

# UTILIZATION OF RENEWABLE POWER FOR THE SYNTHESIS OF LIQUID FUELS USING CO<sub>2</sub> OR BIOMASS FEEDSTOCK

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## Introduction

The conversion of renewable energies such as wind, solar or marine energies to fuels and chemicals could hold the promise of more sustainable routes to the production of fuels and chemicals, especially when coupled with the chemical utilization of more sustainable feedstocks like carbon dioxide or gasified 'waste' biomass feedstock. However, a number of sustainability criteria and technical requirements must be met in order for a reaction route to become a sensible process - and perhaps even a commercial reality. In this paper, we wish to chart this arduous but rewarding landscape within the general context of carbon dioxide abatement, integrated energy systems using renewable power sources, and basic process engineering feasibility. We will focus mostly on carbon dioxide utilization, although many of the results presented here would be applicable to un-shifted, CO<sub>2</sub>-rich synthesis gas derived from biomass. We shall see that the particular nature and distribution of renewable energies as well as the existing chemical engineering technology impose certain fundamental constraints, with regard not just to where and when such technology might be profitably deployed, but also with regard to the type of synthesis routes and process designs that would be best suited for sustainable production of fuels and chemicals from renewable sources of power and carbon. Where possible, we wish to advocate certain approaches that would help realize the coming of age of this renewably-powered chemical industry.

## CO<sub>2</sub> as feedstock for the production of chemicals

'Carbon Capture', which is the extraction of CO<sub>2</sub> emitted by human activities, is widely seen as a key technology for reducing CO<sub>2</sub> emissions from fixed sources. However, subsequent storage of CO<sub>2</sub> without direct economic benefits to the producer is failing to attract official support in significant countries such as India for example, which is a notable coal producer and consumer. This message was made plain to us by a delegation from the Confederation of Indian Industries who visited us in 2010 as part of their fact finding mission on fuel synthesis from CO<sub>2</sub>.

As an alternative to storage, the chemical utilization of carbon dioxide (CO<sub>2</sub>) is a topic of interest as it promises a route for the diversion of anthropogenic CO<sub>2</sub> away from the atmosphere, or the displacement of carbon-emitting processes and products by a process that is a net user of CO<sub>2</sub>.

The CO<sub>2</sub> feedstock for fuel synthesis can be taken from power station, industrial works, gas fields or breweries, but also from second generation biofuel plants relying on gasification (including from syngas without separation of the CO<sub>2</sub> (1), or from biogas (2), or from geothermal sources normally used for power generation in Iceland (for example, the 5,000 t/yr methanol plant being currently built in Svartsengi, Iceland, by Carbon Recycling International (3)).

In fact, CO<sub>2</sub> can be seen as a substantial resource in its own right. Beside chemicals that traditionally use CO<sub>2</sub> for their preparation (e.g. urea or salicylic acid), there is growing interest in the use of CO<sub>2</sub> as a source of fine chemicals, polymers etc. (for example, (4)). In any case, many base chemicals are generated from petrochemicals, the availability and affordability of which is dependent on that of crude oil. When this is the case, a route to these chemicals that would substitute the currently used carbon source for the synthesis by CO<sub>2</sub> reduction would be a handsome solution. As an example, one such product that would be particularly valuable to prepare from CO<sub>2</sub> is ethylene, for the following reasons:

- It is an essential precursor for the production of many polymers (polyethylenes; PVC; polystyrene; polyesters), and it is one of the organic compounds with the biggest world production at 120 Mt/yr
- It is essentially produced by the cracking of light hydrocarbons (5); this results in a carbon footprint of ethylene as produced by the conventional cracking process is substantial, at 1.1 kg per kg ethylene, i.e. 0.7 mol CO<sub>2</sub> / mol ethylene (6);
- There currently is substantial research effort directed at the preparation of organic carbonates and polycarbonates by reacting CO<sub>2</sub> with olefins, including ethylene (7); however, the carbon footprint of ethylene and olefins production by conventional means as highlighted above could offset the advantage offered by any such process from the point of view of CO<sub>2</sub> abatement.

The scope for significant CO<sub>2</sub> abatement on a global scale by this type of utilization is limited: it seems next to impossible to match the size of the markets for these products with the current level of anthropogenic CO<sub>2</sub> emissions (8). Yet this is not so with fuels, since it is their combustion that produces the greatest part of the anthropogenic CO<sub>2</sub> emissions. It seems that if a substantial portion of CO<sub>2</sub> emissions from stationary sources could be recovered and used as carbon sources for fuel production, a great deal of emissions from fossil resource could be displaced. However, we shall see that this approach requires a great deal of care in identifying both the right applications where real environmental and economic benefits might accrue, as well as the right type of processes that will utilize the available primary energy that is required for upgrading CO<sub>2</sub> to a carbon-based fuel.

## CO<sub>2</sub> as feedstock for the production of fuels

If the source of energy that is used to upgrade CO<sub>2</sub> to a carbon-based fuel has a low CO<sub>2</sub> footprint itself (like renewable or nuclear), then the overall result is the avoidance of CO<sub>2</sub> emission by using the carbon at least once more before release into the atmosphere, with displacement of fossil-based fuels.

Typically, the key intermediate is hydrogen produced by electrolysis of water, which then constitutes a straightforward means of converting electrical energy to chemical energy. It is also well known that modern, industrial alkaline electrolyzers in the MW range of rating are able to directly deliver hydrogen at pressures of 30 bar, which will facilitate the utilization of the hydrogen for synthesis. These are also able to handle turndown ratios of at least 6:1 with instant response to changes in load, making them suitable for utilizing wind, solar or marine energy (1, 9).

Once 'low-carbon' hydrogen is available, it is a matter of reacting the CO<sub>2</sub> with it to produce fuels, such as methanol or methane (by direct conversion), dimethyl-ether and synthetic gasoline (both via methanol, or perhaps directly), etc. CO<sub>2</sub> to methanol pilot

units built and operated in Germany and in Japan in the 1990's inspire confidence that this approach is technically successful, and it is possible to design processes for these routes based on existing process technology (9).

These successes however were achieved at steady flow rates of feedstock, and therefore either they would be applicable mostly to correspondingly steady sources of power such as nuclear or hydroelectricity, or they would require substantial buffer storage of hydrogen. The use of renewable power presents particular challenges as well as opportunities, as we shall discuss next.

### Using renewable power wisely

Before discussing the technical difficulties with using renewable power sources for chemical synthesis, it must be borne in mind that direct displacement of carbon-intensive power generation is often the best possible use of renewable power from the point of view of emission abatement, preferable to fuel synthesis. This is particularly true for power grids that have only a limited penetration of renewable power (less than 20% of the total generation mix), i.e. most national transmission grids at the time of writing. The following example which illustrates this problem is taken from the UK, where the average emission factor for the power grid is 0.52 kg CO<sub>2</sub> / kWh<sub>el</sub>. The conversion of 1 MWh<sub>el</sub> of carbon-free electric energy would utilize at best 0.12 t CO<sub>2</sub> to produce 0.51 MWh of fuel, which would allow a reduction of CO<sub>2</sub> emission by the same figure (this estimate neglects any energy cost for the capture and compression of CO<sub>2</sub>, which may be substantial). However, if instead the same 1 MWh<sub>el</sub> is used on the transmission grid to displace other generation sources, the CO<sub>2</sub> savings are (0.52 - 0.12) = 0.4 t CO<sub>2</sub>.

However, in recent years, wind power has achieved significant growth in installed capacity, to the extent that in some situations (for example in Denmark) it has acquired a major share of the production. And yet where it has occurred this success has brought with it preoccupying issues for transmission network operators, stemming from the fact that whenever supply does not match demand the power grid might collapse. At any time a shortfall in supply may occur, and although this can be accommodated by various means ('spinning reserve', hydroelectric storage, importing power, etc.), this has a cost. Likewise, dealing with excess supply (which can destabilize the grid frequency and voltage) can be costly (at best, success is achieved by switching off some suppliers and depressing the price of power on the spot market. At worst, the black out of entire regions can occur!). Therefore, in such a context there is an opportunity for chemical utilization of excesses, and even re-converting back to electricity ('peak shaving'). The high energy density and ease of storage of liquid fuels make them particularly suited for long term (seasonal), bulk storage. Given the monthly and year-on-year variability of renewable power, one could imagine a scenario where CO<sub>2</sub> would be converted to a liquid fuel using this excess energy, and the fuel stored until periods of lean supply of renewable power required its use (for example in gas turbine or fuel cell plants) in order to make up any shortfall on the transmission grid.

The potential for this type of conversion is of a significant scale: Mignard, Harrison and Pritchard (10) evaluated the availability of wind electricity on the Western Danish grid when generation from this source was in excess of local demand, over the years 2000 to 2004. They found a significant correlation between hourly wind power production and hourly net power exports. A significant correlation also existed between production from Combined Heat and Power plant and net exports, but this was a seasonal effect rather than an instant effect. If hourly net exports were primarily attributed to

wind, then between 44 and 84% of the annual wind production could be deemed to be exported, depending on the year. Attributing these same net exports to local CHP would reduce the proportion of wind energy available for export to 4 - 32%; In any case, a large amount of exportable electricity is available at times when most of the wind electricity is produced. However, this electricity could be used in the manufacture of carbon-neutral transport fuels, especially whenever export is not a practical or economical option. This situation could occur, for example, in Western Denmark itself should wind power become prevalent to the same extent in neighboring countries; or with a fairly isolated power system like the UK grid.

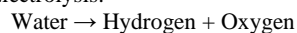
Another context in which conversion of renewable to chemicals can be shown to allow substantial carbon abatement is when the renewable resource is located in remote areas, away from any transmission lines. Mignard and Pritchard (9) evaluated the processes that were readily available for converting CO<sub>2</sub> to either methanol, higher alcohols or petrol, with the CO<sub>2</sub> being shipped to synthesis plants in remote locations where renewable power was abundant, and the fuel product shipped back to centres of consumption for use as transport fuel or re-conversion back to power.

However, there are specific and significant process issues connected with the use of renewable power sources like wind, wave, tidal or solar for powering these processes.

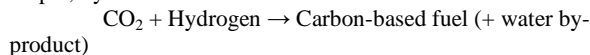
### Technical difficulties arising from the variability or intermittence of power supply

Typically, processes that seek to convert CO<sub>2</sub> to fuels using commercially available technology are of the following type:

Step 1, Electrolysis:



Step 2, Synthesis:



Step 1, which is powered by the renewable energy source, can easily be operated at the variable rate that is imposed by that source, with a turndown ratio of 6:1. However, this is not necessarily so with Step 2 which, if not operable at variable flow rates, will require the use of bulk hydrogen storage to cover periods of low production that can range from hours to weeks. The alternative is excessively frequent shutdown and start-up of the synthesis plant, which is time consuming and inefficient given the process requirements (e.g. heating up of large structures to operating temperatures and build-up of inventories and recycle streams) as well as safety aspects (purging with nitrogen, etc). In the absence of nearby geological storage such as caverns, depleted oil reservoirs, aquifers etc. (which have to be carefully chosen in order to avoid excessive contamination of the hydrogen or unacceptable pressure drop losses leading to large energy penalties), the limitations of compressed H<sub>2</sub> storage can clearly be seen in the following example of a relatively 'small' plant producing 228 t/day (75,000 tpa) of methanol from CO<sub>2</sub> and electrolytic hydrogen.

If the plant required no more than ½ hour of storage of hydrogen in pressurised tanks of ca. 20 m<sup>3</sup>, and these would be cycled between 30 bar (at which H<sub>2</sub> is delivered from the electrolyzers) and perhaps 200 bar (an industry standard), then ½ hour of storage would already require two vessels of 20 m<sup>3</sup> each. However, several hours or days of storage could be necessary in practice to cover a period of 'calm' weather with modest wind or wave. In addition, frequent cycling of

the pressure between high and low values in order to accommodate variations within minutes could subject the tanks to increased risk of embrittlement and subsequent catastrophic mechanical failure.

### Process solutions for handling the variability or intermittence of power supply

Three types of approaches were considered by the author for circumventing the issues that were raised in the previous section

**Long term storage of hydrogen energy.** A first solution might consist in finding suitable means of long term storage for hydrogen. Over ground storage using for example atmospheric pressure floating head tanks soon runs into gigantism (11). Underground storage in caves can be very helpful if available (for example, the refinery complex along the Gulf of Mexico) but the availability of this geological feature would be likely to be too restrictive, especially if geographical matching with either the source of renewable power or the CO<sub>2</sub> source is required.

Perhaps storage of the energy content of the hydrogen rather than the hydrogen itself is desirable, a potential solution being the production of iron sponge by reducing magnetite with hydrogen. Subsequently, the hydrogen and the oxide can be regenerated by contacting the iron with steam, thus re-oxidizing the iron back to magnetite. This type of technique has been developed to pilot scale for the conversion of biomass to hydrogen (via gasification), as well as for power generation by Chemical Looping (which involves a similar concept and the same type of particles). For our purposes, this solution has the advantage of compactness (up to 1.33 mol of hydrogen per mol of iron metal) and the avoiding of pressurized storage. In principle, the energy efficiency of the storage and regeneration cycle can be made as efficient as the most energy efficient method that has been identified so far, which is electrolysis under pressure followed by further pressurization of the hydrogen product (12). However, this result was derived for operation at steady state. The question is whether the process will be as efficient when operated at variable flow rate or intermittently. This is not a straightforward issue to address for this process because of the high temperatures that are required (at least 600 °C for the reduction step, and a couple of 100's °C for the oxidation step – (12)). Efficient energy recovery is required, as well as thermal insulation and operating the reduction step at temperatures no higher than 600 °C (also in order to avoid the use of expensive materials). Another issue is that the equilibrium concentrations of the hydrogen in the feed stream is unfavourable with iron, requiring the recycling of large amounts of unreacted hydrogen. As an alternative, design specifications for alloys and their associated mixed oxides were discussed with respect to suitable thermodynamic properties for avoiding this wastage, and we are currently seeking to develop predictive models for these properties (13).

Although some storage of hydrogen may help, it would be better if the synthesis step itself was able to handle the variability in feed flowrate. Two types of approaches can be proposed: either a robust process design that somehow can handle the variability of hydrogen feedstock, or direct electrolysis of CO<sub>2</sub> that bypass the need for hydrogen generation.

**Reaction steps that can handle a variable flowrate: the example of methanol.** This first approach seems applicable in a limited number of, but fortunately very useful types of reactions. Simulation indicates that, for the case of methanol synthesis from

pure CO<sub>2</sub> + 3H<sub>2</sub> feed, it should be possible to operate the methanol synthesis reactor at variable flow rates, even though some storage is still necessary to smooth the fluctuations. This approach was first tested for CO<sub>2</sub>-rich (i.e., un-shifted) synthesis gas derived from biomass gasification (1), but it is readily extendable to CO<sub>2</sub> plus hydrogen feedstock. Here, we present a straightforward extension of this work to synthesis of methanol from CO<sub>2</sub> rather than biomass. For details regarding the selection, modification and validation of the kinetic model, the reader is referred to the Appendix of the original paper. For an idea of costs, the reader is also referred to the same paper.

Figure 1 represents a simple set up that would allow adiabatic operation of a packed bed reactor that is divided up in two sections: The first section receives the re-heated gases from the recycle after the methanol and water products have been condensed out, i.e. the recycle stream. This has the effect of avoiding rises in temperature above 280 °C, where the highly exothermic methane synthesis might occur and provoke a destructive 'runaway'.

Figure 2 represents the simulated temperature profile along both sections of a reactor (this would be a fairly small scale reactor, corresponding to a ca. 16,000 t/yr methanol plant that would use about 22,000 t CO<sub>2</sub> /yr. This would require a 20 MW<sub>el</sub> electrolysis plant. It can be seen that in both sections the temperature is not able to rise above 275°C even when the contact time is increased by a factor of five with respect to the nominal value, which in principle should ensure safe operation of the reactor. For reference, we also give the methanol yield with respect to CO<sub>2</sub> feed rate (Figure 3).

This flexibility is due to a combination of the thermodynamic equilibrium of conversion to methanol (explaining the flattening portions of the curves in Figure 2), and the quenching effect of the (endothermic) reverse gas shift reaction. The fact that the recycle stream is several times larger than the feed stream to the process (itself due to the high concentration of CO<sub>2</sub> in the feed) is also helping to dampen the variations in feed flow rate.

To be sure, simulating the process in dynamic mode would be required. Control of the overall process will also require a well thought through strategy.

Finally, a store of hydrogen will probably still be required if the process cannot be quickly shut down and restarted during periods of interruption of the power supply. With lengthy catalyst conditioning at very gentle heating rates and sequenced commissioning of the different sections of the plant being part of standard practice, the plant would not be efficiently operated if the availability of power was too erratic. Ways of "mothballing" the plant for quick start-up would need to be examined, including means of keeping the catalyst warm and the gases circulating without further reaction.

**Direct electrolysis of CO<sub>2</sub>.** Synthesis of some fuels may be very difficult with the approaches described in the previous section. For example, with a Fischer-Tropsch or higher alcohol synthesis reaction scheme, the product distribution depends on the reactor residence time. There are other issues regarding process control and safety, especially if 'runaway' reactions are possible.

Thus, if one wished to manufacture ethylene from a steady source of power and CO<sub>2</sub>, one could proceed via the production of ethanol by reacting CO<sub>2</sub> with hydrogen, which seems feasible with current process technology (9), followed by dehydration of the

ethanol to give ethylene, which is the standard industrial process. However, when using renewable power the operation of the first step at variable flow rates is likely to raise considerable difficulties of the type that we have just highlighted.

Direct electrolysis of  $\text{CO}_2$  has been proposed as a means to circumvent this type of problem (14). Essentially,  $\text{CO}_2$  is reduced at a cathode in the presence of water or hydronium ions to give one or several possible products (including carbon monoxide, organic acids, hydrocarbons and oxygenates), while water or the hydroxide ion is reduced at the anode to give oxygen (15).

One could imagine that modular operation of banks of electrolyzers with switching on and off of modules as required would allow relative constancy of the potential across individual cells while the overall load fed to the electrolysis plant varies. This would guarantee that the cells remained in the adequate potential range that yields the desired product distribution. Alternatively or in addition to this, there may be a range of potentials around the nominal value over which the product distribution is relatively constant, although any increase in potential across the cell will generally mean a lower energy efficiency. As an example, we found this to be the case with copper based electrocatalysts for temperatures in the range 0-20°C in aqueous electrolytes. However, both the energy efficiency (as indicated by high overpotentials) and the selectivity are still limited, even though with a copper and iron based electrocatalyst it is possible to get high combined yields of the hydrocarbons methane, ethylene and ethane at current densities (300-400 mA/cm<sup>2</sup>) that could warrant practical applications (14). One issue seems to be the nature of the process, involving multiple electron transfers which makes it difficult to minimize the energy barriers to all the different steps in a simultaneous manner. Recent progress in Density Functional Theory modeling indicates the possibility to identify better catalysts in the future (15).

Another approach consists in electrolysis of  $\text{CO}_2$  at high temperature, in which case the product is carbon monoxide. This was met with success when operating with high temperature, solid oxide electrolyzers ( $T > 600\text{ °C}$ ), provided that steam electrolysis occurred simultaneously so that the nickel-based catalyst was not deactivated (16) (in fact, there probably happens concomitant steam reduction and reverse water gas shift reaction, rather than actual electrochemical reduction of  $\text{CO}_2$  taking place). Advantages here include the direct production of a synthesis gas of adequate ratio for further reaction to liquid fuels, as well as potentially a very high efficiency of the electrolysis cell. One of the issues with an intermittent power source is to preserve the stack from thermo-mechanical degradation if shutdowns are required too often during the year, as testified for example by the specifications given by the European Relhy project (17) (7-14 thermal cycles per year, and temperature kept at 600 °C while non-operating in order to facilitate a quick start-up under one hour in duration). Finally, the synthesis process downstream of the electrolysis plant must still be able to handle a variable feed flow rate.

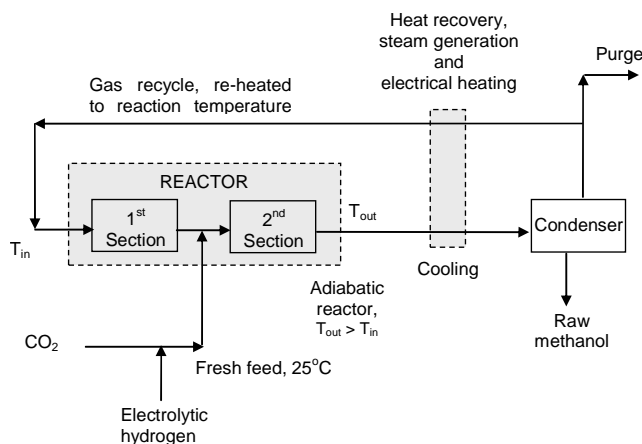
### What next? Conclusions

With existing catalytic and process technologies for the production of hydrogen from water by electrolysis and the production of methanol from syngas by heterogeneous catalysis, it is possible to synthesize liquid fuels like methanol, dimethylether and others products derived from methanol, using feedstocks like  $\text{CO}_2$  or gasified biomass, and hydrogen derived from low carbon sources of power, even at variable rate of supply. It certainly is possible at

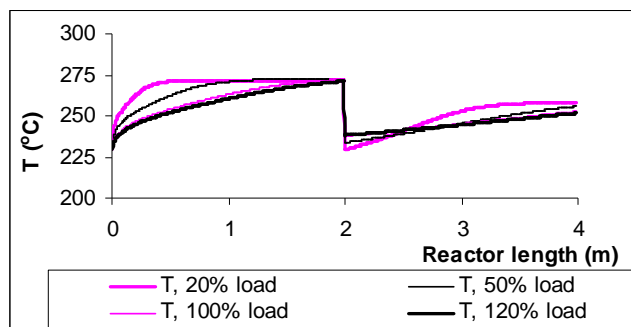
steady load, and it seems likely to be possible if the load varied between 20% and 120% as we demonstrated.

Given the overwhelming effect to the cost of low carbon electricity on the economics of this type of process, it is required to maximize the energy efficiency of this type of process, which is where breakthroughs like steam and  $\text{CO}_2$ -electrolysis assume great importance.

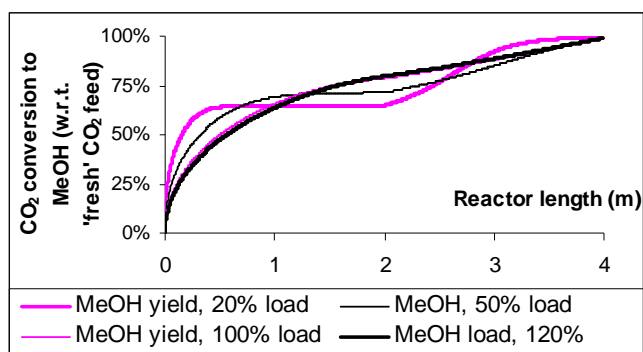
For chemicals like ethylene, a process like  $\text{CO}_2$  electrolysis operating near room temperature would be helpful if it only could be made to operate at energy efficiencies nearer to that of currently available alkaline water electrolysis.



**Figure 1.** Set-up for adiabatic, gas phase methanol reactor which allows operation between 20% and 120 % nominal load without entering runaway, high temperature region.



**Figure 2.** Simulated temperature profiles along a plug-flow methanol reactor with 1000 kg Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst (ICI 51-2), diameter 0.6 m, two lengths of 2 m each, and set up as in Fig. 1.



**Figure 3.** Simulated methanol yield profiles along the same methanol reactor as in Fig. 2.

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