Kirk-Othmer Encyclopedia of Chemical Technology.

FUELS, SYNTHETIC, GASEOUS FUELS

Substitute or synthetic natural gas (SNG) has been known for several centuries. When SNG was first discovered, natural gas was largely unknown as a fuel and was more a religious phenomenon (see Gas, natural) (1). Coal (qv) was the first significant source of substitute natural gas and in the early stages of SNG production the product was more commonly known under variations of the name coal gas (2, 3). Whereas coal continues to be a principal source of substitute natural gas (4) a more recently recognized source is petroleum (qv) (5).

1. Gas from Coal

Coal can be converted to gas by several routes (2, 6–11), but often a particular process is a combination of options chosen on the basis of the product desired, ie, low, medium, or high heat-value gas. In a very general sense, *coal gas* is the term applied to the mixture of gaseous constituents that are produced during the thermal decomposition of coal at temperatures in excess of 500°C (>930°F), often in the absence of oxygen (air) (see Coal conversion processes, gasification) (3). A solid residue (coke, char), tars, and other liquids are also produced in the process:

$$C_{coal} + \text{heat} \longrightarrow C_{char} + \text{tar/liquid} + CO + CO_2 + H_2$$

The tars and other liquids (liquor) are removed by condensation leaving principally hydrogen, carbon monoxide, and carbon dioxide in the gas phase. This gaseous product also contains low boiling hydrocarbons (qv), sulfur-containing gases, and nitrogen-containing gases including ammonia (qv) and hydrogen cyanide. The solid residue is then treated under a variety of conditions to produce other fuels which vary from a purified char to different types of gaseous mixtures (see also Coal conversion processes, carbonization). The amounts of gas, coke, tar, and other liquid products vary according to the method used for the carbonization (especially the retort configuration), and process temperature, as well as the nature (rank) of the coal (3, 11).

The recorded chronology of the coal-to-gas conversion technology began in 1670 when a clergyman, John Clayton, in Wakefield, Yorkshire, produced in the laboratory a luminous gas by destructive distillation of coal (12). At the same time, experiments were also underway elsewhere to carbonize coal to produce coke, but the process was not practical on any significant scale until 1730 (12). In 1792, coal was distilled in an iron retort by a Scottish engineer, who used the by-product gas to illuminate his home (13).

The conversion of coal to gas on an industrial scale dates to the early nineteenth century (14). The gas, often referred to as manufactured gas, was produced in coke ovens or similar types of retorts by simply heating coal to vaporize the volatile constituents. Estimates based on modern data indicate that the gas mixture probably contained hydrogen (qv) (ca 50%), methane (ca 30%), carbon monoxide (qv) and carbon dioxide (qv) (ca 15%), and some inert material, such as nitrogen (qv), from which a heating value of approximately 20.5 MJ/m^3 (550 Btu/ft^3) can be estimated (6).

Table 1. Analyses of Fuel Gases

Type of fuel gas	Gas composition, vol % CO	CO_2	H_2	N_2	O_2	CH_4	Illuminants	Heat value,[a] MJ/m^3
blast-furnace	27.5	10.0	3.0	58.0	1.0	0.5		3.8
producer (bituminous)	27.0	4.5	14.0	50.9	0.6	3.0		5.6
blue-water	42.8	3.0	49.9	3.3	0.5	0.5		11.5
carburetted water	33.4	3.9	34.6	7.9	0.9	10.4	8.9[b]	20.0
retort coal	8.6	1.5	52.5	3.5	0.3	31.4	2.2[c]	21.5
coke-oven	6.3	1.8	53.0	3.4	0.2	1.6	3.7[d]	21.9
natural								
mid-continent		0.8		3.2		96.0		36.1
Pennsylvania				1.1		67.6	31.3[e]	46.0

[a] To convert MJ/m^3 to Btu/ft^3, multiply by 26.86.
[b] 6.7 vol % C_2H_4 plus 2.2 vol % C_6H_6.
[c] 1.1 vol % each of C_2H_4 and C_6H_6.
[d] 2.7 vol % C_2H_4 plus 1.0 vol % C_6H_6.
[e] 31.3 vol % C_2H_6.

Blue gas, or blue-water gas, so-called because of the color of the flame upon burning (10), was discovered in 1780 when steam was passed over incandescent carbon (qv), and the blue-water gas process was developed over the period 1859–1875. Successful commercial application of the process came about in 1875 with the introduction of the carburetted gas jet. The heating value of the gas was low, ca 10.2 MJ/m^3 (275 Btu/ft^3), and on occasion oil was added to the gas to enhance the heating value. The new product was given the name carburetted water gas and the technique satisfied part of the original aim by adding luminosity to gas lights (10).

Coke-oven gas is a by-product fuel gas derived from coking coals by the process of carbonization. The first by-product coke ovens were constructed in France in 1856. Since then they have gradually replaced the old and primitive method of beehive coking for the production of metallurgical coke. Coke-oven gas is produced in an analogous manner to retort coal gas, with operating conditions, mainly temperature, set for maximum carbon yield. The resulting gas is, consequently, poor in illuminants, but excellent as a fuel. Typical analyses and heat content of common fuel gases vary (Table 1) and depend on the source as well as the method of production.

In Germany, large-scale production of synthetic fuels from coal began in 1910 and necessitated the conversion of coal to carbon monoxide and hydrogen.

Water gas reaction $C_{coal} + H_2O \longrightarrow CO + H_2$

The mixture of carbon monoxide and hydrogen is enriched with hydrogen from the water gas catalytic (Bosch) process, ie, water gas shift reaction, and passed over a cobalt–thoria catalyst to form straight-chain, ie, linear, paraffins, olefins, and alcohols in what is known as the Fisher-Tropsch synthesis.

$$n\,CO + (2n+1)\;H_2 \xrightarrow[\text{catalyst}]{\text{cobalt}} C_nH_{2n+2} + n\,H_2O$$

$$2n\,CO + (n+1)\;H_2 \xrightarrow[\text{catalyst}]{\text{iron}} C_nH_{2n+2} + n\,CO_2$$

$$n\,\mathrm{CO} + 2n\,\mathrm{H_2} \xrightarrow[\text{catalyst}]{\text{cobalt}} \mathrm{C}_n\mathrm{H}_{2n} + n\,\mathrm{H_2O}$$

$$2n\,\mathrm{CO} + n\,\mathrm{H_2} \xrightarrow[\text{catalyst}]{\text{iron}} \mathrm{C}_n\mathrm{H}_{2n} + n\,\mathrm{CO_2}$$

$$n\,\mathrm{CO} + 2n\,\mathrm{H_2} \xrightarrow[\text{catalyst}]{\text{cobalt}} \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\ \mathrm{H_2O}$$

$$(2n-1)\ \mathrm{CO} + (n+1)\ \mathrm{H_2} \xrightarrow[\text{catalyst}]{\text{iron}} \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\ \mathrm{CO_2}$$

In Sasolburg, South Africa, a commercial plant using the Fischer-Tropsch process was completed in 1950 and began producing a variety of liquid fuels and chemicals. The facility has been expanded to produce a considerable portion of South Africa's energy requirements (15, 16).

In 1948, the first demonstration of suspension gasification was successfully completed by Koppers, Inc. The product gas was of 11.2 MJ/m^3 (300 Btu/ft^3) calorific value and consisted primarily of a mixture of hydrogen and oxides of carbon. In the United States, so-called second-generation coal gasification processes came into being as a result of the recognized need to develop reliable, domestic energy sources to replace the rapidly diminishing supply of conventional fuels (see Fuel resources) (3, 9). More recently, the biological conversion of coal and synthesis gas (carbon monoxide–hydrogen mixtures) into liquid fuels by methanogenic bacteria has received some attention (17–19).

1.1. Gas Products

The originally designated names of the gaseous mixtures are used herein, with the understanding that since their introduction there may be differences in means of production and in the make-up of the gaseous products. Properties of fuel gases are available (20). There are standard tests to determine properties and character of gaseous mixtures. These tests are accepted by the American Society for Testing and Materials (ASTM), by the British Standards Institution (BSI), by the Institute of Petroleum (IP), and by the International Standards Organization (ISO) (1, 10, 20).

1.1.1. Low Heat-Value Gas

Low heat-value (low Btu) gas (7) consists of a mixture of carbon monoxide and hydrogen and has a heating value of less than 11 MJ/m^3 (300 Btu/ft^3), but more often in the range 3.3–5.6 MJ/m^3 (90–150 Btu/ft^3). The gas is formed by partial combustion of coal with air, usually in the presence of steam (7).

$$2\ \mathrm{C_{coal}} + \mathrm{O_2} \longrightarrow 2\ \mathrm{CO}$$

$$\mathrm{C_{coal}} + \mathrm{H_2O} \longrightarrow \mathrm{CO} + \mathrm{H_2}$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

This gas is of interest to industry as a fuel gas or even, on occasion, as a raw material from which ammonia and other compounds may be synthesized.

The first gas producer making low heat-value gas was built in 1832. (The product was a combustible carbon monoxide–hydrogen mixture containing ca 50 vol % nitrogen). The open-hearth or Siemens-Martin process, built in 1861 for pig iron refining, increased low heat-value gas use (see Iron). The use of producer gas as a fuel for heating furnaces continued to increase until the turn of the century when natural gas began to supplant manufactured fuel gas (see Furnaces, fuel-fired).

The combustible components of the gas are carbon monoxide and hydrogen, but combustion (heat) value varies because of dilution with carbon dioxide and with nitrogen. The gas has a low flame temperature unless the combustion air is strongly preheated. Its use has been limited essentially to steel (qv) mills, where it is produced as a by-product of blast furnaces. A common choice of equipment for the smaller gas producers is the Wellman-Galusha unit because of its long history of successful operation (21).

1.1.2. Medium Heat-Value Gas

Medium heat-value (medium Btu) gas (6, 7) has a heating value between 9 and 26 MJ/m^3 (250 and 700 Btu/ft^3). At the lower end of this range, the gas is produced like low heat-value gas, with the notable exception that an air separation plant is added and relatively pure oxygen (qv) is used instead of air to partially oxidize the coal. This eliminates the potential for nitrogen in the product and increases the heating value of the product to 10.6 MJ/m^3 (285 Btu/ft^3). Medium heat-value gas consists of a mixture of methane, carbon monoxide, hydrogen, and various other gases and is suitable as a fuel for industrial consumers.

1.1.3. High Heat-Value Gas

High heat-value (high Btu) gas (7) has a heating value usually in excess of 33.5 MJ/m^3 (900 Btu/ft^3). This is the gaseous fuel that is often referred to as substitute or synthetic natural gas (SNG), or pipeline-quality gas. It consists predominantly of methane and is compatible with natural gas insofar as it may be mixed with, or substituted for, natural gas.

Any of the medium heat-value gases that consist of carbon monoxide and hydrogen (often called synthesis gas) can be converted to high heat-value gas by methanation (22), a low temperature catalytic process that combines carbon monoxide and hydrogen to form methane and water.

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

Prior to methanation, the gas product from the gasifier must be thoroughly purified, especially from sulfur compounds the precursors of which are widespread throughout coal (23) (see Sulfur removal and recovery). Moreover, the composition of the gas must be adjusted, if required, to contain three parts hydrogen to one part carbon monoxide to fit the stoichiometry of methane production. This is accomplished by application of a catalytic water gas shift reaction.

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The ratio of hydrogen to carbon monoxide is controlled by shifting only part of the gas stream. After the shift, the carbon dioxide, which is formed in the gasifier and in the water gas reaction, and the sulfur compounds formed during gasification, are removed from the gas.

Table 2. Coal Carbonization Methods[a]

Carbonization process	Final temperature, °C	Products	Processes
low temperature	500–700	reactive coke and high tar yield	rexco (700°C) made in cylindrical vertical retorts; coalite (650°C) made in vertical tubes
medium temperature	700–900	reactive coke with high gas yield, or domestic briquettes	town gas and gas coke (obsolete); phurnacite, low volatile steam coal, pitch-bound briquettes carbonized at 800°C
high temperature	900–1050	hard, unreactive coal for metallurgical use	foundry coke (900°C); blast-furnace coke (950–1050°C)

[a] Ref. 29.

The processes that have been developed for the production of synthetic natural gas are often configured to produce as much methane in the gasification step as possible thereby minimizing the need for a methanation step. In addition, methane formation is highly exothermic which contributes to process efficiency by the production of heat in the gasifier, where the heat can be used for the endothermic steam–carbon reaction to produce carbon monoxide and hydrogen.

$$C + H_2O \longrightarrow CO + H_2$$

1.2. Carbonization

Next to combustion, *carbonization* represents one of the largest uses of coal (2, 24–26). Carbonization is essentially a process for the production of a carbonaceous residue by thermal decomposition, accompanied by simultaneous removal of distillate, of organic substances.

$$C_{\text{organic}} \longrightarrow C_{\text{coke/char/carbon}} + \text{liquids} + \text{gases}$$

This process may also be referred to as destructive distillation. It has been applied to a whole range of organic materials, more particularly to natural products such as wood (qv), sugar (qv), and vegetable matter to produce charcoal (see Fuels from biomass). However, in the present context, coal usually yields coke, which is physically dissimilar from charcoal and appears with the more familiar honeycomb-type structure (27).

The original process of heating coal in rounded heaps, the hearth process, remained the principal method of coke production for over a century, although an improved oven in the form of a beehive was developed in the Durham-Newcastle area of England in about 1759 (2, 26, 28). These processes lacked the capability to collect the volatile products, both liquids and gases. It was not until the mid-nineteenth century, with the introduction of indirectly heated slot ovens, that it became possible to collect the liquid and gaseous products for further use.

Coal carbonization processes are generally defined according to process operating temperature. Terms are defined in Table 2.

1.2.1. Low Temperature Carbonization

Low temperature carbonization, when the process does not exceed 700°C, was mainly developed as a process to supply town gas for lighting purposes as well as to provide a smokeless (devolatilized) solid fuel for domestic consumption (30). However, the process by-products (tars) were also found to be valuable insofar as they served as feedstocks (qv) for an emerging chemical industry and were also converted to gasolines, heating oils, and lubricants (see Gasoline and other motor fuels; Lubrication and lubricants) (31).

Coals preferred for the low temperature carbonization were usually lignites or subbituminous, as well as high volatile bituminous, coals (see Lignite and brown coal). These yield porous solid products over the temperature range 600–700°C. Certain of the higher rank (caking) coals were less suitable for the process, unless steps were taken to destroy the caking properties, because of the tendency of these higher rank coals to adhere to the walls of the carbonization chamber.

The options for efficient low temperature carbonization of coal include vertical and horizontal retorts which have been used for batch and continuous processes. In addition, stationary and revolving horizontal retorts have also been operated successfully, and there are also several process options employing fluidized or gas-entrained coal. Coke production from batch-type carbonization of coal has been supplanted by a variety of continuous retorting processes which allow much greater throughput rates than were previously possible. These processes employ rectangular or cylindrical vessels of sufficient height to carbonize the coal while it travels from the top of the vessel to the bottom and usually employ the principle of heating the coal by means of a countercurrent flow of hot combustion gas. Most notable of these types of carbonizers are the Lurgi-Spulgas retort and the Koppers continuous steaming oven (2).

1.2.2. High Temperature Carbonization

When heated at temperatures in excess of 700°C (1290°F), low temperature chars lose their reactivity through devolatilization and also suffer a decrease in porosity. High temperature carbonization, at temperatures $>900^\circ C$, is, therefore, employed for the production of coke (27). As for the low temperature processes, the tars produced in high temperature ovens are also sources of chemicals and chemical intermediates (32).

A newer concept has been developed that is given the name mild gasification (33). It is not a gasification process in the true sense of the word. The process temperature is some several hundred degrees lower, hence the term mild, than the usual gasification process temperature and the objective is not to produce a gaseous fuel but to produce a high value char (carbon) and liquid products. Gas is produced, but to a lesser extent.

Documented efforts at cokemaking date from 1584 (34), and have seen various adaptations of conventional wood-charring methods to the production of coke including the eventual evolution of the beehive oven, which by the mid-nineteenth century had become the most common vessel for the coking of coal (2). The heat for the process was supplied by burning the volatile matter released from the coal and, consequently, the carbonization would progress from the top of the bed to the base of the bed and the coke was retrieved from the side of the oven at process completion.

Some beehive ovens, having various improvements and additions of waste heat boilers, thereby allowing heat recovery from the combustion products, may still be in operation. Generally, however, the beehive oven has been replaced by wall-heated, horizontal chamber, ie, slot, ovens in which higher temperatures can be achieved as well as a better control over the quality of the coke. Modern slot-type coke ovens are approximately 15 m long, approximately 6 m high, and the width is chosen to suit the carbonization behavior of the coal to be processed. For example, the most common widths are ca 0.5 m, but some ovens may be as narrow as 0.3 m, or as wide as 0.6 m.

Several (usually 20 or more, alternating with similar cells that contain heating ducts) of these chambers are constructed in the form of a battery over a common firing system through which the hot combustion gas is conveyed to the ducts. The flat roof of the battery acts as the surface for a mobile charging car from which the coal (25–40 t) enters each oven through three openings along the top. The coke product is pushed from the rear of the oven through the opened front section onto a quenching platform or into rail cars that then move the coke through water sprays. The gas and tar by-products of the process are collected for further processing or for on-site use as fuel.

Most modern coke ovens operate on a regenerative heating cycle in order to obtain as much surplus gas as possible for use on the works, or for sale. If coke-oven gas is used for heating the ovens, the majority of the gas is surplus to requirements. If producer gas is used for heating, much of the coke-oven gas is surplus.

Table 3. Gas Composition Requirements for Substitute Natural Gas and for Power Generation

	Product requirement	
Characteristic	Synthetic natural gas	Power generation
methane content	high, less synthesis required	low, probably means no tars
H_2/CO ratio	high, less shifting required	low, CO more efficient fuel
moisture content	high, steam required for shift	low, lower condensate treatment costs
outlet temperature	low, maximizes methane minimizes sensible heat loss leads to high cold gas efficiency	high, precludes tar formation provides for steam generation reduces cold gas efficiency
gasifier oxidant	O_2 only, cost of N_2 removal excessive	air or O_2, low heating gas value acceptable fuel

The main difference between gas works and coke oven practice is that, in a gas works, maximum gas yield is a primary consideration whereas in the coke works the quality of the coke is the first consideration. These effects are obtained by choice of a coal feedstock that is suitable to the task. For example, use of lower volatile coals in coke ovens, compared to coals used in gas works, produces lower yields of gas when operating at the same temperatures. In addition, the choice of heating (carbonizing) conditions and the type of retort also play a principal role (10, 35).

1.3. Gasification

The *gasification* of coal is essentially the conversion of coal by any one of a variety of processes to produce combustible gases (7, 8, 11, 22, 36–38). Primary gasification is the thermal decomposition of coal to produce mixtures containing various proportions of carbon monoxide, carbon dioxide, hydrogen, water, methane, hydrogen sulfide, and nitrogen, as well as products such as tar, oils, and phenols. A solid char product may also be produced, and often represents the bulk of the weight of the original coal.

Secondary gasification involves gasification of the char from the primary gasifier, usually by reaction of the hot char and water vapor to produce carbon monoxide and hydrogen.

$$C_{\text{char}} + H_2O \longrightarrow CO + H_2$$

The gaseous product from a gasifier generally contains large amounts of carbon monoxide and hydrogen, plus lesser amounts of other gases and may be of low, medium, or high heat value depending on the defined use (Table 3) (39, 40).

The importance of coal gasification as a means of producing fuel gas(es) for industrial use cannot be underplayed. But coal gasification systems also have undesirable features. A range of undesirable products are also produced which must be removed before the products are used to provide fuel and/or to generate electric power (see Power generation) (22, 41).

1.3.1. Chemistry

Coal gasification involves the thermal decomposition of coal and the reaction of the carbon in the coal, and other pyrolysis products with oxygen, water, and hydrogen to produce fuel gases such as methane by internal hydrogen shifts

$$C_{\text{coal}} + H_{\text{coal}} \longrightarrow CH_4$$

Table 4. Gasification Reactions

Reaction	ΔH, kJ[a]
Gasification zone, 595–1205°C	
$C + CO_2 \longrightarrow 2\,CO$	9.65[b]
$CO + H_2O \longrightarrow CO_2 + H_2$	−1.93[c]
$C + H_2O \longrightarrow CO + H_2$	7.76[d]
$C + 2H_2 \longrightarrow CH_4$	−5.21
$C + 2\,H_2O \longrightarrow 2\,H_2 + CO_2$	5.95
Combustion zone, >1205°C	
$2\,C + O_2 \longrightarrow 2\,CO$	−22.6
$C + O_2 \longrightarrow CO_2$	−6.74
Methanation reactions	
$CO + 3\,H_2 \longrightarrow CH_4 + H_2O$	−12.9
$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O$	−11.0
$2\,C + 2\,H_2O \longrightarrow CH_4 + CO_2$	0.62
Others reactions	
$2\,H_2 + O_2 \longrightarrow 2\,H_2O$	
$CO + 2\,H_2 \longrightarrow CH_3OH$	
$2\,C + H_2 \longrightarrow C_2H_2$	
$CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$	

[a] To convert kJ to kcal, divide by 4.184.
[b] Boudouard reaction.
[c] Water gas shift reaction.
[d] Water gas reaction.

or through the agency of added (external) hydrogen

$$C_{coal} + 2\,H_2 \longrightarrow CH_4$$

although the reactions are more numerous and more complex as can be seen in Table 4.

If air is used as a combustant, the product gas contains nitrogen and, depending on design characteristics, has a heating value of approximately $5.6 - 11.2 \times 10^3$ MJ/m^3 (150–300 Btu/ft^3). The use of pure oxygen, although expensive, results in a product gas having a heating value of 11–15 MJ/m^3 (300–400 Btu/ft^3) and carbon dioxide and hydrogen sulfide as by-products.

If a high heat-value gas (33.5–37.3 MJ/m^3 (900–1000 Btu/ft^3)) ie, SNG, is the desired product, efforts must be made to increase the methane content.

Shift conversion reaction $$CO + H_2O \longrightarrow CO_2 + H_2$$

$$CO + 3\,H_2 \longrightarrow CH_4 + H_2O$$

$$2\,CO + 2\,H_2 \longrightarrow CH_4 + CO_2$$

$$CO + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O$$

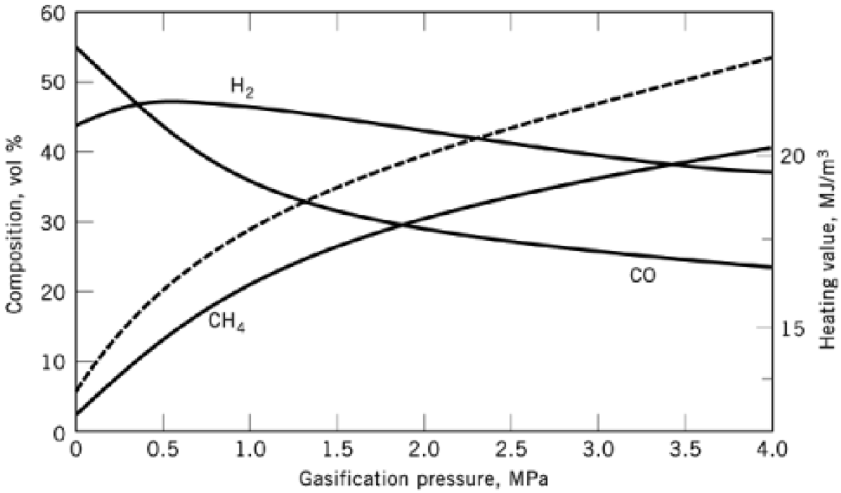

Fig. 1. Variation of (—) gas composition and (- - -) heating value with gasifier pressure. To convert MJ/m^3 to Btu/ft^3, multiply by 26.86. To convert MPa to psi, multiply by 145.

The gasification is performed using oxygen and steam (qv), usually at elevated pressures. The steam–oxygen ratio along with reaction temperature and pressure determine the equilibrium gas composition. The reaction rates for these reactions are relatively slow and heats of formation are negative. Catalysts may be necessary for complete reaction (2, 3, 24, 42, 43).

1.3.2. Process Parameters

The most notable effects in gasifiers are those of pressure (Fig. 1) and coal character. Some initial processing of the coal feedstock may be required. The type and degree of pretreatment is a function of the process and/or the type of coal (see Coal conversion processes, cleaning and desulfurization).

Depending on the type of coal being processed and the analysis of the gas product desired, some or all of the following processing steps may 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-value gas is desired, all of these processing steps are required because coal gasifiers do not yield methane in the concentrations required.

An example of application of a pretreatment option occurs when the coal displays caking or agglomerating characteristics. Such coals are usually not amenable to gasification processes employing fluidized-bed or moving-bed reactors. The pretreatment involves a mild oxidation treatment, usually consisting of low temperature heating of the coal in the presence of air or oxygen. This destroys the caking characteristics of coals.

Gasification technologies for the production of high heat-value gas do not all depend entirely on catalytic methanation, that is, the direct addition of hydrogen to coal under pressure to form methane.

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 a higher overall process efficiency.

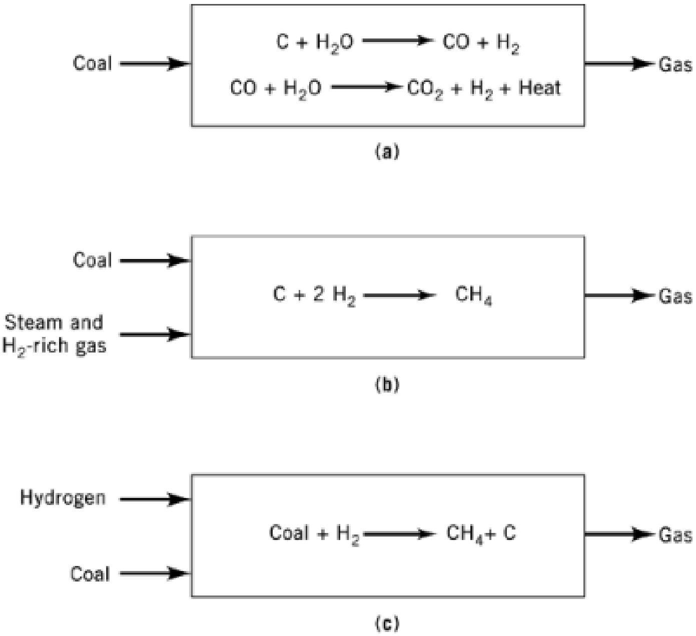

Fig. 2. Chemistry of (**a**) gasifier; (**b**) hydrogasifier; and (**c**) devolatization processes. The gaseous product of (**a**) is of low heating value; that of (**b**) and (**c**) is of intermediate heating value.

There are three fundamental reactor types for gasification processes: (*1*) a gasifier reactor, (*2*) a devolatilizer, and (*3*) a hydrogasifier (Fig. 2). The choice of a particular design is available for each type, eg, whether or not two stages should be involved depending on the ultimate product gas desired. Reactors may also be designed to operate over a range of pressure from atmospheric to high pressure.

Gasification processes have been classified on the basis of the heat-value of the produced gas. It is also possible to classify gasification processes according to the type of reactor and whether or not the system reacts under pressure. Additionally, gasification processes can be segregated according to the bed types, which differ in the ability to accept and use caking coals. Thus gasification processes can be divided into four categories based on reactor (bed) configuration: (*1*) fixed bed, (*2*) moving bed, (*3*) fluidized bed, and (*4*) entrained bed.

In a fixed-bed process the coal is supported by a grate and combustion gases, ie, steam, air, oxygen, etc, pass through the supported coal whereupon the hot produced gases 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. In the moving-bed system (Fig. 3), coal is fed to the top of the bed and ash leaves the bottom with the product gases being produced in the hot zone just prior to being released from the bed.

The fluidized-bed system (Fig. 3) 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 and the result is an expanded bed having greater coal surface area to promote the chemical reaction. These systems, however, have only a limited ability to handle caking coals (see Fluidization).

An entrainment system (Fig. 3) 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.

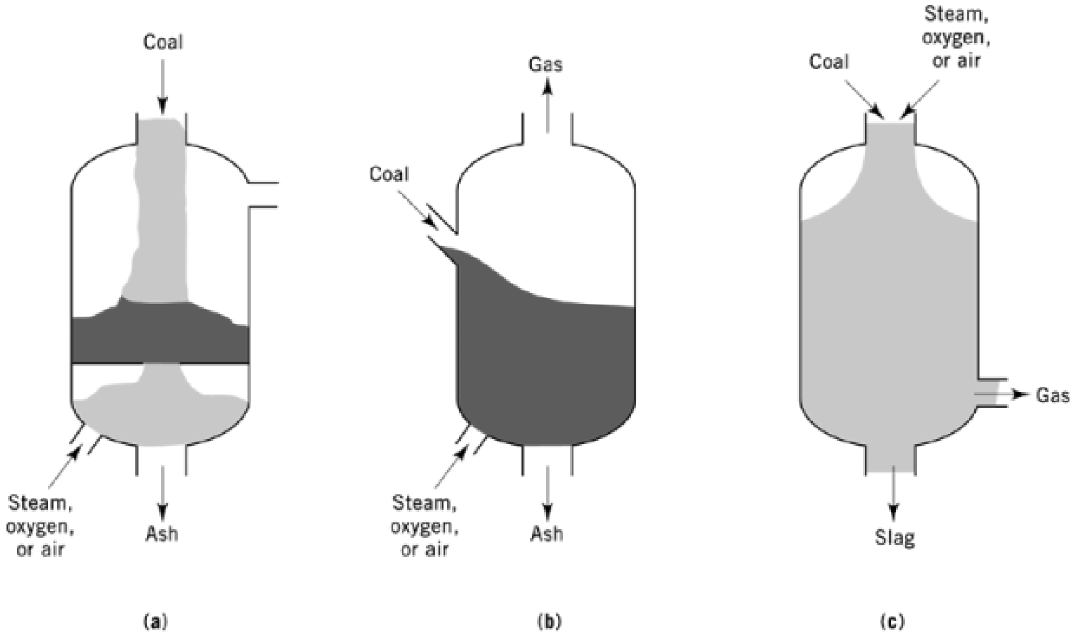

Fig. 3. Gasifier systems: (**a**), moving bed (dry ash); (**b**), fluidized bed; and (**c**), entrained flow.

1.3.3. Gasifier Options

The standard Wellman-Galusha unit, used for noncaking coals, is an atmospheric pressure, air-blown gasifier (Fig. 4) fed by a two-compartment lockhopper system. The upper coal-storage compartment feeds coal intermittently into the feeding compartment, which then feeds coal into the gasifier section almost continuously except for brief periods when the feeding compartment is being loaded from storage. In small units up to 1.5 m internal diameter ash is removed by shaker grates. In larger units, ash is removed continuously from the bottom of the gasifier into an ash-hopper section by a revolving grate.

The grate is constructed of flat, circular steel plates set one above the other with edges overlapping. The grate, revolving eccentrically within the gasifier, causes ash to fall from the coal bed as the space between the grate and the shell increases, and then pushes the ash down into the ash-hopper as the space decreases. The smaller size units are brick-lined, although the larger sizes are unlined and water-jacketed. Combustion air, provided by a fan, passes over the warm (82°C) jacket water causing the water to vaporize to provide the necessary steam for gasification. Gas leaves from above the fuel bed at 428–538°C for bituminous coal.

On the other hand, the agitator type of Wellman-Galusha unit, used for gasification of any type of coal, uses a slowly revolving horizontal arm which also spirals vertically below the surface of the fuel bed to retard channeling and maintain a uniform bed. Use of the agitator not only allows operation with caking coals but also can increase the capacity of the gasifier by about 25% for use with other coals.

The Winkler gasifier (Fig. 5) is an example of a medium heat-value gas producer which, when oxygen is employed, yields a gas product composed mainly of carbon monoxide and hydrogen (43).

In the process, finely crushed coal is gasified at atmospheric pressure in a fluidized state; oxygen and steam are introduced at the base of the gasifier. The coal is fed by lockhoppers and a screw feeder into the bottom of the fuel bed. Sintered ash particles settle on a grate, where they are cooled by the incoming oxygen and steam; a rotating, cooled rabble moves the ash toward a discharge port. The ash is then conveyed pneumatically to a disposal hopper.

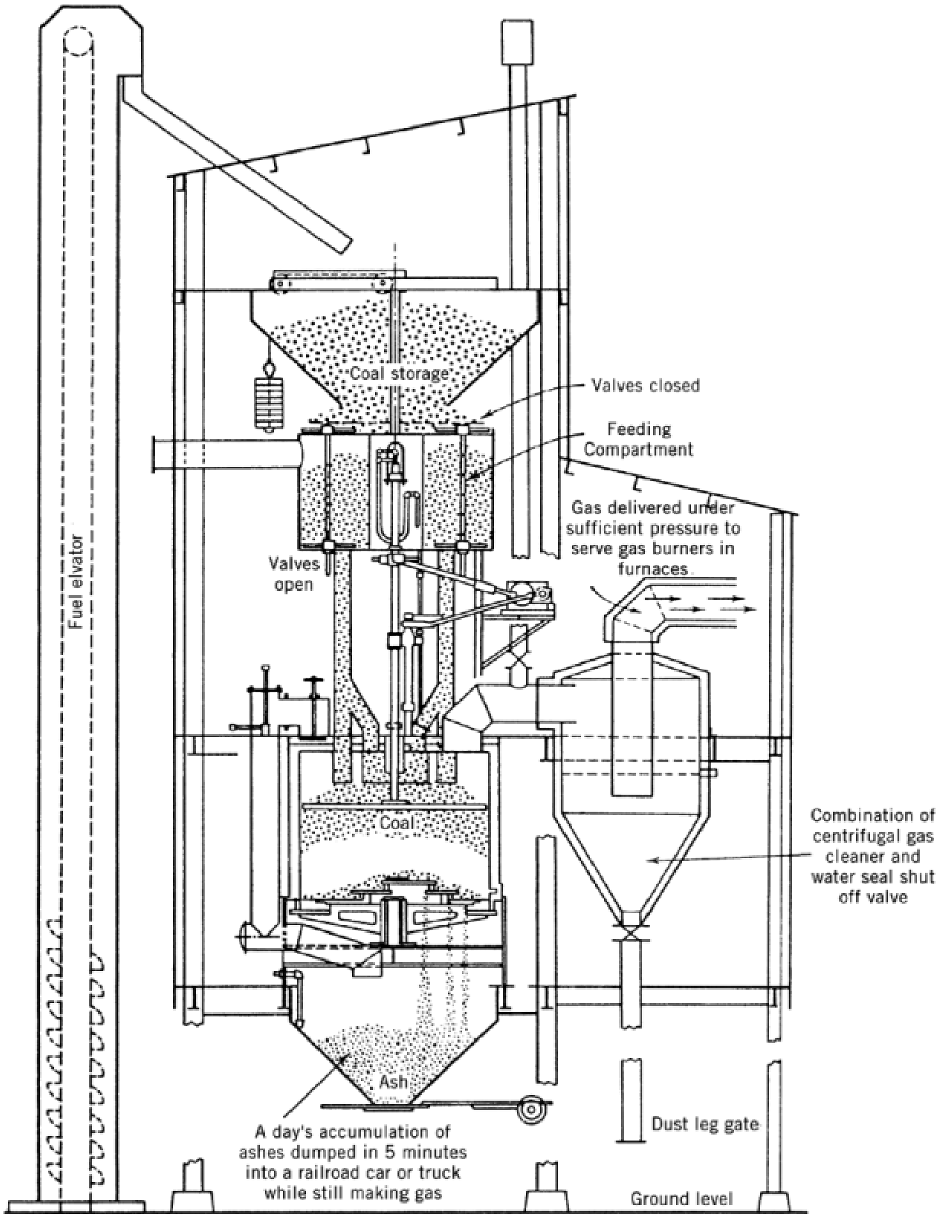

Fig. 4. A Wellman-Galusha agitator-type gas producer.

The gas, along with entrained ash and char particles, which are subjected to further gasification in the large space above the fluid bed, exit the gasifier at 954–1010°C. The hot gas is passed through a waste-heat boiler to recover the sensible heat, and then through a dry cyclone. Solid particles are removed in both units. The gas is further cooled and cleaned by wet scrubbing, and if required, an electrostatic precipitator is included in the gas-treatment stream.

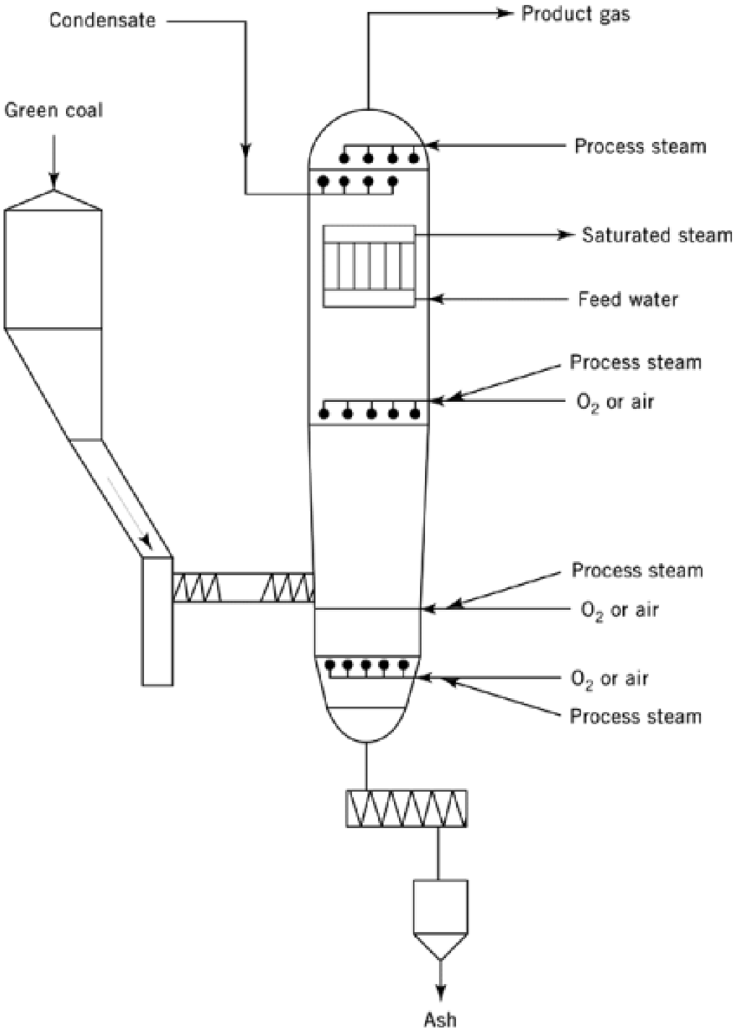

Fig. 5. The Winkler gas producer.

The Koppers-Totzek process is a second example of a process for the production of a medium heat-value gas (44, 45). Whereas the Winkler process employs a fluidized bed, the Koppers-Totzek process uses an entrained flow system. In the Koppers-Totzek process, dried and pulverized coal is conveyed continuously by a screw into a mixing nozzle. From there a high velocity stream of steam and oxygen entrains the coal into a gasifier. The gasifier (Fig. 6) is a cylindrical vessel with a refractory-lining that is designed to conduct a selected amount of heat to a surrounding water jacket in which low pressure process steam is generated. The lining is thin (about 5 cm) and made of a high alumina cast material. In a two-headed gasifier two burner heads are placed 180° apart at either end of the vessel. Four burner heads, 90° apart, are used in a four-headed gasifier. The largest gasifiers are 3–4 m diameter at the middle, tapering to 2–3 m at the burner ends and are about 19 m long. The reactor volume is about 30 m^3 for the two-headed design, and 64 m^3 for the larger, four-headed models.

The process is carried at moderate (slightly above atmospheric) pressures, but at very high temperatures that reach a maximum of 1900°C. Even though the reaction time is short (0.6–0.8 s) the high temperature

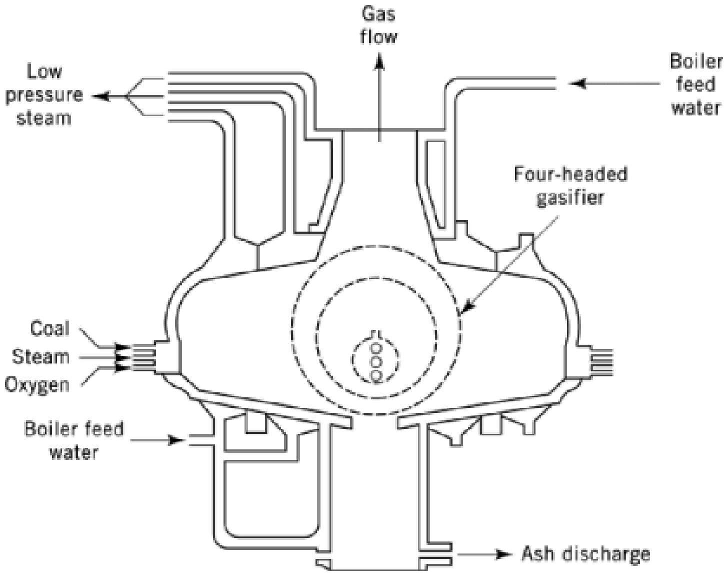

Fig. 6. The Koppers-Totzek gas producer.

prevents the occurrence of any condensable hydrocarbons, phenols, and/or tar in the product gas. The absence of liquid simplifies the subsequent gas clean-up steps.

Normally ca 50% of the coal ash is removed from the bottom of the gasifier as a quenched slag. The balance is carried overhead in the gas as droplets which are solidified when the gas is cooled with a water spray. A fluxing agent is added, if required, to the coal to lower the ash fusion temperature and increase the molten slag viscosity.

Conversion of carbon in the coal to gas is very high. With low rank coal, such as lignite and subbituminous coal, conversion may border on 100%, and for highly volatile A coals, it is on the order of 90–95%. Unconverted carbon appears mainly in the overhead material. Sulfur removal is facilitated in the process because typically 90% of it appears in the gas as hydrogen sulfide, H_2S, and 10% as carbonyl sulfide, COS; carbon disulfide, CS_2, and/or methyl thiol, CH_3SH, are not usually formed.

The production of synthetic natural gas can be achieved by use of the Lurgi gasifier (Fig. 7), which is similar in principle to the Wellman-Galusha unit and is designed for operation at pressures up to 3.1 MPa (450 psi) (46). Three distinct reaction zones are identifiable in a pressurized (1.9–2.9 MPa (280–425 psi)) Lurgi reactor: (*1*) the drying/devolatilization and pyrolysis zone, 370–595°C, nearest the coal feed end, commences the process by converting the coal to a reactive char; (*2*) the gasification zone (595–1205°C); and (*3*) the combustion zone ($>$1205°C), nearest the discharge end, which provides the heat requirements for the endothermic steam–carbon reaction. Equations and reaction enthalpies for the last two zones are given in Table 4.

The operating conditions in the gasifier (temperature and pressure) and the reaction kinetics (residence time, concentration of the constituents, and rate constants) determine the extent of conversion or approach to equilibrium.

The coal is fed through a lockhopper mounted on the top of the gasifier where a rotating distributor provides uniform coal feed across the bed. When processing caking coals, blades attached to the distributor rotate within the bed to break up agglomerates. A revolving grate supports the bed at the bottom and serves as a distributor for steam and oxygen. Solid residue is removed at the bottom of the gasifier through an

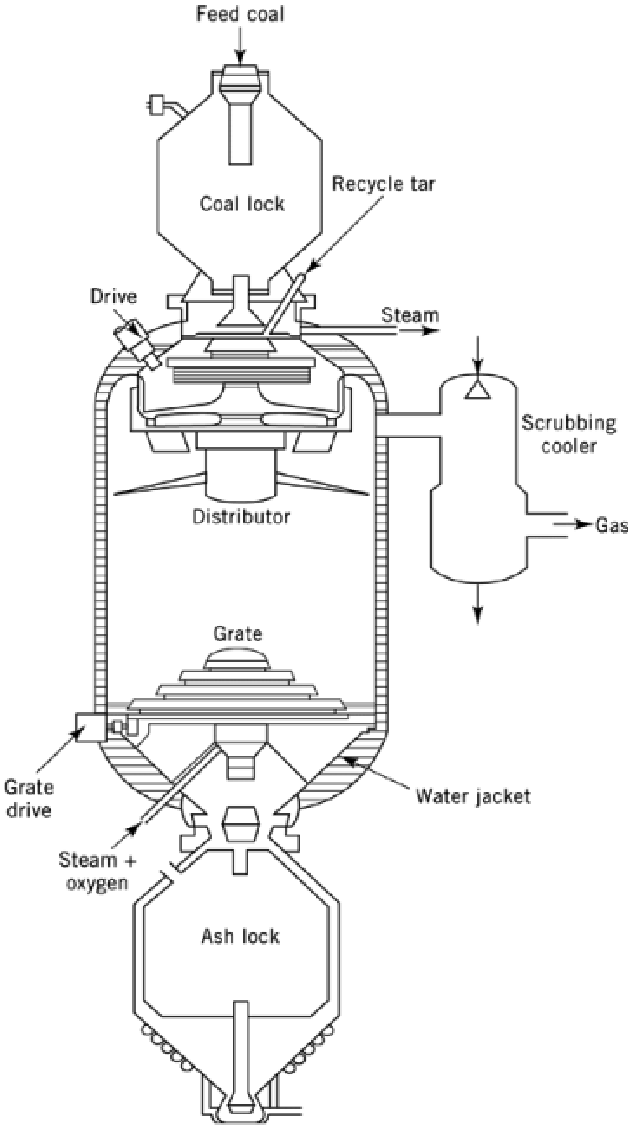

Fig. 7. The pressurized Lurgi gas producer.

ash lockhopper. The entire gasifier vessel is surrounded by a water jacket in which high pressure steam is generated.

Crude gas leaves from the top of the gasifier at 288–593°C depending on the type of coal used. The composition of gas also depends on the type of coal and is notable for the relatively high methane content when contrasted to gases produced at lower pressures or higher temperatures. These gas products can be used as produced for electric power production or can be treated to remove carbon dioxide and hydrocarbons to provide synthesis gas for ammonia, methanol, and synthetic oil production. The gas is made suitable for methanation, to produce synthetic natural gas, by a partial shift and carbon dioxide and sulfur removal.

As in most of the high heat-value processes, the raw gas is in the medium heat-value gas range and can be employed directly in that form. Removing the carbon dioxide raises the heating value, but not enough to render the product worthwhile as a high heat-value gas without methanation.

Methanation of the clean desulfurized main gas (less than 1 ppm total sulfur) is accomplished in the presence of a nickel catalyst at temperatures from 260–400°C and pressure range of 2–2.8 MPa (300–400 psi). Equations and reaction enthalpies are given in Table 4.

Hydrogenation of the oxides of carbon to methane according to the above reactions is sometimes referred to as the Sabatier reactions. Because of the high exothermicity of the methanization reactions, adequate and precise cooling is necessary in order to avoid catalyst deactivation, sintering, and carbon deposition by thermal cracking.

Catalytic methanation processes include (*1*) fixed or fluidized catalyst-bed reactors where temperature rise is controlled by heat exchange or by direct cooling using product gas recycle; (*2*) through wall-cooled reactor where temperature is controlled by heat removal through the walls of catalyst-filled tubes; (*3*) tube-wall reactors where a nickel–aluminum alloy is flame-sprayed and treated to form a Raney-nickel catalyst bonded to the reactor tube heat-exchange surface; and (*4*) slurry or liquid-phase (oil) methanation.

To enable interchangeability of the SNG with natural gas, on a calorific, flame, and toxicity basis, the synthetically produced gas consists of a minimum of 89 vol % methane, a maximum of 0.1% carbon monoxide, and up to 10% hydrogen. The specified minimum acceptable gross heating value is approximately 34.6 MJ/m^3 (930 Btu/ft^3).

In a combined power cycle operation, clean (sulfur- and particulate-free) gas is burned with air in the combustor at elevated pressure. The gas is either low or medium heat-value, depending on the method of gasification.

The hot gases from the combustor, temperature controlled to 980°C by excess air, are expanded through the gas turbine, driving the air compressor and generating electricity. Sensible heat in the gas turbine exhaust is recovered in a waste heat boiler by generating steam for additional electrical power production.

The use of hot gas clean-up methods to remove the sulfur and particulates from the gasified fuel increases turbine performance by a few percentage points over the cold clean-up systems. Hot gas clean-up permits use of the sensible heat and enables retention of the carbon dioxide and water vapor in the gasified fuel, thus enhancing turbine performance. Further, additional power may be generated, prior to combustion with air, in an expansion turbine as the hot product fuel gas is expanded to optimum pressure level for the combined cycle. Future advances in gas turbine technology (turbine inlet temperature above 1650°C) are expected to boost the overall combined cycle efficiency substantially.

More recently, advanced generation gasifiers have been under development, and commercialization of some of the systems has become a reality (36, 41). In these newer developments, the emphasis has shifted to a greater throughput, relevant to the older gasifiers, and also to high carbon conversion levels and, thus, higher efficiency units.

For example, the Texaco entrained system features coal–water slurry feeding a pressurized oxygen-blown gasifier with a quench zone for slag cooling (Fig. 8). In fact, the coal is partially oxidized to provide the heat for the gasification reactions. The Dow gasifier also utilizes a coal–water slurry fed system whereas the Shell gasifier features a dry-feed entrained gasification system which operates at elevated temperature and pressure. The Kellogg Rust Westinghouse system and the Institute of Gas Technology U-Gas system are representative of ash agglomerating fluidized-bed systems.

In response to the disadvantage that the dry ash Lurgi gasifier requires that temperatures have to be below the ash melting point to prevent clinkering, improvements have been sought in the unit; as a result the British Gas-Lurgi GmbH gasifier came into being. This unit is basically similar to the dry ash Lurgi unit insofar as the top of the unit is identical but the bottom has been modified to include a slag quench vessel (Fig. 9). Thus the ash melts at the high temperatures in the combustion zone (up to 2000°C) and forms a slag that runs into the quench chamber, which is in reality a water bath where the slag forms granules of solid

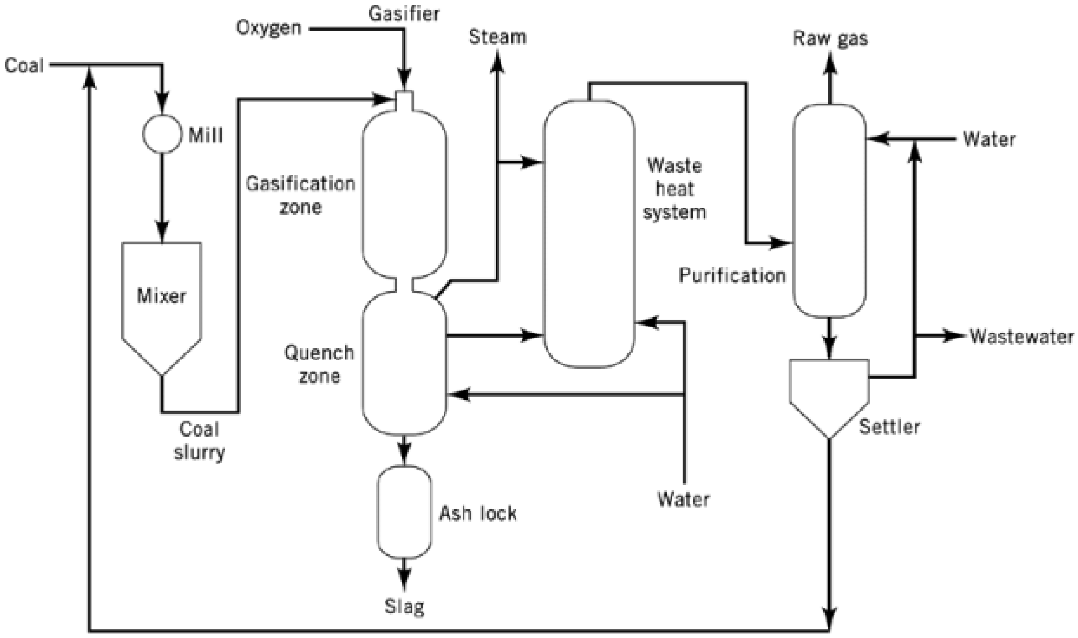

Fig. 8. The Texaco gasification process.

ash. Temperatures and reaction rates are high in the gasification zone so that coal residence time is markedly reduced over that of the dry ash unit.

In summary, these second-generation gasifiers offer promise for the future in terms of increased efficiency as well as for use of other feedstocks, such as biomass. The older, first-generation gasifiers, however, continue to be used.

1.4. Combustion

Coal combustion, not being in the strictest sense a process for the generation of gaseous synfuels, is nevertheless an important use of coal as a source of gaseous fuels. Coal combustion, an old art and probably the oldest known use of this fossil fuel, is an accumulation of complex chemical and physical phenomena. The complexity of coal itself and the variable process parameters all contribute to the overall process (8, 10, 47–50) (see also Combustion science and technology).

There are two principal methods of coal combustion: fixed-bed combustion and combustion in suspension. The first fixed beds, eg, open fires, fireplaces, and domestic stoves, were simple in principle. Suspension burning of coal began in the early 1900s with the development of pulverized coal-fired systems, and by the 1920s these systems were in widespread use. Spreader stokers, which were developed in the 1930s, combined both principles by providing for the smaller particles of coal to be burned in suspension and larger particles to be burned on a grate (10).

A significant issue in combustors in the mid-1990s is the performance of the process in an environmentally acceptable manner through the use of either low sulfur coal or post-combustion clean-up of the flue gases. Thus there is a marked trend to more efficient methods of coal combustion and, in fact, a combustion system that is able to accept coal without the necessity of a post-combustion treatment or without emitting objectionable amounts of sulfur oxides, nitrogen oxides, and particulates is very desirable (51, 52).

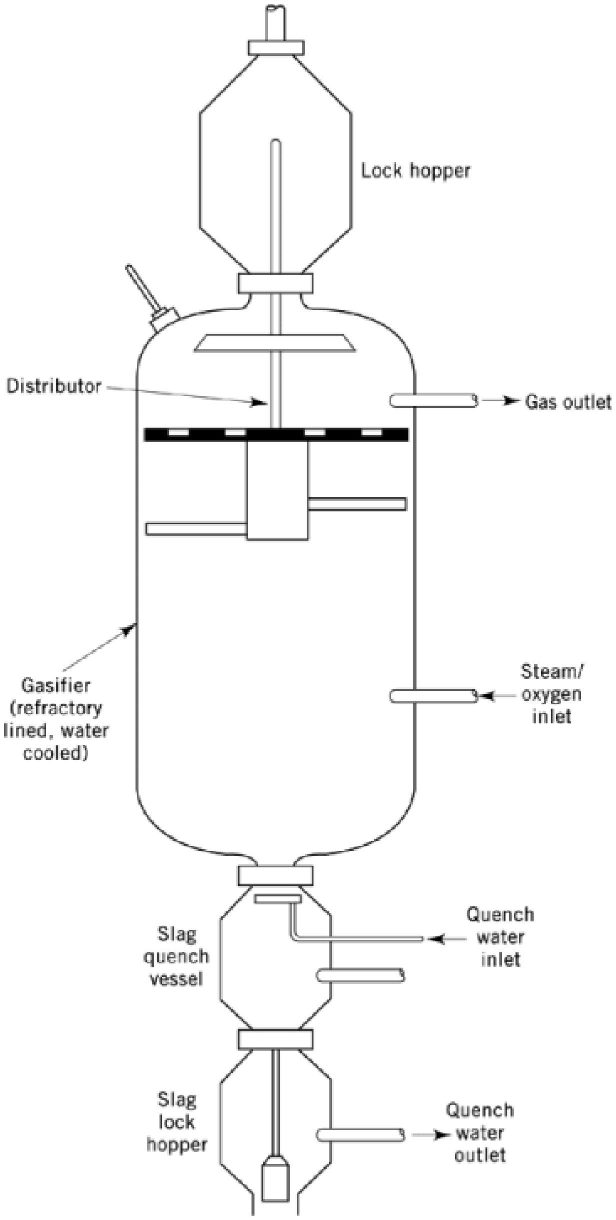

Fig. 9. The British Gas-Lurgi slagging gasifier.

The parameters of rank and moisture content are regarded as determining factors in combustibility as it relates to both heating value and ease of reaction as well as to the generation of pollutants (48). Thus, whereas the lower rank coals may appear to be more reactive than higher rank coals, though exhibiting a lower heat-value and thereby implying that rank does not affect combustibility, environmental constraints arise through the occurrence of heteroatoms, ie, noncarbon atoms such as nitrogen and sulfur, in the coal. At the same time, anthracites, which have a low volatile matter content, are generally more difficult to burn than bituminous coals.

1.4.1. Chemistry

In direct combustion coal is burned to convert the chemical energy of the coal into thermal energy, ie, the carbon and hydrogen in the coal are oxidized into carbon dioxide and water.

$$2\ \mathrm{H_{coal}} + \mathrm{O_2} \longrightarrow \mathrm{H_2O}$$

After burning, the sensible heat in the products of combustion can then be converted into steam that can be used for external work or can be converted directly into energy to drive a shaft, eg, in a gas turbine. In fact, the combustion process actually represents a means of achieving the complete oxidation of coal.

The combustion of coal may be simply represented as the staged oxidation of coal carbon to carbon dioxide

$$2\ \mathrm{C_{coal}} + \mathrm{O_2} \longrightarrow 2\ \mathrm{CO}$$

$$2\ \mathrm{CO} + \mathrm{O_2} \longrightarrow 2\ \mathrm{CO_2}$$

with any reactions of the hydrogen in the coal being considered to be of secondary importance. Other types of combustion systems may be rate-controlled as a result of the onset of the Boudouard reaction (see Table 4).

The complex nature of coal as a molecular entity (2, 3, 24, 25, 35, 37, 53) has resulted in the chemical explanations of coal combustion being confined to the carbon in the system. The hydrogen and other elements have received much less attention but the system is extremely complex and the heteroatoms, eg, nitrogen, oxygen, and sulfur, exert an influence on the combustion. It is this latter that influences environmental aspects.

For example, the conversion of nitrogen and sulfur, during coal combustion, to the respective oxides during combustion cannot be ignored:

$$\mathrm{S_{coal}} + \mathrm{O_2} \longrightarrow \mathrm{SO_2}$$

$$2\ \mathrm{SO_2} + \mathrm{O_2} \longrightarrow 2\ \mathrm{SO_3}$$

$$2\ \mathrm{N_{coal}} + \mathrm{O_2} \longrightarrow 2\ \mathrm{NO}$$

$$2\ \mathrm{NO} + \mathrm{O_2} \longrightarrow 2\ \mathrm{NO_2}$$

$$\mathrm{N_{coal}} + \mathrm{O_2} \longrightarrow \mathrm{NO_2}$$

The sulfur and nitrogen oxides that escape into the atmosphere can be converted to acids by reaction with moisture in the atmosphere (see also Air pollution; Atmospheric models)

Sulfurous acid $SO_2 + H_2O \longrightarrow H_2SO_3$

Sulfuric acid $2\ SO_2 + O_2 \longrightarrow 2\ SO_3$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Nitrous acid $NO + H_2O \longrightarrow H_2NO_2$

Nitric acid $2\ NO + O_2 \longrightarrow 2\ NO_2$

$$NO_2 + H_2O \longrightarrow HNO_3$$

1.4.2. Combustion Systems

Combustion systems vary in nature depending on the nature of the feedstock and the air needed for the combustion process (54). However, the two principal types of coal-burning systems are usually referred to as layer and chambered. The former refers to fixed beds; the latter is more specifically for pulverized fuel.

1.4.2.1. Fixed or Slowly Moving Beds. For fuel-bed burning on a grate, a distillation effect occurs. The result is that liquid components which are formed volatilize before combustion temperatures are reached; cracking may also occur. The ignition of coal in a bed is almost entirely by radiation from hot refractory arches and from the flame burning of volatiles. In fixed beds, the radiant heat above the bed can only penetrate a short distance into the bed.

Consequently, convective heat transfer determines the intensity of warming up and ignition. In addition, convective heat transfer also plays an important part in the overall flame-to-surface transmission. The reaction of gases is greatly accelerated by contact with hot surfaces and, whereas the reaction away from the walls may proceed slowly, reaction at the surface proceeds much more rapidly.

1.4.2.2. Fluidized Beds. Fluidized-bed combustion occurs in expanded beds (Fig. 3) and at relatively lower (925°C) temperatures; high convective transfer rates exist resulting from the bed motion. Fluidized systems can operate under substantial pressures thereby allowing more efficient gas clean-up. Fluidized-bed combustion is a means for providing high heat-transfer rates, controlling sulfur, and reducing nitrogen oxide emissions from the low temperatures in the combustion zone.

There are, however, problems associated with pollution control. Whereas the sulfur may be removed downstream using suitable ancillary controls, the sulfur may also be captured in the bed, thereby adding to the separations and recycle problems. Capture during combustion, however, is recognized as the ideal and is a source of optimism for fluidized combustion.

A fluidized bed is an excellent medium for contacting gases with solids, and this can be exploited in a combustor because sulfur dioxide emissions can be reduced by adding limestone, $CaCO_3$, or dolomite, $CaCO_3 \cdot MgCO_3$, to the bed.

$$2\ SO_2 + O_2 \longrightarrow 2\ SO_3$$

$$SO_3 + CaCO_3 \longrightarrow CaSO_4 + CO_2$$

or

$$2\ SO_2 + O_2 + 2\ CaCO_3 \longrightarrow 2\ CaSO_4 + 2\ CO_2$$

The spent sorbent from fluidized-bed combustion may be taken directly to disposal and is much easier than the disposal of salts produced by wet limestone scrubbing. Alternatively, the spent sorbent may be regenerated using synthesis gas, CO/H_2.

$$CaSO_4 + H_2 \longrightarrow CaO + H_2O + SO_2$$

$$CaSO_4 + CO \longrightarrow CaO + CO_2 + SO_2$$

The calcium oxide product is supplemented with fresh limestone and returned to the fluidized bed. Two undesirable side reactions can occur in the regeneration of spent lime leading to the production of calcium sulfide:

$$CaSO_4 + 4\ H_2 \longrightarrow CaS + 4\ H_2O$$

$$CaSO_4 + 4\ CO \longrightarrow CaS + 4\ CO_2$$

which results in the recirculation of sulfur to the bed.

1.4.2.3. Entrained Systems. In entrained systems, fine grinding and increased retention times intensify combustion but the temperature of the carrier and degree of dispersion are also important. In practice, the coal is introduced at high velocities which may be greater than 30 m/s and involve expansion from a jet to the combustion chamber.

Types of entrained systems include cyclone furnaces, which have been used for various coals. Other systems have been developed and utilized for the injection of coal–oil slurries into blast furnaces or for the burning of coal–water slurries. The cyclone furnace, developed in the 1940s to burn coal having low ash-fusion temperatures, is a horizontally inclined, water-cooled, tubular furnace in which crushed coal is burned with air entering the furnace tangentially. Temperatures may be on the order of 1700°C and the ash in the coal is converted to a molten slag that is removed from the base of the unit. Coal fines burn in suspension; the larger pieces are captured by the molten slag and burn rapidly.

2. Gas from Other Fossil Fuels

As of this writing natural gas is a plentiful resource, and there has been a marked tendency not to use other fossil fuels as SNG sources. However, petroleum and oil shale (qv) have been the subject of extensive research efforts. These represent other sources of gaseous fuels and are worthy of mention here.

2.1. Petroleum

Thermal cracking (pyrolysis) of petroleum or fractions thereof was an important method for producing gas in the years following its use for increasing the heat content of water gas. Many water gas sets operations were converted into oil-gasification units (55). Some of these have been used for base-load city gas supply, but most find use for peak-load situations in the winter.

In the 1940s, the hydrogasification of oil was investigated as a follow-up to the work on the hydrogasification of coal (56, 57). In the ensuing years, further work was carried out as a supplement to the work on thermal cracking (58, 59), and during the early 1960s it became evident that light distillates having end boiling points $<182^\circ C$ and containing no sulfur could be catalytically reformed by an autothermic process to pure methane (60). This method was extensively used in England until natural (North Sea) gas came into use.

Prior to the discovery of plentiful supplies of natural gas, and depending on the definition of the resources (1), there were plans to accommodate any shortfalls in gas supply from solid fossil fuels and from gaseous resources by the conversion of hydrocarbon (petroleum) liquids to lower molecular weight gaseous products.

$$CH_{petroleum} \longrightarrow CH_4$$

2.1.1. Thermal Cracking

In addition to the gases obtained by distillation of crude petroleum, further highly volatile products result from the subsequent processing of naphtha and middle distillate to produce gasoline, as well as from hydrodesulfurization processes involving treatment of naphthas, distillates, and residual fuels (5, 61), and from the coking or similar thermal treatment of vacuum gas oils and residual fuel oils (5).

The chemistry of the oil-to-gas conversion has been established for several decades and can be described in general terms although the primary and secondary reactions can be truly complex (5). The composition of the gases produced from a wide variety of feedstocks depends not only on the severity of cracking but often to an equal or lesser extent on the feedstock type (5, 62, 63). In general terms, gas heating values are on the order of 30–50 MJ/m^3 (950–1350 Btu/ft^3).

2.1.2. Catalytic Processes

A second group of refining operations which contribute to gas production are the catalytic cracking processes, such as fluid-bed catalytic cracking, and other variants, in which heavy gas oils are converted into gas, naphthas, fuel oil, and coke (5).

The catalysts promote steam reforming reactions that lead to a product gas containing more hydrogen and carbon monoxide and fewer unsaturated hydrocarbon products than the gas product from a noncatalytic process (5). Cracking severities are higher than those from thermal cracking, and the resulting gas is more suitable for use as a medium heat-value gas than the rich gas produced by straight thermal cracking. The catalyst also influences the reactions rates in the thermal cracking reactions, which can lead to higher gas yields and lower tar and carbon yields (5).

The basic chemical premise involved in making synthetic natural gas from heavier feedstocks is the addition of hydrogen to the oil:

$$CH_3\,(CH_2)_n\,CH_3 + (n+1)\,H_2 \longrightarrow (n+2)\,CH_4$$

In general terms, as the molecular weight of the feedstock is increased, similar operating conditions of hydrogasification lead to decreasing hydrocarbon gas yields, increasing yields of aromatic liquids, with carbon also appearing as a product.

The principal secondary variable that influences yields of gaseous products from petroleum feedstocks of various types is the aromatic content of the feedstock. For example, a feedstock of a given H/C (C/H) ratio that contains a large proportion of aromatic species is more likely to produce a larger proportion of liquid products and elemental carbon than a feedstock that is predominantly paraffinic (5).

Another option for processing crude oils which are too heavy to be hydrogasified directly involves first hydrocracking the crude oil to yield a low boiling product suitable for gas production and a high boiling product suitable for hydrogen production by partial oxidation (57). Alternatively, it may be acceptable for carbon deposition to occur during hydrogasification which can then be used for heat or for hydrogen production (64, 65).

2.1.3. Partial Oxidation

It is often desirable to augment the supply of naturally occurring or by-product gaseous fuels or to produce gaseous fuels of well-defined composition and combustion characteristics (5). This is particularly true in areas where the refinery fuel (natural gas) is in poor supply and/or where the manufacture of fuel gases, originally from coal and more recently from petroleum, has become well established.

Almost all petroleum fractions can be converted into gaseous fuels, although conversion processes for the heavier fractions require more elaborate technology to achieve the necessary purity and uniformity of the manufactured gas stream (5). In addition, the thermal yield from the gasification of heavier feedstocks is invariably lower than that of gasifying light naphtha or liquefied petroleum gas(es) because, in addition to the production of hydrogen, carbon monoxide, and gaseous hydrocarbons, heavy feedstocks also yield some tar and coke.

As in the case of coal, synthetic natural gas can be produced from heavy oil by partially oxidizing the oil to a mixture of carbon monoxide and hydrogen

$$2\ \mathrm{CH}_{\mathrm{petroleum}} + \mathrm{O}_2 \longrightarrow 2\ \mathrm{CO} + \mathrm{H}_2$$

which is methanated catalytically to produce methane of any required purity. The initial partial oxidation step consists of the reaction of the feedstock with a quantity of oxygen insufficient to burn it completely, making a mixture consisting of carbon monoxide, carbon dioxide, hydrogen, and steam. Success in partially oxidizing heavy feedstocks depends mainly on details of the burner design (66). The ratio of hydrogen to carbon monoxide in the product gas is a function of reaction temperature and stoichiometry and can be adjusted, if desired, by varying the ratio of carrier steam to oil fed to the unit.

To make synthetic natural gas by partial oxidation, virtually all of the methane in the product gas must be produced by catalytic methanation of carbon monoxide and hydrogen. The feed is mixed with recycled carbon and fed, together with steam and oxygen, to a reactor in which partial combustion takes place. Heat from the reaction gasifies the rest of the feed, and by-product coke is formed. The heavier feedstocks tend to produce more carbon than can be consumed through recycling; thus some must be withdrawn. After carbon separation by water scrubbing, the synthesis gas that is available can be converted into hydrogen or into synthetic natural gas by methanation.

2.1.4. Steam Reforming

When relatively light feedstocks, eg, naphthas having ca 180°C end boiling point and limited aromatic content, are available, high nickel content catalysts can be used to simultaneously conduct a variety of near-autothermic reactions. This results in the essentially complete conversions of the feedstocks to methane:

$$CH_3\,(CH_2)_3\,CH_3 + 2\,H_2O \longrightarrow 4\,CH_4 + CO_2$$

Because of limitations on the activity of practical catalysts, this reaction must be carried out in stages, the first of which is carried out at 425–480°C and 1.5–2.9 MPa (200–400 psi) and amounts approximately to the following reaction:

$$C_5H_{12} + 3\,H_2O \longrightarrow 3\,CH_4 + CO_2 + 3\,H_2 + CO$$

In ensuing catalytic stages, usually termed hydrogasification and methanation (not to be confused with the noncatalytic, direct hydrogasification processes described above), the remaining carbon monoxide and hydrogen are reacted to produce additional methane.

2.2. Oil Shale

Oil shale (qv) is a sedimentary rock that contains organic matter, referred to as kerogen, and another natural resource of some consequence that could be exploited as a source of synthetic natural gas (67–69). However, as of this writing, oil shale has found little use as a source of substitute natural gas.

2.3. Biomass

Biomass is simply defined for these purposes as any organic waste material, such as agricultural residues, animal manure, forestry residues, municipal waste, and sewage, which originated from a living organism (70–74).

Biomass is another material that can produce a mixture of carbonaceous solid and liquid products as well as gas:

$$C_{\mathrm{organic}} \longrightarrow C_{\mathrm{coke/char/carbon}} + \mathrm{liquids} + \mathrm{gases}$$

Whereas biomass has not received the same attention as coal as a source of gaseous fuels, questions about the security of fossil energy supplies related to the availability of natural and substitute gas have led to a search for more reliable and less expensive energy sources (75). Biomass resources are variable, but it has been estimated that substantial amounts (up to 20×10^6 mJ$(20 \times 10^{15}$ Btu$)$) of energy, representing ca 19% of the annual energy consumption in the United States. In addition, environmental issues associated with the use of coal have led some energy producers to question the use of large central energy generating plants. However, biomass may be a gaseous fuel source whose time is approaching (see Fuels from biomass).

The means by which synthetic gaseous fuels could be produced from a variety of biomass sources are variable and many of the known gasification technologies can be applied to the problem (70, 71, 76–82). For example, the Lurgi circulatory fluidized-bed gasifier is available for the production of gaseous products from biomass feedstocks as well as from coal (83, 84).

3. Gas Treating

The reducing conditions in gasification reactors effect the conversion of the sulfur and nitrogen in the feed coal to hydrogen sulfide, H_2S, and ammonia, NH_3. Some carbonyl sulfide, COS, carbon disulfide, CS_2, mercaptans, RSH, and hydrogen cyanide, HCN, are also formed in the gasifier. These compounds, along with carbon dioxide, are removed simultaneously, either selectively or nonselectively, from the gas stream in the clean-up stages of the process using commercially available physical or chemical solvents and scrubbing agents (1, 5, 85–88).

Solvents used for hydrogen sulfide absorption include aqueous solutions of ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), and diisopropanolamine (DIPA) among others:

$$2\,RNH_2 + H_2S \longrightarrow (RNH_3)_2\,S$$

$$(RNH_3)_2\,S + H_2S \longrightarrow 2\,RNH_3HS$$

$$2\,RNH_2 + CO_2 + H_2O \longrightarrow (RNH_3)_2\,CO_3$$

$$(RNH_3)_2\,CO_3 + CO_2 + H_2O \longrightarrow 2\,RNH_3HCO_3$$

$$2\,RNH_2 + CO_2 \longrightarrow RNHCOONH_3R$$

These solvents differ in volatility and selectivity for the removal of H_2S, mercaptans, and CO_2 from gases of different composition. Other alkaline solvents used for the absorption of acidic components in gases include potassium carbonate, K_2CO_3, solutions combined with a variety of activators and solubilizers to improve gas–liquid contacting.

Whereas most alkaline solvent absorption (qv) processes result in gases of acceptable purity for most purposes, it is often essential to remove the last traces of residual sulfur compounds from gas streams. This is in addition to ensuring product purity such as the removal of water, higher hydrocarbons, and dissolved elemental sulfur from liquefied petroleum gas. Removal can be accomplished by passing the gas over a bed of molecular sieves (qv), synthetic zeolites commercially available in several proprietary forms. Impurities are retained by the packed bed, and when the latter is saturated it can be regenerated by passing hot clean gas or hot nitrogen, generally in a reverse direction (see also Catalysts, regeneration).

By-product water formed in the methanation reactions is condensed by either refrigeration or compression and cooling. The remaining product gas, principally methane, is compressed to desired pipeline pressures of 3.4–6.9 MPa (500–1000 psi). Final traces of water are absorbed on silica gel or molecular sieves, or removed by a drying agent such as sulfuric acid, H_2SO_4. Other desiccants may be used, such as activated alumina, diethylene glycol, or concentrated solutions of calcium chloride (see Desiccants).

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