

Sustainable Organic Fuels for Transport (SOFT) – A Concept for Compatible Affordable Mobility Using Carbon-Neutral Liquid Fuels

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Abstract: Carbon-neutral liquid fuels offer the possibility of decarbonising transport without the paradigm shifts required by electrification of the vehicle fleet or conversion to a hydrogen economy. The paper describes the SOFT concept (Sustainable Organic Fuels for Transport) in which carbon-neutral liquid fuels provide a route to avoiding the climate change and energy security concerns which currently challenge the transport sector. The low-carbon-number alcohols, and, where necessary, synthetic diesel and kerosene, offer the prospect of continued high levels of affordable mobility through the gradual evolution of the vehicle fleet and fuel distribution infrastructure to one which is broadly compatible with that which pervades today. Vehicle technology to support this transition is described. The production of liquid fuels from air and water are reviewed in which fully-closed carbon cycles are theoretically possible with the development of large-scale renewable energy generation and CO₂ capture from the atmosphere. To expedite air capture, developments in CO₂ concentration and release based on bipolar membrane electrodialysis are described and initial results from a laboratory-scale device are reported.

Keywords: SOFT, carbon-neutral liquid fuels, methanol, ethanol, fuel synthesis, CO₂ capture, electrodialysis.

1. Introduction

On a global basis transport is the fastest growing sector responsible for the accumulation of CO₂ in the atmosphere. It is extremely difficult to decarbonize this sector due to its high dependency on energy-dense fossil fuels – it is also, therefore, vulnerable to issues arising from insecurity of supply.

The three routes most frequently advocated to address these issues are:

- vehicle electrification;
- conversion to a 'hydrogen economy';
- adoption of biofuels.

Of these, only the use of biofuels offers the prospect of an evolutionary transition in technology which results in vehicles of equivalent range and cost to those to which the user is accustomed.

Electrification and adoption of hydrogen require large infrastructure changes, with concomitant costs (which are huge in the case of hydrogen [1]). The incorporation of batteries or hydrogen storage systems and fuel cells will result in vehicles which are much more expensive than current vehicles, both in terms of energy and capital, and will require quantum changes in manufacturing facilities [2]. This will lead to the stranding of the vast assets which inhere in engine production lines and require massive investment in new, often unproven, technologies.

Biofuels, in the form of ethanol and biodiesel, are miscible with current gasoline and diesel formulations respectively and can be used even in high concentration levels with minimum engine and fuel system modification. They can therefore be introduced incrementally, with a fuel supply infrastructure which is broadly similar to the current network. This close compatibility is responsible for the current presence of more than 6 million E85 / gasoline flex-fuel vehicles in the global fleet [3].

The high-profile market presence of biofuels has attracted the scrutiny of political and environmental lobby groups who have raised concerns over their sustainability credentials. The greenhouse gas emissions associated with the direct or indirect conversion of previously uncultivated land, and the land area requirements themselves, have led to forecasts that there is a global *biomass limit* which confines the properly sustainable supply of biofuels to between 20% and 30% of the current transport energy requirement. Biofuels are therefore vulnerable to the accusation that they are a dead end and this is clearly of concern to automobile manufacturers looking to embrace them. This paper will show that biofuels are not merely an ephemeral palliative but can be part of a more universal solution where similar fuels can be synthesized using recycled feed stocks from the ocean and the atmosphere. In this way carbon-neutral liquid fuels for transport can be supplied in full amounts when sufficient renewable energy is made available.

The concept of Sustainable Organic Fuels for Transport (SOFT), which offers a fully renewable

solution based on carbon-neutral liquid fuels, will be posited. This route has the potential to emancipate renewable alcohol, diesel, and kerosene fuels from the constraints imposed by the biomass limit by utilizing renewable energy, carbon in the atmosphere, and hydrogen in the oceans. Methanol is proposed as the base fuel for the light-duty automotive sector, ultimately used in high-efficiency spark-ignition engines. For aircraft, ships, and trucks, where the need for high on-board energy density in order to maintain payloads is paramount, kerosene and diesel can be synthesized. This route enables carbon-neutral liquid fuels to be supplied to the transport sector in full amounts, fuelling all vehicles via an infrastructure which is broadly compatible with the current system in terms of technology and capital cost.

The characteristics of alcohols as spark-ignited fuels are such that, in the form of the low-carbon-number alcohols methanol and ethanol, they are synergistic with the technology trend toward pressure-charged downsized internal combustion engines [4]. In compression-ignition engines with appropriate modifications to either the engine (in the form of spark or glow-plug ignition) or the fuel (in the form of an ignition enhancer) alcohols can achieve equivalent efficiencies to those obtained operating on diesel fuel [5].

To expedite the transition to the SOFT end game a simple low-cost vehicle technology is proposed which enables a spark-ignition engine to run on any combination of gasoline, ethanol, and methanol. Fuel blending concepts which enable methanol to substitute for ethanol in blends in the market now, maintaining the same properties, will also be described. All the concepts and technologies covered in this paper are dealt with in greater detail in reference [2].

2. The Biomass Limit

The presence of biofuels in the market today is driven by their potential to improve energy security, to contribute toward climate change mitigation, *and their compatibility with modern vehicles with minimum modifications*. Their use has been mandated in the EU and US, the former at a level of 5.75% (energy-based) by 2010 [6] and then 10% by 2020 [7], and the latter at a level of 36 billion gallons by 2022 (from 4.7 billion gallons in 2007), 21 billion gallons of which should be produced from non-corn starch feedstock [8]. The EU proposals have recently been revised to require that 'hydrogen and green electricity', together with 'second-generation' biofuels, comprise at least 40% of the transport energy requirement in 2020. Further sustainability criteria, including an obligation for the biofuels to

provide at least 45% GHG saving compared with fossil fuels are also being introduced [9].

The very low rate and efficiency with which plants convert solar energy to biomass severely limits the ability of biofuels to supply the transport fleet. Pressures on land utilization will be brought about by the projected growth in world population whose food consumption patterns are increasingly land-intensive and the rising demand for land to cultivate industrial feedstock [10]. Countries with high population densities are not likely to achieve substantial energy security via the development of biofuels [11] but those with low population densities and an excess of fertile land, such as Brazil, are able to consider them as a replacement for their fossil counterparts.

In order to assess the impact on the climate of biofuel production the effects of land-use change must be considered. These may be direct or indirect effects where, if the land was previously uncultivated or, if there is a usage change, a large one-off release of carbon from the soil into the atmosphere may occur [12,13]. The impact of these emissions can be expressed in terms of 'carbon payback time'. The time required to produce a net benefit from biofuel production chains can vary from 17 years for bioethanol from sugar cane feed stock grown on cleared Brazilian cerrado woodland, to over 400 years for biodiesel from produced from palm oil, grown on drained Indonesian peat forest.

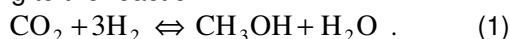
A biomass limit exists for the supply of energy to the transport sector which globally is between 20 and 30% at current usage levels, and is much lower for developed countries with high population densities [14]. Improvements in vehicle fuel efficiency due to downsizing of powertrains, their optimization to operate on the biofuel [15], and low mass, low drag/rolling resistance vehicle technology, together with behavioural mode switching have the potential to extend the biomass limit in developed countries in which the population and automotive transport fuel demand might be in decline. However increased efficiency and even improved crop yields due to advances in biotechnology will not be sufficient to off-set the burgeoning demand for personal mobility in developing countries. There is also an implicit risk in developing a high dependency on biofuels associated with attempting to solve the climate change problem using a feed stock which is itself dependent on an increasingly unstable climate. Nevertheless, with appropriate sustainability criteria in place, biofuels are capable now of delivering reductions in GHG emissions immediately in a sector in which the emissions are growing and which is extremely difficult to de-carbonize. In order for these fuels not to be ultimately viewed as a dead end

however, there is a requirement to find the remaining 70%-80% of the global transport fuel requirement.

3. Beyond the Biomass Limit – Carbon-neutral liquid Fuels

Ethanol and, in particular, methanol can be made renewably from a wide variety of biomass feed stocks but are constrained in the extent to which they can supply the transport fleet to the level imposed by the biomass limit. In this section approaches to synthesizing alcohol and hydrocarbon fuels are described which are theoretically capable of supplying them in sufficient quantities to meet the entire global transport fuel demand.

A plant creates carbohydrates by combining carbon dioxide and water in a biogenic cycle involving photosynthesis; this biomass can then be converted into ethanol or methanol via a variety of means [14]. It is possible to synthesize methanol directly from carbon dioxide by combining it with hydrogen according to the reaction



This can be viewed as a mechanism for liquefying hydrogen chemically using carbon dioxide. Methanol is the simplest organic hydrogen carrier which is liquid at ambient conditions. In the same way that biofuels recycle carbon biologically, a cycle where the carbon in the methanol is recycled artificially by extracting CO_2 from the atmosphere is shown in Figure 1. The energy used to produce hydrogen by the electrolysis of water and that used for the capture and release of the CO_2 should be carbon-neutral. Such cycles have been proposed by a number of previous workers over a period of over 30 years [16-23]. An additional feature of the cycle is to provide a route to synthesizing replacements for petrochemicals via the ready manufacture of olefins from methanol [20,23]. In this way carbon is effectively sequestered allowing the continued exploitation of remaining fossil fuel reserves without causing a net accumulation of CO_2 in the atmosphere.

The separation of CO_2 at higher concentrations is routine in some large industrial plants such as natural gas processing and ammonia production facilities and the future challenges and costs of flue-gas capture are well understood [24]. At up to 15% by volume concentration it might be expected that the energy requirements for flue gas capture would be significantly lower than that for atmospheric capture at 0.0387%. The variation of theoretical CO_2 separation energy with concentration is given by the Gibbs energy as

$$\Delta G = R_{\text{mol}} T \ln \left(\frac{p_0}{p} \right) \quad (2)$$

In equation (2) p is the partial pressure of ambient CO_2 and p_0 the desired pressure in the output stream. At the current atmospheric CO_2 concentration of 387 ppm the theoretical separation energy is in the region of 20 kJ/(mol. CO_2) – this is less than 3% of the higher heating value for methanol (1 mole of CO_2 makes 1 mole of methanol with HHV=726 kJ/mol.). The logarithmic nature of equation (2) means that the energy to separate atmospheric CO_2 is only 4 times higher than that required for flue gas CO_2 separation at 150000 ppm. In fact, due to the higher energy required to capture the marginal concentrations, Keith et al. [28] put the figure for the theoretical ratio of atmospheric capture to flue gas capture at 1.8.

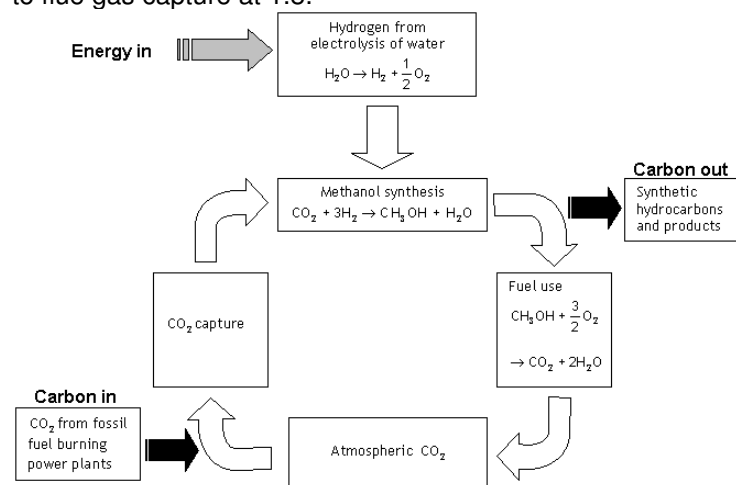


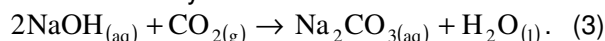
Figure 1: Cycle for sustainable methanol production and use (adapted from Olah et al. [20]).

3.1 Concentrating CO_2 Directly from the Atmosphere

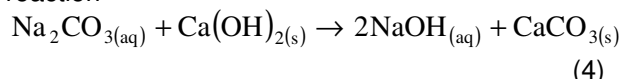
While references can be found from the 1940s that describe research into capturing CO_2 directly from the air [25], and NASA developed devices in the 1970s and 1980s capable of removing CO_2 from enclosed cabin air [26,27], the prospect of climate change due to accumulated atmospheric CO_2 concentrations has caused increased interest over the last decade into cost-effective, energy efficient, high-rate "direct air capture" technologies [28-32].

Concentrating CO_2 from atmospheric concentrations to a stream of pure CO_2 typically involves two steps: capture and extraction. First, the atmosphere is contacted with either a solution or treated surface that selectively captures (absorbs or adsorbs) the CO_2 from the air. Next, the captured CO_2 is extracted from the solution or surface to produce a pure stream of CO_2 . This second step may use thermal [33], chemical and thermal [34-36], or electrochemical methods [17,32,33], among others [33]. This pure stream of CO_2 can then be optionally treated (e.g. dehumidified or pressurized) before sending it to a synthetic liquid fuel reactor.

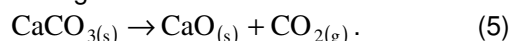
Most approaches to CO₂ concentration that are currently being pursued accomplish the first step of CO₂ capture by contacting air with a caustic liquid capture solution in a 'wet scrubbing' technique that has been known for several decades [25,37]. In the specific case of a sodium hydroxide capture solution, the mechanism is initiated by the absorption of CO₂ in the sodium hydroxide in the reaction



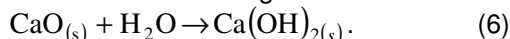
While many research groups propose spray tower capture for the first step, they differ in their approach to the subsequent extraction. Keith et al. [30] and Lackner [33] have both investigated capture via a sodium hydroxide solution, followed by regeneration of the sodium hydroxide via the 'causticization' reaction



which readily transfers 94% of the carbonate ions from the sodium to the calcium cation to produce an emulsion of calcium hydroxide. The calcium carbonate precipitate is filtered from solution and thermally decomposed to release the CO₂ according to the following reaction

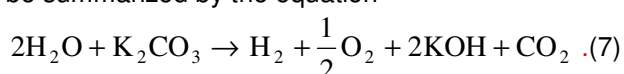


Finally, the calcium hydroxide is regenerated by hydration of the lime according to



The sodium and calcium hydroxide are recycled in two separate loops and there are CO₂ emissions associated with their initial production. Steinfeld et al. have also investigated air capture using both Ca-based [35] and Na-based [36] capture solutions. Keith et al. [30] and Zeman [38] give the net energy requirement for the above processes as about 350 kJ/(mol. CO₂), and indicate that there is scope for significant further improvements on this figure [34]. Lackner [33] gives a figure of '<250 kJ/(mol. CO₂)'.

Steinberg [16] and Stucki [17] have proposed combined electrolysis / electrodialysis units for the production of methanol. Stucki [17] constructed an electrochemical membrane cell which can be used for the regeneration of the potassium (in this case rather than sodium) hydroxide and for simultaneous production of hydrogen at the cathode, obviating the requirement for a second loop for the ion exchange process described above. The overall reaction can be summarized by the equation



In order to demonstrate energy-efficient and scalable atmospheric CO₂ capture that will enable the generation of renewable liquid hydrocarbon fuels the co-authors at PARC initially followed a fuel-cell-

based approach [32] but recent research has focused on electrodialysis. As shown in Figure 2, this approach involves the capture of CO₂ from the air using a spray tower with KOH capture solution, followed by regeneration of the CO₂ via high-pressure electrodialysis. The key innovations in the PARC system are high current densities with active pH control and high-pressure operation of the electrodialysis unit, allowing energy-efficient, high-rate CO₂ separation from the atmosphere in a compact, reliable unit [39].

A schematic of the entire CO₂-capture unit as well as a detailed view of the electrodialytic CO₂ separator are shown in Figures 2(a) and 2(b), respectively. Using well-established techniques [40-42], air is first passed through a spray tower consisting of a counter flow of a 10 - 50% aqueous K₂CO₃ solution at ambient conditions. The capture solution, now loaded with CO₂, is then pressurized (10 - 100 atm, depending on conditions) and introduced into the bipolar membrane electrodialysis (BPMED) unit, see Figure 2(b). The bicarbonate is transferred across the anion exchange membrane to the CO₂-rich acid stream that is held at a constant pH of 3-4 by a combination of acidic buffers and flow-rate control. The capture solution is buffered against excessive pH increases and held at a constant pH of 8-10 by the presence of significant concentrations of bicarbonate and carbonate ions. The capture solution is regenerated by the hydroxyl ion flux from the bipolar membrane and by partially depleting it of bicarbonate via electrodialysis.

The high pressure acid stream is transferred to a gas evolution/separation tank where the pressure is reduced resulting in the release of pure CO₂. The CO₂ is removed and fed to a reactor for the production of fuel. The now CO₂-depleted acid stream is returned to the electrodialysis unit via a re-pressurization pump while the regenerated capture solution is returned to the spray tower. It is important to note that, in the process of concentrating CO₂, both the acid and base solutions are regenerated, resulting in two closed, continuous process loops. This is crucial for commercial application, as it will minimize the amount of solvent required for operation.

It is ultimately envisaged that 100-cell electrodialysis stacks will be used to decrease the fractional energy requirement for H₂ (O₂) gas formation at the cathode (anode) to between 1% and 2%. In parallel to the CO₂ capture, H₂ for fuel production can be produced via electrolysis of water. The separation of the electrodialysis for CO₂ regeneration and electrolysis for H₂ production is in contrast to the approach of Stucki [17], which combines both processes into one unit. Separating the electrodialysis and electrolysis

provides more flexibility to operate independently and optimize the two processes.

BPMED is a well-established technology and has been successfully deployed in commercial applications ranging from organic and amino acid production to hydrofluoric acid recovery since 1986 [43]. Commercially-operating BPMED systems typically achieve high current efficiencies (the fraction of applied current that is applied to the desired ionic transport) of 85% and current densities as high as 100 mA/cm². Regeneration of carbonate/bicarbonate solutions [44,45] and other gas-evolving solutions [45] via electrodialysis has been previously demonstrated on the laboratory scale. A noted deficiency of this process includes "bubble formation", i.e. gas-evolution inside the membrane stack, leading to localized regions of high current density ("current crowding") that damages the membranes due to localized heating. In addition, low conductivity of the solution and poor mixing of the solutions leads to high internal resistances and reduced efficiencies inside the BPMED stack. Despite these problems, low voltages, reasonable current densities, and CO₂ recovery were observed.

that operates at high pressures (> 10 atm). Membrane damage from localized high current density regions is eliminated by preventing gas evolution inside the membrane stack. By instead releasing the gas from solution in a gas evolution tank that is physically separated from the membrane stack, the system allows processing of gas-evolving solutions in a unit that is both compact and reliable. These are both qualities which are essential for commercial applications. It is thought that this would be the first high-pressure BPMED system ever constructed, and although the goal is to optimize the system for CO₂ concentration, the results of this work should also be applicable to other gas-evolving solutions. Assuming a typical BPMED current efficiency of 85% and effective pH control it is estimated that this system will extract CO₂ gas from the capture solution with an energy consumption of approximately 100-150 kJ/(mol. CO₂). This estimate does not include the energy required for spray tower operation, pumping of fluid, or compression and dehumidification of the extracted CO₂. The energy requirements for spray tower operation have been measured at about 5 kJ/(mol. CO₂) [46].

Preliminary results from investigations in to CO₂ concentration and pH control using ambient-pressure electrodialysis at PARC are reported below. CO₂ concentration tests have been performed on a bipolar membrane electrodialysis stack used in the same configuration as shown in Figure 2(b). The stack itself consists of 7 cells, with each membrane having an area of 200 cm². Experiments were performed using K₂CO₃ (10g/l to 100g/l) as input to the base compartment, K₃PO₄ (to provide an initial conductivity of 10 mS/cm) as input to the acid compartment, and KOH (2M) as an electrode solution. Flow rates of 140 l/hr (300 l/hr) were used for the acid and base (electrode) compartments, and the current was tuned between 15 A and 19 A. After a few minutes of operation, gas was visibly bubbling out of solution at the output of the acid compartment. This gas was collected and tested using a gas chromatograph. The chromatograph results for the gas sample (Figure 3(b)) from the electrodialysis unit were compared to chromatograph analysis of bottled N₂ and CO₂, as well a sample of air (Figure 3(a)). The tests with bottled N₂ and CO₂ yielded peaks at 83.6 s and 118.4 s, respectively. As seen from Figure 6(a), the sample of air yields a peak at 80.8 s, consistent with the N₂ peak (for this chromatograph tube, the N₂ and O₂ peaks overlap), whereas no peak is seen at the CO₂ position. For the gas captured from the output of the acid compartment of the electrodialysis stack, Figure 3(b), a large peak at the CO₂ position (117.4 s) can be seen together with a smaller peak at the N₂/O₂ position (81.1 s). The areas under the peaks indicate that this gas is 84% CO₂ and 16% air. This

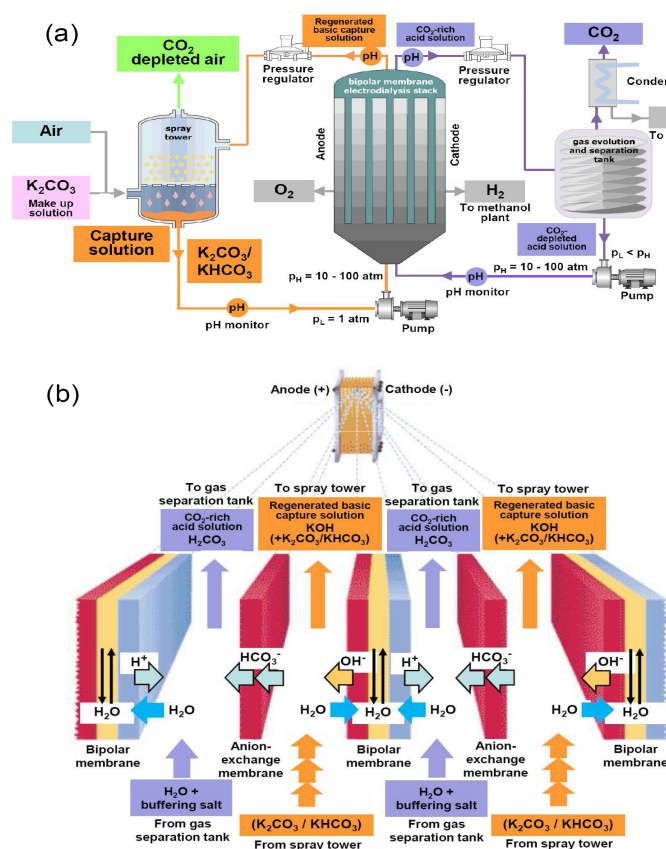


Figure 2: (a) Schematic of atmospheric CO₂ separation system (b) BPMED membrane stack. Portions of this figure courtesy of Ameridia Corp.

It is proposed to solve these problems associated with gas-evolving solutions using a BPMED system

residual air is likely to be the air present in the electro dialysis stack when idle. The fraction of CO_2 in the output gas increases as the electro dialysis unit is run for longer so that the air that was in the stack at start-up is flushed out of the system.

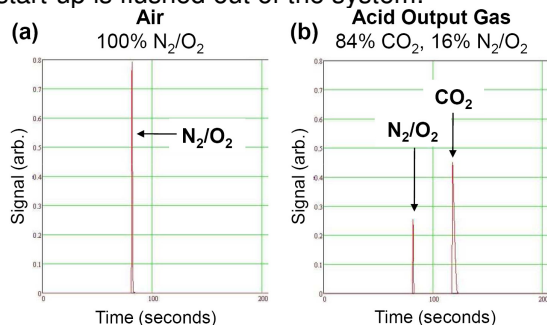


Figure 3: Gas chromatograph data. (a) Sample of air. (b) Sample of gas evolving from the solution exiting the acid compartment.

3.2 Methanol Synthesis from Atmospheric CO_2

In order to produce a stoichiometric mixture for methanol synthesis (eqn. (1)) the hydrogen must be supplied using a separate water electrolyser. Figure 4 shows that by far the largest component of the processes energy requirements for synthesizing methanol is that to produce the hydrogen. An 80% electrolyser efficiency has been assumed together with a conservative CO_2 extraction energy of 250 kJ/(mol. CO_2). This gives a HHV 'wind-to-tank' (WTT) efficiency of 46%, including multi-pass synthesis and re-compression. A CO_2 extraction energy requirement of 125 kJ/(mol. CO_2) gives a WTT efficiency of 50%. It has also been assumed that the heat of reaction generated in forming the methanol can be used elsewhere in the process, e.g. to offset the distillation energy. These figures compare well with the number measured by Specht et al. [18,47] using an electro dialysis process to recover the absorbed CO_2 .

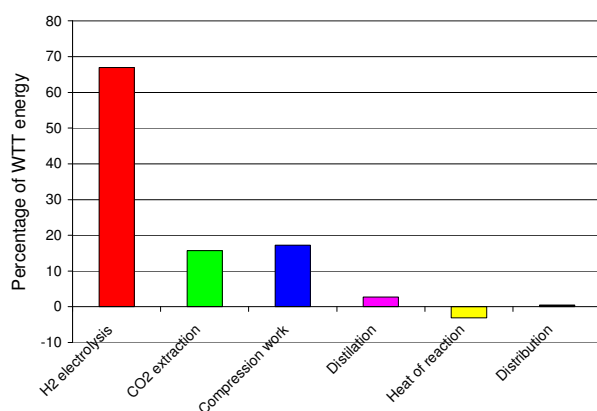


Figure 4: Breakdown of process energy requirements for synthesis of methanol from atmospheric CO_2 and renewable hydrogen.

The mixing time of emitted CO_2 in the atmosphere is easily sufficient to ensure that there is no shortfall in any particular global region, ensuring security of supply for the carbon feed stock component of a carbon-neutral fuel cycle based on methanol.

4. Evolving the Vehicle Fleet

Synthesized methanol would ultimately form the basis of the bulk of the transport fuel requirement, significantly exceeding the availability of properly sustainable biofuels. However, ethanol from biomass is present in the fuel market today and has been mandated to increase in its share in the United States [8]. The miscibility of methanol with ethanol and gasoline supports the gradual transition toward the use of carbon-neutral liquid fuels to replace fossil fuels. In an attempt to illustrate the ease with which vehicles capable of supporting this transition can be provided, a production vehicle was modified to operate on standard 95 RON gasoline (its normal fuel), ethanol, methanol, or any combination of these fuels. The vehicle was a Lotus Exige S, which uses a Toyota 2ZZ-GE engine fitted with a supercharger arrangement and a 'T4e' engine management system engineered by Lotus. The development of electronic engine control systems over the past 30 years has enabled practical realization of flex-fuel vehicles which can operate seamlessly on varying mixtures of ethanol and gasoline. Saab and Ford have shown how the approach can work beneficially within a European architecture, with issues of cold-start addressed down to -25°C ambient temperatures [4] and there are many similar vehicles in other markets around the world.

The fuel system of the vehicle was modified to accept alcohol fuel through the application of alcohol-resistant fuel lines and the fitment of an alcohol sensor (manufactured by Continental Automotive Systems). A fuel pump with increased flow rate was also fitted to account for the lower volumetric energy content of the alcohol fuels. The additional software required was developed within the environment of the production engine management system using spare inputs and outputs for the alcohol sensor. The calibration was developed to deduce the possible range of AFRs for 100% ethanol or 100% methanol in the fuel. Hence no new sensor input was required for the tri-flex-fuel conversion and the standard AFR sensor was retained. Only injector pulse width was influenced by the software and the signal from the AFR sensor.

While identical spark advance was used with methanol and ethanol, some pre-ignition was noticed using the former fuel. Small amounts of pre-ignition can be compensated for in the ignition timing table but methanol shows a greater propensity towards

this phenomenon due to the lower temperature at which it decomposes. Fortunately a significant reduction in pre-ignition can be achieved by avoiding spark plugs with electrodes made from precious metals. Replacing the standard iridium electrodes with copper-cored versions eliminated pre-ignition up to 100% methanol concentration in the fuel.

Compliance with Euro 4 emissions limits on any combination of the three fuels was achieved using the standard vehicle catalyst which was formulated primarily for operation on gasoline [2]. It was found that as the alcohol concentration increases, so the tail pipe CO₂ emissions reduced. Using 88% by volume methanol gave 94% of the CO₂ emissions when operating on gasoline. In a more heavily-downsized engine-vehicle combination the octane rating of the alcohol component, and its reduced need for component protection fuelling, could be more beneficially exploited in the drive cycle.

Using modern control technology the conversion of existing production vehicles to tri-flex-fuel operation on gasoline, ethanol and methanol is straightforward and can be achieved with very low on-cost. From the customer perspective the low additional vehicle cost ensures continued access to personal mobility which is financed by high-cost capital available to the individual to purchase an asset which sits idle for 95% of its lifetime.

4.1 Using Methanol to Extend the Displacement of Gasoline by Ethanol

In addition to the use of tri-flex-fuel vehicles as a means of bringing methanol to market, it may be possible to introduce methanol in a far more pragmatic manner. The aim of the concept outlined below is to exploit the physico-chemical similarities of ethanol and methanol to produce ternary mixtures of the two alcohols with gasoline in a pre-blended form which can be used seamlessly by any existing E85/gasoline flex-fuel vehicle.

Over recent years, the US has, through Corporate Average Fuel Economy (CAFÉ) regulations, encouraged manufacturers in the production of so-called flex-fuel vehicles capable of operating on gasoline or E85 or any mixture of the two. There are issues of fuel availability which the US Energy Independence and Security Act has addressed [8]. In view of the aggressive level of the target stipulated by the latter legislation, and due to the concerns over the sustainability of fuels from some biomass sources, it is desirable to find means of extending the amount of renewable fuel that can be introduced in the short-term. About 2.7 million vehicles capable of operating on high-alcohol-concentration fuels were sold world-wide in 2007.

Since these flex-fuel vehicles are capable of running on any binary fuel blend with a stoichiometric AFR between that of gasoline (14.7:1) and E85 (9.7), methanol can be introduced to produce an equivalent ternary blend of ethanol, methanol, and gasoline with similar properties to the binary ethanol and gasoline mixtures by re-adjusting the amount of gasoline in the mix. This can extend the utilization of a given quantity of ethanol in the market to the benefit of security of fuel supply and, depending on the source of the methanol, greenhouse gas emissions. Three different blend proportions to achieve the same AFR are given in Table 1.

Table 1: Ternary mixtures of ethanol, gasoline and methanol to yield stoichiometric AFR equal to E85.

Ethanol vol. %	Gasoline vol. %	Methanol vol. %
85	15	0
42.5	28.8	28.7
0	42.6	57.3

The second blend in Table 1 is termed E42.5 G28.8 M28.7 to correspond to the volume fraction of the major blend components. It spreads the available ethanol across twice the volume of blended fuel supplied to the market at the same energy level per unit volume. In terms of equivalent energy of gasoline, one litre of ethanol displaces 0.673 litres of gasoline in E85 while, for this ternary blend, the extra methanol supplied enables one litre of ethanol to displace 1.011 litres of gasoline – an increase of about 50%. It is interesting to note in this mixture that the gasoline content, nearly 30%, is almost the same as 'winter-grade E85' (typically E70 G30 M0) and thus it might be expected that this blend would be suitable for year-round use, particularly since methanol is more readily started under cold conditions than ethanol. This implies a greater potential use of ethanol all year round.

5. Sustainable Organic Fuels for Transport

Since biofuels are only capable of supplying about 20% of transport energy in a properly sustainable manner renewable energy must be used to synthesize carbon-neutral liquid fuels. Carbon dioxide extracted from the atmosphere can be combined with hydrogen produced by the electrolysis of water to produce methanol which is the simplest and most effective carbon carrier which is liquid at over the range of ambient conditions normally encountered by land transport. The high energy density of methanol and ethanol relative to non-liquid 'fuel' alternatives makes them suitable for use in light-duty land transport without accepting a significant compromise in vehicle range. In applications where range is crucial, however, synthesizing diesel and kerosene may be a necessary additional step to the fuel production

process, at the sacrifice of an energy penalty (of the order of 10% [14]) and a significant increase in plant cost.

Bandi and Specht [14] and Biedermann et al. [48] describe processes for the Fischer-Tropsch (FT) synthesis of gasoline and diesel from both CO and CO₂ with hydrogen. Methanol can also be used as the base feedstock for synthesizing more complex fuels: a 14000-barrel-per-day methanol-to-gasoline (MTG) plant was built in New Zealand in the early 1980s [14]. The Lurgi MtSynfuels process [14] has the advantage over the conventional FT route that it is easier to downscale and thus may be better suited to the decentralized availability of biomass. The mechanism operates in a similar way to the MTG process, where DME and olefins are created as intermediate products, before hydrogen addition to yield diesel, kerosene, gasoline, or LPG.

Since the low-carbon-number alcohols are superior fuels for internal combustion engines and that their use implies minimal on-cost for new vehicles, it is expedient to use methanol in automotive and light-duty transport applications with spark-ignition powertrains. It can be phased in via the technology described in Section 4.1, and eventually used in optimized engines with high compression ratios, achieving peak fuel conversion efficiencies which match or exceed those of diesel engines [15]. Several authors [20,23,49] have also pointed out the synergies possible from the adoption of methanol as the basis of the transport energy economy and its diverse applicability as a replacement feedstock for the petrochemical industry.

The combination of bio-alcohols, synthetic methanol, and the synthetic hydrocarbons diesel and kerosene, constitute a potentially carbon-neutral system for the provision of fuel for all types of transport in full amounts. Collectively they are *sustainable organic¹ fuels for transportation - SOFT*.

Figure 5 shows how the transition to sustainable organic fuels might occur. In developed countries first generation biofuels, with the exception of sugar cane ethanol, would be phased out, with second generation biofuels replacing them and supplying the fleet up to the biomass limit of about 20%. The remaining fuel demand would be provided by synthetic fuel production from atmospheric CO₂ capture and flue gas capture of CO₂ from power plants burning a mixture of fossil fuel and biomass in combined heat, power, and fuel plants (CHP+F). Developing countries with sufficient land area could produce first generation biofuels at relatively low cost to diversify the use of their produce and provide opportunities for export or manufacture renewable

fuels. It is more expedient to export liquid fuels than 'raw' biomass.

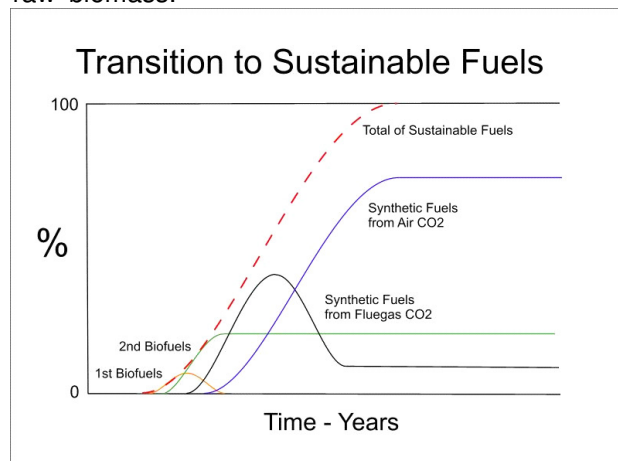


Figure 5: Schematic of possible fuel transition.

A necessary (but not sufficient) factor determining whether any renewable energy carrier or fuel can supply the transport fleet in full amounts is the amount of 'upstream' renewable energy required. The current global transport fuel demand is about 90EJ per annum, equivalent to an average power consumption of 2.85TW. As a first approximation, if it is assumed that the vehicle tank-to-wheel efficiency using sustainable organic fuels is equal to their fossil-fuel replacements and the well-to-tank efficiency of the fuel is taken as 0.5, the ultimate renewable energy demand for powering the transport fleet with such fuels is in the region of 6TW. This is clearly a huge requirement - the world electricity generation in 2006 of 2.06TW. The global wind resource at turbine heights (on- and off-shore) of 96TW [50] is clearly more than capable of providing this power in the long term but synergies and process integration, such as combined heat and power plus fuel plants with district heating, are necessary to maximize the efficiency of energy utilization. Fuel synthesis plants using electrolyzers may be a practical way to overcome the intermittency of renewable energy and could be a route to exploiting 'stranded' renewable energy in remote locations where installation of an electricity grid is not economic.

The lower upstream generating energy demand due to the higher tank-to-wheel efficiencies of battery electric vehicles or, to a lesser extent, hybridized fuel cell vehicles, are possible at large on-cost to vehicles. Full life-cycle analyses of energy requirements have shown that the life-cycle CO₂ emissions for BEVs and HFCVs can be higher, under some operating conditions, than vehicles powered by gasoline-fuelled internal combustion engines due to the higher emissions in the vehicle production process [51,52]. Initial work by the authors indicates that the high embedded GHG

¹ Organic signifying 'carbon containing'.

emissions for BEVs and HFCVs translate in to high embedded energy costs which give a substantial overhead to accommodate the lower tank-to-wheel efficiency of conventional vehicles using carbon-neutral liquid fuels. With optimized alcohol engines operating at their peak efficiency points, enabled by the hybridization assumed for HFCVs, and using the more correct higher heating values, the TTW efficiency superiority of HFCVs reduces to less than 10 percentage points.

The current presence of ethanol-fuelled vehicles in the market in significant numbers [3], and the miscibility of ethanol, methanol, and gasoline, together with the ability to synthesize gasoline, diesel, and kerosene from biomass, methanol, or renewable hydrogen and CO₂ feed stock, allows a soft start to the introduction sustainable organic fuels for transport with renewable methanol as its basis. It could be expedited by the mandating of flex-fuel (or tri-flex-fuel) capability for all new vehicles with spark-ignition engine powertrains from, say, 2015, to coincide with the proposed imposition in the EU of fiscal penalties for exceeding CO₂ emissions targets. Together with the recent US Energy Independence and Security Act [68] this will incentivize the development of second-generation biofuels, with additional criteria to ensure they do not compete with food or create large carbon payback times. With the correct materials selection in the design of the next generation of gasoline/ethanol flex-fuel vehicles, methanol operation could be implemented by software changes when the fuel becomes available.

The rapid recent implementation of methanol as a transport fuel in Sweden and China [2] demonstrates the ease with which the technology can be applied, the low additional cost of the vehicles in which the fuel is used, and the low cost of the fuel distribution infrastructure.

Figure 6 shows that while methanol produced from coal can generate about 2.3 times as much well-to-wheel GHG emissions as gasoline, the GHG emissions from methanol via natural gas are slightly better than those from gasoline - emissions from state-of-the-art plants can be substantially below this level. The GHG emissions from methanol synthesized from flue-gas CO₂ and renewable hydrogen are approximately half those of gasoline – this enables fossil fuels to be used in both the power generation and transport sectors with significant GHG reductions. Using atmospheric CO₂ and renewable hydrogen gives only around 5 per cent of the WTW GHG emissions of gasoline due to the recycling of carbon in the production and use processes [14], making this a pathway to an essentially carbon-neutral liquid fuel. ‘Atmospheric methanol’ is about 3% more energy intensive than

production ‘flue-gas methanol’ but, in addition to being almost carbon-neutral, can be co-located with the renewable energy generation sites, thus avoiding transport of CO₂.

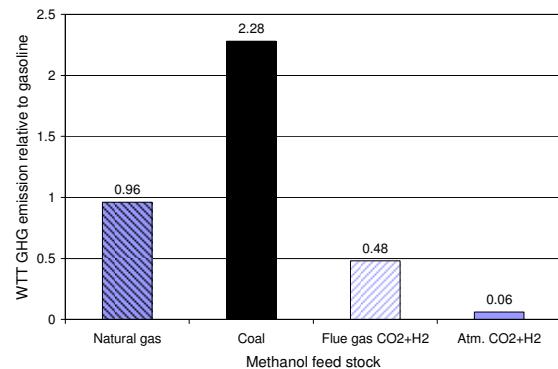


Figure 6: Well-to-wheel GHG emissions for methanol made from different feed stocks. (Adapted from [59]).

6. Conclusions

Fundamental physical and chemical principles dictate that the energy density of batteries and molecular hydrogen is unlikely ever to be competitive with liquid fuels for transport applications. The cost of personal transport incorporating these technologies, which sits idle for 95% of its lifetime, is, and will continue to be, excessive for a high proportion of the market in developed economies. In developing economies, where the majority of the medium to long-term growth in transport is projected, the cost is prohibitively high. The production of sustainable organic liquid fuels is proposed as a route to the continued provision of compatible, affordable, sustainable transport. This approach retains the use of low-cost internal combustion engines and liquid fuel systems. These powertrain systems have high power and energy storage densities, low embedded manufacturing and materials extraction energies; there is considerable potential for further efficiency improvements, especially combined with mild electrification.

Replacement of fossil fuels with carbon-neutral liquid fuels would not compromise current levels of mobility and would enable transport to remain globally compatible. Low-carbon number alcohols can be used for personal mobility and light-duty applications, and synthetic hydrocarbons for applications where maximum energy density is crucial. The technology to enable the evolution, not revolution, from the current vehicle fleet to equivalent-cost vehicles capable of using sustainable methanol has been described in the form of either tri-flex-fuel vehicles capable of running on any combination of gasoline, ethanol, or methanol, or current flex-fuel vehicles which can run on specific pre-blended mixtures of these three fuels. All transport energy can be supplied using biofuels up to

the biomass limit, and beyond it using carbon-neutral liquid fuels made using renewable energy and CO₂ from the atmosphere. The role of biofuels in this transitional route and end-game prevents them being regarded as a dead-end by vehicle manufacturers.

Populations in countries with developing economies have the right to increased mobility as their wealth grows. The current tendency to focus on vehicle CO₂ emissions results in rapid escalation in the large capital commitment required in vehicle purchase. Setting targets for vehicles in terms of energy usage per unit distance travelled (e.g. MJ/km) and targets for fuels / energy carriers in terms of non-renewable carbon (dioxide) per unit energy generated in production / use (e.g. gCO₂/MJ) resolves the tank-to-wheel and well-to-tank emissions in a way in which the parties responsible for their respective contributions are able to take the appropriate responsibilities. It is posited that such a system would accelerate the development of carbon-neutral fuels. The responsibility for de-carbonizing transport would then be more equitably apportioned.

7. Acknowledgements

Anthony Peck of Lotus Engineering carried out the engine calibration work on the Exige 270E tri-flex-fuel vehicle. The authors would also like to acknowledge the insights gained from discussions with Paul Wuebben of South Coast Air Quality Management District, Ben Iosefa of Methanex, Matt Brusstar of EPA, Frank Zeman of New York Institute of Technology, and George Olah, Surya Prakash, and Alain Goeppert of the University of Southern California.

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9. Glossary

AFR	air:fuel ratio
BEV	battery electric vehicle
BPMED	bipolar membrane electrodialysis
DME	Di-methyl ether
EU	European Union
EXX	blend of XX% by volume of ethanol in gasoline
FFV	flex-fuel vehicle
FT	Fischer-Tropsch
GHG	greenhouse gas
HFCV	hydrogen fuel cell vehicle
HHV	higher heating value
ICE	internal combustion engine
LHV	lower heating value
LPG	liquid petroleum gas
MTG	methanol-to-gasoline
MtSynfuels	methanol-to-synfuels
MXX	blend of XX% by volume of methanol in gasoline
ppm	parts per million
RON	research octane number
SOFT	Sustainable Organic Fuels for Transport
TTW	tank-to-wheel
WTT	well (wind)-to-tank
WTW	well (wind)-to-wheel