

Gas Production, 1. Introduction

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1. Types of Gases; General Overview of Production Methods and Characteristics

Gases for industrial or heating uses can be classified in various ways. The most appropriate classification appears by calorific (heating) value ranges, in kJ/m³ (STP):

Water and producer gas	4600 – 12 500
Synthesis and reduction gas	ca. 12 500
Town gas and medium-Btu gas	16 700 – 20 000
Biogas and landfill gas	18 000 – 29 000
High-Btu gas and substitute natural gas (SNG)	25 000 – 37 000

A distinction has deliberately been made between *water gas* and *synthesis gas*, although water gas was formerly used in large quantities for synthesis as well. However, the so-called water gases are based on very specific raw materials and belong to a different generation of production methods compared to synthesis gases produced in modern plants. *Reduction gas* refers to gases used in iron production.

Synthesis gas is the basis for most of the hydrogen (→ Hydrogen) produced, and it is also used as a fuel gas, e.g., in gas turbines (see → Gas Production, 5. Examples of Complex Gas Production Plants, Chap. 3.).

Biogas and *landfill gas* (→ Methane) are produced during biological degradation of organic matter. They may be collected and purified either to be used further (renewable energy) or to prevent air pollution.

1.1. Water Gas and Producer Gas

The terms water gas and producer gas were first used in solid fuel gasification technology. Both types of gas were very important from the 1920s to the 1940s. They were the basis for producing synthesis gas, town gas, and fuel gas. The technology is of only minor importance today because the raw material basis has shifted largely from solid fuels to liquid and gaseous fuels, and high-performance processes have been developed for coal-based synthesis gas, town gas, and grid gas.

Production of Water Gas. Water gas is usually produced in an alternating operation, i.e., by alternately hot blowing a fuel layer with air and gasifying it with steam. Among its various modifications, the production of so-called *blue water gas* from coke was the most common method, yielding gas with high hydrogen and carbon monoxide contents which was suitable for use as synthesis gas. By addition of higher hydrocarbons, the calorific value of water gas could be increased (*carbureting*) so it could be used as town gas.

Although most water gas plants were based on coke, plants also operated with anthracite and noncaking highly volatile types of coal (coal water gas or double gas). Coal with a high volatile matter content gives gases with higher calorific values because gasification gas is supplemented by a considerable amount of devolatilization gas.

In the water gas process with its cyclic mode of operation, coke has two functions: (1) it reacts with blowing air during warm-up and with steam during gasification, and (2) serves as a heat regenerator.

Because of the expensive raw material (coke), complicated batch operation, and relatively low output per gasifier ($6000 - 9000 \text{ m}^3 \text{ (STP)/h}$), this method of producing synthesis and town gases has been replaced by more up-to-date processes. The gas production of synthesis gas plants based on either natural gas (in tubular reformers; see → Gas Production, 2. Processes, Chap. 1.) or heavy oil (by partial oxidation; see → Gas Production, 2. Processes, Chap. 2.), and of modern coal gasification plants (see → Gas Production, 2. Processes, Chap. 3.) is ten times higher than that of water gas plants.

Production of Producer Gas. Producer gas is obtained by supplying a gasification agent consisting of air and steam continuously, rather than cyclically, to a gas producer of the same general design as a water gas producer. This gas has a lower calorific value than water gas because it contains atmospheric nitrogen. Producer gas was obtained from a variety of rotary grate gas producers from the 1920s to the 1940s. Because of its high nitrogen content, which cannot be eliminated at economically justifiable cost, this gas is not suitable for use as synthesis gas; it was employed almost exclusively as fuel gas and as an additive to town gases in municipal works.

In addition to coke, noncaking coals were also used as feedstocks, and a few plants were also built for the gasification of caking bituminous coals under atmospheric conditions and under pressure (Lurgi pressure gasification).

Nature of Water Gas and Producer Gas.

The following is a typical analysis of a water gas, in percent by volume:

Carbon dioxide	5	Hydrogen	50
Carbon monoxide	40	Nitrogen	5

A typical analysis of a producer gas, in percent by volume, is

Carbon dioxide	5.5	Hydrogen	10.5
Carbon monoxide	29.0	Nitrogen	55.0

The higher heating values (HHV) for water gas based on coke and for producer gas are $10\,500 - 12\,500 \text{ kJ/m}^3 \text{ (STP)}$ and $4600 - 6700 \text{ kJ/m}^3 \text{ (STP)}$, respectively.

The nitrogen content of water gas, amounting to ca. 5 vol %, does not originate from coke or coal for the most part, but is due to the fact that air remains in the coke pores on transition from the blowing to the gasification period. This nitrogen content can be lowered by discarding a small fraction of the gas produced at the beginning of the gasification period.

1.2. Synthesis Gas and Reduction Gas

The gas production method used depends on the raw materials. The raw materials are mainly natural gas, naphtha, heavy vacuum residue, and coal (see → Gas Production, 2. Processes). In addition, unconventional fuels such as solid or liquid waste materials or biomass gain interest. However, in the recent decades most of the world production of synthesis gas was based on natural gas and sulfur-rich heavy vacuum residues. Because of more stringent environmental protection requirements, these residues may no longer be burned in boiler plants in many countries, so their market value is often low. Countries that do not have these two raw materials, particularly countries in which no natural gas is available, often use naphtha. Depending on certain boundary conditions such as the relationship between oil and coal prices, as well as local factors and strategic considerations, plants based on coal will continue to be built.

Production of Synthesis Gas. Because synthesis gas is processed under elevated pressure, a trend toward operating gas production plants at increasingly high pressure could be observed. Gas production at higher pressure reduces the cost of compressing synthesis gas to the required synthesis pressure.

Natural Gas as Raw Material (→ Gas Production, 2. Processes, Chap. 1.). Synthesis

gases are produced from natural gas mainly in tubular reformers. If the natural gas contains virtually no nitrogen, a temperature of 750 – 800 °C is sufficient for gas suitable in *ammonia synthesis*. Residual unreacted methane is reformed in a secondary reformer (catalytic partial oxidation with air) with simultaneous adjustment of its nitrogen content.

For normal *methanol synthesis*, reforming is performed in *one step* in a tubular reactor at 850 – 900 °C in order to leave as little methane as possible in the synthesis gas.

For large methanol synthesis plants, Lurgi has introduced a *two-step combination* that gives better results. In the primary tubular reformer, lower temperature (ca. 800 °C) but higher pressure (2.5 – 4.0 MPa instead of 1.5 – 2.5 MPa) are applied. The secondary reformer operates with a fixed catalyst bed as in the case of ammonia synthesis gas, but pure oxygen is used for partial oxidation.

More recently, Lurgi developed another two-step gas production scheme. It is based on catalytic autothermal reforming with an adiabatic prereformer and has economical advantages for very large methanol plants (→ Gas Production, 5. Examples of Complex Gas Production Plants, Chap. 1.).

The various tubular reformer designs differ primarily in the method of firing the catalyst-containing tubes (from the side or top, terraced, or from the bottom). Subsequent developments of combined reforming resulted in the integration of the primary and the secondary reforming step in one apparatus using the thermal energy of the effluent of the autothermal process for heating the steam reformer part (M.W. Kellogg, Uhde). Exxon tested the simultaneous reforming and partial oxidation of natural gas in a reactor with fluidized catalyst. Apart from tubular reformer technology with or without a secondary reformer, partial oxidation (in one step) is still used sporadically for reforming natural gas. This can be performed either noncatalytically (Shell, Texaco) or catalytically (Lurgi). The latter is used especially when low ratios of hydrogen to carbon monoxide are required.

Naphtha as Raw Material (→ Gas Production, 2. Processes, Chap. 1.). The purity of naphtha allows the use of catalysts. Therefore, the production of synthesis and reduction gases

from naphtha is carried out almost exclusively catalytically and at elevated pressure.

Externally heated tubular reformers containing special catalysts are used to produce *hydrogen-rich gases* (e.g., ammonia synthesis). Two processes stand out from the others: they differ in the types of tubular reformers recommended and, primarily, in the type of nickel catalyst used. Topsøe uses a nickel catalyst without alkali; ICI employs one with a definite alkali content.

In future naphtha might replace methanol as a raw material for hydrogen produced on board of vehicles driven by *fuel cells*. Due to the much smaller size of such production units as compared with plants in the petrochemical industry and due to restrictions by volume and by utilities (e.g., steam and water), the production scheme and above all the reactors and heat exchangers for naphtha reforming in vehicles look rather different.

Apart from single-stage tubular reforming, two-stage processes have also proved successful for the production of *gases rich in carbon monoxide*, such as those required for methanol and oxo synthesis. An example of a two-stage process is the Recatro process, developed by BASF – Lurgi. Here, naphtha is converted with relatively little steam in an initial low-temperature adiabatic stage over a special nickel catalyst to produce a rich gas containing ca. 60 – 65 vol% methane plus hydrogen and carbon dioxide. This gas is supplied together with the remaining steam to a conventional tubular reformer to be reformed to carbon monoxide-rich synthesis gas in the presence of a conventional catalyst. The two-stage operation makes carbon dioxide recycling unnecessary in many cases or reduces it considerably.

A few plants using partial oxidation with (Lurgi) or without (Shell, Texaco) catalysts have been built.

Heavy Fuel or Residual Oil as Raw Material (→ Gas Production, 2. Processes, Chap. 1.).

For the production of synthesis and reduction gases from heavy and residual oils, two processes are accepted worldwide: the Shell and the Texaco process, both operating under elevated pressure and noncatalytic. The Texaco process was originally designed for partial oxidation of natural gas; the Shell process, developed later, was tailored from the beginning to gasification of

heavy oil. The differences between the two processes are virtually negligible and involve only details of equipment design.

Coal as Raw Material (→ *Gas Production*, 2. *Processes*, Chap. 3.). Processes employing coal that are used in practice operate on a noncatalytic basis. Various processes operating under *elevated pressure* are available: Lurgi, BGL (British Gas/Lurgi), HTW (High Temperature Winkler), U-Gas, Texaco, Shell and Prenflo. The Koppers – Totzek process and the original Winkler process operate at *atmospheric pressure*. Coal gasification plants for the production of synthesis gas built since the 1950s are based essentially on the Koppers or Lurgi processes.

In view of the distribution of fossil fuels in the world – almost ten times as much coal exists as petroleum and natural gas, and it is distributed relatively uniformly – and the sharp increase in oil prices in the 1970s, efforts have been made in many countries to develop new coal gasification processes tailored to the requirements of particular countries and their coal deposits.

In most processes, the heat required for gasification is provided by partial oxidation with pure oxygen. These processes are based essentially on the following three process arrangements:

1. moving bed,
2. one or more fluidized beds, and
3. entrained-flow systems in which coal dust and the gasification agent are conveyed co-currently.

Combinations of these three process arrangements are being investigated, as are processes applying high-temperature melts.

The overall arrangement of various coal gasification plants, including downstream units, is determined essentially by the composition of the raw gases. The gases produced at increased pressure by the Lurgi and by the BGL gasification processes contain methane, which can be converted to carbon monoxide and hydrogen for downstream ammonia or methanol synthesis, or can be removed before entering the high-pressure compressor. The Koppers – Totzek, the Texaco, as well as the other entrained-flow processes yield a gas without methane, but with a higher specific oxygen consumption. As in all high-temperature gasification processes, gas from the

latter two processes has a high carbon monoxide content, requiring considerable conversion measures for certain syntheses. The gasification processes applied to coal are also suitable for petrol coke if they can cope with its low reactivity and they are also applied when biomass or waste materials are used as fuels.

Production of Reduction Gas. In principle, reduction gas production is very similar to that of synthesis gas. However, iron ore is usually reduced under atmospheric conditions, so reduction gas can be produced at atmospheric or slightly increased pressure. Reduction gases used for the production of sponge iron by various direct reduction processes (→ Iron, Section 2.6.) must meet certain requirements. Generally, the proportion of oxidizing components such as steam and carbon dioxide in the gas mixture produced should be as low as possible, always < 10 %. This goal can be achieved by cooling the gases produced from coal, oil, naphtha, or natural gas and removing carbon dioxide. However, because reduction gases in the shaft furnaces of steel works are needed at high temperature, more cost-effective solutions are being sought and used. In the *Midrex process* natural gas is converted at ca. 1000 °C in the tubular reformer, without the addition of steam, thereby producing only hydrogen and carbon monoxide; the conversion is such that the reformed gases can be used directly in the shaft furnace.

As the recovery of byproducts from coke oven raw gas (benzene, phenol) loses economical attractiveness, reduction gas is considered to be produced from coke oven raw gas by catalytic partial oxidation.

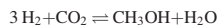
Composition and Aftertreatment. Synthesis gas requirements depend on the intended application.

Ammonia synthesis units now generally operate between 13.0 and 22.0 MPa and require gas with a hydrogen: nitrogen ratio of 3: 1. Impurities are limited in modern processes to < 1 ppm for sulfur and 2 – 10 ppm for oxygen-containing components such as oxygen itself, carbon dioxide, and water. With a view to the economy of synthesis (i.e., the purge gas quantities to be branched off), the methane content of synthesis gas must not exceed 0.5 – 0.8 vol %.

This means that the reformer and gasification gases produced from various raw materials must be conditioned appropriately. If the methane content is originally considerably high it can be lowered by secondary reforming with oxygen or air. Because all reformed gases contain carbon monoxide, they have to be converted, irrespective of the raw materials from which they are produced; this is done by catalytically reacting carbon monoxide with steam to form hydrogen and carbon dioxide (shift conversion). Depending on its residual content after shift conversion, either the carbon monoxide concentration must be lowered (to the ppm range) in a methanation stage or it must be removed at low temperatures by a liquid nitrogen wash. Hydrogen sulfide, organic sulfur compounds, and carbon dioxide have to be removed by appropriate washing procedures.

Similar conditioning and purification processes have to be applied for the production of hydrogen for *fuel cells* ($\rightarrow$ Fuel Cells).

Methanol is generated from carbon monoxide as well as from carbon dioxide:



The preferred reaction path goes via carbon monoxide, some carbon dioxide is required for kinetic reasons. The ratio $(c_{\text{H}_2} - c_{\text{CO}_2}) / (c_{\text{CO}} + c_{\text{CO}_2})$ should generally be between 2.0 and 2.2. The theoretical value derived from adding both reaction equations after pondering

each of them arbitrarily is 2.0. A higher carbon monoxide content is required for fuel methanol synthesis (Lurgi Octamix and others), in which a mixture of methanol and higher alcohols is produced as an additive to motor fuel. For high-pressure methanol synthesis (35.0 MPa), which is still used in a few cases, the presence of methane adds an economic burden (as in ammonia synthesis). It is less important in low-pressure (5.0 – 10.0 MPa) methanol synthesis (ICI, Lurgi) because compression costs for this gas component are practically negligible because of the lower compression ratio required. The content of sulfur compounds in the gas used for low-pressure methanol synthesis, which is based on a special copper-containing catalyst, must be extremely low. The amount of hydrogen sulfide and organic sulfur compounds in the synthesis gas produced from raw materials with relatively high sulfur content can be lowered to ca. 0.1 ppm by special processes (Rectisol for coal and oil gasification gases; hydrogenation of the organic sulfur compounds in the presence of Comox and Nimox catalysts, and subsequent adsorption prior to the reforming of naphtha and natural gas in the tubular reformer).

Purities applicable in methanol synthesis are also required for *oxo synthesis*. However, because the latter often requires a hydrogen: carbon monoxide ratio of ca. 1: 1, the carbon: hydrogen ratio of the feedstock may require that carbon dioxide be recycled or fed to the gasification unit.

For iron ore *reduction gas*, the sulfur content must be reduced to a few parts per million. Table 1 shows typical analysis data for raw gases from various starting materials.

Table 1. Typical raw gas analyses

Feedstocks and processes	Content, vol %						
	H ₂	CO	CH ₄	C ₂₊	N ₂ + Ar	CO ₂	H ₂ S + COS
Coal							
Lurgi pressure gasification	43	12	11.5	1	0.3	32	0.2
BGL	28	57	7.1	0.4	4.2	3	0.3
Koppers – Totzek	30	55	0.1		1.4	13.2	0.3
Texaco	37	41.3	0.1		0.6	20.7	0.3
Oil gasification							
Shell – Texaco	46	47	0.5		0.6	5.5	0.4
Naphtha							
Tubular reformer	67	19	3			11	
Recatro (BASF – Lurgi)	66	22	4			8	
Natural gas							
Tubular reformer	73	16	4			7	

1.3. Town Gas and Medium-Btu Gas

Because natural gas ($\rightarrow$ Natural Gas) has become the preferred fuel gas for households and industry, the production of town and medium-Btu gas from coal and liquid fuels is of minor importance today. High-temperature coking – formerly general practice in town gas works – has disappeared almost completely ($\rightarrow$ Coal Pyrolysis). The following is a brief outline of gasification processes for the production of town gas.

Basis of Production. When charcoal was replaced in the last century by coke from bituminous coal to smelt iron in blast furnaces, large quantities of degasification gas were produced by the carbonization of caking coals. Initially, these gases were largely flared; later on, they were distributed through piping systems supplying gas particularly to the municipalities in the neighborhood of steelworks. The gas grids were large enough to provide sufficient gas from the coke ovens even at times of peak demand; on Sundays and holidays, the gas was flared in the coking plants.

With the increasing demand for grid gas, utilization of the gas system improved, so that towns had to build their own gas production facilities to meet peak requirements. These facilities were based mainly on water gas, which in some cases was carbureted.

Both solid and liquid or gaseous fuels were used as raw materials for town gas production. Liquid hydrocarbons such as fuel oil and, later on, naphtha were preferred, but coal was also used.

Plants using fuel oil are based mainly on a cyclic process arrangement and became very successful since the 1950s. Some of them use straight thermal processes without catalysts, but most employ a catalyst bed. During a blowing phase, a bed of catalytic or noncatalytic material is heated by the combustion of fuel oil with air. After switching to the gasification period, fuel oil is passed over the hot bed along with steam. The ONIA GEGI and SEGAS processes and the Koppers Cwper process have become widely known [1].

The disadvantages of these cyclic processes are their relatively low output and difficulties caused by excessive wear of the switchover mechanism. In addition, as environmental laws

tightened toward the end of the 1950s and beginning of the 1960s, plant operators turned to processes using lighter hydrocarbons and continuous operation. The development of special catalysts (ICI, Topsøe) permitted gas production from readily available liquid feedstocks (such as lighter hydrocarbons and naphtha having a boiling end point up to 200 °C) to be carried out in externally heated tubular reformers. Apart from its higher efficiency, this mode of operation had an additional advantage because the gases produced were available at increased pressure, thus reducing the expenditure for their distribution in pressure gas systems. The methane content of the gases could be increased by keeping reaction temperatures in the tubular reformer low, so that after a cold carbureting stage with propane – butane, standard town gas could be produced.

Cold carbureting was often not applicable because either propane – butane was not available at a reasonable price, or certain standards with respect to dew-point were not met, therefore, modified processes aiming at increased production of methane from naphtha (BASF/Lurgi, British Gas, Japan Gasoline Corp.) were developed. Because methane content increases with decreasing temperature according to thermodynamic equilibrium, appropriate catalysts had to be developed. In these processes, a so-called *rich gas* having a methane content of ca. 65 vol % is produced from naphtha and steam by a slightly exothermic reaction in a shaft reactor at 400 – 490 °C. Because the calorific value and specific gravity of this gas are too high, compared with pertinent standards for town gas, part of it must be reformed in a downstream tubular reformer using commercial catalysts and then remixed with the residual methane-rich gas. Another method of obtaining a leaner gas is to add nitrogen or air. Many European cities built plants of this type with town gas capacities up to $1 \times 10^6 \text{ m}^3 \text{ (STP)/d}$.

Plants that converted propane – butane to town gas via externally heated tubular reformers were built particularly for small capacities. Part of the propane – butane was added to increase the calorific value of the reformed gas after carbon monoxide shift conversion. A few plants produced town gas by reforming natural gas in externally heated tubular reformers for transitional periods. This was done mainly when the consumers' existing piping systems and burners

were to be used, even if a loss in efficiency had to be accepted in converting natural gas to town gas.

Oil gasification by partial oxidation (Shell, Texaco, Lurgi; see → Gas Production, 2. Processes, Section 2.2.2.) has not become important in town gas production because of the high investment cost of such plants. The gases produced, consisting essentially of hydrogen and carbon monoxide must be carbureted to comply with standards.

Along with the development of gas production processes, downstream gas conditioning and gas cleaning units were adapted as well. Carbon monoxide shift conversion plants often reduced the carbon monoxide content to < 3 vol %, sometimes even to < 1 vol %, to eliminate the danger of poisoning.

The *composition* of town and grid gas is given in (→ Gas Production, 6. Analysis and Quality Control). Group A in these tables corresponds to town gas; Group B, to grid gas; and the first gas family, to town and grid gases combined.

1.4. Biogas and Landfill Gas

(→ Methane)

Biogas is the gaseous reaction product from anaerobic digestion of wastewater having a high BOD value or of sludge from wastewater treatment plants. It is used solely as fuel for combustion engines to meet the power requirements of the treatment plant.

Landfill gas is produced by the degradation of organic matter in the waste disposed of in landfills under anaerobic conditions. Because access to oxygen is not strictly controllable, aerobic degradation may occur simultaneously, producing water and carbon dioxide. Landfill gas is recovered via pipelines buried in the landfill. For existing landfills, wells are drilled and lined with tubes to allow the gases to be extracted. Landfill gas is used mostly as fuel gas for cogeneration and in combustion engines after suitable purification.

Composition. Biogas is composed of 60 – 70 vol % methane and 30 – 40 vol % carbon dioxide, depending on the feed and digester temperature (mesophilic – thermophilic).

Landfill gas is composed of 50 – 55 vol % methane, 41 – 45 vol % carbon dioxide, and 1 – 4 vol % nitrogen.

Depending on the nature of landfill waste, the gas may also contain considerable amounts of halocarbons.

1.5. Rich Gas and Substitute Natural Gas (SNG)

Basis of Production. As a result of the doubts concerning gas supplies and their availability to the industrial nations in the 1970s efforts were made to produce synthetic natural gas from the plentiful coal supplies. These efforts were feasible where natural gas accounted for a high percentage of primary energy and cheap domestic coal was available. Thus, a plant was built in North Dakota (United States) which has gone into operation in 1984, producing ca. $3.9 \times 10^6 \text{ m}^3$ (STP)/d of SNG from lignite. In this plant, lignite is gasified in Lurgi pressure gasifiers, and the methane content required is adjusted by reacting carbon monoxide and hydrogen from the raw gas in a methanation stage downstream of the gas cleaning unit. In addition, the Lurgi gasification process has been developed further to produce SNG more economically by increasing gasification pressure to 10.0 MPa (Ruhr 100, see → Gas Production, 2. Processes, Section 3.4.). Here, more than 50 vol % of methane recoverable from coal is produced in the gasification stage proper.

Heavy vacuum residues can also be used as feedstock for SNG production. However, as in coal-based plants, capital investment is relatively high. The discovery of huge new natural gas resources in some areas of the world during the past few years has made the production of SNG less attractive.

Composition. *Rich gases* have a higher calorific value than grid gas, with gross calorific values from about 25 000 kJ/m³ (STP) upward. A rich gas produced from naphtha (British Gas or BASF – Lurgi process) has the following typical analysis, in percent by volume:

Carbon dioxide	21.6	Hydrogen	12.5
Carbon monoxide	0.3	Methane	65.6

Substitute natural gas should differ as little as possible from natural gas. It must be condi-

tioned so that it can be substituted for natural gas. This depends on the following parameters: higher heating value, density, and Wobbe index (see → Gas Production, 6. Analysis and Quality Control, Section 3.1.3.).

In addition the specified content of impurities, particularly sulfur, must not be exceeded. Typical SNG produced in a coal gasification plant in North Dakota has the following analysis, in percent by volume (unless otherwise stipulated):

Methane	96.3	Nitrogen + argon	1.1
Carbon monoxide	0.02	Carbon dioxide	1.2
Hydrogen	1.38	Hydrogen sulfide	4 ppm

2. Raw Materials for Gasification

Gaseous Fuels. Natural gas as raw material is of paramount importance for gasification or reforming (the term reforming is used more commonly for gases) in externally heated tubular reformers to yield synthesis gas for various applications. Plants also reform natural gas by partial oxidation. The composition of natural gases is not important for the technology to be applied, as long as their inerts content is negligible. However, if the nitrogen content rises above 5 – 10 vol %, this may have consequences for the design of ammonia synthesis gas plants operated on the tubular reformer principle.

In certain new energy scenarios, natural gas still plays an important role. Thus, the energy required for natural gas reforming may be supplied—at least partially—by solar collectors or high-temperature nuclear reactors. Liquid motor fuels can be synthesized from synthesis gas. In this way, thermal energy, which is difficult to store and utilize, is converted to energy carriers better adapted to the requirements.

Coke oven gas (→ Coal Pyrolysis) is of minor importance for producing synthesis gas because special expenditures are necessary to remove various impurities from the coke oven gas, and compression costs are high. In older plants, coke oven gas was separated into its individual components by fractionated condensation and distillation at low temperature rather than being reformed (the content of methane and higher hydrocarbons is low anyway); these compo-

nents were then used for synthesis gas production.

Liquid Fuels. In most cases, various fractions of crude oil are used for gasification. Only in very rare cases is unrefined crude oil used directly for gasification because neither its economic nor its technical considerations are optimum.

Liquefied petroleum gas (LPG, a propane – butane mixture; → Liquefied Petroleum Gas) is used for the production of town gas, particularly in smaller capacity plants, and for peak shaving. It is virtually sulfur-free and can be processed without significant problems. *Light naphtha* is utilized for larger town gas plants and for the production of synthesis gas. Generally, fractions boiling at 40 – 110 °C are used, but full-range *straight-run naphtha* with a boiling end point of 150 – 200 °C may also be employed. Depending on its origin, this naphtha has a sulfur content between 30 and 300 ppm. Naphtha must be completely desulfurized because almost all conventional processes for the production of town or synthesis gas include a reaction stage involving catalysts that are very sensitive to sulfur poisoning.

In some cases, LPG and naphtha have also been converted to town and synthesis gas by partial oxidation (thermally or catalytically) with oxygen or oxygen-enriched air. For catalytic partial oxidation, desulfurization to 20 – 50 ppm is sufficient.

Synthesis gas is produced from *high-boiling residues* by partial oxidation with oxygen. Originally, the high-boiling fraction (initial boiling point above 350 °C) from atmospheric distillation units of refineries (→ Oil Refining)—the heavy fuel oil—was used for this purpose. To date even higher viscosity fractions from vacuum distillation and conversion plants are being used increasingly. Because of the more stringent requirements imposed by environmental legislation, these heavy oils can no longer be burned in boiler houses and are, therefore, cheap raw materials for gasification, which also eliminates various pollutants in the residue such as sulfur and heavy metals. To be used in gasification plants, the heavy oil must be suitable for pumping and spraying. Therefore, the oils are preheated to attain the required viscosity.

The ash content of the heavy oils and the composition of the ash affect the operating temperature of gasification plants and the service life of the refractory lining. Vanadium and nickel in ash are particularly harmful.

Apart from petroleum fractions, other liquid fuels may be used for gasification, although they are not very important. These include:

1. tars from bituminous coal and lignite for gasification by partial oxidation;
2. fractions from shale oil ($\rightarrow$ Oil Shale) production, particularly heavy fractions, for gasification by partial oxidation;
3. methanol for producing peak shaving gas in catalytic town gas plants;
4. hydrocarbon condensates from natural gas production for gasification by partial oxidation; and
5. waste from chemical plants (e.g., isobutyraldehyde).

Purity Requirements for Liquid and Gaseous Fuels. Raw materials for gasification plants using catalysts must generally be very pure. Therefore, in most cases, such plants are equipped with special upstream purification units. A certain tolerance regarding the content of impurities can be accepted in cyclic processes that regenerate catalysts in the respective cycles. However, continuous processes important to modern technology require exceptionally pure fuels, especially with respect to sulfur compounds. Catalysts used for these processes thus permit the use only of gaseous fuels (natural gas) and of liquid hydrocarbons up to a boiling end point of ca. 200 °C.

Generally, the lower the operating temperature of the catalytic process, the lower is the residual sulfur content that can be tolerated in the raw materials. How adverse an effect sulfur compounds in the gas have on the active sites of catalysts can be derived from equilibrium conditions governing the reaction of the metallic phase of the catalyst with the sulfur compounds. Most gasification catalysts contain nickel as an active substance. At constant partial pressure of sulfur compounds in the gas, nickel sulfide formation increases with decreasing temperature; a sulfided catalyst no longer provides the desired results regarding reaction direction (danger of carbon formation), speed, and selectivity.

Therefore, light hydrocarbons are desulfurized to < 0.1 ppm of sulfur upstream of plants operated at low catalyst temperature (400 – 700 °C). The sulfur content may often be higher by one or two orders of magnitude in catalytic processes operating above 850 °C.

Solid Fuels. Various solid fuels are not all equally suitable for gasification. In addition, different gasification processes have different fuel requirements.

Because endothermic gasification reactions should be as complete as possible, the suitability of solid fuels for gasification improves as their reactivity increases. This reactivity can be correlated with the oxygen content, which decreases with increasing carbonization (i.e., with increasing age of the fuel).

The classification and designation of various types of coal are different in individual industrial countries ($\rightarrow$ Coal, Chap. 4.). As a rule, however, they depend on volatile matter, which almost always means classification by age of the coal.

Additionally, the following properties of fuels are essential for assessing their suitability for gasification:

Ash content	Coal grain size
Water content	Melting behavior of the ash
Sulfur content	Behavior of the coals on heating
Caking properties	

Because coal gasification adds considerably to the costs of upgraded energy (i.e., the gas), coal used for this purpose should be as cheap as possible. Wherever possible, only coal that is not suitable for other applications and, therefore, has a low market price should be used. Coal produced by open-pit mining is of special interest for gasification.

Almost all solid fuel such as wood, peat, lignite, young and old bituminous coal, and coke, including petrol coke, has been used for gasification. In the future, more use should be made of lignites and younger noncaking or caking bituminous coal, as well as coal with a high ash content (20 – 50 wt %) or sulfur-rich coal which is rarely suitable for other applications.

With regard to various types of petrol coke (delayed, fluid, Lurgi – Ruhr gas (LR) coke, $\rightarrow$ Oil Shale,), their high sulfur and heavy-metal content ($\rightarrow$ Petroleum Coke, Section 3.2.)

Table 2. Comparison of capital cost and energy requirements for an ammonia plant and a methanol plant with a capacity of 1000 t/d based on gaseous, liquid, and solid fuel

	Natural gas	Heavy oil	Coal
Ammonia plant			
Capital cost, %	100	170	225
Energy requirements, %	100	115	135
Methanol plant			
Capital cost, %	90	150	200
Energy requirements, %	95	105	125

renders combustion increasingly difficult in view of pollution control measures. Petrol coke is, therefore, turning into a new potential raw material for gasification.

Gasification of wood has been revived because of increasing interest in renewable raw materials. Emphasis is mainly on the production of clean fuel gas (low sulfur content of wood), but synthesis gas production is also possible with modern fluidized-bed processes.

Suitability of Fuels for Gasification. Considerable differences exist in the complexity of gasification technology applied, depending on whether solid, liquid, or gaseous fuels are used. A general rule is that capital cost and consumption figures are higher for solid than for liquid fuels, and for liquid higher than for gaseous fuels. Therefore, in the production of particular gases, mere comparison of specific energy prices of various fuels is insufficient; individual costs for gasification must be considered as well (see Table 2).

To make end products competitive, the specific energy price of coal must be lower than that of heavy oil, and the latter must be lower than that of natural gas. In principle, this also applies to other solid and liquid fuels with regard to the complexity of the conversion plant based on these particular feedstocks.

Even if fuels of the same physical state are compared, great differences exist in the properties of individual substances, which also affect their suitability for gasification.

3. Physicochemical Basis for Gas Production

Gasification can be described by overall chemical reactions, from which conclusions may be

drawn regarding the conversion of materials and heat of reaction.

Gasification of solid and liquid fuels involves heterogeneous reactions at the phase boundary of particles or droplets and homogeneous reactions in the gas phase. The latter include reactions of components that devolatilize at operating temperature.

The following principles form the basis for calculating gasification processes:

1. *Material Balance.* In establishing a material balance, the total number of atoms of the individual elements in the reactants is equalized to that in the products, irrespective of the distribution of the elements between the individual components (principle of conservation of mass).
2. *Energy Balance.* Energy balance is based on the principle of conservation of energy. Consequently, energy supplied to the system (enthalpy of reactants and heat supplied) is equal to energy removed from it (enthalpy of products and heat removed). In determining enthalpy, formation and phase change energies must be considered.
3. *Chemical Equilibrium.* The equilibrium composition of the gasification product is determined by the temperature-dependent equilibrium constants of reactions going on in the system and by the operating pressure.
4. *Chemical Kinetics.* Because equilibrium is not attained when residence time is too short (for example, because the temperature is too low), the composition of the gasification product in this case is determined by the kinetics of the reactions. In addition, transport phenomena, such as boundary layer or pore diffusion, may have some influence.

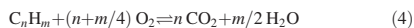
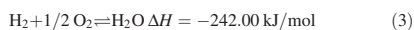
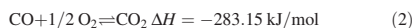
Practical calculation leads to nonlinear equation systems in which the number of unknown quantities is determined essentially by the number of components in the raw gas. The solution may be found iteratively or—if appropriate routines are used—simultaneously. Calculations are particularly complicated when chemical kinetics must be considered.

Reaction Enthalpy of Gasification. Gasification reactions can be described by many

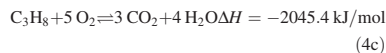
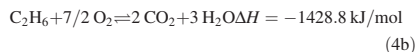
different equations. To calculate the reaction enthalpy of gasification, however, a limitation to certain characteristic reaction groups is sufficient. The reaction enthalpy of all other reactions can be derived by combining these basic equations, and individual reactions have no influence on the total heat balance of a sequence of reactions if the same feedstocks are turned into the same products (Hess's law).

The reaction groups characteristic of gasification can be subdivided as follows (ΔH refers to 0 °C and 0.1 MPa as reference state; ΔH is negative for exothermic reactions and positive for endothermic reactions):

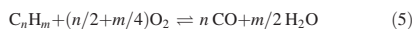
1. Reactions with molecular oxygen (combustion)



For example,



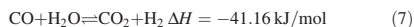
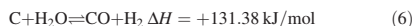
The reaction enthalpy of combustion of other gaseous or liquid fuels is described in the literature (e.g., [2–4]). For *partial combustion* of gaseous or liquid fuels to carbon monoxide and steam,



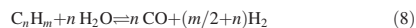
the reaction enthalpy can be calculated from the enthalpies of Equations (4) and (2) as follows:

$$\Delta H(\text{Eq. 5}) = \Delta H(\text{Eq. 4}) - n \Delta H \quad (\text{Eq. 2})$$

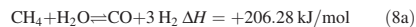
2. Reactions with steam



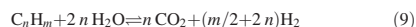
(homogeneous water gas reaction, shift conversion)



For example,



The enthalpy of the reaction of fuels with steam to produce carbon dioxide and hydrogen

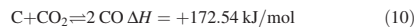


can be determined by

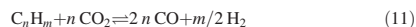
$$\Delta H(\text{Eq. 9}) = \Delta H(\text{Eq. 8}) + n \Delta H \quad (\text{Eq. 7})$$

because Equation 9 may be considered a combination of Equations (8) and (7).

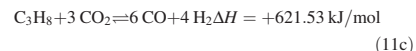
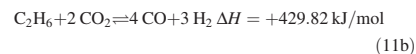
3. Reactions with carbon dioxide



(Boudouard reaction)



For example,



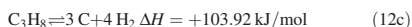
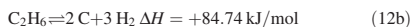
Generally, the reaction enthalpies for hydrocarbon gasification with carbon dioxide (Eq. 11) are obtained from the enthalpies of Equations (8) and 7 as follows:

$$\Delta H(\text{Eq. 11}) = \Delta H(\text{Eq. 8}) - n \Delta H \quad (\text{Eq. 7})$$

4. Hydrocarbon decomposition reactions (soot formation) Hydrocarbon decomposition is described by



For example,



may be considered the reverse of hydrocarbon formation from its elements and is essential for the gasification of hydrocarbons. The reaction enthalpy can be calculated from the combustion enthalpies of the reactants:

$$\begin{aligned} \Delta H(\text{Eq. 12}) &= \Delta H(\text{Eq. 4}) - n \Delta H(\text{Eq. 1}) \\ &\quad - n \Delta H(\text{Eq. 2}) - m/2 \Delta H \end{aligned} \quad (\text{Eq. 3})$$

In calculating the main gas components, side reactions of sulfur compounds (H_2S , COS, etc.) and nitrogen compounds (NH_3 , HCN) are generally neglected because they have no great effect on the numerical distribution of the main gas components. If detailed information on the distribution of secondary components is required, further calculations can be made and the results used for the main gas components.

Chemical Equilibrium. The gasification reactions represented by Equations 1 – 12 are never complete in either of the two possible directions but tend to reach an equilibrium expressed by the equilibrium constant K_p . For Equation 8a, for example, this constant is given by

$$K_p = \frac{p_{\text{CO}} \cdot p_{\text{H}_2}^3}{p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}}} = \frac{x_{\text{CO}} \cdot x_{\text{H}_2}^3}{x_{\text{CH}_4} \cdot x_{\text{H}_2\text{O}}} p^2 = f(T)$$

where x_i represents the mole fraction and p_i the partial pressure of each of the four components, P the total pressure, and T the temperature.

For Equation (7), the carbon monoxide shift conversion (which in nearly any case has to be considered) the equilibrium constant is given by

$$K_p = \frac{p_{\text{CO}_2} \cdot p_{\text{H}_2}}{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}} = \frac{x_{\text{CO}_2} \cdot x_{\text{H}_2}}{x_{\text{CO}} \cdot x_{\text{H}_2\text{O}}} = f(T)$$

In comparison to the steam reforming reaction 8a the equilibrium composition of the shift conversion is not influenced by the total pressure, because simply spoken, the number of molecules on the right and on the left side of Equation 7 is identical. The temperature dependence of the equilibrium constant ($\log K_p$ vs. $1/T$) is shown in Figure 1.

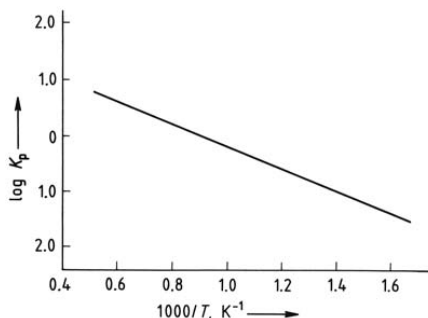


Figure 1. Water gas equilibrium, $K_p = f(1000/T)$

According to the laws of thermodynamics, the equilibrium constant K_p of a reaction can be calculated by means of the Gibbs free energy of the reaction or the free formation energies of the reactants.

Strictly speaking, the equilibrium constant K_p in the above form applies only to ideal gases. At increased pressure (total of ca. 1.0 MPa or more) and near the boiling points of the liquids, the appropriate partial fugacities should be used instead of partial pressures. These fugacities allow for the real behavior of individual gas components. However, in practice, partial pressures can be used for the calculation with sufficient accuracy in most cases.

In heterogeneous reactions, partial pressures of the solids are not taken into account because they are regarded as a function of temperature alone, which is included in the equilibrium constant K_p . However, the free formation energy of the solids must be considered in a thermodynamic calculation of the equilibrium constants.

The three reactions described by Equations (7), (8a) and (10) are almost always sufficient to calculate the theoretical product gas composition of various gasification processes. Table 3 shows the equilibrium constants of these three reactions at different temperatures. In addition equilibrium constants for heterogeneous methane decomposition (Eq. 12a) are given as an example of hydrocarbon decomposition. This equilibrium may also be derived from Equations (7), (8a), and (10). Additionally equilibrium constants for COS hydrogenation and

Table 3. Temperature-dependent equilibrium constants of various reactions

Equation Unit for K_p	(7)	(8a) bar ²	(10) bar	(12a) bar	COS hydrogenation	COS hydrolysis
Temperature, °C						
100					12.4	4.39×10^4
200					19.1	4.26×10^3
300	38.5	6.13×10^{-8}	3.60×10^{-7}	4.36×10^{-3}	24.4	940
400	11.5	5.54×10^{-5}	8.55×10^{-5}	5.56×10^{-2}	28.0	323
500	4.82	9.16×10^{-3}	4.99×10^{-3}	3.76×10^{-1}	30.3	146
600	2.51	4.88×10^{-1}	1.16×10^{-1}	1.66	31.5	79.1
700	1.52	11.8	1.42	5.41	32.1	48.7
800	1.02	159	11.0	14.1	32.2	32.9
900	7.41×10^{-1}	1.38×10^3	59.8	31.2	32.0	23.7
1000	5.71×10^{-1}	8.63×10^3	249	60.6		
1100	4.60×10^{-1}	4.12×10^4	845			
1200	3.84×10^{-1}	1.59×10^5	2.43×10^3			
1300	3.30×10^{-1}	5.16×10^5	6.08×10^3			
1400	2.91×10^{-1}	1.48×10^6	1.36×10^4			
1500	2.61×10^{-1}	3.69×10^6	2.79×10^4			

hydrolysis are included (see → Gas Production, 3. Gas Treating, Chap. 3).



The temperature dependence of the equilibrium constants can be calculated with an equation of the following type

$$\log K_p = A + B/T + C \log T + D \cdot T + E \cdot T^2$$

where T is the absolute temperature in Kelvin. For the various equilibria used in this article the values of the constants $A - E$ are given in Table 4. (The data of Tables 3 and 4 were taken

Table 4. Values of coefficients for calculating the equilibrium constants of various reactions as a function of absolute temperature

Equation	(7)	(8a)
A	-8.000980	-18.98177
B	2456.620	-9520.569
C	1.984098	10.91012
D	$-0.3329441 \times 10^{-3}$	-0.319556×10^{-2}
E	0.563315×10^{-7}	0.3631894×10^{-6}
Equation	(10)	(12a)
A	2.220419	-21.61666
B	-8709.775	-2875.50
C	2.495100	9.505546
D	$-0.6399432 \times 10^{-3}$	$-0.3694027 \times 10^{-2}$
E	0.5280003×10^{-7}	0.5233708×10^{-6}
Equation	COS hydrogenation	COS hydrolysis
A	5.956145	4.485945
B	-566.2154	1568.825
C	-1.309130	-1.681947
D	0.5766548×10^{-4}	0.7452208×10^{-3}
E	$-0.1222679 \times 10^{-7}$	$-0.1160356 \times 10^{-6}$

from the ASPEN program [5] which uses in this case the correlations cited in [6]. Minor differences with respect to other literature data may occur.)

A general assessment of tendencies in gasification reactions is facilitated by the Le Châtelier – Braun principle that a system in equilibrium tries to evade a change forced upon it. For example, in Equation (8a), an increase in total pressure results in increased methane formation because the number of gaseous molecules on the right side of Equation (8a) is higher than that on the left. A pressure increase in reactions proceeding without a change in the number of molecules, such as the homogeneous water gas reaction (Eq. 7) has almost no effect.

Reaction Sequence for Various Gasification Processes. No statements can be made on the basis of thermodynamics regarding the chronological sequence of gasification reactions. Calculations must include reaction kinetics. Frequently, however, the required data are not available. Approximation methods must then be used to calculate product gas composition. A common method involves use of K_p values which, according to experience, reflect the actual final state but pertain to a temperature other than that prevailing at the end of the reactor.

Some processes employ catalysts to accelerate the reaction and enhance reaction kinetics in order to approach equilibrium. Selective catalysts promote desirable reactions at the expense of undesirable ones (e.g., carbon formation

according to Boudouard). Generally, reaction rate increases as temperature increases. Gasification, therefore, approaches equilibrium more easily at higher than at lower temperature.

Tubular Reactor Reforming. When reforming hydrocarbons, especially methane, in externally heated tubular reactors, conversion of the hydrocarbons with steam to yield carbon oxides and hydrogen (according to Eqs. 8 and 9) must be considered basic reactions. The composition of the product gas is determined by the simultaneous equilibrium between Equations (7) and (8a).

Because soot formation should be suppressed, the Boudouard reaction (Eq. 10) and hydrocarbon decomposition (Eq. 12 and, especially, 12a) are essential for an assessment of the reaction system.

Rich-Gas Process. When naphtha is reformed catalytically with steam in a shaft reactor to yield gases with a high methane content, the endothermic gasification reactions (Eqs. 8 and 9) must be considered as starting reactions, whose products are then transformed in an exothermic methanation reaction described by Equation (8). The final condition of the reforming process is determined by Equations (7) and (8a).

Oil Gasification. In oil gasification with oxygen and steam, partial combustion of hydrocarbons (Eq. 4), as well as steam and carbon dioxide gasification of carbon (Eqs. 8 and 11), must be considered to proceed more or less simultaneously. Product gas composition is determined by the final state of the simultaneous equilibrium among the reactions described in Equations (7), (8a), and (10).

Coal Gasification. The first step in a coal gasification reaction (e.g., with oxygen and steam in countercurrent mode of operation) is exothermic combustion of carbon to carbon dioxide, according to Equations (1) and (2). The carbon dioxide formed then reacts with hot carbon to yield carbon monoxide in an endothermic reaction (Eq. 6). This in turn reacts with steam to produce either hydrogen and carbon dioxide (according to Eq. 7) or methane and carbon dioxide (by the reverse of Eq. 11a). The latter occurs particularly at increased gasifica-

tion pressure. Carbon monoxide and hydrogen are also produced by direct endothermic carbon gasification with steam (Eq. 6). In entrained-flow gasification processes, the reaction sequence described is mostly overlapping. The mode of reaction essentially determines the temperature profile in a gas producer.

The composition of gasification gas is determined by a more or less accurate adjustment of the simultaneous equilibrium among the shift conversion reaction (Eq. 7), the methane reforming reaction (Eq. 8a), and the Boudouard reaction (Eq. 10).

4. Characteristics of the Basic Processes

In most cases, the aim is to produce gases with high hydrogen and carbon monoxide content. This applies to all synthesis gases and also to town gas. Depending on the particular requirements, the carbon monoxide content may be reduced with steam to yield hydrogen and carbon dioxide. To produce such gases from various solid, liquid, and gaseous fuels, heat must be supplied to support the endothermic reactions. Thus, different processes can be classified according to the type of heat supply.

On the other hand, processes for producing gases with high methane content, such as rich gas and SNG, in principle require no external heat supply because methane formation is exothermic. Therefore, the process characteristics of this group are different.

Trends in the past decades have shifted from processes operated under atmospheric conditions to those operated at elevated pressure. This has resulted in economic advantages because the subsequent chemical syntheses [ammonia, methanol, oxo ($\rightarrow$ Oxo Synthesis) and Fischer-Tropsch synthesis ($\rightarrow$ Coal Liquefaction)] operate at more or less elevated pressure, which removes the cost of compressing the high-volume synthesis gas. Moreover, plants operating under pressure can be designed for higher capacity due to their smaller gas volume, which again means savings in capital costs.

An essential criterion is whether catalysts are used. With catalysts, a better approximation to reaction equilibria is attained and undesired byproducts are mostly avoided. However,

catalysts can thus far be used successfully only for gaseous feeds and for distillate liquid feeds.

Cyclic Processes. Cyclic processes use heat carriers consisting of refractory brick lining (in regenerators, air heaters, etc.) or beds of ceramic material, which may be appropriately impregnated to impart catalytic properties to them. Regenerative heating is provided by hot flue gases from the combustion of liquid or gaseous fuels. During gasification, the heat carrier transfers its heat to the raw material to be converted. The process is suitable for liquid and gaseous feedstocks. Any carbon black deposited during the reforming period can be burned off after the system is switched back to heating. The process is not suitable for operation at elevated pressure.

Processes using circulating heat carriers are similar to cyclic gasification except for being continuous processes circulating the heat carrier in a closed loop. This carrier is heated by hot flue gases and then fed to a reaction section in which its heat is used for gasification. In addition to sensible heat, some heat carriers used in the past also produced heat through reaction with gas components (producing CaCO_3 from burned lime and CO_2). Any carbon formed in the process can be burned off in the heating zone. The process is generally suitable for gaseous, liquid, and solid fuels. The circulating heat carrier may consist of granular catalytic or noncatalytic solids, or of liquids (such as slag baths) and circulating gas. Although system design does not altogether exclude elevated operating pressure, the necessary design and operating conditions would be difficult to meet.

Autothermal Processes. Autothermal processes produce the heat required for gasification through partial combustion of the fuel to be converted in the reactor. Oxygen or air – if nitrogen in the air is not a ballast in the product gas – is added for this purpose. The process may operate with or without catalysts. If catalysts are used, the temperature can be kept lower because a closer approach to equilibrium is ensured. However, the catalytic process cannot be used to gasify heavy and residual oils because most of these oils contain ash particles that contaminate the catalyst. Also, because of the ash content, catalysts for coal gasification are not applied, so far. Either

the catalyst would have to be very cheap so that it could be disposed of along with the ash, or it would have to be recovered by a very complex procedure.

Processes applying baths of molten slag, iron, or salts as heat carriers and reaction promoters have been used and are still being developed. A characteristic of autothermal processes is that the oxygen added to generate heat is chemically bound in the product gas, so the ratio of hydrogen to carbon monoxide in the product is lower than in other processes. This type of process is applied to solid, liquid, and gaseous fuels.

Processes Involving Externally Heated Walls. Processes using externally heated walls include tubular reforming, which is used widely today. To keep the tube stresses resulting from elevated pressure and temperature to a minimum, all tubular reformers employ a catalyst filling in the tubes, which allows lower reaction temperature.

Modern materials permit tubes to be designed for wall temperatures of ca. 900 °C (in special cases even 1000 °C at atmospheric pressure) and pressures up to 4.0 MPa. All gaseous hydrocarbons (with low unsaturated hydrocarbon content) and distillate liquid fuels are suitable feedstocks. When liquid hydrocarbons are used, demands on the catalysts are extremely high. Virtually ash-free fuels are used almost exclusively to heat the tubes because ash constituents (salts, metals) would damage tube walls.

Reactors with externally heated walls are also used in gas production from solid feedstocks. This process technology offers the opportunity to employ nonfossil energy (heat from nuclear reactors, solar energy) for gasification.

Rich-Gas Processes. Because no external heat supply is required for rich-gas processes, the equipment and process loops can be chosen freely. In most systems, a catalyst is applied because methane formation is favored by lower temperature. Apart from the unfavorable equilibrium position, the risk of carbon deposits resulting from the Boudouard reaction is higher at increased temperature, and other byproducts are formed as well. All the processes operate at elevated pressure because this promotes methane formation.

Because catalysts are highly sensitive with respect to attrition, reactors are normally of the fixed- rather than the fluidized- or entrained-bed type. Raw materials must be virtually free of all substances that may poison catalysts, particularly sulfur compounds.

5. Product Gas Treatment

Each gasification plant requires gas treatment facilities to purify product gases and also, in many cases, to condition them. Whereas the gas purification system eliminates the components that would affect downstream processing or utilization of these gases, the purpose of a conditioning system is to adjust gas components to the appropriate ratio. The ratio of hydrogen to carbon monoxide, especially, must be matched to the requirements of downstream synthesis or reduction units and other gas consumers.

The task of gas purification and conditioning is most complex downstream of plants gasifying solid fuels. Capital investment in these purification units can be much higher than that required for the gasification plant itself. Treatment of gases produced through gasification of high molecular mass liquid hydrocarbons (heavy oils, vacuum residues) is also rather expensive. Generally, the smaller the molecules from which a gas is produced, the lower is the capital investment required in treatment facilities. The costs of gas purification are also strongly dependent on the amount and type of impurities in the feedstock, particularly its content of sulfur and trace elements.

Whereas most catalytic gasification processes have some purification facilities (removing sulfur, lead, chlorine) upstream of the gasification stage, the impurities in noncatalytic processes should be removed only from the product gas.

Impurities in the Gasification Gas. Depending on the type and composition of feedstock and the type of gasification process used, a gas purification plant must handle the following impurities:

- Dust (coal gasification)
- Carbonization products, tar, gas liquor (coal gasification)
- Carbon (Heavy-oil gasification)

- Oxygen (coal gasification, oil gasification)
- Cyanic compounds (coal gasification, oil gasification)
- Nitrogen oxides (coal gasification, oil gasification)
- Carbon dioxide (all gasification processes)
- Hydrogen sulfide, carbonyl sulfide, organic sulfur
- compounds (all noncatalytic gasification processes)
- Ammonia (all gasification processes)

Other gas components, even if they occur only in trace amounts, require specific measures to prevent long-range damage or malfunction of the plant. This is particularly true for the gasification of coal and heavy oils. Such components may include volatile metal compounds and high molecular mass organic compounds.

5.1. Purification Processes

Because of the large number of impurities, along with their widely varying content and combinations, a variety of gas purification processes are available to meet the requirements of downstream processing (synthesis, in particular) and of industrial and municipal consumers (town gas). *Ammonia synthesis*, for instance, tolerates only ca. 5 ppm (mL/m³) of oxygen compounds (e.g., O₂, CO, CO₂, and H₂O), and the sulfur content must be < 1 ppm (mL/m³).

Methanol synthesis, on the other hand, requires a sulfur content of < 0.1 ppm (mL/m³) and the stoichiometric ratio $(c_{\text{H}_2} - c_{\text{CO}_2})/(c_{\text{CO}} + c_{\text{CO}_2})$ must be adjusted to ca. 2 (see → Gas Production, 5. Examples of Complex Gas Production Plants, Section 1.2.). To achieve this ratio, the gas must contain a certain amount of carbon monoxide – a factor that influences the selection of gasification and purification processes and also raises the question of whether an additional process stage is required to convert carbon monoxide into hydrogen and carbon dioxide. Carbon dioxide need not be removed completely so the general plant design can be simplified considerably.

Reduction gases for direct reduction of iron ore may contain sulfur on the order of 7 ppm (mL/m³), but the content of water and carbon dioxide should not exceed 5 vol %.

If several gas purification plants are combined for optimum effect, perhaps including gas conditioning facilities as well, possible interaction should be checked carefully. Interactions could occur because of solvents contained in the gas, depending on their vapor pressure, different operating behavior, etc. If fuel gas is produced for a combined power cycle (see → Gas Production, 5. Examples of Complex Gas Production Plants, Chap. 3.), the gas purification plant must meet the load change requirements of such plants.

Gas purification processes may be classified as follows:

Adsorption. Adsorption describes the retention of impurities by solids, either through physical deposition or through chemical reaction (chemisorption) (→ Adsorption, see also → Gas Production, 3. Gas Treating, Chap. 6.). Whenever solids have to be reused (e.g., for economic reasons), batchwise operation is necessary because the laden solids must be regenerated.

Sulfur compounds are eliminated by using beds of iron hydroxide and zinc oxide (especially for desulfurizing gaseous and liquid feedstocks for catalytic gasification). Activated carbon is favored in special cases for cleaning gases containing high molecular mass organic sulfur compounds.

Molecular sieves (→ Adsorption; → Zeolites) have been developed for selective removal of particular gases. They can be used not only for carbon dioxide, sulfur compounds, and steam, but also for diatomic gases.

Gas purification systems based on the adsorption (and chemisorption) principle are preferred when small quantities of impurities must be eliminated or small gas throughputs must be purified.

Absorption. A general distinction is made between physical and chemical absorption processes. Physical processes (→ Absorption, 1. Fundamentals, Section 1.4., see also → Gas Production, 3. Gas Treating, Chap. 5.) are particularly suitable for high pressure, high impurity content, and large gas throughput. The processes available differ in solvents used, mode of plant operation, operating temperature, method of energy recovery, and potential for recovering several components more or less separately. The

selection of appropriate solvents is determined to a large extent by their specific solubility coefficients for the desired gases and by their selectivity.

Chemical absorption systems (→ Absorption, 1. Fundamentals, Section 1.5.) can be used at elevated or atmospheric pressure. They are particularly suitable whenever the absolute quantity of impurities to be removed is small. Conventional processes differ mainly in the degree of purity that can be achieved and the amount of energy (normally steam) required for regeneration. Numerous processes also use some combination of physical and chemical absorption principles.

Special Wash Processes. Special applications include the removal of solids entrained with gases in the form of dust or carbon black, dust-laden tar, and high molecular mass or unsaturated hydrocarbons that tend to form gums.

5.2. Conditioning

For nearly all applications, gasification gases not only must be purified but also conditioned to obtain the optimum proportions of desirable gas components (→ gas Production, 3. Gas Treating, Chap. 2., → gas Production, 3. Gas Treating, Chap. 3., → gas Production, 3. Gas Treating, Chap. 4.).

Carbon Monoxide Shift Conversion.

Prominent among gas conditioning processes is catalytic carbon monoxide shift conversion, which is based on water gas equilibrium (Eq. 7). By this process, the hydrogen content of a gas can be increased as desired at the expense of its carbon monoxide content. This is important not only for ammonia synthesis but also for town and grid gas production. The process permits the gas to be adjusted to the standard density and Wobbe index, and also enables nontoxic, low-carbon monoxide town gas to be produced, in conformity with current regulations.

Carbon monoxide shift conversion requires the addition of steam, which can be done in one of several ways. Steam at the appropriate pressure may be added directly to the gas to be converted. If steam is not available in sufficient quantities and under economically justifiable conditions, a

so-called saturator cooler loop is often used. With this arrangement, gas entering the conversion section is humidified by circulating hot water, and unreacted steam in the gas leaving this stage is recondensed and recycled to the saturator. A distinction is also made between high- and low-temperature conversion, the latter being provided downstream of the former to reduce the residual carbon monoxide content of the gas to a minimum (e.g., for ammonia synthesis). Shift conversion catalysts for sulfur-free gases are based on iron (high temperature shift) or copper (low temperature shift). They are supplied as oxides and reduced during operation. For gases containing sulfur compounds the shift catalysts are based on cobalt and molybdenum. They are active only as sulfides.

Methanation. Another gas conditioning method is methanation, the conversion of carbon monoxide, carbon dioxide, and hydrogen to methane according to Equations (8a) and (9). A methanation stage is included in many ammonia synthesis plants to ensure a high degree of purity of the synthesis gas. Similarly, a methanation step is indispensable if a high-methane gas for SNG production is to be obtained.

Other Processes. The following processes may also be regarded as gas conditioning.

If the calorific value of town gas, grid gas, or SNG is insufficient, the gasification gas may be carbureted by adding C_3 and C_4 hydrocarbons or, less frequently, small quantities of high molecular mass hydrocarbons. On the other hand, too high a calorific value can be reduced by adding nitrogen, air, or oxygen.

For certain syntheses, gases must be dried. Drying is also necessary in pipelines, to protect the piping from corrosion where a risk of water condensation in the presence of carbon dioxide exists. In addition, the formation of gas hydrates is avoided.

Unlike town gas produced in the past from coke oven batteries, the town gas obtained today through gasification no longer contains any chemical compounds that produce a manifest odor. Therefore, such gases are now odorized artificially so that leaks occurring in the piping or at the consumer's facilities can be detected easily.

To recover particular components from a gas stream (e.g., H_2 from purge gas), pressure-swing

adsorption (PSA) ($\rightarrow$ Adsorption) or membrane processes ($\rightarrow$ Membranes and Membrane Separation Processes) can be used. The PSA principle is based on the fact that the adsorption capacity of molecular sieves ($\rightarrow$ Zeolites) differs for different gases. Generally, heavier or polar gas components are adsorbed preferentially. When a gas mixture is passed over a molecular sieve bed, the component least amenable to adsorption (e.g., H_2) remains in the gas whereas other components are adsorbed.

Gas separation by membranes is based on the differences in permeation coefficients of different gas components. Permeation denotes the sequence of absorption (solution) of the component in the membrane material, diffusion through the membrane, and desorption. The permeation rate of a species increases with its solubility and its diffusion coefficient in the membrane material. Membranes may consist of ceramic or metallic materials, organic liquids, or polymers.

Both processes, PSA and membrane separation, can be used to advantage for gases at elevated pressure.

To remove traces of higher hydrocarbons (e.g., compressor lubricants) from gases, beds of activated carbon are used. For recovery of low-boiling compounds, as well as purification from traces of higher boiling compounds, cryogenic processes ($\rightarrow$ Cryogenic Technology) can be applied. These employ primarily liquid methane or nitrogen to absorb higher boiling gases such as carbon monoxide.

5.3. Byproducts

Some gasification processes yield byproducts along with the desired gas (see also $\rightarrow$ Gas Production, 4. Handling of Byproducts). A comparison of different gasification processes should, therefore, always consider such byproducts and assess their importance. Environmental protection, too, plays an important role because it imposes stringent conditions on pollutant discharge.

Many gasification plant feedstocks contain sulfur, and sulfur often constitutes the main byproduct. Whether this is best recovered in the form of elemental sulfur or sulfuric acid is worth considering.

Other coal gasification processes have coke as a byproduct.

Gasification involving coal carbonization processes can produce a large number of byproducts such as tar, oil, gasoline, phenols, cresols, ammonia, and organic acids. Certain liquid byproducts may even contain solids whose elimination would result in additional costs. Because of this, processes have been developed to recycle certain liquid fractions to the gasification plant if their market value is low.

Heavy-oil gasification plants yield carbon as a byproduct. Attempts to use it for special industrial applications have been successful, but demand for the specific qualities of carbon is limited. Therefore, processes are being developed to recycle most of this carbon to the gasification stage. These and processes where carbon is burnt in conventional power stations at little extra cost are of major interest.

Gas liquor is a product of almost all gasification processes. Depending on its composition and on plant requirements, this gas liquor can either be treated for use as boiler feed water or

cooling water, or be discharged to receiving water via chemical or biological effluent treatment plants.

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