2 Gasification of Coal

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2.1 BACKGROUND

Conversion of coal by any of the processes to produce a mixture of combustible gases is termed *coal gasification*, even though a large number of chemical reactions other than so-called gasification reactions are involved. Even though the product gases of coal gasification involve combustible chemical species, the purpose of gasification is not limited to generation of gaseous fuel, because the product gas can be easily processed to generate other valuable chemical and petrochemical feedstock. Commercial gasification of coal generally entails the controlled partial oxidation of the coal to convert it into desired gaseous products. The coal can be heated either directly by combustion or indirectly by another heat source. A gasifying medium is typically passed over (or through) the heated coal to provide intimate molecular contact for chemical reaction. The gaseous reactants react with carbonaceous matters of coal (i.e., coal hydrocarbons) or with other primary decomposition products of coal to produce gaseous products. Not all the gaseous products generated by such processes are desirable from the standpoints of fuel quality, further processing, and environmental issues. Therefore, coal gasification is always performed in connection with downstream processes, not only for final applications but also for gas-cleaning purposes. The primary emphases of coal gasification may be on electricity generation via *integrated gasification combined cycle* (IGCC) types, on syngas production for pipeline applications, on *hydrogen production*, or on synthesis of *liquid fuels* and petrochemicals as alternative sources of raw materials. With the advent of a hydrogen economy, the role of coal gasification in generation of hydrogen may become even more important.[75]

Conversion of coal from its solid form to a gaseous fuel (or, gaseous chemical) is widely practiced today. During earlier years (1920–1940), coal gasification was being employed to produce *manufactured gas* in hundreds of plants worldwide, and such plants were called *manufactured gas plants* (MGPs). This technology became obsolete in the post–World War II era because of the abundant supply of petroleum and natural gas at affordable prices. With the advent of the *oil embargo* in the early 1970s and subsequent increases and fluctuations in petroleum prices, as well as the natural gas and petroleum shortage experienced during the beginning of the 21st century, the interest in coal gasification as well as its further commercial exploitation was revived. Recently, surging interest in fuel cell technology also prompted keen interest in coal gasification as a means of obtaining reliable and inexpensive hydrogen sources. Many major activities in research, development, and the demonstration of coal gasification have recently resulted in significant improvements in conventional technology, and thus made coal gasification more competitive in modern fuel markets.[1]

The concept of electric power generation based on coal gasification received its biggest boost in the 1990s when the U.S. Department of Energy's Clean Coal Technology Program provided federal cost sharing for the first true commercial-scale IGCC plants in the U.S. Tampa Electric Company's Polk Power Station near Mulberry, FL, is the nation's first "greenfield" (built as a brand new plant, not a retrofit) commercial gasification combined cycle power station.[75] The plant, dedicated in 1997, is capable of producing 313 MW of electricity and removing more than 98% of sulfur in coal that is converted into commercial products. On the other hand, the Wabash River Coal Gasification Repowering Project was the first full-size commercial gasification combined cycle plant built in the U.S., located outside West Terre Haute, IN. The plant started full operations in November 1995. The plant is capable of producing 292 MW of electricity and is still one of the world's largest single-train IGCCs operating commercially.[75]

Coal gasification includes a series of reaction steps that convert coal containing C, H, and O, as well as impurities such as S and N, into *synthesis gas* and other forms of 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. The proportions of the resultant product gases (CO, CO_2, CH_4, H_2, H_2O, N_2, H_2S, SO_2, etc.) depend 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.

Coal gasification technology can be utilized in the following energy systems of potential importance:

1. Production of fuel for use in electric power generation units
2. Manufacturing synthetic or substitute natural gas (SNG) for use as pipeline gas supplies
3. Producing hydrogen for fuel cell applications
4. Production of synthesis gas for use as a chemical feedstock
5. Generation of fuel gas (low-Btu or medium-Btu gas) for industrial purposes

Coal is the largest recoverable fossil fuel resource in the U.S. as well as in the world. Synthesis gas production serves as the starting point for production of a variety of chemicals. The success of the Tennessee Eastman Corp. in producing acetic anhydride from coal shows the great potential of using coal as petrochemical feedstock.[2] A major concern for such a technology involves the contaminants in coal. Coal contains appreciable amounts of sulfur, which is of principal concern to the downstream processes because many catalysts that might be used in the production of chemicals are highly susceptible to *sulfur poisoning*. Coals also contain nonnegligible amounts of alkali metal compounds that contribute to the fouling and *corrosion* of the reactor vessels in the form of slag. Further, coal also contains a number of trace elements that may also affect downstream processes and potentially create environmental and safety risks. If coal gasification is to be adopted to produce certain target chemicals, the choice of the specific gasification technology becomes very critical because a different process will produce a different quality (or composition) of synthesis gas as well as alter the economics of production.

Synthesis gas (SG) is a very important starting material for both fuels and petrochemicals. Synthesis gas is also called *syn gas* or *syngas*. It can be obtained from various sources including petroleum, natural gas, coal, biomass, and even municipal solid wastes (MSWs). Syngas is conveniently classified, based on its principal composition, as: (1) H_2-rich gas, (2) CO-rich gas, (3) CO_2-rich gas, (4) CH_4-rich gas, etc. Principal fuels and chemicals directly made from syngas include hydrogen, carbon monoxide, methane, ammonia, methanol, dimethylether, gasoline, diesel fuel, ethylene, isobutylene, mixture of C_2-C_4 olefins, C_1-C_5 alcohols, ethanol, ethylene glycol, etc.[74]

Secondary fuels and chemicals synthesized via methanol routes include formaldehyde, acetic acid, gasoline, diesel fuel, methyl formate, methyl acetate, acetaldehyde, acetic anhydride, vinyl acetate, dimethylether, ethylene, propylene, isobutylene, ethanol, C_1-C_5 alcohols, propionic acid, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), benzene, toluene, xylenes, ethyl acetate, a methylating agent, etc. The synthesis route of such chemicals via methanol as an intermediate is called *indirect synthesis*.

2.2 SYNGAS CLASSIFICATION BASED ON ITS HEATING VALUE

Depending on the heating values of the resultant synthesis gases produced by gasification processes, product gases are typically classified as three types of gas mixtures[3]:

1. *Low-Btu gas* consisting of a mixture of carbon monoxide, hydrogen, and some other gases with a heating value typically less than 300 Btu/scf.
2. *Medium-Btu gas* consisting of a mixture of methane, carbon monoxide, hydrogen, and various other gases with a heating value in the range of 300–700 Btu/scf.
3. *High-Btu gas* consisting predominantly of methane with a heating value of approximately 1000 Btu/scf. It is also referred to as *SNG*.

Coal gasification involves the reaction of coal carbon (precisely speaking, macromolecular coal hydrocarbons) and other pyrolysis products with oxygen, hydrogen, and water to provide fuel gases.

2.2.1 LOW-BTU GAS

For production of low-Btu gases, air is typically used as a combusting (or gasifying) agent. As air, instead of pure oxygen, is used, the product gas inevitably contains a large concentration of undesirable constituents such as nitrogen or nitrogen-containing compounds. Therefore, it results in a low heating value of 150–300 Btu/scf. Sometimes, this type of gasification of coal may be carried out *in situ*, i.e., underground, where mining of coal by other techniques is not economically favorable. For such *in situ* gasification, low-Btu gas may be a desired product. Low-Btu gas contains 5 principal components with around 50% v/v nitrogen, some quantities of hydrogen and carbon monoxide (combustible), carbon dioxide, and some traces of methane. The presence of such high contents of nitrogen classifies the product gas as low Btu. The other two noncombustible components (CO_2 and H_2O) further lower the heating value of the product gas. The presence of these components limits the applicability of low-Btu gas to chemical synthesis. The two major combustible components are hydrogen and carbon monoxide; their ratio varies depending on the gasification conditions employed. One of the most undesirable components is hydrogen sulfide (H_2S), which occurs in a ratio proportional to the sulfur content of the original coal. It must be removed by gas-cleaning procedures before product gas can be used for other useful purposes such as further processing and upgrading.

2.2.2 MEDIUM-BTU GAS

In the production of medium-Btu gas, pure oxygen rather than air is used as combusting agent, which results in an appreciable increase in the heating value, by about 300–400 Btu/scf. The product gas predominantly contains carbon monoxide and hydrogen with some methane and carbon dioxide. It is primarily used in the *synthesis of methanol*, higher hydrocarbons via *Fischer–Tropsch synthesis*, and a variety of other chemicals. It can also be used directly as a fuel to generate steam or to drive a gas turbine. The *H_2-to-CO ratio* in medium-Btu gas varies from 2:3 (CO-rich) to more than 3:1 (H_2-rich). The increased heating value is attributed to higher contents of methane and hydrogen as well as to lower concentration of carbon dioxide, in addition to the absence of nitrogen in the gasifying agent.

2.2.3 HIGH-BTU GAS

High-Btu gas consists mainly of pure methane (>95%) and, as such, its heating value is around 900–1000 Btu/scf. It is compatible with natural gas and can be used as a synthetic or substitute natural gas (SNG). This type of syngas is usually produced by catalytic reaction of carbon monoxide and hydrogen, which is called the *methanation reaction*. The feed syngas usually contains carbon dioxide and methane in small amounts. Further, steam is usually present in the gas or added to the feed to alleviate carbon fouling, which alters the catalytic effectiveness. Therefore, the pertinent chemical reactions in the methanation system include:

$$3H_2 + CO = CH_4 + H_2O$$
$$2H_2 + 2CO = CH_4 + CO_2$$

$$4H_2 + CO_2 = CH_4 + 2H_2O$$
$$2CO = C + CO_2$$
$$CO + H_2O = CO_2 + H_2$$

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 syngas mixture of H_2 and CO, the desired H_2-to-CO ratio of the feed syngas is around 3:1. The large amount of H_2O 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 above are quite strongly exothermic except the forward water gas shift (WGS) reaction, which is mildly exothermic, the heat release depends largely on the amount of CO present in the feed syngas. For each 1% of CO in the feed syngas, an adiabatic reaction will experience a 60°C temperature rise, which may be termed as *adiabatic temperature rise*.

A variety of metals exhibit catalytic effects on the methanation reaction. In the order of catalytic activity, Ru > Ni > Co > Fe > Mo. Nickel is by far the most commonly used catalyst in commercial processes because of its relatively low cost and also of reasonably high catalytic activity. Nearly all the commercially available catalysts used for this process are, however, very susceptible to sulfur poisoning and 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 lower than 0.5 ppm in order to maintain adequate catalyst activity for a long period of time. Therefore, the objective of the catalyst development has been aimed at enhancing the *sulfur tolerance* of the catalyst.

Some of the noteworthy commercial methanation processes include Comflux, HICOM, and direct methanation. Comflux is a Ni-based, pressurized fluidized bed (PFB) process converting CO-rich gases into SNG in a single stage, where both methanation and WGS reaction take place simultaneously. The HICOM process developed by British Gas Corporation is a fixed bed process, which involves a series of methanation stages using relatively low H_2-to-CO ratio syngas. Direct methanation is a process developed by the Gas Research Institute (GRI), which methanates equimolar mixtures of H_2 and CO, producing CO_2 rather than H_2O (steam) in addition to methane:

$$2\ H_2 + 2\ CO = CH_4 + CO_2$$

The catalyst developed is claimed to be unaffected by sulfur poisoning and, as such, the process can be used to treat the raw, quenched gas from a coal gasifier with no or little pretreatment.[76]

2.3 COAL GASIFICATION REACTIONS

In coal gasification, four principal reactions are crucial:

1. Steam gasification
2. Carbon dioxide gasification

3. Hydrogasification
4. Partial oxidation reaction

In most gasifiers, several of these reactions, along with the WGS reaction, occur simultaneously. Table 2.1 shows the *equilibrium constants* for these reactions as functions of temperature. The same data are plotted in Figure 2.1, as $\log_{10} K_p$ vs. $1/T$. From the figure, the following are evident and significant:

1. The plots of $\log_{10} K_p$ vs. $1/T$ are nearly linear for all reactions.
2. The exothermicity of reaction is on the same order as the slope of the plot of $\log_{10} K_p$ vs. $1/T$ for each reaction.
3. By the criterion of $K_p > 1$ (i.e., $\log_{10} K_p > 0$), it is found that hydrogasification is thermodynamically favored at lower temperatures, whereas CO_2 and steam gasification reactions are thermodynamically favored at higher temperatures.
4. The equilibrium constant for the WGS reaction is the weakest function of the temperature among all the compared reactions, as clearly evidenced in the plot. This also means that the equilibrium of this reaction can be reversed relatively easily by changing the imposed operating conditions.

2.3.1 STEAM GASIFICATION

The steam gasification reaction is endothermic, i.e., requiring heat input for the reaction to proceed in its forward direction. Usually, an excess amount of steam is also needed to promote the reaction.

TABLE 2.1
Equilibrium Constants for Gasification Reactions

		$\log_{10} K_p$					
T, K	**1/T**	**I**	**II**	**III**	**IV**	**V**	**VI**
300	0.003333	23.93	68.67	15.86	20.81	4.95	8.82
400	0.0025	19.13	51.54	10.11	13.28	3.17	5.49
500	0.002	16.26	41.26	6.63	8.74	2.11	3.43
600	0.001667	14.34	34.4	4.29	5.72	1.43	2
700	0.001429	12.96	29.5	2.62	3.58	0.96	0.95
800	0.00125	11.93	25.83	1.36	1.97	0.61	0.15
900	0.001111	11.13	22.97	0.37	0.71	0.34	0.49
1000	0.001	10.48	20.68	0.42	0.28	0.14	1.01
1100	0.000909	9.94	18.8	1.06	1.08	0.02	1.43
1200	0.000833	9.5	17.24	1.6	1.76	0.16	1.79
1300	0.000769	9.12	15.92	2.06	2.32	0.26	2.1
1400	0.000714	8.79	14.78	2.44	2.8	0.36	2.36

Note: Reaction I: $C + \frac{1}{2}O_2 = CO$; Reaction II: $C + O_2 = CO_2$; Reaction III: $C + H_2O = CO + H_2$; Reaction IV: $C + CO_2 = 2\ CO$; Reaction V: $CO + H_2O = CO_2 + H_2$; Reaction VI: $C + 2\ H_2 = CH_4$.

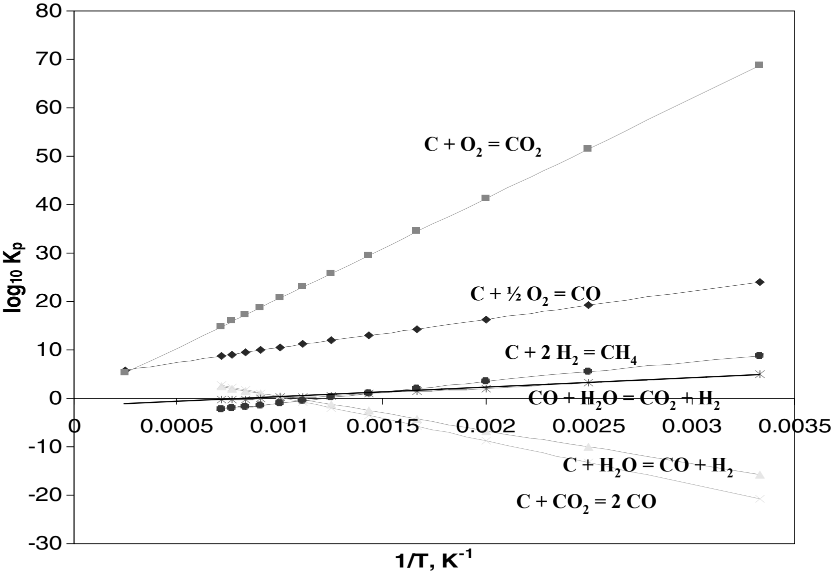

FIGURE 2.1 Equilibrium constant (*K*p) for gasification reactions.

$$C\ (s) + H_2O\ (g) = CO\ (g) + H_2\ (g) \qquad \Delta H^\circ_{298} = 131.3\ \text{kJ/mol}$$

However, excess steam used in this reaction hurts the thermal efficiency of the process. Therefore, this reaction is typically combined with other gasification reactions in practical applications. The H_2-to-CO ratio of the product syngas depends on the synthesis chemistry as well as process engineering. Two reaction mechanisms[77,78] have received most attention for the carbon-steam reactions over a wide range of practical gasification conditions.

Mechanism A[77]

$$C_f + H_2O = C(H_2O)_A$$
$$C(H_2O)_A \rightarrow CO + H_2$$
$$C_f + H_2 = C(H_2)_B$$

In the given equations, C_f denotes free carbon sites that are not occupied, $C(H_2O)_A$ and $C(H_2)_B$ denote chemisorbed species in which H_2O and H_2 are adsorbed onto the carbon site, "=" means the specific mechanistic reaction is reversible, and "→" means the reaction is predominantly irreversible. In Mechanism A, the overall gasification rate is inhibited by hydrogen adsorption on the free sites, thus reducing the availability of the unoccupied active sites for steam adsorption. Therefore, this mechanism may be referred to as *inhibition by hydrogen adsorption.*

Mechanism B[78]

$$C_f + H_2O = C(O)_A + H_2$$
$$C(O)_A \rightarrow CO$$

On the other hand, in Mechanism B, the gasification rate is affected by competitive reaction of chemisorbed oxygen with hydrogen, thus limiting the conversion of chemisorbed oxygen into carbon monoxide. Therefore, this mechanism may be referred to as *inhibition by oxygen exchange.*

Both mechanisms are still capable of producing the rate expression for steam gasification of carbon in the form of[4]:

$$r = k_1 p_{H2O}/(1 + k_2 p_{H2} + k_3 p_{H2O})$$

which was found to correlate with the experimental data quite well. This type of rate expression can be readily derived by taking pseudo–steady state approximation on the adsorbed species of the mechanism.

It has to be clearly noted here that the mechanistic chemistry discussed in this section is based on the reaction between carbon and gaseous reactants, not for reactions between coal and gaseous reactants. Even though carbon is the dominant atomic species present in coal, its reactivity is quite different from that of coal or coal hydrocarbons. In general, coal is more reactive than pure carbon, for a number of reasons, including the presence of various reactive organic functional groups and the availability of catalytic activity via naturally occurring mineral ingredients. It may now be easy to understand why anthracite, which has the highest carbon content among all ranks of coal, is most difficult to gasify or liquefy. Alkali metal salts are known to catalyze the steam gasification reaction of carbonaceous materials, including coals. The order of catalytic activity of alkali metals on coal gasification reaction is $Cs > Rb > K > Na > Li$. In the case of catalytic steam gasification of coal, carbon deposition reaction may affect the catalysts' life by fouling the catalyst active sites. This carbon deposition reaction is more likely to take place whenever the steam concentration is lacking.

2.3.2 CARBON DIOXIDE GASIFICATION

The reaction of coal with CO_2 may be approximated or simplified as the reaction of carbon with carbon dioxide, for modeling purposes. Carbon dioxide reacts with carbon to produce carbon monoxide and this reaction is called *Boudouard reaction.* This reaction is also endothermic in nature, similar to the steam gasification reaction.

$$C\,(s) + CO_2\,(g) = 2\,CO\,(g) \qquad \Delta H^\circ_{298} = 172.5\ \text{kJ/mol}$$

The reverse reaction is a carbon deposition reaction that is a major culprit of carbon fouling on many surfaces, such as process catalyst deactivation. This gasification reaction is thermodynamically favored at high temperatures ($T > 680°C$), which is also quite similar to the steam gasification. The reaction, if carried out alone, requires high temperature (for fast reaction) and high pressure (for higher reactant concentrations) for significant conversion. However, this reaction in practical gasification applications is almost never attempted as a solo chemical reaction, because of a variety of factors including low conversion, slow kinetic rate, low thermal efficiency, unimpressive process economics, etc.

There is general agreement that experimental data on the rate of carbon gasification by CO_2 fit an empirical equation of the form[4]:

$$r = k_1 p_{CO2}/(1 + k_2 p_{CO} + k_3 p_{CO2})$$

where p_{CO} and p_{CO2} are partial pressures of CO and CO_2 in the reactor. This rate equation is shown to be consistent with at least two mechanisms whereby carbon monoxide retards the gasification reaction.[4]

Mechanism A

$$C_f + CO_2 \rightarrow C(O)_A + CO$$
$$C(O)_A \rightarrow CO$$
$$CO + C_f = C(CO)_B$$

Mechanism B

$$C_f + CO_2 = C(O)_A + CO$$
$$C(O)_A \rightarrow CO$$

In both mechanisms, carbon monoxide retards the overall reaction rate. The retardation is via carbon monoxide adsorption to the free sites in the case of Mechanism A, whereas it is via reaction of chemisorbed oxygen with gaseous carbon monoxide to produce gaseous carbon dioxide in Mechanism B.

As mentioned earlier when discussing steam gasification, the CO_2 gasification rate of coal is different from that of the carbon-CO_2 rate for the very same reason. Generally, the carbon-CO_2 reaction follows a global reaction order on the CO_2 partial pressure that is around one or lower, i.e., $0.5 < n < 1$, whereas the coal-CO_2 reaction follows a global reaction order on the CO_2 partial pressure that is one or higher, i.e., $1 < n < 2$. The observed higher reaction order for the coal reaction is also based on the high reactivity of coal for the multiple reasons described earlier.

2.3.3 HYDROGASIFICATION

Direct addition of hydrogen to coal under high pressure forms methane. This reaction is called *hydrogasification* and may be written as:

$$\text{Coal} + H_2 = CH_4 + \text{Carbonaceous matter}$$

Or,

$$C\ (s) + 2\ H_2\ (g) = CH_4\ (g) \qquad \Delta H°_{298} = -74.8\ \text{kJ/mol}$$

This reaction is exothermic and is thermodynamically favored at low temperatures ($T < 670°C$), unlike both steam and CO_2 gasification reactions. However, at low temperatures, the reaction rate is inevitably too slow. Therefore, high temperature is always required for kinetic reasons, which in turn requires high pressure of hydrogn, which is also preferred from equilibrium considerations. This reaction can be catalyzed by K_2CO_3, nickel, iron chlorides, iron sulfates, etc. However, use of catalyst in coal gasification suffers from serious economic constraints because of the low raw material value, as well as difficulty in recovering and reusing the catalyst. Therefore, catalytic coal gasification has not been practiced much.

2.3.4 PARTIAL OXIDATION

Combustion of coal involves reaction with oxygen, which may be supplied as pure oxygen or as air, and forms carbon monoxide and carbon dioxide. Principal chemical reactions between carbon and oxygen involve:

$$C\ (s) + O_2\ (g) = CO_2\ (g) \qquad \Delta H°_{298} = -393.5\ \text{kJ/mol}$$

$$C\ (s) + 1/2\ O_2\ (g) = CO\ (g) \qquad \Delta H°_{298} = -111.4\ \text{kJ/mol}$$

If sufficient air or oxygen is supplied, combustion proceeds sequentially through vapor-phase oxidation and ignition of volatile matter to eventual ignition of the residual char. Certainly, it is not desirable to allow the combustion reaction to continue too long, because it is a wasteful use of carbonaceous resources.

Even though the combustion or oxidation reactions of carbon may be expressed in terms of simple stoichiometric reaction equations, partial oxidation involves a complex reaction mechanism that depends on how fast and efficiently combustion progresses. The reaction pathway is further complicated because of the presence of both gas-phase homogeneous reactions and heterogeneous reactions between gaseous and solid reactants. The early controversy involving the carbon oxidation reaction centered on whether carbon dioxide is a primary product of the heterogeneous reaction of carbon with oxygen or a secondary product resulting from the gas-phase oxidation of carbon monoxide.[4] Oxidation of carbon involves at least the following four carbon-oxygen interactions, of which only two are stoichiometrically independent:

$$C + 1/2\ O_2 = CO$$

$$CO + 1/2\ O_2 = CO_2$$

$$C + CO_2 = 2\ CO$$

$$C + O_2 = CO_2$$

Based on a great deal of research work, including isotope labeling studies, it is generally agreed concerning the carbon-oxygen reaction that[4]:

1. CO_2, as well as CO, is a primary product of carbon oxidation.
2. The ratio of the primary products, CO to CO_2, is generally found to increase sharply with increasing temperature.
3. There is disagreement in that the magnitude of the ratio of the primary products is a sole function of temperature and independent of the type of carbon reacted.

Further details on the carbon oxidation can be found from a classical work done by Walker et al.[4]

Combustion or oxidation of coal is much more complex in its nature than oxidation of carbon. Coal is not a pure chemical species; rather, it is a multifunctional, multispecies, heterogeneous macromolecule that occurs in a highly porous form (typical porosity of 0.3–0.5) with a very large available internal surface area (typically in the range of 250–700 m^2/g). The internal surface area of coal is usually expressed in terms of specific surface area, which is an intensive property that is a measure of the internal surface area available per unit mass. Therefore, coal combustion involves a very complex system of chemical reactions that occur both simultaneously and sequentially. Further, the reaction phenomenon is further complicated by transport processes of simultaneous heat and mass transfer. The overall rate of coal oxidation, both complete and partial, is affected by a number of factors and operating parameters, including the reaction temperature, O_2 partial pressure, coal porosity and its distribution, coal particle size, types of coal, types and contents of specific mineral matter, heat and mass transfer conditions in the reactor, etc.

Kyotani et al.[5] determined the reaction rate of combustion for 5 different coals in a very wide temperature range between 500 and 1500°C to examine the effects of coal rank (i.e., carbon content) and catalysis by coal mineral matter. Based on their experimental results, the combustion rates were correlated with various char characteristics. It was found that in a region where chemical reaction rate is controlling the overall rate, i.e., typically in a low-temperature region where the kinetic rate is much slower than the diffusional rate of reactant, the catalytic effect of mineral matter is a determining factor for coal reactivity. It was also found that for high-temperature regions where the external mass transfer rate controls the overall rate, the reactivity of coal decreased with increasing coal rank. When the external mass transfer rate limited (or controlled) the overall rate of reaction, the mechanistic rate of external mass transfer is the slowest of all mechanistic rates, including the surface reaction rate and the pore diffusional rate of reactant and product. Such a controlling regime is experienced typically at a high-temperature operation, as the intrinsic kinetic rate is far more strongly correlated against the temperature than the external mass transfer rate is.

2.3.5 WATER GAS SHIFT (WGS) REACTION

Even though the WGS 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 synthesis gas, this reaction equilibrium is least sensitive to the temperature variation. In other words, its equilibrium constant is least strongly dependent on the temperature. Therefore, this reaction equilibrium can be reversed in a variety of practical process conditions over a wide range of temperatures. WGS reaction in its forward direction is mildly exothermic as:

$$CO\ (g) + H_2O\ (g) = CO_2\ (g) + H_2\ (g) \qquad \Delta H°_{298} = -41.2\ \text{kJ/mol}$$

Even though all the participating chemical species are in the form of a gas, scientists believe that this reaction predominantly takes place at the heterogeneous surfaces of coal and also that the reaction is catalyzed by carbon surfaces. As the WGS reaction is catalyzed by many heterogeneous surfaces and the reaction can also take place homogeneously as well as heterogeneously, a generalized understanding of the WGS reaction has been very difficult to achieve. Even the kinetic rate information in the literature may not be immediately useful or applicable to a practical reactor situation.

Syngas product 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 were to obtain a high yield of methane, it would be preferred to have the molar ratio of hydrogen to carbon monoxide at 3:1, based on the following methanation reaction stoichiometry:

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

If the objective of generating syngas is the synthesis of methanol via vapor-phase low-pressure process, the stoichiometrically consistent ratio between hydrogen and carbon monoxide would be 2:1. In such cases, the stoichiometrically consistent syngas mixture is often referred to as *balanced gas*, whereas a syngas composition that is substantially deviated from the principal reaction's stoichiometry is called *unbalanced gas.*

If the objective of syngas production is to obtain a high yield of hydrogen, it would be advantageous to increase the ratio of H_2 to CO by further converting CO (and H_2O) into H_2 (and CO_2) via WGS reaction. However, if the final gaseous product is to be used in fuel cell applications, carbon monoxide and carbon dioxide must be removed to acceptable levels by a process such as acid gas removal or other adsorption processes. In particular, for hydrogen proton exchange membrane (PEM) fuel cell operation, carbon monoxide and sulfurous species must be thoroughly removed from the hydrogen gas.

The WGS reaction is one of the major reactions in the steam gasification process, where both water and carbon monoxide are present in ample amounts. Even though all four chemical species involved in the WGS reaction are gaseous compounds at the reaction stage of most gas processing, the WGS reaction, in the case of steam gasification of coal, predominantly takes place heterogeneously, i.e., on the solid surface of coal. If the product syngas from a gasifier needs to be reconditioned by the WGS 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. Many investigators have studied the WGS reaction over a variety of catalysts including iron, copper, zinc, nickel, chromium, and molybdenum. Significant efforts have been made in developing a robust catalyst system that has superior sulfur tolerance and wider applicable temperature range.

2.4 SYNGAS GENERATION VIA COAL GASIFICATION

2.4.1 Classification of Gasification Processes

In the earlier section, the different types of synthesis gas were classified. Similarly, there are a large number of widely varying gasification processes. The gasification processes can be classified basically in two general ways: (1) by the Btu content of the product gas,[6] and (2) by the type of the reactor hardware configuration, as well as by whether the reactor system is operated under pressure or not.

The following processes for conversion of coal to gases are grouped according to *the heating value of the product gas.*

Medium- or High-Btu Gas Gasification Processes

1. Lurgi gasifier
2. Synthane gasifier
3. Atgas molten iron coal gasifier

Low- or Medium-Btu Gas Gasification Processes

1. Koppers-Totzek gasifier
2. Texaco gasifier
3. Shell gasifier
4. Kellogg's molten salt gasifier
5. CO_2-acceptor gasification process
6. U-gas process

Low-Btu Gas Only Gasification Process

1. Underground *in situ* gasification process

Based on the reactor configuration, as well as by the method of contacting gaseous and solid streams, gasification processes can also be categorized into the following four types[3]:

1. *Fixed or moving bed:* In the fixed bed reactor, coal is supported by a grate and the gasifying media (steam, air, or oxygen) pass upward through the supported bed, whereby the product gases exit from the top of the reactor. Only noncaking coals can be used in the fixed bed reactor. On the other hand, in the moving bed reactor, coal and gaseous streams move countercurrently, i.e., coal moves downward by gravity while gas passes upward through the coal bed. The temperature at the bottom of the reactor is higher than that at the top. Because of the lower temperature at the top for coal devolatilization, relatively large amounts of liquid hydrocarbons are also produced in this type of gasifier. In both types of reactor, the

residence time of the coal is much longer than that in a suspension reactor, thus providing ample contact time between reactants. Ash is removed from the bottom of the reactor as dry ash or slag. Lurgi and Wellman-Galusha gasifiers are examples of this type of reactor. It should be clearly understood that a moving bed reactor is classified as a kind of fixed bed reactor, because solids in the bed stay together regardless of the movement of the hardware that supports the bed.

2. *Fluidized bed:* It uses finely pulverized coal particles. The gas (or gasifying medium) flows upward through the bed and fluidizes the coal particles. Owing to the ascent of particles and fluidizing gas, larger coal surface area is made available, which positively promotes the gas-solid chemical reaction, which in turn results in enhancement in carbon conversion. This type of reactor allows intimate contact between gas and solid coal fines, at the same time providing relatively longer residence times than entrained flow reactor. Dry ash is either removed continuously from the bed, or the gasifier is operated at such a high temperature that it can be removed as agglomerates. Such beds, however, have limited ability to handle caking coals, owing to operational complications in fluidization characteristics. Winkler and Synthane processes use this type of reactor.
3. *Entrained bed:* This type of reactor is also referred to as *entrained flow reactor*, because there is no bed of solids. This reactor system uses finely pulverized coal particles blown into the gas stream before entry into the reactor, with combustion and gasification occurring inside the coal particles suspended in the gas phase. Because of the entrainment requirement, high space velocity of gas stream and fine powdery coal particles are very essential to the operation of this type of process. Because of the very short residence time (i.e., high space velocity) in the reactor, a very high temperature is required to achieve good conversion in such a short period of reaction time. This can also be assisted by using excess oxygen. This bed configuration is typically capable of handling both caking and noncaking coals without much operational difficulty. Examples of commercial gasifiers that use this type of reactor include the Koppers-Totzek gasifier and Texaco gasifier.
4. *Molten salt bath reactor:* In this reactor, coal is fed along with steam or oxygen in the molten bath of salt or metal operated at 1,000–1,400°C. Ash and sulfur are removed as slag. This type of reactor is used in Kellogg and Atgas processes.[7]

2.4.2 HISTORICAL BACKGROUND OF COAL GASIFICATION AND ITS COMMERCIALIZATION

It was known as early as the 17th century that gas could be produced by simply heating the coal, i.e., pyrolysis of coal in modern terms. Around 1750, in England, coal was subjected to pyrolysis to form gases that were used for lighting.[8] With the invention of the Bunsen gas burner (at atmospheric pressure), the potential of heating was opened to gas combustion. In 1873, cyclic carbureted water gas process was developed by Thaddeus S. C. Lowe for gas production. In this process, water gas

(H_2 + CO) was produced by reacting hot coke (i.e., smokeless char) with steam via a simplified reaction of $C + H_2O = CO + H_2$. Heat for the reaction was supplied by combustion energy by introducing air intermittently to burn a portion of the coke. The development of coal-to-gas processes was a major breakthrough in Europe during those days, because coal was the principal fuel available besides wood. By the early 1920s, there were at least five *Winkler fluid bed processes* being operated, all of which were air-blown, producing 10 million scf/h of producer gas. Some of them were later converted to use oxygen instead of air in order to produce nitrogen-free syngas.

The *Lurgi process* was developed to manufacture town gas by complete gasification of brown coal in Germany. In 1936, the first commercial plant based on this process went operational. It produced 1 million scf/d of town gas from low-rank lignite coal. By 1966, there were at least ten Lurgi plants at a number of places in Europe and Asia producing synthesis gas.

In 1942, Heinrich Koppers in Germany developed the *Koppers-Totzek (K-T) suspension gasification process* based on the pilot plant work initiated four years earlier. The first industrial plant was built in France around 1949, which produced 5.5 million scf/d of synthesis gas that was later used to produce ammonia and methanol. By the early 1970s, there were at least 20 K-T plants built all over the world. All of them used oxygen as primary gasification medium, thus producing nitrogen-free syngas.

Winkler, Lurgi, and Koppers-Totzek processes all employed steam and oxygen (or air) to carry out gasification. Most of these developments were originated and perfected in Europe. However, very little development of these processes had taken place in the U.S. until the energy crisis of the 1970s, mainly because of the discovery of natural gas as a convenient fuel and also because of the relatively stable supply of liquid petroleum until then. After the oil embargo of 1973, very active research and development efforts were conducted for cleaner use of coal resources in coal gasification, coal liquefaction, clean coal technology, IGCC, etc. Since then, most coal power plants have significantly upgraded their quality of operation in terms of energy efficiency, by-products, emission control, and profitability.

2.4.3 GENERAL ASPECTS OF GASIFICATION

The kinetic rates and extents of conversion for various gasification reactions are typically functions of temperature, pressure, gas composition, and the nature of the coal being gasified. The rate of reaction is intrinsically higher at higher temperatures, whereas the equilibrium of the reaction 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 gasification reactions such as carbon-hydrogen reaction producing methane are favored at high pressures (>70 atm) and relatively lower temperatures (760–930°C), whereas low pressures and high temperatures favor the production of syngas (i.e., carbon monoxide and hydrogen) via steam or carbon dioxide gasification reaction.

Supply and recovery of heat is a key element in the gasification process from the standpoints of economics, design, and operability. Partial oxidation of char with steam and oxygen leads to generation of heat and synthesis gas. Another way to produce a hot gas stream is via the cyclic reduction and oxidation of iron ore. The type of coal being gasified is also important to the gasification and downstream operations. Only suspension-type gasifiers such as entrained flow reactor can handle any type of coal, but if caking coals are to be used in fixed or fluidized bed, special measures must be taken so that coal does not agglomerate (or cake) during gasification. If such agglomeration does happen, it would adversely affect the operability of the gasification process. In addition to this, the chemical composition, the volatile matter (VM) content, and the moisture content of coal also play important roles in the coal processing during gasification. The S and N contents of coal seriously affect the quality of the product gas, as well as the gas-cleaning requirements. The sulfur content of coal typically comes from three different sources of coal sulfur, namely, pyritic sulfur, organic sulfur, and sulfatic sulfur. The first two are more dominant sulfur forms, whereas weathered or oxidized coals have more sulfatic forms than fresh coals. Sulfurous gas species can be sulfur dioxide, hydrogen sulfide, or mercaptans, depending on the nature of the reactive environment. If the reactive environment is oxidative, the sulfur dioxide is the most dominant sulfur-containing species in the product gas.

2.4.4 GASIFICATION PROCESSES

2.4.4.1 Lurgi Gasification

The Lurgi gasification process is one of the several processes for which commercial technology has been fully developed.[9]

Since its development in Germany before World War II, this process has been used in a large number of commercial plants throughout the world. This process produces low- to medium-Btu gas as product gas. It may be classified as a fixed bed process in which the reactor configuration is similar to that of a typical fixed bed reactor. The older version of Lurgi process is *dry ash gasification* process that differs significantly from the more recently developed *slagging gasification process.*

The dry ash Lurgi gasifier is a pressurized vertical reactor that accepts crushed noncaking coals only.[10] The coal feed is supported at the base of the reactor by a revolving grate through which the steam and oxygen mixture is introduced and the ash removed. This process takes place at around 24 to 31 atm and in the temperature range of 620 to 760°C. The residence time in the reactor is about 1 h. Steam introduced from the bottom of the reactor provides the necessary hydrogen species, and the heat is supplied by the combustion of a portion of the char. The product gas from a high-pressure reactor has a relatively high methane content compared to a nonpressurized gasifier. The high methane content of the product gas is a result of the relatively low gasification temperature. If oxygen is used as an injecting (and gasifying) medium, the exiting gas has a heating value of approximately 450 Btu/scf. The crude gas leaving the gasifier contains a substantial amount of condensable products including tar, oil, phenol, etc., which are separated in a devolatilizer, where gas is cleaned to remove unsaturated hydrocarbons and naphtha. The gas is then subjected to methanation ($CO + 3H_2 = CH_4 + H_2O$) to produce a high-Btu gas (pipeline quality).

Recent modification of the Lurgi process called *slagging Lurgi gasifier* has been developed to process caking coals.[3] Therefore, the operating temperature of this gasifier is kept higher and the injection ratio of steam is reduced to 1–1.5 mol/mol of oxygen. These two factors cause the ash to melt easily and, therefore, the molten ash is removed as a slag. Coal is fed to the gasifier through a lock hopper system and distributor. It is gasified with steam and oxygen injected into the gasifier near the bottom. The upward movement of hot product gases provides convective heat transfer and makes the preheating and devolatilization of coal easier. Both volatile matter liberated from coal and devolatilized char react with gasifying media, i.e., steam and oxygen. The molten slag formed during the process passes through the slag tap hole. It is then quenched with water and removed through a slag lock hopper. The amount of unreacted steam passing through the system has to be minimized in this process for high energy efficiency. Also, the high operating temperature and fast removal of product gases lead to higher output rates in a slagging Lurgi gasifier than a conventional dry ash Lurgi unit.

The conventional Lurgi gasification is widely recognized for its role as the gasifier technology for South Africa's Sasol complex. A typical product composition for oxygen-blown operation is given in Table 2.2. As can be seen, the H_2-to-CO ratio is higher than 2:1. It is also noted that a relatively large amount of CO_2 is present.

2.4.4.1.1 Lurgi Dry-Ash Gasifier

In this gasifier, coal sized between 1.5 in. and 4 mesh reacts with steam and oxygen in a slowly moving bed. The process is operated semicontinuously. A schematic of a Lurgi pressure gasifier is shown in Figure 2.2.[11] The gasifier is equipped with the following hardware parts[12]:

1. An automated *coal lock chamber* for feeding coal from a coal bin to the pressurized reactor. This device is often called a *coal lock hopper.*
2. A *coal distributor* through which coal is uniformly distributed into the moving bed.
3. A *revolving grate* through which the steam and oxygen are introduced into the reacting zone (coal bed) and the ash is removed.
4. An *ash lock chamber* for discharging the ash from the pressurized reactor into an ash bin, where the ash is cooled by water quenching.
5. A *gas scrubber* in which the hot gas is quenched and washed before it passes through a waste heat boiler.

The gasifier shell is water-cooled and steam is produced from the water jacket. A motor-driven distributor is located at the top of the coal bed, which evenly distributes the feed coal coming from the coal lock hopper. The grate at the bottom of the reactor is also driven by a motor to discharge the coal ash into the ash lock hopper. The section between the inlet and outlet grates has several distinct zones. The topmost zone preheats the feed coal by contacting with the hot crude product gas that is ready to leave the reactor. As the coal gets heated, devolatilization and gasification reactions proceed at temperatures ranging from 620 to 760°C. Devolatilization of coal is accompanied by gasification of the resulting char. The interaction

TABLE 2.2
Typical Lurgi Gas Products

Species	Mole Percentage
CO	16.9
H_2	39.4
CH_4	9.0
C_2H_6	0.7
C_2H_4	0.1
CO_2	31.5
H_2S + COS	0.8
N_2 +Ar	1.6

Source: From Lloyd, W.G., *The Emerging Synthetic Fuel Industry*, Thumann, A., Ed., Atlanta, GA: Fairmont Press, 1981, pp.19–58. With permission.

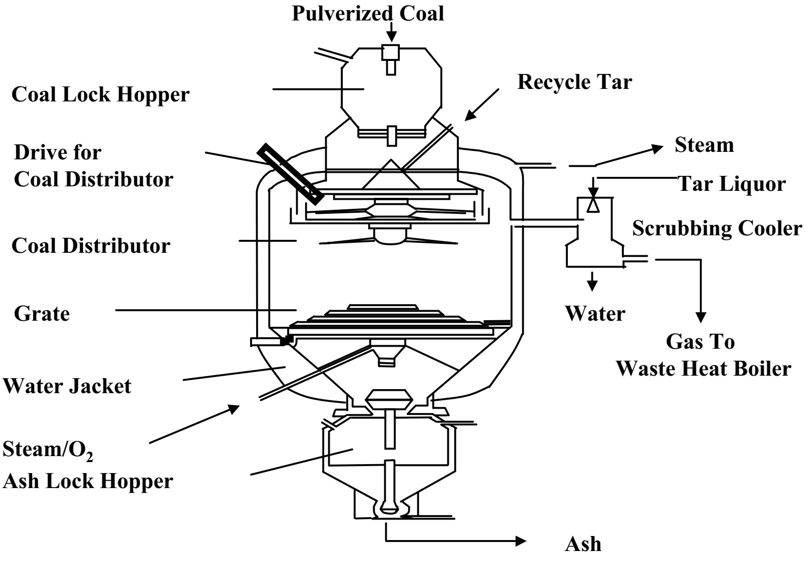

FIGURE 2.2 Lurgi nonslagging pressure gasifier.

between devolatilization and gasification is a determining factor in the kinetics of the process, as well as of the product compositions.

The bottom of the bed is the combustion zone, where coal carbon reacts with oxygen to yield mainly carbon dioxide. The exothermic heat generated by this reaction provides the heat for gasification and devolatilization, both of which are endothermic reactions. By utilizing the exothermic heat of combustion in the gasification and devolatilization, both of which are endothermic, energy integration within the gasifier is accomplished. More than 80% of the coal fed is gasified, the remainder being burned in the combustion zone. The portion of feed coal burned for *in situ* heat generation may be called *sacrificial coal*. The temperature of the combustion zone must be selected in such a way that it is below the ash fusion point but high enough to ensure complete gasification of coal in subsequent zones. This temperature is also determined by the steam-to-oxygen ratio.

The material and energy balance of the Lurgi gasifier is determined by the following process variables:

1. Pressure, temperature, and steam-to-oxygen ratio.
2. The nature of coal: The type of coal determines the nature of gasification and devolatilization reaction. Lignite is the most reactive coal, for which reaction proceeds at 650°C. On the other hand, coke is the least reactive, for which minimum temperature required for chemical reaction is around 840°C. Therefore, more coal is gasified per unit mole of oxygen for lignite compared to other types (ranks) of coal. The higher the coal rank (i.e., the carbon content of coal), the lower the coal reactivity.
3. The ash fusion point of the coal, which limits the maximum operable temperature in the combustion zone, which in turn determines the steam-to-oxygen ratio.
4. Both the amount and chemical composition of the volatile matter of the coal, which influence the quality and quantity of tar and oils produced.

The Lurgi gasifier has relatively high thermal efficiency because of its medium-pressure operation and the countercurrent gas-solid flow. At the same time, it consumes a lot of steam and the concentration of carbon dioxide in the crude product gas is high, as shown in Table 2.2. Also, the crude gas leaving the gasifier contains a substantial amount of carbonization products such as tar, oil, naphtha, ammonia, etc. These carbonization products are results of devolatilization, pyrolytic reactions, and secondary chemical reactions involving intermediates. This crude product gas is passed through a scrubber, where it is washed and cooled down by a waste heat boiler.

2.4.4.1.2 Slagging Lurgi Gasifier

This gasifier is an improved version of the Lurgi dry-ash gasifier. A schematic[11] of slagging Lurgi gasifier is shown in Figure 2.3. The temperature of the combustion zone is kept higher than the ash fusion point. This is achieved by using a smaller amount of steam than dry-ash Lurgi gasifier, thus lowering the steam/oxygen ratio. The ash is removed from the bottom as slag, not as dry ash. Therefore, the process can handle *caking coals*, unlike the conventional dry-ash gasifier. The main advantage of this gasifier over the conventional dry-ash gasifier is that the yield of carbon monoxide and hydrogen is high and the coal throughput also increases many times. The steam consumption is also minimized.[13]

2.4.4.2 Koppers-Totzek Gasification

This gasification process uses entrained flow technology, in which finely pulverized coal is fed into the reactor with steam and oxygen.[14,15] The process operates at

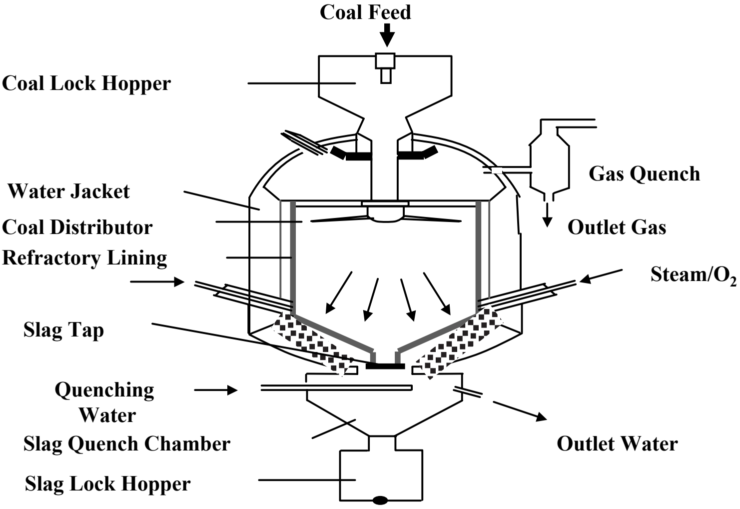

FIGURE 2.3 A schematic of slagging Lurgi gasifier.

atmospheric pressure. As with all entrained flow reactors, the space time in the reactor is very short. The gasifier itself is a cylindrical, refractory-lined coal burner with at least two burner heads through which coal, oxygen, and steam are charged. The burner heads are spaced either 180° (with the two-headed design) or 90° apart (with the four-headed arrangements) and are designed such that steam covers the flame and prevents the reactor refractory walls from becoming excessively hot. The reactor typically operates at a temperature of about 1400–1500°C and atmospheric pressure. At this high temperature, the reaction rate of gasification is extremely high, i.e., by orders of magnitude higher than that at a temperature in a typical fixed bed reactor. About 90% of carbonaceous matter is gasified in a single pass, depending on the type of coal. Lignite is the most reactive coal, for which reactivity approaches nearly 100%.[3]

In contrast to moving bed or fluidized bed reactors, this gasifier has very few limitations on the nature of feed coal in terms of caking behavior and mineral matter (ash) properties. Because of very high operating temperatures, the ash agglomerates and drops out of the combustion zone as molten slag and subsequently gets removed from the bottom of the reactor. The hot effluent gases are quenched and cleaned. This gas product contains no tar, ammonia, or condensable hydrocarbons and is predominantly synthesis gas. It has a heating value of about 280 Btu/scf and can be further upgraded by reacting with steam to form additional hydrogen and carbon dioxide via WGS reaction.

2.4.4.2.1 Koppers-Totzek Gasifier

This gasifier is one of the most significant entrained bed gasifiers in commercial operation today. It accepts almost any type of coal, including caking coal, without any major operational restrictions. It has the highest operating temperature (around 1400–1500°C) of all the conventional gasifiers. There are two versions in terms of process equipment design, a two-headed and a four-headed burner type. A schematic of a Koppers-Totzek

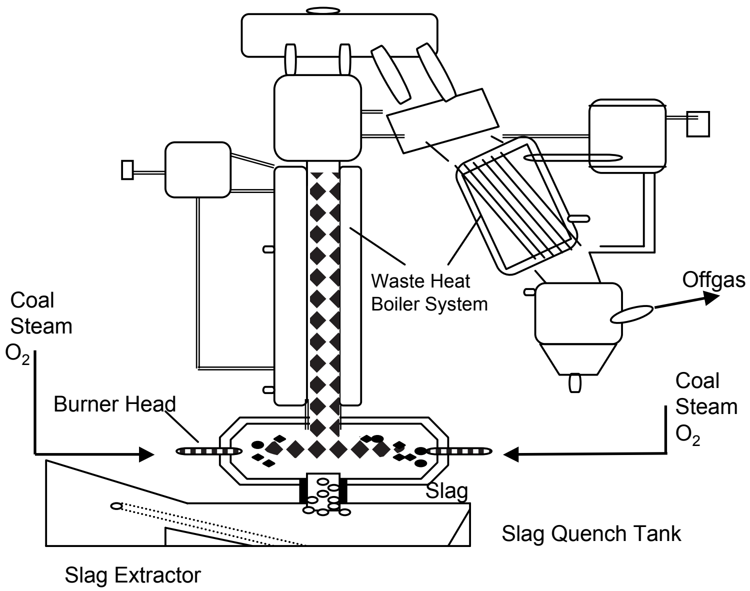

FIGURE 2.4 A schematic of Koppers-Totzek gasifier (two-headed burner design).

two-headed gasifier[16] is shown in Figure 2.4. The original version designed in 1948 in Germany was two-headed, with the heads mounted at the ends, i.e., 180° apart. The gasifier as such is ellipsoidal in shape and horizontally situated. Each head contains two burners. The shell of the gasifier is water-jacketed and has an inner refractory lining. Design of four-headed gasifiers began in India around 1970. In this design, burner heads are spaced 90°, instead of 180° as in two-headed ones. All the burner heads are installed horizontally. The capacity of a four-headed burner gasifier is larger than its two-headed counterpart.[17]

2.4.4.2.2 Features of the Koppers-Totzek Process

The Koppers-Totzek process has been very successfully operated commercially and some of the process features are summarized as follows:

1. *High capacity:* These process units are designed for coal feed rates up to 800 tons per day, or about 42 million scf/d of 300-Btu gas.
2. *Versatility:* The process is capable of handling a variety of feedstocks, including all ranks of solid fuels, liquid hydrocarbons, and pumpable slurries containing carbonaceous materials. Even feedstocks containing high sulfur and ash contents can be readily used in this process. Therefore, this process is not limited only to coal.
3. *Flexibility:* The changeover from solid fuel feed to liquid fuels involves only a change in the burner heads. Multiple feed burners permit wide variations in turndown ratio (defined as the numeric ratio between the highest and the lowest effective system capacity). This process is capable of instantaneous shutdown with full production resumable in a remarkably short time, only 30 min.

4. *Simplicity of construction:* There is no complicated mechanical equipment or pressure-scaling device required. The only moving parts in the gasifiers are the moving screw feeders for solids or pumps for liquid feedstocks.
5. *Ease of operation:* Control of the gasifiers is achieved primarily by maintaining carbon dioxide concentration in the clean gas at a reasonably constant value. Slag fluidity at high process temperatures may be visually monitored. Gasifiers display good dynamic responses.
6. *Low maintenance:* Simplicity of design and a minimum number of moving parts require little maintenance between the scheduled annual maintenance events.
7. *Safety and efficiency*: The process has a track record of over 50 years of safe operation. The overall thermal efficiency of the gasifier is 85 to 90%. The time on stream (TOS) or availability is better than 95%.

2.4.4.2.3 Process Description of Koppers-Totzek Gasification

The Koppers-Totzek gasification process, whose flow schematic is shown in Figure 2.5, employs partial oxidation of pulverized coal in suspension with oxygen and steam. The gasifier is a refractory-lined steel shell encased with a steam jacket for producing low-pressure process steam as an energy recovery scheme. A two-headed gasifier is capable of handling 400 tons per day of coal. Coal, oxygen, and steam are brought together in opposing gasifier burner heads spaced 180° apart (in the two-headed case). In the case of four-headed gasifiers, these burners are 90° apart. The

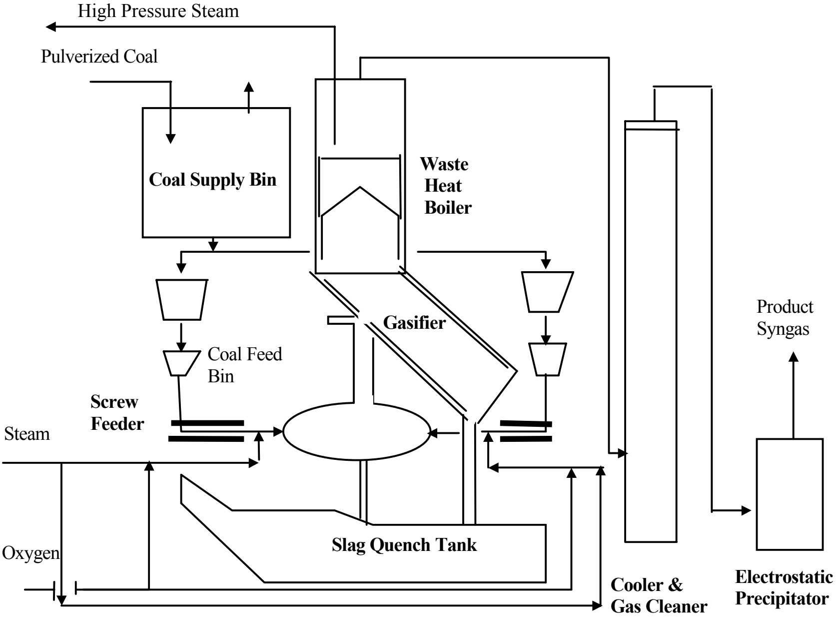

FIGURE 2.5 A schematic of the Koppers-Totzek gasification process.

four-head design can handle up to 850 tons of coal per day. Exothermic reactions due to coal combustion produce a flame temperature of approximately 1930°C, which is lowered by heat exchange with a steam jacket. Gasification of coal is almost complete and instantaneous. The carbon conversion depends on the reactivity of coal, approaching 100% for lignites. The lower the rank of coal, the higher the conversion.

Gaseous and vapor hydrocarbons evolving from coal at moderate temperature are passed through a zone of very high temperature, in which they decompose so rapidly that there is no coagulation of coal particles during the plastic stage. Thus, any coal can be gasified irrespective of the caking property, ash content, or ash fusion temperature. As a result of the endothermic reactions occurring in the gasifier between carbon and steam and radiation to the refractory walls, the reactor temperature decreases from 1930°C (flame temperature) to 1500°C. At these conditions, only gaseous products are produced with no tars, condensable hydrocarbons, or phenols formed. Typical compositions of Koppers-Totzek gaseous products are shown in Table 2.3.

Ash in the coal feed becomes molten in the high-temperature zone. Approximately 50% of the coal ash drops out as slag into a slag quench tank below the gasifier. The remaining ash is carried out of the gasifier as fine fly ash. The gasifier outlet is equipped with water sprayers to drop the gas temperature below the ash fusion temperature. This cooling prevents slag particles from adhering to the tubes of the waste heat boiler, which is mounted above the gasifier.

The raw gas from the gasifier passes through the waste heat boiler, where high-pressure steam up to 100 atm is produced via waste heat recovery. After leaving the waste heat boiler, the gas at 175–180°C is cleaned and cooled in a highly efficient scrubbing system, which reduces the entrained solids to 0.002–0.005 grains/scf or less and further lowers the temperature from 175 to 35°C. If the gas coming out of the Koppers-Totzek process is to be compressed to high pressures for chemical synthesis, electrostatic precipitators (ESPs) are used for further cleaning. Several gasifiers can share common cleaning and cooling equipment, thus reducing the capital cost.

TABLE 2.3
Typical Raw Product Gas Compositions of Koppers-Totzek Gasifier (oxygen-blown type)

Component	Percentage
CO	52.5
H_2	36.0
CO_2	10.0
H_2S + COS	0.4
N_2 + Ar	1.1

Note: Average heating value = 286 Btu/scf; all percentages are in volume percent.

Source: From Lloyd, W.G., *The Emerging Synthetic Fuel Industry*, Thumann, A., Ed., Atlanta, GA: Fairmont Press, 1981, pp. 19–58.

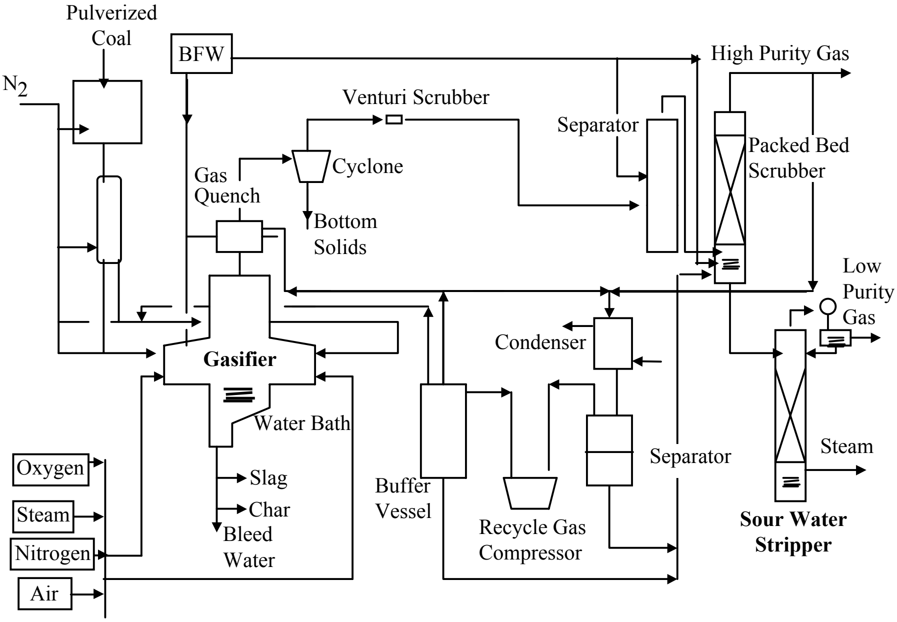

FIGURE 2.6 A schematic of shell gasification process.

The cool, cleaned gas leaving the gas cleaning system still contains sulfur compounds that must be removed to meet the final gas specifications. The type of the desulfurization system chosen depends on the end uses and the pressure of the product gas. For low pressures and low-Btu gas applications, there are a number of chemically reactive processes, such as *amine and carbonate processes.* At higher pressures, physical absorption processes such as *Rectisol process* can be used. The choice of the process also depends on the desired purity of the product gas and its selectivity with respect to the concentration of carbon dioxide and sulfides. Advances in gas cleaning have been quite significant in recent years, owing to more stringent environmental regulations.[18]

2.4.4.3 Shell Gasification

The Shell coal gasification process was developed by Royal Dutch and Shell group in the early 1970s. It uses a pressurized, slagging entrained flow reactor for gasifying dry pulverized coal.[19] Similar to the Koppers-Totzek process, it has the potential to gasify widely different ranks of coals, including low-rank lignites with high moisture content. Unlike other gasifying processes, it uses *pure oxygen* as the gasifying medium, for gasification via partial oxidation. Shell Global Solutions licenses two versions of gasification technologies, i.e., one for liquid feedstock applications and the other for coal and petroleum coke. A schematic of the Shell coal gasification process is given in Figure 2.6. The process has the following features[20]:

1. Almost 100% conversion of a wide variety of coals, including high-sulfur coals, lignites, and coal fines

2. High thermal efficiency in the range of 75 to 80%
3. Efficient heat recovery through production of high-pressure superheated steam
4. Production of clean gas without any significant amount of by-products
5. High throughput
6. Environmental compatibility

Coal before feeding to the gasifier vessel, is crushed and ground to less than 90-μm size. This pulverized and dried coal is fed through diametrically opposite diffuser guns into the reaction chamber.[21] The coal is then reacted with the pure oxygen and steam, where flame temperature reaches as high as 1800–2000°C. A typical operating pressure is around 30 atm. Raw product gas typically consists of mainly carbon monoxide (62–63%) and hydrogen (28%), with some quantities of carbon dioxide. A water-filled bottom compartment is provided in which molten ash is collected. Some amount of ash is entrained with the synthesis gas, which is then recycled along with the unconverted carbon. A quench section is provided at the reactor outlet to lower the gas temperature. Removal of particulate matter from the raw product gas is integrated with the overall process. This removal system typically consists of *cyclones and scrubbers*. The main advantage of this section is elimination of solid-containing wastewater, thus eliminating the need for filtration.

2.4.4.4 Texaco Gasification

The Texaco process also uses entrained flow technology for gasification of coal. It gasifies coal under relatively high pressure by injection of oxygen (or air) and steam with concurrent gas/solid flow. Fluidized coal is mixed with either oil or water to make it into *pumpable slurry*. This slurry is pumped under pressure into a vertical gasifier, which is basically a pressure vessel lined inside with refractory walls. The slurry reacts with either air or oxygen at high temperature. The product gas contains primarily carbon monoxide, carbon dioxide, and hydrogen with some quantity of methane. Because of high temperature, oil or tar is not produced. This process is basically used to manufacture *CO-rich synthesis gas*.[3] A schematic of the Texaco gasification process is shown in Figure 2.7.

This gasifier evolved from the commercially proven Texaco partial oxidation process[10] used to gasify crude oil and hydrocarbons. Its main feature is the *use of coal slurry feed*, which simplifies the coal-feeding system and operability of the gasifier. The gasifier is a simple, vertical, cylindrical pressure vessel with refractory linings in the upper partial oxidation chamber. It is also provided with a slag quench zone at the bottom, where the resultant gases and molten slag are cooled down. In the latter operation, large amounts of high-pressure steam can be obtained, which boosts the thermal efficiency of the process. Another important factor that affects the gasifier thermal efficiency is the water content of the coal slurry. This water content should be minimized because a large amount of oxygen must be used to supply the heat required to vaporize the slurry water. This gasifier favors high-energy dense coals so that the water-to-energy ratio in the feed is small. Therefore, eastern U.S. bituminous coals are preferable to lignites for this gasifier. The gasifier operates at around 1100–1370°C and a pressure of 20–85 atm.

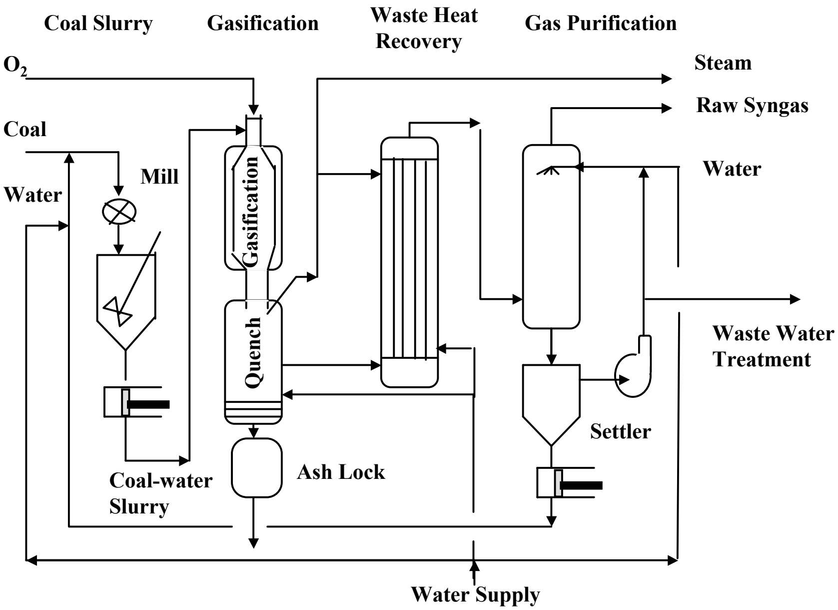

FIGURE 2.7 A schematic of Texaco gasification process.

The product gases and molten slag produced in the reaction zone pass downward through a water spray chamber and a slag quench bath, where the cooled gas and slag are then removed for further treatment. The gas, after being separated from slag and cooled, is treated to remove carbon fines and ash. These fines are then recycled to the slurry preparation system, while the cooled gas is treated for acid gas removal and elemental sulfur is recovered from the hydrogen sulfide (H_2S)-rich stream.

2.4.4.5 *In Situ* Gasification

In situ gasification, or underground gasification, is a technology for recovering the energy content of coal deposits that cannot be exploited either economically or technically by conventional mining (or *ex situ*) processes. Coal reserves that are suitable for *in situ* gasification have low heating values, thin seam thickness, great depth, high ash or excessive moisture content, large seam dip angle, or undesirable overburden properties. A considerable amount of investigation has been performed on *underground coal gasification (UCG)* in the former USSR and in Australia, but it is only in recent years, that the concept has been revived in Europe and North America as a means of fuel gas production. In addition to its potential for recovering deep, low-rank coal reserves, the UCG process may offer some advantages with respect to its resource recovery, minimal environmental impact, operational safety, process efficiency, and economic potential. The aim of *in situ* gasification of coal is to convert coal hydrocarbons into combustible gases by combustion of coal seam in the presence of air, oxygen, or steam.

The basic concepts of underground coal gasification may be illustrated by Figure 2.8.[22] The basic principles of *in situ* gasification are still very similar to those involved

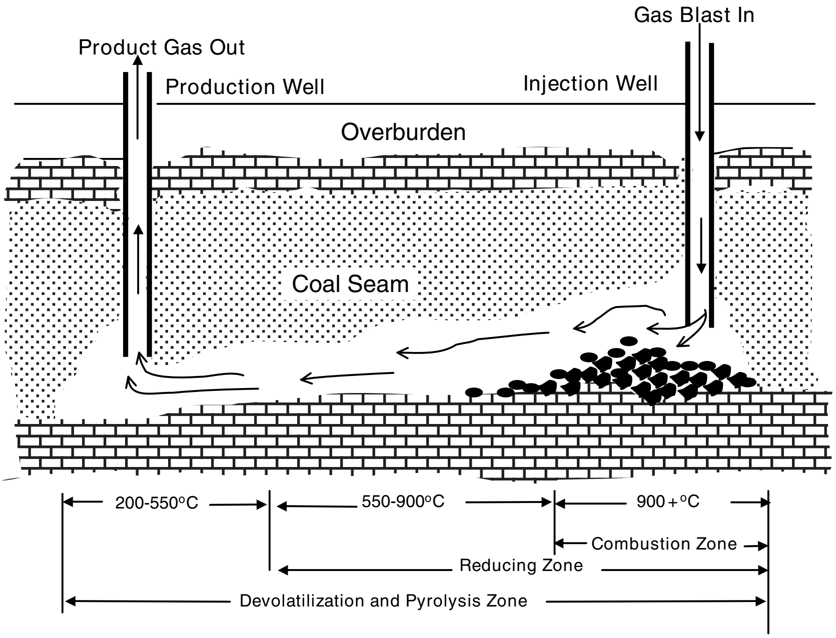

FIGURE 2.8 A schematic of *in situ* underground gasification process.

in the above-ground (*ex situ*) gasification of coal. Combustion process itself could be handled in either *forward* or *reverse* mode. Forward combustion involves movement of the combustion front and injected air in the same direction, whereas in reverse combustion, the combustion front moves in the opposite direction to the injected air. The process involves drilling and subsequent linking of the two boreholes to enable gas flow between the two. Combustion is initiated at the bottom of one borehole called *injection well* and is maintained by the continuous injection of air.

As illustrated in Figure 2.8, in the initial reaction zone, carbon dioxide is generated by reaction of oxygen (air) with the coal, which further reacts with coal to produce carbon monoxide by the Boudouard reaction ($CO_2 + C = 2CO$) in the reduction zone. Further, at such high temperatures, the moisture present in the seam may also react with carbon to form carbon monoxide and hydrogen via the steam gasification reaction ($C + H_2O = CO + H_2$). In addition to all these basic gasification reactions, coal decomposes in the pyrolysis zone owing to high temperatures to produce hydrocarbons and tars, which also contribute to the product gas mix. The heating value from the air-blown *in situ* gasifier is roughly about 100 Btu/scf. The low heat content of the gas makes it uneconomical for transportation, making it necessary to use the product gas on site. An extensive discussion on *in situ* gasification can be found in references by Thompson[23] and by Gregg and Edgar.[24] A noteworthy R&D effort in underground coal gasification has also been conducted by the Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia. CSIRO researchers have developed a model to assist with the implementation of this technology.[25] A number of other trials and trial schemes were evaluated in Europe, China, India, South Africa, and the U.S.

2.4.4.5.1 Potential Possibility of Using Microbial Processes for In Situ *Gasification*

Juntgen[26] in his review article has explored the possibilities of using microbiological techniques for *in situ* conversion of coal into methane. Microorganisms have been found that grow on coal as a sole carbon source. Both forms of sulfur, namely organic and inorganic (pyritic and sulfatic), are claimed to be removable by biochemical techniques, and microorganisms are able to grow, in principle, in narrow pore structures of solids. The conversion of large-molecular-weight aromatics, including polynuclear aromatics (PNAs), is also potentially feasible. An important precursor of developing such new process techniques for *in situ* coal conversion in deep seams is the knowledge of coal properties, both physical and chemical, under the prevailing conditions. The two most important coal properties, which dictate the *in situ* processes, are the *permeability* of coal seam, including the overburden and the *rank* of coal. For microbial conversion of coal, microporosity also becomes an important parameter. The permeability of coal seam in great depths is usually quite small due to high rock overburden pressure. However, accessibility is very important for performing *in situ* processes. There are several ways to increase the permeability of the coal seams at great depths.[26] Some of these ideas are very similar to those used in *in situ* oil shale retorting as discussed in Chapter 8.

The main advantage of using microbiological techniques is that the reaction takes place at ambient temperatures. Progress made in developing these types of processes is quite notable. A remarkable effect of such reactions in coal is that the microorganisms can penetrate into fine pores of the coal matrix, and can also create new pores if substances contained in the coal matrix are converted into gaseous compounds.

However, the most difficult and complex problem associated with microorganism-based reactions is the transition from solely oxidative processes to methane-forming reactions. There are at least three reaction steps involved: (1) the aerobic degradation of coal to biomass and high-molecular-weight products, (2) an anaerobic reaction leading to the formation of acetate, hydrogen, and carbon monoxide, and (3) the conversion of these products to methane using methanogenic bacteria. Methanogenic bacteria belong to a group of primitive microorganisms, the *Archaea*. They give off methane gas as a by-product of their metabolism, and are common in sewage treatment plants and hot springs, where the temperature is warm and oxygen is absent. Advantages of these processes over other conversion processes are lower conversion temperature and more valuable products.[26] However, an intensive investigation must be conducted to adapt reaction conditions and product yields to conditions prevailing in coal seams at great depth, where transport processes play a significant role in the overall reaction.

2.4.4.5.2 Underground Gasification System

The underground gasification system involves three distinct sets of operations: pregasification, gasification, and further processing and utilization. Pregasification operations provide access to the coal deposit and prepare it for gasification. Connection between the inlet and outlet through the coal seam is achieved via shafts and boreholes. Linking can be achieved through several means, such as pneumatic, hydraulic, or electric linking, and using explosives, etc. Sometimes, partial linking

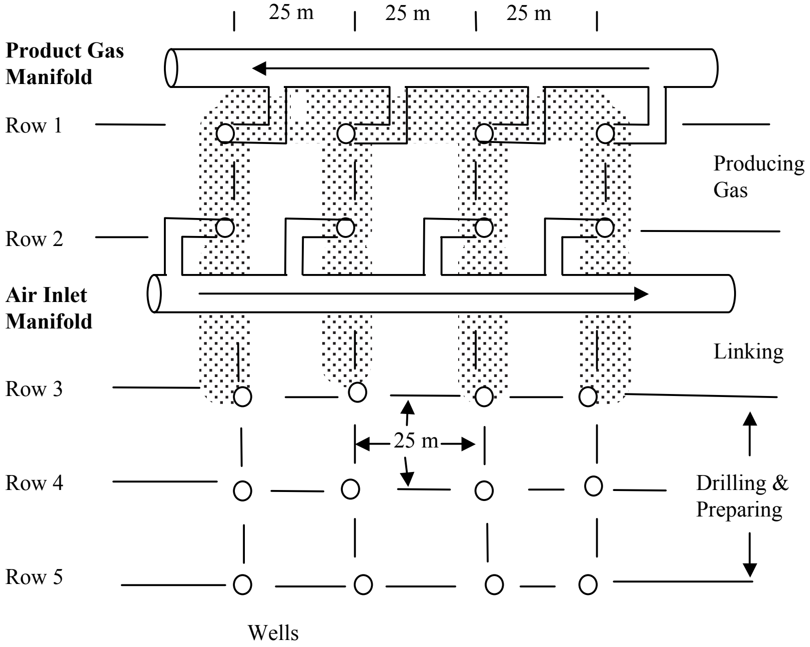

FIGURE 2.9 Plane view of linked-vertical-well underground gasification plant operated near Moscow.

may also be accomplished by taking advantage of the natural permeability of the coal seam. Among all the linking methods, only directionally drilled boreholes provide positive connections between inlet and outlet sections and all other methods permit a certain degree of uncertainty to play a role in the system. A schematic view of a *linked-vertical-well underground gasification* plant operated near Moscow[22] is shown in Figure 2.9.

The gasification operations that allow reliable production of low-Btu gas consist of input of gasifying agents such as air or oxygen and steam (or alternating air and steam), followed by ignition. Ignition can be managed either by electrical means or by burning solid fuels. Ignition results in contact between gasifying agents and coal organics at the flame front. The flame front may advance in the direction of gas flow *(forward burning)* or in the direction opposite to the gas flow (*backward burning*). During these operations, the major technical difficulties and challenges are in the area of process control. Owing to the unique nature of underground gasification, there inherently exists problems of controllability and observability.

The next, and most important, operation is the utilization of the product gas, and it requires a coupling between the gas source and the energy demand. The product gas can be either used as an energy source to produce electricity on site or can be upgraded to a high-Btu pipeline-quality gas for transmission. In some other applications, it could be utilized near the deposit as a hydrogen source, as a reducing agent, or as a basic raw material for manufacture of other chemicals. With realization of the hydrogen economy, the product gas may have good potential as a hydrogen source. Generally speaking, there are no major technical problems involved with the utilization of product gas, apart from potential environmental concerns.

2.4.4.5.3 Methods for Underground Gasification

There are two principal methods that have been tried successfully, *shaft methods* and *shaftless methods* (and combinations of the two).[24,25,27] Selection of a specific method to be adopted depends on such parameters as the natural permeability of the coal seam, the geochemistry of the coal deposit, the seam thickness, depth, width and inclination, closeness to metropolitan developments, and the amount of mining desired. Shaft methods involve driving of shafts and drilling of other large-diameter openings that require underground labor, whereas shaftless methods use boreholes for gaining access to the coal seam and do not require labor to work underground.

2.4.4.5.3.1 Shaft Methods

1. *Chamber or warehouse method:* This method requires the preparation of underground galleries and the isolation of coal panels with brick wall. The blast of air for gasification is applied from the gallery at the previously ignited face of one side of the panel, and the gas produced is removed through the gallery at the opposite side of the panel. This method relies on the natural permeability of the coal seam for airflow through the system. Gasification and combustion rates are usually low, and the product gas may have variable composition from time to time. To enhance the effectiveness, coal seams are precharged with dynamites to rubblize them in advance of the reaction zone by a series of controlled explosions.
2. *Borehole producer method:* This method typically requires the development of parallel underground galleries and are located about 500 ft. apart within the coal bed. From these galleries, about 4-in.-diameter boreholes are drilled about 15 ft. apart from one gallery to the opposite one. Electric ignition of the coal in each borehole can be achieved by remote control. This method was originally designed to gasify substantially flat-lying seams. Variations of this technique utilize hydraulic and electric linking as alternatives to the use of boreholes.
3. *Stream method:* This method can be applied to steeply pitched coal beds. Inclined galleries following the dip of the coal seam are constructed parallel to each other and are connected at the bottom by a horizontal gallery or “fire-drift.” A fire in the horizontal gallery initiates the gasification, which proceeds upward with air coming down one inclined gallery and gas leaving through the other. One obvious advantage of the stream method is that ash and roof material drop down, tend to fill void space, and do not tend to choke off the combustion zone at the burning coal front. However, this method is structurally less suitable for horizontal coal seams because of roof collapse problems.

2.4.4.5.3.2 Shaftless Methods

In shaftless methods, all development, including gasification, is carried out through a borehole or a series of boreholes drilled from the surface into the coal seam. A general approach has been to make the coal bed more permeable between the inlet and outlet boreholes by a chosen linking method, ignite the coal seam, and then gasify it by passing air and other gasifying agents from the inlet borehole to the outlet borehole.

2.4.4.5.3.3 Percolation or Filtration Methods

This is the most direct approach to accomplish shaftless gasification of a coal seam using multiple boreholes. The distance required between boreholes depends on the seam permeability. Lower-rank coals such as lignites have a considerable natural permeability and, as such, can be gasified without open linking. However, higher-rank coals such as anthracites are far less permeable, and it becomes necessary to connect boreholes by some efficient linking techniques that will increase the permeability and fracture of the coal seam so that an increased rate of gas flow can be attained. Air or air/steam is blown through one borehole, and product gas is removed from another borehole. Either forward or reverse combustion can be permitted by this method. As the burn-off (a combination of combustion and gasification) progresses, the permeability of the seam also increases and compressed air blown through the seam helps enlarge cracks or openings in the seam. When the combustion of a zone nears completion, the process is transferred to the next pair of boreholes and continues. In this operation, coal ash and residues should be structurally strong enough to prevent roof collapse.

2.4.4.5.4 *Potential Problem Areas with* In Situ *Gasification*

There are several issues why the *in situ* gasification processes may not be able to produce a high-quality and constant quantity of product gas, recover a high percentage of coal energy in the ground, and control the groundwater contamination. Potential problem areas in commercial exploitation of this technology are discussed in the following text.

2.4.4.5.4.1 Combustion Control

Combustion control is essential for controlling the product gas quality as well as the extent of coal conversion. The reactive contacting between the coal and the gasifying agent should be such that the coal is completely *in situ* gasified, all oxygen in the inlet gas is consumed, and the production of fully combusted carbon dioxide and water is minimized. In a typical *in situ* coal gasification process, as the processing time goes by, the heating value of the product gas decreases. This may be attributable to increasingly poor contact of gas with the coalface, because of large void volumes and from roof collapse. The problem of efficient contacting needs to be solved satisfactorily in this process.

2.4.4.5.4.2 Roof Structure Control

After the coal is burned off, a substantial roof area is left unsupported. Uncontrolled roof collapse causes nontrivial problems in the combustion control, and also seriously hinders successful operation of the overall gasification process. Further, it potentially results in the leakage of reactant gases, seepage of groundwater into the coal seam, loss of product gas, and surface subsidence above the coal deposit.

2.4.4.5.4.3 Permeability, Linking, and Fracturing

An underground coal bed usually does not have a sufficiently high permeability to permit the passage of oxidizing gases through it without a serious pressure drop.

Also, intentional linking methods such as pneumatic, hydraulic, and electric, as well as fracturing with explosives, do not result in a uniform increase in permeability throughout the coal bed. They also tend to disrupt the surrounding strata and worsen the leakage problems. Therefore, the use of boreholes is proved to provide a more predictable method of linking and is a preferred technique.

2.4.4.5.4.4 Leakage Control

This is one of the most important problems because the loss of substantial amount of product gas can adversely affect the recovered amount of the product gas as well as the gasification economics. Further, the inlet reactant gases should not be wasted. Influx of water can also affect the control of the process. Leakage varies from site to site and also depends on a number of factors including geological conditions, depth of coal seam, types of boreholes and their seals, and permeability of coal bed.

Based on the above considerations, it is imperative that *in situ* gasification never be attempted in a severely fractured area, in shallow seams, or in coal seams adjoining porous sedimentary layers. It is also essential to prevent roof collapse and to properly seal inlet and outlet boreholes after operation.

2.4.4.5.5 Monitoring of Underground Processes

Proper monitoring of the underground processes is a necessary component of successful operation and design of an underground gasification system. *A priori* knowledge of all the parameters affecting the gasification is required so that adequate process control philosophy can be adopted and implemented for controlling the operation. These factors include the location, shape, and temperature distribution of the combustion front, the extent and nature of collapsed roof debris, the permeability of coal seam and debris, the leakage of reactant and product gases, the seepage of groundwater, and the composition and yield of the product gases.

2.4.4.5.6 Criteria for an Ideal Underground Gasification System

The following are the criteria for successful operation of an ideal underground coal gasification system:

1. The process must be operable on a large scale.
2. The process must ensure that no big deposits of coal are left ungasified or partially gasified.
3. The process must be controllable so that desired levels, in terms of quality and quantity, of product gases are consistently produced.
4. The mechanical features must ensure that they should be able to control undesirable phenomena such as groundwater inflow and leakage (as outflow) of reactants and products.
5. The process should require little or no underground labor, either during operation or even during the installation of the facilities.

2.4.4.6 Winkler Process

This is the oldest commercial process employing fluidized bed technology.[28] The process was developed in Europe in the 1920s. There are more than 15 plants in operation today all over the world with the largest having an output of 1.1 million scf/d. In this process, pulverized coal is dried and fed into a fluidized bed reactor by means of a *variable speed screw feeder*. The gasifier operates at atmospheric pressure and a temperature of 815–1000°C. Coal particles react with oxygen and steam to produce offgas rich in carbon monoxide and hydrogen. The relatively high operating temperature leaves very little tar and liquid hydrocarbons in the product gas stream. The gas stream that may carry up to 70% of the generated ash is cleaned by water scrubbers, cyclones, and electrostatic precipitators (ESPs). Unreacted char carried over by the fluidizing gas stream is further converted by secondary steam and oxygen in the space above the fluidized bed. As a result the maximum temperature occurs above the fluidized bed. To prevent ash fines from melting at a high temperature and forming deposits in the exit duct, gas is cooled by a radiant boiler before it leaves the gasifier. Raw hot gas leaving the gasifier is passed through a waste heat recovery section. The gas is then compressed and goes through WGS reaction. The product gas has a heating value of about 275 Btu/scf. The thermal efficiency of the process runs approximately 75%.

2.4.4.6.1 Process Description

In the early 1920s, Winkler, an employee of Davy Power Gas Inc., conceived the idea of using a fluidized bed for gasifying the coal. The first commercial unit was built in 1926. Since then, more than 30 producers and 15 installations have put this process into operation for coal gasification.

In earlier facilities, dryers were used, prior to the introduction of coal into the gas generator, to reduce the coal moisture to less than 8%. It was later realized that as long as the feed coal could be sized, stored, and transported without plugging, dryers could be omitted. Without dryers, moisture in the coal is vaporized in the generator with the heat provided by using additional oxygen for combustion reaction. Drying the coal in the generator also offers an additional advantage, i.e., elimination of an effluent stream, the dryer stack, which would require further treatment of particulate and sulfur removal.

2.4.4.6.2 Gasifier (Gas Generator)

A schematic of a Winkler fluidized bed gasifier[22] is shown in Figure 2.10. Pulverized coal is fed to the gasifier through variable-speed feeding screws. These screws not only control the coal feed rate, but also serve to seal the gasifier by preventing steam from wetting the coal and blocking the pathway by agglomeration. A high-velocity gas stream flows upward from the bottom of the gasifier. This gas stream fluidizes the bed of coal, as well as intimately mixes the reactants, thus bringing them into close contact. Fluidization helps the gas-to-solid mass transfer. This also helps in attaining an isothermal condition between the solid and the gas stream, which permits the reactions to reach equilibrium in the shortest possible time. Gasification chemistry in the Winkler gasifier is based on a combination of combustion reaction and WGS reaction.

$$C + O_2 = CO_2$$

$$C + 1/2\ O_2 = CO$$

$$C + H_2O = H_2 + CO$$

$$CO + H_2O = CO_2 + H_2$$

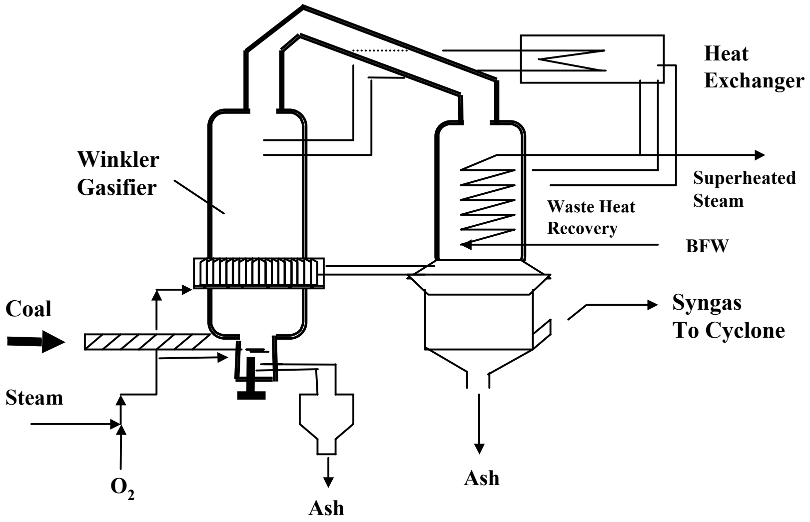

FIGURE 2.10 A schematic of Winkler gasification process.

In the preceding reactions, carbon was used instead of coal only for illustrative purposes. Therefore, the actual reactions in the gasifier are much more complex. Owing to the relatively high temperatures of the process, nearly all the tars and heavy hydrocarbons are reacted.[29]

As a result of the fluidization, the ash particles get segregated according to particle size and specific gravity. About 30% of the ash leaves through the bottom, whereas 70% is carried overhead. The lighter particles carried upward along with the produced gas are further gasified in the space above the bed. Therefore, the quantity of gasifying medium injected into this bed must be adjusted proportionally to the amount of unreacted carbon being carried over. If it is too little, ungasified carbon gets carried out of the generator, resulting in a slightly lower thermal efficiency, and if it is too much, product gas is unnecessarily consumed by combustion. The maximum temperature in the generator occurs in the space above the fluidized bed because of this secondary (further) gasification.

A radiant boiler installed immediately above the bed cools the hot product gas down to 150–205°C before it leaves the generator. This helps prevent the fly ash from getting sintered on the refractory walls of the exit duct. The sensible heat recovered by the radiant boiler generates superheated steam and is used to preheat the boiler feed water (BFW), as an energy integration scheme. The typical gas composition from a Winkler gasifier is shown in Table 2.4. As can be seen from the data, the product gas is rich in carbon monoxide, making the resultant gas a CO-rich syngas.

2.4.4.6.3 Features of the Winkler Process

The following are the chief characteristics of the Winkler process:

1. A variety of coal feeds of widely different ranks, ranging from lignite to coke, can be gasified. Petrologically, younger lignite is more reactive than older counterparts of bituminous and anthracite. With more reactive coal,

the required gasification temperature decreases, whereas the overall gasification efficiency increases. For less reactive coals, however, the energy losses through unburned solids inevitably increase.

2. Coal with high ash content can be gasified without difficulty. Although high-ash-content coals result in increased residues and incombustible materials, usually they are less expensive; and thus, sources of feed coal can be greatly expanded. Winkler gasifier is not sensitive to variations in the ash content during operation.
3. Winkler gasifier can also gasify liquid fuels in conjunction with coal gasification. The addition of supplementary liquid feeds results in an increase in production and heating value of the product gas, thereby boosting the process economics favorably.
4. Winkler gasification is very flexible in terms of the capacity and turndown ratio. It is limited at the lower end by the minimum flow required for fluidization and at the upper end by the minimum residence time required for complete combustion of residues.
5. Shutdown can be very easily facilitated by stopping the flows of oxygen, coal, and steam, and can be achieved within minutes. Even for hard coals (with low permeability), which are difficult to ignite, the heat loss during shutdown may be reduced by brief injection of air into the fuel bed.
6. Maintenance of the gas generator is straightforward, because it consists only of a brick-lined reactor with removable injection nozzle for the gasification medium.

From a more recent study, the high-temperature Winkler (HTW) process was chosen to be well suited for gasification of the lignite found in the Rhine area of Germany. The suitability was based on its temperature for gasification and the fluidized bed reactor configuration.[71] The study also discusses the selection criteria of gasification processes. Rhinebraun AG has operated a demonstration plant of HTW process at Berrenrath, Germany since 1986.[79] A variety of feedstocks other than coal, namely plastic wastes, household refuse, and sewage sludge, were successfully processed.[79]

TABLE 2.4
Typical Winkler Gas Products

Component	O_2-Blown (%)	Air-Blown (%)
CO	48.2	22.0
H_2	35.3	14.0
CH_4	1.8	1.0
CO_2	13.8	7.0
N_2 + Ar	0.9	56.0

Note: Heating value, Btu/scf: O_2-blown = 288; air-blown = 126.

Source: From Lloyd, W.G., *The Emerging Synthetic Fuel Industry*, Thumann, A., Ed., Atlanta, GA: Fairmont Press, 1981, pp.19–58.

2.4.4.7 Wellman-Galusha Process

This process has been in commercial use for more than 40 years. It is capable of producing low-Btu gas; to be specific, using air (as a gasifying medium) for fuel gas or using oxygen (as a gasifying medium) for synthesis gas. There are two types of gasifiers for this process, namely, *the standard type without agitator* and *the modified type with agitator*. The rated capacity of the agitated type is about 25% more than that of a standard type gasifier of the same size. The agitated type can handle volatile caking bituminous coals, whereas the nonagitated type would have technical difficulties with this type of coal.[3] A schematic of a *Wellman-Galusha agitated gasifier*[11] is shown in Figure 2.11.

This gasifier can be classified under the categories of a fixed bed or moving bed type reactor. The gasifier shell is water-jacketed and, hence, the inner wall of the reactor vessel does not require a refractory lining. The gasifier operates at about 540–650°C and at atmospheric pressure. Pulverized coal is fed to the gasifier from the top through a lock hopper and vertical feed pipes, whereas steam and oxygen are injected at the bottom of the bed through tuyeres. The fuel valves are operated to maintain constant flow of coal to the gasifier, which also helps in stabilizing the bed, thus maintaining the quality of the product gas. The injected air or oxygen passes over the water jacket and generates the steam required for the process. A rotating grate is located at the bottom of the gasifier to remove ash from the bed uniformly. An air-steam mixture is introduced underneath the grate and is evenly distributed through the grate into the bed. This gasifying medium passes through the ash, combustion, and gasifying zones in this specific order, while undergoing a variety of chemical reactions. The product gas contains hydrogen, carbon monoxide, carbon dioxide, and nitrogen (if air is used as an injecting medium), which being

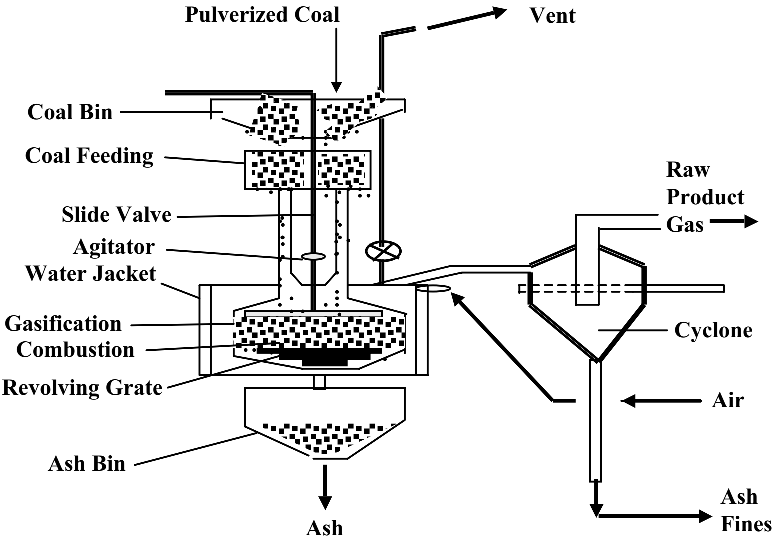

FIGURE 2.11 A schematic of agitated Wellman-Galusha gasifier.

TABLE 2.5
Typical Wellman-Galusha Products (air-blown)

Component	Percentage
CO	28.6
H_2	15.0
CH_4	2.7
N_2	50.3
CO_2	3.4

Note: Heating value (dry) = 168 Btu/scf.

Source: From Lloyd, W.G., *The Emerging Synthetic Fuel Industry*, Thumann, A., Ed., Atlanta, GA: Fairmont Press, 1981, pp.19–58.

hot, dries and preheats the incoming coal before leaving the gasifier. The typical product composition of a Wellman-Galusha gasifier is presented in Table 2.5.

The product gas is passed through a cyclone separator, where char particles and fine ash are removed. It is then cooled and scrubbed in a direct-contact countercurrent water cooler and treated for sulfur removal. If air is used as an oxidant as illustrated in Table 2.5, low-Btu gas is obtained owing to the presence of a large amount of nitrogen; if oxygen is used, then medium-Btu gas would be produced.

Unlike the standard Wellman-Galusha gasifier, the agitated version is equipped with a slowly revolving horizontal arm that spirals vertically below the surface of the coal bed to minimize channeling. This arm also helps in providing a uniform bed for gasification.

2.4.4.8 The U-GAS Process

The process was developed by the Institute of Gas Technology (IGT), Des Plaines, IL, to produce gaseous product from coal in an efficient and environmentally acceptable manner. The product gas may be used to produce low-Btu gas, medium-Btu gas, and SNG for use as fuels, or as chemical feedstocks for ammonia, methanol, hydrogen, oxo-chemicals, etc., or for electricity generation via an *IGCC*. Based on extensive research and pilot plant testing, it has been established that the process is capable of handling large volumes of gas throughput, achieving a high conversion of coal to gas without producing tar or oil, and causing minimum damage to the environment.

The U-GAS process is based on a single-stage, fluidized bed gasifier, as shown in Figure 2.12. The gasifier accomplishes four principal functions in a single stage, namely: (1) decaking coal, (2) devolatilizing coal, (3) gasifying coal, and (4) agglomerating and separating ash from char. Coal of about 0.25-in. diameter is dried and pneumatically injected into the gasifier through a lock hopper system. In the fluidized bed reactor, coal reacts with steam and oxygen at a temperature of 950–1100°C. The temperature of the bed is determined based on the type of coal feed and is controlled

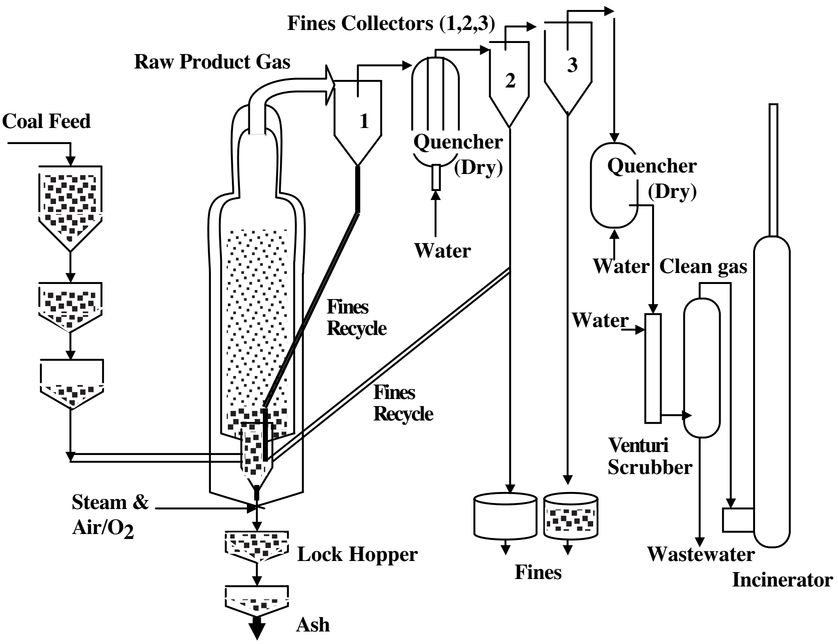

FIGURE 2.12 A schematic of U-gas process.

to prevent slagging conditions of ash. The pressure may be flexible, typically ranging from 50 to 350 psi, and is largely determined based on the ultimate use of the final product gas. Oxygen may be substituted with air. In the gasifier, coal is rapidly gasified producing H_2, CO, CO_2, and small amounts of CH_4. The fluidized bed is always maintained under reducing conditions and, as such, all sulfur species present in coal is converted into H_2S. Simultaneously with gasification, the ash is agglomerated into spherical particles that grow in size and are separated from the bed into water-filled ash hoppers, from which they are withdrawn as slurry. A portion of fluidizing gas enters the gasifier section through an inclined grid, whereas most of the remaining entering gas flows upward at a high velocity through the ash-agglomerating zone and forms a relatively hot zone within the bed.

Coal fines elutriated from the bed are collected by two external cyclones. Fines from the first cyclone are returned to the bed, whereas those from the second cyclone are sent to the ash-agglomerating zone. Raw product gas is virtually free of tar and oils, thus simplifying the ensuing energy recovery and gas purification steps. The pilot plant operated by the IGT has a gasifier made of a mild-steel, refractory-lined vessel with an I.D. of 3 ft. and a height of about 30 ft.

An IGCC process based on the IGT U-GAS process was developed by Tampella Power Company, Finland, which later became Carbona Inc. The choice of the IGT process is based on its excellent carbon conversion, as well as its versatility with a wide range of coals and peat. Enviropower Inc. originally licensed the U-gas technology and developed it as Enviropower gasification technology. Later, Enviropower's gasification business was taken over by Carbona Inc. Carbona has developed the technology applicable to biomass gasification and is developing a pressurized fluidized bed gasification plant for the 55 MW cogeneration project with Ignifluid Boilers India Ltd. (IBIL), Chennai, India. The plant is designed for multifuel operation, including biomass.[70]

2.4.4.9 Catalytic Coal Gasification

In recent years, the study of catalytic gasification has received attention because it requires less thermal energy input but yields higher carbon conversion. Studies on the catalysis of coal gasification have twofold objectives: (1) to understand the kinetics of coal gasification that involves active mineral matter and (2) to design possible processes using these catalysts. The use of catalysts lowers the gasification temperature, which favors product composition under equilibrium conditions as well as high thermal efficiency. However, under normal conditions a catalytic process cannot compete with a noncatalytic one unless the catalyst is quite inexpensive or highly active at low temperatures. Recovery and reuse of catalyst in the process is undesirable and unattractive in coal gasification because of the expensive separation efforts and the low cost of coal and coal gas. Research on catalysis covers mainly three subjects: basic chemistry, application-related problems, and process engineering. Juntgen[30] published an extensive review article on catalytic gasification. Nishiyama[31] also published a review article, which features some possibilities for a well-defined catalytic research effort. The article contains the following observations:

1. Salts of alkali and alkaline earth metals as well as transition metals are active catalysts for gasification.
2. The activity of a particular catalyst depends on the gasifying agent as well as the gasifying conditions.
3. The main mechanism of catalysis using alkali and alkaline earth metal salts in steam and carbon dioxide gasification involves the transfer of oxygen from the catalyst to carbon through the formation and decomposition of the C-O complex, i.e., C(O).

The mechanism of hydrogasification reactions catalyzed by iron or nickel is still not very clear. But a possible explanation is that the active catalyst appears to be in the metallic state and there are two main steps for the mechanism. These are hydrogen dissociation and carbon activation.[32–36] For the latter case, carbon dissolution into and diffusion through a catalyst particle seems logical. Gasification proceeds in two stages, each of which has a different temperature range and thermal behavior, so that a single mechanism cannot explain the entire reaction. Thus, the catalyst is still assumed to activate the hydrogen.

Calcium as a catalyst has also been studied by several investigators.[37–45] This catalyst has a very high activity in the initial period when it is well dispersed in the other promoter catalyst, but with increasing conversion, the activity drops. The chemical state and dispersion are studied by chemisorption of carbon dioxide, x-ray diffraction (XRD), and some other analytical techniques. They confirmed the existence of two or more states of calcium compounds, as well as the formation of a surface oxygen complex.

Compared to other heterogeneous catalytic systems, the catalysis in gasification is complex because the catalyst is very short-lived and effective only while in contact with the substrate, which itself changes during the course. As such, the definition of the activity for such systems is not very straightforward. For an alkali metal catalyst, the rate increases owing to the change in the catalyst dispersion and also to the increase in the ratio of catalyst/carbon in the later stage of gasification. Other possible explanations for the rate increase could be the change in surface area by pore opening, and the change in chemical state of the catalyst. At the same time, there are some changes that deactivate the catalyst, for example, agglomeration of catalyst particles, coking, and chemical reaction with sulfur or other trace elements. Coking causes fouling on the catalyst surface as well as sintering the catalyst, whereas reaction with sulfur poisons the catalytic activity.

The activity of the catalyst also depends on the nature of the substrate and gasifying conditions. The main properties of the substrate related to the activity are: (1) reactivity of the carbonaceous constituents, (2) catalytic effect of minerals, and (3) effect of minerals on the activity of added catalyst. The following general trends have been observed in reference to the factors affecting the activity of the catalysts:

1. Nickel catalysts are more effective toward lower-rank coals because they can be more easily dispersed into the coal matrix owing to higher permeability of the coal, whereas the efficiency of potassium catalyst is independent of the rank. In any case, the coal rank alone, as given by the carbon content, cannot predict catalyst activity.
2. The internal surface area of coal char relates to the overall activity of the catalyst. It can be related to the number of active sites in cases when the amount of catalyst is large enough to cover the available surface area. For an immobile catalyst, the conversion is almost proportional to the initial surface area.
3. Pretreatment of coal before the catalytic reaction often helps in achieving higher reaction rates. Although the pretreatment of coal may not be directly applicable as a practical process, a suitable selection of coal types or processing methods could enhance the activity of catalysts.
4. The effect of coal mineral matter on the catalyst effectiveness is twofold. Some minerals such as alkali and alkaline-earth metals catalyze the reaction, whereas others such as silica and alumina interact with the catalyst and deactivate it. In general, demineralization results in enhancement of activity for potassium catalysts, but only slightly so for calcium and nickel catalysts.

The method of catalyst loading is also important for activity management. The catalyst should be loaded in such a way that a definite contact between both solid and gaseous reactants is ensured. It was observed that when the catalyst was loaded from an aqueous solution, a hydrophobic carbon surface resulted in finer dispersion of the catalyst when compared to a hydrophilic surface.

The most common and effective catalysts for steam gasification are oxides and chlorides of alkali and alkaline-earth metals, separately or in combination.[46] Xiang et al. studied the catalytic effects of the Na–Ca composite on the reaction rate, methane conversion, steam decomposition, and product gas composition, at reaction temperatures of 700–900°C and pressures from 0.1 to 5.1 MPa. A kinetic expression was derived with the reaction rate constants and the activation energy determined at elevated pressures. Alkali metal chlorides such as NaCl and KCl are very inexpensive, and hence preferred as catalyst raw materials for catalytic gasification. However, their activities are quite low compared to the corresponding carbonates because of the strong affinity between alkali metal ion and chloride ion. Takarada et al.[47] have attempted to make Cl-free catalysts from NaCl and KCl by an ion exchange technique. The authors' ion-exchanged alkali metals to brown coal from an aqueous solution of alkali chloride using ammonia as a pH-adjusting agent. Cl ions from alkali chloride were completely removed by water washing. This Cl-free catalyst markedly promoted the steam gasification of brown coal. This catalyst was found to be catalytically as active as alkali carbonate in steam gasification. During gasification, the chemical form of active species was found to be in the carbonate form and was easily recovered. Sometimes, an effective way of preparing the catalyst is physical mixing K-exchanged coal with the higher-rank coals.[48] This direct contact between K-exchanged and higher-rank coal resulted in enhancement of gasification rate. Potassium was found to be a highly suitable catalyst for catalytic gasification by the physical mixing method. Weeda et al.[49] studied the high-temperature gasification of coal under product-inhibited conditions whereby they used potassium carbonate as a catalyst to enhance the reactivity. They performed temperature-programmed experiments to comparatively characterize the gasification behavior of different samples. However, the physical mixing method is likely to be neither practical nor economical for large-scale applications. Some researchers[50] have recovered the catalysts used, in the form of a fertilizer of economic significance. They used a combination of catalysts consisting of potassium carbonate and magnesium nitrate in the steam gasification of brown coal. The catalysts along with coal ash were recovered as potassium silicate complex fertilizer.

In addition to the commonly used catalysts such as alkali and alkaline-earth metals for catalytic gasification, some less-known compounds made of rare earth metals as well as molybdenum oxide (MoO_2) have been successfully tried for steam and carbon dioxide gasification of coal.[51–53] Some of the rare earth compounds used were $La(NO_3)_3$, $Ce(NO_3)_3$, and $Sm(NO_3)_3$. The catalytic activity of these compounds decreased with increasing burn-off (i.e., conversion) of the coal. To alleviate this problem, coloading with a small amount of Na or Ca was attempted and the loading of rare earth complexes was done by the ion exchange method.

Coal gasification technology could benefit from the development of suitable and effective catalysts that will help catalyze steam decomposition and carbon/steam reaction. Batelle Science & Technology International[54] has developed a process in which calcium oxide was used to catalyze the hydrogasification reaction. It was also shown that a reasonably good correlation exists between the calcium content and the reactivity of coal chars with carbon dioxide. Other alkali metal compounds, notably chlorides and carbonates of sodium and potassium, can also enhance the gasification rate by as much as 35–60%. In addition to the oxides of calcium, iron, and magnesium, zinc oxides are also found to substantially accelerate gasification rates by 20–30%.

Some speculative mechanisms have been proposed by Murlidhara and Seras[54] as to the role of calcium oxide in enhancing the reaction rate. For instance, coal organic matter may function as a donor of hydrogen, which then may be abstracted by calcium oxide by a given mechanism as described in Scheme 1. Scheme 2 explains the mechanism of generating oxygen-adsorbed CaO sites and subsequent desorption of nascent oxygen, which in turn reacts with organic carbon of coal to form carbon monoxide. Scheme 3 explains direct interaction between CaO and coal organics, which results in liberation of carbon monoxide. The scheme further explains an oxygen exchange mechanism that brings the reactive intermediates back to CaO.

Scheme 1:

$$\text{Organic} \rightarrow \text{Organic}^{*} + H_2$$

$$CaO + 2H_2 \rightarrow CaH_2 + H_2O$$

$$\text{Organic}^{*} + CO_2 \rightarrow 2CO$$

$$CO_2 + CaH_2 \rightarrow CaO + CO + H_2$$

Scheme 2:

$$CaO + CO_2 \rightarrow CaO(O) + CO$$

$$CaO(O) \rightarrow CaO + (O)$$

$$C + (O) \rightarrow CO$$

Scheme 3:

$$CaO + 2C \rightarrow CaC_x + CO$$

$$CaC_x + \text{Organic (oxygen)} \rightarrow CaO + \text{Organic}^{*}$$

Exxon (currently, ExxonMobil) has reported that impregnation of 10–20% of potassium carbonate lowers the optimum temperature and pressure for steam gasification of bituminous coals, from 980 to 760°C and from 68 to 34 atm, respectively.[55] In their commercial-scale plant design, the preferred form of make-up catalyst was identified as potassium hydroxide. This catalyst aids the overall process in several ways. First, it increases the rate of gasification, thereby allowing a lower gasification temperature. Second, it prevents swelling and agglomeration when handling caking coals, which is another benefit of a lower gasification temperature. Most importantly, it promotes the methanation reaction because it is thermodynamically more favored at a lower temperature. Therefore, in this process, the production of methane is thermodynamically and kinetically favored in comparison to synthesis gas. A catalyst recovery unit is provided after the gasification stage to recover the used catalyst.

2.4.4.10 Molten Media Gasification

Generally speaking, molten media may mean one of the following: molten salt, molten metal, or molten slag. When salts of alkali metals and iron are used as a medium to carry out the coal gasification, it is referred to as *molten media gasification*. The molten medium not only catalyzes the gasification reaction, but also supplies the necessary heat and serves as a heat exchange medium.[3,56] There have been several distinct commercial processes developed over the years:

1. Kellogg-Pullman molten salt process
2. Atgas molten iron gasification process
3. Rockwell molten salt gasification
4. Rummel-Otto molten salt gasification

Schematics of a Rockwell molten salt gasifier and a Rummel–Otto single-shaft gasifier are shown in Figure 2.13[11] and Figure 2.14,[22] respectively.

2.4.4.10.1 Kellogg Molten Salt Process

In this process, gasification of coal is carried out in a bath of molten sodium carbonate (Na_2CO_3) through which steam is passed.[57] The molten salt produced by this process offers the following advantages:

1. The steam–coal reaction, being basic in nature, is strongly catalyzed by sodium carbonate, resulting in complete gasification at a relatively low temperature.
2. Molten salt disperses coal and steam throughout the reactor, thereby permitting direct gasification of caking coals without carbonization.
3. A salt bath can be used to supply heat to the coal undergoing gasification.
4. Owing to the uniform temperature throughout the medium, the product gas obtained is free of tars and tar acids.

Crushed coal is picked up from lock hoppers by a stream of preheated oxygen and steam and carried into the gasifier. In addition, sodium carbonate recycled from the ash rejection system is also metered into the transport gas stream and the combined coal, salt, and carrier are admitted to the gasifier. The main portion of the preheated oxygen and steam is admitted into the bottom of the reactor for passage through the salt bath to support the gasification reactions. Along with the usual gasification reactions, sulfur entering with the coal accumulates as sodium sulfide (Na_2S) to an equilibrium level. At this level, it leaves the reactor according to the following reaction:

$$Na_2CO_3 + H_2S \rightarrow Na_2S + CO_2 + H_2O$$

Ash accumulates in the melt and leaves along with the bleed stream of salt, where it is rejected and sodium carbonate is recycled. The bleed stream of salt is

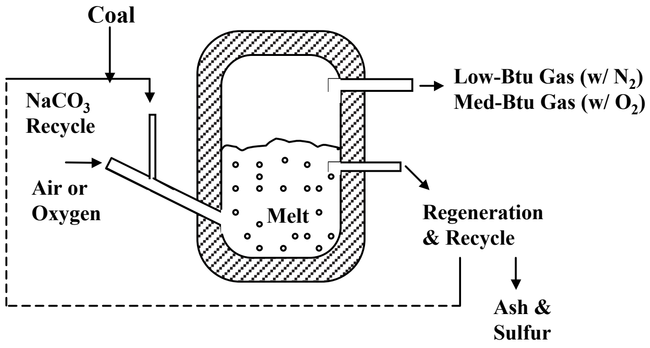

FIGURE 2.13 A schematic of Rockwell molten salt gasifier.

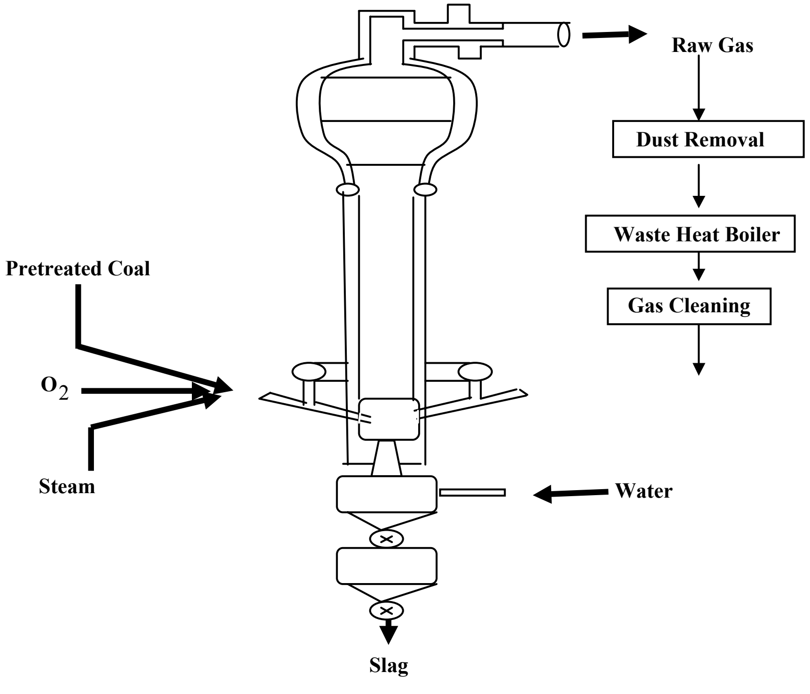

FIGURE 2.14 Rummel-Otto single-shaft gasifier.

quenched in water to dissolve sodium carbonate (Na_2CO_3) and permit rejection of coal ash by filtration. The dilute solution of sodium carbonate is further carbonated for precipitation and recovery of sodium bicarbonate ($NaHCO_3$). The filtrate is recycled to quench the molten salt stream leaving the reactor. The sodium bicarbonate filtrate cake is dried and heated to regenerate to sodium carbonate for recycle to the gasifier. The gas stream leaving the gasifier is processed to recover the entrained salt and the heat, and is further processed for conversion to the desired product gas such as synthesis gas, pipeline gas, or SNG.

2.4.4.10.2 Atgas Molten Iron Coal Gasification

This process is based on the molten iron gasification concept in which coal is injected with steam or air into a molten iron bath. Steam dissociation and thermal cracking of coal volatile matter generate hydrogen and carbon monoxide, i.e., principal ingredients of synthesis gas. The coal sulfur is captured by the iron and transferred to a lime slag from which elemental sulfur can be recovered as a by-product. The coal dissolved in the iron is removed by oxidation to carbon monoxide with oxygen or air injected near the molten iron surface. The Atgas process uses coal, steam, or oxygen to yield product gases with heating values of about 900 Btu/scf.

The Atgas molten iron process has several inherent advantages over the gas-solid contact gasification in either fixed or fluidized bed reactors.[58] They are:

1. Gasification is carried out at low pressures; hence, the mechanical difficulty of coal feeding in a pressurized zone is eliminated.
2. Coking properties, ash fusion temperatures, and generation of coal fines are not problematic.
3. The sulfur content of coal does not cause any environmental problem as it is retained in the system and recovered as elemental sulfur from the slag. Elemental sulfur by-product helps the overall process economics.
4. The system is very flexible with regard to the physical and chemical properties of the feed coal. Relatively coarse size particles can be handled without any special pretreatment.
5. Formation of tar is suppressed owing to very high-temperature operation.
6. The product gas is essentially free of sulfur compounds.
7. Shutdown and start-up procedures are greatly simplified compared to fixed bed or fluidized bed reactors.

Coal and limestone are injected into the molten iron through tubes using steam as a carrier gas. The coal goes through devolatilization with some thermal decomposition of the volatile constituents, leaving the fixed carbon and sulfur to dissolve in iron whereupon carbon is oxidized to carbon monoxide. The sulfur, in both organic and pyritic forms (FeS_2), migrates from the molten iron to the slag layer where it reacts with lime to produce calcium sulfide (CaS).

The product gas, which leaves the gasifier at approximately 1425°C, is cooled, compressed, and fed to a shift converter (WGS reactor) in which a portion of carbon monoxide is reacted with steam via WGS reaction to attain a CO-to-H_2 ratio of 1:3. The carbon dioxide produced is removed from the product gas, and the gas is cooled again. It then enters a methanator in which carbon monoxide and hydrogen react to form methane via $CO + 3H_2 = CH_4 + H_2O$. Excess water is removed from the methane-rich product. The final gaseous product has a heating value around 900 Btu/scf.

2.4.4.11 Plasma Gasification

Plasma gasification is a nonincineration thermal process that uses extremely high temperatures in an oxygen-free or oxygen-deprived environment to completely decompose input material into very simple molecules. The extreme heat, aided by the absence of an oxidizing agent such as oxygen, decomposes the input material into basic molecular structure species. The plasma gasification or plasma pyrolysis process was originally developed for treatment of waste materials. However, the process can be very effectively applied to coal gasification or oil shale pyrolysis, capitalizing on its high thermal efficiency, as long as the input energy for plasma generation can be obtained effectively via energy integration or some other inexpensive source of energy. When the plasma gasification is applied to carbonaceous materials such as coal and oil shale kerogen, by-products are normally a combustible gas and an inert slag. Product gas can be cleaned by conventional technologies, including cyclone, scrubbers, and ESPs. Cyclone/scrubber effluents can normally be recycled for further processing.

Plasma is often mentioned as the fourth state. Electricity is fed to a plasma torch that has two electrodes, creating an arc through which inert gas is passed. The inert gas heats the process gas to a very high temperature, as high as 25,000°F. The temperature at a location several feet away from the torch can be as high as 5,000–8,000°F, at which temperature the carbonaceous materials are completely destroyed and broken down into their elemental forms. Furthermore, there is no tar or furan involved or produced in this process. Ash or mineral matter would become completely molten and flow out of the bottom of the reactor. Therefore, the plasma reactor is not specific to any particular kind of coal for gasification. Figure 2.15 illustrates how the plasma torch operates.[59]

When applied to waste materials such as municipal solid waste (MSW), plasma gasification possesses unique advantages for the protection of air, soil, and water resources through extremely low limits of air emissions and leachate toxicity. Because the process is not based on combustion of carbonaceous matters, generation of *greenhouse chemicals*, in particular carbon dioxide, is far less than from any other conventional gasification technology. Furthermore, air emissions are typically orders of magnitude below the current regulations. The slag is monolithic and the leachate

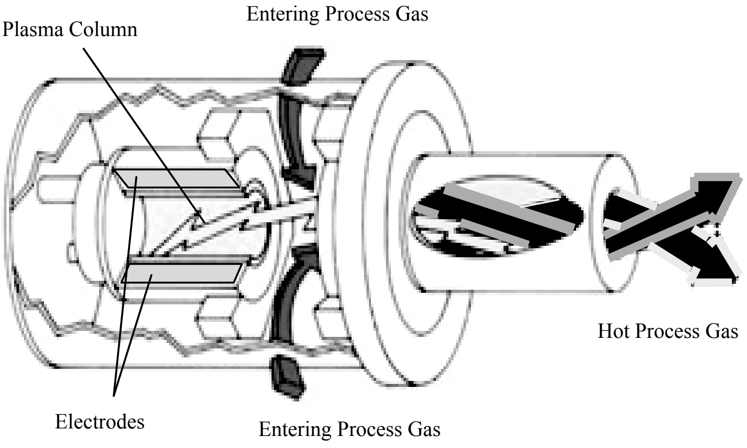

FIGURE 2.15 Plasma torch. (From Recovered Energy, Inc. Web site, http:www.recoveredenergy.com/d_plasma.html, 2004. With permission.)

levels are orders of magnitude lower than the current EP-toxicity standard, which is one of the four criteria for hazardous waste classification.[72] Slag weight and volume reduction ratios are typically very large; for example, in the case of biomedical wastes they are 9:1 and 400:1, respectively. Even though the data for a variety of coals are not readily available in the literature, both the mass reduction ratio and the volume reduction ratio for coals are believed to be significantly higher than those for nonplasma gasification technology, thus substantially reducing the burden of waste and spent ash disposal problem.

Activities in Canada and Norway are noteworthy in the technology development of plasma gasification. Resorption Canada Limited (RCL)[60] is a private Canadian entity that was federally incorporated to develop and market industrial processes based on plasma arc technology. They have amassed extensive operating experience in this technology, covering a wide variety of input materials including environmental, biomedical, and energy-related materials and resources.

2.5 MATHEMATICAL MODELING OF COAL GASIFIERS

As research and development continues on new and efficient coal gasification concepts, mathematical modeling provides insight into their operation and commercial potential. The influence of design variables and processing conditions on the gasifier performance must be *a priori* determined before any commercial processes are designed. Such models are then used as tools for design modifications, scaling, and optimization.

Coal gasification is performed in different types of reactors in which, depending on the type of gas–solid contact, the bed can be moving, fluidized, entrained, or made up of molten salts. Of these, a moving bed configuration may be the most widely used because of its high coal conversion rates and thermal efficiency.

Different approaches have been used to model various types of reactors. There are mainly two kinds of models. The first kind is the thermodynamic or equilibrium model, which is easier to formulate; but it generates only certain restrictive information such as offgas compositions in a limiting case. The other type of model is the kinetic model, which predicts kinetic behavior inside the reactor. The time-dependent behavior of the process can be either steady state or dynamic in nature. Adanez and Labiano[61] have developed a mathematical model of an atmospheric moving bed countercurrent coal gasifier and studied the effect of operating conditions on the gas yield and composition, process efficiency, and longitudinal temperature profiles. The model was developed for adiabatic reactors. It assumes that the gasifier consists of four zones with different physical and chemical processes taking place. They are the zones for: (1) coal preheating and drying, (2) pyrolysis, (3) gasification, and (4) combustion, followed by the ash layer, which acts as a preheater of the reacting (i.e., entering) gases. In reality, however, there is no physical distinction between the zones, and the reactions occurring in each zone vary considerably. The model uses the *unreacted shrinking core model* to define the reaction rate of the coal particles.[73] The unreacted shrinking core model assumes that the dimension (as often represented by the particle size) of unreacted core (of the remaining coal particle) is progressively shrinking as the coal gets reacted. The most critical parameter in the operation of these moving bed gasifiers with dry ash extraction is the longitudinal temperature profile, because the temperature inside the reactor must not exceed the ash-softening (or ash-oozing) point at any time, in order to avoid ash fusion or oozing. The model also takes into account the effect of coal reactivity, particle size, and steam/oxygen ratio. To partially check the validity of the model, predicted data on the basis of the model were compared to real data on the product gas composition for various coals, and good agreement was attained. The authors have concluded that the reactivity of the coals and the emissivity of the ash layer must be known accurately, as they have a strong influence on the temperature profiles, the maximum temperature in the reactor, and its capacity for processing coal.

Lim et al.[62] have developed a mathematical model of a spouted bed gasifier based on simplified first-order reaction kinetics for the gasification reactions. The spouted bed gasifier has been under development in Canada and Japan.[63,64] The spout is treated as a plug flow reactor (PFR) of a fixed diameter with cross-flow into the annulus. The annulus is treated as a series of steam tubes, each being a plug flow reactor with no axial dispersion. The model calculates the composition profile of various product gases in the spout as a function of the height, radial composition profiles, and average compositions in the annulus at different heights, the average compositions exiting the spout and annulus, and the flow rates and linear velocities in the spout and annulus. The model has been further developed as a two-region model including an enthalpy balance.[80]

Monazam et al.[65] have developed a similar model for simulating the performance of a cross-flow coal gasifier. Gasification in a cross-flow gasifier is analogous to the batch gasification in a combustion pot. Therefore, the model equations for kinetics as well as mass and energy balances formulated were based on a batch process. In the cross-flow coal gasifier concept, operating temperatures are much higher than 1000°C and, as such, the diffusion through the gas film and ash layer is a critical factor. The model also assumes shrinking unreacted core model for kinetic formulations. Simulation results of the model were compared to the experimental data obtained in batch and countercurrent gasification experiments, and good agreement was attained. It was also concluded that the performance of the gasifier depends on the gas-solid heat transfer coefficient, whereas the particle size and the bed voidage had a significant effect on the time required for complete gasification.

Watkinson et al.[66] have developed a mathematical model to predict the gas composition and yield from coal gasifiers. Gas composition depends on the contacting pattern of blast and fuel, temperature and pressure of the operation, composition of the blast, and form of fuel feeding. The authors have presented a calculation method and the predicted data have been compared to the operating data from nine different types of commercial and pilot-scale gasifiers, including Texaco, Koppers-Totzek, and Shell, Winkler-fluidized bed, and Lurgi dry ash as well as Lurgi slagging moving bed gasifier. The model consists of elemental mass balances for C, H, O, N, and S, chemical equilibria for four key chemical reactions, and an optional energy balance. The four key reactions were partial oxidation, steam gasification, Boudouard reaction, and WGS reaction. Predictions were most accurate for entrained flow systems, less accurate for fluidized bed gasifiers, and uncertain for moving bed reactors. This was due to the lower temperatures and uncertain volatile yields in the latter ones resulting in deviation between the calculated and experimentally reported values.

Lee et al.[67] developed a single-particle model to interpret kinetic data of coal char gasification with H_2, CO_2, and H_2O. Their model yields asymptotic analytical solutions taking into account all the major physical factors that affect and contribute to the overall gasification rate. Some of the factors taken into account involved changing magnitudes of internal surface area, porosity, activation energy, and effective diffusivity as functions of conversion (or burnoff). Their model closely describes the characterizing shape of the conversion vs. time curves as determined by CO_2 gasification studies. The curve shape under certain restrictions leads to a "universal curve" of conversion vs. an appropriate dimensionless time. The model developed is mathematically very simple, and all the parameters in the model equation have physical significance. Therefore, the model is applicable to a wide variety of coals having different physicochemical and petrological properties. The number of adjustable parameters in this model is only two. Their model predictions were compared against experimental data obtained using a novel thermobalance reactor, and excellent agreement was attained.[67]

Gururajan et al.[68], in their review, critically examined many of the mathematical models developed for fluidized bed reactors. The review is primarily concerned with the modeling of bubbling fluidized bed coal gasifiers. They also discuss the rate processes occurring in a fluidized bed reactor and compare some of the reported models in the literature with their presentation.

When a coal particle is fed into a gasifier, it undergoes several physicochemical transformations, which include: (1) drying, (2) devolatilization, and (3) gasification of the residual char in different gaseous atmospheres. These heterogeneous reaction-transport phenomena are accompanied by a number of supplementary reactions that are homogeneous in nature. Detailed kinetic studies are an important prerequisite for the development of a mathematical model. Mathematical models for a bubbling fluidized bed coal gasifier can be broadly classified into two kinds, i.e., thermodynamic (or equilibrium) and kinetic (or rate) models. Thermodynamic models predict the equilibrium compositions and temperature of the product gas based on a given set of steam/oxygen feed ratios, the operating pressure, and the desired carbon conversion. These models are independent of the type of the gasifier and based on the assumption of complete oxygen consumption. Therefore, they cannot be used to investigate the influence of operating parameters on the gasifier performance. The kinetic model, on the other hand, predicts the composition and temperature profiles inside the gasifier for a given set of operating conditions and reactor configurations and hence can be used to evaluate the performance of the gasifier. They are developed by combining a suitable hydrodynamic model for the fluidized bed with appropriate kinetic schemes for the reactive processes occurring inside the gasifier. Various rate models may be classified into four groups on the basis of hydrodynamic models used.[68] They are:

1. Simplified flow models
2. Davidson-Harrison type models
3. Kunii-Levenspiel type models
4. Kato-Wen type models

The same review[68] also examined and compared the different types of models. Although many investigators have compared their model predictions with experimental data, a detailed evaluation of the influence of model assumptions on its predictions has not been reported. Although efforts have been made to compare the predictions of different models, an attempt to evaluate the model with experimental data from different sources has not been made.

Gururajan et al. in their review article[68] have developed a model of their own for a bottom feeding bubbling fluidized bed coal gasifier based on the following assumptions:

1. The bubble phase is in plug flow and does not contain any particles, whereas the emulsion phase is completely mixed and contains the particles in fluidized conditions.
2. Excess gas generated in the emulsion phase passes into the bubble phase. The rate of this excess per unit bed volume is constant.
3. The coal particles in the feed are spherical, homogeneous, and uniform in size.
4. Only WGS reaction occurs in the homogeneous gas phase.
5. External mass transfer and intraparticle diffusion are assumed to be negligible in the char gasification reactions.
6. Entrainment, abrasion, agglomeration, or fragmentation of the bed particles is assumed to be negligible.
7. The gasifier is at a steady state and is isothermal.

All the model equations are derived on the basis of the preceding assumptions. The model predictions were compared with the experimental data from three pilot-scale gasifiers reported in the literature.[68] They concluded that the predictions were more sensitive to the assumptions regarding the combustion/decomposition of the volatiles and the products of char combustion than to the rate of char gasification. Hence, in pilot-scale gasifiers, owing to the short residence time of coal particles, the carbon conversion and the product gas yields are mainly determined by the fast-rate coal devolatilization, volatiles combustion/decomposition and char combustion, and also by the slow-rate char gasification reactions. This explains why models based on finite-rate char gasification reactions are able to fit the same pilot-scale gasification data.

A better understanding of coal devolatilization, decomposition of the volatiles, and char combustion under conditions prevailing in a fluidized bed coal gasifier is very important for the development of a model with good predictive capability. There is a strong need to investigate the kinetics of gasification of coal and char in synthesis gas atmospheres and to obtain experimental data for the same coal and char in a pilot-scale plant.

It is well known that there are many physical changes occurring when the coal char particles are gasified. There have been many attempts to unify these dynamic changes through various normalizing parameters such as half-life, coal rank, reactivity, or surface area. According to the study by Raghunathan and Yang,[69] the experimental char conversion vs. time data from different experiments can be unified into a single curve where time is considered to be normalized time, $t/t_{1/2}$, $t_{1/2}$ being the half-life of the char-gas reaction. This unification curve with only one parameter is then fitted into the rate models commonly used, e.g., the *grain model* and the *random pore model.* With the aid of reported correlations for unification curves, a master curve is derived to approximate the conversion–time data for most of the gasification systems. Also, as the half-life (more precisely, half-conversion time) is simply related to the average reactivity, it can be generally used as a reactivity index for characterizing various char-gas reactions. Further, conversions up to 70% can be predicted with reasonable accuracy over a wide range of temperatures.

A great deal of effort has been devoted to mathematically modeling a variety of gasifiers and reaction conditions in order to obtain design- and performance-related information. Numerous simplified models and asymptotic solutions have been obtained for coal gasification reactors along with a large database of digital simulation of such systems.

2.6 FUTURE OF COAL GASIFICATION

The roles of coal gasification have been changing constantly based on the societal demands of the era. We observed in the past century that the principal roles and foci of coal-derived syngas shifted from domestic heating fuel, to feedstock for Fischer–Tropsch (F-T), to petrochemical feedstocks, to starting materials for alternative fuels, to IGCC, and to hydrogen sources. With the advent of hydrogen economy, coal gasification has again taken center stage as a means for producing hydrogen for fuel cell applications.[75] Further, coal gasification technology can also be easily applied to biomass and solid waste gasification with minor modifications. Unlike coal, biomass is not only renewable, but also available inexpensively, often free of charge. Coal can also be coprocessed together with a variety of other materials, including petroleum products, scrap tires, biomass, municipal wastes, sewage sludge, etc. With advances in flue gas desulfurization, coal gasification can be more widely utilized in process industries. In electric power generation, IGCC has contributed tremendously to improvement of power generation efficiency, thus keeping the cost of electric power competitive against all other forms of energy. Keen interest in methanol and dimethylether is rekindled due to the ever-rising cost of conventional clean liquid fuel. In order to use coal gasification technology in hydrogen production, the steam gasification process, which is essentially very similar to the hydrocarbon reformation process, needs to be refined further. Therefore, more advances are expected in the areas of product gas cleaning, separation and purification, feedstock flexibility, and integrated or combined process concepts.

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