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History and Background

1.1 Introduction

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 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, the term *natural gas* is the generic term that is applied to the mixture of gases 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) (Table 1.1) that is commonly associated with petroliferous (petroleum-producing, petroleum-containing) geologic formations (Mokhatab et al., 2006; Speight, 2007, 2014a) and that has been extended to gases and liquids from the recently developed shale formations (Speight, 2017b) as well as gas (biogas) produced from biological sources (John and Singh, 2011; Ramroop Singh, 2011; Singh and Sastry, 2011).

For clarification, natural gas (also called marsh gas and swamp gas in older texts and more recently landfill gas) is not the same as town gas, which is manufactured from coal, and the terms coal gas, manufactured gas,

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Table 1.1 Constituents of natural gas.

Name	Formula	Vol. %
Methane	CH_4	>85
Ethane	C_2H_6	3–8
Propane	C_3H_8	1–5
Butane	C_4H_{10}	1–2
Pentane$^+$	C_5H_{12}	1–5
Carbon dioxide	CO_2	1–2
Hydrogen sulfide	H_2S	1–2
Nitrogen	N_2	1–5
Helium	He	<0.5

Pentane$^+$: pentane and higher molecular weight hydrocarbon derivatives up to octane as well as benzene and toluene.

producer gas, and syngas (synthetic natural gas [SNG]) are also in regular use for gases produced from coal (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 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. 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 nineteenth century and early twentieth 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 twentieth 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), it was used for paving streets (road asphalt). The coal tar asphalt has been replaced by asphalt produced from crude oil (Speight, 2014a, 2015b). Thus, prior to the development of resources, virtually all fuel and lighting gas was manufactured from coal, and the history of and analysis of natural gas has its roots in town gas

analysis 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.

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, 2007, 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; Speight, 2008, 2011a, b, c; Rasi et al., 2011). Any gas sold, however, to an industrial or domestic consumer must meet the designated specification that is designed according to the use of the gas.

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 vital information about the behavior of natural gas during recovery, wellhead processing, transportation, gas processing, and use. 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, Use, and the Need for Analysis

Natural gas is a versatile, clean-burning, and efficient fuel that is used in a wide variety of applications. In the late nineteenth century and in the early twentieth 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 twenty-first century progresses, the discovery of large reserves 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. The fastest-growing use of natural gas is for the generation of electric power and, to a large extent, has been a replacement fuel of 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.

Natural gas-fired 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 for base load power as well as for 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 but also as a 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:

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

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

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 associated (or contract) laboratory operations to perform the necessary high numbers of analyses 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 analyze pressure–volume–temperature (PVT) relationships and phase behavior of reservoir fluids (i) to estimate the amount of oil or gas in a reservoir, (ii) to develop a recovery process for a crude oil or gas field, (iii) to determine an optimum operating condition in a gas–liquid separator unit, (iv) to determine the need for a wellhead processing system to protect a pipeline from corrosion, and (v) 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 as determined in an analytical laboratory dictate otherwise. For these reasons accurate knowledge of the properties of the gas is an extremely increasingly important aspect of gas technology. Analysis of the gas during production operations is also an essential practice.

Typically, in field operations, the composition of natural the 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 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 is necessary to collect representative samples of gas from high-pressure cylinders for analysis by gas chromatography in the laboratory (Chapter 6). In terms of gas analysis, the concept of obtaining a representative sample of the gas for analysis cannot be overstressed (Chapter 6).

1.2.1 History

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). In the current contact, it is perhaps at least as awe inspiring – considering the history of the use of other fossil fuels such as coal and crude oil during the twentieth 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 twentieth century caused a back-and-forth concern about the future lack of energy-producing fuels (Speight, 2011a, 2014a; Speight and Islam, 2016).

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, 2007, 2014a). 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. Sometimes, events such as lightning strikes would ignite natural gas that was escaping from vents through the crust of the Earth. 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. The (realistic or legendary) story is that 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.

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 seawater, removing the salt as a residue product, after which the water was condensed and, therefore, drinkable (Abbott, 2016).

Natural gas was discovered and identified in America as early as 1620, when French explorers discovered natives igniting gases that were seeping into and around Lake Erie (Table 1.2). However, Britain was the first country to commercialize the use of natural gas, and 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 environmentally friendly, than modern natural gas that comes from underground.

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, 2007). 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 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

Table 1.2 Abbreviated timeline for the use of natural gas.

1620	French missionaries recorded that Indians in what is now New York state ignited gases in the shallows of Lake Erie and in the streams flowing into the lake
1785	HousNNatural gas is introduced for home lighting and streetlighting
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

by-product because, as any gas-containing reservoirs were tapped during the drilling process, the drillers were forced to discontinue the drilling operations to 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.

1.2.2 Use

Throughout the nineteenth century, natural gas was used almost exclusively as source of light, but because of the lack of any transport infrastructure that prevented the transportation of the gas to distant markets, the use was localized to areas close by where the gas was discovered. However, in 1890 with the invention of leakproof pipeline coupling, transportation of natural gas to long-distance customers became possible and finally achieved practicality in the early 1920s with additional advances in pipeline technology. Finally, after World War II, the use of natural gas underwent a marked increase as pipeline networks and natural gas storage systems underwent rapid development.

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 that included the use of natural gas by industrial consumers. As the use of natural gas has increased and diversified, the need for analysis related to gas composition has also increased. Natural gas has many applications: for domestic use, industrial use, and 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.

1.2.3 The Need for Analysis

To satisfy the modern use of natural gas, analytical methods are applied to all aspects of gas production and use and include (i) gas in the reservoirs, (ii) associated gas, (iii) nonassociated gas, (iv) unconventional gas, including coalbed methane (CBM), tight shale gas, and gas from gas hydrates, (v) determining the quality of gas reserves; (vi) determining the suitability of the gas for use, (vii) the ability of the gas to conform to regulation, and (viii) the effect of natural gas on the environment.

However, the primary need for analysis of natural gas came with the recognition by the producers and the consumers that natural gas – a product of nature – is a gaseous mixture and that the composition of the gas will differ according to the reservoir from which the gas was produced. While natural gas consists predominantly of methane, with higher molecular weight (MW) hydrocarbon derivatives such as ethane, propane, and butane present as minor constituents, there are also the nonflammable (inert) constituents such as nitrogen, carbon dioxide, water (vapor), and helium. It is these other nonmethane constituents that give rise to the need not only for compositional analysis of the gas but also for the determination of other properties that are relevant to the ultimate use of the gas.

Up to the introduction of gas chromatography in the 1950s, the analysis of natural gas and other fuel gases, such as coal gas (Speight, 2013b) and refinery process gas (Speight, 2014a), was performed using chemical absorption (chemisorption) and/or combustion methods (Speight, 2015a). These methods relied upon the selective absorption of different constituents (either in their original form or after reaction with other chemicals), e.g. carbon dioxide was determined by absorption in a solution of potassium hydroxide (chemisorption) followed by titration to determine the amount of the gas absorbed:

$$CO_2 + 2KOH = K_2CO_3 + H_2O$$

But in the early 1960s, chromatography had replaced the adsorption methods as the major analytical method applied to natural gas and other fuel gases.

Although the specification of the natural gas from a source is typically negotiated between the supplier and the customer, the gas must meet specification that is provided by various governmental and environmental bodies. The main aspects that should be covered include, but are not limited to, (i) properties such as gas quality, heating value, and Wobbe index; (ii) impurities, such as oxygen, inert gases, carbon dioxide, and sulfur compounds; (iii) hydrocarbon

dew point, which prevents condensation of hydrocarbon liquids in the pipeline; and (iv) water content, which prevents water dropout and hydrate formation and corrosion in the pipeline.

Each of the categories enumerated in the preceding paragraph requires detailed analysis (and thence knowledge) of the properties of natural gas, and to understand the applicability of the analytical methods, it is helpful for the reader to understand (i) the origin of natural gas; (ii) the production of natural gas; (iii) the transportation of natural gas; (iv) the refining of natural gas, including gas cleaning; and (v) the influence of natural gas on the environment.

First and foremost, although covered in name by a generic term, natural gas varies in composition, and therefore quality, as well as other properties depending on the source of the gas. Therefore, it is essential that gas composition and properties should be determined by a series of standard test methods (Chapter 6) in order to choose and predict a suitable use for the gas. For example, it is often assumed that gases with the same heat content (calorific value [CV], heating value) are interchangeable, but this is not necessarily the case. Since all gas-fired equipment is designed to operate within a particular range of gas specification, the use of gases outside this range can lead to a range of issues from poor quality combustion to equipment damage and ultimately dangerous operation. As a result, gas interchangeability relates to more than just a parameter for the heat content. In fact, interchangeability is governed by a general umbrella property often referred to as *gas quality*, which is, in turn, a function of gas composition and specific gravity as well as any other property (or properties) that are relevant to the use of the gas. Thus, the essence of natural gas interchangeability relies on knowledge of the necessary properties of the gas, which are derived from application of a series of standard test methods that are accepted on an international basis.

The various purposes to be served by the analytical data and the necessary accuracy with which each constituent of each type of gas must be known in order to serve each specific purpose are then estimated. These estimates afford the first criterion by means of which the suitability of analytical methods and apparatus may be judged, but they are subject to revision when more is known about the limiting attainable accuracies of the analytical methods (Shepherd, 1947). Thus, because of the worldwide use of natural gas and the potential for gas from different wells to vary in composition, there is a need to apply a series of standard test to the gas in order that it can meet sales specifications (Table 1.3).

Gases analyzed include hydrocarbon derivatives (C_1–C_{6+}) such as methane, ethane, propane, isobutane, *n*-butane, isopentane, *n*-pentane, and hexane, plus higher MW hydrocarbon derivative. Nonhydrocarbon impurities include hydrogen, nitrogen, carbon monoxide, carbon dioxide, oxygen, mercury, sulfur-containing compounds such as hydrogen sulfide and thiols (also called

Table 1.3 Examples of standard test methods for natural gas (ASTM, 2017).

ASTM D1070 Standard Test Methods for Relative Density of Gaseous Fuels
ASTM D1071 Standard Test Methods for Volumetric Measurement of Gaseous Fuel Samples
ASTM D1072 Standard Test Method for Total Sulfur in Fuel Gases
ASTM D1142 Standard Test Method for Water Vapor Content of Gaseous Fuels by Measurement of Dew-Point Temperature
ASTM D1826 Standard Test Method for Calorific (Heating) Value of Gases in Natural Gas Range by Continuous Recording Calorimeter
ASTM D1945 Standard Test Method for Analysis of Natural Gas by Gas Chromatography
ASTM D1946 Standard Practice for Analysis of Reformed Gas by Gas Chromatography
ASTM D1988 Standard Test Method for Mercaptans in Natural Gas Using Length-of-Stain Detector Tubes
ASTM D3588 Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels
ASTM D4084 Standard Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)
ASTM D4150 Standard Terminology Relating to Gaseous Fuels
ASTM D4810 Standard Test Method for Hydrogen Sulfide in Natural Gas
ASTM D4891 Standard Test Method for Heating Value of Gases in Natural Gas Range by Stoichiometric Combustion
ASTM D4984 Standard Test Method for Carbon Dioxide in Natural Gas Using Length-of-Stain Detector Tubes
ASTM D5287 Standard Practice for Automatic Sampling of Gaseous Fuels
ASTM D5454 Standard Test Method for Water Vapor Content of Gaseous Fuels Using Electronic Moisture Analyzers
ASTM D5503 Standard Practice for Natural Gas Sample-Handling and Conditioning Systems for Pipeline Instrumentation
ASTM D5504 Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
ASTM D5954 Standard Test Method for Mercury Sampling and Measurement in Natural Gas by Atomic Absorption Spectroscopy
ASTM D6228 Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection
ASTM D6273 Standard Test Methods for Natural Gas Odor Intensity
ASTM D6350 Standard Test Method for Mercury Sampling and Analysis in Natural Gas by Atomic Fluorescence Spectroscopy

mercaptans, R—SH), and water. As an example of the need for a standard test method, natural gas composition analysis is applied to all phases of natural gas exploration and production, from the reservoir to recovery at the wellhead, initial processing prior to transportation, processing, storage, and distribution as well as liquefied natural gas-related activities. Natural gas composition includes testing for the following:

- Methane, CH_4
- Ethane, C_2H_6
- Propane, C_3H_8
- Butane, C_4H_{10}
- Carbon dioxide, CO_2
- Oxygen, O_2
- Nitrogen, N_2
- Hydrogen sulfide, H_2S
- Thiols (mercaptans), RSH
- Trace of rare gases
- Trace metals

Because of the presence of the nonmethane constituents, the energy density of the gas also differs. Since delivery of natural gas to the consumer is billed according to the energy quantities calculated from the gas analysis and the measured volume of gas, it is essential to analyze the gas composition as accurately as possible.

Moreover, the analysis of natural gas is carried out for many reasons: (i) identification of specific constituents, commonly minor constituents such as odorants, (ii) identification of the source of the gas either by fingerprinting or by molar composition, (iii) the application areas of increasing importance such as calculation (or estimation) of physical properties, and (iv) the measurement of gas quality when compared to the specification for use. However, the amount of detail that is required from the analysis depends upon the reason for the analysis, i.e. identification of source of the gas by molar composition might be done in some circumstances by an analysis up to pentane with a composite number for the presence of the higher MW hydrocarbon derivatives (such as the hexane and hydrocarbon derivatives up to, and including, C_8 or C_{10} hydrocarbon derivatives). Such data may also be suitable for estimation of the CV, assuming a single bulk contribution to the CV from this higher MW group (Chapter 6).

Direct methods of measurement of physical properties, particularly CV and relative density, are common and in some cases mandatory (Chapter 6). Chromatographic analysis followed by calculation of a property is a popular alternative for several reasons: (i) the apparatus is relatively inexpensive, (ii) the

analysis will show why a change in property has occurred in addition to measuring the change, and (iii) a sufficiently detailed analysis allows several properties to be calculated at the same time. Nevertheless, the investigator should be aware of the risks of the use of *average values*, which may produce data that are not truly representative of the behavior of the gas mixture. Furthermore, in the case of property calculations related to phase changes, such as the hydrocarbon dew point, much more detail is needed about the distribution of the higher MW hydrocarbon derivatives. Briefly, the dew point is the temperature to which a given volume of gas must be cooled, at constant barometric pressure, for vapor to condense into liquid. Thus, the dew point is the saturation point that will vary as the carbon number of the hydrocarbon increases or decreases, thereby leading to results that are not consistent with the true behavior of the gas.

In summary, natural gas testing includes the analysis of conventional and shale gas, liquefied natural gas, and other hydrocarbon condensates and components (ASTM, 2017). The standard test methods that are cited within this book are, for convenience, the standard test methods developed by ASTM International (formerly the American Society for Testing and Materials) (ASTM, 2017). For example, standard test methods that might be used or consulted for comparison are (i) the British Standards (BS), which are the standards produced by BSI Group, located in Chiswick, London, which is incorporated under a Royal Charter and is formally designated as the national standards body (NSB) for the United Kingdom; (ii) the International Organization for Standardization (ISO), located in Geneva, Switzerland; and (iii) the German Institute for Standardization (DIN), located in Berlin, Germany, which publishes a variety of test methods that are applicable to determining the properties and behavior of natural gas and processed gases. Other organizations are available in several countries (Table 1.4) that might also be consulted as source of standard test methods.

However, the application of standard test methods need not (or does not) typically end with analysis of the gas. The mineralogy of the reservoir can (and often does) play a major role in the ability of the gas to be produced at the wellhead. Thus, there may be a need for the mineralogical analysis of samples of the reservoir rock.

1.3 Reservoirs

Natural gas is derived from aquatic plants and animals that lived and died hundreds of millions of years ago. Their remains mixed with mud and sand in layered deposits that, over the millennia, were geologically transformed into sedimentary rock. Gradually the organic matter decomposed and eventually formed petroleum (or a related precursor), which migrated from the original

Table 1.4 Examples of standards organizations in various countries (listed alphabetically).

Organization	Acronym	Country
American National Standards Institute	ANSI	United States
Badan Standardisasi Nasional	BSN	Indonesia
Brazilian National Standards Organization	ABNT	Brazil
British Standards Institution	BSI	United Kingdom
Bureau of Indian Standards	BIS	India
Bureau of Standards Jamaica	BSJ	Jamaica
Colombian Institute of Technical Standards and Certification	ICONTEC	Colombia
Deutsches Institut für Normung	DIN	Germany
Dirección General de Normas	DGN	Mexico
Ente nazionale italiano di unificazione	UNI	Italy
Estonian Centre for Standardisation	EVS	Estonia
Euro-Asian Council for Standardization, Metrology and Certification	GOST	Russia (Soviet Union)
Finnish Standards Association	SFS	Finland
French Association for Standardization	AFNOR	France
Instituto Argentino de Normalización y Certificación	IRAM	Argentina
Instituto Português da Qualidade	IPQ	Portugal
Japanese Industrial Standards Committee	JISC	Japan
Jabatan Standard Malaysia	DSM	Malaysia
Korean Agency for Technology and Standards	KATS	Korea (Republic)
Luxembourg Institute for Standardization	ILNAS	Luxembourg
Nederlandse Norm	NEN	Netherlands
Romanian Standards Association	ASRO	Romania
South African Bureau of Standards	SABS	South Africa
Spanish Association for Standardization and Certification	AENOR	Spain
Standardization Administration of China	SAC	China
Standards Australia	SAI	Australia
Standards Council of Canada	SCC	Canada
Standards New Zealand	SNZ	New Zealand
Standards Norway	SN	Norway
Standards Organisation of Nigeria	SON	Nigeria
Swedish Standards Institute	SIS	Sweden
Swiss Association for Standardization	SNV	Switzerland

source beds to more porous and permeable rocks, such as *sandstone* and *siltstone*, where it finally became entrapped. Such entrapped accumulations of petroleum are called *reservoirs*. A series of reservoirs within a common rock structure or a series of reservoirs in separate but neighboring formations is commonly referred to as an *oil field*. A group of fields is often found in a single geologic environment known as a *sedimentary basin* or *province*.

When a hydrocarbon reservoir is identified, it is important to also identify the types of fluids that are present, along with their main physicochemical characteristics. Generally, that information is obtained by performing a PVT analysis on a fluid sample of the reservoir. Conventional production measurements, such as a drill stem test (DST), are the typical parameters that can be measured almost immediately after a well is completed, as well as to obtain preliminary values of properties such as molar percentage of heptane and heavier components (% mole of C_{7+}), MW of the original fluid, maximum retrograde condensation (MRC), and dew-point pressure (P_d). Most of these properties are essential for exploitation of gas condensate reservoir, and their early availability will allow engineers to carry out reservoir studies that will ensure an efficient exploitation and maximize the final recovery of the liquids present in the reservoir. The only parameter needed to use these correlations is the value of the gas–condensate ratio (GCR) of the fluid during the early stage of production. These empirical equations should be valid for any gas condensate reservoir worldwide, although a range of usability is proposed for a better performance of the correlations. Moreover, just as crude oil can vary in composition, natural gas can also vary in composition. Differences in natural gas composition occur between different reservoirs, and two wells in the same field may also yield gaseous products that are different in composition (Speight, 1990; Mokhatab et al., 2006; Speight, 2007, 2014a).

Just as processes play a role in determining the composition and type of gaseous products, reservoirs (especially reservoir mineralogy) also play a major role in determining the composition and, hence, the behavior of natural gas. Different minerals adsorb gases at different rates, leading to a requirement for determining the mineralogical composition of the rock within the reservoir. The data related to mineralogical composition can lead to estimates of the gaseous constituents not produced through a well and the mean by which these constituents are held within the reservoir. In addition, the pressure within the reservoir may also be a major influence on the properties of the gas as it appears at the wellhead. For example, reservoir pressure varies depending on the depth, and because of the pressure, some of the typically gaseous constituents (at STP) of natural gas may be in liquid form and therefore appear at the surface as liquids (gas condensate) (Chapter 10).

In addition to the natural gas found in reservoirs that contain crude oil, there are also reservoirs in which natural gas may be the sole occupant. Again,

the principal constituent of natural gas is methane, but other hydrocarbon derivatives, such as ethane, propane, and butane, may also be present but in lower proportions than those found in natural gas from crude oil reservoirs. Carbon dioxide is also a common constituent of natural gas. Trace amounts of rare gases, such as helium, may also occur, and certain natural gas reservoirs are a source of these rare gases.

On a worldwide scale, there are many reservoirs that produce gas condensate, and each reservoir will produce gas condensate with its own unique composition. However, in general, gas condensate has a specific gravity ranging from 0.5 to 0.8 and is composed of higher MW hydrocarbon derivatives such as pentane, hexane, heptane, and even octane, nonane, and decane in some cases. Propane and butane, normally gases at standard temperature and pressure, may also occur in gas condensate as gases soluble in the liquid hydrocarbon derivatives. In addition, gas condensate may contain additional impurities such as hydrogen sulfide, thiols (mercaptans, RSH), carbon dioxide, cyclohexane (C_6H_{12}), and low MW aromatics such as benzene (C_6H_6), toluene (C_6H5CH_3), ethylbenzene ($C_6H_5CH_2CH_3$), and xylene derivatives ($H_3CC_6H_4CH_3$) (Mokhatab et al., 2006; Speight, 2007, 2014a).

The composition of the gas condensate can have a major influence on the production of gas and condensate at the wellhead. For example, when condensation occurs in the reservoir, the phenomenon known as condensate blockage can halt flow of the liquids to the wellbore. Hydraulic fracturing is the most common mitigating technology in siliciclastic reservoirs (reservoirs composed of clastic rocks), and acidizing is used in reservoirs composed of carbonate mineral rocks (generally referred to as carbonate reservoirs) (Speight, 2016a). Briefly, clastic rocks are composed of fragments, or clasts, of preexisting minerals and rock. A clast is a fragment of geological detritus, chunks, and smaller grains of rock broken off other rocks by physical weathering. The geological term *clastic* is used with reference to sedimentary rocks as well as to particles in sediment transport whether in suspension or as bed load and in sedimentary deposits.

1.4 Conventional Gas

Natural gas resources, like crude oil resources, are typically divided into two categories: (i) conventional gas and (ii) unconventional gas (Mokhatab et al., 2006; Speight, 2007, 2014a). For the purposes of this text, the term unconventional gas resources also include CBM and natural gas from shale formations and from tight formations as well as biogas and landfill gas (John and Singh, 2011; Ramroop Singh, 2011; Singh and Sastry, 2011; Speight, 2011c, 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.

In addition, there are several general definitions that have been applied to natural gas from conventional formations that can also be applied to gas from tight formations. 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 MW hydrocarbon derivatives. *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 MW 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 MW constituents have been removed. In natural gas technology, residue gas is natural gas from which the higher MW constituents have been removed during gas processing operations (Chapter 4) to leave methane (the lower-boiling constituent) as residue gas.

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 is emitted from the well. This 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) or butane (C_4H_{10}) may be present in condensate by dissolution in 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 ethylbenzene ($C_6H_5C_2H_5$) may also be present (Mokhatab et al., 2006; Speight, 2007, 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, 2007, 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, have higher concentrations of higher MW 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 MW hydrocarbon derivatives.

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 (i) primary thermogenic degradation of organic matter, (ii) secondary thermogenic decomposition of petroleum, and (iii) biogenic degradation of organic matter. Gas generated by thermogenic and biogenic pathways may both exist in the same shale reservoir. After generation, the gas is stored in the reservoir formation in three different ways: (i) *adsorbed gas*, which is physically attached (adsorption) or chemically attached (chemisorption) to organic matter or to clay minerals; (ii) nonadsorbed gas, also known as *free gas* (also referred to as *nonassociated gas*), which occurs within the pore spaces in the reservoir rock or in spaces created by the rock cracking (fractures or microfractures); and (iii) solution gas, also referred to as *associated gas*, which is gas that exists in solution in liquids such as petroleum and 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 (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.

1.4.1 Associated Gas

Crude oil cannot be produced without producing some associated gas, which consists of low-boiling hydrocarbon constituents that are emitted from solution in the crude oil as the pressure is reduced on the way to, and on, the surface. Well completion designs 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; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a, 2017a). Crude oil in the reservoir with minimal or no dissolved associated gas is rare and, as *dead crude oil*, 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; Hsu and Robinson, 2006; Mokhatab et al., 2006; Gary et al., 2007; Speight, 2014a, 2017a).

After the production fluids are brought to the surface, the gas is treated to separate out the higher MW NGLs, which are treated in a liquefied petroleum gas (LPG) processing (refining) plant to provide propane and butane, either separately or as a mixture of the two. By definition, NGLs include ethane, propane, butanes, pentanes, and higher MW hydrocarbon derivatives (C_{6+}). The higher MW hydrocarbon derivative product is commonly referred to as *natural gasoline* or *gas condensate*. The LPG is stored ready for transport, and the nonvolatile residue (i.e. nonvolatile under the conditions of the separation process), after 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, 2007, 2014a).

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. When referring to NGLs in the natural gas stream, the term *gallons per thousand cubic feet* of gas is used as a measure of hydrocarbon richness.

Thus, in the case of associated gas, crude oil may be assisted up the wellbore by gas lift (Mokhatab et al., 2006; Speight, 2007, 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 exit 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) (Table 1.5). The higher-boiling residue, after propane and butane are removed, is the 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.

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 of the gas is as fuel for the gas

Table 1.5 General properties of unrefined natural gas (left-hand number) and refined natural gas (right-hand number).

Relative molar mass	20–16
Carbon content (% w/w)	73–75
Hydrogen content (% w/w)	27–25
Oxygen content (weight % w/w)	0.4–0
Hydrogen-to-hydrogen atomic ratio	3.5–4.0
Density relative to air at 15 °C	1.5–0.6
Boiling temperature (°C/1 atm)	−162
Autoignition temperature (°C)	540–560
Octane number	120–130
Methane number	69–99
Vapor flammability limits (% v/v)	5–15
Flammability limits	0.7–2.1
Lower heating/calorific value ($Btu\,lb^{-1}$)	900
Methane concentration (% v/v)	100–80
Ethane concentration (% v/v)	5–0
Nitrogen concentration (% v/v)	15–0
Carbon dioxide concentration (% v/v)	5–0
Sulfur concentration (ppm, w/w)	5–0

turbines on-site. This gas is treated in a fuel gas plant to ensure it is clean and at the correct pressure. The start-up 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), and mercaptans (thiols; RSH), as well as trace amounts of other constituents, may also be present. Thus, there is no single composition of components that 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.

1.4.2 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 MW hydrocarbon derivatives may also be present but in lower quantities than found in associated gas.

Thus, *nonassociated gas* (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.

Processing of nonassociated gas is somewhat less complicated than processing of 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 MW constituents that 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, 2007, 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 that 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 water and is later recovered in a glycol plant (Mokhatab et al., 2006; Speight, 2007, 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 LGP plant. Alternatively, the lower-boiling constituents of the NGLs may be used as feedstock for the production of petrochemicals (Parkash, 2003; Hsu and Robinson, 2006; Gary et al., 2007; Speight, 2014a, 2017a).

Finally, another aspect of gas processing that requires attention (Chapter 4) 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 4). 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 counterflow of hot pressurized water.

1.4.3 Refinery Gas

The terms *refinery gas* and *petroleum gas* are often used to identify LPG or even gas that emanates from the top of a refinery distillation column. Refinery gas varies in composition and volume, depending on crude origin and on any additions to the crude made at the loading point – in this sense, it is probably the most difficult gas to analyze. Furthermore, it is not uncommon to reinject low MW hydrocarbon derivatives such as propane and butane into the crude before dispatch by tanker or pipeline. This results in a higher vapor pressure of the crude, but it allows one to increase the quantity of light products obtained at the refinery. Since light ends in most petroleum markets command a premium, while in the oil field itself propane and butane may have to be reinjected or flared, the practice of *spiking* crude oil with LPG is becoming common.

Thus, *refinery gas* (*fuel gas*) is the noncondensable gas that is obtained during distillation of crude oil or treatment (cracking, thermal decomposition) of petroleum. Refinery gas is produced in considerable quantities during the different refining processes and is used as fuel for the refinery itself and as an important feedstock to produce petrochemicals. It consists mainly of hydrogen (H_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and olefins ($RCH{=}CHR^1$, where R and R^1 can be hydrogen or a methyl group) and may also include off-gases from petrochemical processes. Olefins such as ethylene ($CH_2{=}CH_2$, boiling point: –104 °C, –155 °F), propene (propylene, $CH_3CH{=}CH_2$, boiling point: –47 °C, –53 °F), butene (butene-1, $CH_3CH_2CH{=}CH_2$, boiling point: –5 °C, 23 °F), *iso*-butylene ($(CH_3)_2C{=}CH_2$, –6 °C, 21 °F), *cis*- and *trans*-butene-2 ($CH_3CH{=}CHCH_3$, boiling point: ca. 1 °C, 30 °F), and butadiene ($CH_2{=}CHCH{=}CH_2$, boiling point: –4 °C, 24 °F) as well as higher-boiling olefins are produced by various refining processes.

Still gas is broad terminology for low-boiling hydrocarbon mixtures and is the lowest boiling fraction isolated from a distillation (*still*) unit in the refinery. If the distillation unit is separating light hydrocarbon fractions, the still gas will be almost entirely methane with only traces of ethane (CH_3CH_3) and ethylene ($CH_2{=}CH_2$). If the distillation unit is handling higher-boiling fractions, the still gas might also contain propane ($CH_3CH_2CH_3$), butane ($CH_3CH_2CH_2CH_3$),

and their respective isomers. *Fuel gas* and still gas are terms that are often used interchangeably, but the term *fuel gas* is intended to denote the product's destination – to be used as a fuel for boilers, furnaces, or heaters.

In a series of processes commercialized as Platforming, Powerforming, Catforming, and Ultraforming, paraffinic and naphthenic (cyclic nonaromatic) hydrocarbon derivatives are converted into aromatics in the presence of hydrogen and a catalyst or isomerized to more highly branched hydrocarbon derivatives. Catalytic reforming processes thus not only result in the formation of a liquid product of higher octane number but also produce substantial quantities of gases. The latter are rich in hydrogen but also contain hydrocarbon derivatives from methane to butanes, with a preponderance of propane ($CH_3CH_2CH_3$), *n*-butane ($CH_3CH_2CH_2CH_3$), and isobutane [$(CH_3)_3CH$]. The composition of these gases varies in accordance with reforming severity and reformer feedstock. Since all catalytic reforming processes require substantial recycling of a hydrogen stream, it is normal to separate reformer gas into a propane ($CH_3CH_2CH_3$) and/or a butane [$CH_3CH_2CH_2CH_3/(CH_3)_3CH$] stream, which becomes part of the refinery LPG production, and a lighter gas fraction, part of which is recycled. In view of the excess of hydrogen in the gas, all products of catalytic reforming are saturated, and there are usually no olefin-type gases present in either gas stream.

A second group of refining operations that contributes to gas production is that of the catalytic cracking processes. These include Thermofor catalytic cracking and other variants in which heavy gas oils are converted into cracked gas, LPG, catalytic naphtha, fuel oil, and coke by contacting the heavy hydrocarbon with the hot catalyst. Both catalytic and thermal cracking processes, the latter being now largely used to produce chemical raw materials, result in the formation of unsaturated hydrocarbon derivatives, particularly ethylene ($CH_2=CH_2$), as well as propylene (propene, $CH_3CH=CH_2$), isobutylene [isobutene, $(CH_3)_2C=CH_2$], and the *n*-butenes ($CH_3CH_2CH=CH_2$, and $CH_3CH=CHCH_3$) in addition to hydrogen (H_2), methane (CH_4), and smaller quantities of ethane (CH_3CH_3), propane ($CH_3CH_2CH_3$), and butane isomers [$CH_3CH_2CH_2CH_3$, $(CH_3)_3CH$]. Diolefins such as butadiene ($CH_2=CHCH=CH_2$) are also present.

Additional gases are produced in refineries with coking or visbreaking facilities for the processing of their heaviest crude fractions. In the visbreaking process, fuel oil is passed through externally fired tubes and undergoes liquid-phase cracking reactions, which result in the formation of lighter fuel oil components. Oil viscosity is therefore reduced, and some gases, mainly hydrogen, methane, and ethane, are formed. Substantial quantities of both gas and carbon are also formed in coking (both fluid coking and delayed coking) in addition to the middle distillate and naphtha. When coking a residual fuel oil or heavy gas oil, the feedstock is preheated and contacted with hot carbon (coke), which causes extensive cracking of the feedstock constituents of higher MW

to produce lower MW products ranging from methane, via LPG(s) and naphtha, to gas oil and heating oil. Products from coking processes tend to be unsaturated, and olefin-type components predominate in the tail gases from coking processes.

A further source of refinery gas is hydrocracking, a catalytic high-pressure pyrolysis process in the presence of fresh and recycled hydrogen. The feedstock is again heavy gas oil or residual fuel oil, and the process is mainly directed at the production of additional middle distillates and gasoline. Since hydrogen is to be recycled, the gases produced in this process again must be separated into lighter and heavier streams; any surplus recycle gas and the LPG from the hydrocracking process are both saturated.

Both hydrocracker and catalytic reformer tail gases are commonly used in catalytic desulfurization processes (Table 1.6). In the latter, feedstocks ranging from light to vacuum gas oils are passed at pressures of 500–1000 psi with hydrogen over a hydrofining catalyst. This results mainly in the conversion of organic sulfur compounds to hydrogen sulfide:

$$[S]_{\text{feedstock}} + H_2 \rightarrow H_2S + \text{hydrocarbon derivatives}$$

The process also produces some light hydrocarbon derivatives by hydrocracking.

The first and most important aspect of gaseous testing is the measurement of the volume of gas. However, in all cases, it is the composition of the gas in terms of *hydrocarbon type* that is more important in the context of application.

Table 1.6 Origin of petroleum-related gases.

Gas	Origin
Natural gas	Occurs naturally with or without the presence of crude oil in the reservoir
	A gaseous combination of low-boiling hydrocarbon derivatives
	Predominantly C_1 up to and including C_4 hydrocarbon derivatives
	May also contain gas condensate (C_{5+} hydrocarbon derivative) or natural gasoline (also C_{5+} hydrocarbon derivatives)
Refinery gas process gas	A combination of gases produced by distillation
	Products from the cracking of crude oil
	Consists of C_2 to C_4 hydrocarbon derivatives including olefin gases
	Boiling range of approximately −51–−1 °C (−60–30 °F)
Tail gas	A combination of hydrocarbon derivatives from the distillation of products from catalytically cracked feedstocks
	Predominantly of C_1 to C_4 hydrocarbon derivatives

For example, in petrochemical applications, the presence of propylene and butylene above 10% v/v can have an adverse effect on hydrodesulfurization prior to steam reforming. On the other hand, petrochemical processes, such as in the production of *iso*-octane from *iso*-butane and butylene, can require the exclusion of the saturated hydrocarbon derivatives. Furthermore, refinery gas specifications will vary depending on the gas quality available and the end use. For fuel uses, gas as specified above presents little difficulty used as supplied. Alternatively, a gas of constant Wobbe index, say, for gas turbine use, could readily be produced by the user. Part of the combustion air would be diverted into the gas stream by a Wobbe index controller, which would be preset to supply the gaseous fuel at the lowest Wobbe index of the undiluted gas.

Still gas is a term reserved for low-boiling hydrocarbon mixtures that represent the lowest boiling fraction isolated from an atmospheric distillation unit (*still*) in the refinery (Table 1.6). Typically, the still gas will contain methane, ethane (CH_3CH_3), propane ($CH_3CH_2CH_3$), butane ($CH_3CH_2CH_2CH_3$), and their respective isomers. If cracked products have been recycled to the atmospheric distillation unit, the still gas may also contain volatile olefins such as ethylene ($CH_2{=}CH_2$).

1.5 Unconventional Gas

There are several types of unconventional gas resources that are currently produced: (i) shale gas and tight natural gas, natural gas that occurs in low-permeability shale formations; (ii) geopressurized zones, natural underground formations that are under unusually high pressure for their depth; (iii) CBM, natural gas that occurs in conjunction with coal seams; and (iv) methane hydrates, natural gas that occurs at low-temperature and high-pressure regions such as the sea bed and is made up of a lattice of frozen water, which forms a *cage* around the methane (Mokhatab et al., 2006; Speight, 2007, 2013b, 2014a).

Typically, natural gas produced from shale reservoirs and other tight reservoirs has been classed under the general title *unconventional gas*. The production process requires stimulation by horizontal drilling coupled with hydraulic fracturing because of the extremely low permeability of the reservoir rocks that prohibits natural movement of the gas to a well. Moreover, maximization or optimization of reservoir producibility can only be achieved by a thorough understanding of the occurrence and properties of the shale gas resources as well as the producibility of the gas from the reservoir (Kundert and Mullen, 2009).

The boundary between conventional gas and unconventional gas resources is not well defined, because they result from a continuum of geologic conditions. Coal seam gas, more frequently called coalbed methane, is frequently referred to as unconventional gas. Tight shale gas and gas hydrates are also placed into the category of *unconventional gas*.

1.5.1 Gas in Geopressurized Zones

Geopressurized zones are natural underground formations that are under high pressure that is not always expected from the depth of the zone. These areas are formed by layers of clay minerals that are deposited and compacted on top of (or above) more porous, absorbent material such as sandstone or silt. Water and natural gas that are present in this clay formation are forced out by the rapid compression and enter the more porous sandstone or silt deposits. The natural gas or crude oil is deposited in this sandstone or silt under very high pressure (*geopressure*). Geopressurized zones are typically located at great depths – on the order of usually 10 000–25 000 ft below the surface of the Earth. The combination of the above factors makes the extraction of natural gas or crude oil located in geopressurized zones quite complicated (Speight, 2017b).

1.5.2 Coalbed Methane

Just as natural gas is often located in the same reservoir as with crude oil, it can also be found trapped within coal seams, where it is often referred to as coalbed methane (or *coal bed methane*, sometimes referred to as *coalmine methane*). Coalbed methane is a generic term for the methane found in most coal seams. To the purist, coalmine methane is the fraction of CBM that is released during the mining operation (referred to in the older literature as *firedamp* by miners because of its explosive nature). In practice, the terms coalbed methane and coalmine methane may usually refer to different sources of gas – both forms of gas, whatever the name, are equally dangerous to the miners. Methane in coalbeds is a gas formed as part of the geological process of coal generation and is contained in varying quantities within all coal. CBM is exceptionally pure compared with conventional natural gas, containing only very small proportions of higher MW hydrocarbon derivatives such as ethane and butane and other gases (such as hydrogen sulfide and carbon dioxide).

CBM is found within geological formations of coal deposits (Speight, 2013b). Because coal is a solid, very high carbon content mineral, there are usually no liquid hydrocarbon derivatives contained in the produced gas. The coalbed (coal seam) must first be dewatered to allow the trapped gas to flow through the formation to produce the gas. Consequently, CBM usually has a lower heating value and elevated levels of carbon dioxide, oxygen, and water that must be treated to an acceptable level, given the potential to be corrosive. However, the occurrence of methane in coal seams is not a new discovery, and methane (also called *firedamp*) was known to coal miners for at least 150 years (or more) before it was *rediscovered* and developed as CBM (Speight, 2013b). The gas occurs in the pores and cracks in the coal seam and is held there by

underground water pressure. To extract the gas, a well is drilled into the coal seam, and the water is pumped out (*dewatering*), which allows the gas to be released from the coal and brought to the surface.

CBM is predominantly methane extracted from coalbeds (coal seams) and has become an important source of energy in the United States, Canada, and other countries. The gas is adsorbed into the solid matrix of the coal and is often referred to as *sweet gas* because of its lack of hydrogen sulfide. Unlike natural gas from conventional reservoirs, CBM contains very little higher MW hydrocarbon derivatives such as propane or butane or condensate. It often contains up to a few percent of carbon dioxide. Some coal seams contain little methane, with the predominant coal seam gas being carbon dioxide. In fact, CBM has been suggested with sufficient justification that the materials comprising a coalbed fall broadly into the following two categories: (i) volatile low MW materials (components) that can be liberated from the coal by pressure reduction, mild heating, or solvent extraction and (ii) materials that will remain in the solid state after the separation of volatile components.

Typically, with some exceptions, coalbed gas is typically in excess of 90% v/v methane and, subject to gas composition data, may be suitable for introduction into a commercial pipeline with little or no treatment (Rice, 1993; Levine, 1993; Mokhatab et al., 2006; Speight, 2007, 2013a). Methane within coalbeds is not structurally trapped by overlying geologic strata, as in the geologic environments typical of conventional gas deposits (Speight, 2007, 2013a, 2014a). Only a small amount (on the order of 5–10% v/v) of the CBM is present as free gas within the joints and cleats of coalbeds. Most of the CBM is contained within the coal itself (adsorbed to the sides of the small pores in the coal).

As the coal forms from the organic detritus (the precursor material), large quantities of methane-rich gas are produced and subsequently adsorbed onto the surface and within the pore system of the coal matrix. Because of its many natural cracks and fissures, as well as its porous nature, coal in the seam has a large internal surface area and can store much more gas than a conventional natural gas reservoir of similar rock volume. If a seam is disturbed, either during mining or by drilling into it before mining, methane is released from the surface and interior of the coal. This methane then leaks into any open spaces such as fractures in the coal seam (known as *cleats*). In these fractures, the coalmine methane mixes with nitrogen and carbon dioxide (CO_2). Boreholes or wells can be drilled into the seams to recover the methane. Large amounts of coal are found at shallow depths, where wells to recover the gas are relatively easy to drill at a relatively low cost. At greater depths, increased pressure may have closed the fractures, or minerals may have filled the fractures over time, lowering the permeability and thereby making it more difficult for the methane (and any other gases) to move through the coal seam.

The primary (or natural) permeability of coal is very low, typically ranging from 0.1 to 30 mD, and because coal is a very weak (low modulus) material and

cannot take much stress without fracturing, it is almost always highly fractured and cleated. The resulting network of fractures commonly gives coalbeds a high secondary permeability (despite coal's typically low primary permeability). Groundwater, hydraulic fracturing fluids, and methane gas can more easily flow through the network of fractures. Because hydraulic fracturing generally enlarges preexisting fractures in addition to creating new fractures, this network of natural fractures is very important to the extraction of methane from the coal (Speight, 2013b, 2016b).

The gas from coal seams can be extracted by using technologies that are similar to those used to produce conventional gas, such as using wellbores. However, complexity arises from the fact that the coal seams are generally of low permeability and tend to have a lower flow rate (or permeability) than conventional gas systems, gas is only sourced from close to the well, and as such a higher density of wells is required to develop a CBM resource as an unconventional resource (such as tight gas) than a conventional gas resource.

Technologies such as horizontal and multilateral drilling with hydraulic fracturing are sometimes used to create longer, more open channels that enhance well productivity, but not all coal seam gas wells require application of this technique (Speight, 2013a, 2016b). Water present in the coal seam, either naturally occurring or introduced during the fracturing operation, is usually removed to reduce the pressure sufficiently to allow the gas to be released, which leads to additional operational requirements, increased investment, and environmental concerns. There are some horizontally drilled CBM wells and some that receive hydraulic fracturing treatments. However, some CBM reservoirs are also underground sources of drinking water, and as such, there are restrictions on hydraulic fracturing operations. CBM wells are mostly shallow, as the coal matrix does not have the strength to maintain porosity under the pressure of significant overburden thickness.

1.5.3 Gas in Tight Formations

The term *tight formation* refers to a formation consisting of extraordinarily impermeable, hard rock (Speight, 2013a). Tight formations are relatively low-permeability, nonshale, sedimentary formations that can contain oil and gas. A *tight reservoir* (*tight sands*) is a low-permeability sandstone reservoir that produces primarily dry natural gas. A tight gas reservoir is one that cannot be produced at economic flow rates or recover economic volumes of gas unless the well is stimulated by a large hydraulic fracture treatment and/or produced using horizontal wellbores. This definition also applies to CBM and tight carbonate reservoirs – shale gas reservoirs are also included by some observers (but not in this text). Typically, tight formations that formed under marine conditions contain less clay and are more brittle and thus more suitable for

hydraulic fracturing than formations formed in freshwater that may contain more clay. The formations become more brittle with an increase in quartz content (SiO_2) and carbonate content (such as calcium carbonate, $CaCO_3$, or dolomite, $CaCO_3{\cdot}MgCO_3$).

By way of explanation and comparison, in a conventional sandstone reservoir, the pores are interconnected so that natural gas and crude oil can flow easily through the reservoir and to the production well. However, in tight sandstone formations, the pores are smaller and are poorly connected (if at all) by very narrow capillaries, which results in low permeability and immobility of the natural gas. Such sediments typically have an effective permeability of less than 1 millidarcy (<1 mD).

Shale is a sedimentary rock characterized by low permeability (Aguilera and Radetzki, 2014; Khosrokhavar et al., 2014), mainly compositing of mud, silts, and clay minerals, but, however, this composition varies with burial depth and tectonic stresses (Moslemizadeh et al., 2015). Shale reservoirs have a permeability that is three orders times less than tight gas reservoirs (Khosrokhavar et al., 2014). Natural gas and light tight oil (sometime erroneously referred to as shale oil – by way of definition, shale oil is the liquid product produced by the decomposition of the kerogen component of oil shale) are confined in the pore spaces of these impermeable rocks. The gas in a shale formation is present as a free gas in the pore spaces or is adsorbed by clay minerals and organic matters (Ross and Bustin, 2009). The free gas will be produced upon well completion, but the production of adsorbed gas depends on the pressure drop needed for desorption. It is, therefore, essential to know the relative amounts of free and adsorbed gas in shales. On the other hand, oil shale is a kerogen-rich petroleum source rock that was not buried under the correct maturation conditions to experience the temperatures required to generate oil and gas (Speight, 2014a, AAPG, 2015).

Natural gas from shale formations and other formations designated as and tight formations (i.e. formations having zero to extremely low permeability) offers additional energy-producing resources. This gas can be recovered from such formations that typically function as both the reservoir rock and the source rock. The tight formations that yield gas and oil are organic-rich shale formations that were previously regarded only as source rocks as well as seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas development.

In addition, the gas storage properties of such formations are quite different to conventional reservoirs. In the case of shale formations, the natural gas present in the matrix system of pores – similar to that found in conventional reservoir rocks – is accompanied by gas that is bound to, or adsorbed on, the surface of inorganic minerals the formation, especially clay minerals that are often present in shale. The relative contributions and combinations of free gas from matrix porosity and from desorption of adsorbed constituents is a key

determinant of the production profile of the well. Thus, by definition, *shale gas* is the hydrocarbon gas present in organic-rich, fine-grained sedimentary rocks (shale and associated lithofacies). The gas is generated and stored *in situ* in gas shale as both adsorbed gas (on organic matter) and free gas (in fractures or pores). As such, shale containing gas is a self-sourced reservoir. Low-permeable shale requires extensive fractures (natural or induced) to produce commercial quantities of gas.

In terms of chemical makeup, shale gas is typically a dry gas composed primarily of methane (60–95% v/v), but some formations do produce wet gas (Table 1.7). The Antrim and New Albany plays have typically produced water and gas. Gas shale formations are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas development.

Tight gas is the fastest-growing natural gas resource in the United States and worldwide because of several recent developments. Advances in horizontal drilling technology allow a single well to pass through larger volumes of a shale gas reservoir and, thus, produce more gas. The development of hydraulic fracturing technology has also improved access to shale gas deposits. This process requires injecting large volumes of water mixed with sand and fluid chemicals into the well at high pressure to fracture the rock, increasing permeability and production rates.

Table 1.7 Composition of dry gas, wet gas, and gas condensate.

Component or property	Dry gas	Wet gas	Condensate
CO_2	0.10	1.41	2.37
N_2	2.07	0.25	0.31
C_1	86.12	92.46	73.19
C_2	5.91	3.18	7.80
C_3	3.58	1.01	3.55
i C_4	1.72	0.28	0.71
n C_4	—	0.24	1.45
i C_5	0.50	0.13	0.64
n C_5	—	0.08	0.68
C_6	—	0.14	1.09
C_{7+}	—	0.82	8.21
Molecular weight C_{7+}	—	132	184
Specific gravity C_{7+}	—	0.750	0.816

Briefly, to further define the terms *dry gas* and *wet gas* in quantitative measures, the term *dry* natural gas indicates that there is less than 0.1 gal (1 gal, US = 264.2 m^3) of gasoline vapor (higher MW paraffins) per 1000 ft^3 (1 ft^3 = 0.028 m^3). The term *wet natural gas* indicates that there are such paraffins present in the gas, in fact more than 0.1 gal/1000 ft^3.

The shale formations that yield gas and oil are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas development. On the other hand, the crude oil from shale formations is a light, highly volatile crude oil that contains more of the volatile hydrocarbon derivatives (C1–C4) than many conventional crude oils. In addition, the gas and oil storage properties of shale are quite different to conventional reservoirs. In the case of shale formations, the natural gas and crude oil present in the matrix system of pores – like the gas found in conventional reservoir rocks – is accompanied by gas or oil that is bound to, or adsorbed on, the surface of inorganic minerals in the shale. The relative contributions and combinations of free gas and oil from matrix porosity and from desorption of adsorbed constituents are a key determinant of the production profile of the well.

Natural gas from shale and tight formations offer additional energy-producing resources that can be recovered from shale formations that typically function as both the reservoir rock and the source rock. In terms of chemical makeup, shale gas is typically a dry gas of which methane is the primary constituent, but some formations do produce wet gas. The shale formations that yield gas are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas development. In the case of shale formations, the natural gas present in the matrix system of pores – like that found in conventional reservoir rocks – is accompanied by gas that is bound to, or adsorbed on, the surface of inorganic minerals in the shale. The relative contributions and combinations of free gas from matrix porosity and from desorption of adsorbed constituents is a key determinant of the production profile of the well.

1.5.4 Gas Hydrates

In addition to CBM (Section 1.5.2), another relatively new and possibly large source of methane that can be expected to extend the availability of natural gas is *methane hydrate* (also called *gas hydrate* and *methane ice*). Their production technologies have only recently been developed, and these sources are now becoming economically competitive.

Methane hydrates (also called *methane clathrates*) are a resource in which a large amount of methane is trapped within a crystal structure of water, forming

a solid that resembles ice (Kvenvolden and McMenamin, 1980; Kvenvolden, 1995; Lorenson and Collett, 2000; Buffett and Archer, 2004; Gao et al., 2005; Gao, 2008; USGS, 2011). Natural gas hydrates are solids that form from a combination of water and one or more hydrocarbon or nonhydrocarbon gases. In physical appearance, gas hydrates resemble packed snow or ice. In a gas hydrate, the gas molecules (such as methane, hence the name *methane hydrates*) are trapped within a cagelike crystal structure composed of water molecules. Gas hydrates are stable only under specific conditions of pressure and temperature. Under an appropriate pressure, they can exist at temperatures significantly above the freezing point of water. The maximum temperature at which gas hydrate can exist depends on pressure and gas composition. For example, methane plus water at 600 psia forms hydrate at 5 °C (41 °F), while at the same pressure, methane with 1% v/v propane forms a gas hydrate at 9.4 °C (49 °F). Hydrate stability can also be influenced by other factors, such as salinity (Edmonds et al., 1996).

Estimates of the global inventory of methane clathrate have exceeded 10^{19} g of carbon (MacDonald, 1990a, b; Gornitz and Fung, 1994), which is comparable with estimates of potentially recoverable coal, oil, and natural gas. The proximity of this methane reservoir to the seafloor has motivated speculations about a release of methane in response to climate change (MacDonald, 1990b). Increases in temperature or decreases in pressure (through changes in sea level) tend to dissociate clathrate, releasing methane into the near-surface environment. Release of methane from clathrate has been invoked to explain abrupt increases in the atmospheric concentration of methane during the last glacial cycle.

On a unit volume basis, gas hydrates contain a high amount of gas. For example, 1 cubic yard of hydrate disassociates at atmospheric temperature and pressure to form approximately 160 cubic yards of natural gas plus 0.8 cubic yards of water (Kvenvolden, 1993). The natural gas component of gas hydrates is typically dominated by methane, but other natural gas components (e.g. ethane, propane, carbon dioxide) can also be incorporated into a hydrate. The origin of the methane in a hydrate can be either thermogenic gas or biogenic gas. Bacterial gas formed during early digenesis of organic matter can become part of a gas hydrate in continental shelf sediment. Similarly, thermogenic gas leaking to the surface from a deep thermogenic gas accumulation can form a gas hydrate in the same continental shelf sediment (Collett, 2002; Gupta, 2004; Collett et al., 2009; Demirbaş, 2010a, b, c; Chong et al., 2016).

Generally, methane clathrates are common constituents of the shallow marine geosphere, and they occur both in deep sedimentary structures and form outcrops on the ocean floor. Methane hydrates are believed to form by migration of gas from depth along geological faults, followed by precipitation, or crystallization, on contact of the rising gas stream with cold seawater. When

drilling in petroleum-bearing and gas-bearing formations submerged in deep water, the reservoir gas may flow into the wellbore and form gas hydrates owing to the low temperatures and high pressures found during deepwater drilling. The gas hydrates may then flow upward with drilling mud or other discharged fluids. When the hydrates rise, the pressure in the annulus decreases and the hydrates dissociate into gas and water. The rapid gas expansion ejects fluid from the well, reducing the pressure further, which leads to more hydrate dissociation (sometimes explosive dissociation) and further fluid ejection.

As might be anticipated, the gas that is evolved from gas hydrates under laboratory conditions is composed of the following hydrocarbon gases: methane (C1), ethane (C2), and the sum C3+, composed of propane (C3), isobutane (*i*-C4), and *n*-butane (*n*-C4) (Lorenson and Collet, 2000). Other hydrocarbon gases present in some sediments include neopentane (neo—C5), isopentane (*i*-C5), *n*-pentane (*n*-C5), cyclopentane (cycloC5), neohexane (neo—C6), isohexane (*i*-C6), *n*-hexane (*n*-C6), isoheptane (*i*-C7), and methylcyclohexane (Lorenson and Collet, 2000). The composition of the gaseous product varies over a considerable range. Hydrogen sulfide (H_2S) has been detected in gas hydrates, but because hydrogen sulfide is water soluble and the gas hydrate dissociation measurements have the potential to be contaminated with some sediment and pore water, it is also possible that in some cases hydrogen sulfide may not have existed within the gas hydrate structure (Lorenson and Collet, 2000).

1.5.5 Coal Gas

Coal gas is any gaseous product that is produced by gasification of coal or by carbonization of coal. Most of these products have been replaced by natural gas (the city and town gas works is an industry of the past) but still find use in some parts of the world. The products of coal gasification are varied insofar as the gas composition varies with the system employed. It is emphasized that the gas product must be first freed from any pollutants such as particulate matter and sulfur compounds before further use, particularly when the intended use is a water–gas shift or methanation.

Low-heat-content gas (low-Btu gas) is produced when the oxygen is not separated from the air (ca. 150–300 Btu ft^{-3}). This gas is also the usual product of *in situ* gasification of coal, which is used essentially as a technique for obtaining energy from coal without the necessity of mining the coal. The process is a technique for utilization of coal that cannot be mined by other techniques. The nitrogen content of low-heat-content gas ranges from somewhat less than 33% v/v to slightly more than 50% v/v and cannot be removed by any reasonable means; the presence of nitrogen at these levels renders the product gas to be low heat content. The nitrogen also strongly limits the applicability of the gas to chemical synthesis. Two other noncombustible components (water, H_2O,

and carbon dioxide, CO) further lower the heating value of the gas; water can be removed by condensation and carbon dioxide by relatively straightforward chemical means. The two major combustible components are hydrogen and carbon monoxide; the H_2/CO ratio varies from approximately 2 : 3 to 3 : 2, but methane may also make an appreciable contribution to the heat content of the gas. Of the minor components hydrogen sulfide is the most significant, and the amount produced is, in fact, proportional to the sulfur content of the feed coal. Any hydrogen sulfide present must be removed by one, or more, of several procedures. Low-heat-content gas is of interest to industry as a fuel gas or even, on occasion, as a raw material from which ammonia, methanol, and other compounds may be synthesized.

Medium-heat-content gas (medium-Btu gas) has a heating value in the range of 300–550 Btu ft^{-3}, and the composition is much like that of low-heat-content gas, except that there is virtually no nitrogen. The primary combustible gases in medium-heat-content gas are hydrogen and carbon monoxide. Medium-heat-content gas is considerably more versatile than low-heat-content gas; like low-heat-content gas, medium-heat-content gas may be used directly as a fuel to raise steam or used through a combined power cycle to drive a gas turbine, with the hot exhaust gases employed to raise steam, but medium-heat-content gas is especially amenable to synthesize methane (by methanation), higher hydrocarbon derivatives (by Fischer–Tropsch synthesis), methanol, and a variety of synthetic chemicals. The reactions used to produce medium-heat-content gas are the same as those employed for low-heat-content gas synthesis, the major difference being the application of a nitrogen barrier (such as the use of pure oxygen) to keep diluent nitrogen out of the system.

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

High-heat-content gas (high-Btu gas) is essentially pure methane and often referred to as *synthetic natural gas* or *substitute natural gas*. However, to qualify as substitute natural gas, a product must contain at least 95% methane; the energy content of SNG is 980–1080 Btu ft^{-3}. The commonly accepted approach to the synthesis of high-heat-content gas is the catalytic reaction of hydrogen and carbon monoxide:

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

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

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

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

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

1.5.6 Biogas

On the other hand, biogas is gas produced from biological materials either by fermentation or by pyrolysis, while landfill gas is, as the name implied, gas produced during the *in situ* maturation of landfill materials, which can include municipal waste and industrial waste. Thus, *biomass* is the collective name for *renewable materials* that includes (i) energy crops grown specifically to be used as fuel, such as wood or various types of grass; (ii) agricultural residues and by-products, such as straw, sugarcane fiber, rice hulls, and animal waste; and (iii) residues from forestry, construction, and other wood-processing industries. Biomass is a renewable resource that has received great attention due to environmental considerations and the increasing demands of energy worldwide. It has a negligible content of sulfur, nitrogen, and ash that produces lower emissions of sulfur dioxide, nitrogen oxides, and soot than conventional fossil fuels. Following from this, a *biofuel* is any fuel that is derived from biomass. A biofuel has also been defined as any fuel with an 80% v/v minimum content of materials derived from living organisms harvested within the 10 years preceding its manufacture.

Biogas (often predominantly methane, also called biogenic gas and sometimes incorrectly known as swamp gas) typically refers to a biofuel gas produced by anaerobic digestion or fermentation of organic matter including manure, sewage sludge, municipal solid waste, biodegradable waste, or any other biodegradable feedstock under anaerobic conditions. Depending on where it is produced, biogas is also called swamp gas, marsh gas, landfill gas, and digester gas.

Biogas is produced by certain types of bacteria (methanogens) during the process of breaking down organic matter in an oxygen-free environment. Examples of biomass are (i) wood and wood-processing wastes; (ii) agricultural crops and waste materials; (iii) food, yard, and wood waste in garbage; and (iv) animal manure and human sewage, which are all potential sources of biogas (biogenic gas). Biogas production (typically an anaerobic process) is a multi-step biological process where the originally complex and large organic solid wastes are progressively transformed in simpler and smaller-sized organic compounds by different bacteria strains up to have a final energetically worthwhile gaseous product and a semisolid material (digestate) that is rich in nutrients and thus suitable for its utilization in farming.

The composition of biogas varies depending upon the composition of the waste material in the landfill and the anaerobic digestion process. Landfill gas typically has methane concentration around 50%. Advanced waste treatment technologies can produce biogas with 55–75% v/v methane; often air is introduced (5% by volume) for microbiological desulfurization. For example, the constituents (by volume) of biogas generally are methane (50–75%), carbon dioxide (25–50%), nitrogen (0–10%), hydrogen (0–1%), hydrogen sulfide (0–3%), and oxygen (0–2%).

Biogas is characterized based on the chemical composition and the physical characteristics that result from it, including the methane content (Esposito et al., 2012). It is primarily a mixture of methane (CH_4) and inert carbonic gas (CO_2). However, the name biogas covers a wide variety of gases resulting from specific treatment processes, starting from various organic waste such as industrial waste, animal waste, or waste of domestic origin waste. Different sources of production lead to different specific compositions of the biogas (Table 1.8).

Table 1.8 Examples of biogas composition.

Constituents	Source-1	Source-2	Source-3
Methane, CH_4% v/v	50–60	60–75	60–75
Carbon dioxide, CO_2% v/v	38–34	33–19	33–19
Nitrogen, N_2% v/v	5–0	1–0	1–0
Oxygen, O_2% v/v	1–0	<0,5	<0,5
Water, H_2O% v/v	6 (40 °C)	6 (40 °C)	6 (40 °C)
Hydrogen sulfide, H_2S mg m^{-3}	100–900	1000–4000	3000–10 000
Ammonia, NH_3 mg m^{-3}	—	—	50–100

Source-1: Household waste.
Source-2: Wastewater treatment plant sludge.
Source-3: Agricultural waste.

Biogas is produced by methanogenic organisms in swamps and marshes by the decomposition of organic (both animal and plant) matter. The anaerobic (low or no oxygen present in the system) decomposition produces methane, carbon dioxide, a small amount of hydrogen, and a small amount of heat. Acidity, the carbon to nitrogen ratio of the feedstock, temperature, and percentage of solids are factors that influence the quality and quantity of biogas produced. Normally, cow manure, enriched by vegetable matter, is the ideal feedstock. The other principal type of biogas is wood gas, which is produced by gasification of wood or another biomass. This type of biogas is composed primarily of nitrogen, hydrogen, and carbon monoxide, with trace amounts of methane. Industrial anaerobic digesters and mechanical biological treatment systems are becoming increasingly popular. Methane is a potent greenhouse gas but is also a very clean, easy-burning fuel, and hence harnessing it from natural sources such as landfills is beneficial to the natural environment.

Biogas presents characteristics interesting to compare with natural gas and propane. It is a gas appreciably lighter than air; it produces twice as less calories by combustion with equal volume of natural gas. The presence of hydrogen sulfide, carbon dioxide, and water makes biogas very corrosive and requires the use of adapted materials. The composition of a gas issued from a digester depends on the substrate, its organic matter load, and the feeding rate of the digester.

When biogas is sent to processing for impurity removal, the characteristics of the resulting purified biogas are similar to that of a natural gas. In this instance the producer of the biogas can utilize the local gas distribution networks. The gas must be very clean to reach pipeline quality. Water (H_2O), hydrogen sulfide (H_2S), and particulates are removed if present at high levels or if the gas is to be completely cleaned. Carbon dioxide is less frequently removed, but it must also be separated to achieve pipeline quality gas. If the gas is to be used without extensive cleaning, it is sometimes cofired with natural gas to improve combustion. Biogas cleaned up to pipeline quality is called renewable natural gas. In this form the gas can be used in any application in which natural gas is used. The heating value of the raw biogas is on the order of 600 Btu ft^{-3} (5340 cal m^{-3}). The raw gas will burn in an engine, but corrosion can occur unless proper materials of construction are selected.

1.5.7 Landfill Gas

Landfill gas, which is often included under the umbrella definition of biogas, is also produced from the decay of organic wastes (such as municipal solid waste that contains organic materials), but these wastes may not be biomass-type materials (Lohila et al., 2007; Staley and Barlaz, 2009; Speight, 2011c). Landfills

offer another underutilized source of biogas. When municipal waste is buried in a landfill, bacteria break down the organic material contained in garbage such as newspapers, cardboard, and food waste, producing gases such as carbon dioxide and methane. Rather than allowing these gases to go into the atmosphere, where they contribute to global warming, landfill gas facilities can capture them, separate the methane, and combust it to generate electricity, heat, or both.

Thus, landfill gas is another source of biogas generated from the decomposition of the biodegradable organic fraction of municipal solid waste by microorganisms. This generally occurs under semicontrolled conditions in a landfill; its constituents depend on the composition and age of the waste. Large variations may exist in the composition of landfill gas due to differences in sources of municipal solid waste and operating conditions at the landfill. The three main gas constituents, namely, methane (CH_4), carbon dioxide (CO_2), and hydrogen sulfide (H_2S), are used to characterize landfill gas.

The gas is a complex mix of different gases created by the action of microorganisms within a landfill. Typically, landfill gas is composed of 45–60% v/v methane, 40–60% v/v carbon dioxide, 0–1.0% v/v hydrogen sulfide, 0–0.2% v/v hydrogen (H_2), trace amounts of nitrogen (N_2), low MW hydrocarbon derivatives (dry volume basis), and water vapor (saturated). The specific gravity of landfill gas is approximately 1.02–1.06. Trace amounts of other volatile organic compounds comprise the remainder (typically, 1–2% v/v or less), and these trace gases include a large array of species, such as low MW hydrocarbon derivatives. Other minor components include hydrogen sulfide, nitrogen oxides, sulfur dioxide, nonmethane volatile organic compounds, polycyclic aromatic hydrocarbon derivatives, polychlorinated dibenzodioxin derivatives, and polychlorinated dibenzofuran derivatives (Brosseau, 1994; Rasi et al., 2007). All of the aforementioned agents are harmful to human health at high doses.

The gases produced within a landfill site can be collected for various uses, such as direct utilization on-site in a boiler or any type of combustion system, providing heat. Electricity can also be generated on-site through the use of microturbines, steam turbines, or fuel cells (Sullivan, 2010). The landfill gas can also be sold off-site and sent into natural gas pipelines. This approach requires the gas to be processed into pipeline quality, e.g. by removing various contaminants and components. As should be expected, the amount of methane that is produced varies significantly based on the composition of the waste (Staley and Barlaz, 2009). The efficiency of gas collection at landfills directly impacts the amount of energy that can be recovered – closed landfills (those no longer accepting waste) collect gas more efficiently than open landfills (those that are still accepting waste).

Landfill gas collection is typically accomplished through the installation of wells installed vertically and/or horizontally in the waste mass. Design

heuristics for vertical wells call for about one well per acre of landfill surface, whereas horizontal wells are normally spaced about 50–200 ft apart on center. Efficient gas collection can be accomplished at both open and closed landfills, but closed landfills have systems that are more efficient, owing to greater deployment of collection infrastructure since active filling is not occurring. On average, closed landfills have gas collection systems that capture approximately 84% v/v of produced gas, compared with approximately 67% v/v for open landfills.

Landfill gas can also be extracted through horizontal trenches instead of vertical wells. Both systems are effective at collecting. Landfill gas is extracted and piped to a main collection header, where it is sent to be treated or flared. The main collection header can be connected to the leachate collection system to collect condensate forming in the pipes. A blower is needed to pull the gas from the collection wells to the collection header and further downstream. However, landfill gas cannot be distributed through utility natural gas pipelines unless it is cleaned up to less than 3% carbon dioxide and a few parts per million of hydrogen sulfide, because carbon dioxide and hydrogen sulfide corrode the pipelines (Speight, 2014b). The presence of carbon dioxide will lower the energy level of the gas below requirements for the pipeline. Siloxane derivatives in the gas will form deposits in gas burners and need to be removed prior to entry into any gas distribution or transmission system. Consequently, it may be more economical to burn the gas on-site or within a short distance of the landfill using a dedicated pipeline. Water vapor is often removed, even if the gas is burned on-site. If low temperatures condense water out of the gas, siloxane derivatives can be lowered as well because they tend to condense out with the water vapor. Other nonmethane components may also be removed to meet emission standards, to prevent fouling of the equipment, or for environmental considerations. Cofiring landfill gas with natural gas improves combustion, which lowers emissions.

Finally, although not strictly a gas, landfill gas condensate is a liquid that is produced in landfill gas collection systems. The condensate is removed as the gas is withdrawn from landfills. Production of condensate may be through natural or artificial cooling of the gas or through physical processes such as volume expansion. Condensate is composed principally of water and organic compounds. Often the organic compounds are not soluble in water, and the condensate separates into a watery (aqueous) phase and a floating organic (hydrocarbon) phase. This organic fraction may comprise up to 5% of the liquid.

The organic phase varies in volume and composition among sites and may range from less than 1 to 5% (by volume) of the total mixture. In general, the aqueous phase is mostly water and trace organic compounds. The organic phase consists principally of hydrocarbon derivatives, xylene isomers, chloroethane derivatives, chloroethylene derivatives, benzene, toluene, other priority

pollutants, and trace moisture. However, a larger number of acid and base/neutral compounds are present in the aqueous than in the organic phase of the condensate. Concentration levels may be orders of magnitude higher in the organic phase than the aqueous phase and are dependent upon the types of compounds in the landfill (Briggs, 1988).

1.5.8 Flue Gas

Flue gas (sometimes called *exhaust gas* or *stack gas*) is gas that is generated through, in the current context, the combustion of a carbonaceous fuel. The steam generators in large power plants and the process furnaces in large refineries petrochemical plants, and incinerators, burn considerable amounts of carbonaceous fuels and therefore emit large amounts of flue gas to the ambient atmosphere. As with other gases, the composition of flue gas depends on the type of fuel and the combustion conditions, e.g. the air ratio value. Many flue gas components are air pollutants and must therefore, due to governmental regulations, be eliminated or minimized by special cleaning procedures before the gas is released to the atmosphere.

A typical flue gas from the combustion of a carbonaceous fuel contains varying amounts of nitrogen oxides (NOx), sulfur dioxide (SO_2), and particulate matter. The nitrogen oxides are derived from the nitrogen in the ambient air as well as from any nitrogen-containing compounds in the fuel. The sulfur dioxide is derived from any sulfur-containing compounds in the fuel. The particulate matter is composed of very small particles of solid materials and very small liquid droplets, which give flue gases their smoky appearance.

When burning coal, hydrogen chloride and hydrogen fluoride may be present in the flue gas as well as hydrocarbon derivatives and heavy metals in case of incineration of waste materials. In many countries, as part of a national environmental protection program, exhaust gases must comply with strict governmental regulations regarding the limit values of pollutants such as dust, sulfur and nitrogen oxides, and carbon monoxide. To meet these limit values, combustion plants are equipped with flue gas cleaning systems such as gas scrubbers and dust filters.

Thus, as environmental regulations regarding sulfur dioxide emissions have been enacted in many countries, sulfur dioxide is removed from flue gases by a variety of methods. Examples of common flue gas cleaning processes are (i) wet scrubbing process, which uses a slurry of alkaline sorbent, usually limestone or lime, or seawater to scrub the gases; (ii) spray-dry scrubbing process, which uses similar sorbent slurries as described in the first category; (iii) wet sulfuric acid process, which allows the recovery of sulfur in the form of commercial quality sulfuric acid; (iv) a process commonly referred to as a SNOX flue gas desulfurization process, which removes sulfur dioxide, nitrogen oxides, and particulate matter from flue gases; and (v) a dry sorbent injection process,

which introduces powdered hydrated lime or other sorbent materials into the exhaust ducts to eliminate sulfur dioxide and sulfur trioxide from the process emissions.

1.6 Natural Gas and Energy Security

In terms of reserves, natural gas is produced on all continents except Antarctica. The proved reserves of natural gas are of the order of 6588.8 trillion cubic feet ($1\,\text{Tcf} = 1 \times 10^{12}\,\text{ft}^3$), of which approximately 374 Tcf exist in the United States and Canada (BP, 2017). It should also be remembered that the total gas resource base (like any fossil fuel or mineral resource base) is dictated by economics. Therefore, when resource data are quoted, some attention must be given to the cost of recovering those resources. Most importantly, the economics must also include a cost factor that reflects the willingness to secure total, or a specific degree of, energy independence. The total proved reserves of natural gas generally taken to be those quantities that geological and engineering information indicates with reasonable certainty can be recovered in the future from known reservoirs under existing economic and operating conditions.

A common misconception about natural gas is that resources are being depleted at an alarming rate and the supplies are quickly running out. In fact, there is a vast amount of natural gas estimated to still be retrieved from a variety of reservoirs. However, many proponents of the rapid-depletion theory believe that price spikes indicate that natural gas resources are depleted beyond the point of no return. However, price spikes of any commodity are not always caused by waning resources but can be the outcome of other forces at work in the marketplace.

Energy security is the continuous and uninterrupted availability of energy to a specific country or region. The security of energy supply conducts a crucial role in decisions that are related to the formulation of energy policy strategies. The economies of many countries are dependent on the energy imports in the notion that their balance of payments is affected by the magnitude of the vulnerability that the countries have in crude oil and natural gas (Speight, 2011b).

Energy security has been an on-again-off-again political issue in the United States since the first Arab oil embargo in 1973. Since that time, the speeches of various presidents and the Congress of the United States have continued to call for an end to the dependence on foreign oil and gas by the United States. The congressional rhetoric of energy security and energy independence continues, but meaningful suggestions of how to address this issue remain few and far between.

The energy literature and numerous statements by officials of oil-and-gas-producing and oil-and-gas-consuming countries indicate that the concept of

energy security is elusive. Definitions of energy security range from uninterrupted oil supplies to the physical security of energy facilities to support for biofuels and renewable energy resources. Historically, experts and politicians referred to *security of oil supplies* as *energy security*. Only recently policy makers started to include natural gas supplies in the portfolio of energy definitions.

The security aspects of natural gas are similar, but not identical, to those of oil. Compared with oil imports, natural gas imports play a smaller role in most importing countries – mainly because it is less costly to transport liquid crude oil and petroleum products than natural gas. Natural gas is transported by pipeline over long distances because of the pressurization costs of transmission; the need to finance the cost of these pipelines encourages long-term contracts that dampen price volatility.

The past decade has yielded substantial change in the natural gas industry. Specifically, there has been rapid development of technology allowing the recovery of natural gas from shale formations. Since 2000, rapid growth in the production of natural gas from shale formations in North America has dramatically altered the global natural gas market landscape. Indeed, the emergence of shale gas is perhaps the most intriguing development in global energy markets in recent memory.

Beginning with the Barnett shale in northeast Texas, the application of innovative new techniques involving the use of horizontal drilling with hydraulic fracturing has resulted in the rapid growth in production of natural gas from shale. Knowledge of the shale gas resource is not new as geologists have long known about the existence of shale formations, and accessing those resources was long held in the geology community to be an issue of technology and cost. In the past decade, innovations have yielded substantial cost reductions, making shale gas production a commercial reality. In fact, shale gas production in the United States has increased from virtually nothing in 2000 to over 10 billion cubic feet per day (bcfd, 1×10^9 ft^3 per day) in 2010, and it is expected to more than quadruple by 2040, reaching 50% or more of total US natural gas production by the decade starting in 2030.

Natural gas – if not disadvantaged by government policies that protect competing fuels, such as coal – stands to play a very important role in the US energy mix for decades to come. Rising shale gas production has already delivered large beneficial impacts to the United States. Shale gas resources are generally located in close proximity to end-use markets where natural gas is utilized to fuel industry, generate electricity, and heat homes. This offers both security of supply and economic benefits.

The *Energy Independence and Security Act of 2007* (originally named the *Clean Energy Act of 2007*) is an Act of Congress concerning the energy policy of the United States. The stated purpose of the act is "to move the United States toward greater energy independence and energy security, to increase the

production of clean renewable fuels, to protect consumers, to increase the efficiency of products, buildings, and vehicles, to promote research on and deploy greenhouse gas capture and storage options, and to improve the energy performance of the Federal Government, and for other purposes."

The bill originally sought to cut subsidies to the petroleum industry in order to promote petroleum independence and different forms of alternative energy. These tax changes were ultimately dropped after opposition in the Senate, and the final bill focused on automobile fuel economy, development of biofuels, and energy efficiency in public buildings and lighting. It was, and still is, felt by many observers that there should have been greater recognition of the role that natural gas can play in energy security. In fact, viewed from the perspective of the energy-importing countries as a whole, diversification in oil supplies has remained constant over the last decade, while diversification in natural gas supplies has steadily increased. Given the increasing importance of natural gas in world energy use, this is an indicator of an increase in overall energy security (Cohen et al., 2011).

However, natural gas is an attractive fuel, and its attraction is growing because of its clean-burning characteristics, compared with oil or coal, and because of its price advantage, on an energy equivalent basis, compared with oil. Accordingly, analysts predict significant future growth in natural gas consumption worldwide and growth in the trade of natural gas. Significant investments are being made to meet this future demand by bringing so-called stranded gas (including *shale gas*) to market.

Current trends suggest that natural gas will gradually become a global commodity with a single world market, just like oil, adjusted for transportation differences. The outcome of a global gas market is inevitable; once this occurs, the tendency will be toward a world price of natural gas, as with oil today, and the prices of oil and gas each will reach a global equivalence based on energy content (Deutch, 2010).

These trends also indicate the need for continuing development of methods for the analysis of natural gas.

1.7 Natural Gas Regulations

No matter what one can hear from various pundits, it is advantageous to accept that natural gas is dangerous – when mixed with air, it can form an explosive mixture at specific low concentrations, between a lower explosion limit (LEL) and an upper explosion limit (UEL). However, it can burn as a flame at the point of leakage. In an open land installation, the gas normally disperses quickly. However, in a closed system, simple explosions and boiling liquid expanding vapor explosions (BLEVE) can (will) cause serious damage. The latter is caused if a flame impinges on a vessel containing liquefied gas. Adequate

ventilation is required by all safety codes for all enclosed spaces. It is possible to prevent a catastrophe by a chain of preventive measures. Insofar as the condition of the environment is important to floral and faunal life on Earth, any serious disturbance of the environment (pollution) can have serious consequences for continuation of this life.

Furthermore, all carbon-based fuels produce carbon dioxide and water when they are burned. Because of higher atomic ratio of hydrogen to carbon atom, natural gas produces less carbon dioxide per unit of energy than higher MW hydrocarbon derivatives (such as crude oil constituents) or coal. Also, natural gas impurities can be selectively and relatively easily removed and be completely converted by combustion, resulting in lower emissions of particulate matter. However, any releases of methane and ethane to the atmosphere should be minimized.

In the United States, the regulation of natural gas production has traditionally occurred primarily at the state level with most states that produce natural gas and crude oil issuing more rigorous standards that take primacy over federal regulations, as well as additional regulations that control areas not covered at the federal level, such as hydraulic fracturing. Within states, regulation is carried out by a range of agencies.

1.7.1 General Aspects

The specific regulations vary considerably among states, such as different depths for well casing, levels of disclosure on drilling and fracturing fluids, or requirements for water storage. Currently, many states that produce natural gas and crude oil have varying hydraulic fracturing regulations, specifically regulations related to (i) the disclosure of the components of hydraulic fracturing fluids, (ii) the proper casing of wells to prevent aquifer contamination, and (iii) management of wastewater from flow-back and produced water. The disposal of wastewater by underground injection has emerged as a concern for state regulators due to large interstate flows of wastewater to states with suitable geology for the water disposal as well as the potential for seismic activity near some well sites.

In terms of the development of unconventional natural gas and crude oil resources, a major environmental concern is the potential contamination of watercourses. Apart from water, which makes up 99.5% v/v of the hydraulic fracturing fluid, the fluid also contains chemical additives to improve the process performance. The additives are varied and can include acid, friction reducer, surfactant, gelling agent, and scale inhibitor (Speight, 2016b). The composition of the fracturing fluid is tailored to differing geological features and reservoir characteristics to address challenges, including scale buildup, bacterial growth, and proppant transport. Unfortunately, in the past many of the chemical compounds used in the hydraulic fracturing process lacked

scientifically based maximum contaminant levels, making it more difficult to quantify their risk to the environment (Colborn et al., 2011). Moreover, uncertainty about the chemical makeup of fracturing fluids persists because of the limitations on required chemical disclosure (Centner, 2013; Maule et al., 2013; Centner and O'Connell, 2014).

The measures required by state and federal regulatory agencies in the exploration and production of natural gas from deep tight formations have been very effective, for example, in protecting drinking water aquifers from contamination. In fact, a series of federal laws govern most environmental aspects of natural gas development (Table 1.9). However, federal regulation may not always be the most effective way of assuring the desired level of environmental protection. Therefore, most of these federal laws have provisions for granting primacy to the state governments, which have usually developed their own sets of regulations. By statute, the different states may adopt these standards of their own, but they must be at least as protective as the federal principles they replace and, as a result, may be more protective to address local conditions.

State regulation of the environmental practices related to natural gas and crude oil development can more easily address the regional- and state-specific character of the activities, compared with a one-size-fits-all management by the federal level. Some of these factors include geology, hydrology, climate, topography, industry characteristics, development history, state legal structures, population density, and local economics, and, thus, the regulation of natural gas and crude oil production is a detailed monitoring of each stage of the development through the many controls at the state level. Each state has the necessary powers to regulate, permit, and enforce all activities – from drilling and fracturing of the well to production operations, to managing and disposing of wastes, to abandoning and plugging the production well(s). These state powers are a means of assuring that natural gas and crude oil operations do not have an adverse impact on the environment.

Moreover, because of the regulatory makeup of each state – which can vary from state to state – different states take different approaches to the regulation and enforcement of resource development, but the laws of each state generally give the state agency responsible for natural gas and crude oil development the discretion to require whatever is necessary to protect the environment, including human health. In addition, most have a general prohibition against pollution from natural gas and crude oil production. Most of the state requirements are written into rules or regulations, but some of the regulations may be added to permits on a case-by-case basis because of (i) environmental review, (ii) on-site inspections, (iii) commission hearings, and (iv) public comments.

Finally, the organization of regulatory agencies within the different states where natural gas and crude oil is produced varies considerably. Some states have several agencies that oversee different aspects (with some inevitable

Table 1.9 Examples of federal laws (*listed alphabetically*) in the United States to monitor hydraulic fracturing projects.

Act	Purpose
Clean Air Act	Limits air emissions from engines, gas processing equipment, and other sources associated with drilling and production
Clean Water Act	Regulation of surface discharges of water associated with natural gas and crude oil drilling and production, as well as storm water runoff from production sites
Energy Policy Act	Exempted hydraulic fracturing companies from some regulations; may disclose chemicals through a report submitted to the regulatory authority, but in some instances, chemical information may be exempt from disclosure to the public as trade secrets
NEPA[a]	Requires that exploration and production on federal lands be thoroughly analyzed for environmental impacts
NPDES[b]	Requires tracking of any toxic chemicals used in fracturing fluids
Oil Pollution Act	Regulation of ground pollution risks relating to spills of materials or hydrocarbon derivatives into the water table; also regulated under the Hazardous Materials Transportation Act
Safe Drinking Water Act	Directs the underground injection of fluids from natural gas and crude oil activities; disclosure of chemical content for underground injections; after 2005, see Energy Policy Act
TSCA[c]	Suggestion that this act be used to regulate the reporting of hydraulic fracturing fluid information

NB: The Fracturing Responsibility and Awareness of Chemicals Act (the FRAC Act) was an attempt to define hydraulic fracturing as a federally regulated activity under the Safe Drinking Water Act; no significant moves or passage of this act at the time of writing (https://www.congress.gov/bill/114th-congress/senate-bill/785/text).

[a] National Environmental Policy Act.

[b] National Pollutant Discharge Elimination System.

[c] TSCA, Toxic Substances Control Act.

overlap powers) of natural gas and crude oil operations, particularly the requirements that protect the environment. In different states, the various approaches have developed over time to create a structure that best serves the consumers, nonconsumers, and the various industries. The one constant is that in each state where natural gas and crude oil is produced, there is one agency that has the responsibility for issuing permits for gas and oil development projects. The permitting agencies work with other agencies in the

regulatory process and often serve as a central organizing body and a useful source of information about activities related to natural gas and crude production.

1.7.2 Federal Regulation of the Industry

Since the Energy Policy Act passed in 2005, natural gas and crude oil production in the United States has grown significantly, and this rapid growth – along with continued reports of environmental effects – has led to renewed calls for the federal government to provide increased regulation or guidance. This pressure led to the introduction to Congress in 2009 of the Fracturing Responsibility and Awareness of Chemicals Act (the FRAC Act) to define hydraulic fracturing as a federally regulated activity under the Safe Drinking Water Act (Table 1.9). The proposed Act requires the energy industry to disclose the chemical additives used in the hydraulic fracturing fluid. The Act did not receive any action, was reintroduced in 2011, and appears to have been held in limbo since that time.

In the absence of new federal regulations, the various states that produce natural gas and crude oil by hydraulic fracturing have continued to use existing natural gas and crude oil and environmental regulations to manage natural gas and crude oil development, as well as introducing individual state regulations for hydraulic fracturing (Table 1.9). In fact, the current regulations comprise an overlapping collection of federal, state, and local regulations and permitting systems, and these regulations cover different aspects of the development and production of a natural gas and crude oil with the intention that the regulations combine to manage any potential impact on the surrounding environment, including any effects on water management. However, the hydraulic fracturing process has not previously been regulated under current laws, and, therefore, in terms of water management, emissions management, and site activity, the existing regulations are being (must be) reassessed for suitability for application to the hydraulic fracturing process. In the meantime, many states (including Wyoming, Arkansas, and Texas) have already implemented regulations requiring disclosure of the materials used in hydraulic fracturing fluids, and the US Department of the Interior has indicated an interest in requiring similar disclosure for sites on federal lands.

The Bureau of Land Management (BLM) of the Department of the Interior has proposed draft rules for natural gas and crude oil production on public lands, and these proposals would require disclosure of the chemical components used in hydraulic fracturing fluids. The proposed rule requires that an operations plan be submitted to the relevant authority – prior to initiation of the hydraulic fracturing project – that would allow BLM to evaluate groundwater protection designs based on (i) a review of the local geology, (ii) a review of any anticipated surface disturbance, and (iii) a review of the proposed

management and disposal of project-related fluids. In addition, BLM would require submittal of the information necessary to confirm wellbore integrity before, during, and after the stimulation operation. Furthermore, before hydraulic fracturing commenced, the company would have to certify that the fluids comply with all applicable federal, state, and local laws, rules, and regulations. After the conclusion of the hydraulic fracturing stage of the project, a follow-up report would be required in which the actual events that occurred during fracturing activities would be summarized, and this report would have to include the specific chemical makeup of the hydraulic fracturing fluid.

On 17 April 2012, the US Environmental Protection Agency released new performance standards and national emission standards for hazardous air pollutants in the natural gas and crude oil industries. These rules include the first federal air standards for hydraulically fractured gas wells, along with requirements for other sources of pollution in the natural gas and crude oil industry that currently are not regulated at the federal level. These standards require either flaring or *green completion* on natural gas wells developed prior to 1 January 2015, with only green completions allowed for wells developed on and after that date.

Briefly, *green completion* requires natural gas companies to capture the gas at the wellhead immediately after well completion instead of releasing it into the atmosphere or flaring the gas. Thus, the green completion systems are systems to reduce methane losses during well completion. After a new well completion or workover, the wellbore and formation must be cleaned of debris and fracturing fluid. Conventional methods for doing this include producing the well into an open pit or tank to collect sand, cuttings, and reservoir fluids for disposal. Typically, the natural gas that is produced is vented or flared, and the large volume of natural gas that is lost may not only affect regional air quality. When using green completion systems, gas and hydrocarbon liquids are physically separated from other fluids (a form of wellhead gas processing) – there is no venting or flaring of the gas – and delivered directly into equipment that holds or transports the hydrocarbon derivatives for productive use. Furthermore, by using portable equipment to process natural gas and natural gas condensate, the recovered gas can be directed to a pipeline as sales gas. The use of truck-mounted or trailer-mounted portable systems can typically recover more than half of the total gas produced.

1.7.3 Natural Gas and the Environment

Natural gas, although often cited as a relatively clean fuel, is also capable of producing emissions that are detrimental to the environment. While the major constituent of natural gas is methane, there are components such as carbon dioxide (CO), hydrogen sulfide (H_2S), and mercaptans (thiols; R — SH), as well as trace amounts of sundry other emissions. The fact that methane has a

foreseen and valuable end use makes it a desirable product, but in several other situations it is considered a pollutant, having been identified a greenhouse gas.

Also, a characteristic feature of natural gas that contains hydrogen sulfide is the presence of carbon dioxide (generally in the range of 1–4% v/v). In cases where the natural gas does not contain hydrogen sulfide, there may also be a relative lack of carbon dioxide. A sulfur removal process must be very precise, since natural gas contains only a small quantity of sulfur-containing compounds that must be reduced several orders of magnitude. Most consumers of natural gas require less than 4 ppm in the gas.

Acid rain occurs when the oxides of nitrogen and sulfur that are released to the atmosphere during the combustion of fossil fuels are deposited (as soluble acids) with rainfall, usually at some location remote from the source of the emissions. It is generally believed (the chemical thermodynamics are favorable) that acidic compounds are formed when sulfur dioxide and nitrogen oxide emissions are released from tall industrial stacks. Gases such as sulfur oxides (usually sulfur dioxide, SO_2) as well as nitrogen oxides (NO_x) react with the water in the atmosphere to form acids:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$2NO + H_2O \rightarrow 2HNO_2$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + H_2O \rightarrow HNO_3$$

Acid rain has a pH less than 5.0 and predominantly consists of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). As a point of reference, in the absence of anthropogenic pollution sources, the average pH of rain is –6.0 (slightly acidic; neutral pH = 7.0). In summary, the sulfur dioxide that is produced during a variety of processes will react with oxygen and water in the atmosphere to yield environmentally detrimental sulfuric acid. Similarly, nitrogen oxides will also react to produce nitric acid.

Another acid gas, hydrogen chloride (HCl), although not usually considered to be a major emission, is produced from mineral matter and the brines that often accompany petroleum during production and is gaining increasing recognition as a contributor to acid rain. However, hydrogen chloride may exert severe local effects because it does not need to participate in any further chemical reaction to become an acid. Under atmospheric conditions that favor a buildup of stack emissions in the areas where hydrogen chloride is produced, the amount of hydrochloric acid in rainwater could be quite high.

In addition to hydrogen sulfide and carbon dioxide, natural gas may contain other contaminants, such as mercaptans (R—SH) and carbonyl sulfide (COS). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes are also capable of removing the acid gas impurities to very low levels when the acid gases are there in low to medium concentrations in the gas.

At the global level there is concern that the increased use of any hydrocarbon-based fuels will ultimately raise the temperature of the planet (*global warming*), as carbon dioxide reflects the infrared or thermal emissions from the Earth, preventing them from escaping into space (*greenhouse effect*). Whether the potential for global warming becomes real will depend upon how emissions into the atmosphere are handled. There is considerable discussion about the merits and demerits of the global warming theory, and the discussion is likely to continue for some time. Be that as it may, the atmosphere can only tolerate pollutants up to a limiting value. And that value needs to be determined. In the meantime, efforts must be made to curtail the use of noxious and foreign (nonindigenous) materials into the air.

There are a variety of processes that are designed for sulfur dioxide removal from gas streams (Speight, 2014a), but scrubbing process utilizing limestone ($CaCO_3$) or lime [$Ca(OH)_2$] slurries has received more attention than other gas scrubbing processes. Most of the gas scrubbing processes are designed to remove sulfur dioxide from the gas streams; some processes show potential for removal of nitrogen oxide(s).

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