



Natural Gas

Fuel for the
21st Century

Vaclav Smil

WILEY

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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 (CO₂). 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 CO₂ 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, NO₂, N₂O) from combustion (be it of fossil fuels, fuel wood, or emissions from forest and grassland fires), lightning, and bacterial metabolism; sulfur oxides (SO₂ and SO₃) mainly from the combustion of coal and liquid hydrocarbons, nonferrous metallurgy, and also volcanic eruptions; hydrogen sulfide (H₂S) from anaerobic decomposition and from volcanoes; ammonia (NH₃) from livestock and from volatilization of organic and inorganic fertilizers; and dimethyl sulfide (C₂H₆S) 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 $\text{CH}_4\text{:CO}_2$ 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 . Reproduced from http://upload.wikimedia.org/wikipedia/commons/7/70/Terrace_field_yunnan_china_denoised.jpg. © Wikipedia Commons.

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 infiammabile 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 $\text{C}_n\text{H}_{2n+2}$. When in 1866 August Wilhelm von Hofmann proposed a systematic nomenclature of hydrocarbons, that series became known as alkanes (alkenes are C_nH_{2n} ; alkynes are $\text{C}_n\text{H}_{2n-2}$).

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 $1,400\text{ kg/m}^3$. 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