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Towards Oil Independence Through Renewable Methanol Chemistry

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Introduction

Coal, oil, and natural gas, so called fossil fuels, since the industrial revolution in the 18th century have provided mankind with cheap, accessible energy, fuels, and raw materials for varied products and materials. What nature has given us as a most precious gift is however increasingly consumed and depleted. Petroleum oil was recognized to be an essential source for illuminating oil in the 1860s followed by its use for heating and varied other applications including eventually electricity generation. It became essential for the production of transportation fuels after the introduction of internal combustion engines for cars and other vehicles, followed by planes and other means of transportation. Its use as a raw material for petrochemical and chemical products also gained great significance. The demand for oil continues to expand owing to a growing population and increase in standard of living. Our oil reserves are however limited and the majority of the remaining reserves are located in the Middle East and other politically sensitive regions setting the trend for great uncertainty. New discoveries (including shale gas), advanced technologies, savings, and improved methods of use, as well as changing economic climates have extended the availability of relatively "cheap oil", albeit only by decades. By all estimates we will continue to face an increased shortage and thus increase in prices. At the end of the century this will result in inevitable fundamental changes in the availability and use of oil. Now is clearly the time to develop new feasible substitutes for petroleum oil.[1,2]

To overcome problems of diminishing oil resources, the world is already shifting to more-abundant natural gas, but even this will last only for a limited time. We clearly must find ways to live increasingly without oil while meeting the needs of world's growing population and safeguarding the quality of our environment. The questions of our carbon conundrum have been discussed in excellent books.[1,2]

It is not in the scope of this Essay to discuss in any depth either humankind's energy needs or energy availability. Most energy on earth is basically coming, or is derived in one way or other, from the sun. We are essentially not "producing" energy, only collecting what nature gives us or can be "liberated" from the energy of the atoms either by nuclear fission or in the future by controlled nuclear fusion. The Essay centers on feasible ways to replace diminishing natural petroleum oil based on renewable methanol chemistry developed in continuation of our previous work in hydrocarbon chemistry.[3] A monograph with Goeppert and Prakash[4] discusses in more depth and detail the background of the field and gives credit to the extensive and valuable work of others in the field. It emphasizes, however, primarily my approach and ongoing development of the methanol economy which I began to pursue in the 1990s.

Methanol as a Feasible and Economic Substitute for Oil

Our coal and natural gas sources and reserves greatly exceed those of oil. The need for their feasible conversion into synthetic oil and derived hydrocarbon products by technological processes was recognized early and pursued since.

To produce synthetic oil and its products, two approaches were successfully developed in the past. One is based on the liquifaction of coal, which started in the 1920s in Germany with the Fischer–Tropsch syn-gas chemistry to convert abundant coal to liquids. Later the chemistry was extended to the conversion of natural gas into liquids (natural-gas-to-liquids (GTL) technologies). Neither routes are, however, renewable or safeguard our environment. Processes based on synthesis gas (syn-gas) are still widely used by the chemical and petrochemical industry. Syn-gas is a complex variable composition mixture of CO and H_2 ranging from ratios of 1:1 to 1:3. Its use in preparing synthetic oil products involves multi-stage and complex technology with all its limitations and cost. The syn-gas composition can be adjusted by separate steam and dry reforming, water-gas shift reaction, and other steps. Our developed "bireforming" process in contrast produces exclusively a 1:2 $CO:H_2$ gas composition named "metgas" for the only purpose of producing methanol.

I consider the books by Daniel Yergin "*The Prize*" followed by "*The Quest*"[5,6] written for the general public, discussing the great question of energy and security and the remaking of the modern world, an excellent source for those interested in the historical background of our oil conundrum.

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In the earlier essay "*Beyond Oil and Gas: The Methanol Economy*"[7] I have discussed the concept and ongoing development of relevant new chemistry to use methanol (at the time prepared exclusively from fossil-fuel-based syn-gas) as a transportation fuel, as an energy storage medium (a convenient "liquid hydrogen" carrier), and as raw material to produce the products and materials now derived primarily from oil. References and full credit to the extensive significant previous work and developments are given in our monograph and several review articles.[8,10,11]

Yergin also discusses alternative energy sources, such as hydrogen, geothermal, solar, wind, as well as atomic energy pointing out their advantages but also limitations (availability, cost, safety, need for storage, transportation). It should be pointed out that methanol was previously used to a limited degree in California as a transportation fuel in the 1980s–1990s (as M-15, M-85, and even M-100) but was abandoned subsequently. Significant development was also made in commercial-methanol-to-gasoline (MTG) conversion by Mobil in New Zealand. These efforts, however, were subsequently also abandoned as the effects of temporary major oil crises were soon forgotten. The establishment of OPEC, and making available plentiful supplies caused the world oil market to settle down to a less than $20 a barrel level. It held for a time but prices have since increased fivefold owing to increased use and demand and diminishing reserves. They are now around the $100 a barrel level and will inevitably continue to increase with intermittent periods of price fluctuation.

The Methanol Economy concept outlined in my earlier Essay[7] is by now much further developed. Progress is also being made towards practical applications. Carbon Recycling International in Iceland completed and operates the first commercial CO_2-to-renewable-methanol plant based on geothermal sources (Figure 1). There is increasing interest in methanol and its derived products (synthetic gasoline, Diesel oil, dimethyl ether (DME), and varied chemical products) for replacing diminishing petroleum oil in a growing number of countries from China to the EU and also the USA.

Figure 1. The "George Olah Carbon Dioxide to Renewable Methanol Plant" of Carbon Recycling International in Iceland based on local geothermal energy. The first commercial carbon dioxide recycling plant operating in the world (Courtesy: K. C. Tran, CEO, Carbon Recycling International, Iceland).

All carbon-containing fuels and materials upon their combustion or oxidative use generate CO_2. Capture and recycling of CO_2 to methanol (CCR) instead of just capturing and storing it (CCS), makes methanol renewable and is an essential part of the methanol economy. The hydrogen needed can be generated from natural gas, shale gas, and other methane sources or by electrolysis (or cleavage) of water. Carbon recycling to renewable methanol can use any available alternative energy for the required heat of processes. It allows increasing independence from petroleum oil providing transportation fuels and derived chemical products and materials. It is not considered to be the only or the ultimate solution to our carbon conundrum but it is a feasible and economic approach.

We have in recent years also developed a method for the use of methanol to generate electricity in a fuel cell, that is, the direct oxidation methanol fuel cell (DMFC). Using it in a reversed way it can operate as a regenerative fuel cell to recycle CO_2.[4] Carbon dioxide recycling further mitigates the effect of excessive CO_2 emissions that contribute to increasing global warming and climate change.[8b]

The chemical carbon recycling supplements nature's photosynthetic cycle. Our relevant discoveries and intellectual property of the new renewable methanol chemistry are disclosed and protected in a series of some 25 patents and patent applications. Continuing scientific publications and our monograph in its second expanded and updated edition published in 2009 give much descriptions and details.[4]

Methanol is a convenient liquid at ambient temperature and can be readily stored, transported, and distributed using essentially existing infrastructure. Methanol is an excellent fuel for varied internal combustion engines. It can be readily converted by dehydration to dimethyl ether (DME), which is a clean burning high cetane fuel, capable of replacing Diesel fuel. Methanol itself can be directly used as a fuel in recently developed spark-ignition-assisted Diesel engines. DME can also replace liquefied petroleum gas (LPG), compressed natural gas (CNG), and liquefied natural gas (LNG) in many applications including heating and cooking (in stoves). Besides its use as a fuel, methanol can be readily transformed to ethylene and propylene, thus replacing oil as the raw material for key products of the petrochemical and chemical industry. As it is today for petroleum, it is estimated that the chemical use of methanol will however represent less than 10% of the transportation fuel use. Recent discoveries of new natural gas sources, such as shale gas, coalbed methane, and eventually methane hydrates which are more plentiful than conventional natural gas reserves, expands the gas sources for the discussed methanol chemistry.

The carbon dioxide required for the methanol chemistry can come from diverse natural and anthropogenic sources, including exhausts from the combustion of natural (shale) gas. Initially, for conversion into methanol, high-concentration exhausts of power plants, varied chemical plants, cement plants, fermentation plants (breweries) can be used as well as varied natural sources, such as CO_2 accompanying natural gas, geothermal wells. Eventually, even the carbon dioxide content of the air can be utilized.[9] The increasing carbon dioxide content of our atmosphere (ca. 390 ppm) is a significant contributing factor to global warming. The separation and recycling of CO_2 is feasible when cheap energy is available and is being explored. For the chemical CO_2 recycling, non-fossil-based energy, such as solar, wind, hydro, geothermal, or even nuclear (with the risks of accidents and effects of natural catastrophes significantly reduced), is becoming increasingly available.

As CO_2 is naturally recycled from the atmosphere through photosynthesis, the use of agricultural- and natural-carbon-based biofuels, such as corn- or sugar-derived bioethanol, vegetable-oil-based biodiesel is increasingly being developed. However, these fuels interfere with the food chain, drive food prices up, and have considerable negative impact on the environment. Vegetation and non-edible crops, waste biomass and cellulosic materials can be used in contrast in a sustainable manner. All biofuels, however, supplement only a small part of our overall fuel requirements.

Production of Renewable Methanol

For a long time, methanol production was based on fossil fuels (oil, natural gas, or coal) by conventional syn-gas chemistry.[8] Haldor Topsøe developed[8f] the partial oxidation of natural gas based on an autothermal reforming process in which CO_2 is partially recycled in a processes called trireforming. It uses in situ combustion of natural gas with added oxygen (or air) to provide the process heat thus generating much CO_2, which besides recycling can be separated and stored (CCS). This multistep process involves, however, substantial expense and waste.

In contrast to conventional syn-gas mixtures, our renewable methanol chemistry generates only a 1:2 CO:H_2 mixture called "metgas" in a single-step process exclusively for methanol production. Methanol is produced from methane (or natural gas), CO_2, and steam in a 3:1:2 ratio in what is called bireforming. As mentioned, the methane (or natural gas) needed can come from varied sources. Carbon dioxide is available from varied natural or industrial sources and when needed is pre-purified from accompanying impurities, primarily H_2S which can poison catalysts. The process operates advantageously in a pressurized flow system at temperatures of 800–1000 °C and pressures of 5–40 bar over a nickel-based catalyst [Eq. (1)]. The conversion of metgas into methanol is well developed and practical with very high yields and purity.

$$3\,CH_4 + CO_2 + 2\,H_2O \rightarrow 4\,CO + 8\,H_2 \rightarrow 4\,CH_3OH \qquad (1)$$

Natural or shale gas containing higher alkanes can also be directly used in the bireforming process. Adjustment of the steam and CO_2 ratios allows the production of metgas with the CO/H_2 ratio of 1:2. In the more distant future our very large methane hydrate sources on the continental shelves of the oceans or under arctic tundras should be able to provide methane for many centuries.

Necessary water can come from any source but must be "clean", purified from salt (in case of seawater) and other impurities. Our atmosphere itself contains, depending on location, 2–8 % of moisture that can also be separated and used in bireforming.

The one-step bireforming route offers other overall advantages since many natural gas sources contain significant amount of CO_2. Such methane/CO_2 mixtures can be easily adjusted for bireforming avoiding the need for prior separation.[10,11]

CO_2 can also be converted into methanol by hydrogenation over heterogeneous catalysts. Catalysts based on copper–zinc oxide–alumina can for example be used to produce methanol at 220–250 °C and 10–30 bar pressure. Hydrogen can be generated by water electrolysis (a mature technology). One third of the hydrogen is however converted into water [Eq. (2)].

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \qquad (2)$$

In fact, such a technology is already being used commercially in Iceland by Carbon Recycling International (CRI). The required CO_2 is separated from the geothermal steam. The present annual production of 3500 tonnes is planned to be increased to 35 000 tonnes. In Japan, Mitsui Chemicals is operating an approximately 100 tonnes per year^1 pilot plant using CO_2 obtained as a byproduct from other processes. Research and development in other countries is being actively pursued.

An electrochemical CO_2 recycling route is also being developed and involves initial selective reduction to formic acid [Eq. (3)]. Formic acid is then converted with methanol into methyl formate, which is catalytically reduced with hydrogen to give exclusively two mole equivalents of methanol [Eq. (4)].[10,11] Formic acid itself is an excellent hydrogen carrier.[12]

$$CO_2 + 2\,H^+ + 2\,e^- \rightarrow HCOOH \qquad (3)$$

$$HCOOH \xrightarrow{CH_3OH} HCOOCH_3 + H_2O \xrightarrow{2\,H_2} 2\,CH_3OH \qquad (4)$$

CO_2 can also be electrochemically reduced to CO on gold-based electrocatalysts. Combining such a process with electrolysis, metgas can be produced at the cathode of the electrolyzer for the production of methanol [Eq. (5)].[10,11]

$$\begin{aligned} CO_2 + 2\,H_2O \xrightarrow[\text{Au Cathode}]{\text{Electrolyzer}} CO + 2\,H_2\ &(\text{at the cathode})\,/ \\ 1.5\,O_2\ &(\text{at the anode}) \end{aligned} \qquad (5)$$

Our proposed CCR is also suited for the conversion of carbon emissions of coal- or natural-gas-burning power plants into methanol and even renewable methanol.[10,11] It can diminish or make fossil-fuel-burning power plants emission's close to carbon neutral.

Conclusions

The suggestion and development of a carbon cycle to produce renewable methanol by chemical recycling of carbon dioxide allows substantially carbon-neutral production and the use of methanol. It can be achieved by bireforming with currently available methane (natural gas) sources or by CO_2 hydrogenation with hydrogen produced through water electrolysis. Energy for the processes can come from any conventional (off-peak period) or alternative energy sources. With decreasing fossil-fuel reserves, hydro, geothermal, and atomic energy, but primarily wind and solar energy are going to be used. In the long term, our atmosphere itself can be the source material for CO_2 and water. With inexhaustible solar energy they can produce methanol and oxygen using electrochemical or hydrogenative chemical conversion according to the overall process shown in Equation (6).[10,11]

$$CO_2 + 2\,H_2O \xrightarrow{\text{Solar energy}} CH_3OH + 1.5\,O_2 \qquad (6)$$

Progress takes time, but I believe that the foundations of an effective and practical carbon recycling, which converts CO_2 into renewable methanol (CCR), have been laid and are being increasingly translated into practical industrial use. For the rest of the century the use of natural (shale) gas and methane sources will continue, and when such sources are depleted, water cleavage will provide the required hydrogen for recycling CO_2 in which case renewable or atomic energy sources will be used. Humankind can replace the use of petroleum oil through the renewable methanol chemistry through CCR. At the same time, the methanol economy is capable of minimizing harmful environmental effects of CO_2 emissions (global climate change). Our technological carbon capture and recycling offers a sustainable and practical solution to our carbon-based-fuel and feed-stock conundrum, supplementing nature's own photosynthetic carbon cycle.

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