Natural Gas

Fuel for the 21st Century

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WILEY

Preface

This book, my 36th, has an unusual origin. For decades, I have followed an unvarying pattern: as I am finishing a book, I had already chosen a new project from a few ideas that had been queuing in my mind, sometimes coming to the fore just in a matter of months and in two exceptional cases (books on creating and transforming the twentieth century) after a wait of nearly two decades. But in January 2014, as I was about to complete the first draft of my latest book (*Power Density*: *A Key to Understanding Energy Sources and Uses*), I was still undecided what to do next. Then I got an e-mail from Nick Schulz at ExxonMobil who is also a reader (and a reviewer) of my books, asking me if I had considered writing a book about natural gas akin to my two beginner's guides (to energy and to oil) published by Oneworld in Oxford in, respectively, 2006 and 2008.

I had written about natural gas in most of my energy books, but in January 2014, the idea of a book solely devoted to it was not even at the end of my mental book queue. But considering all the attention natural gas has been getting, it immediately seemed an obvious thing to do. And because there are so many components and perspectives to the natural gas story—ranging from the fuel as a key part of the United States' much publicized energy revolution to its strategic value in Russia's in its dealings with Europe and to its role in replacing coal in the quest for reduced greenhouse gas emissions—it was no less obvious that I will have to approach the task in my usual interdisciplinary fashion and that I will dwell not only with what we know but also describe and appraise many unknowns and uncertainties that will affect the fuel's importance in the twenty-first century.

I began to write this natural gas book on March 1, 2014, intent on replicating approach and coverage of the two beginner’s guides: the intended readers being reasonably well educated (but not energy experts) and the coverage extending to all major relevant topics (be they geological, technical, economical, or environmental). But as the writing proceeded, I decided to depart from that course because I realized that some of the recent claims and controversies concerning natural gas require more detailed examinations. That is why the book is thoroughly referenced (the two guides had only short lists of suggested readings at the end), why it is significantly more quantitative and longer than the two guides, and why I dropped the word *primer* from its initial subtitle.

To many forward-looking energy experts, this may seem to be a strangely retrograde book. They would ask why dwell on the resources, extraction, and uses of a fossil fuel and why extol its advantages at a time when renewable fuels and decentralized electricity generation converting solar radiation and wind are poised to take over the global energy supply. That may be a fashionable narrative—but it is wrong, and there will be no rapid takeover by the new renewables. We are a fossil-fueled civilization, and we will continue to be one for decades to come as the pace of grand energy transition to new forms of energy is inherently slow. In 1990, the world derived 88% of its primary commercial energy (leaving aside noncommercial wood and crop residues burned mostly by rural families in low-income nations) from fossil fuels; in 2012, the rate was still almost 87%, with renewables supplying 8.6%, but most of that has been hydroelectricity and new renewables (wind, solar, geothermal, biofuels) provided just 1.9%; and in 2013, their share rose to nearly 2.2% (Smil, 2014; BP, 2014a).

Share of new renewables in the global commercial primary energy supply will keep on increasing, but a more consequential energy transition of the coming decades will be from coal and crude oil to natural gas. With this book, I hope to provide a solid background for appreciating its importance, its limits, and a multitude of its impacts. This goal dictated the book’s broad coverage where findings from a number of disciplines (geochemistry, geology, chemistry, physics, environmental science, economics, history) and process descriptions from relevant engineering practices (hydrocarbon exploration, drilling, and production; gas processing; pipeline transportation; gas combustion in boilers and engines; gas liquefaction and shipping) are combined to provide a relatively thorough understanding of requirements, benefits, and challenges of natural gas ascendance.

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1

Valuable Resource with an Odd Name

Natural gas, one of three fossil fuels that energize modern economies, has an oddly indiscriminate name. Nature is, after all, full of gases, some present in enormous volumes, others only in trace quantities. Nitrogen (78.08%) and oxygen (20.94%) make up all but 1% of dry atmosphere’s volume, the rest being constant amounts of rare gases (mainly argon, neon, and krypton altogether about 0.94%) and slowly rising levels of carbon dioxide (CO_2). The increase of this greenhouse gas has been caused by rising anthropogenic emissions from combustion of fossil fuels and land use changes (mainly tropical deforestation), and CO_2 concentrations have now surpassed 0.04% by volume, or 400 parts per million (ppm), about 40% higher than the preindustrial level (CDIAC, 2014).

In addition, the atmosphere contains variable concentrations of water vapor and trace gases originating from natural (abiogenic and biogenic) processes and from human activities. Their long list includes nitrogen oxides (NO, NO_2, N_2O) from combustion (be it of fossil fuels, fuel wood, or emissions from forest and grassland fires), lightning, and bacterial metabolism; sulfur oxides (SO_2 and SO_3) mainly from the combustion of coal and liquid hydrocarbons, nonferrous metallurgy, and also volcanic eruptions; hydrogen sulfide (H_2S) from anaerobic decomposition and from volcanoes; ammonia (NH_3) from livestock and from volatilization of organic and inorganic fertilizers; and dimethyl sulfide (C_2H_6S) from metabolism of marine algae.

But the gas whose atmospheric presence constitutes the greatest departure from a steady-state composition that would result from the absence of life on the Earth is methane (CH_4), the simplest of all hydrocarbons, whose molecules are composed only of hydrogen and carbon atoms. Methane is produced during strictly anaerobic decomposition of organic matter by species of archaea, with *Methanobacter*, *Methanococcus*, *Methanosarcina*, and *Methanothermobacter* being the major methanogenic genera. Although the gas occupies a mere 0.000179% of the atmosphere by volume (1.79 ppm), that presence is 29 orders of magnitude higher than it would be on a lifeless Earth (Lovelock and Margulis, 1974). The second highest disequilibrium attributable to life on the Earth is 27 orders of magnitude for NH_3.

Methanogens residing in anaerobic environments (mainly in wetlands) have been releasing CH_4 for more than three billion years. As with other metabolic processes, their activity is temperature dependent, and this dependence (across microbial to ecosystem scales) is considerably higher than has been previously observed for either photosynthesis or respiration (Yvon-Durocher et al., 2014). Methanogenesis rises 57-fold as temperature increases from 0 to 30°C, and the increasing CH_4:CO_2 ratio may have important consequences for future positive feedbacks between global warming and changes in carbon cycle.

Free-living methanogens were eventually joined by archaea that are residing in the digestive tract (in enlarged hindgut compartments) of four arthropod orders, in millipedes, termites, cockroaches, and scarab beetles (Brune, 2010), with the tropical termites being the most common invertebrate CH_4 emitters. Although most vertebrates also emit CH_4 (it comes from intestinal anaerobic protozoa that harbor endosymbiotic methanogens), their contributions appear to have a bimodal distribution and are not determined by diet. Only a few animals are intermediate methane producers, while less than half of the studied taxa (including insectivorous bats and herbivorous pandas) produce almost no CH_4, while primates belong to the group of high emitters, as do elephants, horses, and crocodiles.

But by far the largest contribution comes from ruminant species, from cattle, sheep, and goats (Hackstein and van Alen, 2010). Soil-dwelling methanotrophs and atmospheric oxidation that produces H_2O and CO_2 have been methane's major biospheric sinks, and in the absence of any anthropogenic emissions, atmospheric concentrations of CH_4 would have remained in a fairly stable disequilibrium. These emissions began millennia before we began to exploit natural gas as a fuel: atmospheric concentration of CH_4 began to rise first with the expansion of wet-field (rice) cropping in Asia (Ruddiman, 2005; Figure 1.1).

Figure 1.1 Methanogens in rice fields (here in terraced plantings in China’s Yunnan) are a large source of CH_4.

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Existence of inflammable gas emanating from wetlands and bubbling up from lake bottoms was known for centuries, and the phenomenon was noted by such famous eighteenth-century investigators of natural processes as Benjamin Franklin, Joseph Priestley, and Alessandro Volta. In 1777, after observing gas bubbles in Lago di Maggiore, Alessandro Volta published *Lettere sull’ Aria inflammabile native delle Paludi*, a slim book about “native inflammable air of marshlands” (Volta, 1777). Two years later, Volta isolated methane, the simplest hydrocarbon molecule and the first in the series of compounds following the general formula of C_nH_{2n+2}. When in 1866 August Wilhelm von Hofmann proposed a systematic nomenclature of hydrocarbons, that series became known as alkanes (alkenes are C_nH_{2n}; alkines are C_nH_{2n-2}).

The second compound in the alkane series is ethane (C_2H_6), and the third one is propane (C_3H_8). The fossil fuel that became known as natural gas and that is present in different formations in the topmost layers of the Earth's crust is usually a mixture of these three simplest alkanes, with methane always dominant (sometimes more than 95% by weight) and only exceptionally with less than 75% of the total mass (Speight, 2007). C_2H_6 makes up mostly between 2 and 7% and C_3H_8 typically just 0.1–1.3%. Heavier homologs—mainly butane (C_4H_{10}) and pentane (C_5H_{12})—are also often present. All C_2–C_5 compounds (and sometimes even traces of heavier homologs) are classed as natural gas liquids (NGL), while propane and butane are often combined and marketed (in pressurized containers) as liquid petroleum gases (LPG).

Most natural gases also contain small amounts of CO_2, H_2S, nitrogen, helium, and water vapor, but their composition becomes more uniform before they are sent from production sites to customers. In order to prevent condensation and corrosion in pipelines, gas processing plants remove all heavier alkanes: these compounds liquefy once they reach the surface and are marketed separately as NGL, mostly as valuable feedstocks for petrochemical industry, some also as portable fuels. Natural gas processing also removes H_2S, CO_2, and water vapor and (if they are present) N_2 and He (for details, see Chapter 3).

1.1 METHANE'S ADVANTAGES AND DRAWBACKS

No energy source is perfect when judged by multiple criteria that fully appraise its value and its impacts. For fuels, the list must include not only energy density, transportability, storability, and combustion efficiency but also convenience, cleanliness, and flexibility of use; contribution to the generation of greenhouse gases; and reliability and durability of supply. When compared to its three principal fuel alternatives—wood, coal, and liquids derived from crude oil—natural gas scores poorly only on the first criterion: at ambient pressure and temperature, its specific density, and hence its energy density, is obviously lower than that of solids or liquids. On all other criteria, natural gas scores no less than very good, and on most of them, it is excellent or superior.

Specific density of methane is 0.718 kg/m^3 (0.718 g/l) at 0°C and 0.656 g/l at 25°C or about 55% of air's density (1.184 kg/m^3 at 25°C). Specific densities of common liquid fuels are almost exactly, 1,000 times higher, with gasoline at 745 kg/m^3 and diesel fuel at 840 kg/m^3, while coal densities of bituminous coals range from 1,200 to 1,400 kg/m^3. Only when methane is liquefied (by lowering its temperature to −162°C) does its specific density reach the same order of magnitude as in liquid fuels (428 kg/m^3), and it is equal to specific density of many (particularly coniferous) wood species, including firs, cedars, spruces, and pines.

Energy density can refer to the lower heating value (LHV) or higher heating value (HHV); the former rate assumes that the latent heat of vaporization of water produced during the combustion is not recovered, and hence it is lower than HHV that accounts for the latent heat of water vaporization. Volumetric values for methane are 37.7 MJ/m^3 for HHV and 33.9 MJ/m^3 for LHV (10% difference), while the actual HHVs for natural gases range between 33.3

MJ/m^3 for the Dutch gas from Groningen to about 42 MJ/m^3 for the Algerian gas from Hasi R’Mel. Again, these values are three orders of magnitude lower than the volumetric energy density of liquid fuels: gasoline’s HHV is 35 GJ/m^3 and diesel oil rates nearly 36.5 GJ/m^3. Liquefied natural gas (50 MJ/kg and 0.428 kg/l) has volumetric energy density of about 21.4 GJ/m^3 or roughly 600 times the value for typical natural gas containing 35–36 MJ/m^3.

Methane’s low energy density is no obstacle to high-volume, low-cost, long-distance terrestrial **transport**. There is, of course, substantial initial capital cost of pipeline construction (including a requisite number of compression stations), and energy needed to power reciprocating engines, gas turbines, or electric motors is the main operating expenditure. But as long as the lines and the compressors are properly engineered, there is no practical limit to distances that can be spanned: multiple lines bring natural gas from supergiant fields of Western Siberia to Western Europe, more than 5000 km to the west. Main trunk of China’s West–East pipeline from Khorgas (Xinjiang) to Guangzhou is over 4,800 km long, and eight major branches add up to the total length of 9,100 km (China.org, 2014). Moreover, pipelines transport gas at very low cost per unit of delivered energy and can do so on scales an order of magnitude higher than the transmission of electricity where technical consideration limit the maxima to 2–3 GW for single lines, while gas pipelines can have capacities of 10–25 GW (IGU, 2012).

Undersea pipelines are now a proven technical option in shallow waters: two parallel 1,224 km long lines of the Nord Stream project built between 2010 and 2012 between Russia and Germany (from Vyborg, just north of Sankt Petersburg to Lubmin near Greifswald in Mecklenburg-Vorpommern) to transport 55 Gm^3/year were laid deliberately in the Baltic seabed in order to avoid crossing Ukraine or Belarus before reaching the EU (Nord Stream, 2014). Crossing deep seas is another matter: low energy density of natural gas precludes any possibility of shipborne exports at atmospheric pressure, and the only economic option for intercontinental shipments is to liquefy the gas and carry it in insulated containers on purpose-built tankers; this technique, still much more expensive than pipeline transportation, will be appraised in detail in Chapter 5. Methane's low energy density is also a disadvantage when using the fuel in road vehicles, and once again, the only way to make these uses economical is by compression or liquefaction of the gas (for details, see Chapter 7).

Low energy density would be a challenge if the only **storage** option would be as uncompressed gas in aboveground tanks: even a giant tank with 100 m in diameter and 100 m tall (containing about 785,000 m^3 or roughly 28 TJ) would store gas for heating only 500 homes during a typical midcontinental Canadian winter. Obviously, volumes of accessible stores must be many orders of magnitude higher, high enough to carry large midlatitude cities through long winters. The easiest, and the most common, choice is to store the fuel by injecting it into depleted natural gas reservoirs; other options are storage in aquifers (in porous, permeable rocks) and (on a much smaller scale but with almost perfect sealing) in salt caverns.

High **combustion efficiency** is the result of high temperatures achievable when burning the gas in large boilers and, better yet, in gas turbines. Gas turbines are now the single most efficient fuel convertors on the market and that high performance can be further boosted by combining them with steam turbines. When exiting a gas turbine, the exhaust has temperature of 480–600°C, and it can be used to vaporize water, and the resulting steam runs an attached steam turbine (Kehlhofer, Rukes, and Hannemann, 2009). Such combined cycle generation (CCG, or combined cycle power plants, CCPP) can achieve overall efficiency of about 60%, the rate unsurpassed by any other mode of fuel combustion (Figure 1.2). And modern natural gas-fired furnaces used to heat North America’s houses leave almost no room for improvement as they convert 95–97% of incoming gas to heat that is forced by a fan through ducting and floor registers into rooms.

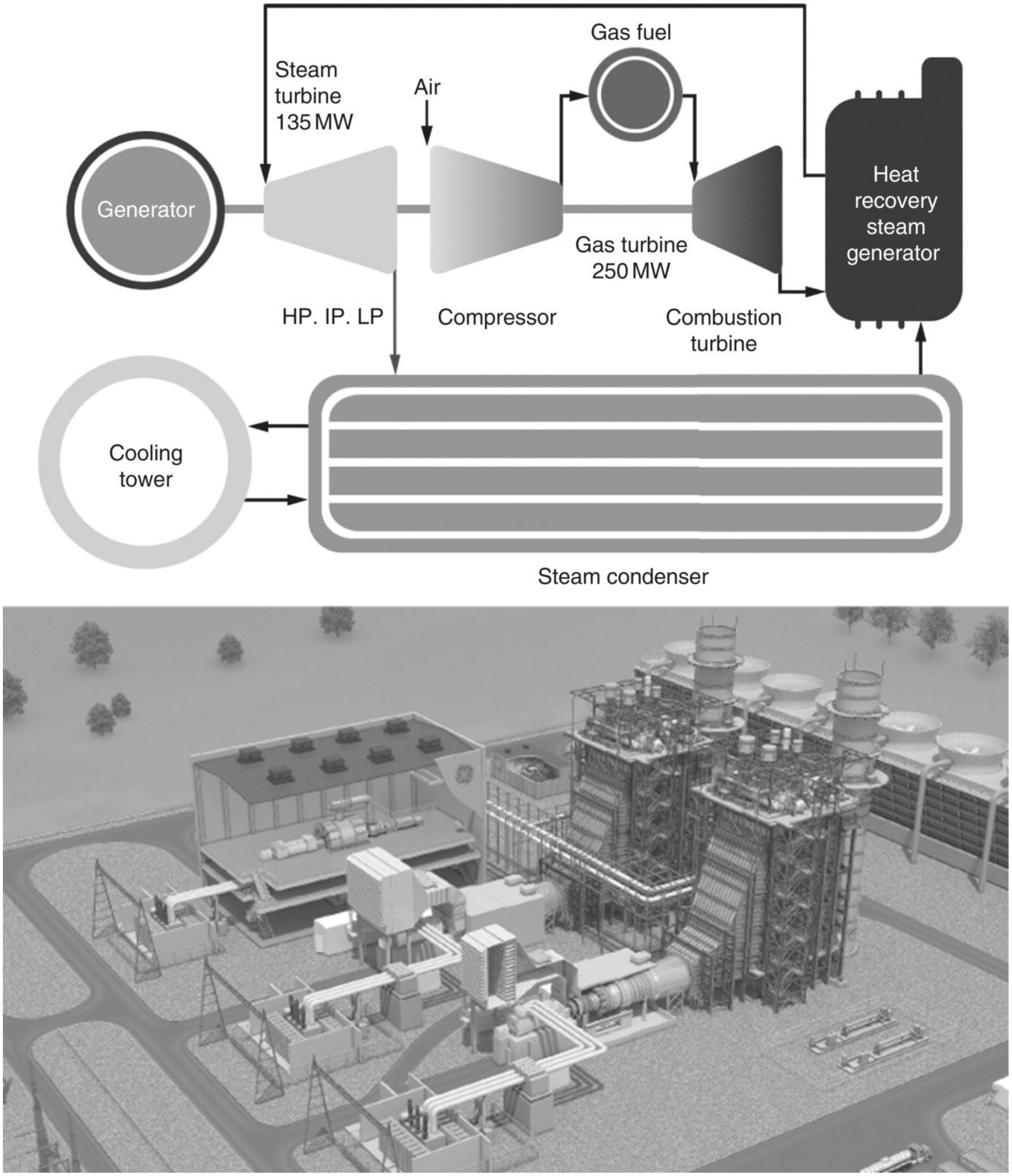

Figure 1.2 Combined cycle gas turbine: energy flow and a model of GE installation.

Reproduced courtesy of General Electric Company.

Little needs to be said about the **convenience of use**. The only chore an occupant has to do in houses heated by natural gas is to set a thermostat to desired levels (with programmable thermostats, this can be done accurately with specific day/night or weekday/weekend variations)—and make sure that the furnace is checked and cleaned once a year. Electronic ignition, now standard on furnaces as well as on cooking stoves, has eliminated wasteful pilot lights, and auto reignition makes the switching a one-step operation (turning a knob to desired intensity) instead (as is the case with standard electronic ignition) of turning a knob to on position (to open a gas valve), waiting a second for ignition, and then turning a knob to a preferred flame intensity.

Combination of these desirable attributes—safe and reliable delivery by pipelines from fields and voluminous storages, automatic dispensation of the fuel by electronically controlled furnaces, effortless control of temperature settings for furnaces and stoves, and low environmental impact—means that natural gas is an excellent source of energy for densely populated cities that will house most of the world's population in the twenty-first century. As Ausubel (2003, 2) put it, "the strongly preferred configuration for very dense spatial consumption of energy is a grid that can be fed and bled continuously at variable rates"—and besides electricity, natural gas is the only energy source that can be distributed by such a grid and used directly in that way.

As for the **cleanliness of use**, electricity is the only competitor at the point of final consumption. Combustion of pure methane, or a mixture of methane and ethane, produces only water and carbon dioxide $\left(CH_4 + O_2 \rightarrow H_2O + CO_2\right)$. There are no emissions of acidifying sulfur oxides (as already noted, H_2S is stripped from natural gas before it is sent through pipelines), while heating houses with coal or fuel oil generates often fairly high emissions of SO_2. Moreover, coal combustion produces high concentrations of particulate matter (diameters of <10 µm, PM_{10}), and the smallest particles (diameter <2.5 µm, $PM_{2.5}$) are also fairly abundant when burning heavier liquids, while combustion of natural gas emits only a small fraction of the finest particulate matter compared to the burning of solid or liquid fuels.

Similarly, natural gas is a superior choice when generating electricity in large power plants. Coal burning in large central stations remains a globally dominant way of thermal electricity generation, and even with appropriate modern air pollution controls (electrostatic precipitators to capture more than 99% of fly ash produced by the combustion of finely pulverized coal in boilers; flue gas desulfurization to remove more than 80% of SO_2 produced by oxidation of coal's organic and inorganic sulfur), to generate a unit of electricity, it releases five to six times more $PM_{2.5}$ and PM_{10} and in many cases more than 1,000 times as much SO_2 as does the combustion of natural gas (TNO, 2007).

No other form of energy has a higher **flexibility of use** than electricity: commercial flying is the only common final conversion that it cannot support, as it can be used for heating, lighting, cooking, and refrigeration; for supplying processing heat in many industries, powering all electronic gadgets and all stationary machinery; for propelling vehicles, trains, and ships; and for producing metals (electric arc furnaces and electrochemical processes). Natural gas shares the flying limitation with electricity—but otherwise, the fuel is remarkably flexible as its common uses range from household space heating and cooking to peak electricity generation and from powering compressors in nitrogen fertilizer plants to propelling LNG tankers (for details, see Chapter 4).

Because climate change and the future extent of global warming have become major concerns of public policy, **contribution to the generation of greenhouse gases** has emerged as a key criterion to assess desirability of fuels. On this score, natural gas remains unsurpassed as its combustion generates less CO_2 per unit of useful energy than does the burning of coal, liquid fuels, or common biofuels (wood, charcoal, crop residues). In terms of kg CO_2/GJ, the descending rates are approximately 110 for solid biofuels, 95 for coal, 77 for heavy fuel oil, 75 for diesel, 70 for gasoline, and 56 for natural gas (Climate Registry, 2013). Moreover, high-temperature coal combustion in large power stations also produces much higher volumes of the other two most important greenhouse gases: more than 10 times as much CH_4 and more than 20 times as much N_2O per unit of generated electricity (details in Chapter 7).

Reliability of supply is perhaps best demonstrated by the fact that inhabitants of large northern cities hardly ever think about having their gas supply interrupted because such experiences are exceedingly rare. There may be a temporary problem with a distribution line bringing the gas to a house, and there are rare—and in a great majority of cases perfectly preventable—explosions. A widely reported explosion that leveled two apartment buildings, killed 7, and injured more than 60 in New York’s East Harlem on March 12, 2014, is a good illustration of such an avoidable accident. Several residents said that they “smelled gas in the area for several days” (Slattery and Hutchinson, 2014). That unmistakable smell is butanethiol (butyl mercaptan, $C_4H_{10}S$) that is added to odorless natural gas in order to detect even tiny leaks by smell (humans can detect as little as 10 parts per billion of the skunk-like odor).

Nor are there any great uncertainties about the reliability of international gas supply. The most notable case of interrupted supply took place in January 2009 when Gazprom cut off all flows of Russian gas to Ukraine (also affecting the deliveries to more than half a dozen European countries whose gas must flow through the Ukrainian lines) due to the unpaid accumulated debt for previous deliveries (Daly, 2009). The flow was restored after 13 days, but by March 2014, new Ukrainian debts threatened a reprise of 2009, although Gazprom maintained that the EU consumers west of the Ukraine would not be affected. Another threat of export interruption (following Russia’s annexation of Crimea and fighting in the Eastern Ukraine) was averted by a deal conclude in late October 2014. But this unique, albeit recurrent, threat is not a reflection of general natural gas trading practices, rather an exception due to an unsettled nature of Russia’s relations with its neighbors in the post-Soviet era.

Durability of supply is, of course, the function of resources in place and of our technical and managerial capabilities to translate their substantial part into economically recoverable commodities—and natural gas ranks high on all of these accounts. Natural gas is present in abundance in the topmost crust in several formations, but until recently, only three kinds of gaseous hydrocarbons dominated commercial production. They are natural gases associated with crude oils, a very common occurrence in nearly all of the world’s major oil reservoirs; these gases may be present in separate layers in a reservoir containing oil and gas, they may accumulate on top of oil as gas caps, or they may be (another common occurrence) dissolved in crude oil. Usual cutoff for associated gas is when a gas/oil ratio is less than 20,000 ft^3 per barrel (in SI units about 350 m^3 of gas per 100 l of oil).

In contrast, nonassociated natural gas comes from gas fields, that is, from hydrocarbon reservoirs whose gas/oil ratio exceeds the rate noted in the preceding paragraph. The two common categories of nonassociated natural gas are wet (also called rich) gas that is extracted from reservoirs where methane dominates but where heavier alkanes (NGL) account for a substantial share of hydrocarbon mixtures, while dry natural gas comes from reservoirs where prolonged heat processing produced gas mixtures containing more than 90% or even more than 95% of methane and only small amounts of ethane and other alkanes.

These three conventional resources continue to dominate global extraction of natural gas, but some countries and regions are now producing increasing quantities of gaseous fuel from coal beds and from shales, while extraction of gas from methane hydrates still awaits additional technical advances before becoming commercial. All resource totals are always only temporary best estimates, but in this instance, their magnitude guarantees generations of future use: the best recent assessments of recoverable resources indicate that the global peak of natural gas extraction is most likely no closer than around 2050 or perhaps even after 2070. Another reassuring perspective shows that during the past three decades (between 1982 and 2012), the world gas consumption rose 2.3-fold, but the global reserve/production ratio has remained fairly constant, fluctuating within a narrowband of 55–65 years and not signaling any imminent radical shifts.

This brief review shows that natural gas is an exceptional source of primary energy for all modern economies—not only because it combines a number of practical advantages and benefits but also because it either fits existing infrastructures or because any further expansion of extraction, transportation, and use can rely on proven and economical technical and managerial arrangements. This book will offer a concise, but systematic, review of key aspects that define and delimit the fuel’s great potential during the twenty-first century: its biogenic origins, crustal concentrations, and widespread distribution; its exploration, extraction, processing, and pipeline transportation; its common uses for heat and electricity generation and as a key feedstock for many chemical syntheses; its pipeline and intercontinental exports and the emergence of global trade; diversification of its commercial sources; and the fuel’s role in energy transitions and environmental consequences of its combustion.

Given the scope of the coverage and the length of the text, it is easy to appreciate that writing this book was a serial exercise in exclusion; at the same time and with every key topic, I have tried to go sufficiently below the shallows that now dominate the (web page-like) writings about technical, environmental, and economic complexities for nonexperts. That is why I hope that those readers who will persevere (and tolerate what I always think of as a necessary leavening by many requisite numbers) will be rewarded by acquiring a good basis for an unbiased and deeper understanding of a critical segment of modern energy use and of its increasing importance.

2

Origins and Distribution of Fossil Gases

Many gases encountered in the biosphere are of organic (biogenic) origin: as already explained in the previous chapter, methane is actually the best example of a gas whose concentration is orders of magnitude higher than it would be on a lifeless Earth. Other gases generated by microbial metabolism include hydrogen (H_2), hydrogen sulfide (H_2S), carbon monoxide and dioxide (CO and CO_2), nitric oxide (NO), nitrous oxide (N_2O), and ammonia (NH_3), while photosynthesis releases huge volumes of oxygen (O_2), and all animal metabolism emits CO_2. But many of these gases are also of inorganic origins: CO from incomplete combustion of fuels and CO, H_2S, and SO_2 from volcanic eruptions—and methane was found in hydrothermal vents at the bottom of the Pacific Ocean and in other crustal fluids.

Given these realities, we have to ask if all fossil methane, or at least an overwhelming majority of its presence in the crust’s topmost layer, is of biogenic origin (arising from transformation of organic matter) or if a significant share of it (if not most of it) is abiogenic, arising from processes that have not required metabolism of living organisms. These obvious questions have been asked and answered: debates about the origin of natural gas have been a part of a wider inquiry about the genesis of fossil hydrocarbons, with the consensus coming on the side of their organic provenance and with dissenters arguing that inorganic process is a better way to explain the genesis of vast gas volumes in the Earth's upper crust.

I will recount this contest in the first section of this chapter before I get into a fairly systematic review of the known global distribution of natural gas resources and a few closer looks at major resource endowments in key producing countries and at some of the world's most notable natural gas fields. In the chapter's final section, I will assess the development of our understanding of the world's natural gas resources (whose total cannot be quantified with satisfactory accuracy) as well as the progression of natural gas reserves (whose appraisal, while far from perfect, offers a much more revealing understanding of realistic, economic prospects for exploiting the fuel).

2.1 BIOGENIC HYDROCARBONS

A widely accepted conclusion is that natural gas was formed by thermal decomposition (under temperatures of 150–200°C and higher), primarily of crude oil in reservoirs and, to a lesser degree, of organic matter in shales that were the source rock for the liquids (Hunt, 1995; Selley, 1997; Buryakovsky et al., 2005). But organic origins of oils are not as obvious as those of coals which contain fossilized trunks and imprints of leaves of trees that grew during the Carboniferous periods (360–286 million years ago) and in more recent pre-Quaternary eras (many lignites are younger than 10 million years). While coals are fossilized phytomass of the largest photosynthesizers, crude oils originated mostly from dead biomass of the smallest photosynthetic organism, single-cell phytoplankton composed mostly of cyanobacteria (photosynthetic bacteria that used to be known erroneously as blue-green algae) and diatoms (unicellular and colonial algae enclosed in siliceous cell walls), and from dead zooplankton (dominated by foraminifera, amoeboid protists with food-catching pseudopodia). In addition, there were secondary contributions of dead algal phytomass, invertebrate and fish zoomass, and assorted dead organic matter carried to oceans and lakes by rivers.

But there is no simple, direct path to transform microbial biomass into a pool of oil hydrocarbons: they originated mostly from nonhydrocarbon organic compounds (carbohydrates, proteins, and lipids) that were transformed by bacteriogenesis (microbial metabolism) followed by lengthy thermogenesis (heat processing within sediments). The process begins with gradual accumulation of dead biomass in coastal or lake sediments followed by aerobic microbial degradation releasing CO_2 and then by anaerobic fermentation releasing CH_4 and H_2S, and burial and compaction of organic matter in anoxic sediments produced complex mixtures of large organic molecules. These insoluble kerogens arise from different materials—mainly from algae in lacustrine settings, from plankton and some algae in marine formations, and mainly from higher plants in terrestrial environments—and they could be up to 10% (commonly just 1–2%) of the mass in shales and limestones, the usual source rocks of fossil hydrocarbons. Rate of their formation and their eventual concentration is an outcome of competing processes of accumulation, destruction, and dilution of organic matter.

Kerogens subjected to higher temperatures and pressures in buried sediments will be eventually degraded by a process that is very similar to deliberate actions in crude oil refineries: thermal cracking breaks up complex molecules, and kerogens are first transformed into dark (black or brown), near-solid bitumens. This transformative process, resulting in bitumen (dark, very viscous but inflammable organic matter) appears to be almost as old as life itself: residues of asphaltic pyrobitumen were found in Australia’s Pilbara shales and were dated to 3.2 billion years ago (Rasmussen, 2000). Eventual cracking of bitumens produces lighter molecules of liquid hydrocarbons, and increasing temperatures mark the principal stages of the process (McCarthy et al., 2011).

Transformation of sediments rich in organic matter to sedimentary rocks (diagenesis) takes place usually at less than 50°C and at a depth of less than 1 km. Thermal cracking (catagenesis) is most effective between 65 and 150°C and typically at depths of 2–4 km. Heavier liquid molecules are formed at temperatures between 80 and 120°C, and catagenesis at higher temperature results in higher shares of lighter alkanes and in gradually increasing gas/oil ratio, and any prolonged thermal processing above 200°C produces only dry gas. Finally, metagenesis converts much of the remaining kerogen into methane and nonhydrocarbon gases at 150–200°C. Stolper et al. (2014), using an isotopic technique, delimited formation temperatures of thermogenic gases between 157 and 221°C (Figure 2.1).

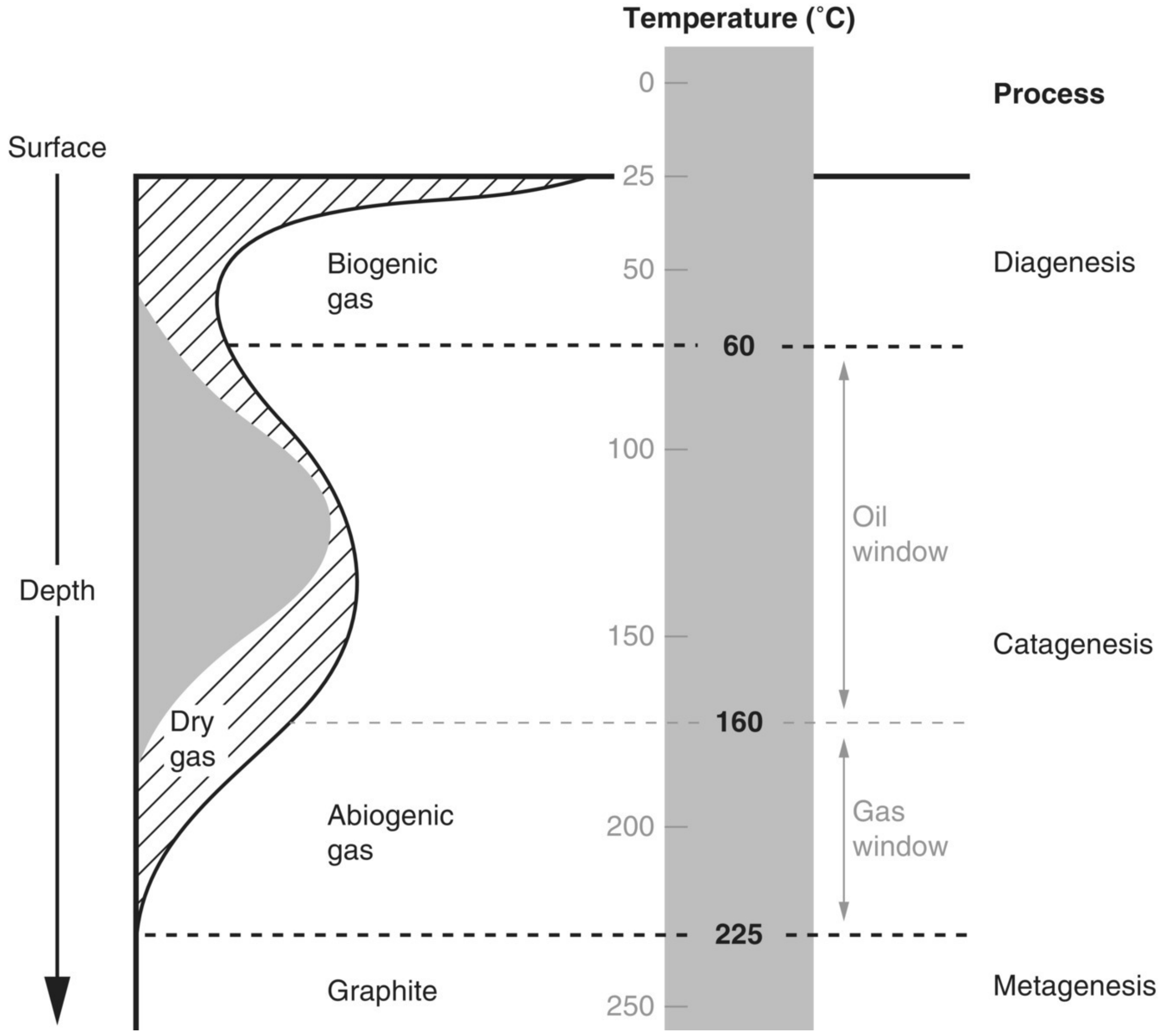

Figure 2.1 Diagenesis, catagenesis, and metagenesis.

Hydrocarbons in young (Cretaceous, 145–65 million years ago) reservoirs tend to be mostly heavy crude oils, lighter crude oils come from Jurassic or Triassic formations (younger than 250 million years), and the lightest alkanes are often of Permian or Carboniferous age (up to 350 million years old). As a result, the composition of hydrocarbon reservoirs spans a huge range from the extreme of highly viscous bitumen through heavy oils not accompanied by any gas to combinations of liquid and gaseous compounds (ranging from oils with only a small amount of dissolved gas to mixtures of oil, gas, and natural gas liquids) and to the other extreme of nearly pure methane with only a marginal presence of natural gas liquids.

Efficiency of this long process of transforming ancient biomass carbon into carbon in marketed fossil fuels can be quantified in terms of right orders of magnitude (Dukes, 2003). During coal formation, up to 15% of plant carbon ends up in peat, up to 90% of peat carbon is preserved in coal, and the now dominant opencast extraction can get up to 95% of coal in place from thick and level seams. This means that the overall carbon recovery factor (which is the fraction of carbon's original content in ancient phytomass that remains in extracted fuel) can be as high as 13%—or, restating this in reverse, that some eight units of ancient carbon (with the most common range of 5–20 units) was transformed into one unit of carbon in marketed coal.

In contrast, carbon preservation rates were much lower in marine and lacustrine sediments, and hydrocarbon recovery rate is only rarely close to 50%. As a result, the overall recovery factor for carbon sequestered in crude oil carbon could be as high as nearly 1% and lower than 0.0001%. Common rate of 0.01% means that 10,000 units of ancient carbon in aquatic biomass were transformed into 1 unit of carbon in marketed crude oil, and subsequent catagenesis and metagenesis, even if operating with 80% efficiency, would result in more than 12,000 units of carbon in ancient aquatic phytomass and zoomass to produce a unit of carbon in methane and natural gas liquids.

But what if hydrocarbons were of inorganic, rather than biogenic, origin? That was assumed by Dmitri Ivanovich Mendeleev, Russia's leading nineteenth-century chemist, and that has been an alternative to the biogenic explanation offered by the so-called Russian–Ukrainian hypothesis about the abiogenic formation of oil and gas in abyssal environments. The theory was first formulated during the early 1950s, and it had been championed by its proponents in the USSR and by some Western geologists (Kudryavtsev, 1959; Simakov, 1986; Glasby, 2006). According to the theory, formation of highly reduced hydrocarbons with high energy content from highly oxidized organic molecules with low energy content would violate the second law of thermodynamics, and high pressures deeper in the Earth’s mantle are the best explanation for the formation of such reduced molecules.

Porfir’yev (1959, 1974) had also argued that abiogenic formation of giant oil fields is a better explanation of their origins than assuming truly gigantic accumulations of organic material that would be needed to create such structures. Modern interpretation of the abiogenic theory was summarized in a paper published in the *Proceedings of the National Academy of Sciences* and authored by Jason F. Kenney (a leading American advocate of inorganic origins of hydrocarbons) and his Russian colleagues. They recounted the experiments that produced a range of petroleum fluids in an apparatus replicating pressure (50 MPa) and temperature (up to 1500°C) 100 km below the surface (Kenney et al., 2002).

A kindred alternative was advocated by Thomas Gold, an American astrophysicist (Gold, 1985, 1993). Gold noted the presence of abiogenic hydrocarbons on planetary bodies devoid of life and maintained that methane can form by combining hydrogen and carbon under high temperatures and pressures in the outer mantle, and after this mantle-derived methane migrates it is then converted to heavier hydrocarbons in the upper layers of the Earth’s crust. If true, this would have two profound consequences: hydrocarbons created by degassing from the mantle would be much more plentiful than is indicated by estimates attributed to biogenic formation; and perhaps the most intriguing consequence of abiogenic hydrocarbon formation, existing reservoirs could be gradually recharged (albeit at a very slow rate) by continuing formation of oil and gas (Mahfoud and Beck, 1995; Gurney, 1997).

But the alternative explanations of oil and gas origins have not aged well. Once the Russian–Ukrainian theory became better known abroad (starting in the mid-1970s), it was repeatedly dismissed by most of the European and North American petroleum geologists who favor the consensus explanation that excludes any major contribution by abiogenic origins of hydrocarbons. This consensus view is strongly supported by geological and geochemical evidence, and it has been strengthened by the use of the latest analytical methods (Glasby, 2006; Sephton and Hazen, 2013). I will note here half a dozen of major realities that undermine the abiogenic hypothesis.

The upper mantle is too oxidizing to allow the persistence of significant amounts of H_2 or CH_4; hydrocarbons formed from outgassed methane should be (but are not) concentrated largely along major tectonic discontinuities (faults and convergent zones); modern understanding of fluid and gas migration explains many previously puzzling hydrocarbon occurrences; biomarkers (including porphyrins and lipids) are derived from organic molecules; and isotopic analyses show a match between carbon isotope ratios in hydrocarbons and in terrestrial and marine plants. Lollar et al. (2002) used isotopic analysis of carbon and hydrogen to show a clear distinction between thermogenic and abiogenic hydrocarbons, and due to the absence of appropriate isotopic signatures in economically important reservoirs, they ruled out the occurrence of globally significant abiogenic alkanes.

This does not mean that there are no hydrocarbons of inorganic origin and that we have satisfactory explanation for the formation of all major hydrocarbon deposits. Gold may have overstated his case for abiogenic methane, but he was right when he posited the existence of what he called deep hot biosphere (Gold, 1998), assemblages of extremophilic bacteria living deep underground, up to several km below the Earth’s surface, others deep below the deep-sea bottom. That claim was initially dismissed by the prevailing scientific consensus only to be confirmed later by incontrovertible and amazing findings of such organisms (Reith, 2011). And Milkov’s recent explanation of the formation of giant gas pools in Western Siberia is an excellent illustration of complexities involved in the genesis of hydrocarbons (Milkov, 2010).

Dry gas pools in the northern part of the West Siberian Basin contain about 11% of the world’s conventional gas reserves and account for 17% of current global gas extraction, but none of the proposed hypotheses of their origin (thermogenic gas from deep source rocks, microbial gas from dispersed organic matter, thermogenic gas from coal) are consistent with actual molecular and isotopic composition of extracted gases. Milkov argues that a significant (but unquantified) share of those shallow dry gases is the result of methanogenic biodegradation of petroleum rather than the outcome of thermogenesis. This also illustrates the complexities of postformation hydrocarbon histories. Oil and gas originating in kerogen-rich source rocks will almost invariably migrate through porous and hence permeable reservoir rocks and will be held in place by impermeable traps to hold the liquid in place: we find gas (and oil) only in those places where all of these conditions are appropriately combined.

2.2 WHERE TO FIND NATURAL GAS