Alternative Energy Sources

# Beyond Oil and Gas: The Methanol Economy**

*George A. Olah**

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Oil and natural gas together with coal, the main fossil fuels, not only remain our major energy sources but they are also the feedstocks for a great variety of manmade materials and products that range from gasoline and diesel oil to varied petrochemical and chemical products, including synthetic materials, plastics, and pharmaceuticals. What nature gave us as a gift, formed over the course of eons, is being used up rather rapidly. Fossil fuels continue to be significantly depleted and will become increasingly costly. Thus we need to search for new sources and solutions.

All fossil fuels are mixtures of hydrocarbons, which contain varying ratios of carbon and hydrogen. Upon their combustion, they are irreversibly used up: carbon is converted into carbon dioxide and hydrogen into water. On a related note, the increase of the $CO_2$ content of the atmosphere is considered a major manmade cause of global warming.

## Coal and the Industrial Revolution

Coal is considered to have been formed during the so-called carboniferous period some 300 million years ago from the anaerobic decomposition of then-living plants. Its use for heating purposes began slowly and became more widespread in the 16th and 17th centuries mainly in England as a replacement for wood, which was becoming scarcer. Coal became dominant in the 18th century with the invention of the steam engine and the industrial revolution, which was also fueled by coal, that followed. In the 19th and 20th centuries, coal continued to satisfy the ever-increasing energy demand of mankind, and today it is used primarily for generating electricity.[1] Whereas our coal reserves may last for another two or three centuries, the mining of coal (except in areas suited for surface strip mining) is increasingly affected by socio-economical, safety, and environmental difficulties.

## Oil and Natural Gas

Since the latter half of the 19th century, petroleum oil and natural gas have become increasingly important and dominant energy sources and raw materials for chemicals and manmade materials. They are certainly the most convenient fossil-fuel sources.

Much has been said over the years about the extent of our available oil and gas resources. At first glance, estimated world oil and gas reserves look impressive. These reserves seem not to have diminished in the last 50 years[2] owing to continuous developments and improved technologies that have allowed exploration, production, and recovery from increasingly difficult-to-access areas, such as the depths of the seas and inhospitable land areas from deserts to the Arctic. Conservation of energy and secondary and tertiary recovery from previously exploited fields are significant, but will not fundamentally change the long-range outlook.

Besides petroleum oil and natural gas (and also coal), we have additional sources of "heavy" hydrocarbons, such as heavy-oil deposits in Venezuela, oil shales in various geological formations including the US Rocky Mountains, and vast tar sand deposits in the Canadian province Alberta. The relatively stable hydrates of methane, as found under the Siberian tundras and along the continental shelves of the oceans, represent significant possibilities for natural gas deposits in the future. They will all eventually be exploited, although the difficulties and expense involved are extensive.

Besides the size of oil reserves (1–1.5 trillion barrels or some 200 billion metric tons), one must also consider our expanding world population, which exceeds 6 billion now and will probably approach 9–10 billion by the mid-21st century, as well as increasing standards of living and demand in countries such as China and India if one wants to predict how long the estimated oil reserves may last. Present estimates of our proven oil reserves reveal that they would last for some 40 years at the current rate of consumption. Natural gas reserves are comparable but somewhat larger. New developments and improved recovery methods, however, could extend these estimates significantly.

## Alternative Energy Sources

To satisfy mankind's ever-increasing energy needs, one has to consider all feasible alternative energy sources. Hydro- and geothermal energy are used where Nature makes it feasible, but no

[*] Prof. Dr. G. A. Olah
Loker Hydrocarbon Research Institute and Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661 (USA)
Fax: (+1) 213-740-5087
E-mail: olah@usc.edu

[**] An identically titled monograph that discusses various aspects of the methanol economy is being published by Wiley-VCH.

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major new sources have been found. Energy from the sun and wind, and waves and tides of the seas all have real potential and are increasingly exploited, but their use on such a large scale so as to substitute fossil fuels is not likely to significantly affect our energy outlook in the foreseeable future.[3]

## Atomic Energy

Probably the greatest technological achievement of the 20th century was to harness the energy of the atom. Regretfully, as it was first achieved by building the atomic bomb, in subsequent years public opinion increasingly turned against atomic energy, even for peaceful uses. Over the last few decades, relatively few new atomic power plants were constructed. There is even strong sentiment to close them down altogether in some countries, although others such as France depend on them for some 80% of their electricity needs. Progress has been made to limit the use of atomic energy to only peaceful uses and to improve its safety aspects, including the storage and disposal of radioactive waste. I believe that our society, which was able to build the atomic bomb, can and will solve these problems. In my opinion, the decline of the atomic energy industry is most regrettable. Whether or not one supports atomic energy, in the long term it is the most feasible and massive energy source for mankind.[4] Conservation and use of alternate energy sources are most desirable, but they cannot replace, by themselves, the "classic" energy sources in fulfilling mankind's enormous energy demand.

## Energy Storage and Distribution

Despite their nonrenewable nature and diminishing resources, fossil fuels and particularly oil and gas will maintain their leading role as the most convenient source of transportation fuels and energy sources as long as they last. A vast infrastructure exists for their transport and distribution. As transportation fuels for our cars, trucks, and airplanes, they can be used in the form of their convenient products (liquid gasoline, diesel fuel) or as compressed natural gas. They are also the basic raw materials for chemical products and materials that are essential to our everyday life. However, the bulk of fossil fuels is utilized in power plants to generate electricity. From whatever source electricity is generated, its storage on a large scale is still unresolved; for example, batteries are inefficient and bulky. It is thus necessary to also find, besides new energy sources, efficient means to store and distribute energy.

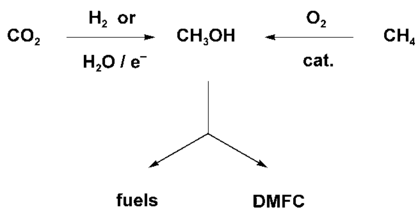
## The Hydrogen Economy and Its Difficulties

With our diminishing resources of fossil fuels, there is urgent need to develop feasible new and safe ways to store and distribute energy from whatever sources it is generated (atomic or alternate) as well as to produce efficiently manmade hydrocarbons.

One approach that was proposed and has been much discussed recently is the generation of hydrogen and its use as a clean fuel—the so-called "hydrogen economy". Hydrogen is not a natural energy source on earth as it is incompatible with the high oxygen content of our atmosphere. Whereas it is indeed clean burning to form water, its generation is a highly energy-consuming process, which itself is not necessarily clean. Presently it is mainly produced by the reforming of fossil fuels to give syngas (synthetic gas), a mixture of CO and $H_2$. The generated CO can also be used in the water gas shift reaction to yield more hydrogen. In this process, however, at least 20% of the energy of the fossil fuel is lost as heat. Hydrogen can also be produced by the electrolysis of water, a process that does not produce $CO_2$ nor involve a source of fossil fuels. Our oceans represent inexhaustible water sources that can be split by atomic energy or any of the alternate energies to produce hydrogen. Despite this, hydrogen is not convenient either as a means to store energy or for its subsequent use as a fuel. The handling of volatile (b.p.: −253°C) and potentially explosive hydrogen gas necessitates special conditions: high pressure, use of special materials to minimize diffusion and leakage, and extensive safety precautions. Even so, any leaks could represent explosion hazards, which limits its potential use. Regardless, the U.S.[5] and other governments as well as major industries seem to be increasingly committing themselves to develop the hydrogen economy. Besides the mentioned difficulties of hydrogen storage and distribution, the development of the needed infrastructure for the hydrogen economy, in my view, is also economically prohibitive, although this infrastructure may eventually be developed. The volumetric power density of liquid hydrogen is also a drawback at only one-third of that of gasoline, while liquefying hydrogen requires considerable amounts of energy.[6]

## The Methanol Economy and Its Advantages

Methanol, which is presently prepared from fossil-fuel-based syn-gas, can also be prepared by direct oxidative conversion of natural gas (methane) or reductive conversion of atmospheric carbon dioxide with hydrogen (Scheme 1). In this way, hydrogen can

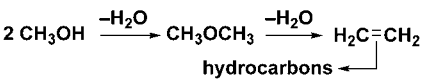



*Scheme 1.* Production of methanol from atmospheric carbon dioxide or from natural gas (methane), and its use as a fuel. DMFC: direct methanol fuel cell.

be stored by converting it into methanol—a convenient liquid fuel and raw material for synthetic hydrocarbons and their products—with carbon dioxide from industrial effluents or the atmosphere. This opens up the possibility of an alternative energy source to diminishing oil and gas resources and would lead to a feasible "methanol economy".

Owing to the serious limitations of the hydrogen economy, I have been proposing for some time now the methanol economy as a reasonable alternative.[7] Methanol provides an efficient means to store energy and can be used as a convenient fuel as well as a raw material for manmade hydrocarbons and their products.

Methanol is an excellent fuel in its own right and it can also be blended with gasoline, although it has half the volumetric energy density relative to gasoline or diesel. It is also used in the direct methanol fuel cell (DMFC) that we developed jointly with the Jet Propulsion Laboratory of Caltech.[8] In this electrochemical cell, methanol is directly oxidized with air to carbon dioxide and water to produce electricity, without the need to first generate hydrogen. This greatly simplifies the fuel-cell technology and makes it available to a wide scope of applications: for example, to provide power to cellular phones and computers (already under development) and eventually to motor scooters and cars, or even to use it in large electricity-generating facilities. It was also found that methanol can be conveniently converted into ethylene or propylene in the MTO (methanol-to-olefins) process (Scheme 2). In turn, these olefins can be used to produce hydrocarbon fuels and their products,[9] which are presently obtained from oil and gas. UOP, based on the earlier work of Jule Rabo and coworkers,[9d] developed an industrial process for the production of ethylene from methanol using acidic zeolite catalysts, and industrial plants based on this process are now under development.[9e]



***Scheme 2.*** Conversion of methanol into ethylene (or propylene) on the way to hydrocarbons and their products.

In contrast to hydrogen gas, methanol is a convenient and safe liquid (b.p.: 64.7 °C). Whereas it is toxic when internally ingested and is frequently quoted as a poison, so are gasoline and diesel fuel. Some suggestions were made to use ethanol as a fuel as it can be made by fermentation from agricultural products. However, its use as a fuel has many drawbacks, and even Brazil is limiting its ambitious program to convert sugar cane into ethanol fuel. The overall economics to produce agriculture-based ethanol to replace fossil fuels is also not favorable. In fuel cells, ethanol encounters further difficulties as cleavage of C–C bonds is more difficult than cleavage of C–H bonds. Interestingly, it was Lenin that supported the industrial use of agricultural alcohol after the Bolshevik Revolution, but even the Russians resisted the "misuse" of their beloved vodka and the plan was abandoned.

At present, methanol is produced nearly exclusively from syn-gas, which is obtained by catalytic reforming of fossil fuels.[9b] As long as natural gas remains quite abundant, it seems reasonable to convert it directly (without first producing syn-gas) into methanol. In our research, much progress was made in the direct oxidative conversion of methane into methanol. As mentioned earlier, large resources of methane are tied up as gas hydrates in vast areas of sub-Arctic tundras and under the seas in the areas of the continental shelves.

## *Chemical Recycling of $CO_2$*

As mentioned earlier, methanol can be also obtained by the reduction of carbon dioxide with hydrogen. Flue gases of coal- or fossil-fuel-burning power plants may be an abundant source of readily isolable carbon dioxide for the foreseeable future. Many industrial exhausts also contain considerable concentrations of carbon dioxide. Water can provide the required hydrogen. Instead of just sequestration, this process would recycle carbon dioxide into useful fuel and provide a source of hydrocarbons.

For the long-range solution to mankind's hydrocarbon needs as well as for efficient storage of energy that will eventually be generated from nonfossil fuel sources, the utilization of atmospheric carbon dioxide itself through its reduction to methanol offers a feasible new alternative. However, the content of carbon dioxide in the atmosphere is low at 0.037 %. Thus, new efficient ways to separate $CO_2$ are needed. One way is membrane separation technology, another is the use of selective absorption methods; here our ongoing research has led to significant advances to allow practical separation of atmospheric $CO_2$ from air. Besides, in the conversion of $CO_2$ to methanol, volatile hydrogen gas is converted into a convenient, safe liquid. If we can produce methanol efficiently on a large scale from atmospheric carbon dioxide and hydrogen, it could replace oil and gas both as a fuel and as a chemical raw material.

Atmospheric carbon dioxide is available to everybody on earth. The methanol economy thus eventually can liberate mankind from reliance on fossil fuels. The required hydrogen can be obtained from the electrolysis of water of the seas—an unlimited source. The electrical energy will be provided by atomic energy, which will be made safer and solved of problems pertaining to radioactive waste disposal, as well as by all suitable alternate energy sources (sun, wind, and hydroelectric). Alternatively, direct aqueous electrochemical reduction of $CO_2$ can be used,[7b] and photochemical reduction of $CO_2$ is also feasible. I believe that it is reasonable to consider the methanol economy as a practical and sensible approach to eventually replace fossil fuels. It can provide a feasible and safe way to store energy, to make available a convenient liquid fuel, and assure mankind an unlimited source of hydrocarbons, while at the same time mitigating the dangers of global warming owing to the greenhouse effect of carbon dioxide. In contrast to highly volatile hydrogen, methanol is a convenient liquid. Its use does not necessitate the development of a new and extremely costly and unproven infrastructure, nor does it suffer the great difficulties of safety as with the use of hydrogen.

The hydrogenation of carbon dioxide either by catalytic conversion with $H_2$ or by electrochemical reduction, including the reverse use of the direct methanol fuel cell,[7b] produces formic acid and formaldehyde besides methanol. It is possible, however, to further convert formic acid and formaldehyde into methanol and allow an overall high yield of methanol to be obtained. The direct oxidation of methane, which is still available from natural gas sources, into methanol also should be considered. This also always produces significant amounts of formaldehyde and formic acid. Higher selectivities to obtain methanol were reported only under low-conversion conditions.[10] With this in mind, we were successful in dramatically increasing the yields of methanol by the secondary conversion of formaldehyde/formic acid into methanol.

I suggest that carbon dioxide recycled by chemical reduction will provide an essential source of methanol for use as a fuel as well as a raw material for synthetic hydrocarbons and their products. Nature, of course, recycles carbon dioxide in the photosynthesis of plants by using water and solar energy in a process catalyzed by chlorophyll. However, the formation of hydrocarbons from plant life is a very slow process that requires hundreds of millions of years, although much faster bacterial conversion is feasible.

Methanol was suggested before as a fuel and a bridge to a renewable energy future,[11] however, these suggestions were never followed up by implementation. The reason, besides economic and practical factors, most probably was that methanol that originates from syn-gas generated from fossil fuel does not alleviate our dependence on fossil fuels.

The methanol economy through chemical recycling of carbon dioxide will eventually free mankind from dependence on diminishing natural fossil fuels. At the same time, recycling excess $CO_2$ from industrial gases and the atmosphere will mitigate a major man-made cause of global warming. The collection and sequestration of $CO_2$ in subterranean cavities or at the bottom of the seas is costly and does not provide a permanent solution, nor does it resolve our future needs for hydrocarbons. The still-controversial Kyoto agreement on global warming, which aims to limit $CO_2$ emissions, would be made more feasible by the availability of new technology, such as the chemical recycling of excess atmospheric carbon dioxide.

Ultimately all of our energy comes from the sun. As the sun will last for at least 4.5 billion years, there is an enormous amount of time for mankind to devise methods for harnessing its energy. We cannot in any way imagine advances of future generations. Discussion of what will happen beyond our present oil and gas economy relates to only the foreseeable future. Nevertheless, to find efficient ways to store energy and to produce convenient hydrocarbon-based fuels and products while mitigating global warming by recycling carbon dioxide is essential to our life and has long-range significance.

In the suggested methanol economy, methanol will be used as 1) a convenient energy-storage material, 2) a fuel, and 3) a feedstock to synthesize hydrocarbons and their products.

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