NATURAL GAS

A Basic Handbook

SECOND EDITION

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History and use

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1.1 Introduction

Natural gas (also called marsh gas and swamp gas in older texts) is a gaseous fossil fuel that is found in oil fields and natural gas field. While it is commonly grouped in with other fossil fuels and sources of energy, there are many characteristics of natural gas that make it unique. The term natural gas is often extended to gases and liquids from the recently developed shale formations (Kundert and Mullen, 2009; Aguilera and Radetzki, 2014; Khosrokhavar et al., 2014; Speight, 2017b) as well as gas (biogas) produced from biological sources (John and Singh, 2011; Ramroop Singh, 2011; Singh and Sastry, 2011). However, for the purposes of this book, the petroliferous natural gas is placed under the category of conventional gas, while petroliferous gas from tight formations and the nonpetroliferous gases (such as biogas and landfill gas) are placed under the term *nonconventional gas* (sometime called *unconventional gas*) (Chapter 3: Unconventional gas).

Although the terminology and definitions involved with the natural gas technology are quite succinct, there may be those readers that find the terminology and definitions somewhat confusing. *Terminology* is the means by which various subjects are named so that reference can be made in conversations and in writings and so that the meaning is passed on. *Definitions* are the means by which scientists and engineers communicate the nature of a material to each other either through the spoken or through the written word. Thus, the terminology and definitions applied to natural gas (and, for that matter, to other gaseous products and fuels) are extremely important and have a profound influence on the manner by which the technical community and the public perceive that gaseous fuel. For the purposes of this book, natural gas and those products that are isolated from natural gas during recovery [such as natural gas liquids (NGLs), gas condensate, and natural gasoline] are a necessary part of this text. Thus:

Conventional gas
    Associated gas
    Nonassociated gas
    Gas condensate
Unconventional gas
    Gas hydrates
    Biogas
    Coalbed methane
    Coal gas
    Flue gas
    Gas in geopressurized zones
    Gas in tight formations

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Landfill gas
Manufactured gas
Refinery gas
Shale gas
Synthesis gas

A more meaningful categorization of these gases would be as fuel gases with a third category that includes the gases produced in manufacturing processes. Thus:

Conventional natural gas
    Associated gas
    Nonassociated gas
    Gas condensate
Unconventional gas
    Gas hydrates
    Coalbed methane
    Gas in geopressurized zones
    Gas in tight formations
    Shale gas
Manufactured gas
    Biogas
    Coal gas
    Flue gas
    Landfill gas
    Refinery gas
    Synthesis gas

These categorizations are based on the source of the gas or the method of production of the gas which also has some relationship to the composition of the gas. Nevertheless, whatever, the source or origin, natural gas and other fuel gases are vital components of the energy supply of the world and form a necessary supply chain for energy production:

reservoir gas → produced gas – wellhead gas → transported gas → stored gas → sales gas

Specifically, the term *natural gas* is the generic term that is applied to the mixture of and gaseous hydrocarbon derivatives and low-boiling liquid hydrocarbon derivatives (typically up to and including hydrocarbon derivatives such as *n*-octane, $CH_3(CH_2)_6CH_3$, boiling point 125.1–126.1°C, 257.1–258.9°F) (Tables 1.1 and 1.2) that is commonly associated with petroliferous (petroleum-producing, petroleum-containing) geologic formations (Mokhatab et al., 2006; Speight, 2014a).

From a chemical standpoint, natural gas is a mixture of hydrocarbon compounds and nonhydrocarbon compounds with crude oil being much more complex than natural gas (Mokhatab et al., 2006; Speight, 2012, 2014a). The fuels that are derived from this natural product supply more than one quarter of the total world energy supply. The more efficient use of natural gas is of paramount importance and the technology involved in processing both feedstocks will supply the industrialized nations of the world for (at least) the next five decades until suitable alternative forms of energy (such as biogas and other nonhydrocarbon fuels) are readily available (Boyle, 1996; Ramage, 1997; Rasi et al., 2007, 2011; Speight, 2011a,b,c, 2008). Any gas sold, however, to an industrial or domestic consumer must meet designated specification that is designed according to the use of the gas.

Table 1.1 Constituents of natural gas

Constituent	Formula	% v/v
Methane	CH_4	>85
Ethane	C_2H_6	3–8
Propane	C_3H_8	1–5
n-Butane	C_4H_{10}	1–2
iso-Butane	C_4H_{10}	<0.3
n-Pentane	C_5H_{12}	1–5
iso-Pentane	C_5H_{12}	<0.4
Hexane, heptane, octane[a]	C_nH_{2n+2}	<2
Carbon dioxide	CO_2	1–2
Hydrogen sulfide	H_2S	1–2
Oxygen	O_2	<0.1
Nitrogen	N_2	1–5
Helium	He	<0.5

[a] Hexane (C_6H_{14}) and higher molecular weight hydrocarbon derivatives up to octane as well as benzene (C_6H_6) and toluene ($C_6H_5CH_3$).

Table 1.2 Differentiation of the constituents of natural gas

Hydrocarbon constituents	
Dry gas or natural gas	Methane (CH_4)
	Ethane (C_2H_6)
Liquefied petroleum gas	Propane (C_3H_8)
	n-Butane (C_4H_{10})
	iso-Butane (C_4H_{10})
Natural gas liquids	Pentane isomers (C_5H_{15})
	Hexane isomers (C_6H_{14})
	Heptane isomers (C_7H_{16})
	Octane isomers (C_8H_{18})
	Condensate ($\geq C_5H_{12}$)
	Natural gasoline ($\geq C_5H_{12}$)
	Naphtha ($\geq C_5H_{12}$)
Nonhydrocarbon constituents	
	Carbon dioxide (CO_2)
	Hydrogen sulfide (H_2S)
	Water (H_2O)
	Nitrogen (N_2)
	Carbonyl sulfide (COS)

Typically, in field operations, the composition of natural gas (which affects the specific gravity), especially of associated gas, can vary significantly as the product flowing out of the well can change with variability of the production conditions as

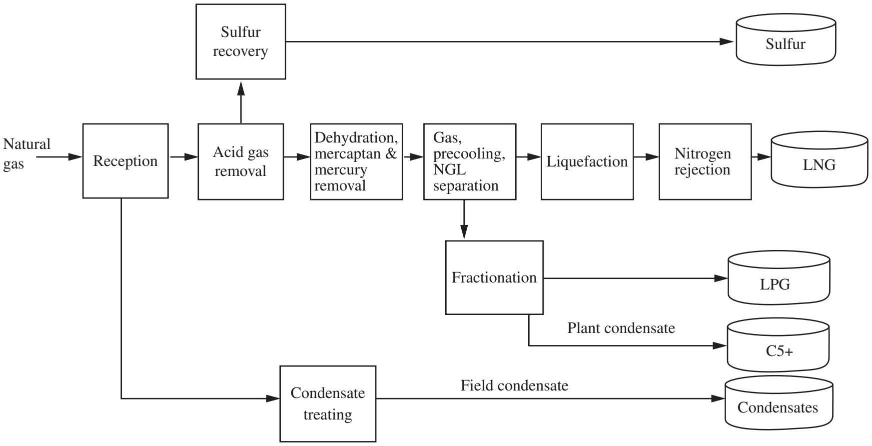

Figure 1.1 Typical gas processing sequence.

well as the change of pressure as gas is removed from the reservoir (Burruss and Ryder, 2003, 2014). Constituents of the gas that were in the liquid phase under the pressure of the reservoir can revert to the gas phase as the reservoir pressure is reduced by gas removal.

As a result, it should not be a surprise that at each stage of natural gas production, wellhead treating, transportation, and processing, analysis of the gas to determine the composition and properties of the gas by standard test methods is an essential part of the chemistry and technology of natural gas. Use of analytical methods offers (Speight, 2018) vital information about the behavior of natural gas during recovery, wellhead processing, transportation, gas processing, and use (Fig. 1.1). The data produced from the test methods are the criteria by means of which the suitability of the gas for use and the potential for interference with the environment.

1.2 History

Natural gas is a naturally occurring gaseous fossil fuel that is found in gas-bearing formations, oil-bearing formations—coalbed methane is often referred to (incorrectly) as natural gas or as coal gas due to lack of standardization of the terminology (Levine, 1993; Speight, 2013b, 2014a). For clarification, natural gas is not the same as town gas, although the history of natural gas cleaning prior to sales has its beginnings in town gas cleaning (Speight, 2013a).

Town gas is a generic term referring to manufactured gas produced for sale to consumers and municipalities. The terms coal gas, manufactured gas, producer gas, and syngas [synthetic natural gas (SNG)] are also used for gas produced from coal. Depending on the processes used for its creation, town gas is a mixture of hydrogen, carbon monoxide, methane, and volatile hydrocarbons with small amounts of carbon dioxide and nitrogen as impurities.

Thus, town gas is manufactured from coal and the terms coal gas, manufactured gas, producer gas, and synthesis gas (syngas), and SNG are also in regular use for gases produced from coal (Chapter 3: Unconventional gas) (Speight, 2013b). Also, by way of definition and clarification, town gas is a flammable gaseous fuel made by the destructive distillation of coal. It contains a variety of calorific gases including hydrogen, carbon monoxide, methane, and other volatile hydrocarbon derivatives, together with small quantities of noncalorific gases such as carbon dioxide and nitrogen. Town gas, although not currently used to any great extent in the United States, is still generated and used in some countries and is used in a similar way to natural gas in the United States. This is a historical technology and is not usually economically and environmentally competitive with modern sources of natural gas.

Most town gas-generating plants located in the eastern United States in the late 19th century and early 20th century were ovens that heated bituminous coal in airtight chambers to produce coke through the carbonization process. The gas driven off from the coal was collected and distributed through networks of pipes to residences and other buildings where it was supplied to industrial and domestic users—natural gas did not come into widespread use until the last half of the 20th century. The coal tar collected in the bottoms of the gashouse ovens was often used for roofing and other waterproofing purposes, and when mixed with sand and gravel (aggregate) was used for paving streets (road asphalt). The coal tar asphalt has been replaced by asphalt produced from crude oil (Speight, 2014a, 2015, 2018; ASTM, 2017). Thus, prior to the development of resources, virtually all fuel and lighting gas was manufactured from coal and the history of natural gas has its roots in town gas production and use (Speight, 2013b). Thus, with the onset of industrial expansion after World War II, natural gas has become one of the most important raw materials consumed by modern industries to provide raw materials for the ubiquitous plastics and other products as well as feedstocks for the energy and transportation industries.

1.2.1 Timeline

Natural gas has been known for many centuries, but initial use for the gas was more for religious purposes rather than as a fuel. For example, gas wells were an important aspect of religious life in ancient Persia because of the importance of fire in their religion. In classical times these wells were often flared and must have been, to say the least, awe inspiring (Forbes, 1964).

These types of gas leaks became prominent in the religions of India, Greece, and Persia where the inhabitants of the region were unable to explain the origin of the fires and regarded the origin of the flames as divine, or supernatural, or both. As a result, the energy value of natural gas was not recognized until approximately 900 BC in China and the Chinese drilled the first known natural gas well in 211 BC. Crude pipelines (probably state-of-the-art pipelines at the time) were constructed from bamboo stems to transport the gas, where it was used to boil sea water, removing the salt as a residue product, after which the water was condensed and, therefore, drinkable (Abbott, 2016).

The uses of natural gas did not necessarily parallel its discovery. In fact, the discovery of natural gas dates from ancient times in the Middle East. During recorded historical time, there was little or no understanding of what natural gas was, it posed somewhat of a mystery to man. Sometimes, such things as lightning strikes would ignite natural gas that was escaping from under the Earth's crust. This would create a fire coming from the Earth, burning the natural gas as it seeped out from underground. These fires puzzled most early civilizations and were the root of much myth and superstition. One of the most famous of these types of flames was found in ancient Greece, on Mount Parnassus approximately 1000 BC. A goat herdsman came across what looked like a *burning spring*, a flame rising from a fissure in the rock. The Greeks, believing it to be of divine origin, built a temple on the flame. This temple housed a priestess who was known as the Oracle of Delphi, giving out prophecies she claimed were inspired by the flame.

In Europe, natural gas was unknown until it was discovered in Great Britain in 1659 and Britain was the first country to commercialize the use of natural gas. In 1785, natural gas produced from coal was used to light houses, as well as streetlights. Manufactured natural gas of this type (as opposed to naturally occurring gas) was first brought to the United States in 1816, when it was used to light the streets of Baltimore, Maryland. This manufactured gas was much less efficient, and less environment-friendly, than modern natural gas that comes from underground.

Naturally occurring natural gas was discovered and identified in America as early as 1626, when French explorers discovered natives igniting gases that were seeping into and around Lake Erie (Table 1.3).

In 1821 in Fredonia, United States, residents observed gas bubbles rising to the surface from a creek. William Hart, considered as America's *father of natural gas*, dug there the first natural gas well in North America (Speight, 2014a). In 1859, Colonel Edwin Drake, a former railroad conductor (the origin of the title "Colonel" is unknown but seemed to impress the townspeople), dug the first well. Drake found

Table 1.3 Abbreviated timeline for the use of natural gas

1620	French missionaries recorded that Indians ignited gases near Lake Erie
1785	Natural gas is introduced for home lighting and street lighting
1803	Gas lighting system patented in London by Frederick Winsor
1812	First gas company founded in London
1815	Metering for households, invented in 1815 by Samuel Clegg
1816	First US gas company (using manufactured gas) founded in Baltimore
1817	First natural gas from the wellhead used in Fredonia, NY for house lighting
1840	Fifty or more US cities were burning public utility gas
1850	Thomas Edison postulated replacing gas lighting by electric lighting
1859	Carl Auer von Welsbach in Germany developed a practical gas mantle
1885	Depleted reservoirs are used for the first time to store gas

crude oil and natural gas at 69 ft below the surface of the Earth. More recently, natural gas was discovered because of prospecting for crude oil. However, the gas was often an unwelcome by-product because, as any gas containing in the reservoirs were tapped during the drilling process, the drillers were forced to discontinue the drilling operations that allow the gas to vent freely into the air. Currently, and particularly after the crude oil shortages of the 1970s, natural gas has become an important source of energy in the world.

Throughout the 19th century, natural gas was used almost exclusively as source of light and its use remained localized because of lack of transport structures, making difficult to transport large quantities of natural gas through long distances. There was an important change in 1890 with the invention of leak proof pipeline coupling but transportation of natural gas to long distance customers did not become practical until the 1920s as a result of technological advances in pipelines. Moreover, it was only after World War II that the use of natural gas grew rapidly because of the development of pipeline networks and storage systems.

1.2.2 Formation

Although covered in more detail elsewhere (Chapter 2: Origin and production), it is pertinent at this point, to give a brief coverage of the formation of natural gas to place it in context.

Just as crude oil is a product of decomposed organic matter (often referred to as organic debris or detritus), natural gas is also a product of the decomposition of organic matter. The organic matter is the remains of ancient flora and fauna that was deposited over the past 550 million years. This organic debris is mixed with mud, silt, and sand on the sea floor, gradually becoming buried over time. Sealed off in an oxygen-free (anaerobic) environment and exposed to increasing amounts of pressure and an unknown amount of heat, the organic matter underwent a decomposition process in which hydrocarbons (and nonhydrocarbons) were the products that converted it into hydrocarbons. The lowest boiling of these hydrocarbons exist in the gaseous state under normal conditions and become known collectively as natural gas. In the purest hydrocarbon form, natural gas is a colorless, odorless gas composed primarily of methane. These hydrocarbons are highly flammable compounds.

Thus, natural gas, like crude oil and often occurring in conjunction with crude oil, has been generated over geological time from deep-lying source rock, sometimes called the *kitchen*, which contains organic debris. Nevertheless, the actual chemical paths involved in the maturation of the organic debris are largely unknown and, therefore, subject to speculation.

Thus, it has been speculated, but not absolutely accepted (Speight, 2014a), that the deeper and hotter the source rock, the more likelihood of gas being produced. However, there is considerable discussion about the heat to which the organic precursors have been subjected. Cracking temperatures (≥300°C, ≥572°F) are not by any means certain as having played a role in natural gas formation. Maturation of the organic debris through temperature effects occurred over geological time (millennia) and shortening the time to laboratory time and increasing the temperature to above and beyond the cracking temperature (at which the chemistry changes) does not offer conclusive proof of natural gas (and crude oil) formation involving high temperatures (Speight, 2014a). Once the natural gas has formed, its fate depends on two critical characteristics of the surrounding rock: (1) porosity and (2) permeability.

The term *porosity* refers to the amount of empty space contained within the grains of a rock. Highly porous rocks, such as a sandstone formation, typically has a porosity on the order of 5%−25% v/v (percent volume of the rock), which gives the formation a substantial amount of space for the storage of fluids—the term *reservoir fluids* includes natural gas, crude oil, and water. On the other hand, the term *permeability* is a measure of the degree to which the pore spaces in a rock are interconnected and, therefore amenable to fluid flow. A highly permeable rock will permit gas and liquids to flow easily through the rock, while a low-permeability rock will not allow fluids to pass through. This latter term is characteristic of shale formations and tight formations (Chapter 3: Unconventional gas).

After natural gas forms, it will tend to rise toward the surface through pore spaces in the rock because of its low density compared to the surrounding rock. Thus, at some point during or after the maturation process, the gas and crude oil migrated from the source rock either upward or sideways or in both directions (subject to the structure of the accompanying and overlying geological formations) through the underground sediments through fissures and faults until the gas enters a geological formation (*reservoir*) that retains or *traps* the gas through the presence of impermeable basement rock and cap rock. Has this not occurred, there is the distinct likelihood that most of the natural gas would percolate through the surface formations and escape into the atmosphere.

It is rare that the source rock and the reservoir were one and the same and the reservoir may be many miles from the source rock. Thus, a natural gas field may have a series of layers of crude oil/gas and gas reservoirs in the subsurface. In some instances, the natural gas and crude oil parted company leading to the occurrence of reservoirs containing only gas (nonassociated gas).

The techniques to discover gas are essentially those used to discover crude oil (Speight, 2014a). When using seismic techniques, gas slows down the velocity of the seismic waves to produce a characteristic and stronger reflection. Over time, as more knowledge of a hydrocarbon province is obtained, better recognition of the characteristics and amplitude of the seismic reflection from gas can lead to a greater chance of success.

Thus, potential natural gas reservoirs can be located with seismic testing methods similar to those used for petroleum exploration (Chapter 2: Origin and production) (Speight, 2014a). In such tests, gas prospectors use seismic trucks or more advanced three-dimensional tools that involve setting off a series of small charges near the surface of the Earth to generate seismic waves thousands of feet below ground in underlying rock formations. By measuring the travel times of these waves through the Earth at acoustic receivers (*geophones*), geophysicists can construct a pictorial representation of the subsurface structure and identify potential gas deposits. However, to verify whether the rock formation actually contains economically recoverable quantities of natural gas or other hydrocarbons, an exploratory well must be drilled. Once the viability of a site is determined, vertical wells are drilled to penetrate the overlying impermeable cap rock and reach the reservoir. Natural buoyancy and reservoir pressure then brings the gas to the surface, where it can be processed and sent to the consumers.

1.3 Conventional gas

Natural gas resources, like crude oil resources, are typically divided into two categories: (1) conventional gas and (2) unconventional gas (Mokhatab et al., 2006; Islam, 2014; Speight, 2014a; AAPG, 2015). For the purposes of this text, the term unconventional gas resources also include coalbed methane and natural gas from shale formations and from tight formations as well as biogas and landfill gas (Brosseau, 1994; Briggs, 1988; Rice, 1993; John and Singh, 2011; Ramroop Singh, 2011; Singh and Sastry, 2011; Speight, 2011a, 2017b). Conventional gas is typically found in reservoirs with a permeability greater than 1 milliDarcy (>1 mD) and can be extracted by means of traditional recovery methods. In contrast, unconventional gas is found in reservoirs with relatively low permeability (<1 mD) and hence cannot be extracted by conventional methods (Speight, 2016a,b).

1.3.1 Associated gas

Associated or *dissolved* natural gas occurs either as free gas in a petroleum reservoir or as gas in solution in the petroleum. Gas that occurs as a solution in the petroleum is *dissolved* gas, whereas the gas that exists in contact with the petroleum (*gas cap*) is *associated* gas (Fig. 1.2).

Crude oil cannot be produced without producing some associated gas, which consists of low-boiling hydrocarbon constituents that are emitted from solution in

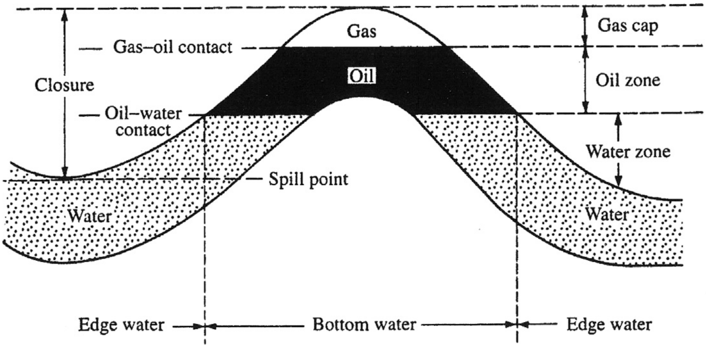

Figure 1.2 An anticlinal reservoir containing oil and associated gas.

the crude oil as the pressure is reduced on the way to, and on, the surface. Designs for well completion and reservoir management protocols are used to minimize the production of associated gas to retain the maximum energy in the reservoir and thus increase ultimate recovery of the crude oil (Parkash, 2003; Gary et al., 2007; Hsu and Robinson, 2017; Speight, 2014a, 2017a).

Crude oil in the reservoir with minimal or no dissolved associated gas (*dead crude oil* or *dead oil*) is rare and is often difficult to produce as there is little reservoir energy to drive the oil into the production well and to the surface. Thus, *associated* or *dissolved* natural gas occurs either as free gas or as gas in solution in the petroleum. Gas that occurs as a solution in the petroleum is *dissolved* gas whereas the gas that exists in contact with the petroleum is *associated* gas—the *gas cap* is an example of associated gas (Parkash, 2003; Mokhatab et al., 2006; Gary et al., 2007; Hsu and Robinson, 2017; Speight, 2014a, 2017a).

After the production fluids are brought to the surface, the gas is treated to separate out the higher molecular weight NGLs which are treated in a liquid petroleum gas (LPG) processing plant (refining plant) to provide propane and butane, either separately or as a mixture of the two. By definition, NGLs include ethane, propane, butanes, and pentanes and higher molecular weight hydrocarbon derivatives (C_{6+}). While NGLs are gaseous at underground pressure, these constituents condense at atmospheric pressure and turn into liquids. The composition of natural gas can vary by geographic region, the geological age of the deposit, the depth of the gas, and many other factors. Natural gas that contains a lot of NGLs and condensates is referred to as wet gas, while gas that is primarily methane, with little to no liquids in it when extracted, is referred to as dry gas.

These liquids are hydrocarbon derivatives that are removed (condensed) as a liquid from a hydrocarbon stream (natural gas) that is typically in a vapor phase (i.e., natural gas). They are kept in a liquid state for storage, shipping, and consumption. There has been a movement to classify NGLs are components of natural gas that are separated from the gas state in the form of liquids on the basis of vapor pressure, for example: (1) low vapor pressure—condensate and (2) high vapor pressure—liquefied natural gas and/or LPG. However, the boundaries drawn in this manner are arbitrary and caution is advised when using such a classification scheme.

Mixtures of these higher molecular weight hydrocarbon derivatives are often referred to as gas condensate or natural gasoline and the mixture has the characteristics of low-boiling naphtha produced in a refinery by distillation and cracking processes (Parkash, 2003; Gary et al., 2007; Hsu and Robinson, 2017; Speight, 2014a, 2017a). The LPG stored is ready for transport and the nonvolatile residue (i.e., nonvolatile under the conditions of the separation process), after the propane and butane are removed, is gas condensate (or, simply, condensate), which is mixed with the crude oil or exported as a separate product (low-boiling naphtha) (Mokhatab et al., 2006; Speight, 2014a).

Thus, in the case of associated gas, crude oil may be assisted up the wellbore by gas lift (Mokhatab et al., 2006; Speight, 2014a) in which the gas is compressed into the annulus of the well and then injected by means of a gas lift valve near the bottom of the well into the crude oil column in the tubing. At the top of the well the crude oil and gas mixture passes into a separation plant (consisting of high-pressure and low-pressure separators) in which the gas pressure is reduced considerably in two stages. The crude oil and water exits the bottom of the lower pressure separator, from where it is pumped to tanks for separation of the crude oil and water. The gas produced in the separators is recompressed and the gas that comes out of solution with the produced crude oil (surplus gas) is then treated to separate out the NGLs that are treated in a gas plant to provide propane and butane or a mixture of the two (LPG). The higher boiling residue, after the propane and butane are removed, is condensate, which is mixed with the crude oil or exported as a separate product. At each stage of this process (often referred to under the collective term *wellhead processing*), the composition of the gaseous and liquid products should be monitored to determine separator efficiency as well as for safety reasons (Colborn et al., 2011).

The gas itself is then *dry* and, after compression, is suitable to be injected into the natural gas system where it substitutes for natural gas from the nonassociated gas reservoir. Pretreated associated gas from other fields can also enter the system at this stage. Another use for the gas is as fuel for the gas turbines on site. This gas is treated in a fuel gas plant to ensure it is clean and at the correct pressure. The startup fuel gas supply will be from the main gas system, but facilities exist to collect and treat low-pressure gas from the various other plants as a more economical fuel source.

Other components such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), mercaptans (thiols; RSH), as well as trace amounts of other constituents may also be present. Thus, there is no single composition of components which might be termed *typical natural gas* because of the variation in composition of the gas from different reservoirs, even from different wells from the same reservoir. Methane and ethane constitute the bulk of the combustible components; carbon dioxide (CO_2) and nitrogen (N_2) are the major noncombustible (inert) components.

1.3.2 Nonassociated gas

In addition to the natural gas found in petroleum reservoirs, there are also those reservoirs in which natural gas is the sole occupant and is referred to as *nonassociated gas*. As with associated gas, the principal constituent of nonassociated gas is methane—higher molecular weight hydrocarbon derivatives may also be present but in lower quantities than found in associated gas. Carbon dioxide is also a common constituent of nonassociated natural gas and trace amounts of rare gases, such as helium, may also occur, and certain natural gas reservoirs are a source of these rare gases.

Thus, *nonassociated ga*s (sometimes called *gas well gas*) is produced from geological formations that typically do not contain much, if any, crude oil, or higher boiling hydrocarbon derivatives (*gas liquids*) than methane. The nonassociated gas recovery system is somewhat simpler than the associated gas recovery system. The gas flows up the well under its own energy, through the wellhead control valves and along the flow line to the treatment plant.

The nonassociated gas recovery system is somewhat simpler than the associated gas recovery system. The gas flows up the well under its own energy, through the wellhead control valves and along the flow line to the treatment plant. Treatment requires the temperature of the gas to be reduced to a point dependent upon the pressure in the pipeline so that all liquids that would exist at pipeline temperature and pressure condense and are removed.

Processing of nonassociated gas is somewhat less complicated than processing associated gas. Typically, nonassociated gas flows up the production well under the reservoir energy and then through the wellhead control valves and along the flow line to the wellhead processing plant. At this stage, the first processing option is to reduce the temperature of the gas to a point dependent upon the pressure in the pipeline so that the higher molecular weight constituents which would exist as liquids at the temperature and pressure of the pipeline condense to a liquid phase and are removed in a separator. The temperature is reduced by expanding the gas through a Joule–Thomson valve, although other methods of removal do also exist (Mokhatab et al., 2006; Speight, 2014a). Briefly, the Joule–Thomson effect (also known as the Joule–Kelvin effect, the Kelvin–Joule effect, or the Joule–Thomson expansion) relates to the temperature change of a gas or liquid when it is forced through a valve while kept insulated so that no heat is exchanged with the environment.

Water in the gas stream must also be removed to mitigate the potential for the formation of gas hydrates (Gornitz and Fung, 1994; Collett, 2002; Buffett and Archer, 2004; Collett et al., 2009; Demirbaş, 2010a,b,c; Boswell and Collett, 2011; Chong et al., 2016) which would block flow lines and have the potential for explosive dissociation. One method for water removal from the gas stream, involves the injection of ethylene glycol ($HOCH_2CH_2OH$, also referred to as *glycol*) which combines with the water and is later recovered in a glycol plant (Mokhatab et al., 2006; Speight, 2014a). The treated gas then passes from the top of the treatment vessel and into the pipeline. The water is treated in a glycol plant to recover the glycol and the fraction of the natural gas stream that has been isolated as NGLs is sent, as additional feedstock, to the LPG plant. Alternatively, the lower boiling constituents of the NGLs may be used as feedstock for the production of petrochemicals (Parkash, 2003; Gary et al., 2007; Hsu and Robinson, 2017; Speight, 2014a, 2017a).

Finally, one other aspect of gas processing that requires attention (Chapter 3: Unconventional gas) and is worthy of mention here, is the removal of sulfur from natural gas. The potential of sulfur-containing constituents, such as hydrogen sulfide (H_2S) and mercaptans (RSH) to corrode shipping equipment (such as pipelines) is high—especially in the presence of water (Speight, 2014b). Once the hydrogen sulfide has been removed by a suitable wellhead treatment process—it is environmentally undesirable to flare the hydrogen sulfide, so where there are significant quantities in the gas stream, it is converted into elemental sulfur and used for the manufacture of sulfuric acid and other products (Chapter 3: Unconventional gas). The sulfur can be transported over long distances by being pumped as a liquid at a temperature on the order of 120°C (248°F) through an insulated pipeline, which is maintained at this temperature by a counter flow of hot pressurized water.

Finally, it would be remissed if other types of gases were not included here since these gases are becoming a blend stock for natural gas in many gas processing operations.

1.3.3 Gas condensate

Gas condensate (sometimes referred to as *condensate*) is a mixture of low-boiling hydrocarbon liquids obtained by condensation of the vapors of these hydrocarbon constituents either in the well or as the gas stream emits from the well. Gas condensate is predominately pentane (C_5H_{12}) with varying amounts of higher-boiling hydrocarbon derivatives (up to C_8H_{18}) but relatively little methane or ethane; propane (C_3H_8), butane (C_4H_{10}) may be present in condensate by dissolution in the liquids. Depending upon the source of the condensate, benzene (C_6H_6), toluene ($C_6H_5CH_3$), xylene isomers ($CH_3C_6H_4CH_3$), and ethyl benzene ($C_6H_5C_2H_5$) may also be present (Mokhatab et al., 2006; Speight, 2014a).

The terms *condensate* and *distillate* are often used interchangeably to describe the liquid produced in tanks, but each term stands for a different material. Along with large volumes of gas, some wells produce a water-white or light straw-colored liquid that resembles low-boiling naphtha (Mokhatab et al., 2006; Speight, 2014a). The liquid has been called *distillate* because it resembles the products obtained from crude oil in refineries by distilling the volatile components from crude oil.

Lease condensate, so-called because it is produced at the lease level from oil or gas wells, is the most common type of gas condensate and is typically a clear or translucent liquid. The API gravity of lease condensate ranges between 45 and 75°API but, on the other hand, lease condensate with a lower API gravity can be black or near black color and, like crude oil, has higher concentrations of higher molecular weight constituents. This condensate is generally recovered at atmospheric temperatures and pressures from wellhead gas production and can be produced along with large volumes of natural gas and lease condensates with higher API gravity contains more NGLs, which include ethane, propane, and butane, but not many higher molecular weight hydrocarbon derivatives.

1.3.4 Other definitions

In addition to the definitions presented earlier, there are several other definitions that have been applied to natural gas from conventional formations that can also be applied to gas from any source.

Rich gas has a high heating value and a high hydrocarbon dew point. However, the terms *rich gas* and *lean gas*, as used in the gas processing industry, are not precise indicators of gas quality but only indicate the relative amount of NGLs in the gas stream. Thus, *lean* gas is gas in which methane is the predominant major constituent with other hydrocarbon constituents in the low minority, while *wet* gas contains considerable amounts of the higher molecular weight hydrocarbon derivatives than dry gas (Table 1.4). When referring to NGLs in the natural gas stream, the

Table 1.4 Composition of dry gas, wet gas, and gas condensate

Component	Dry gas	Wet gas	Condensate
Carbon dioxide, CO_2	0.10	1.41	2.37
Nitrogen, N_2	2.07	0.25	0.31
Methane, CH_4	86.12	92.46	73.19
Ethane, C_2H_6	5.91	3.18	7.80
Propane, C_3H_8	3.58	1.01	3.55
n-Butane, n-C_4H_{10}		0.24	1.45
iso-Butane, i-C_4H_{10}	1.72	0.28	0.71
n-Pentane, n-C_sH_{12}	–	0.08	0.68
iso-Pentane, i-C_sH_{12}	0.50	0.13	0.64
Hexane isomers, C_6H_{14}	–	0.14	1.09
Heptane isomers-plus[a], $\geq C_7H_{16}$	–	0.82	8.21

[a] Indicates higher molecular weight hydrocarbons.

term *gallons per thousand cubic feet* of gas is used as a measure of hydrocarbon richness.

Sour gas contains hydrogen sulfide and the equally odorous mercaptans, whereas *sweet* gas contains very little, if any, hydrogen sulfide or mercaptan. *Residue gas* is natural gas from which the higher molecular weight hydrocarbon derivatives have been extracted and *casinghead gas* is derived from crude oil but is separated at the separation facility at the wellhead.

The term residue (as in *residue gas*) is used in relation to gas as a direct opposite as it is applied to crude oil in a refinery. In the refinery, the residue is the distillation residue of crude oil from which the lower molecular weight constituents have been removed. In natural gas technology, residue gas is natural gas from which the higher molecular weight constituents have been removed during gas processing operations (Chapter 3: Unconventional gas and Chapter 7: Process classification) to leave methane (the lower boiling constituent) as residue gas.

Other terms applied to natural gas typically apply to the method by which the gas occurs in the reservoir. By way of explanation, natural gas is generated by any combination of (1) primary thermogenic degradation of organic matter, (2) secondary thermogenic decomposition of petroleum, and (3) biogenic degradation of organic matter. Gas generated by thermogenic and biogenic pathways may both exist in the same shale reservoir.

After production, the gas is stored in the reservoir formation in three different ways: (1) by adsorption, which refers to *adsorbed gas* that is physically attached (adsorption) or chemically attached (chemisorption) to organic matter or to clay minerals, (2) nonadsorbed gas, which refers to *free gas* (also referred to as *nonassociated gas*) that occurs within the pore spaces in the reservoir rock or in spaces created by the rock cracking (fractures or microfractures), and (3) by solution, also referred to as *associated gas*, which is gas that exists in solution in liquids such as petroleum, heavy oil, and (in the current context) in the gas condensate that occurs in some tight reservoirs with the gas (Speight, 2014a).

The amount of adsorbed gas component (which is, typically, methane) usually increases with an increase in organic matter or surface area of organic matter and/or clay. On the beneficial side, a higher free-gas (nonassociated) content in unconventional tight reservoirs generally results in higher initial rates of production because the free gas resides in fractures and pores and, when production is commenced moves easier through the fractures (induced channels) relative to any adsorbed gas. However, the high, initial flow rate will decline rapidly to a low steady rate as the nonassociated gas is produced leaving the adsorbed gas to move to the well as it is slowly released from the shale.

1.4 Use

Natural gas is a versatile, clean-burning, and efficient fuel that is used in a wide variety of applications as well as for the production of a variety of chemicals, especially when the natural gas is used as the starting point for the production of synthesis gas (a mixture of hydrogen and carbon monoxide) and thence to the various chemicals (Table 1.5).

After the discovery by the Chinese more than 2000 years ago that the energy in natural gas could be harnessed and used as a heat source, the use of natural gas has grown (Mokhatab et al., 2006; Speight, 2014a). In the late 19th century and in the early 20th century, natural gas played a subsidiary role to coal gas insofar as coal gas was used for street lighting and for building lighting and provided what was known as gaslight (Mokhatab et al., 2006; Speight, 2013b). However, as the 20th century progressed and moved into the 21st century, the discovery of large reserves

Table 1.5 Examples of routes to chemicals from natural gas via synthesis gas

Starting material	Intermediate	Product
Methane	Synthesis gas	Oxo synthesis Alcohols Aldehydes Fischer–Tropsch synthesis Naphtha Diesel Kerosene Lubricants Waxes Carbonylation Formic acid Methanol Acetic acid Dimethyl ether Formaldehyde

of natural gas in various countries as well as improved distribution of gas has made possible a wide variety of uses in homes, businesses, factories, and power plants and natural gas is becoming a global energy source (Nersesian, 2010; Hafner and Tagliapietra, 2013).

However, the uses of natural gas did not necessarily parallel its discovery and during recorded historical time, there was little or no understanding of what natural gas was, it posed somewhat of a mystery to man. Prior to the development of natural gas supplies and transmission in the United States during 1940s and 1950s, virtually all fuel and lighting gas was manufactured, and the by-product coal tar was an important feedstock for the chemical industry. The development of manufactured gas paralleled that of the industrial revolution and urbanization.

However, in the current contact, it is perhaps at least as awe-inspiring if not predictable considering the current attention to the environment—considering the history of the use of other fossil fuels such as coal and crude oil during the 20th century—that the use of natural gas is superseding the use of crude oil and coal in many countries. During that time, natural gas was generally flared as a product of limited use until the depletion of crude oil reserves in the late 20th century caused a back-and-forth concern about the future lack of energy-producing fuels (Speight, 2011a, 2014a; Speight and Islam, 2016).

Once the transportation of natural gas was possible over considerable distances, the increased use of natural gas led to innovations from the discovery of new uses for natural gas which included the use of natural gas by industrial consumers. In fact, the fastest growing use of natural gas is for the generation of electric power and, to a large extent, has been a replacement fuel many formerly coal-fired power plants and oil-fired power plants. Natural gas power plants usually generate electricity in gas turbines (which are derived from jet engines), directly using the hot exhaust gases from the combustion process.

As the use of natural gas has increased and diversified, the need for knowledge of the composition of the gas has also increased (Mokhatab et al., 2006; Speight, 2018). Natural gas has many applications: for domestic use, for industrial use, and for transportation. In addition, natural gas is also a raw material for many common products such as paints, fertilizer, plastics, antifreeze, dyes, photographic film, medicines, and explosives. Along with these newer uses, there has been an increased need not only for the compositional analysis of natural gas but also for analytical data that provide other information about the behavior of natural gas.

Natural gas-fired power plants are currently among the cheapest power plants to construct which is a reversal of previous trends where operating costs were generally higher than those of coal-fired power plants because of the relatively high cost of natural gas. In addition, natural gas-fired plants have greater operational flexibility than coal-fired power plants because they can be fired up and turned down rapidly. Because of this, many natural gas plants in the United States were originally used to provide additional capacity (peak capacity) at times when electricity demand was especially high, such as the summer months when air conditioning is widely used. During much of the year, these natural gas peak plants were idle, while coal-fired power plants typically provided base-load power. However, since

2008, natural gas prices in the United States have fallen significantly, and natural gas is now increasingly used as base-load power as well as intermediate-load power source in many cities. Natural gas can also be used to produce both heat and electricity simultaneously [cogeneration or combined heat and power (CHP)]. Cogeneration systems are highly efficient, able to put 75%−80% of the energy in gas to use. Trigeneration systems, which provide electricity, heating, and cooling, can reach even higher efficiencies using natural gas.

Natural gas also has a broad range of other uses in industry, not only as a source of both heat and power and as source of valuable hydrogen that is necessary for crude oil refining as well as for producing plastics and chemicals. Most hydrogen gas (H_2) production, for example, comes from reacting high temperature water vapor (steam) with methane—steam-methane reforming reaction followed by the water gas shift reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{ (steam-methane reforming reaction)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (Water-gas shift reaction)}$$

Natural gas-fired plants have greater operational flexibility than coal plants because they can be fired up and turned down rapidly. Because of this, many natural gas plants were originally used to provide peaking capacity at times when electricity demand was especially high, such as the summer months when air conditioning is widely used. During much of the year, the natural gas peak-plants were in low use or idle, while coal-fired power plants typically provided base load power. However, (1) with the current (and projected prolonged) plentiful supplies of natural gas, (2) lower natural gas prices, and (3) the projected environmental benefits of natural gas use vis-à-vis coal, natural gas is now increasingly used as a base and intermediate load power source in many places.

The integrated gasification combined cycle plant can be used as an example of the benefits of gas-fired power generation. The natural gas is combusted in a gas turbine unit that is connected to a generator after which the hot exhaust gases are then passed through a heat exchanger to generate steam for a steam turbine. By using this approach, a natural gas combined cycle power plant can reach efficiencies at least on the order of 50%, compared to a lower efficiency (30%−35%) for a similar megawatt size coal-fired power plant.

Furthermore, the hydrogen produced from natural gas can itself be used as a fuel. The most efficient way to convert hydrogen into electricity is by using a fuel cell, which combines hydrogen with oxygen to produce electricity, water, and heat. Although the process of reforming natural gas to produce hydrogen still has associated carbon dioxide emissions, the amount released for each unit of electricity generated is much lower than for a combustion turbine.

As part of the industrial use of natural gas, there is the need for analysis before the products (in this context, the gaseous products) are used by industrial and domestic consumers. Detection of even the slightest amounts of impurities can be an indication of process inefficiency and whether or not the gas is suitable for the designated use. In fact, one of the most important tasks in gas technology, especially in the context of petroleum-related natural gas is the need for reliable values of the volumetric and thermodynamic properties for pure low-boiling hydrocarbon derivatives and their mixtures. These properties are important in the design and operation of much of the processing equipment (Poling et al., 2001).

For example, reservoir engineers and process engineers use pressure-volume-temperature relationships and phase behavior of reservoir fluids (1) to estimate the amount of oil or gas in a reservoir, (2) to develop a recovery process for a crude oil or gas field, (3) to determine an optimum operating condition in a gas–liquid separator unit, (4) to determine the need for a wellhead processing system to protect a pipeline from corrosion, and (5) to design suitable gas processing options. However, the most advanced design approaches or the most sophisticated simulation experiments cannot guarantee the optimum design or operation of a unit (or protection of a pipeline) if the physical properties are not known. For these reasons accurate knowledge of the properties of the gas is an extremely increasingly important aspect of gas technology.

Natural gas can also be used to produce both heat and electricity simultaneously (CHP). Cogeneration systems are highly efficient, able to put 75%–80% of the energy in gas to use. *Trigeneration* systems, which provide electricity, heating, and cooling, can reach even higher efficiencies.

Natural gas sees a broad range of other industrial uses, as a source of both heat and power and as an input for producing plastics and chemicals. For example, most of the hydrogen gas production comes from reacting high temperature water vapor (steam) with methane. The resulting hydrogen has wide use in crude oil refineries in order to produce marketable products from heavy crude oil, extra heavy cried oil and tar sand bitumen (Speight, 2014a, 2017a) as well as to produce ammonia for fertilizer. Although the process of reforming natural gas to hydrogen still has associated carbon dioxide emissions, the amount released for each unit of electricity generated is much lower than for a combustion turbine.

Hydrogen produced from natural gas can itself be used as a fuel—the most efficient way to convert hydrogen into electricity is by using a fuel cell, which combines hydrogen with oxygen to produce electricity, water, and heat:

$$2H_2 + O_2 \rightarrow 2H_2O + \text{Heat}$$

Compressed natural gas (CNG) has been used as a transportation fuel (Chapter 5: Recovery, storage, and transportation), mostly in public transit. The natural gas, which is compressed at over 3000 psi to 1% of the volume that the gas would occupy at normal atmospheric pressure, can be burned in an internal combustion engine that has been appropriately modified. Approximately 0.1% v/v of the natural gas consumed in the United States has been used to power vehicles, representing the energy content of more than 5 million barrels of oil (US EIA, 2012).

Compared to gasoline, vehicles powered by CNG emit less carbon monoxide, nitrogen oxides (NO_x), and particulate matter. However, a disadvantage of CNG is the low energy density compared with the higher energy density of liquid fuels. A gallon of CNG has approximately one quarter of the energy in a gallon of

Table 1.6 Natural gas liquids (NGLs), uses, products, and consumers

NGL	Chemical formula	Uses	Other uses
Ethane	C_2H_6	Ethylene production Power generation	Plastics Antifreeze Detergents
Propane	C_3H_8	Heating fuel Transportation petrochemical feedstock	Plastics
Butanes: *n*-butane and *iso*-butane	C_4H_{10}	Petrochemical feedstock Refinery feedstock Blend stock for gasoline	Plastics Synthetic rubber
Condensate	C_5H_{12} Higher boiling hydrocarbons	Petrochemical feedstock Additive to gasoline Diluent for heavy crude oil	Solvents

gasoline and, therefore, vehicles powered by CNG require larger fuel tanks (compared to vehicles powered by liquid fuels).

Thus, a more suitable use for natural gas in the transportation sector may be as a resource to generate electricity for plug-in vehicles or hydrogen for fuel cell vehicles, which can reduce emissions savings on the order of 40% (or more).

NGLs which are, by definition, hydrocarbon derivatives also have use other than fuel components (Table 1.6) because of the hydrocarbon constituents. Thus, there are many uses for NGLs that span almost all sections of the industrial chemicals economy. NGLs are used as feedstocks for petrochemical plants, burned for space heat and cooking, and blended into vehicle fuel.

The chemical composition of NGLs from different sources is similar, yet their applications vary widely. Ethane occupies the largest share of the filed production of NGLs and is used almost exclusively to produce ethylene, which is then converted into plastic products. By contrast, the majority of the propane, by contrast, is burned for heating, although a substantial amount is used as petrochemical feedstock. A blend of propane and butane, sometimes referred to as *autogas* (*auto-gas*), is a popular fuel in some parts of Europe, Turkey, and Australia. Natural gasoline (pentanes plus) can be blended into various kinds of fuel for combustion engines and is useful in energy recovery from wells and tar sand (oil sand) deposits.

A challenge with the use of NGLs is that they are (1) expensive to handle, (2) store, and (3) transport compared to refined products. NGLs are highly flammable and require high pressure and/or low temperature to be maintained in the liquid state for shipping and handling. The flammability of these liquids necessitates the use of special trucks, ships, and storage tanks.