Methanol Production for Renewable Energy Storage and Distribution

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ABSTRACT

Certain processes for methanol production that use neither fossil fuel nor biological feedstock are examined. Because the source for the required carbon is CO_2 scrubbed from the air, combustion of the resulting methanol produces zero net CO_2 emission. The energy that drives the production process is thus cleanly stored and distributed in the form of methanol. The existing fossil fuel infrastructure can be highly leveraged for that storage and distribution. Proposals are given for the role that such methanol production might serve in facilitating the use of various energy sources, with focus on those that are renewable. A prototype of such a methanol production system using proven technologies is described. Conditions and alternative technologies for achieving economic viability are examined. Some solutions that methanol storage offers in addressing several major problems faced by the energy industry are discussed.

Keywords: methanol, electrochemical, Fischer-Tropsch, sequestration, DMFC

1 CLEAN METHANOL

Commercial methanol is typically produced from fossil fuel feedstock. The term 'clean methanol' is used here to describe methanol that is instead produced by alternative processes which share the following characteristics:

- The energy used to drive the process comes from neither a fossil fuel nor a biological source.
- The energy is largely used in extracting hydrogen from water.
- The required carbon is obtained by scrubbing carbon dioxide from the air.
- The hydrogen and carbon dioxide are combined exothermically to form methanol.

The prototype described in Section 3 shows how proven technologies may be combined into one example of such a process. When the resulting methanol is consumed in either traditional combustion or in a direct methanol fuel cell (DMFC), the water and carbon dioxide are returned to the environment. Figure 1 shows the complete cycle for the water, carbon dioxide, and oxygen used in the process; there is zero net CO_2 emission. The energy is effectively transported from a source that may be intermittent and/or

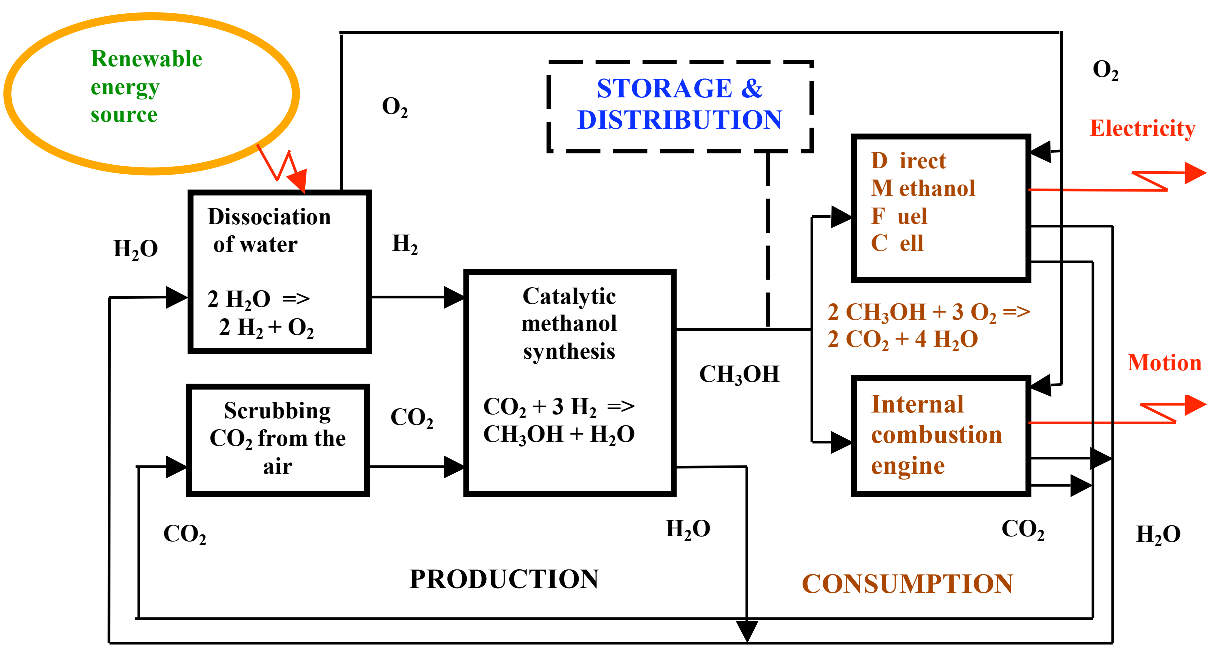

Figure 1: The Methanol Energy Cycle

inconveniently located to where it is needed for consumption, especially for transportation and heating.

2 VERSUS OTHER ENERGY SOURCES

Clean methanol may either complement or compete with other energy sources and means of distribution, both traditional and nascent, as follows:

2.1 Fossil Fuel: Coal, Oil, Natural Gas

Fossil fuels provide the largest source of energy for transportation and heating. With almost no change to the distribution infrastructure for gasoline, clean methanol can be blended with gasoline to reduce net CO_2 emission. With minor changes in infrastructure, clean methanol is a direct gasoline replacement with lower energy density, but with higher octane rating for good acceleration properties [1]. While methanol itself is a poor diesel replacement, dehydration of methanol according to:

$$2\ CH_3OH \Rightarrow CH_3OCH_3 + H_2O \quad (1)$$

yields dimethyl ether, a good diesel replacement, though requiring infrastructure changes for pressurized storage. Since power plants using coal and natural gas can fairly easily be replaced by those using liquid fuel, clean methanol offers a long term path to zero net CO_2 emission for most fossil fuel energy applications.

2.2 Solar, Wind

Solar and wind have both the advantage and disadvantage of being widely dispersed; available almost anywhere, but difficult to aggregate for efficiency especially near populous areas where energy consumption is greatest. Aside from local solar heating, solar and wind mostly supply the electric grid, but intermittent availability leads to peak power issues. Clean methanol production can complement solar and wind by enabling the use of sites far from the electric grid, by storing energy for peak periods, and by providing a path for renewable energy to be used for transportation and heating.

2.3 Geothermal, Hydro, Nuclear

Like solar and wind, these sources primarily supply the electric grid. Only hydro can be called renewable. Geothermal and hydro sources may be located far from the electric grid, in which case clean methanol can provide a means of distribution that avoids costly transmission lines. Nuclear can benefit from locating methanol production facilities near sources of uranium ore and waste storage, avoiding the transport of radioactive materials. As for solar and wind, clean methanol offers a path to make these energy sources available for transportation and heating.

2.4 The Electric Grid

The U.S. electric grid relies heavily on fossil fuel generation. Over time, other energy sources can be used instead, but fuel fired power plants are good for handling peak power and for avoiding excessively long transmission lines. Clean methanol can serve as fuel for those plants in keeping with a goal of zero net CO_2 emission. Electricity for transportation requires costly batteries, and electricity for heating is more costly than fuel combustion heating. Clean methanol thus remains a preferred transportation and heating solution in the long term.

2.5 Hydrogen

Hydrogen, while a clean energy source, faces severe storage and safety problems particularly for transportation and residential heating. Clean methanol can be viewed as a hydrogen storage solution, achieving high energy density and safety by binding the hydrogen to carbon in the form of liquid methanol. Analogous to hydrogen fuel cells, transportation grade DMFCs can provide direct conversion to electricity for clean and quiet vehicles.

2.6 Biofuel

Wood, the oldest biomass fuel, is still used in the third world despite frequently devastating deforestation. Corn based ethanol competes with an important food/feed use of corn. Even cellulose based ethanol competes for valuable agricultural land. The net solar energy/acre/year captured in biofuel is far less than can be obtained by covering that acre with PV panels (factor of 40 less) or by producing clean methanol from the PV electricity (factor of 20 less).

3 PROTOTYPE SYSTEM

Figure 2 shows the major subsystems of a prototype under development. One square meter of PV panels is chosen as the energy source, with 12v battery storage to span periods of intermittent sunlight. The scrubbing unit has 25 square meters of fabric, through which drips a K_2CO_3 solution with excess KOH. The KOH absorbs CO_2 from air, being converted first to all K_2CO_3 and finally to a solution with excess $KHCO_3$. A novel electrochemical cell (patent pending – US# 60/982,778) uses multiple chambers both to recover KOH from the K_2CO_3 solution, and to evolve H_2 and CO_2 in the correct proportion (3:1) required for methanol conversion. The gas is mixed and compressed to 50 bar and fed to a pipe filled with catalyst and maintained at 225°C. The conversion uses a modified Fischer-Tropsch process with a $Cu/Zn/Al_2O_3$ catalyst. At ideal 100% conversion efficiency, the output would be equal parts methanol and water that are separated and condensed by a distillation unit, with added stages to separate undesirable fractions. In Figure 3, chambers C1 and C4 contain H_2SO_4 solution and evolve O_2 which is

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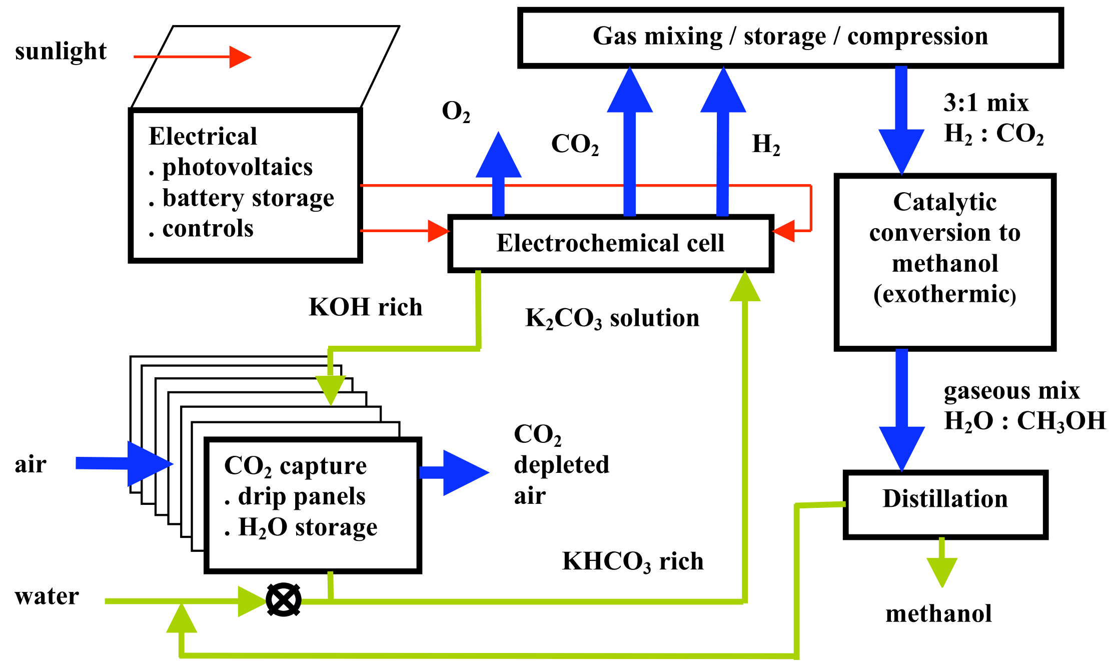

Figure 2: Prototype System Diagram

released. Chamber C2 receives $KHCO_3/K_2CO_3$ solution, and evolves CO_2 which is collected. Chamber C3 produces KOH solution which is removed, and evolves H_2 which is collected. All membranes are DuPont™ NAFION®; M1 and M3 pass H+ ions and M2 passes K+ ions.

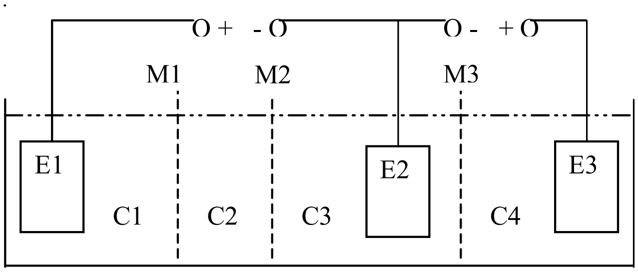

Figure 3: Multiple Chamber Electrochemical Cell

The prototype establishes a base level of cost and efficiency for a small system, allowing the evaluation of subsystem alternatives. The electrochemical cell shows the efficiency of KOH recovery when coupled with electrolysis of water. A particular challenge is temperature control in a small exothermic system. A phase change liquid surrounds the reaction chamber, is well insulated from ambient, and transfers heat in its gaseous form to the cooling fins of a condensing unit; a heat pipe approach. Different phase change materials, all operating at near atmospheric pressure, are used for the various stages of the distillation unit as well. The prototype allows various techniques to be tried for separating and disposing of, or reusing, undesired fractions. Comparing PV energy input to methanol output gives an overall conversion efficiency for the process, with an expected 20% energy loss in the exothermic reaction.

4 ACHIEVING ECONOMIC VIABILITY

A simple definition of achieving economic viability is the ability to produce methanol at a cost per gallon no more than about half that of gasoline, to account for the lower energy density. Methanol from fossil fuel met this criterion as recently as a few years ago after which methanol price rose more sharply than gasoline price. Clean methanol production requires higher capital investment and process energy, but consumes no fossil fuel.

Factors that contribute to economic viability for clean methanol include the following:

- Feedstock cost is negligible, so viability depends largely on energy and capital cost.
- Improvements in process energy efficiency contribute directly to lower energy cost. Energy sources that are currently unusable may be available at low energy cost.
- In the short term, capital cost is reduced by good site specific system design and economies of scale. As for many industries in the past, continuing capital cost reduction can be expected from technological innovation.
- Any rise in price for fossil fuel comparatively greater than the rise in price for other energy sources favors clean methanol production from those other sources.
- In some cases, the value of reduced CO_2 emission is being recognized with carbon credits that might be viewed as a subsidy for defraying the cost of the CO_2 scrubbing equipment in the clean methanol process.

Section 5 examines some cases where underutilized energy sources and carbon credits are important. For the rest of this section, the focus is on process improvements for better energy efficiency and reduced capital cost.

While use of PV panels for capturing solar energy followed by electrolysis of water is straightforward, a solar thermal approach may achieve better energy efficiency. Multistage water splitting is needed to separate H_2 and O_2 to prevent recombination. One option is thermal reduction of a metal oxide (releasing O_2) followed by exposure of the metal to water (releasing H_2). Lower temperature options include sulfur cycles where a maximum temperature of only 850^{o}C is needed to reduce a sulfate to a sulfite:

$$2\ SO_3 \Rightarrow 2\ SO_2 + O_2 \quad (2)$$

One sulfur cycle particularly appropriate for solar includes a photocatalytic stage [2]. For a geothermal energy source that doesn't reach the temperature required for sulfate reduction, high temperature electrolysis of water may be used instead for increased efficiency.

Scrubbing CO_2 (and CO) from a concentrated source like a fossil fuel plant flue is more efficient than scrubbing it from air. Methanol derived from such CO_2 feedstock cannot be said to contribute zero net CO_2 emission, but it does mitigate the effect of the emission from the original fossil fuel with respect to total combustion fuel use.

Reclaiming some of the energy lost in the exothermic catalytic conversion would also increase energy efficiency. One attractive option is to conduct high temperature electrolysis of water (steam) at the 225^{o}C temperature of the catalytic reaction. The heat of reaction then contributes directly to creating additional H_2 feedstock.

A promising future approach skips the generation of H_2 and the catalytic conversion altogether. Production of methanol in an electrochemical cell directly from CO_2 and water has been demonstrated at high Faradic efficiency, but only low rate [3]. A reversible DMFC has the potential to dramatically reduce the capital cost of clean methanol production while maintaining high energy efficiency, allowing for much smaller cost effective systems.

5 METHANOL BASED SOLUTIONS

5.1 Reduced CO_2 Emission Transportation

As the third world approaches a first world standard of living, the need to find transportation options with lower impact on global CO_2 levels becomes urgent. Rising fossil fuel cost and carbon credits makes clean methanol a viable solution. With minimal change to infrastructure needed, this solution can be implemented faster than alternatives.

5.2 Tapping Underutilized Energy Sources

To replace fossil fuels, other energy sources must be more fully utilized. Iceland has geothermal energy beyond that needed for local heating and electricity. The Congo River represents a largely untapped hydro source. Offshore wind is mostly unused at present. And many sparsely populated regions with good solar exposure are both unforested and unsuitable for agriculture. For such cases, installing electrical transmission from the source to where energy is needed might be impractical, whereas transporting methanol by tanker or pipeline is more feasible.

5.3 Intermittent Energy Sources

At present, the small fraction of electricity produced by wind and solar is easily consumed by the grid. If wind and solar succeed in supplying a major fraction of electrical needs, however, their intermittent nature becomes a problem. Generating capacity designed for peak power must fully discount any available wind and solar. Wind and solar capacity greater than off peak needs would sometimes be wasted. Production and storage of methanol during off peak periods, to be consumed by fuel fired generating facilities during peak periods, offers a solution that prevents waste, fits well into the existing infrastructure, and achieves the goal of zero net CO_2 emission for electrical generation.

5.4 Carbon Sequestration

Having removed CO_2 from the air during methanol production, the cleanest environmental solution would be to keep it out of circulation altogether. If dehydration of methanol continues beyond the stage of dimethyl ether described in Section 2.1, the result is ethylene.

$$CH_3OCH_3 \Rightarrow CH_2CH_2 + H_2O \quad (3)$$

Ethylene and other olefins made from methanol are precursors in producing plastics and a variety of industrial chemicals [4]. There is no economic incentive for sequestration by storing carbon based material in underground caverns. Producing plastic building materials from clean methanol, on the other hand, can be nearly self funding. Modest carbon credits for reducing atmospheric CO_2 should be sufficient to bring about a market driven program of carbon sequestration.

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