lead to process or even refinery shutdown (Speight, 2011a, 2011b).

In the future, computer models for process unit and refinery economics and operations will also be optimized and integrated into plant operations via process computer controls. Alternate fuels for power generation will continue to push crude processing toward higher value products, such as transportation fuels and chemicals. Otherwise, the heavy crude oil and tar sand bitumen that are considered uneconomical to transport to a refinery will be partially refined at their source to facilitate transport, and there will be a new emphasis on partial or full upgrading *in situ* during recovery operations (Speight, 2009, 2014). In addition, alternative energy sources may become increasingly involved with petroleum, leading to the concept of *alternative energy systems* (Szklo & Schaeffer, 2005) in which petroleum refining is integrated with the production of energy from other energy sources.

Thus, *refinery flexibility* will be a key target, especially when related to the increased use of renewable energy sources. And, the industry can begin to work toward such flexibility by incorporating gasification technology into the refinery system as an equal partner in energy production.

In summary, gasification is the only technology allowing refineries to a achieve a zero residue target, as opposed conversion technologies, such as thermal cracking, coking, catalytic cracking, deasphalting, and hydroprocessing, which can only reduce the volume of bottoms, with the complication that the residue qualities generally get worse with the degree of conversion. The flexibility of gasification permits refineries to handle any kind of refinery residue, including petroleum coke and tank bottoms, as well as refinery sludge, while producing a range of value added products, electricity, steam, hydrogen, and various chemicals based on synthesis gas chemistry. The environmental performance of gasification is unmatched because no other technology for processing low-value refinery residues can come close to achieving the emission levels that result from gasification.

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Biomass gasification for synthetic liquid fuel production

11

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11.1 Introduction

Biomass is organic material that has stored sunlight in the form of chemical energy, and this resource has the advantages of high yield, low pollution emissions, carbon neutrality, and wide availability. Biomass contains mainly carbon, hydrogen, oxygen, and traces of nitrogen and sulfur, and biomass can be converted to fuel and chemicals using the technology for converting fossil fuels. However, biomass is different from fossil fuels, such as coal, in that it has high moisture and volatile content, lower carbon content, higher oxygen content, and a lower heating value, not to mention more sodium, potassium (alkaline), and chlorine. Hence, the thermochemical conversion behavior of biomass is very different from the behavior of coal and other fossil fuels. It is therefore necessary to fully understand the properties and mechanisms of biomass conversion in detail.

Gasification is the conversion of biomass to gaseous fuel by heating the biomass in a gasification medium such as air, oxygen, steam, or their mixture. Distinguished from combustion, gasification converts the intrinsic chemical energy of the carbon in the biomass into a flammable gas. During biomass gasification, biomass feedstock is promptly heated up and devolatilized, forming tar, permanent gas, and solid char. Then the tar and solid char undergo cracking, oxidization, and reduction to form gaseous products as the final products. These products mainly consist of carbon monoxide, carbon dioxide, methane, hydrogen, water vapor, and some light hydrocarbon, known as syngas, which can be used to power gas engines and gas turbines or as a chemical feedstock to produce high rank fuels, such as liquid fuels, hydrogen, and carbon-containing chemicals.

Gasification is a complex process. It is affected by many factors, such as reactor configuration, operating conditions, gasifying agent, biomass properties, and so on. When air is used as a gasifying agent, the heating value of the gas product is very low, only 3-4 MJ/m^3, while it increases to over 10 MJ/m^3 with pure oxygen. Moreover, the gas product contains more H_2 and hydrocarbon with a heating value of 13-20 MJ/m^3 with water steam. Also, high temperature and longer residence time might be favorable for more H_2.

The basic reactions occurring in the gasification process are mainly the thermal cracking of biomass, which comprises complete and partial reactions, the water gas shift reaction, and the methanation reaction. Higher temperatures are favorable for char gasification and water gas shift reaction, as more H_2 and CO are formed.

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In ideal gasification systems, there should be no excess tar, no nitrogen, and no methane in the gaseous product, and the gas yield should be over 80%. Although remarkable progress has been achieved in recent years in gasification technology, low gas productivity and high tar content in the gas are still two bottlenecks that have blocked the wider utilization of biomass gasification. The main problem might be attributed to low carbon conversion and high tar content. It has been noted that increasing char conversion improves efficiency, while increasing tar conversion improves gas utilization.

Removal of tar has been one of the most important technical subjects in the development of biomass gasification. Tar is formed during the biomass pyrolysis process, and it experiences cracking, condensing, and reformation. The tar is changed from mixed oxygenates to larger polycyclic aromatic hydrocarbon (PAH) dominated with temperature increasing from 400 °C to more than 900 °C. Higher temperatures are favorable for tar cracking, but the efficiency is limited. Catalytic cracking is the prevalent and efficient choice for tar cracking. Three distinct groups of catalyst materials have been the subjects of published research on biomass gasification. They are dolomite catalysts, alkali metal and alkali earth metal catalysts, and nickel catalysts. The nickel-based catalysts showed excellent catalytic effects on tar cracking, especially for H_2-enriched gas.

Currently, many novel technologies have been invented to reduce tar and upgrade syngas quality, and biomass-staged gasification is one of the most promising. During staged gasification, biomass was pyrolyzed at 500 °C to organic vapor and solid char; after pyrolization, the volatile material was catalytically reformed at 800-1000 °C, while the char was combusted to provide heat for pyrolysis. As organic compounds contain more oxygen, which is easily cracked, the tar content in syngas is quite low. Because of the special properties of biomass char, which is characterized by high porosity and rich alkali content, this char was also can be used as a catalyst, and organic vapor reformed through the char bed was combined with char water shifting during steam gasification. It has been shown that char is a very efficient catalyst. Recently, a three-staged fluidized gasifier showed cold gasification efficiency of ~82% and carbon conversion at 97%.

As a result of the high purity of H_2, the sorption-enhanced steam gasification of biomass is a novel one-step conversion technology that is being developed. CO_2 sorbents (CaO, etc.) are introduced into the process of biomass steam gasification to continuously remove the CO_2 *in situ* as soon as it is formed during the gasification process. The Ca-Ni complex attracted great interest because of the high CO_2 capture and tar-cracking feature that resulted in a higher purity of H_2. It has been pointed out that 80% (vol.) H_2 can be derived in syngas. Also, some metal oxides were involved with chemical looping biomass steam gasification.

Mathematical and computational modeling is used to easily illustrate the expected results at low financial cost, and such modeling has support a wide range of investigations related to biomass gasification. Mathematical modeling can be categorized into three sections: equilibrium, kinetic, and neural networks, each of which might play a critical role in the development of biomass gasification.

Biomass gasification has shown unique advantages; however, with syngas, there are still some challenges, such as particulates, hydrocarbons, and alkali compounds in gas products.

11.2 Properties of biomass resources

11.2.1 Background

The world's current energy requirements are largely met by fossil fuels, such as oil, coal, and natural gas, which are estimated to account for 80% of the world's energy consumption (Fernando, Adhikari, Chandrapal, & Murali, 2006; Xiao, Meng, Le, & Takarada, 2011). The increase in fuel costs, limited fuel sources, and environmental problems, such as global warming and acid rain, are all problems caused by the usage of fossil fuels. These crises have prompted mankind to look for renewable energy in order to meet the increasing energy demand. Among renewable energy resources, biomass is the only one that can produce not only heat and electricity, but also fuels.

Biomass-based energy accounted for roughly 10% of world's total primary energy supply in 2009. Most of this biomass energy is consumed in developing countries for cooking and heating via very inefficient open fires or simple cook stoves with considerable impact on health (smoke pollution) and the environment (deforestation). Modern bioenergy supply, on the other hand, is comparably small, but has been growing steadily in the last decade. A total of 280 TWh of bioenergy electricity, or 1.5% of the world's electricity generation, was produced globally in 2010, and 8 EJ of bioenergy for heat were used in the industrial sector (Xiao *et al.*, 2011).

11.2.2 Origins of biomass resources

Biomass is plant material derived through photosynthesis, a set of reactions in through which CO_2 in the air, water, and sunlight produce the carbohydrates that form the building blocks of biomass.

The solar energy that drives photosynthesis is stored in the chemical bonds of the structural components of biomass (Peter, 2002), and biomass is the term used to describe all biologically produced matter. Biomass resources include wood and wood wastes, agricultural crops and their waste by-products, municipal solid waste (MSW), animal wastes, waste from food processing, and aquatic plants and algae. On average, the majority of biomass energy is produced from wood and wood waste (64%), followed by MSW (24%), agricultural waste (5%), and landfill gases (5%) (Demirbas, 2000).

11.2.3 Properties of biomass materials

Biomass can be used for fuels, power production, and products that would otherwise be made from fossil fuels, and it can provide an array of benefits. The use of biomass energy has the potential to greatly reduce greenhouse gas emissions. Biomass releases carbon dioxide that is largely balanced by the carbon dioxide captured in during its formation. Burning biomass produces 90% less sulfur than burning coal, and the use of biomass can reduce dependence on foreign oil because biofuels are the only renewable fuel that can be transported as a liquid (Demirbas, 2001). However, when compared to coal, biomass also has several shortcomings.

Table 11.1 shows the comparison of fixed carbon content, volatile matter, moisture content, heating value, and bulk density between coal and biomass. As can be seen, coal has a higher bulk density, higher heating value, and lower moisture content. Compared to pulverized coal fuels, biomass is generally more volatile, has more moisture, and has a lower heating value than coal. In general, biomass energy densities are approximately one-tenth of fossil fuels, such as petroleum or high-quality coal. In coal, the ratio of volatiles to fixed carbon content is low, always less than one. In biomass, however, this ratio is as high as four. This volatile-to-fixed-carbon ratio describes how easily a fuel is volatilized and affects the subsequent system and products. The high volatility is considered an advantage for biomass and allows the fuel to burn at a high power output (Demirbas, 2004).

The difference between the O/C and H/C ratios of solid fuels can be illustrated using a Van Krevelen diagram, as shown in Figure 11.1. The composition of the ash-free organic components of biomass is relatively uniform. The major components are carbon, oxygen, and hydrogen. Most biomass also contains a small proportion of nitrogen. A comparison of biomass with coal shows clearly that there are higher proportions of oxygen and hydrogen in biomass. Consequently, the higher oxygen and hydrogen content reduce the energy value of biomass as a fuel, due to the lower energy contained in carbon–oxygen and carbon–hydrogen bonds, than in carbon–carbon bonds.

Table 11.1 Proximate and ultimate analysis of biomass resources

	Proximate analysis/wt.%				**Ultimate analysis/wt.%**				
Samples	M_{ad}	V_{ad}	A_{ad}	FC_{ad}	**C**	**H**	**N**	**S**	$\mathrm{O_a}$
Cotton stalk	5.10	72.98	3.09	16.73	45.22	6.34	1.15	0.34	46.94
Corn stalk	5.02	70.17	8.25	16.56	42.68	6.21	1.22	0.32	49.57
Rape straw	5.49	74.32	6.27	13.93	44.87	6.60	0.82	0.20	47.51
Wheat straw	4.38	68.52	12.91	14.20	40.36	5.95	0.55	0.27	52.87
Rice straw	5.04	82.12	7.74	5.10	37.52	5.92	0.86	0.14	42.78
Tobacco stem	3.64	68.52	21.7	6.14	36.10	4.85	2.64	0.77	55.63
Pine	15.30	70.40	0.20	14.19	51.01	6.00	0.10	0.02	42.90
Poplar	6.80	79.70	1.30	12.20	41.39	5.27	0.25	0.27	39.13
Bamboo	4.60	72.83	0.73	21.70	48.37	6.11	0.27	0.08	45.17
Rice husk	6.33	60.35	16.75	16.57	48.61	5.45	0.45	0.13	55.36
Peanut shell	9.13	56.62	1.52	31.86	60.53	7.12	1.92	0.35	30.08
Coal	2.29	30.65	28.07	36.84	56.72	2.76	1.05	0.53	2.00

ad, based on air dried basis; a, determined by difference.

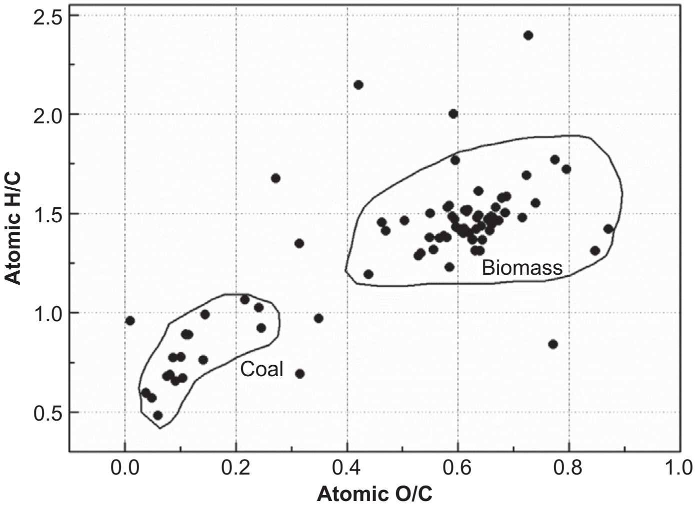

Figure 11.1 Relationship between H/C and O/C of biomass and coal.

Research shows that the mineral composition of coal and biomass has a strong impact on processing, application, and environmental and technological concerns related to these fuels. For biomass, variability in mineral content among plants can be considerable, as it depends on genetic and environmental factors, as well as physiological and morphological differences between crops. Table 11.2 presents the ash compositions of typical biomass and coal samples. It clearly shows that the ash compositions of biomass and coal are different. Biomass ash is mainly composed of K, Na, Mg, Al, Ca, and P, in the form of oxides, silicates, and chlorides, while coal ash consists mainly of Al and Si in the form of oxides. The ash from biomass also contains high alkali metal content, which can lead to corrosion in the gasifier instruments and downstream setup.

11.3 Biomass gasification

Biomass gasification is an important thermal chemical process that converts any carbonaceous biomass to gaseous products. Compared with traditional coal gasification, biomass gasification takes place at a lower temperature (~900 °C) due to the essential nature of biomass. The high content of volatiles and some intrinsic catalytic metals (like potassium, calcium) in biomass also tend to increase its reactivity. Additionally, biomass makes no contribution to net green house gas emissions, and its low sulfur and nitrogen contents make it a greener and cleaner option to fossil fuels.

The product of gasification, syngas, mainly contains H_2, CO, CO_2, CH_4, and some C_{2+} hydrocarbons. Different uses of syngas show the flexibility of biomass gasification and thus allow it to be integrated with various industrial routes, such as gas engines for power generation, Fischer-Tropsch (FT) Synthesis for DME, methanol,

Table 11.2 Ash composition of typical biomass

Samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	Cl
Corn stalk	0.68	3.55	1.75	40.97	5.81	3.74	25.14	6.48	0.59	11.15
Wheat straw	1.13	0.96	1.51	53.76	2.75	3.71	21.33	4.20	0.59	10.09
Rice straw	0.96	2.33	0.91	51.99	2.49	6.50	17.81	7.68	0.84	7.09
Poplar	0.74	4.14	6.85	26.83	7.03	5.52	8.21	34.8	3.76	1.49
Cotton stalk	2.43	6.40	5.82	18.21	7.14	9.45	17.07	26.09	3.8	2.76
Rape straw	1.06	0.38	0.21	4.05	2.69	21.23	35.40	25.70	0.71	8.22
Tobacco stem	0.38	5.88	-	0.12	4.05	7.96	21.20	31.36	0.08	28.16
Pine	12.84	5.56	6.50	16.47	2.42	7.64	7.76	24.89	4.57	8.77
Bamboo	-	4.48	-	19.22	6.36	8.18	49.22	6.02	3.13	1.06
Rice husk	-	0.84	1.06	87.47	0.81	1.30	3.02	1.64	2.38	0.52
Peanut shell	0.20	4.76	8.21	23.11	8.20	10.63	25.69	11.07	6.07	1.09
Coal	-	-	29.7	50.4	1.1	-	3.6	1.9	7.9	-

carbon-containing chemicals, methane, substitute gas, H_2, and gas fuels (Delgado, Aznar, & Corella, 1997).

Biomass gasification involves a complex series of chemical reactions, as shown in Figure 11.2. A good understanding of the basic biomass gasification reactions is fundamental to the planning, design, operation, troubleshooting, and process improvement of a gasification plant. In a typical gasification process, the following stages are usually take place: drying, pyrolysis, char and tar gasification. The detailed reactions that occur during gasification are summarized in Table 11.3.

Biomass materials are preheated and dried at 100-200 °C, before undergoing the pyrolysis stage. As the initial stage of gasification, pyrolysis partially removes carbon from the feed but does not add hydrogen. It takes place at relatively low temperatures in the range of 200-700 °C, without the use of a gasifying agent. During pyrolysis, a portion of biomass is transformed into condensable hydrocarbon tars, gases, and solid char (R1). Thereafter, a series of reactions occur in the gasifier, including a homogeneous gas-phase reaction and a heterogeneous gas-solid char gasification reaction shown as reactions (R2-R14). Char experiences partial (R2) and complete combustion (R3), as well as water gas reaction (R5) and hydrogasification (R6), which involves adding hydrogen to carbon to produce fuel with a higher hydrogen-to-carbon (H/C) ratio. Among all the reactions, R3 releases the most energy. In gas phase gasification reactions, volatiles undergo oxidation (R7-R9), steam reforming (R13), and cracking

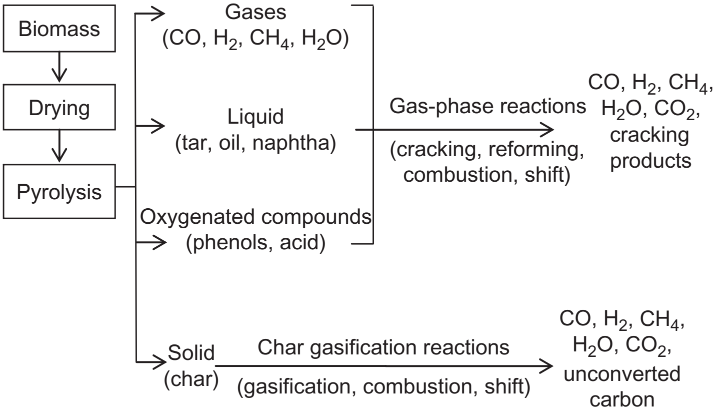

Figure 11.2 Basic chemistry of the biomass gasification process.

Table 11.3 **Main chemical reactions of biomass gasification**

Reaction	**ΔH_{298}, kJ mol^{-1}**	**Number**
Pyrolysis		
Biomass → char + tar + H_2O + light gas ($CO + H_2 + CO_2 + CH_4 + C_2 + \cdots$)	Endothermic	R1
Char combustion		
$C + 0.5O_2 \rightarrow CO$	−111	R2
$C + O_2 \rightarrow CO_2$	−394	R3
Char gasification		
$C + CO_2 \rightarrow 2CO$	172	R4
$C + H_2O \rightarrow CO + H_2$	131	R5
$C + 2H_2 \rightarrow CH_4$	−75	R6
Homogeneous volatile oxidation		
$CO + 0.5O_2 \rightarrow CO_2$	−254	R7
$H_2 + 0.5O_2 \rightarrow H_2O$	−242	R8
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	−283	R9
$CO + H_2O \rightarrow CO_2 + H_2$	−41	R10
$CO + 3H_2 \rightarrow CH_4 + H_2O$	−88	R11
Tar reactions		
$C_nH_m + (n/2)O_2 \rightarrow nCO + (m/2)H_2$	Endothermic	R12
$C_nH_m + nH_2O \rightarrow nCO + (m/2 + n)H_2$		R13
$C_nH_m \rightarrow (m/4)CH_4 + (n - m/4)C$		R14
$C_nH_m + (2n - m)H_2 \rightarrow nCH_4$		R15

Source: Zhang *et al*. (2010).

(R14). The water-gas shifting (WGS) reaction (R10) is of great importance because it plays a significant role in generating hydrogen (Matsumura *et al*., 2005). The methanation reaction (R11) always proceeds in the absence of any catalyst. Both R10 and R11 can proceed in either direction, depending on the specific temperature, pressure, and concentration of the reacting species. Above all, it can be seen that the product gas from gasification is a mixture mainly consists of H_2, CO_2, CO, CH_4 and water vapor.

11.4 Biomass gasification properties

11.4.1 Influence of feedstock characteristics

11.4.1.1 Biomass type

Different biomass with different physical and chemical characteristics, such as particle size and moisture content, may affect the gasification behavior.

Van Der Drift, Van Doorn, and Vermeulen (2001) investigated gasification behaviors of ten biomass feedstocks in circulating fluidized bed (CFB) with air at 850 °C, as shown in Figure 11.3. It was found that the main combustible gases are CO (10%) and H_2 (~8%), with trace amounts of methane and ethane (3-4 vol.%). The higher heat value (HHV) of the gas product was quite low, around 5MJ/m^3. However, gasification of different biomass samples resulted in variant fuel gas properties. The HHV of gas

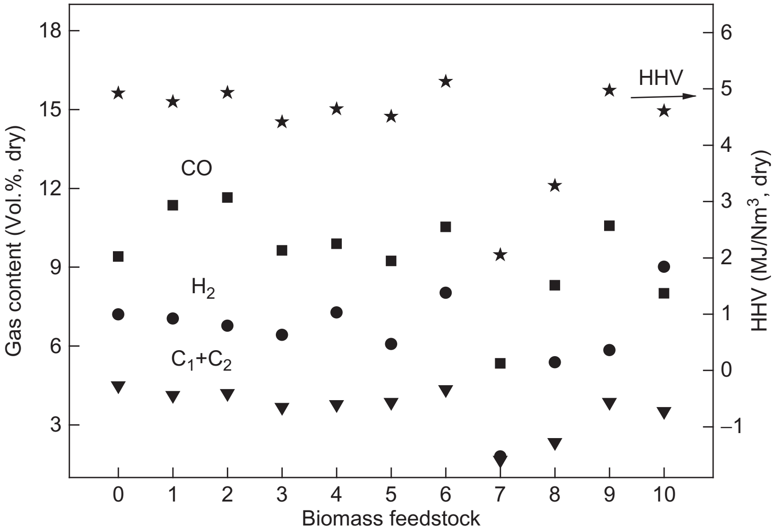

Figure 11.3 Synthesis gas distribution produced by the gasification of different biomass materials in a circulating fluidized-bed gasifier (0 – Willow, 1 – Demolition, 2 – Park wood, 3 – Chip board material, 4 – Verge grass, 5 – Demolition wood + paper residue sludge, 6 – Demolition wood + sewage sludge, 7 – Woody excess fraction of ODW, 8 – Park wood, 9 – Railrode ties, 10 – Cacao shells) (Van Der Drift *et al*., 2001).

fuel decreased significantly with the increase of water ash content in the biomass samples. For samples 7 and 8, the results might be attributed to some volatiles being removed by biocomposition, and because the ash and water content was very high.

Herguido, Corella, and Gonzalez-Saiz (1992) investigated the steam gasification behavior of four different biomass types. They found that the gas yield that resulted from sawdust and straw gasification was much higher than that from chips and thistles. The higher yield might be attributed to the higher volatile content in sawdust and straw. However, they also pointed out that the different sizes and shapes of the particles of each biomass is also a concern. As char from the sawdust particles showed much larger porosity and smaller particle diameter, the gasification reactivity of the solid sawdust char is much higher. In regard to the gas distribution, a clear difference based on the different biomass used. Sawdust showed higher H_2, while straw produced higher CO content, but the lowest H_2 yield. However, the variation decreased with the increase in gasification temperature, as shown in Figure 11.4.

Gani and Naruse (2007) analyzed the effect of cellulose and lignin content on biomass pyrolysis and combustion. For the biomass with higher cellulose content, the pyrolysis rate became faster, while the biomass feedstock with higher lignin content gave a slower pyrolysis rate. Thus, the cellulose and lignin content in the biomass were two important parameters used to evaluate the pyrolysis characteristics. Lv *et al.* (2010) found that gasification activity was considerably influenced by the content of cellulose and lignin in biomass.

Fushimi and Tsutsumi (2012) studied the gasification of cellulose and lignin and found that cellulose is easy to convert with higher reactivity, while lignin is quite difficult to convert at lower temperature. Wu, Wang, Huang, and Williams (2013) found that cellulose produces the highest amount of hydrogen, 5.8 mmol H_2 g^{-1} sample during gasification in the absence of steam and catalyst, while lignin produced only a 1.8 mmol H_2 g^{-1} sample with more CH_4 being formed. Also, cellulose pyrolysis/

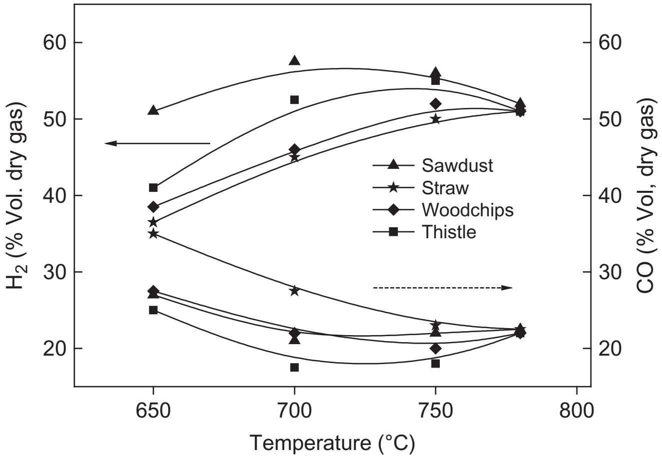

Figure 11.4 Effect of temperature on hydrogen and carbon monoxide concentrations in the gas (Herguido *et al.*, 1992).

gasification produced the highest CO concentration (44.4 vol.%), but the highest CO_2 concentration (27.3 vol.%) was observed for hemicelluloses (Wu, Wang, Huang, & Williams, 2013). More tar was also found to result from hemicellulose gasification, indicating that hemicelluloses might not produce high quality syngas (Fushimi & Tsutsumi, 2012).

11.4.1.2 Particle size

As mentioned above, particle size shows great effects on the gasification operation and the product gas composition. Lv *et al.* (2004) selected four size ranges of biomass particles to be used in a fluidized bed gasifier (Table 11.4). They found that fine particles are favorable for gas production with higher heat values and carbon conversion efficiency of biomass. As gas yield and composition are related to the heating rate of the biomass particles, high heating rates produce more light gases and less char and condensate. Smaller particles have larger surface area, and as a result, they also have a faster heating rate.

However, size control is expensive and energy intensive, so obtaining the optimal biomass particle requires a trade off. Fine and irregular-shaped feed particles may impede gas flow through the bed and result in increasing carbon conversion and a large pressure drop leading to irregular axial temperature profiles and “rat holes” or channeling of the pyrolysis and combustion zones (Cummer & Brown, 2002). On the contrary, fuel reactivity, such as slow gasifier startups and poor gas quality, may be a problem with excessively large particles. Due to the high degree of turbulence and good heat-transfer characteristics, fluidized bed gasifiers tend to be more forgiving to smaller-sized fuel particles.

11.4.1.3 Moisture content

The high moisture content of feedstock has shown a negative influence on the thermal process efficiency and is usually the most energy-intensive part of the gasification process. High-moisture fuels will result in more tar formation and low gasification temperatures. As seen in Figure 11.5, a decrease in moisture content from 25.5% to 9.5% can result in increases of 8.5% for CCE and 20.8% for CGE. In high moisture conditions, the gas also tended to have lower H_2 and CO contents and a higher CO_2 content

Table 11.4 Influence of particle size on the properties of biomass gasification (Lv *et al.*, 2004)

Biomass particle size (mm)	0.6-0.9	0.45-0.6	0.3-0.45	0.2-0.3
Average size (mm)	0.75	0.53	0.38	0.25
Gas yield (Nm^3/kg biomass)	1.53	1.93	2.37	2.57
Gas LHV (kJ/Nm^3)	6976	7937	8708	8737
Carbon conversion efficiency (%)	77.62	84.4	90.60	95.10
Steam decomposition (SD) (%)	32.34	42.55	52.67	56.45

Source: Lv *et al.* (2004).

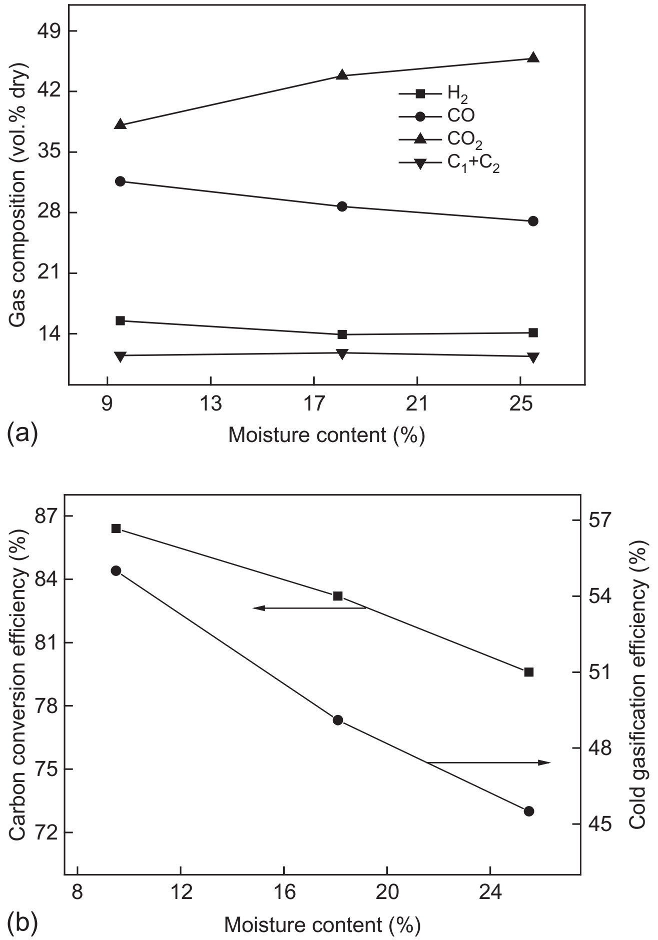

Figure 11.5 Influence of moisture content on (a) gas composition, (b) carbon conversion efficiency (CCE) and cold gasification efficiency (CGE) (Kaewluan & Pipatmanomai, 2011).

(Kaewluan & Pipatmanomai, 2011). The influences of the moisture content of biomass on tar species are available in detail in other literature (Ahrenfeldt, Egsgaard, Stelte, Thomsen, & Henriksen, 2012). Processing wet fuels can also bring about erratic gasifier operation, longer startup times, and higher energy consumption. Hence, air-drying or some other form of pretreatment, such as torrefaction, should be an efficient way to remove excess moisture.

11.4.2 Gasification parameters

There is a series of parameters that are crucial for the efficiency of gasification, and thus the optimum values of these factors should be maintained to ensure a constant quality with high process performance.

11.4.2.1 Gasification temperature

As it controls the cracking and conversion of biomass, temperature plays a vital role in gasification. Figure 11.6 provides the gasification property under different temperatures during sawdust gasification (Chen, Li, Yang, Yang, & Zhang, 2008). A higher operating temperature (>800 °C) is always favorable for higher hydrogen and lower tar content yield (decrease from 13.2 to 6.5 g/m^3) in the product gas. Meanwhile, temperature not only influences the amount of tar, but also the tar composition by changing the chemical reactions during gasification (Devi, Ptasinski, & Janssen, 2003; Meng, De Jong, Fu, & Verkooijen, 2011; Mayerhofer *et al.*, 2012). The effects of temperature on tar are shown in detail in the section on tar. With the rise of temperature, the carbon conversion rate increases, as does the thermal efficiency, but the rising temperature may cause more severe fouling and slagging problems when the

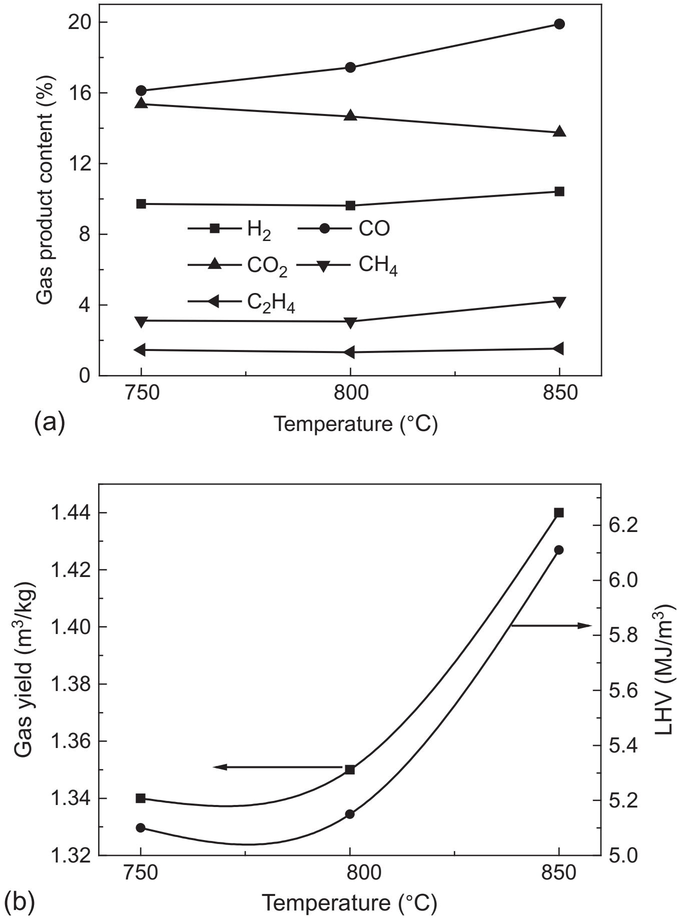

Figure 11.6 Influence of gasification temperature on (a) gas composition, (b) gas yield and LHV (Chen *et al.*, 2008).

biomass has higher contents of K, Cl, and other inorganic materials. Therefore, the optimal temperature is based on the conversion and application condition.

11.4.2.2 Gasifying agent

The gasifying agent, which is normally a gas such as oxygen, air, subcritical water, carbon dioxide, or their mixtures, or supercritical water, is an indispensable medium for biomass gasification. The selectivity of the gasification reactions varies with different gasifying agents, thus affecting the composition and LHV of produced gas (Devi *et al.*, 2003). Table 11.5 shows the gas product properties when the gasification process involves different agents (Gil, Corella, Aznar, & Caballero, 1999). A steam medium is preferred if high hydrogen content and higher heating value are required for syngas utilization, especially in a small-scale operation unit. But steam has its drawbacks, as it results in high tar content (60-95 g/kg compared with 3.7-61.9 g/kg produced by air), so downstream purification is needed. When using the medium of air or oxygen, most of the heat used to drive the reaction is generated by partial oxidation and exothermic combustion reactions inside the gasifier. Air has gained popularity as the most practical gasifying agent in biomass power plants due to its low cost and availability. However, the LHV of the product gas is quite low with air gasification due to the dilution of nitrogen. Other research has shown how the properties of the product gas can vary with the specific content of the

Table 11.5 **Gas product properties with variant gasifying agents (Gil *et al.*, 1999)**

	Air	**(Pure) Steam**	**Steam-O_2 mixtures**
Operating conditions			
ER	0.18-0.45	0	0.24-0.51
S/B (kg/kg daf)	0.08-0.66	0.53-1.10	0.48-1.11
T (°C)	780-830	750-780	785-830
Gas composition			
H_2 (vol.%, dry basis)	5.0-16.3	38-56	13.8-31.7
CO (vol.%, dry basis)	9.9-22.4	17-32	42.5-52.0
CO_2 (vol.%, dry basis)	9.0-19.4	13-17	14.4-36.3
CH_4 (vol.%, dry basis)	2.2-6.2	7-12	6.0-7.5
C_2H_n (vol.%, dry basis)	0.2-3.3	2.1-2.3	2.5-3.6
N_2 (vol.%, dry basis)	41.6-61.6	0	0
Steam (vol.%, wet basis)	11-34	52-60	38-61
Yields			
Tars (g/kg daf)	3.7-61.9	60-95	2.2-46
Char (g/kg daf)	na[a]	95-110	5-20
Gas (Nm^3/kg daf)	1.25-2.45	1.3-1.6	0.86-1.14
LHV (MJ/Nm^3)	3.7-8.4	12.2-13.8	10.3-13.5

na, not available. *Source:* Gil *et al.* (1999).

gasifying agent, the ER (Narvaez, Orio, Aznar, & Corella, 1996), the S/B ratio (Franco, Pinto, Gulyurtlu, & Cabrita, 2003; Pinto *et al.*, 2003), and the gasifying agent ratio(GR) (Aznar *et al.*, 1997; Pinto *et al.*, 2003).

11.4.2.3 Gasification pressure

Pressure also influences gasification behavior. As shown in Figure 11.7, Mayerhofer investigated the effects of pressure on gas composition and tar content (Mayerhofer *et al.*, 2012). The enhancement of WGS reactions under pressurized conditions makes the gas composition shift to higher CH_4 and CO_2 content, while CO decreases. Figure 11.7b indicates that an increase in total tar content was observed when pressure increased from 0.1 to 0.25 MPa. But an opposite trend in tar content has also been reported (Wolfesberger, Aigner, & Hofbauer, 2009). Furthermore, the syngas

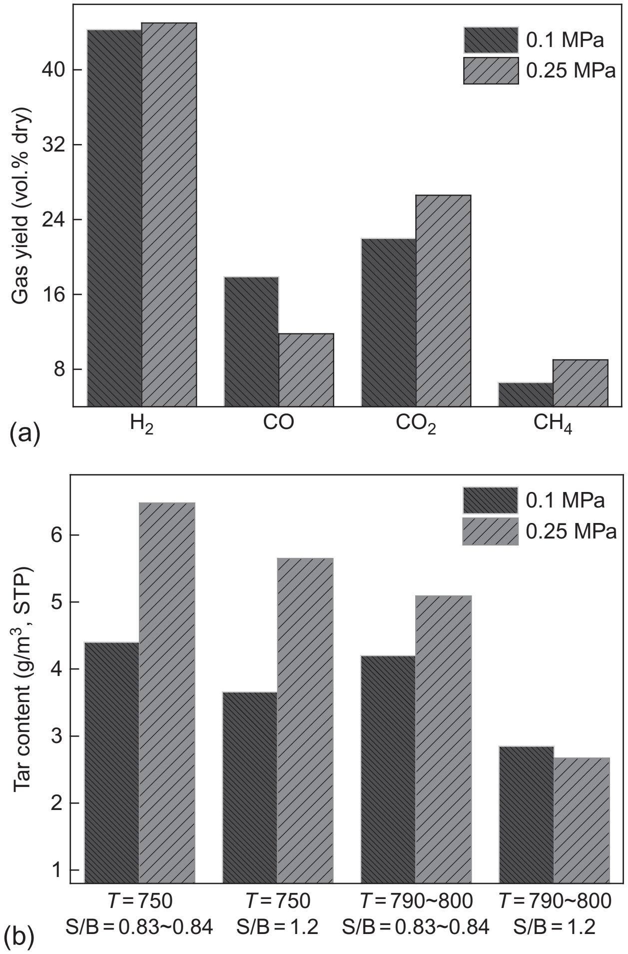

Figure 11.7 Influence of pressure on gas yield and tar content (Mayerhofer *et al.*, 2012).

produced at high pressures is favorable for downstream high-pressure units, such as turbines and FT synthesis. However, high-pressure gasification seems uneconomical when extra equipment is needed to ensure the stability of the over-pressurized gasification conditions. Other operational conditions, such as the bed material in fluidized beds (Meng *et al.*, 2011) and the biomass feeding rate (Lv *et al.*, 2007), influence gas distribution and tar formation as well.

11.5 The biomass gasifier

A gasifier is the device in which biomass gasification takes place. Hundreds of different gasifier models can be categorized into three types, as shown in Figure 11.8: updraft, downdraft, and fluidized beds. All of these types have the same four reaction zones: drying, pyrolysis, combustion, and reduction. However, the zones are distributed differently in each type.

In a typical updraft gasifier (Figure 11.8a), the preheated gasifying agent enters the reactor from the bottom and flows upward, and the producer gas leaves from the top of the reactor where incoming biomass is added. This type of gasifier is more forgiving with respect to fuel moisture, as the heat transfer is enhanced with the counter flow arrangement. The disadvantage of the updraft gasifier is the high tar yield because the tar formed during pyrolysis is partly taken away by producer gas.

In a downdraft gasifier (Figure 11.8b), the reaction zones differ from those of updraft gasifiers. Compared with the updraft gasifier, some large molecular tars can be decomposed by thermal cracking in the downdraft type, leaving a clean gaseous

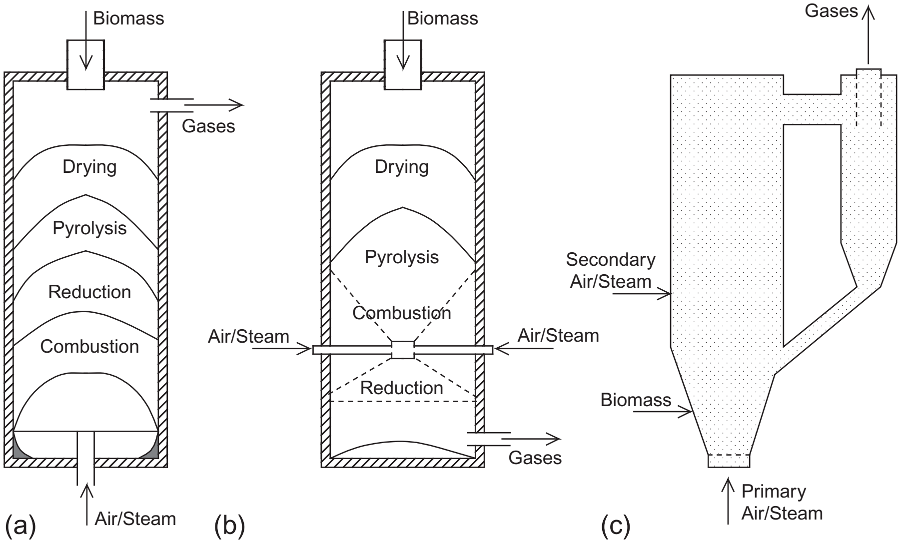

Figure 11.8 Schematic structure of different gasifiers (a) updraft, (b) downdraft, and (c) fluidized bed.

product with less concentrations of tar and thus benefitting the downstream equipment. For this reason, the downdraft gasifier has the widest applications, especially for small-scale engines and heating supply.

In a fluidized bed gasifier, oxygen or steam enters at the bottom of the reactor, carrying biomass, which has been reduced to a fine particle size, upward through a bed of heated silica particles. The biomass is decomposed in the hot bed, forming char and gaseous product. Fluidized bed gasifiers can be further classified into bubbling fluidized bed and circulating fluidized bed (Figure 11.8c). Fluidized beds typically operate in the temperature range of 800-1000 °C, which avoids the ash agglomeration and sintering, allowing the safe operation of fuel with high ash content. Additionally, the large thermal inertia and vigorous mixing benefit the flexibility of various biomass feed rates and compositions.

The advantages and disadvantages of different types of gasifiers are summarized in Table 11.6. The gasifier plays a vital role in a gasification plant, and it is responsible for keeping syngas production as steady as possible. The selection of the gasifier type will depend on feedstock properties, the reaction conditions, the desired end use, and the quantity of the producer gas required.

Table 11.6 **Properties of biomass gasification reactor types**

Advantages	**Disadvantages**
Fixed/moving bed, updraft	
Simple and reliable design	Large tar production
High carbon conversion efficiency	Potential channeling, bridging, and clinkering
Low dust levels in gas	Small feed size
High thermal efficiency	Low-output
Fixed/moving bed, downdraft	
Simple, inexpensive process	Minimum feed size
Low tar content in product gas	Limited ash content allowable in feed
	Limits to scale up capacity
	Potential for bridging and clinkering
Fluidized bed	
Short residence time	Low char conversion rate
High ash fuels acceptable	The efficiency is not high
Excellent heat and mass exchange	High product gas temperature
Flexible feed rate and composition	High tar and fines content in gas
Uniform temperature distribution in gasifier	Possibility of high C content in fly ash
High CH_4 in product gas	Complicated operation
High volumetric capacity	
Able to pressurize	

Source: Arena (2012), Knoef and Ahrenfeldt (2005), Pan *et al*., (1999), Sridhar *et al*. (2001), Wang *et al*. (2008), and Zhang *et al*. (2013).

11.6 The formation and cracking of tar

One of the main barriers for the application of biomass gasification is the presence of tar in the gas product, which may cause severe problems for downstream equipment. Tar has been widely defined in the gasification literature. Li and Suzuki (2009) considered "tars" to be condensable fractions of the organic gasification products that largely consisted of aromatic hydrocarbons, including benzene. Devi *et al.* (2003) describe tar as a complex mixture of condensable hydrocarbons, such as single to multiple ring aromatic compounds, other oxygen-containing hydrocarbons, and complex PAHs. The formation and cracking of tar is critical in biomass gasification in order to produce high quality gas fuel.

11.6.1 Formation mechanism of tar

The characteristics of tar mainly depend on the composition of the tar, particularly the tar's heavy compound content. The components of tar are very complex, and more than 200 kinds can be detected in a single sample. This diversity of components is due to the fact that tar is formed from volatiles during biomass pyrolysis, and the composition of volatiles is dependent on temperature. The main composition of liquid tar obtained from variable temperatures is shown in Figure 11.9. When the temperature is below 550 °C, the

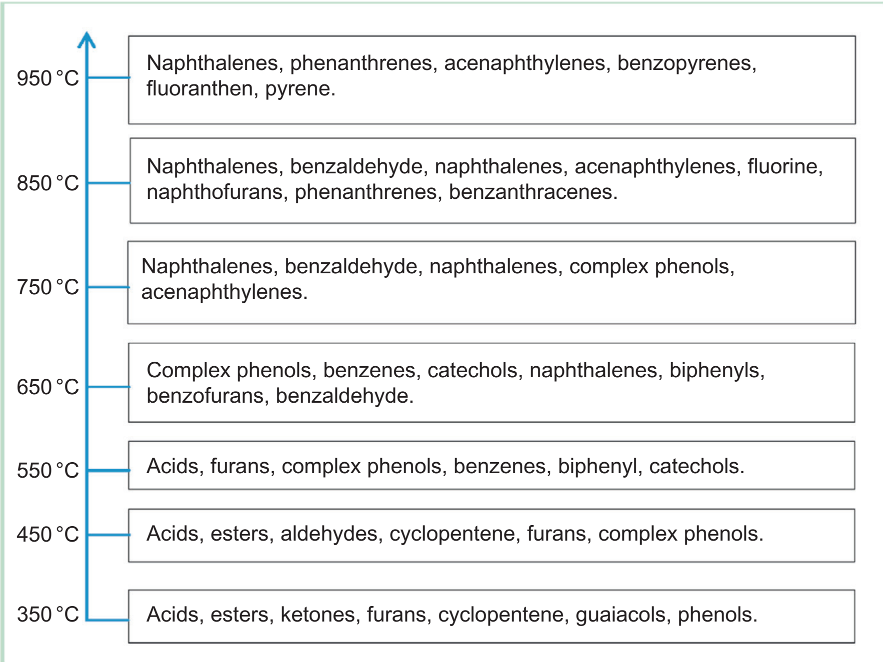

Figure 11.9 Typical chemical components in biomass tars (Chen *et al.*, 2012; Devi, Ptasinski, & Janssen, 2003).

volatiles are formed from the direct degradation of cellulose and hemicellulose. Therefore, most of the resulting tar is formed by low-molecular-weight and oxygen-containing compounds, such as acids, esters, ketones, furans, cyclopentene, guaiacols, and phenols. This type of tar easily undergoes further reforming. With the temperature increasing up to 650 °C, complex phenols replace these low-molecular-weight and oxygen-containing compounds (Hernández, Ballesteros, & Aranda, 2013; Zheng, Zhu, Guo, & Zhu, 2006). However, during the secondary reaction of the volatiles, the elimination reactions of the oxygen-containing functional groups produce some aromatic compounds containing benzenes, naphthalenes, biphenyls, benzofurans, and benzaldehyde. Above 650 °C, the molecular weight and the number of aromatic rings within the tar components increase significantly because of the generation of a large number of PAHs. Although complex phenols are observed in the tar obtained at 750 °C, the weight content of complex phenols is rather lower, and the branched structures become uncomplicated. As the temperature rises to 950 °C, the dehydrogenation condensation reaction generates some PAHs with more than three aromatic rings, such as acenaphthylenes, benzopyrenes, fluoranthen, and pyrene, which are the precursors of the particulate matter called "soot" (Chen, Yang, Wang, Zhang, & Chen, 2012; Qin, Feng, & Li, 2010), The thermal stability of such tar is very high, so it is difficult to crack and remove.

11.6.2 Tar cracking

Tar removal is seen as one of the greatest technical challenges to overcome for the successful development of advanced, commercially viable gasification technologies (Minlne & Evans, 1998; Li & Suzuki, 2009). Tar cracking technology can be divided into two basic methods: thermal cracking and catalytic cracking. However, the former method is not considered to be a feasible option, as it requires temperatures higher than 1100 °C to achieve high cleaning efficiency, and it also produces soot (Aznar, Corella, Delgado, & Lahoz, 1993).

In comparison with high temperature thermal cracking, catalytic cracking is highly efficient. Catalysts used in biomass conversion can be divided into three distinct groups. They are dolomite catalysts, alkali metal and alkali earth metal catalysts, and nickel-based catalysts.

11.6.2.1 Dolomite

Dolomite is a magnesium ore with the general formula $MgCO_3 \cdot CaCO_3$. The use of dolomite as a catalyst in biomass gasification has attracted much attention (Xu, Donald, Byambajav, & Ohtsuka, 2010). The chemical composition of dolomite varies from source to source, but it generally contains 30 wt.% CaO, 21 wt.% MgO, and 45 wt.% CO_2. Dolomite also contains the trace minerals SiO_2, Fe_2O_3, and Al_2O_3. Orío, Corella, and Narváez (1997) investigated four different dolomites from different places for oxygen-steam gasification of wood in a downstream catalytic reactor. They found that the catalytic activity was different.

Delgado *et al.* (1997) investigated the use of Norte dolomite and compared it with calcite (CaO) and magnesite (MgO) for the steam reforming of biomass tars. They investigated the effects of temperature, contact time, and the particle diameter of the catalysts and reported that tar conversion increased with the temperature of the catalyst bed, and complete elimination was observed at 840 °C. Vassilatos, Taralas, Sjöström, and Björnbom (1992) also studied the effect of temperature, catalyst contact time, and steam-carbon ratio. They found that higher temperatures resulted in an increase in the gas yield. An increase in the gas-catalyst contact time led to an increase in the destruction of tar present in the gas, with a maximum being reached at 0.3 kg h/ Nm^3. Increasing contact time produced more H_2 and CO due to tar conversion reactions and the water-gas shift reaction.

Chen *et al.* (2008) compared the catalytic properties of dolomite, olivine, and magnesite in fluidized bed gasifier. They found that catalyst addition showed great catalytic effect on biomass gasification, and the release of light gas products (H_2, CH_4, and CO) was enhanced greatly. However, in the Chen study, the biomass samples showed variant adoptability. Tar removal efficiency varied from 48.1% to 70.5%, while sawdust gasification showed the highest tar removing efficiency with the addition of dolomite.

Dolomite is a cheap, disposable catalyst that can significantly reduce the tar content of the product gas from a gasifier. It may be used as a primary catalyst, dry-mixed with biomass, or, more commonly, placed in a downstream reactor, in which case it is often referred to as a guard bed.

11.6.2.2 Alkali metal and alkaline-earth metals catalysis

Much research has also considered the use of alkali metal catalysts for the elimination of tar and the upgrading of the product gas. These catalysts are often added directly to the biomass by dry-mixing or wet-impregnation. When added in this way, the catalyst is difficult to recover, and, as a result, this form of catalyzing tar cracking is not always cost effective for the gasification process. It also leads to an increase in the ash content remaining after char gasification, and the disposal of this ash is predicted to become a problem for the technology over the coming years.

In a study of the catalytic properties of potassium (K) on char gasification with potassium-loaded woody biomass, Sueyasu *et al.* (2012) found that the catalysis of K reduced the heavy tar content to 20 mg/m^3 N, and the concentration of hydrogen in the product gas exceeded 50 vol.% dry. Mudge, Baker, Mitchell, and Brown (1985) studied the catalytic steam gasification of wood using alkali carbonates and naturally occurring minerals, which were either impregnated or mixed with the biomass. They considered the effectiveness of four different primary catalysts and of different catalyst concentrations at 550, 650, and 750 °C. The order of activity was reported as being potassium carbonate > sodium > carbonate > Trona ($Na_3H(CO_3)_2$) $2H_2O$ > Borax ($Na_2B_4O_710H_2O$) Impregnated catalysts had little or no carbon deposition, as compared to the mixed catalysts, and carbon deposition resulted in deactivation. In the paper, the Mudge team also reported that the impregnation decreased particle agglomeration.

11.6.2.3 Nickel-based catalysts

The most significant body of literature published on hot gas cleaning for biomass gasification concerns nickel-based catalysts. Several groups have investigated a system of raw gas cleaning that involves a dolomite or alkali catalyst for the removal of up to 95% of the tar, followed by the adjustment of the gas composition reforming of the methane and the remaining tar using a nickel-steam-reforming catalyst. Steam and dry reforming reactions are catalyzed by metals of group VIIIA. Among these catalysts, nickel is the most widely used in the industry. Nickel catalysts are designed for steam reforming of hydrocarbons and methane. Using these catalysts at temperatures >740 °C generally produces an increase in the hydrogen and carbon monoxide content of the exiting gas, as well as the elimination or reduction of the hydrocarbon and methane content.

Modification of nickel catalysts through the addition of promoters has also been investigated (Arauzo, Radlein, Piskorz, & Scott, 1997; Bangala, Abatzoglou, & Chornet, 1998). Arauzo *et al.* (1997) reported on the addition of magnesium and potassium to a nickel alumina catalyst. The magnesium substitution was made at two different levels, resulting in two catalysts, namely $Ni_2MgAl_8O_{16}$ and $NiMgAl_4O_8$. Magnesium was added to increase the physical strength of the catalyst and its resistance to attrition. Partial replacement of nickel by magnesium improved the strength of the resultant catalyst, but the replacement also produced a 14% lower gas yield and an increase in the char yield. The CO and H_2 yields decreased slightly with nickel content. The magnesium modified the catalyst structure and pore size distribution, with the unmodified catalyst containing a higher fraction of wider macropores. Arauzo and colleagues further proposed that the magnesium should inhibit the reduction of the nickel. Carbon deposition was reported as the cause of deactivation. However, the kinetics of catalyst deactivation depend on many factors, such as catalyst type, bed temperature, gas residence time, steam/biomass ratio, catalyst particle size, and, above all, the tar content of the raw gas (Herguido *et al.*, 1992). Researchers have energetically sought a variety of reasonable catalysts for tar reforming and removal. Some catalysts performed with high tar reforming efficiency and excellent catalysis property, such as the nano-architectured $Ni_5TiO_7/TiO_2/Ti$ compound, palygorskite-supported Fe, and Ni catalyst. Further research work on tar elimination during biomass gasification is needed to identify reasonable catalysts that efficiently eliminate tar in an environmentally friendly manner (no secondary pollution), with low cost and easy regeneration based on tar types and content (Xu *et al.*, 2010).

11.7 Char gasification

Another critical issue blocking the widespread use of biomass gasification is the lower carbon conversion efficiency of the process. Biomass gasification consists of two stages: the pyrolysis or release of volatiles and the gasification of the residual char. The release of volatiles is very fast, while char conversion is a gas-solid oxidation reaction, and as a result, it is the rate-limiting step in the overall conversion process (Bridgwater, 1995).

Chars from biomass tend to have higher gasification reactivity than those from coal (Miura, Hashimoto, & Silveston, 1989). As biomass contains much higher volatile content, char particles show a more porous surface structure and carbonaceous matter (Keown, Li, Hayashi, & Li, 2008). Wu, Yip, Tian, Xie, and Li (2009) found that biochar has highly heterogeneous and disordered structures, that easily react with the gasify agent.At the same time, the alkali and alkaline earth metallic (AAEM) species in biomass have a catalytic influence on char gasification. It was found that K and Ca increased the gasification rate significantly (Mitsuoka *et al.*, 2011). Especially with the addition of K_2CO_3, char gasification can be shifted to a much lower temperature (600-700 °C). Furthermore, tar content in the gas product is decreased sharply as a result of this process (Sueyasu *et al.*, 2012).

Aside from biomass composition, the pyrolysis condition also plays a critical role in char structure and gasification reactivity. Cetin, Moghtaderi, Gupta, and Wall (2004) found that char reactivity increased with increases in the pyrolysis heating rate and decreases in pyrolysis pressure. Under high heating rates, the char particles underwent plastic deformation (melted), developing a structure different than that of the virgin biomass. Pressure was also found to influence the physical and chemical structures of char particles. Klose and Wolki (2005) found that the reaction rate of biomass char is generally proportional to the reactive surface area. The surface-related reaction rates for the studied biomass chars are comparable to surface-related reaction rates for coal chars at similar reaction temperatures

During char gasification, the structure and gasification reactivity also differ greatly. The highly heterogeneous and disordered structures in the char are selectively consumed during steam gasification, leading to the enrichment of larger aromatic ring systems, which are much more ordered and difficult to further convert (Wu *et al.*, 2009). Consequently, a high char conversion for biomass is difficult to attain in gasification units. For example, one study found that carbon conversion reaches 80% in fluidized bed gasifier only after half an hour at 800 °C. Higher temperatures might accelerate the conversion, but 20 min is still necessary for full carbon conversion, as is shown in Figure 11.10, based on calculation (Gómez-Barea, Ollero, *et al.*, 2013).

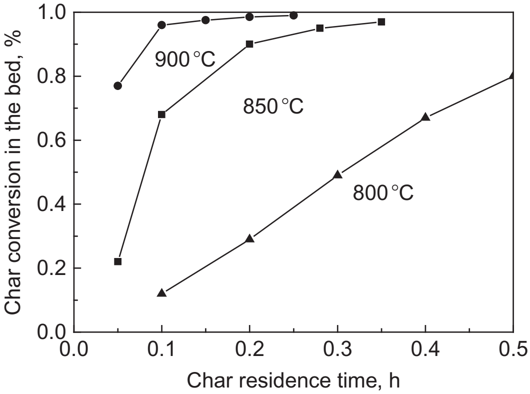

Figure 11.10 Effect of temperature and char residence time on char conversion in an FBG (Gómez-Barea, Ollero, & Leckner, 2013).

For pilot, experimental, and industrial running, carbon conversion is much lower. Hence, measures should be taken to improve char gasification, thus ensuring a higher carbon conversion ratio and gasification efficiency.

11.8 Novel technology for biomass gasification

11.8.1 Staged gasification

Low carbon (char) conversion and high tar content in the gas are the two main problems that have blocked the development of biomass gasification (Gómez-Barea *et al.*, 2013). Therefore, tar cracking and char gasification are two critical issues for syngas quality upgrading. Higher temperature is favorable for tar removal and char gasification (Hasler & Nussbaumer, 1999; Sutton, Kelleher, & Ross, 2001). But a new challenge is arising, as biomass facilities may be at risk of agglomeration at high temperatures, due to the release of a high proportion of alkali metals from certain feedstocks such as agricultural straws (Nilsson, Gomez-Barea, Fuentes Cano, & Ollero, *et al.*, 2012). Staged gasification is a suitable way to reach high char conversion, while yielding a gas with a low concentration of heavy tar (Nilsson *et al.*, 2012; Gómez-Barea, Ollero, *et al.*, 2013). Gas produced by stage gasification is ideal for direct thermal applications, including gas engines, boilers, and fuel cells.

Staged gasification creates at least two different temperature zones and various thermal levels in the gasification bed by staging the oxidant. The biomass gets devolatilized at relatively low temperatures and then gasified at elevated temperatures with the remaining oxidant. As is shown in Figure 11.11, the process is divided into two parts: the pyrolysis stage at temperatures of 350∼600 °C and the gasification stage at temperatures of 800-1000 °C. This process is convenient for the optimization of simultaneous char conversion and tar cracking.

Early in the 1994, Bui, Loof, and Bhattacharya (1994) found that tar yield in multistage reactors for thermal gasification was a factor of 40 times lower than the tar yield produced by one-stage gasification. Henriksen, *et al.* (Brandt, Larsen, & Henriksen, 2000; Henriksen *et al.*, 2006) designed a 75-kw two-stage fixed-bed gasifier that has been operated for more than 2000 h, and this gasifier has produced product with a tar content <15 mg/m^3. Šulc *et al.* (2012) found that two-stage gasification systems can significantly decrease aromatic compounds with two or more benzene rings. Stage gasification of biomass not only sharply decreases the tar yield, but it also can increase the LHV of the resulting syngas. Hamel, Hasselbach, Weil, and Krumm (2007) produced high calorific value gas in a bubbling fluidized bed-fixed bed stage gasification system, and when using this process, the LHV of gas from MSW steam gasification increased to 14 MJ/Nm^3. As for the release of AAEM and the reaction rate of gasification at about 800 °C lower than traditional conditions, Sharma, Saito, and Takanohashi (2008) studied the effects of K_2CO_3 catalytic gasification characteristics on ash-washed coal, and they pointed out that the low temperature of coal gasification (<650 °C) is feasible. Sueyasu *et al.* (2012) proposed a two-stage conversion of biomass into gas, during which pyrolysis occurs at 500-600 °C and steam reforming/

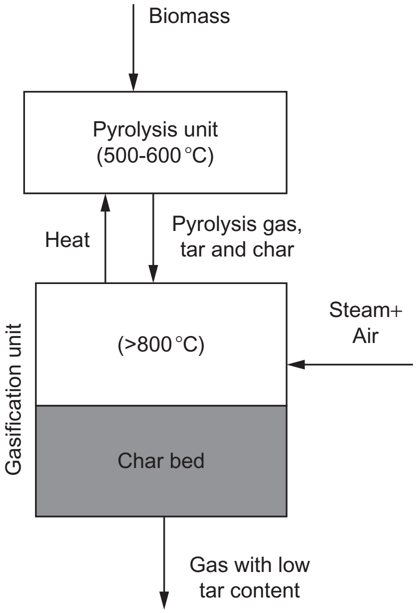

Figure 11.11 The schematic system of biomass-staged gasification (Gómez-Barea, Leckner, *et al.*, 2013).

gasification occurs at 600-700 °C, with the K_2CO_3 catalyst being recycled. The addition of K can obviously increase the gasification characteristics of pine sawdust at low temperature. As a reslt of adding potassium, the concentration of hydrogen in the product gas exceeded 50 vol.%, and the tar yield was as low as 20 mg/Nm^3.

Furthermore, the produced char can be gasified in the second stage and as the heat-carrier or catalyst for the further conversion of tar. Gómez-Barea (Gómez-Barea, Leckner, *et al.*, 2013; Gómez-Barea, Ollero, *et al.*, 2013) has proposed the three-stage concept shown in Figure 11.12, which includes fluidized bed devolatilization (first stage), the non-catalytic air/steam reforming of the gas from the devolatilizer (second stage), and the chemical filtering of gas in a moving bed supplied with the char generated in the devolatilizer (third stage). Air and steam can be injected at various points, such as the devolatilizer, steam reformer, and seal, with different proportions of the two reactants. The fuel is fed near the bed's surface and has to circulate down to the bottom before leaving the bed. The devolatilizer, where a high yield of fresh tar is generated, is operated at relatively low temperatures (700-750 °C). The fresh tar compounds are drastically reduced in the reformer, where a temperature of up to 1200 °C is created. The injection of steam into the reformer avoids coking and polymerization of the tar. The gas is then filtered through a moving bed made of char which comes from the loop seal. The loop seal can be operated as an oxidizer fed with enriched air or as a light reformer fed with H_2O, depending on the fuel's reactivity and ash properties. The char filter also cools down the gas through an endothermic char gasification reaction with steam, while the char also acts as a catalytic filter promoting tar decomposition reactions with steam.

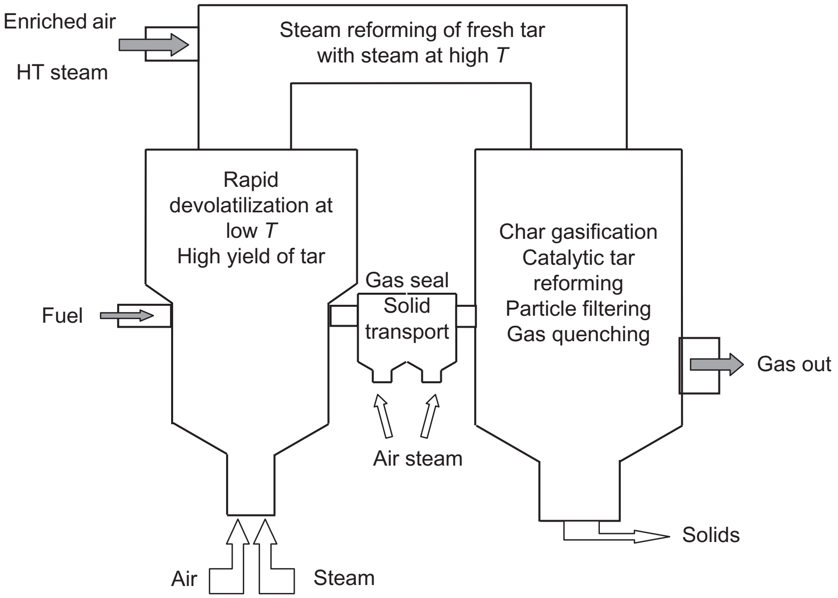

Figure 11.12 Basic conceptual design of the three-stage gasification process (Gómez-Barea, Leckner, Villanueva Perales, Nilsson, & Fuentes Cano, 2013; Gómez-Barea, Ollero, *et al*., 2013).

In the new three-stage system, the char conversion is up to 98%, leading to higher process efficiency. By optimizing the operating condition of air and steam in the three-stage system, the cold gas efficiency and gas HHV can increase to 0.81 and 6.9 MJ/Nm^3 dry gas respectively. When using 40 vol.% oxygen-enriched air instead of typical air, the cold gas efficiency increases to almost 0.85, and the resulting gas can have an HHV of 10.8 MJ/Nm^{3}dry gas. Given that the heavy tar content is lower than 0.01 g/Nm^3, being virtually converted in the system, the obtained low dew point gas can be burned in a gas engine, and as a result, this gas is ideal for power production.

Nowadays, staged gasification tends to involve large-scale applications and continuous operation. The University of Canterbury has built a 100 kW fast internal circulating fluidized bed gasification system that incorporates two closely coupled fluidized bed stages, a bubbling bed for gasification and a fast circulating bed for combustion (Brown, Dobbs, Devenish, & Gilmour, 2006). This duality provides a medium calorific value producer gas suitable for use as a fuel in a gas engine or gas turbine. Steam gasification is used in the bubbling fluid bed, at ~800 °C, to form a product gas that is rich in hydrogen. Residual char is transferred with bed material to the circulating fluid bed, where it is combusted, along with LPG, to heat the bed material. The hot bed material is then circulated back to the gasification stage, providing heat for the endothermic gasification reactions. On the other hand, char, char-supported catalysts, and ilmenite are investigated for the steam reforming of biomass tar, as opposed to the use of a precious metal catalyst. Min *et al*. (Min, Asadullah, *et al*., 2011; Min, Yimsiri, Asadullah, Zhang, & Li, 2011) clearly indicated that the chars from the pyrolysis and gasification of biomass could support a new class of cheap industrial catalysts with superior performance. Char would not only disperse the catalysts, but it would also interact with the catalysts to enhance their involvement in the steam reforming of tar. The physical and chemical property of support could play important roles for the activities of the catalysts and the reaction pathways of the catalysts. The char-supported iron/nickel catalysts exhibited much higher activity for the reforming of tar than char itself. So the utilization of pyrolysis char as catalyst support is another research point.

11.8.2 Sorption-enhanced steam gasification of biomass for H_2 production

Together with electricity, hydrogen is considered to be one of the two main terminal energies produced by gasification in the twenty-first century. Hydrogen can also be utilized for ammonia production and, with suitable CO concentrations, for methanol and FT synthesis. Through the use of a calcium oxide (CaO) sorbent for carbon dioxide (CO_2) capture, the steam gasification of biomass offers a potential means for the renewable and sustainable hydrogen (H_2) production.

Sorption-enhanced steam gasification of biomass is a novel one-step conversion technology developed for high-concentration H_2 production. In this process, CO_2 sorbents are introduced into the process of biomass steam gasification for the continuously *in situ* removal of CO_2 as soon as it was formed in the gasification process. As a result, the chemical equilibrium of the gasification reactions changes, and the process produces more H_2 (Hanaoka *et al*., 2005; Harrison, 2009). The gasification unit, the WGS unit, and the CO_2 separation unit are integrated into a single-stage reactor in this process, in order to achieve *in situ* CO_2 removal, energy integration of the endothermic gasification and exothermic WGS and CO_2 sorption processes, facility and process simplification, and steam usage reduction. As a result, the overall efficiency and economic feasibility of biomass gasification are improved.

Considering the spent CO_2 sorbent regeneration, the whole H_2 production process is a looping system, and the circulation between sorption and desorption ceaselessly transforms each cycle. With CaO as an example, the principle of this process could be described as shown in Figure 11.13 (Koppatz *et al*., 2009), and the main reactions that take place in the process could be summarized as follows:

$$\text{Biomass steam gasification}: \quad C_xH_yO_z(\text{Biomass}) + (1-y)H_2O \rightarrow CO + (0.5x + 1 - y)H_2 \tag{R16}$$

$$\text{WGS reaction}: \quad CO + H_2O \rightarrow CO_2 + H_2,\ \Delta H = -41.2\,\text{kJ/mol} \tag{R17}$$

$$CO_2\text{absorption}: \quad CaO + CO_2 \rightarrow CaCO_3,\ \Delta H = -178.3\,\text{kJ/mol} \tag{R18}$$

Li *et al*. (2011) have reported that a H_2 concentration of 94.92% could be obtained at the gasification temperature of 600-700 °C, with the atmospheric pressure being appropriate for chemical equilibrium. Marquard-Möllenstedt *et al.* (2004) also

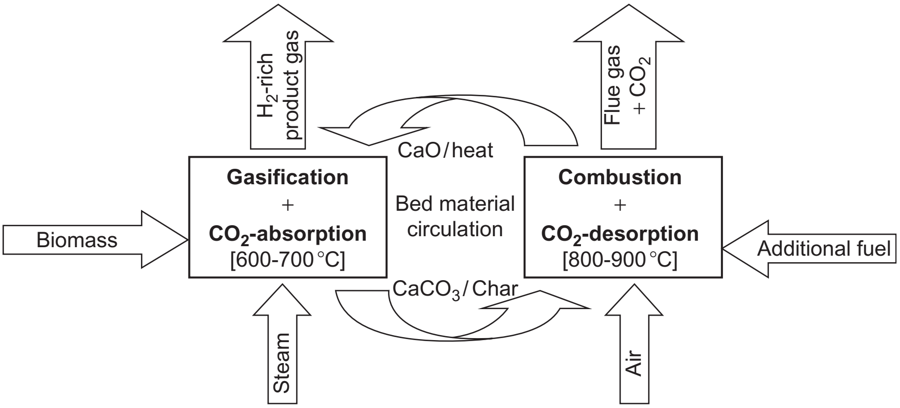

Figure 11.13 The principle of CaO-based sorption-enhanced steam gasification of biomass. Adapted from Koppatz *et al.* (2009).

reported that the H_2 concentration could increase from 40% to about 75%, with the addition of CaO, while the CO_2 concentration decreased significantly.

CaO-enhanced steam gasification of biomass still has several advantages: (1) the temperature of the CaO carbonation reaction coincides with the temperatures required for biomass gasification; (2) CaO also has a catalytic effect on the process of biomass gasification and tar cracking and reforming. Considering the appropriate conditions of the CaO carbonation reaction, the optimized carbonation temperature is between 600 and 700 °C at atmospheric pressure. In this temperature range, biomass steam gasification enhanced by CaO sorption could produce a high H_2 concentration.

However, due to the lower temperature (600-700 °C) of this process compared to the conventional gasification process (800-900 °C), and the reaction activity of H_2O is relatively low compared to air, and although the H_2 concentration is very high, the conversion rate of biomass and total carbon is still low. This low conversation rate is due to the fact that a portion of the carbon remains in the solid char, and other parts go into the liquid tars, thus resulting in the lower H_2 yield, as shown in Figure 11.14. To improve the biomass/carbon conversion rate and the H_2 yield, two methods could be used:

(1) Increase the gasification temperature to enhance the reaction rate and accelerate the gasification process, thereby improving the biomass conversion rate and the H_2 yield. Considering that the temperature necessary for CO_2 absorption would enter the high range under pressurized conditions, a feasible solution might be high-temperature pressurized gasification, such as the HyPr-RING process (Lin, Harada, Suzuki, & Hatano 2002; Lin, Suzuki, Hatano, & Harada, 2001) or pressurized fluidized bed gasification (Han *et al.*, 2011).

(2) Introduce the catalysts into the gasification process to enhance the gasification reaction rate, as well as the selectivity and conversion rate of the reforming reaction of tars and carbonaceous gases. Introducing catalysts would realize the high conversion rate of biomass and the high H_2 selectivity in the product gas at relatively low temperatures. Such catalysts include Fe/CaO (calcined dolomite) and Ni/CaO (calcined dolomite) catalysts (Di Felice *et al.*, 2009; Di Felice, Courson, Foscolo, & Kiennemann, 2011), Ni-Mg-Al-CaO catalysts

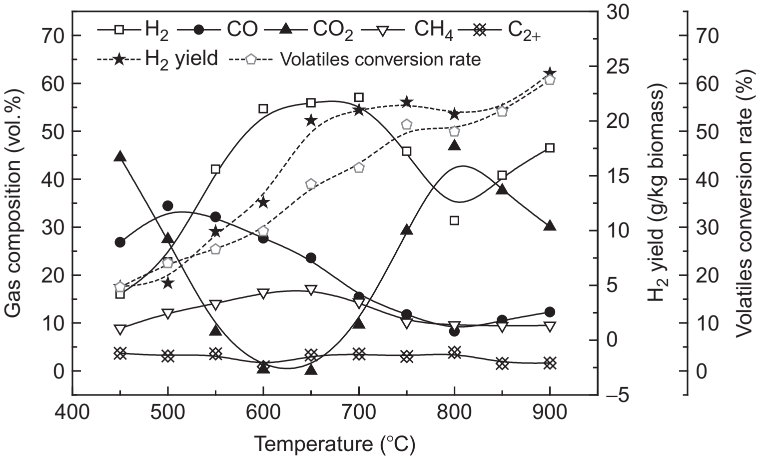

Figure 11.14 Gasification properties of CaO-sorption-enhanced biomass fast pyrolysis/steam gasification.

(Nahil *et al.*, 2013), and Pd-Co-Ni + dolomite catalysts (Fermoso, Rubiera, & Chen, 2012), etc. For example, Nahil *et al.* (2013) found that over 80% H_2 was produced with a Ni-Mg-Al-CaO bed during biomass gasification.

11.9 Mathematical simulation of biomass gasification

In order to understand the biomass gasification process and to optimize the design and operation of the biomass gasifier, implementers must conduct an extensive investigation of biomass gasification behavior and the involved operating parameters. However, performing experiments is impossible and dangerous in some cases. Instead, mathematical modeling can give us the expected result. So far, many investigations involved mathematical and computational approaches. Overall, mathematical modeling can be categorized into the use of equilibrium, kinetic, and neural networks (Ahmed, Ahmad, Yusup, Inayat, & Khan, 2012).

11.9.1 Thermodynamic equilibrium models

The “equilibrium model” refers to thermodynamic equilibrium models, such as models of chemical reaction equilibrium, which are based on the minimization of the Gibbs free energy of the system. Gibbs free energy is minimized when the species of a reaction system reach equilibrium and will no longer experience any change over time.

Mansaray, Ghaly, Al-Tawell, Ugursal, and Hamdullahpur (2000) simulate rice husk gasification based on material balance, energy balance, and chemical equilibrium relations. Their model attempted to predict the core, annulus, and exit temperatures; the mole fractions of the combustible components of the gas; the higher heating value of the gas; and the overall carbon conversion under various operating conditions, including bed height, fluidization velocity, equivalence ratio, and the moisture content of rice husk.

However, the definition of chemical equilibrium implies that the residence time is long enough to allow the chemical reactions to reach stasis, which is rarely reached in real gasifier. Hence, in some research, the models employed the restricted equilibrium method (Doherty, Reynolds, & Kennedy, 2009), and the temperature approach for the gasification reactions was specified. Li *et al*. (2004) introduced a phenomenological model that incorporated experimental results regarding unconverted carbon and methane to account for non-equilibrium factors, and this model predicted product gas compositions, heating value, and cold gas efficiency in good agreement with the experimental data.

Thermodynamic equilibrium models, which only take into account thermodynamic limitations, inherently disregard specific reaction mechanisms that are independent of the gasifier design (Jand, Brandani, & Foscolo, 2006). Also, the results may not be achieved at low temperatures, so the calculations may not be representative of the real situation, when kinetic constraints become the major factor (Ju *et al*., 2009). Hence, thermodynamic equilibrium models cannot produce accurate results, but these models are efficient for the process of optimizing and prediction (Ju *et al*., 2009; Mahishi & Goswami, 2007).

11.9.2 Kinetics models

Kinetic models differ from thermodynamic equilibrium models, as they describe the char reduction process using kinetic rate expressions obtained from experiments, thereby permitting better simulation of the experimental data when the residence time of gas and biomass is relatively short.

Kaushal, Abedi, and Mahinpey (2010) developed a one-dimensional steady state model with two phases (bubble and emulsion) and two zones (bottom dense bed and upper freeboard). This model was based on global reaction, kinetic, mass, and energy balances of biomass gasification in bubbling fluidized gasifiers, and it is capable of predicting temperature, solid hold up, and gas concentration along the reactor's major axis.

Wu, Zhang, Yang, and Blasiak (2013) built a two-dimensional computational fluid dynamics (CFD) model to study the gasification process in a downdraft configuration, considering drying, pyrolysis, combustion, and gasification reactions. The gas and solid phases were resolved using an Euler-Euler multiphase approach, with exchange terms for the momentum, mass, and energy.

Miao *et al*. (2013) developed a new mathematical model that combined hydrodynamics with chemical reaction kinetics to predict the overall performance of a biomass gasification process in fluidized beds. The fluidized bed gasifier was divided into two distinct sections: a dense region at the bottom and a dilute region at the top. Each section was divided into a number of small cells, over which mass and energy balances were applied. The model is capable of predicting the bed temperature distribution along the gasifier, the concentration and distribution of each species in the vertical direction of the bed, the composition and heating value of produced gas, the gasification efficiency, the overall carbon conversion, and the produced gas production rate well.

Kinetic models provide essential information on kinetic mechanisms to describe the conversion during biomass gasification, which is crucial in designing, evaluating, and improving gasifiers. These kinetic models are accurate and detailed, but they are also computationally intensive. In addition, the basic experiment data is necessary when constructing and running the models. Sometimes, thermodynamic equilibrium models have been combined with kinetic models. Lee, Yang, Yan, and Liang (2007) extracted substitutable gas phase compositions from thermodynamic calculations, before entering the gas phase compositions into the Sandia PSR code to consider the potential kinetic constraints involved in the pyrolysis. Lee and colleagues also hoped to obtain the distributions of gas products. The result, in this case, is much closer to the realistic situation (Lee *et al.*, 2007).

11.9.3 Neural networks model

Artificial neural networks are normally based on mathematical regression to correlate input and output streams to and from process units. Such models principally rely on a large number of experimental data. Guo, Li, Cheng, Lu, and Shen (2001) created a hybrid neural network model for the purpose of predicting biomass gasification profiles at atmospheric pressure with steam. Artificial neural networks differ from traditional regression because they have more potential for finding the unseen structure (Guo *et al.*, 2001).

Each type of model has its own strengths and limitations, as mentioned above. In order to achieve efficient calculation and design, Brown, Fuchino, and Mar Chal (2006) combined the three models together, given that fuels and chars are defined as pseudospecies with properties derived from their ultimate analyses, and tars are defined as a subset of known molecular species with their distribution determined by equilibrium calculations. While the reforming of gas, tar, and char formation was explained by applying reaction temperature differences to a complete set of stoichiometric equations, the changes in temperature related to fuel composition and operational variables were determined with nonlinear regression via an artificial neural network. This method improves the accuracy of equilibrium calculations and reduces the amount of required data by preventing the neural network from learning atomic and heat balances.

11.10 Conclusion and future trends

Biomass is an accepted form of renewable energy, and it plays a pivotal role in helping the world reduce the environmental impacts of burning fossil, such as global warming and acid rain. Gasification is a versatile thermochemical conversion process that produces a gas mixture of CH_4, CO, and H_2. The relative yields of these substances are determined by operating conditions, such as the gasification agent and reactor configurations.

Catalyzed tar reforming is essential to biomass gasification, and this chapter summarizes the effects and activities of three types catalyst (dolomite, alkali metals, and nickel). These catalysts effectively increase gas productivity and reduce carbon deposition. Dolomite and alkali metals are often mixed with biomass feedstocks, and studies showed that Ni metal was most productive as a secondary catalyst located in a downstream reactor.

Staged biomass gasification is an optimum choice for biomass gasification with high char conversion and low tar content, and the three-stage biomass gasifier has approached 98% carbon conversion efficiency. Sorption-enhanced steam gasification, on the other hand, is a novel one-step conversion technology developed for the production of high concentration H_2 from biomass. The H_2 concentration could increase from 40% to about 75% or higher as CaO or a CaO-based catalyst is added.

Biomass gasification has shown unique advantages. With syngas, however, there are still some challenges, such as particulates, hydrocarbons, and alkali compounds in the gas product. A lot of research is needed regarding the gasification process, and academia and industry must continue to develop and demonstrate new technologies, with the intention of creating large-scale real-world applications.

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Waste gasification for synthetic liquid fuel production

12

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12.1 Introduction

Waste is an unavoidable by-product of human activity, and rising living standards have led to increases in the quantity and complexity of generated waste, while industrial diversification and the provision of expanded healthcare facilities have added substantial quantities of industrial and biomedical waste. Waste disposal (landfill) operations are being stretched to the limit, and suitable disposal areas are in short supply. The potential for rainwater and snowmelt to carry the chemical constituents of waste from landfills into the groundwater table is of immediate concern. Thus, the management and safe disposal of the growing volume of waste is extremely important.

Gasification is a unique process that transforms any carbon-based material, such as municipal solid waste (MSW), into energy without burning it by converting the carbonaceous components of the waste into gaseous products, including synthesis gas, which is of prime importance in the current context. Gasification also allows for the removal of pollutants and impurities, resulting in clean gas that can be converted into electricity and valuable products (Chapters 1 and 6). With gasification, MSW and other types of wastes are no longer environmental threats, but feedstocks for gasifiers. Instead of generating costs associated with disposal and landfill management, this waste can now serve as a feedstock for a gasification process, reducing disposal costs and landfill space, while producing electricity and fuels.

Initially, the gasification process was applied to coal as a means of producing fuel gases, chemicals, and electricity, but gasification has evolved considerably in terms of utilization of feedstocks other than coal, as well as the technologies used for the process. As a result, gasification now represents a significant advance over the incineration process (Chapters 1 and 2) (E4Tech, 2009; Malkow, 2004; Orr & Maxwell, 2000; Speight, 2008, 2011a, 2011b, 2013a, 2013b, 2014). In order to understand the advantages of the gasification of waste compared to incineration, one must understand the differences between the two processes.

Incineration, which does have a place in waste disposal operations, uses MSW as a fuel (Mastellone *et al.*, 2010). The waste is burned with high volumes of air to form carbon dioxide and heat. In a waste-to-energy plant that uses incineration, the hot gaseous products are used to generate steam, which is then used in a steam turbine to generate electricity. On the other hand, gasification converts MSW into usable synthesis gas, and the production of this synthesis gas makes gasification different from the incineration process. In the gasification process, the MSW is not a fuel but a

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feedstock for a high-temperature chemical conversion process. Instead of only making heat and electricity, as is done with incineration, gasification produces synthesis gas that can be turned into higher-value commercial products such as transportation fuels, chemicals, fertilizers, and substitute natural gas.

In addition, one of the concerning features of MSW incineration is the formation and reformation of toxic dioxins and furans, especially from PVC plastics (polyvinyl chloride plastics). These toxins enter exhaust streams via three pathways: (1) by decomposition into low-molecular-weight volatile constituents, (2) by reforming in which lower molecular weight constituents combine to form new products, and (3) by the unusual step of passing through the incinerator without change. Incineration does not always allow adequate control of these processes.

With respect to MSW disposal, gasification is significantly cleaner than incineration. In the high temperature environment required for gasification, materials with higher molecular weights, such as plastics, are effectively decomposed to synthesis gas, which can be cleaned and processed before any further use. Dioxins and furans need sufficient oxygen to form, and the oxygen-deficient atmosphere in a gasifier does not provide the environment needed for the formation of dioxins and furans. When the synthesis gas is primarily used as a fuel for making heat, it can be cleaned as necessary *before* combustion, a measure that cannot occur in incineration.

Thus, waste-to-energy plants based on gasification are high-efficiency power plants that utilize MSW as fuel rather than conventional sources of energy such as coal or petroleum. The cogasification of waste with biomass, coal, petroleum residua, and biomass is always an option, however (Speight, 2011a, 2011b, 2013a, 2013b, 2014). In either case, such plants recover the thermal energy contained in the waste in highly efficient boilers that generate steam to be used to drive turbines for electricity production.

This chapter presents descriptions of the various types of waste and the recovery of energy from waste by gasification, illuminating the benefits of the process, including (1) the reduction of the total quantity of waste depending on the waste composition and the gasification technology employed, (2) the reduction of environmental pollution, and (3) the improved commercial viability of the waste disposal project due to the sale of energy and related products.

12.2 Waste types

Also called *garbage* or *trash* in the United States, waste is a substance, object, or collection of substances and objects selected for disposal or required to be disposed of by the provisions of local, regional, or national laws. In addition, waste is also a substance or object that is not the prime product of a process or processes. The initial user has no further use for this product in terms of the stated objectives of production, transformation, or consumption, and, as result, he or she wishes to dispose of it. Wastes may be generated during the extraction of raw materials, the processing of raw materials into intermediate and final products, the consumption of final products, and other human activities.

12.2.1 Solid waste

Solid waste is a general term that includes garbage; rubbish; refuse; sludge from a wastewater treatment plant, water supply treatment plant, or air pollution control facility; sewage sludge; and other discarded material, including solid, liquid, semisolid, or contained gaseous material resulting from industrial, municipal, commercial, mining, and agricultural operations, as well as from community and institutional activities. Whether natural or of human origin, oil, dirt, rock, sand, and other inert solid materials used to fill land are not classified as waste if the objective of the fill is to make the land suitable for the construction of surface improvements. Solid waste does not include waste materials that result from activities associated with the exploration, development, or production of oil, gas, geothermal resources, or other substances or materials regulated by local or federal governments.

Solid waste that is typically excluded from gasification feedstocks includes uncontaminated solid waste resulting from the construction, remodeling, repair, and demolition of utilities, structures, and roads, as well as uncontaminated solid waste resulting from land clearing. Such waste includes, but is not limited to, bricks, concrete, other masonry materials, soil, rock, wood (including painted, treated, and coated wood and wood products), land clearing debris, wall coverings, plaster, drywall, plumbing fixtures, nonasbestos insulation, roofing shingles, other roof coverings, asphaltic pavement, glass, plastics that are not sealed in a manner that conceals other wastes, empty buckets (10 gallons or less in size and having no more than 1 inch of residue remaining on the bottom), electrical wiring and components containing no hazardous liquids, and pipe and metals that are incidental to any of the above.

In summary, as used in this text, the term *solid waste* refers to any unwanted or discarded carbonaceous (containing carbon) or hydrocarbonaceous (containing carbon and hydrogen) material that originates from a variety of sources and is not a liquid or a gas. Furthermore, the disposal of a wide variety of wastes has become an important problem because the traditional means of disposal in a landfill has become much less acceptable in recent years due to concerns about the environmental impacts of the practice. Newer and stricter regulation of the conventional disposal methods has made waste processing for resource recovery much more favorable economically.

However, before moving on to the various aspects of the gasification process, it is worthwhile to describe in more detail the types of waste that arise from human activities and which might be suitable for gasification.

12.2.2 Municipal solid waste

MSW is solid waste resulting from, or incidental to, municipal, community, commercial, institutional, and recreational activities, and it includes garbage, rubbish, ashes, street cleanings, dead animals, medical waste, and all other nonindustrial solid waste.

MSW is generated by households, offices, hotels, shops, schools, and other institutions. The major components of MSW are food waste, paper, plastic, rags, metal, and glass, although demolition and construction debris is often included in collected waste, as are small quantities of hazardous waste, such as electric light bulbs, batteries, automotive parts, and discarded medicines and chemicals.

MSW is a negatively priced, abundant, and essentially renewable feedstock. The composition of MSW (Table 12.1) can vary from one community to the next, but the overall differences are not substantial. In fact, there are several types of waste that might also be classified within the MSW umbrella (Table 12.2).

The heat content of raw MSW depends on the concentration of combustible organic materials in the waste and its moisture content. Typically, raw MSW has a heating value of approximately half that of bituminous coal (Speight, 2013a). The moisture content of raw MSW is usually 20% w/w.

12.2.3 Industrial solid waste

Industrial solid waste is solid waste resulting from or incidental to any process of industry, manufacturing, mining, or agricultural operations. Industrial solid waste is classified as either *hazardous* or *nonhazardous*. Hazardous industrial waste includes any industrial solid waste or combination of industrial solid wastes identified or listed as a hazardous waste. Nonhazardous industrial waste is an industrial solid waste that is not identified or listed as a hazardous waste.

Industrial solid waste encompasses a wide range of materials of varying environmental toxicity. Typically, this range includes paper, packaging materials, waste from food processing, oils, solvents, resins, paints and sludge, glass, ceramics, stones, metals, plastics, rubber, leather, wood, cloth, straw, and abrasives. As with MSW, the absence of a regularly updated and systematic database on industrial solid waste ensures that the exact rates of generation are largely unknown.

A generator of industrial solid waste must classify the waste as:

- Class 1 waste: The class of waste includes any industrial solid waste or mixture of industrial solid wastes with a concentration level or physical or chemical characteristics that make it toxic; corrosive; flammable; a strong sensitizer or irritant; or a generator of sudden pressure

Table 12.1 General composition of municipal solid waste

Component	% (w/w)
Paper	33.7
Cardboard	5.5
Plastics	9.1
Textiles	3.6
Rubber, leather, “other”	2.0
Wood	7.2
Horticultural wastes	14.0
Food wastes	9.0
Glass and metals	13.1

Source: EPA 530-S-97-015, 1997.

Table 12.2 Sources and types of waste

Source	Typical waste generators	Types of solid wastes
Residential	Single and multifamily dwellings	Food wastes, paper, cardboard, plastics, textiles, leather, yard wastes, wood, glass, metals, ashes, special wastes (e.g., bulky items, consumer electronics, white goods, batteries, oil, tires), and household hazardous wastes.)
Industrial	Light and heavy manufacturing, fabrication, construction sites, power and chemical plants	Housekeeping wastes, packaging, food wastes, construction and demolition materials, hazardous wastes, ashes, special wastes
Commercial	Stores, hotels, restaurants, markets, office buildings, etc.	Paper, cardboard, plastics, wood, food wastes, glass, metals, special wastes, hazardous wastes
Institutional	Schools, hospitals, prisons, government centers	Same as commercial
Construction and demolition	New construction sites, road repair, renovation sites, demolition of buildings	Wood, steel, concrete, dirt, etc.
Municipal services	Street cleaning, landscaping, parks, beaches, other recreational areas, water and wastewater treatment plants	Street sweepings; landscape and tree trimmings; general wastes from parks, beaches, and other recreational areas; sludge
Process (manufacturing, etc.)	Heavy and light manufacturing, refineries, chemical plants, power plants, mineral extraction and processing	Industrial process wastes, scrap materials, off-specification products, tailings
Agriculture	Crops, orchards, vineyards, dairies, feedlots, farms	Spoiled food wastes, agricultural wastes, hazardous wastes (e.g., pesticides)

by decomposition, heat, or other means, Class 1 wastes may also pose a substantial present or potential danger to human health or the environment when improperly processed, stored, transported, or disposed of or otherwise.

- Class 2 waste: This class of waste consists of any individual industrial solid waste or combination of industrial solid wastes that are not described as hazardous, Class 1, or Class 3.
- Class 3 waste: The class of waste consists of inert and essentially insoluble industrial solid waste, usually including, but not limited to, materials such as rock, brick, glass, dirt, and certain plastics and rubbers that are not readily decomposable.

12.2.4 Biosolids

Biosolids include livestock waste, agricultural crop residues, and agroindustrial by-products. In most traditional, sedentary agricultural systems, farmers use the land application of raw or composted agricultural wastes as a means of returning valuable nutrients and organics back into the soil, and this practice remains the most widespread means of disposal. Similarly, fish farming communities commonly integrate fish rearing with agricultural activities such as livestock husbandry, vegetable and paddy cultivation, and fruit farming.

Many countries with agriculture-based economies use agricultural wastes to produce biogas through anaerobic digestion (Speight, 2008, 2011a). The biogas (approximately 60% v/v methane) is primarily used directly for cooking, heating, and lighting, while the slurry from the anaerobic digesters is used as liquid fertilizer, feed supplements for cattle and pigs, and a medium for soaking seeds.

12.2.5 Biomedical waste

Biomedical waste refers to the waste materials produced by hospitals and health care institutions, which have been increasing over the past four decades to meet the medical and health care requirements of the growing world population. Until recent years, little attention was paid to biomedical wastes, which are potentially hazardous to human health and the environment. In fact, serious concern has arisen regarding the potential for spreading pathogens, as well as causing environmental contamination due to the improper handling and management of clinical and biomedical waste.

Regulated medical waste (RMW) is a waste stream that contains potentially infectious material, also called *red bag waste* or *biohazardous waste*. RMW is regulated on a state-by-state basis, but it also falls under the Bloodborne Pathogen Standard as defined by the US Office of Safety and Health Administration. Such wastes are subject to state and federal regulations, may not be suitable as gasification feedstock, and require higher processing temperatures to assure complete disposal of the constituents.

12.3 Feedstock properties and plant safety

When using the described waste streams in a waste-to-energy gasification plant, one must consider the feedstocks' varied constituents, as well as any safety and health issues that might arise from the use of such feedstocks.

In fact, feedstock materials typically comprise biomass waste (or biomass), MSW, refuse-derived fuel (RDF), or solid recovered fuel, and the composition of these waste materials does not always allow for accurate predictions about how the feedstocks will behave during the gasification process (Speight, 2011a).

12.3.1 Feedstock properties

The individual feedstock constituents typically have their own hazards, including fire, dust explosion, and toxic gas formation, but when constituents are used in combination, handling the combined feedstocks may require extra precautions to ensure safety. For example, where feed materials such as biomass wood are stored in large piles, there is potential for selfheating or spontaneous ignition, which is always an issue when coal is stockpiled (Speight, 2013a, 2013b). Wood fuel is a source of nutrients for microbes, and in the presence of moisture, microbial activity can lead to the generation of heat in the wood over time, resulting in selfignition. Other feed safety considerations include hazards associated with dust, such as explosion hazards requiring protection through hot particle detection and explosion venting.

12.3.2 Plant safety

The gasification process produces a highly flammable gaseous mixture, including hydrogen and the extremely toxic carbon monoxide. In plant sections where pressure buildup exists, there is a risk of gas escaping into the atmosphere. Therefore, precautions are necessary to prevent such escape of toxic or environmentally destructive gases. The areas outside the equipment must be adequately ventilated to prevent buildup of an explosive atmosphere, but also to prevent poisoning due to carbon monoxide accumulation. Carbon monoxide detection equipment should be provided to detect possible leaks.

Thus, the gasification of waste introduces a series of safety issues that are, in fact, closely related to safety issues in chemical processing plants. These hazards are well understood in the chemical processing industries, where safety techniques, including hazard and operability, layers of protection analysis, and safety integrity level (SIL), have evolved to ensure the safe design and operation of plants. Crossindustry cooperation will result in quicker, safer implementation of new technology, greatly reducing the risk of a catastrophic incident.

Unlike conventional energy plants, which are numerous, waste gasification plants do not yet follow uniform design standards, and this variability makes the construction and operation of a waste gasification plant particularly challenging. Although guidance is now becoming available, the multitude of gasification technologies and available reactor configurations often defy the application of recommended practices. The chemical processing industry has a wealth of experience with the techniques required to ensure that plants meet the high standards of employee safety, however, and implementing these techniques to gasification is necessary to ensure safety and meet environmental standards.

12.4 Fuel production

Solid waste gasification includes a number of physical and chemical interactions that occur at temperatures generally higher than 600 °C (1110 °F), with the exact temperature depending on the reactor type and the waste characteristics, such as the ash softening and melting temperatures (Arena, 2012; Higman & van der Burgt, 2003). Different types of waste gasification processes are classified on the basis of oxidation medium. Gasification types include partial oxidation with air, oxygen-enriched air, or pure oxygen; steam gasification; and plasma gasification. Some processes are operated with oxygen-enriched air. Oxygen-enriched air is a mixture of nitrogen and oxygen with an oxygen content higher than 21% v/v but less than 50% v/v. This medium produces a gas with a higher heating value as a consequence of the reduced nitrogen content, and as a result, gasification with oxygen-enriched air can carry out autothermal processes at higher temperatures, without the expensive consumption of oxygen (Mastellone, Santoro, Zaccariello, & Arena, 2010a). The partial oxidation process using pure oxygen generates synthesis gas free (or almost free) of atmospheric nitrogen. The steam gasification option generates a high hydrogen concentration, as well as nitrogen-free synthesis gas with a medium heating value. In this case, steam is the only gasifying agent, and the process does not include exothermic reactions. The steam process does need an external source of energy, however, for the endothermic gasification reactions.

Regardless of the medium used, two main steps have been proposed for the thermal degradation of MSW: (1) thermal degradation at temperatures from 280 to 350 °C (535-660 °F) consisting mainly of the decomposition of any waste biomass component into low-boiling hydrocarbons (methane, ethane, and propane) and (2) thermal degradation at temperatures from 380 to 450 °C (715-840 °F) for the processing of polymer components, such as plastics and rubber. The polymer component can also involve significant amounts of benzene derivatives, such as styrene (Kwon, Westby, & Castaldi, 2009). However, the complexity of MSW should warrant more complex thermal decomposition regimes than the two proposed.

In the case of plasma gasification (Lemmens *et al.*, 2007; Moustakas, Fatta, Malamis, Haralambous, & Loizidou, 2005), the heat source of the gasifier is one or more plasma arc torches that create an electric arc and produce a very high temperature plasma gas (up to 15,000 °C, 27,000 °F). This gas, in turn, allows temperature control independent from fluctuations in the feed quality and the supply of a gasification agent (air, oxygen, or steam). As a result, the gasifier can operate consistently despite variations in the feeding rate, moisture content, and elemental composition of the waste material: plasma gasifiers can therefore accept feedstocks of variable particle size, containing coarse lumps and fine powders, with minimal feed preparation (Gomez *et al.*, 2009).

12.4.1 Preprocessing

Gasification is a thermochemical process that generates a gaseous, fuel-rich product (Chapter 1), and regardless of how the gasifier is designed (Chapter 2), two processes must take place in order for the gasifier to produce a useable fuel gas. In the first stage, pyrolysis releases the volatile components of the fuel at temperatures below 600 °C (1110 °F). The by-product of pyrolysis that is not vaporized is *char* and consists mainly of fixed carbon and ash. In the second gasification stage, the char that remains after pyrolysis is either reacted with steam or hydrogen or combusted with air or pure oxygen. Gasification with air results in a nitrogen-rich, low-Btu fuel gas. Gasification with pure oxygen results in a higher quality mixture of carbon monoxide and hydrogen and virtually no nitrogen. Gasification with steam (steam reforming) (Chapter 6) also results in a synthesis gas that is rich in hydrogen and carbon dioxide, with only minor amounts of impurities (Richardson, Rogers, Thorsness, Wallman, & Leininger, 1995). Typically, the exothermic reaction between the feedstock carbon and oxygen provides the heat energy required to drive the pyrolysis and char gasification reactions.

MSW is not a homogenous waste stream. Given that inorganic materials (metals, glass, concrete, and rocks) do not enter into the thermal conversion reactions, part of the energy that could be used to gasify the feedstock is expended in heating the inorganic materials to the pyrolysis reactor temperature. Then the inorganic materials are then cooled in cleanup processes, and the heat energy is lost, reducing the overall efficiency of the system. To make the process more efficient, some preprocessing of the waste is typically required and includes the separation of thermally nondegradable material, such as metals, glass, and concrete debris. Preprocessing may include sorting, separation, size reduction, and densification (for reducing overall volume of feedstock being fed into the gasifier). Such preprocessing techniques are common in the waste recycling industry for recovery of paper, glass, and metals from the MSW streams.

Thus, the first function of the front-end (preprocessing) system is to accept solid waste directly from the collection vehicle and to separate the solid waste into two parts, combustible waste and noncombustible waste. The front-end separation produces the feedstock for the gasification process.

In order to enhance the process before gasification begins, feedstock pregasification systems (preprocessing systems) extract metals, glass, and inorganic materials, resulting in the increased recycling and utilization of materials. In addition, a wide range of plastics cannot be recycled as feedstocks for gasification. Thus, the main steps involved in preprocessing MSW are analogous to the preprocessing of coal (Speight, 2013a, 2013b) or biomass (Speight, 2008, 2011a). These steps include (1) manual or mechanical sorting, (2) shredding, (3) grinding, (4) blending with other materials, (5) drying, and (6) pelletization. The purpose of pre-processing is to produce a feed material with, as best as can be achieved, near-consistent physical characteristics and chemical properties. Preprocessing operations are also designed to produce a material that can be safely handled, transported, and stored prior to the gasification process. In addition, particle size or pellet size affects the product distribution (Luo *et al*., 2010).

If the MSW has a high moisture content, a dryer may be added to the preprocessing stage to lower the moisture content of the waste stream to 25% w/w, or lower (CH2MHill, 2009). Lowering the moisture content of the feedstock increases its heating value, and as a result, the system becomes more efficient. The waste heat or fuel produced by the system can be used to dry the incoming MSW.

In some cases, the preprocessing operation may be used for the production of a combustible fraction (a solid fuel) from MSW and from mixed waste, and its thermal conversion requires two basic and distinct subsystems, the *front-end* and the *back-end*. The combustible fraction recovered from mixed MSW has been given the name RDF.

The composition of the recovered combustible fraction is a mixture that has higher concentrations of combustible materials, such as paper and plastics, than those present in the parent mixed MSW.

The main components or unit operations of a front-end subsystem are usually any combination of size reduction, screening, magnetic separation, and density separation (e.g., air classification). The types and configurations of unit operations selected for the front-end design depend on the types of secondary materials that will be recovered and on the desired quality of the recovered fuel fraction. The designer or supplier of the thermal conversion system must specify the fuel quality.

Typically, systems that recover a combustible fraction from mixed MSW utilize size reduction, screening, and magnetic separation. Some designs and facilities have used screening, followed by size reduction in the form of pretrommel screening (a trommel is a drum screen), as the fundamental foundation of the system design, while others have reversed the order of these two operations. A number of considerations enter into the determination and selection of the optimum order of screening and size reduction for a given application. Among others, the considerations include composition of the waste. The system design may also include other unit operations, such as manual sorting, magnetic separation, air classification, and pelletization (i.e., densification), as the need arises for recovery of other materials, such as aluminum, and for achieving the desired specification of the solid fuel product (Diaz & Savage, 1996).

12.4.2 Gasifier types

The gasifier is the core of the gasification system and is a *vessel* where the feedstock reacts with oxygen (or air) at high temperatures (Chapters 1 and 10) (E4Tech, 2009). In order to accommodate the different feedstocks and process requirements, there are several gasifier designs (Chapter 2), which are distinguished by (1) the use of wet or dry feedstock, (2) the use of air or oxygen, (3) the flow direction within the gasifier (upflow, downflow, or circulating flow), and (4) the cooling process for the synthesis gas and other gaseous products.

12.4.2.1 Counter-current fixed bed gasifier

In the countercurrent fixed bed gasifier (*updraft gasifier*), the gasification agent (steam, oxygen, and/or air) flows through a fixed bed of waste in countercurrent configuration. The ash is either removed in the dry condition or as a slag. The slagging gasifiers have a lower ratio of steam to carbon, achieving temperatures higher than the ash fusion temperature. The nature of the gasifier means that the fuel must have high mechanical strength and must ideally be noncaking so that it will form a permeable bed, although recent developments have reduced these restrictions to some extent. The throughput for this type of gasifier is relatively low, but the thermal efficiency is high as the temperatures in the exiting gas are relatively low. Tar can be recycled to the gasifier, methane production can be significant at typical operation temperatures, and the product gas must be extensively cleaned before use.

In the fixed-bed or moving-bed gasifier, a deep bed of waste is present in almost all the volume of the reactor, and different zones can be distinguished, with a sequence that depends on the flow direction of the waste and gasification medium. These zones are not physically fixed and move upward and downward depending on operating conditions, so that they can overlap to some extent. In the updraft reactors, the waste is fed in at the top of the gasifier, and the oxidant intake is at the bottom, so that the waste moves countercurrently to the gases, successively passing through different zones (drying, pyrolysis, reduction, and oxidation). The fuel is dried in the top of the gasifier, so that waste with high moisture content can be used. Some of the resulting char falls and burns to provide heat. The methane and tar-rich gas leave at the top of the gasifier, and the ash falls from the grate for collection at the bottom.

12.4.2.2 Cocurrent fixed bed gasifier

The cocurrent fixed bed gasifier (*downdraft gasifier*) is similar to the countercurrent fixed-bed gasifier type, except that the gasification agent flows in a cocurrent configuration with the descending waste. Heat needs to be added to the upper part of the bed, either by combusting small amounts of the fuel or from external heat sources. The produced gas leaves the gasifier at a high temperature, and most of this heat is often transferred to the gasification agent added in the top of the bed, resulting energy efficiency is on level with the efficiency of the countercurrent type. The downdraft gasifier is configured so that the tar product must pass through a hot bed of char, and, as a result, the tar yield is much lower than the tar yield in the countercurrent fixed-bed gasifier.

In the downdraft gasifier, the waste is fed in at the top of the gasifier, while the oxidant is introduced from the top or the sides so that waste and gases move in the same direction. It is possible to distinguish the same zones of updraft gasifiers but in a different order. Some of the waste is burned, falling through the gasifier throat to form a bed of hot char that the gases pass through. This configuration ensures a high quality synthesis gas with relatively low tar content, which leaves at the base of the gasifier, with ash collected under the grate.

12.4.2.3 Fluidized-bed gasifier

In the fluidized-bed gasifier, fuel waste feedstock is fluidized in oxygen and steam or air. The ash is removed dry or as heavy agglomerates that are no longer capable of fluidization. The temperatures are relatively low in dry ash gasifiers, so the fuel must be highly reactive, and low-grade coals are particularly suitable. The agglomerating gasifiers have slightly higher temperatures and are suitable for higher rank coals. Fuel throughput in the fluidized-bed gasifiers is higher than in the fixed-bed units, but not as high as the throughput for the entrained-flow gasifier.

Fluidized-bed gasifiers include bubbling bed designs and circulating fluidized-bed designs. These are commonly used to enhance turbulence for more complete gasification of low quality, low reactivity feedstocks. Fluidized-bed gasifiers operate at low pressures and temperatures, use air instead of oxygen, and have longer feedstock residence times, along with relatively low throughput.

In a fluidized-bed gasifier, the flow of gaseous oxidant (air, oxygen, or oxygen-enriched air) is directed upwards through a distributor plate so that it permeates a bed of inert material (typically, silica sand, or olivine) located at the gasifier bottom, which contains the waste. The superficial gas velocity (the ratio between gas volumetric flow rate and the cross-sectional area) is several times larger than the *minimum fluidization velocity* that causes the drag forces on the particles to equal the weight of the particles in the bed and gives it a fluidlike behavior. This fluidlike state produces an intense mixing and gas-solid contact that allow very high heat and mass transfer. Once formed, the synthesis gas moves upwards along the vertical space above the bed height, called the *freeboard*, and leaves the reactor.

The conversion efficiency in a fixed-bed unit may be low due to the elutriation (separation of lighter particles from heavier particles) of the carbonaceous material. However, the recycling or subsequent combustion of solids can be used to increase conversion. Fluidized-bed gasifiers are most useful for fuels that form highly corrosive ash that would damage the walls of slagging gasifiers. Certain types of waste and biomass fuels generally contain high levels of corrosive ash, and the fluidized-bed gasifier is also appropriate for cogasification of these feedstocks.

12.4.2.4 Entrained-flow gasifier

In the entrained-flow gasifier, dry pulverized solids, such as preprocessed MSW, or waste slurry is gasified with oxygen in cocurrent flow. Air is also used, but much less frequently (Suzuki & Nagayama, 2011). However, when used in slurry-feed gasifiers, high-moisture feedstocks result in inefficient gasification and poor carbon conversion. When changes in the feedstock are anticipated, bench-scale or short-term testing can be used to optimize gasifier operation. Slurry-fed gasification is not recommended for MSW due to its high moisture content; dry-feed gasifiers are more applicable to MSW (CH2MHill, 2009).

The gasification reactions take place in a dense cloud of very fine particles. Most coals are suitable for this type of gasifier because of the high operating temperatures, and thus, cogasification of coal with pelletized solid waste is an option. However, the waste feedstock particles must be much smaller than they are in other types of gasifiers. In other words, the waste must be pulverized, which requires somewhat more energy than for the other types of gasifiers. By far the most energy consumption related to entrained-flow gasification is not the milling of the fuel but the production of oxygen used for the gasification.

The high temperatures and pressures in this process lend themselves to a higher throughput than can be achieved with other gasifiers, but thermal efficiency is somewhat lower, as the gas must be cooled before it can be cleaned with existing technology. Because of the high temperatures, tar and methane are not present to any great extent (if at all) in the product gas, but the oxygen requirement is higher than for the other types of gasifier units. All entrained-flow gasifiers remove the major part of the ash as a slag, as the operating temperature is well above the ash fusion temperature.

A smaller fraction of the ash is produced either as a very fine dry fly ash or as black fly ash slurry. Some fuels, in particular certain types of waste and biomass, can form slag, that is, corrosive for the ceramic inner walls that serve to protect the gasifier outer wall. However some entrained-flow types of gasifiers do not possess a ceramic inner wall, but have an inner water or steam cooled wall covered and, to some extent, protected by partially solidified slag. As a result, these types of gasifiers do not suffer severe adverse effects from corrosive slag.

If the waste is likely to produce ash with a very high ash fusion temperature, limestone or dolomite can be mixed with the waste prior to gasification (He *et al.*, 2009), and the mixing is usually sufficient to lower the fusion temperature of the ash.

Most modern large-scale gasification systems utilize the entrained-flow design. However, for MSW, fixed-bed and fluidized-bed designs predominate due to MSW's low reactivity, high moisture content, and high mineral matter content (high propensity for ash formation) (CH2MHill, 2009).

12.4.2.5 Other types

The *rotary kiln gasifier* is used in several applications, varying from the processing of industrial waste to cement production, and the reactor accomplishes two objectives simultaneously: (1) moving solids into and out of a high-temperature reaction zone and (2) assuring thorough mixing of the solids during the reaction.

The kiln is typically comprised of a cylindrical steel shell lined with abrasion-resistant refractory to prevent overheating of the metal, and it is usually inclined slightly toward the discharge port. The movement of the solids being processed is controlled by the speed of rotation (~1.5 rpm).

The *moving grate gasifier* is based on the system used for waste combustion in a waste-to-energy process. The constant-flow grate feeds the waste feedstock continuously to the incinerator furnace and provides movement of the waste bed and ash residue toward the discharge end of the grate. During the operation, stoking and mixing of the burning material allows some flexibility in the composition of the fuel for the gasifier. The thermal conversion takes place in two stages: (1) the primary chamber for gasification of the waste (typically at an equivalence ratio of 0.5) and (2) the secondary chamber for high temperature oxidation of the synthesis gas produced in the primary chamber.

The unit is equipped with a horizontal oil-cooled grate that is divided into several separate sections, each with a separate primary air supply, and a water-cooled guillotine-type controller that is installed at the inlet of the gasification unit to control the thickness of the fuel bed. The oxidation in the secondary chamber is facilitated by multiple injections of air and recycled flue gas (Grimshaw & Lago, 2010). As with the fluidized-bed gasifiers, a distinct benefit of the moving grate gasifiers is that the process can accommodate wet feedstocks (Hankalin, Helanti, & Isaksson, 2011).

12.4.3 Process design

After being preprocessed into suitable particle-size pieces or fed directly (if a gas or liquid), the waste is injected into the gasifier, along with a controlled amount of air or oxygen. The high temperature conditions in the gasifier decompose the feedstock, eventually forming synthesis gas, which consists primarily of hydrogen, carbon monoxide, and, depending upon the specific gasification technology, smaller quantities of methane, carbon dioxide, hydrogen sulfide, and water vapor. Typically, 70-85% w/w of the carbon in the feedstock is converted into synthesis gas.

The ratio of carbon monoxide to hydrogen depends in part upon the hydrogen and carbon content of the feedstock and the type of gasifier used, but the ratio can be adjusted or *shifted* downstream of the gasifier through the use of catalysts. This ratio is important in determining the type of product to be manufactured (electricity, chemicals, fuels, hydrogen) (Chapters 1 and 6). For example, a refinery would use a synthesis gas consisting primarily of hydrogen, which is important in producing transportation fuels (Speight, 2011b, 2014). Conversely, a chemical plant will require synthesis gas with approximately equal proportions of hydrogen and carbon monoxide, both of which are basic building blocks for a broad range of products, including consumer and agricultural products such as fertilizers, plastics, and fine chemicals (i.e., complex, single, or pure chemical compounds). Thus, the inherent flexibility of the gasification process to adapt to feedstock requirements and the desired product slate can lead to the production of one or more products from the same process.

As a result of gasifier selection and the prerequisites for the use of the selected reactor, the correct design of the front-end system is obviously a necessity for the successful operation of a waste-to-energy facility. The key function of the preprocessing system is the segregation of the combustible components from the noncombustible components. In the production of a RDF, particular attention must be paid to the combustion unit in which the fuel is to be burned. For example, in order to facilitate handling, storage, and transportation, it may be necessary to produce a densified fuel (i.e., a pelletized fuel) that meets necessary specifications (Pellet Fuels Institute, 2011).

Processing MSWs for the production of a fuel is a seemingly straightforward process in terms of design and system operation. The performance and operation of the processing system is strongly and fundamentally determined by the feedstock, the type of equipment chosen, and the location of the equipment in the overall processing configuration. Although some of the equipment available for waste processing applications may be well suited to the processing tasks of other industries, such as mining, waste differs substantially from the raw materials that serve as feedstocks for other industries.

The failure to recognize and account for feedstock differences can result in operational problems at waste processing facilities, such as use of equipment that was improperly applied, the use of equipment that was improperly designed, or the use of equipment that was improperly operated. Plant operators and designers must now be aware of the need for a thorough understanding of the operating parameters of each piece of equipment as those parameters pertain specifically to waste preprocessing and gasification. This need for specialized knowledge extends to a detailed familiarization with the physical and chemical characteristics of the waste feedstocks (Savage, 1996).

In summary, gasification technology is selected on the basis of feedstock properties and quality, gasifier operation, the desired product slate, and product quality. The main reactors used for gasification of MSW are fixed-bed and fluidized-bed units.

Larger capacity gasifiers are preferable for treatment of MSW because they allow for variable fuel feed, uniform process temperatures due to highly turbulent flow through the bed, good interaction between gases and solids, and high levels of carbon conversion (Chapter 2).

12.4.4 Plasma gasification

While the main types of gasifiers (Chapter 2) can be adapted for use with various waste feedstocks, plasma gasification is the object of much interest in connection with treatment of MSW.

Plasma is a high temperature, highly ionized (electrically charged) gas capable of conducting an electrical current. Plasma technology has evolved into a valuable processing option using very high temperatures (Ducharme, 2010; E4Tech, 2009; Fabry, Rehmet, Rohani, & Fulcheri, 2013; Gomez *et al*., 2009; Heberlein & Murphy, 2008; Kalinenko *et al*., 1993; Leal-Quirós, 2004; Lemmens *et al*., 2007; Messerle & Ustimenko, 2007; Moustakas *et al*., 2005). Plasma is formed by passing an electrical discharge through a gas such as air or oxygen (O_2), whereupon the interaction of the gas with the electric arc dissociates the gas into electrons and ions, causing the temperature to increase significantly. In theory, plasma temperatures often exceed 6000 °C (10,830 °F), but measurement of the temperature is not always possible, and the temperature range may be speculative.

There are two basic types of plasma torches, the *transferred torch* and the *nontransferred torch*. The transferred torch creates an electric arc between the tip of the torch and a metal bath or the conductive lining of the reactor wall. In the nontransferred torch, the arc is produced within the torch itself. The plasma gas is fed into the torch and heated, and it then exits through the tip of the torch.

In the plasma-based process, the gasifier is heated by a plasma torch system located near the bottom of the reactor vessel. In the gasifier, the feedstock is charged into a vertical reactor vessel (refractory lined or water-cooled) at atmospheric pressure. A superheated blast of air, which may be enriched with oxygen, is provided to the bottom of the gasifier, at the stoichiometric amount required for gasification. The amount of introduced air is controlled so that a low velocity of the upward flowing gas is maintained and the pulverized (small particle) feedstock can be fed directly into the reactor. Additional air and/or steam can be provided at different levels of the gasifier to assist with the pyrolysis and gasification components of the process. The temperature of the synthesis gas leaving the top of the gasifier is maintained above 1000 °C (1830 °F), and at this temperature, tar formation is eliminated.

The high operating temperatures in the plasma gasifier decompose the feedstock (and all hazardous and toxic components) and dramatically increase the kinetics of the various reactions occurring in the gasification zone, converting all organic materials into hydrogen (H_2) and carbon monoxide (CO). Any residual materials, from inorganic constituents and heavy metals, will be melted and produced as a vitrified slag, that is, highly resistant to leaching. *Magmavication* or *vitrification* is the result of the interaction between plasma and inorganic materials: in the presence of a coke bed or cokelike products in the cupola or reactor, a vitrified material is produced that can be used in the manufacture of architectural tiles and construction materials (Leal-Quirós, 2004).

Plasma gasification is increasingly considered for conversion of all types of waste, including MSW and hazardous waste, into electricity and other valuable products. The process produces the maximum amount of energy from waste, and different types of feedstocks, such as MSW and hazardous waste, can be mixed, avoiding the time-consuming and costly step of sorting the feedstock by type before it is fed into the gasifier. This makes plasma gasification an attractive option for managing different types of waste streams.

However, the main challenge facing plasma gasification is the skepticism among some observers regarding the process's ability to fully convert MSW. Synthesis gas cleanup processes and oxygen separation methods could be improved to make the economics competitive, but public perception is the real deterrent to market penetration. More experience with operating the technology in the various countries, such as the United States, and using the process with MSW in particular would help the community recognize plasma gasification as a viable component of a waste management program.

12.5 Process products

By general definition, the goal of the gasification process is to produce gaseous products, in particular synthesis gas from which hydrogen can be isolated on an as-needed basis (Chapter 6). Furthermore, the product gas resulting from waste gasification contains carbon dioxide, tar, particulate matter, halogens or acid gases, heavy metals, and alkaline compounds, depending on the feedstock composition and the particular gasification process. Downstream power-generating and gas-cleaning equipment typically requires removal of these contaminants.

12.5.1 Synthesis gas

As with many gasification processes, *waste gasification* is intended o produce a gas that can be used as fuel gas or used for hydrocarbons or chemicals production. In either case, the gas is synthesis gas, mixtures of carbon monoxide and hydrogen, and the yield and composition of the gas and related byproducts are dependent upon the properties and character of the feedstock, the gasifier type, and the conditions in the gasifier (Chapters 1 and 2) (Orr & Maxwell, 2000).

The raw synthesis gas produced in the gasifier contains trace levels of impurities that must be removed prior to its ultimate use. After the gas is cooled, virtually all the trace minerals, particulates, sulfur, mercury, and unconverted carbon are removed using commercially proven cleaning processes common to the gas processing, chemical, and refining industries (Gary, Handwerk, & Kaiser, 2007; Hsu & Robinson, 2006; Mokhatab, Poe, & Speight, 2006; Speight, 2007, 2014). For feedstocks containing mercury, more than 90% w/w of the mercury can be removed from the synthesis gas using relatively small and commercially available activated carbon beds.

12.5.2 Carbon dioxide

Carbon dioxide can also be removed during the synthesis gas cleanup stage using a number of commercial technologies (Mokhatab *et al*., 2006; Speight, 2007). In fact, carbon dioxide is routinely removed with a commercially proven process in gasification-based ammonia, hydrogen, and chemical manufacturing plants. Gasification-based plants for the production of ammonia are equipped to separate and capture approximately 90% v/v of their carbon dioxide, and gasification-based methanol plants separate and capture approximately 70% v/v of the produced carbon dioxide. In fact, the gasification process is considered to offer a cost-effective and efficient means of capturing carbon dioxide during the energy production process.

12.5.3 Tar

For the purposes of this text, tar is any condensable or noncondensable organic material in the product stream, and it is largely intractable and comprised of aromatic compounds.

When MSW is gasified, significant amounts of tar are produced, and if tar is allowed to condense (condensation temperatures range from 200 to 600 °C or 390-1110 °F), it can cause coke to form on fuel-reforming catalysts; deactivate sulfur removal systems; erode compressors, heat exchangers, and ceramic filters; and damage gas turbines and engines. Noncondensable tar can also cause problems for advanced power conversion devices, such as fuel cell catalysts, and complicate environmental emissions compliance.

The amount and composition of tars are dependent on the fuel, the operating conditions, and the secondary gas phase reactions, and tar can be divided into three categories based on the reaction temperature ranges in which it forms (Table 12.3). This categorization is important for assessing gasification processes, as the effectiveness of conversion and removal systems depends greatly on the specific tar composition and the concentration of tars in the fuel gas.

Table 12.3 General classification of tars

Category	Formation temperature	Constituents
Primary	400-600 °C 750-1110 °F	Mixed oxygenates, Phenolic ethers
Secondary	600-800 °C 1110-1470 °F	Alkyl phenols, Heterocyclic ethers
Tertiary	800-1000 °C 1470-1830 °F	Polynuclear aromatic hydrocarbons Phenolic ethers

The primary tars are mixed oxygenates and are a product of pyrolysis. As gasification takes over at higher temperatures, the primary products thermally decompose to lesser amounts of secondary and tertiary products and a greater quantity of light gases. Tertiary products are the most stable and difficult to crack catalytically. Provided that there is adequate gas-mixing, primary and tertiary tars are mutually exclusive in the product gas. Both lignin and cellulose in the fuel result in the formation of tertiary tar compounds. However, lignin-rich fuels have been shown to form heavier tertiary aromatics more quickly.

Both physical and chemical treatment processes can reduce the presence of tar in the product gas. The physical processes are classified into wet and dry technologies, depending on whether water is used. Various forms of wet or wet/dry scrubbing processes are commercially available, and these are the most commonly practiced techniques for the physical removal of tar.

Wet physical processes involve tar condensation, droplet filtration, and gas/liquid mixture separation. Cyclones, cooling towers, venturi scrubbers, baghouses, electrostatic precipitators, and wet/dry scrubbers are the primary tools in this process. The main disadvantage of using wet physical processes is that the tar is transferred to wastewater, so the heating value is lost, and the water must be disposed of in an environmentally acceptable way. Wastewater that contains tar is classified as *hazardous waste*, and treatment and disposal of the wastewater can add significantly to the overall cost of the gasification plant.

Dry tar removal using ceramic, metallic, or fabric filters are alternatives to wet tar removal processes. However, at temperatures above 150 °C (300 °F), tars can become semisolid and adhesive, causing operational problems with such barriers. As a result, dry tar removal methods are rarely implemented. Injection of activated carbon into the product gas stream or in a granular bed may also reduce tars through adsorption and collection with a baghouse. The carbonaceous material containing the tars can then be recycled back to the gasifier to encourage further thermal and/or catalytic decomposition. On other words, the tar is recycled to extinction.

Chemical tar treatment processes are the most widely practiced in the gasification industry. They can be divided into four generic categories: thermal, steam, partially oxidative, and catalytic processes. Thermal destruction has been shown to break down aromatics at temperatures above 1000 °C (1830 °F). However, such high temperatures can have adverse effects on heat exchangers and refractory surfaces due to ash-sintering in the gasification vessel. The introduction of steam does encourage reformation of primary and some secondary oxygenated tar compounds, but it has a lesser effect on many nitrogen-containing organic compounds.

The presence of oxygen during gasification has been shown to accelerate both the destruction of primary tar products, and the formation of aromatic compounds from phenol cracking increases when the oxygen content of the gas is low (less than 10% v/v). Only above 10% v/v was a decrease in the amount of tertiary tars observed. A net increase in the carbon monoxide may also be observed as the product from the oxidative cracking of tar. Benzene levels are not usually affected by the presence of oxygen.

The most widely used and studied tar cracking catalyst is dolomite, which is a mixture of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$). Dolomite has been shown to work more effectively when placed in a vessel downstream from the gasifier and in a low carbon monoxide environment. However, when used within the gasifier, catalytic materials often accumulate a layer of coke that causes rapid loss of catalytic efficiency.

The specific tar conversion and destruction processes chosen depend on the nature and composition of the tars present, as well as the intended end-use equipment. However, the advantages of recycling the tar product for further treatment include increased waste-to-energy efficiency, lower emissions, and lower effluent treatment costs. Although progress had been made in mitigating tar formation and increasing tar removal, the lack of affordable, effective tar removal processes continues to provide a barrier to the widespread commercialization of integrated gasification combined cycle power generation using MSW.

12.5.4 Particulate matter

The detrimental effect of particulate matter on the atmosphere has been of some concern for several decades. Chemicals ejected into the atmosphere and from fossil fuel combustion, such as mercury, selenium, and vanadium, are particularly harmful to the flora and fauna. There are many types of particulate collection devices in use, and they involve a number of different principles for the removal of particles from gasification product streams (Speight, 2013a, 2013b). However, the selection of an appropriate particle removal device must be based upon equipment performance as anticipated or predicted under the process conditions. To enter into a detailed description of the various devices available for particulate removal is well beyond the scope of this text, but the reader should be aware of the equipment available for particulate removal and the means by which this might be accomplished: (1) cyclones, which are particle collectors that have many potential applications in coal gasification systems; (2) electrostatic precipitators, which are efficient collectors of fine particulate matter and are capable of reducing the amount of submicron particles by 90% or more, while also collecting liquid mists and dust; (3) granular-bed filters, which comprise a class of filtration equipment that is distinguished by a bed of separate, closely packed granules that serve as the filter medium for collecting particulates at high temperatures and pressures; (4) wet scrubbers, which represent a simple method to clean exhaust air or exhaust gas, removing toxic or smelling compounds via close contact with fine water drops in a cocurrent or countercurrent flow of the gas stream.

12.5.5 Halogens/acid gases

The principal combustion products of halogen-containing organic waste are either hydrogen halides, such as hydrogen chloride (HCl) or hydrogen bromide (HBr), or metal halides, such as mercuric chloride ($HgCl_2$) or mercurous chloride (HgCl). Thee substances volatilize out of the reactor along with the other gases. In the gasification of *pure* MSW, which does not contain coal, biomass, or any other added feedstock, hydrogen chloride is the prevailing chlorine-containing product. Bromine constituents can accumulate to a greater extent in the bottom ash, but in the presence of hydrogen, bromine is transformed to hydrogen bromide (HBr), which is readily removed, along with the HCl, by scrubbing systems, thus causing no emission problems.

A significant advantage of gasification is that it takes place in a reducing atmosphere, which prevents sulfur and nitrogen compounds from oxidizing. As a result, most of the elemental nitrogen or sulfur in the waste stream ends up as hydrogen sulfide (H_2S), carbonyl sulfide (COS), nitrogen (N_2) or ammonia (NH_3), rather than sulfur oxides (SOx) or nitrogen oxides (NOx). The reduced sulfur species can then be recovered as elemental sulfur at efficiencies between 95% w/w and 99% w/w, or converted to a sulfuric acid by-product (Mokhatab *et al*., 2006; Speight, 2007).

The typical sulfur removal and recovery processes used to treat the raw synthesis gas are the same as commercially available methods used in other industrial applications, such as oil refining and natural gas recovery (Speight, 2007, 2008, 2014). One process commonly used to remove sulfur compounds is the selective-amine (olamine) technology, which extracts sulfur species from the synthesis gas using an amine-based solvent or related agent in an absorber tower. The reduced sulfur species removed in the solvent stripper are converted to elemental sulfur in a sulfur recovery process such as the Selectox/Claus process.

When MSW is gasified, nitrogen in the fuel is converted primarily to ammonia that, when fired in a turbine or other combustion engine, forms nitrogen oxide, a harmful pollutant. Removal of ammonia and other nitrogen compounds in the product gas prior to combustion can be accomplished with wet scrubbers or by catalytic destruction. Catalytic destruction of ammonia has been studied with dolomite and iron-based catalysts. This technique is of interest because tars are simultaneously decomposed (cracked) to lower weight gaseous compounds. Destruction of 99% v/v of the ammonia in the gas stream has been demonstrated with these catalysts.

If the product gas is first cooled, wet scrubbing with lime is also an effective ammonia removal technique. Gasification processes that use pure oxygen, steam, or hydrogen will only have nitrogen contents brought in through the fuel stream. Typical MSW has a nitrogen content of less than 1% w/w.

12.5.6 Heavy metals

Trace amounts of metals and other volatile materials are also present in MSW. These are typically toxic substances that pose ecological and human health risks when released into the environment.

Mercury found in the fly ash and flue gas is likely to be in the elemental form, but when oxidizing conditions are prevalent in the gasifier, the presence of hydrogen chloride (HCl) and chlorine (Cl_2) can cause some of the elemental mercury to form mercuric chloride ($HgCl_2$):

$$Hg + 4HCl + O_2 \leftrightarrow 2HgCl_2 + 2H_2O$$

$$Hg + Cl_2 \leftrightarrow HgCl_2$$

Volatilized heavy metals (or heavy metals that are entrained in the gas stream due to the high gas velocity) that are not collected in the gas cleanup system can bioaccumulate in the environment, where they can be carcinogenic and damage human nervous systems (Speight & Arjoon, 2012). For this reason, mercury must be removed from the product gas prior to combustion or further use. However, there has been extraordinary success removing heavy metals with activated carbon, baghouses, filters, and electrostatic precipitators (Mokhatab *et al.*, 2006; Speight, 2007, 2013a).

12.5.7 Alkalis

The primary elements causing alkali slagging are potassium, sodium, chlorine, and silica. Sufficient volatile alkali content in a feedstock causes a reduction in the ash fusion temperature and promotes slagging and/or fouling. Alkali compounds in the ash from the gasification of MSW can cause serious slagging in the boiler or gasification vessel. Sintered or fused deposits can form agglomerates in fluidized beds and on grates. Potassium sulfate (K_2SO_4) and potassium chloride (KCl) have been found to mix with flue dust and deposit or condense on the upper walls of the gasifier.

Alkali deposit formation is a result of particle impaction, condensation, and chemical reaction. Unfortunately, most deposits occur subsequent to gasification and cannot always be predicted solely on the basis of analysis of the feedstock. There are two characteristic temperature intervals for alkali metal emission. A small fraction of the alkali content is released below 500 °C (930 °F) and is attributed to the decomposition of the organic structures. Another fraction of alkali compounds is released from the char residue at temperatures above 500 °C (930 °F).

Thus, the presence of alkali metals in gasification processes is known to cause several operational problems. Eutectic systems consisting of alkali salts are formed on the surfaces of fly ash particles or on the fluidized bed material. The eutectic system is a mixture of chemical compounds or elements that have a single chemical composition that solidifies at a lower temperature than any other composition made up of the same ingredients. The semisolid or adhesive particle surfaces can lead to the formation of bed material agglomerates, which must be replaced by fresh material. The deposition of fly ash particles and the condensation of vapor-phase alkali compounds on heat-exchanging surfaces lower the heat conductivity and may eventually require temporary plant shutdowns for the removal of deposits.

The challenges of removing alkali vapor and particulate matter are closely connected, since alkali metal compounds play an important role in the formation of new particles as well as the chemical degradation of ceramic barrier filters used in some hot gas cleaning systems. The most convenient method is to cool the gas and condense out the alkali compounds.

12.5.8 Slag

Most solid and liquid feed gasifiers produce a hard glasslike by-product (*slag*, also called *vitreous frit*) that is composed primarily of sand, rock, and any minerals (or thermal derivatives thereof) originally contained in the gasifier feedstock. Slag is the result of gasifier operation at temperatures above the fusion or melting temperature of the mineral matter. Under these conditions, nonvolatile metals are bound together in a molten form until it is cooled in a pool of water at the bottom of a quench gasifier or by natural heat loss at the bottom of an entrained bed gasifier. Volatile metals, such as mercury, if present in the feedstock, are typically not recovered in the slag, but are removed from the raw synthesis gas during cleanup. Depending upon the type of mineral matter in the feedstock, the slag is usually nonhazardous and can be used in roadbed construction, cement manufacturing, or in roofing materials.

Slag production is a function of the amount of mineral matter present in the gasifier feedstock, so materials such as MSW, as well as coal and biomass, produce much more slag than petroleum residua. Regardless of the character of the feedstock, as long as the operating temperature is above the fusion temperature of the ash (as in the modern gasification technologies under discussion), slag will be produced. Aside from being influenced by the waste feedstock, the physical structure of the slag is sensitive to changes in operating temperature and pressure, and, in some cases, physical examination of the appearance of the slag can provide a good indication of carbon conversion in the gasifier.

Furthermore, because the slag is in a fused vitrified state, it rarely fails the toxicity characteristic leaching procedure protocols for metals (Speight & Arjoon, 2012). Slag is not a good substrate for binding organic compounds, so it is usually found to be nonhazardous, exhibiting none of the characteristics of a hazardous waste. Consequently, it may be disposed of in a nonhazardous landfill, or sold as an ore for the recovery of metals concentrated within its structure. The hardness of slag also makes it suitable as an abrasive or roadbed material, as well as an aggregate in concrete formulations (Speight, 2013a, 2014).

12.6 Advantages and limitations

Gasification has several advantages over the traditional disposal of MSW and other waste materials by combustion. The process takes place in a low oxygen environment that limits the formation of dioxins and large quantities of sulfur oxides (SOx) and nitrogen oxides (NOx).

Furthermore, the process requires just a fraction of the stoichiometric amount of oxygen necessary for combustion. As a result, the volume of process gas is low, requiring smaller and less expensive gas cleaning equipment. The lower gas volume is reflected in the higher partial pressure of contaminants in the off-gas, thus favoring more complete adsorption and particulate capture according to chemical thermodynamics:

$$\Delta G = -RT\ln(P_1/P_2)$$

ΔG is the Gibbs free energy of the system, T is the temperature, P_1 is the initial pressure, and P_2 is the final pressure. The lower gas volume also means a higher partial pressure of contaminants in the off-gas, which favors more complete adsorption and particulate capture.

In fact, one of the important advantages of gasification is that the contaminants can be removed from the synthesis gas prior to its use, thereby eliminating many of the types of after-the-fact (postcombustion) emission control systems required by incineration plants. Whether generated using conventional gasification or plasma gasification, the synthesis gas can be used in reciprocating engines or turbines to generate electricity, or it can be further processed to produce substitute natural gas, chemicals, fertilizers, or transportation fuels, such as ethanol. In summary, the gasification of waste generates a gas product that can be integrated with combined cycle turbines, reciprocating engines, and, potentially, fuel cells that convert fuel energy to electricity more than twice as efficiently as conventional steam boilers.

Furthermore, the ash produced from gasification is more amenable to use, as it exits from the gasifier in a molten form so that, after quench-cooling, it forms a glassy, *nonleachable* slag that can be used for cement, roofing shingles, asphalt filler, or sandblasting. Some gasifiers are designed to recover valuable molten metals in a separate stream, taking advantage of the ability of gasification technology to enhance recycling.

On the other hand, during gasification, tars, heavy metals, halogens, and alkaline compounds are released within the product gas and can cause environmental and operational problems. Tars are high molecular weight organic gases that ruin reforming catalysts, sulfur removal systems, and ceramic filters, and tars can increase the occurrence of slagging in boilers and on other metal and refractory surfaces. Alkalis can increase agglomeration in fluidized beds that are used in some gasification systems, and they can also ruin gas turbines during combustion. Heavy metals are toxic and bioaccumulate if released into the environment. Halogens are corrosive and are a cause of acid rain if emitted to the environment. The key to achieving cost-efficient, clean energy recovery from MSW gasification will be overcoming problems associated with the release and formation of these contaminants.

In terms of power generation, the coutilization of waste with biomass and/or with coal may provide economies of scale that help achieve the above-identified policy objectives at an affordable cost. In the some countries, governments propose cogasification processes as being well suited for community-sized developments, suggesting that waste should be dealt with in smaller plants serving towns and cities, rather than moved to large, central plant, thus satisfying the so-called *proximity principal*.

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Gasification for synthetic liquid fuel production: past, present, and future

13

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13.1 Introduction

Projections indicate that fossil fuels, such as coal and petroleum, will continue to dominate the energy market for at least 50 years before biomass and other forms of alternative energy take hold (Speight, 2011a, 2011b, 2013a, 2013b). Furthermore, some authorities estimate that the era of fossil fuels will near its end when cumulative production reaches 85% of the initial total reserves (Hubbert, 1962). These claims may or may not have some merit. In fact, the relative scarcity of petroleum, as compared to a few decades ago, is real, but it seems likely that the remaining reserves will continue to provide an adequate supply of energy to the world for several decades (Banks, 1992; Krey *et al.*, 2009; MacDonald, 1990; Martin, 1985; Speight, 2011c, 2013a, 2013b, 2014). The environmental issues that result from fossil fuel use are undeniable, however, and they require serious and continuous attention.

Technologies that ameliorate the effects of fossil fuel combustion on acid rain deposition, urban air pollution, and global warming must be vigorously pursued (Bending *et al.*, 1987; Vallero, 2008). This is a challenge that must not be ignored, as the effects of acid rain on the soil and water leave no doubt about the need to control its causes (Mohnen, 1988). Indeed, the recent emergence of new energy strategies and research and development programs indicate that society has begun to recognize the need to address fossil fuel use and its environmental impacts (Stigliani & Shaw, 1990; United States Department of Energy, 1990; United States General Accounting Office, 1990).

While regulations on greenhouse gases, such as carbon dioxide (CO_2), would be an immediate hurdle to the deployment of coal plants, gasification plants are better able to deal with carbon dioxide. However, with the continued uncertainty of carbon dioxide regulation, the industry is reluctant to make large investments in projects with high emissions of carbon dioxide because a cost-effective solution for reducing such emissions is not yet available. Nevertheless, the need to reduce greenhouse gas emissions can encourage the use of gasification in the long run because the carbon dioxide from a gasification plant is more amenable to capture.

As new technologies are developed, emissions may be reduced by repowering, a process through which aging equipment is replaced by more advanced and efficient substitutes. Such repowering might involve exchanging an aging unit for a newer

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combustion chamber, such as the atmospheric fluidized-bed combustor or the pressurized fluidized-bed combustor.

Indeed, many countries have recognized the vast quantity of atmospheric pollutants produced by fossil fuel use, and they have began to institute industrial emission standards. For a substance such as sulfur dioxide, the various standards are not only very specific but will become more stringent with the passage of time. In addition, heavy fines and jail terms may be issued to any pollution-minded miscreants who seek to flaunt the laws (Vallero, 2008). Nevertheless, increasing global fossil fuel use will require more stringent approaches to environmental protection than humankind has ever implemented. The need to protect the environment is strong.

13.2 Applications and products

Hydrogen and carbon monoxide, the major components of synthesis gas, are the basic building blocks of a number of other products, including fuels, chemicals, and fertilizers. In addition, a gasification plant can be designed to produce more than one product at a time (*coproduction* or *polygeneration*), such as electricity and chemicals (e.g., methanol or ammonia).

13.2.1 Chemicals and fertilizers

The process of producing energy through gasification has been in use for more than 100 years. Gasification was initially developed in the 1800s to produce town gas for lighting and heating, before being replaced by electricity and natural gas. It then continued to be used in blast furnaces. The gasification of coal was more significant in the production of synthetic chemicals, however, and it has been serving this function since the 1920s. The concept is now being considered as a means of producing much-needed chemicals, with the added benefit that low-value carbonaceous and hydrocarbonaceous feedstocks can also be gasified in a large chemical reactor. The resulting synthesis gas is cleansed and then converted into high-value products such as synthetic fuels, chemicals, and fertilizers.

Typically, the chemical industry uses gasification to produce methanol, as well as a variety of other chemicals, such as ammonia and urea, which form the foundation of nitrogen-based fertilizers and a variety of plastics. The majority of the world's operating gasification plants are designed to produce chemicals and fertilizers.

13.2.2 Substitute natural gas

Gasification can also be used to convert coal into *substitute natural gas* (SNG) by using a *methanation* reaction in which the coal-based synthesis gas, which ismostly carbon monoxide and hydrogen, can be converted to methane.

Also called synthetic natural gas, SNG is an artificially produced version of natural gas that can be derived from coal, biomass, petroleum coke, or solid waste.

The carbon-containing mass can be gasified, and the resulting synthesis gas converted to methane, the major component of natural gas. There are several advantages associated with producing SNG. In times when natural gas is in short supply, SNG from coal could be a major driver for energy security by diversifying energy options and reducing imports of natural gas, thus helping to stabilize fuel prices.

Biomass and other low-cost feedstocks, such as municipal waste, can also be used along with coal to produce SNG. The use of biomass would reduce greenhouse gas emissions, as biomass is a carbon-neutral fuel. In addition, the development of SNG technology would also boost the other gasification-based technologies, including hydrogen generation and the integrated gasification combined cycle (IGCC).

As it is identical to conventional natural gas (methane, CH_4), SNG can be transported in existing natural gas pipeline networks and used to generate electricity, produce chemicals and fertilizers, or heat homes and businesses. For many countries that lack natural gas resources, SNG enhances domestic fuel security by displacing imported natural gas that is likely to be supplied in the form of *liquefied natural gas*.

13.2.3 Hydrogen for petroleum refining

The use of hydrogen in thermal processes is perhaps the single most significant advance in refining technology during the twentieth century, and hydrogen is now employed in most refineries. In fact, now and in the future, refineries must deal with the changing availability of crude oil feedstocks and the conversion of these feedstocks into refined, transportation fuels, while complying with increasingly stringent clean fuel regulations. Refineries must also adjust to the decreasing heavy fuel oil demand and increasing supply of heavy, high-sulfur crude oils. Hydrogen network optimization can allow refineries to address clean fuel trends, to meet growing demands for transportation fuel, and to profit from their crudes (Long, Picioccio, & Zagoria, 2011). A key element of a refinery's hydrogen network analysis involves the capture of hydrogen in its fuel streams in a manner that extends its flexibility and processing options. Thus, innovative hydrogen network optimization will be a critical factor influencing refineries' future operational flexibility and profitability in a world of shifting crude feedstock supplies and ultra-low-sulfur gasoline and diesel fuel.

The process of upgrading heavy oils, residua, and related feedstocks evolved out of hydrodesulfurization processes (Ancheyta & Speight, 2007; Rana, Sámano, Ancheyta, & Diaz, 2007; Speight, 2014). In the early days, the goal was desulfurization, but the processes were later adapted to a 10-30% partial conversion operation. This new process was intended to achieve desulfurization and obtain low-boiling fractions simultaneously, by increasing severity in the operating conditions. However, as refineries have evolved and feedstocks have changed, refining heavy feedstocks has become a major issue for refineries, and several process configurations have emerged to accommodate the heavy feedstocks (Khan & Patmore, 1997; Speight, 2011a, 2014; Speight & Ozum, 2002).

As one of the two major components of synthesis gas, hydrogen is used to produce high-quality gasoline, diesel fuel, and jet fuel that meet the requirements for clean fuels in state and federal clean air regulations. Hydrogen is also used to upgrade heavy crude oil and tar sand bitumen. Refineries can gasify low-value residuals, such as petroleum coke, asphalts, tars, and some oily wastes from the refining process, to generate both the required hydrogen and the power and steam needed to run the refinery.

Thus, the gasification of petroleum residua, petroleum coke, and other feedstocks, such as biomass (Speight, 2008, 2011a, 2011b, 2014), to produce hydrogen and power may become an attractive option for refiners. The premise that the gasification section of a refinery will be the *garbage can* for deasphalter residues, high-sulfur coke, and other refinery wastes is worthy of consideration. Other processes such as ammonia dissociation, steam-methanol interaction, or electrolysis are also available for hydrogen production, but economic factors and feedstock availability affect the choice between processing alternatives.

13.2.4 Transportation fuels

Gasification is the foundation for converting coal and other solid feedstocks and natural gas into transportation fuels, such as gasoline, ultraclean diesel fuel, jet fuel, naphtha, and synthetic oils. Two options are available for converting carbonaceous feedstocks to motor fuels via gasification.

In the first option, the synthesis gas undergoes an additional process, the *Fischer-Tropsch reaction* (FT), to convert it to a liquid petroleum product. The FT process, with coal as a feedstock, was invented in the 1920s. Germany used FT-based technology during World War II, and it has been utilized in South Africa for decades. Currently, Malaysia and the Middle East also use FT processes with natural gas as the feedstock. In the second option, the *methanol-to-gasoline* process, the synthesis gas is first converted to methanol via a commercially used process, and the methanol is then converted to gasoline by reacting it over catalysts.

FT synthesis produces hydrocarbons of different chain lengths from a gaseous mixture of hydrogen and carbon monoxide. The higher-molecular-weight hydrocarbons can be hydrocracked to form diesel of excellent quality, among other products. The fraction of short-chain hydrocarbons is used in a combined-cycle plant with the remainder of the synthesis gas. As a result, the transportation sector will increasingly rely on fuel production through the gasification of biomass and the conversion of the gaseous products to FT fuels. However, large-scale, pressurized biomass gasification systems are necessary with particular attention given to the system's gas-cleaning section.

13.2.5 Transportation fuels from tar sand bitumen

Tar sand deposits (oil sands deposits) can be found in many countries throughout the world, and these feedstocks may comprise more than 65% v/v of the total world oil reserve. The two largest deposits are in Canada and Venezuela. The Canadian tar sands are distributed in three major deposits thought to cover more than 54,000 square miles (140,000 km^2), and the Alberta Energy and Utilities Board estimates that ~1.6 trillion barrels (1.6×10^{12} bbls) of crude oil equivalent are contained within the tar sand deposits of Canada. Of this amount, more than 170 billion barrels (170×10^9 bbls) are considered recoverable, but this amount is dependent on current oil prices.

Gasification is a commercially proven technology that can be used to convert petroleum coke into synthesis gas, and it is also being recognized as a means to economically generate hydrogen, power, and steam for tar sand operators in northeastern Alberta, Canada.

The tar sand deposits in Alberta are estimated to contain as much recoverable bitumen as the petroleum available from the vast oil fields of Saudi Arabia. However, converting the raw bitumen to saleable products requires extracting the bitumen from the sand and refining the separated bitumen to transportation fuels. The mining process requires massive amounts of steam to separate the bitumen from the sand, and the refining process demands large quantities of hydrogen to upgrade the raw distillates to saleable products. Residual materials from the bitumen-upgrading process include petroleum coke, deasphalted residua, vacuum residua, all of which contain unused energy that can released and captured for use by gasification. Traditionally, tar sand operators have utilized natural gas to produce the steam and hydrogen needed for the mining, upgrading, and refining processes.

Oil sands operators have most often utilized natural gas to produce the steam and hydrogen needed for the mining, upgrading, and refining processes. However, a number of operators will soon gasify coke to supply the necessary steam and hydrogen. Not only will gasification displace expensive natural gas as a feedstock, it will also enable the extraction of useable energy from what is otherwise a very low-value product (coke). In addition, traditional oil sand operations consume large volumes of water, but, with gasification, black water from the mining and refining processes can be recycled to the gasifiers, using a wet feed system, thus reducing fresh water usage and waste water management costs.

13.2.6 Power generation

Converting coal to power through gasification technology allows the continued use of domestic supplies of coal without the high level of air emissions associated with conventional coal-burning technologies. One of the advantages of the coal gasification technology is that it offers the polygeneration: coproduction of electric power, liquid fuels, and chemicals from hydrogen and the syngas generated from gasification.

Furthermore, an *integrated gasification combined cycle* power plant (IGCC power plant) combines the gasification process with a combined-cycle power block consisting of one or more gas turbines and a steam turbine. Clean synthesis gas is combusted in high-efficiency gas turbines to produce electricity. The excess heat from the gas turbines and from the gasification reaction is then captured, converted into steam, and sent to a steam turbine to produce additional electricity.

In the IGCC power plant, which is focused on power generation, the clean synthesis gas is combusted in high-efficiency gas turbines to generate electricity with very low emissions. The gas turbines used in these plants are slight modifications of proven, natural gas combined-cycle (NGCC) gas turbines that have been specially adapted for use with synthesis gas. For IGCC power plants that include carbon dioxide capture, these gas turbines are adapted to operate on synthesis gas with higher levels of hydrogen. Although state-of-the-art gas turbines are commercially ready for the high-hydrogen synthesis gas, there is a movement to develop the next generation of even more efficient gas turbines ready for carbon dioxide capture-based IGCC power plants.

The *heat recovery steam generator* (HRSG) captures heat in the hot exhaust from the gas turbines and uses it to generate additional steam that is used to make more power in the steam turbine portion of the combined-cycle unit. In most IGCC power plant designs, steam recovered from the gasification process is superheated in the HRSG to increase the overall efficiency output of the steam turbines. As a result, the IGCC combination, which includes a gasification plant, two types of turbine generators (gas and steam), and the HRSG, is clean and efficient.

Biomass fuel producers, coal producers, and, to a lesser extent, waste companies are enthusiastic about supplying cogasification power plants, and these producers realize the benefits of cogasification with alternate fuels. Cogasification technology can capitalize on a reliable coal supply with gate-fee waste, as well as biomass that allows the use of a larger plant than could be supplied just with waste and biomass. In addition, the technology offers a future option for hydrogen production and fuel development in refineries. In fact, when hydrogen is particularly valuable, oil refineries and petrochemical plants provide opportunities for gasifiers (Speight, 2011a).

13.2.7 Waste-to-energy gasification

Municipalities are spending millions of dollars each year to dispose of solid waste that, in fact, contains valuable unused energy. In addition to the expense of collecting this waste, they must also contend with increasingly limited landfill space, the environmental impacts of landfilling, and stringent bans on the use of incinerators. As a result of these challenges, municipalities are increasingly looking to gasification as a solution, transforming waste into energy rather than burying it.

The traditional waste-to-energy plant, which is based on mass-burn combustion on an inclined grate, has low public acceptability despite the very low emissions achieved over the last decade with modern flue gas cleanup equipment. This lack of popular support for mass-burn operations has led to companies having difficulty obtaining planning permissions to construct the new waste-to-energy plants that are needed. After much debate, various governments have allowed options for advanced waste conversion technologies (gasification, pyrolysis, and anaerobic digestion), but these same governments will only give credit to the proportion of electricity generated from nonfossil waste.

Gasification can convert municipal, construction, and demolition wastes that cannot otherwise be recycled into electric power or other valuable products, such as chemicals, fertilizers, and SNG. Instead of paying to dispose of these wastes, municipalities are generating income by using the wastes as valuable feedstocks for a gasifier. Gasifying municipal and other waste streams reduces the need for landfill space, decreases the generation of methane (a potent greenhouse gas) generated by bacterial action as the landfill matures, and reduces the potential for groundwater contamination from landfill sites.

Coutilization of waste and biomass with coal may provide economies of scale that help achieve the above-identified policy objectives at an affordable cost. In some countries, governments propose cogasification processes as being well suited for community-sized developments, suggesting that waste should be dealt with in smaller plants serving towns and cities, rather than moved to large, central plants, thus satisfying the so-called *proximity principal*, or the tendency to band similar entities together to achieve a common goal.

Municipalities' use of gasifiers to dispose of waste and create energy is almost a return to the days when gasification first became commercially available and every small town had a gasification plant to produce gas (hence the name *town gas*) for heating and lighting purposes.

However, it is important to add that gasification does not compete with recycling. In fact, gasification complements existing recycling programs through the creation of an added-value product (energy). Many materials, including a wide range of plastics, cannot currently be recycled or recycled any further and are ideal candidates for feedstocks in the gasification process. As the amount of waste generated increases in line with an increase in the population, and recycling rates increase to the point of overburdening the system, gasification will alleviate any potential bottlenecks through the generation of energy.

13.2.8 Biomass gasification

Biomass comprises a wide range of materials, including energy crops such as switch grass and miscanthus, agricultural sources such as corn husks, wood pellets, lumbering and timbering wastes, yard wastes, construction and demolition waste, and biosolids (treated sewage sludge). Gasification helps recover the energy locked in these materials. Gasification can convert biomass into electricity and products, such as ethanol, methanol, fuels, fertilizers, and chemicals. Thus, in addition to using the traditional coal, petroleum coke, and other traditional feedstocks, gasifiers can be designed to convert biomass.

Biomass usually has a high moisture content (along with carbohydrates and sugars). The presence of high levels of moisture in the biomass reduces the temperature inside the gasifier, which then reduces the efficiency of the gasifier. Therefore, many biomass gasification technologies require that the biomass be dried to reduce its moisture content before it is fed into the gasifier.

As with many solid feedstocks, biomass can come in a range of sizes. In many biomass gasification systems, the biomass must be processed to a uniform size or shape so that it might be fed into the gasifier at a consistent rate and to ensure that as much of the biomass is gasified as possible. However, beyond the issue of biomass availability, including the seasonal factors associated with many of the biomass feedstocks, another major concern is that more energy is expended in collecting and preparing the biomass than is generated through actual gasification, and technical hurdles to biomass use remain. In general, many countries seem to be increasingly using biomass feedstocks in response to environmental and regulatory factors, rather than free-market forces. Without tax credits or similar incentives, biomass is unlikely to be used as a base-load feedstock, and market entry is likely to involve cogasification or other blended use (Clayton, Stiegel, & Wimer, 2002).

Most biomass gasification systems use air as a gasifying agent, instead of oxygen, which is typically used in large-scale industrial and power gasification plants. Gasifiers that use oxygen require an air separation unit to provide the gaseous or liquid oxygen, and air separation is usually not cost-effective at the smaller scales used in biomass gasification plants. Thus, air-blown gasifiers use the oxygen in the air for the gasification reactions.

In general, biomass gasification plants are much smaller than the typical coal or petroleum coke gasification plants used in the power, chemical, fertilizer, and refining industries. As such, they are less expensive to build and have a smaller *facility footprint*. While a large industrial gasification plant may take up 150 acres of land and process 2500-15,000 tons per day of feedstock such as coal or petroleum coke, the smaller biomass plants typically process 25-200 tons of feedstock per day and take up <10 acres.

Currently, most ethanol in the United States is produced from the fermentation of corn. Vast amounts of corn, and the land, water, and fertilizer required to grow it, are needed to produce ethanol. As more corn is being used, some observers have raised concerns about the decreasing availability of food corn. Gasifying biomass, such as corn stalks, husks, and cobs, and other agricultural waste products, to make ethanol and synthetic fuels such as diesel and jet fuel can help break this energy-food competition.

Biomass, such as wood pellets, yard wastes, and crop wastes, and energy crops, such as switch grass and waste from pulp and paper mills, can be used to produce ethanol and synthetic diesel. The biomass is first gasified to produce syngas (synthesis gas) and then converted via catalytic processes to these downstream products.

Each year, municipalities spend millions of dollars collecting and disposing of wastes, such as yard wastes (grass clippings and leaves) and construction and demolition debris. While some municipalities compost yard wastes, composting requires a separate collection by a city, which is an expense many cities just can't afford. Yard waste and the construction and demolition debris can also take up valuable landfill space, shortening the life of a landfill. With gasification, this material is no longer a waste, but a feedstock for a biomass gasifier. And, as opposed to paying to dispose of and manage a waste for years in a landfill, using it as a feedstock reduces disposal costs and landfill space and converts wastes into power and fuels.

Thus, the benefits of biomass gasification include (1) converting what would otherwise be a waste product into high-value products, (2) reducing the need for landfill space for disposal of solid wastes, (3) decreasing methane emissions from landfills, (4) reducing the risk of groundwater contamination from landfills, and (5) producing ethanol from nonfood sources. Thus, municipalities, as well as the paper and agricultural industries, would be well advised to use gasification to reduce the disposal costs associated with these wastes, as well to produce electricity and other valuable products from these waste materials. While still relatively new, biomass gasification shows a great deal of promise. A key advantage of gasification is that it can convert nonfood biomass materials, such as corn stalks and wood wastes, to alcohols. Furthermore, unlike traditional process for making alcohols, biomass gasification does not remove food-based biomass, such as corn, from the economy.

13.3 Environmental benefits of gasification-based systems

The careless combustion of fossil fuels can account for the large majority of the sulfur oxides and nitrogen oxides released to the atmosphere. If a technology can succeed in reducing the amounts of these gases in the atmosphere, it should also succeed in reducing the amounts of urban smog, those odorous brown and gray clouds that are often visible over cityscapes and lead to the deposition of acid rain:

$$SO_2 + H_2O \rightarrow H_2SO_4 (\text{sulfurous acid})$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4 (\text{sulfuric acid})$$

$$2NO + H_2O \rightarrow HNO_2 + HNO_3 (\text{nitrous acid} + \text{nitric acid})$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + H_2O \rightarrow HNO_3 (\text{nitric acid})$$

In the United States, a growing awareness of the environmental impacts of fossil use has led the government to adopt the Clean Fossil Fuels Program to facilitate the development of pollution abatement technologies. This new attention to pollution has also led to successful partnerships between government and industry (United States Department of Energy, 1993). In addition, new laws, such as the 1990 Clean Air Act Amendments in the United States, have the potential to encourage the controlled clean use of fossil fuels (Stensvaag, 1991; United States Congress, 1990). There will be a cost associated with clean use, but industry is supportive of the measure and confident that the goals can be met.

Besides fuel and product flexibility, gasification-based systems offer significant environmental advantages over competing technologies, particularly coal-to-electricity combustion systems. Gasification plants can readily capture carbon dioxide, the leading greenhouse gas, much more easily and efficiently than coal-fired power plants. In many instances, this carbon dioxide can be sold, creating additional value from the gasification process.

Carbon dioxide captured during the gasification process can be used to help recover oil from otherwise depleted oil fields. The Dakota Gasification plant in Beulah, North Dakota, captures its carbon dioxide, while making SNG, and it then sells the carbon dioxide for enhanced oil recovery. Since 2000, this plant sent its captured carbon dioxide via pipeline to EnCana's Weyburn oil fields in Saskatchewan, Canada, where it is used for enhanced oil recovery. As a result, more than five million tons of carbon dioxide has been sequestered.

13.3.1 Carbon dioxide capture

In a gasification system, carbon dioxide can be captured using commercially available technologies, such as the *water gas shift reaction*, before it is vented into the atmosphere. Converting the carbon monoxide to carbon dioxide and capturing it prior to combustion is more economical than removing carbon dioxide after combustion, effectively "decarbonizing" or, at least, reducing the carbon in the synthesis gas.

Gasification plants manufacturing ammonia, hydrogen, fuels, or chemical products routinely capture carbon dioxide as part of the manufacturing process. According to the Environmental Protection Agency, the higher thermodynamic efficiency of the IGCC process minimizes carbon dioxide emissions, relative to the emissions of other technologies. IGCC plants offer a least-cost alternative for capturing carbon dioxide from a coal-based power plant. In addition, facilities using IGCC will experience a lower energy penalty than other technologies if carbon dioxide capture is required. While carbon dioxide capture and sequestration will increase the cost of all forms of power generation, an IGCC plant can capture and compress carbon dioxide at one-half the cost of a traditional pulverized coal plant. Other gasification-based options, including the production of motor fuels, chemicals, fertilizers, and hydrogen, have even lower carbon dioxide capture and compression costs, which will provide a significant economic and environmental benefit in a carbon-constrained world.

13.3.2 Lower air emissions

Gasification can achieve greater air emission reductions at lower cost than other forms of coal-based power generation, such as supercritical pulverized coal. Coal-based IGCC offers the lowest emissions of sulfur dioxide, nitrogen oxides, and particulate matter of any coal-based power production technology. In fact, a coal IGCC plant is able to achieve low air-emissions rates that approach those of a NGCC power plant. In addition, mercury emissions can be removed from an IGCC plant at one-tenth the cost of removal from a coal combustion plant. Technology exists today to remove more than 90% w/w of the volatile mercury from the synthesis gas in a coal-based gasification plant.

13.3.3 Solids generation

During gasification, virtually all of the carbon in the feedstock is converted to synthesis gas. The mineral material in the feedstock separates from the gaseous products, and the ash and other inert materials melt and fall to the bottom of the gasifier as a non-leachable, glasslike solid or other marketable material. This material can be used for many construction and building applications. In addition, more than 99% w/w of the sulfur can be removed using commercially proven technologies, prior to being converted into marketable elemental sulfur or sulfuric acid.

13.3.4 Reduced water use

Gasification uses ~14-24% v/v less water to produce electric power from coal, compared to other coal-based technologies, and water losses during operation are about 32-36% v/v less than the losses incurred by other coal-based technologies. This is a major issue in many countries, including the United States, where water supplies have already reached critical levels in certain regions.

13.4 A process for now and the future

Gasification differs from more traditional energy-generating process, in that it is not a combustion process, but rather a conversion process. Instead of the carbonaceous feedstock being wholly burned in air to create heat for the production of steam to drive turbines, the feedstock to be gasified is combined with steam and limited oxygen in a heated, pressurized vessel. The atmosphere inside the vessel is deficient in oxygen leading to a complex series of reactions in the feedstocks that produce synthesis gas. Moreover, using current technologies, the synthesis gas can be cleaned beyond current and proposed environmental regulatory requirements, as demonstrated by commercial chemical production plants that require ultraclean synthesis gas to protect the integrity of expensive catalysts. The clean synthesis gas can be combusted in turbines or engines using more efficient higher-temperature cycles than the conventional steam cycles associated with burning carbonaceous fuels, and as a result, the use of clean synthesis gas allows for possible efficiency improvements. Synthesis gas can also be used in fuel cells and fuel cell-based cycles with yet even higher efficiencies and exceptionally low emissions of pollutants.

Furthermore, one of the major challenges of the twenty-first century is finding a way to meet national and global energy needs, while minimizing the impact on the environment. There is extensive debate surrounding this issue, certain areas of focus have emerged: (1) production of cleaner energy from conventional fuel sources and alternative technologies, (2) use of energy sources that are environmentally sound and economically viable, (3) investment in a variety of technologies and resources to produce clean energy to meet energy needs. Gasification technologies will help to answer these challenges.

13.4.1 The process

As a time-tested, reliable and flexible technology, gasification will be an increasingly important component of this new energy equation, even leading petroleum refineries to evolve, as more gasification units are added to them (Speight, 2011a). Any investment in gasification will yield valuable future returns in clean, abundant, and affordable energy from a variety of sources (Speight, 2008, 2011b).

Gasification is an environmentally sound way to transform any carbon-based material, such as coal, refinery by-products, biomass, or even waste, to energy by producing synthesis gas that can be converted into electricity and valuable products, such as transportation fuels, fertilizers, SNG, or chemicals (Chadeesingh, 2011; Speight, 2013a).

Gasification has been used on a commercial scale for ~100 years by the coal, refining, chemical, refining, and lighting industries. It is currently playing an important role in meeting energy needs in many countries, and it will continue to play an increasingly important role as an economical manufacturing technology that produces clean, abundant energy. And, while gasification has typically been used in industrial applications, the technology is increasingly being adopted in smaller-scale applications to convert biomass and waste to energy and products.

Gasification is the cleanest, most flexible, and most reliable way to use fossil fuels and a variety of other carbonaceous or hydrocarbonaceous feedstocks. It can convert low-value materials into high-value products, such as chemicals and fertilizers, SNG, transportation fuels, electric power, steam, and hydrogen. The process can also be used to convert biomass, municipal solid waste, and other materials (that are normally burned as fuel) into a clean gas. In addition, gasification provides the most cost-effective means of capturing carbon dioxide, a greenhouse gas, when generating power with fossil fuel feedstock. Many countries also depend on high-cost imported petroleum and natural gas from politically unstable regions of the world, and gasification allows these countries to use of domestic resources to generate energy.

In fact, gasifiers can be designed to use a single material or a blend of feedstocks of the following types: (1) solids, such as coal, petroleum coke, biomass, wood waste, agricultural waste, household waste, and hazardous waste; (2) liquids, such as petroleum resids (including used or recovered road asphalts), tar sand bitumen, and liquid wastes from chemical plants and other processing plants; and (3) gas, such as natural gas or refinery and chemical processing off-gas.

The specific gasification technology used determines the output of the most sought-after products of the process, synthesis gas and hydrogen, and smaller quantities of methane, carbon dioxide, hydrogen sulfide, and water vapor are also produced, with 70-85% of the carbon in the feedstock typically converted into synthesis gas. The ratio of carbon monoxide to hydrogen depends in part upon the hydrogen and carbon content of the feedstock and the type of gasifier used, but this ratio can also be adjusted downstream of the gasifier through use of catalysts. This inherent flexibility of the gasification process means that it can produce one or more products from the same process.

Another benefit of gasification is carbon dioxide removal during the synthesis gas cleanup stage, using a number of proven commercial technologies (Mokhatab, Poe, & Speight, 2006; Speight, 2007). In fact, carbon dioxide is routinely removed in gasification-based ammonia, hydrogen, and chemical manufacturing plants. Gasification-based ammonia plants already separate and capture ~90% v/v of the carbon dioxide, and gasification-based methanol plants capture ~70% v/v of the carbon dioxide. Thus, the gasification process offers the most cost-effective and efficient means of capturing carbon dioxide during the energy production process.

Other by-products include slag – a glass-like product – composed primarily of sand, rock, and minerals originally contained in the gasifier feedstock. This slag is non-hazardous and can be used in roadbed construction, cement manufacturing, and the manufacture of roofing materials. Also, in most gasification plants, more than 99% w/w of the feedstock sulfur is removed and recovered either as elemental sulfur or sulfuric acid.

In addition, plasma gasification is increasingly being used to convert all types of waste, including municipal solid waste and hazardous waste, into electricity and other valuable products. Plasma is an ionized gas that is formed when an electrical charge passes through a gas. Plasma torches generate extremely high temperatures that can initiate and intensify gasification reactions, increasing the rate of those reactions and making gasification more efficient. The plasma system can also convert different types of mixed feedstocks, such as municipal solid waste and hazardous waste, removing the expensive step of sorting the feedstock by type before it is fed into the gasifier. These significant benefits make plasma gasification an attractive option for managing different types of wastes.

13.4.2 Refineries of the future

As it enters the twenty-first century, the petroleum refining industry is experiencing its greatest innovations driven by the increasing supply of heavy oils with decreasing quality, as well as the rapidly increasing demand for clean and ultraclean vehicle fuels and petrochemical raw materials. As feedstocks to refineries change, there must be an accompanying change in refinery technology. This change requires a movement from conventional means of refining heavy feedstocks that typically use coking technologies to more innovative processes, including hydrogen management, that will produce the maximum amounts liquid fuels from the feedstock and maintain emissions within environmental compliance (Davis & Patel, 2004; Lerner, 2002; Penning, 2001; Speight, 2008, 2011a).

To meet the challenges from changing restructured over the years from simple crude trends in product slate and the stringent distillation operations into increasingly specifications imposed by environmental complex chemical operations involving legislation, the refining industry in the near transformation of crude oil into a variety of future will become increasingly flexible and refined products with specifications that meet innovative with new processing schemes, users requirements.

During the next 20-30 years, the evolution of petroleum refining and refinery configurations will likely focus on process modification with some new innovations emerging (Speight, 2014). Predictably, the industry will move on to deep conversion of heavy feedstocks, higher hydrocracking and hydrotreating capacity, and more efficient processes.

High-conversion refineries will begin to use gasification to produce alternative fuels and to enhance equipment usage. When cost begins to prohibit the production of superclean transportation fuels using conventional technologies, refineries will also move toward gasification to meet the increasing demand for fuels synthesized from simple basic reactants (e.g., synthesis gas). FT plants and IGCC systems will also be integrated with or even into refineries, offering the advantage of high-quality products (Stanislaus *et al*., 2000). The Sasol refinery in South Africa provides an example of a facility to be centered on gasification technology (Couvaras, 1997). The refinery would produce synthesis gas to be used in manufacturing liquid fuels via FT processes.

In fact, gasification to produce synthesis gas can proceed from any carbonaceous material, including biomass. The inorganic components of the feedstock, such as metals and minerals, are trapped in an inert and environmentally safe form as char, which may have use as a fertilizer. Biomass gasification is therefore one of the most technically and economically convincing forms of energy generation for a potentially carbon-neutral economy.

A modified version of steam reforming, known as autothermal reforming, combines partial oxidation near the reactor inlet with conventional steam reforming further along the reactor, and as a result, it improves the overall reactor efficiency and increases the flexibility of the process. Partial oxidation processes using oxygen instead of steam also found wide application for synthesis gas manufacture, with the special feature that they could utilize low-value feedstocks such as heavy petroleum residua. In recent years, catalytic partial oxidation employing very short reaction times (milliseconds) at high temperatures (850-1000 °C, 1560-1830 °F) has been providing yet another approach to synthesis gas manufacture (Hickman & Schmidt, 1993).

As petroleum supplies decrease, the desirability of producing gas from other carbonaceous feedstocks will increase, especially in those areas where natural gas is in short supply. Natural gas costs are also likely to increase, allowing coal gasification to compete as an economically viable process. Current research, both in the laboratory and at pilot-plants, should lead to the invention of new process technology by the end of the century, thus accelerating the industrial use of coal gasification.

The conversion of the gaseous products of gasification into synthesis gas still requires additional steps after purification, but the gases produced during this process, such as carbon monoxide, carbon dioxide, hydrogen, methane, and nitrogen, can be used as fuels or as raw materials for chemical or fertilizer manufacture.

13.4.3 Economic aspects

As with any manufacturing unit, a gasification plant is capital intensive, but its operating costs can be lower than those faced by many other manufacturing processes or coal combustion plants. A gasification plant can use low-cost feedstocks, such as petroleum coke or high-sulfur coal, converting them into high-value products. So, it increases the use of available energy in the feedstocks, while reducing disposal costs. Ongoing research, development, and demonstration investment efforts show potential to substantially decrease current gasification costs even further, increasing the economic attractiveness of gasification.

In addition, gasification has a number of other significant economic benefits: (1) the principal gasification by-products (sulfur, sulfuric acid, and slag) are marketable; (2) gasification can produce a number of high-value products at the same time (cogeneration or polygeneration), helping a facility offset its capital and operating costs, while diversifying its risks; (3) gasification offers wide feedstock flexibility, because a gasification plant can be designed to vary the mix of the solid feedstocks or to run on natural gas or liquid feedstocks when desirable; (4) gasification units require less emission control equipment because they generate fewer emissions, further reducing the plant's operating costs.

Investment in gasification also involves the construction, operation, and maintenance of large-scale plants, and as a result, it increases business for suppliers at home and abroad, while creating domestic jobs in sectors such as construction and machine operation that cannot be outsourced to overseas workers.

13.4.4 Market outlook

The forecast for growth of gasification capacity focuses on two areas: large-scale industrial and power generation plants and the small-scale biomass and waste-to-energy plants.

Worldwide, the capacity of gasification for industry and power generation is projected to grow 70% by 2015, with 81% of the growth occurring in developing markets. The prime movers behind this expected growth are the chemical, fertilizer, and coal-to-liquids industries in China, tar sands in Canada, polygeneration (hydrogen and power or chemicals) in the United States, and refining in Europe. In fact, China has focused on gasification as part of its overall energy strategy. The industrial and power gasification industry in the United States faces a number of challenges, however, including rising construction costs and uncertainty about policy-based incentives and regulations. Despite these challenges, the industrial and power gasification capacity in the United States is expected to grow.

A number of factors will contribute to this expansion. Volatile oil and natural gas prices will make low-cost and abundant domestic resources with stable prices increasingly attractive as feedstocks, and gasification processes will be able to comply with more stringent environmental regulations because their emission profiles are already substantially less than more conventional technologies.

In fact, there is a growing consensus that carbon dioxide management will be required in power generation and energy production. Given that the gasification process allows carbon dioxide to be captured in a cost-effective and efficient manner, it will be an increasingly attractive choice for the continued use of fossil fuels. In terms of the number of plants in the United States, the greatest growth is likely to occur in the biomass and waste-to-energy gasification areas. Because they are smaller in scale, these plants are easier to finance, easier to permit, and require less time to construct. In addition, municipal and state restrictions on landfills and incineration and a growing recognition that these materials contain valuable sources of energy are driving the demand for these plants.

Finally, a number of factors will contribute to the growing interest in waste and biomass gasification: (1) restrictions on landfill space, (2) efforts to reduce costs associated with waste management, (3) growing recognition that waste and biomass contain unused energy that can be captured and converted into energy and valuable products, (4) the availability of nonfood biomass for conversion into valuable energy products.

13.5 Conclusions

The most obvious issue with fossil fuel use relates to its effects on the environment. As technology evolves, the means to reduce the damage done by fossil fuel use also evolves, and the world is on the verge of adopting alternative energy sources. In the meantime, gasification offers alternatives to meet future fuel demand, while reducing potentially harmful emissions.

Recent policy aimed at tackling climate change and resource conservation, such as the Kyoto Protocol, the deliberations at Copenhagen in 2009, and the Landfill Directive of the European Union, stimulated the development of renewable energy and landfill diversion technology, thus providing renewed impetus for developing gasification technology. However, even though they are the fastest growing source of energy, renewable sources of energy will still represent only 15% of the world energy requirements in 2035 (up from the current estimation of 10%), and divesting from fossil fuels does not mean an end to environmental emissions. Petroleum, tar sand bitumen, coal, natural gas, and perhaps oil shale will still be dominant energy sources, and their use will grow at a relatively robust rate for at least the next two decades. These estimates provide a reality check for those hoping to implement clean technologies, and they should head it, if they hope to reduce greenhouse gas emissions, while satisfying future energy demands (EIA, 2013).

Gasification could now be proposed as a viable alternative solution for waste treatment with energy recovery. On the other hand, the gasification process still faces some technical and economic problems, mainly related to the highly heterogeneous nature of municipal solid wastes and related feeds and the relatively limited number of plants (~100) worldwide with continuous experience using this technology under commercial conditions. In the aggressive working environment of municipal solid waste management, with its uncompromising demand for reasonable cost, high reliability, and operational flexibility, it could be premature to indicate that gasification is the thermal processing strategy of the future, or even a strong competitor for combustion systems, at least for all waste-to-energy plants.

The success of any advanced thermal technology is determined by its technical reliability, environmental sustainability, and economic convenience. Around one hundred gasification-based waste-to-energy plants, mainly in Japan but now also in Korea and Europe, have logged years of continuous operation, demonstrating technical reliability. Environmental performance is also one of the greatest strengths of gasification technology, which often is considered a sound response to the increasingly restrictive regulations applied around the world, and independently verified emissions tests indicate that gasification is able to meet existing emissions limits and can have a great effect on the reduction of landfill use.

Economic aspects are probably the biggest obstacle to market penetration, because gasification-based waste-to-energy conversion tends to have operating and capital costs higher than those of conventional combustion-based waste-to-energy (in the order of about 10%), mainly as a consequence of the ash-melting system or the added complexity of the technology.

The evidence of the last decade or so indicates the convenience of constructing gasification plants having a capacity less than approximately 120,000 tons feedstocks per year. In order to achieve a wider market penetration, advanced gasification technologies must be able to provide cheaper synthesis and gas cleaning, while conveniently meeting defined specifications and obtaining higher electric energy conversion efficiencies. Nevertheless, the performance and experience of the commercial waste gasifiers in operation illustrate that gasification processes can indeed compete with conventional moving-grate or fluidized-bed combustion systems.

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