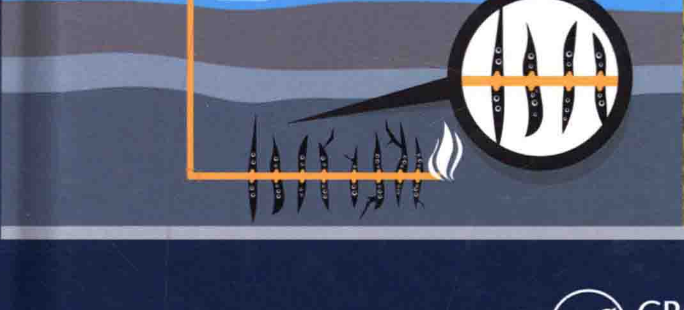
Chemical Energy from Natural and Synthetic Gas

Yatish T. Shah



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Engineering – Chemical

Chemical Energy from Natural and Synthetic Gas

"If you have a focused interest in the field of utilization and chemical transformation of natural and/or synthetic gas, this is one book you cannot live without. Two thumbs up!"
—Sunggyu Lee, Ohio University, USA

"This will be a first of its kind book which provides information on natural gas as well as synthesis gas…. serve[s] as a knowledge base for students or researchers interested or working in this area."
—Sandeep Kumar, Old Dominion University, Norfolk, Virginia, USA

Commercial development of energy from renewables and nuclear is critical to long-term industry and environmental goals. However, it will take time for them to economically compete with existing fossil fuel energy resources and their infrastructures. Gas fuels play an important role during and beyond this transition away from fossil fuel dominance to a balanced approach to fossil, nuclear, and renewable energies. ***Chemical Energy from Natural and Synthetic Gas*** illustrates this point by examining the many roles of natural and synthetic gas in the energy and fuel industry, addressing it as both a "transition" and "end game" fuel. The book describes various types of gaseous fuels and how are they are recovered, purified, and converted to liquid fuels and electricity generation and used for other static and mobile applications. It emphasizes methane, syngas, and hydrogen as fuels, although other volatile hydrocarbons are considered. It also covers storage and transportation infrastructure for natural gas and hydrogen and methods and processes for cleaning and reforming synthetic gas. The book also deals with applications, such as the use of natural gas in power production in power plants, engines, turbines, and vehicle needs.

- Presents a unified and collective look at gas in the energy and fuel industry, addressing it as both a "transition" and "end game" fuel.
- Emphasizes methane, syngas, and hydrogen as fuels.
- Covers gas storage and transport infrastructure.
- Discusses thermal gasification, gas reforming, processing, purification and upgrading.
- Describes biogas and bio-hydrogen production.
- Deals with the use of natural gas in power production in power plants, engines, turbines, and vehicle needs.

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Chemical Energy from Natural and Synthetic Gas

Dedication

This book is dedicated to my family: Mary, James, Rebecca, Jonathan, Heather, Keith, Laura, and my eight grandchildren.

Preface

As the world is engaged in realigning the energy and fuel portfolio, which is currently fossil fuel dominated, to one that is more balanced between fossil, nuclear, and renewable energies, one source of fuel that is considered as playing the role of not only a "bridge or transition fuel" but also an "ultimate or end fuel" is gas. While for several decades coal and oil have been the dominant forces for heating, electrical power generation, and fuel for transportation industry, recent concerns about global warming and carbon emissions from these sources have led to more push toward the use of renewable energy sources such as biomass, waste, solar, wind, geothermal, and water, as well as more recognition of carbon-free nuclear energy. Unfortunately, the commercial development of energy and fuel from renewables will take time to economically compete with existing fossil energy resources and their infrastructure.

The development of renewable and nuclear energy at the large scale faces many challenges. Biomass has low mass and energy density compared to coal and oil. They are difficult to transport long distances and they are not as easy to store as coal and oil. The same is true for waste. In general, municipal solid waste is also highly heterogeneous and it can only be used from local sources. For these reasons, the development of stand-alone, large-scale, and sustainable power or fuel plants from these sources is highly problematic. Small-scale plants cannot compete with the economy of scale of fossil fuel plants. Furthermore, the infrastructure for their storage and transport is not well developed. Their penetration in the energy and fuel industry may require a different strategy than one used for fossil fuels. This different strategy is addressed in my previous book *Energy and Fuel Systems Integration*, CRC Press, New York (2015). Similarly, both solar and wind energy are time and location dependent and cannot provide large-scale sustainable power without backup power supply by fossil or nuclear energy or backup energy storage. Their large-scale implementation will also require hybrid energy system strategy. The possible hybrid structures for this purpose are also discussed in my previous book. Solar and wind energy are not highly energy efficient and their infrastructures also need to be further developed. The large-scale commercial experience for power generation from these sources of energy is in its early stages of development.

While enhanced geothermal system has an enormous potential for its role in energy and fuel industry, the needed infrastructure and commercial experience for it to become a reality is also still at the development stage. Finally, as shown in my book *Water for Energy and Fuel Production*, CRC Press, New York (2014), water also has an enormous potential for providing unlimited supply of energy and fuel; however, both infrastructure and commercial experience to tap this still needs to be developed. Nuclear energy, in some parts of the world, still suffers from social and political acceptance and, as shown in my previous book *Energy and Fuel Systems Integration*, CRC Press, New York (2015), it will require a different strategy (more toward helping renewable energy penetration and its use for nonelectrical applications) to gain more public acceptance.

While the world must pursue, more aggressively, obtaining energy and fuels from renewable sources, the resolutions of the issues outlined in the previous paragraph will take time. While renewable sources of energy and fuel have distinct advantages over fossil fuels, their commercial production must economically compete with fossil fuels. In the meantime, one fuel that has the potential to be a true "transition or bridge fuel" or even the "ultimate or end fuel" is gas. This book illustrates this point by examining all the roles of natural and synthetic gas in the energy and fuel industry.

Gaseous compounds containing carbon and/or hydrogen are what make gas a source of energy and fuel. These compounds, such as methane, ethane, propane, butane (and other volatile hydrocarbons), syngas (mixture of hydrogen and carbon monoxide), and hydrogen have high heating values and can be used to generate energy and other types of fuels. These fuels can be basically obtained from two sources: natural and man-made. Gas from a natural source (obtained from underground) recovered by conventional or unconventional method is called natural gas. This gas predominantly contains methane as a source of energy and fuel. Man-made gas is called "synthetic gas" and it can be obtained by three different methods, as detailed later. The composition of synthetic gas varies depending on the process used to produce it. While natural gas only comes from nonrenewable sources, synthetic gas can come from both nonrenewable and renewable sources.

Just like coal and oil, natural gas is a fossil fuel obtained from underground, from the bottom of the ocean or from an arctic environment. In the past, natural gas was recovered from relatively shallow and easy-to-access natural gas reservoirs by conventional drilling techniques. Just like conventional oil well, this source of natural gas is rapidly depleting. Natural gas often contains oil, and this type of gas is called associated gas. Natural gas can also be obtained from stand-alone pure gas reservoirs, called nonassociated gas.

Recent developments in and success of the process of hydraulic fracturing and horizontal (or directional) drilling have allowed successful access to gas trapped in deeper (even more than 15,000 ft) and tighter and more compressed matrices underground. These techniques have allowed us to access unconventional gas such as deep gas, tight gas, gas from geo-pressurized zones, shale gas, and gas from coal bed methane. In the United States, the biggest revolution occurred in the production of shale gas. Along with these unconventional gas sources, gas hydrates (mixture of water and methane) are obtained from the ocean floor and in arctic conditions. All these combined unconventional gas resources have vast potential, and our improved ability to tap them has led us into the "gas age." With recent successes, the United States is now the world's leading producer of natural gas. This expanding supply has allowed us to replace coal by natural gas in power plants and diesel oil in large vehicles by Liquid Natural Gas (LNG), Liquid Petroleum Gas or Liquid Propane Gas (LPG), and Compressed Natural Gas (CNG). This "shale gas" revolution has allowed us to replace more harmful coal and oil by gas, which has made it a "transition or bridge fuel." Thus, we are slowly transitioning from a coal and oil–based economy to a natural gas–based economy.

Natural gas or methane is cleaner than coal and oil. It contains significantly larger hydrogen to carbon ratio (4) compared to the ones for coal (less than 1) and refined oil (around 1.2–1.6). It does not contain other harmful chemicals that cannot be handled upfront and are prevented from emission into the environment. Unlike coal, natural gas can be used for both large- and small-scale (like micro turbines and engines) power applications in a convenient manner. While natural gas has low mass and energy density compared to oil, LNG, LPG, and CNG have been found to be good substitutes for diesel oil in large vehicles and their use is both economically and environmentally competitive and gaining ground. A gallon of CNG has about 25% of the energy content of a gallon of diesel fuel and LNG has 60% of the volumetric energy density of diesel fuel. LPG has a typical specific calorific value of 46.1 MJ/kg compared with 42.5 MJ/kg for fuel oil and 43.5 MJ/kg for premium-grade gasoline. However, its energy density per volume (26 MJ/L) is lower than either that of gasoline or fuel oil. Its density (about 0.5–0.58 kg/L) is lower than that of gasoline (about 0.71–0.77 kg/L). All old coal-based power plants in the United States are gradually being replaced by those operated by natural gas. Natural gas usage in power plants is expected to double by 2040 and surpass that of coal. Similarly, the use of natural gas is expected to surpass that of oil by 2025.

Synthetic gas can be produced by three distinct methods: (a) thermal gasification of all carbonaceous materials or refining of oil to produce hydrocarbons such as propane, butane, etc.; (2s) anaerobic digestion of cellulosic waste; and (3) hydrothermal processes involving either gasification in the presence of steam, sub- and supercritical water, and/or hydrogen for all carbonaceous materials or water dissociation to produce hydrogen. These three methods produce synthetic gas of different compositions.

Unlike coal- and petroleum-based oil, gas can be produced synthetically by gasification and reforming of both nonrenewable and renewable carbonaceous materials. The feedstock for the production of synthetic gas can be coal, oil, biomass, waste, or a mixture of these. The thermal gasification of coal is a commercially proven technology. The refining of oil to produce hydrocarbons such as propane, butane, etc., is also a commercial technology. The gasification of other feedstock (like biomass, waste, etc.) is also being aggressively developed at both small and large scales. Cogasification of coal/biomass/waste mixtures is gaining momentum due to its impact on carbon emission into the environment.

Unlike natural gas, synthetic gas contains many fuel components, such as all volatile hydrocarbons, hydrogen, carbon monoxide, and other gaseous impurities depending on the nature of feedstock and gasification conditions. Synthetic gas produced in this manner has been given many names, such as "producer gas," "town gas," "wood gas," "syngas," "water gas," etc., depending on its composition. Producer gas can also be described as high-, medium-, or low-Btu gas depending on its methane and nitrogen concentrations. Thus, synthetic gas can replace natural gas for heating and power production. The most useful form of synthetic gas for liquid fuel production is "syngas," which is a mixture of hydrogen and carbon monoxide that can be converted to a variety of liquid fuels and chemicals by the well-recognized Fischer–Tropsch synthesis, iso-synthesis, oxo-synthesis, and methanol and mixed alcohol production processes. Often, gas produced by the gasification technology is called by the generic name "synthesis gas," which is synonymous to "syngas." Unlike natural gas, the sources for synthesis gas are unlimited.

Both methane and hydrogen can also be produced by the biological process of "anaerobic digestion," which can be carried out in the absence of oxygen and with the help of suitable microorganisms. The gas produced by this method is called "biogas" or "bio-hydrogen." With the use of methanogenic bacteria, the "biogas" produced mainly contains methane and carbon dioxide. Landfill gas is a type of "biogas" largely containing methane and carbon dioxide. Anaerobic digestion processes can also produce bio-hydrogen with the help of appropriate microorganisms. In the presence of methanogenic bacteria, the produced "biogas" has a methane concentration of about 55% (the remainder being mostly carbon dioxide) as opposed to conventional natural gas that has a methane concentration of about 95%. The methane concentration in "biogas" is, however, very similar to that in "shale gas." Biogas can be refined to produce "bio-syngas," which is very similar to syngas produced from thermal gasification technologies.

The third type of synthetic gas is hydrogen or gas concentrated with hydrogen produced by two separate methods. Gas containing a high concentration of hydrogen can be produced by gasification in the presence of steam and sub- and supercritical water with or without hydrogenation of all carbonaceous materials. These processes are generally considered as "hydrothermal gasification." The second method involves the dissociation of water by electrolysis and photocatalytic, photobiological, thermal, thermochemical, and other novel methods. These methods generally produce pure hydrogen. Many consider hydrogen to be the "ultimate fuel" because it contains no carbon. The world will be much safer and cleaner if all the energy is provided from carbon-free sources. Thus, technological developments and commercialization of all types of "synthetic gas production," and in particular hydrogen production, will make large-scale synthetic gas production the end game (not just a transition game like natural gas) for energy and fuel industry.

Natural and synthetic gas can be converted to syngas with the desired composition of hydrogen and carbon monoxide by the process of "gas reforming" so that the mixture can be used to produce liquid fuels, fuel additives, and chemicals via Fischer–Tropsch synthesis, iso-synthesis, oxo-synthesis, and others. Gas reforming is one of the most important technologies for natural and synthetic gas and its further development can transform the role of gas from a "bridge fuel" to more of an "end fuel" through the production of syngas and hydrogen from methane and other carbonaceous materials. One type of gas reforming, namely, dry reforming, which involves the use of carbon dioxide to convert synthetic gas or carbonaceous materials to syngas, can also be an answer to reduce carbon dioxide emission. The book critically evaluates the effectiveness of various available technologies for gas reforming. Further developments in various types of reforming processes will further accentuate the role of "synthetic gas" as the "ultimate fuel."

Unlike coal and oil, natural gas, and various types of synthetic gas, can be easily cleaned up and upgraded to the desired level so that using them for power, heat, and liquid fuel applications does not result in harmful emissions into the environment. Both natural and synthetic gases also need to be cleaned to prepare them for storage and the transport. The book evaluates all the available technologies to clean and upgrade gas coming from different sources.

One of the reasons natural gas is becoming so important in the energy and fuel industry is that its storage and transportation infrastructure is well established and it is constantly expanding. The concept of gas grid, analogous to smart electrical grid, is being developed and this will make gas, heat, and electricity the dominant future forces of the energy and fuel industry. Natural gas storage technologies in all its forms (natural gas, LNG, LPG, CNG) are well established on a regional basis and progress is constant. While the natural gas infrastructure can be used for hydrogen in small quantities (5 to 15 vol%), the storage and transportation infrastructure for hydrogen is still at the research stage. Once that is developed, gas will truly become the "ultimate fuel." The book evaluates storage and transportation options for natural gas, syngas, and hydrogen.

The book also evaluates various end usages of natural gas, syngas, and hydrogen. Various gas-to-liquid fuel technologies and the role of hydrogen in refinery industries are assessed. Hydrogen is the most valuable commodity in the fuel industry. The book evaluates the role of methane, syngas, and hydrogen in large- and small-scale power production. Over next twenty years, gas will be the most dominant fuel in the power industry, surpassing coal and oil by a large margin. ExxonMobil predicts that by 2040, gas will generate 30% of the total electricity as opposed to its current value of 20%. The use of gas in small-scale power generation is rapidly rising. The use of gas for various heating purposes will also rapidly expand. Another area where the use of gas is rapidly expanding is the vehicle industry where LNG, LPG, and CNG are replacing gasoline and diesel fuels, and the use of fuel cell is on rise. The use of hydrogen for both stationary and mobile fuel cells is gaining momentum. The book evaluates all of these applications of gas in a critical manner.

In summary, this book differs from numerous other books on natural gas, synthesis gas, and hydrogen published previously in that it presents the unified and collective role of gas in the energy and fuel industry. It addresses both the "transition" as well as the "end game" role of gas. Most people believe hydrogen and electricity will be the pivotal sources of energy in the future. Syngas chemistry for the production of liquid fuels and chemicals has a vast future because syngas can be obtained from both natural gas and man-made synthetic gas. The development of smart gas grid will make the use of gas for heat, power, and liquid fuel unavoidable in the years to come.

This comprehensive book on natural and synthetic gas will be useful to all researchers involved in the development of new technologies for energy and fuel. It will be a good reference for graduate courses on energy and fuel and can serve as a graduate-level text on the subject of gas as a source of fuel and energy.

Author

Dr. Yatish T. Shah received his BSc in chemical engineering from the University of Michigan, Ann Arbor, Michigan and MS and ScD in chemical engineering from Massachusetts Institute of Technology, Cambridge, Massachusetts. He has more than 40 years of academic and industrial experience in energy-related areas. He was chairman of the Department of Chemical and Petroleum Engineering at the University of Pittsburgh, dean of the College of Engineering at the University of Tulsa and Drexel University, chief research officer at Clemson University, and provost at Missouri University of Science and Technology, University of Central Missouri, and Norfolk State University. He was also a visiting scholar at Cambridge University in the United Kingdom and a visiting professor at the University of California, Berkley, and Institut für Technische Chemie I der Universität Erlangen, Nürnberg, Germany. Dr. Shah has written six books related to energy: *Gas-Liquid-Solid Reactor Design* (published by McGraw-Hill, 1979), *Reaction Engineering in Direct Coal Liquefaction* (published by Addison-Wesley, 1981), *Cavitation Reaction Engineering* (published by Plenum Press, 1999), *Biofuels and Bioenergy—Processes and Technologies* (published by CRC Press, 2012), *Water for Energy and Fuel Production* (published by CRC Press, 2014) *and Energy and Fuel Systems Integration* (CRC Press, 2015). He has also published more than 250 refereed reviews, book chapters, and research technical publications in the areas of energy, environment, and reaction engineering. He is an active consultant to numerous industries and government organizations in the energy areas.

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