2009-01-2764

Extending the Supply of Alcohol Fuels for Energy Security and Carbon Reduction

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ABSTRACT

The paper critiques proposals for de-carbonizing transport and offers a potential solution which may be attained by the gradual evolution of the current fleet of predominantly low-cost vehicles via the development of carbon-neutral liquid fuels. The closed-carbon cycles which are possible using such fuels offer the prospect of maintaining current levels of mobility with affordable transport whilst neutralizing the threat posed by the high predicted growth of greenhouse gas emissions from this sector.

Approaches to de-carbonizing transport include electrification and the adoption of molecular hydrogen as an energy carrier. These two solutions result in very expensive vehicles for personal transport which mostly lie idle for 95% of their life time and are purchased with high-cost capital. The total cost of ownership of such vehicles is high and the impact of such vehicles in reducing greenhouse gas emissions from transport is therefore likely to be low due to their unaffordability for a large number of customers. Conversely, powertrains and fuel systems capable of using renewable alcohols in high concentrations have minimal additional cost over existing models as they are made from abundant materials with low embedded energy levels.

The use of ethanol and methanol in internal combustion engines is reviewed and it is found that the efficiency and performance of engines using these fuels exceeds that of their fossil fuel counterparts. Low-carbon-number alcohols and, where necessary, more energy-dense hydrocarbons can be supplied using feed stocks from the biosphere up to the biomass limit from biofuels and, beyond the biomass limit, from the atmosphere and oceans using captured CO_2 and hydrogen electrolysed from water. Using the hydrogen in a synthesized fuel rather than as an independent energy carrier can be thought of as a pragmatic implementation of the hydrogen economy. This avoids the extremely high infrastructure and distribution costs which accompany the use of molecular hydrogen.

The production of liquid fuels from CO_2 and water are reviewed in which fully-closed carbon cycles are theoretically possible with the development of large-scale renewable energy generation and CO_2 capture from the atmosphere. An approach to the latter problem where CO_2 concentration and release based on bipolar membrane electrodialysis, developed by the co-authors from PARC, is described in detail and initial results from a laboratory scale device are reported.

The development of a Tri-Flex-Fuel vehicle, capable of operating on any combination of gasoline, ethanol, and methanol, using a single fuel system is also described. The low additional technology and materials costs of such vehicles demonstrates that compatible, affordable transport can be developed which provides a feasible means of vehicle *evolution* towards decarbonized transport without the consequences of huge stranded assets which would be imposed on the automotive industry by the revolution which would be required to mass-produce hydrogen fuel cell vehicles and battery-electric vehicles.

INTRODUCTION

Security of energy supply and climate change are the principal factors motivating the consideration of alternatives to fossil fuels in the near-to-medium-term. The desirability of securing national energy supply via exploitation of indigenous resources has the concomitant benefit of avoiding the excessive transfer of wealth in exchange for imported energy. The estimate that in 2007 the global transfer payments to the 13 OPEC countries was about $\$1\text{x}10^{12}$ [1] highlights the influence of this factor on the formulation of future transport energy policy for nations dependent on imported oil.

The longer-term concerns regarding security of energy supply are centred around the fact that oil is a depletable commodity on a human timescale. Speculation over the proximity of the global peak oil scenario and the dwindling reserves of cheaply exploitable oil to which the Western oil companies have access [2] are causing growing concerns regarding resource depletion. Significant new capacity is required to compensate for declines in existing production. It is estimated that $\$1\text{x}10^{12}$ investment in new capacity (equivalent to the transfer of wealth mentioned above) is required to meet projected demand in 2015 and that 64 million barrels per day of additional capacity is required by 2030 to meet demand growth and off-set decline – this is new capacity and is equivalent to six times the current capacity of Saudi Arabia [3,4].

In addition to causing resource depletion the world's growing population and energy demand per capita are leading to a rapid increase in greenhouse gas (GHG) emissions [5]. Concern over climate change is now escalating to the extent that it is clear that deep reductions in anthropogenic GHG emissions will be necessary across all sectors in order to stabilize the global average surface temperature. Over the past 10 years GHG emissions from transport have produced the highest rates of growth in any sector and by 2030 energy use and carbon emissions from transport are predicted to grow by 80% relative to current levels [6]. With a vast number of mobile emitters and an extremely high dependency on fossil fuels, transport is one of the most difficult sectors to tackle.

Large improvements in vehicle efficiency are promised only by what is likely to be prohibitively expensive vehicle technology such as widespread electrification or, to a lesser degree, the adoption of hybridized hydrogen fuel cell powertrain units. Using these technologies to provide personal mobility via vehicles with operating ranges and performance levels which are comparable to those to which we are accustomed will require the customer to accept a large increase in cost. Moreover, the majority of the growth in transport is likely to occur in countries with developing economies [7]; the types of vehicles via which personal mobility will be propagated in these economies will, by economic necessity, be based on low-cost powertrain and fuel system technologies. Legislation requiring 80% reduction in GHG emissions over 1990 levels [8], such as that enacted in the UK, cannot rely on improvements in vehicle efficiency alone – it is also necessary to decarbonise the fuels and energy carriers with which the vehicles are energized.

Internal combustion engines are made from cheap and abundant materials and are capable of burning a wide variety of fuels, including those which are carbon neutral. They have low-cost fuel systems capable of storing fuel with high on-board energy densities which can be re-filled from simple re-fuelling stations by self-service. It is argued in the present work that such powertrains, using carbon-neutral liquid fuels, offer the best potential for a long-term solution to de-carbonising transport. The paper develops the case for *sustainable organic*[1] *fuels* which are capable of supplying the transport fleet in full amounts, enabling vehicles and the fuel distribution infrastructure to transform via *evolution* rather than revolution. Vehicle technologies are described which can operate on mixtures of alcohol fuels and gasoline; in particular the development of a tri-flex-fuel car is described. Factors which limit the supply of biofuels and impose an effective biomass limit are discussed together with approaches to circumventing this constraint on fuel supply by synthesizing fuels from renewable hydrogen electrolysed from water and carbon feed stocks extracted from the atmosphere. A technology based on bi-polar membrane electrodialysis is described for concentrating and releasing extracted CO_2 and initial results for a laboratory-scale device operating this principle are presented.

ELECTRICITY AND HYDROGEN AS TRANSPORT ENERGY CARRIERS

2.1 Electrification

The tank-to-wheel efficiency of an electric vehicle is about 4 times higher than that of a gasoline fuelled spark-ignition engine over a drive cycle such as the NEDC and this gives electrification the obvious appeal of potentially minimizing the investment in the upstream energy generation. In order for this advantage to be converted into a significant reduction in carbon dioxide emissions however, it is essential to de-carbonize the upstream energy supply or implement a widespread carbon capture and storage approach. Electrification of the vehicle fleet has the additional theoretical attraction that most of the various forms of renewable energy are conveniently converted to electricity and utilizing this in the grid to power electric vehicles removes the conversion losses involved in manufacturing a chemical energy carrier. An infrastructure for supplying end-user vehicles at low rates of charge is available to those with access to electricity supplies which are close to where their vehicles are parked. However transmission lines required to convey the renewable electricity from the remote locations in which it may be generated to the locations in which it is required is often not readily available and would be extremely expensive to install.

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[1] 'Organic' meaning 'carbon-containing'.

Batteries are fundamentally limited by their very low net gravimetric and volumetric energy densities, as shown for lead-acid, nickel-metal hydride, and lithium ion batteries in Figure 1. To match the range of a conventional gasoline vehicle with a 50 litre fuel tank would require approximately a 100 kWh battery. Such a battery would be capable of storing a similar quantity of energy to approximately 12 litres of gasoline, but the 4 times greater tank-to-wheel efficiency of the electric vehicle would give parity in range. A tank containing 50 litres of gasoline would weigh about 46 kg; a 100 kWh battery would weigh 600-1000 kg, depending on the technology and the permissible depth of discharge.

Battery cost estimates vary enormously depending on the detailed material content, permissible depth of discharge, and a variety of other factors. The most optimistic medium-term estimates for a lithium-ion battery at 100,000 units per annum production levels are in the region of \$250/(kWh). This puts the cost of a 100 kWh battery at \$25,000. More common price estimates are in the range \$800-\$1000/(kWh) [9], putting a 100 kWh battery at over \$80,000. Cell durability is a major concern for electric vehicles and failure of the battery to last the life of the vehicle will compound the high initial cost so that the total cost of ownership over the vehicle lifetime would be substantially higher than those of current vehicles. Durability can generally be increased by reducing the maximum permissible depth of discharge but this has the effect of over-specifying the battery size thus increasing the cost further [9].

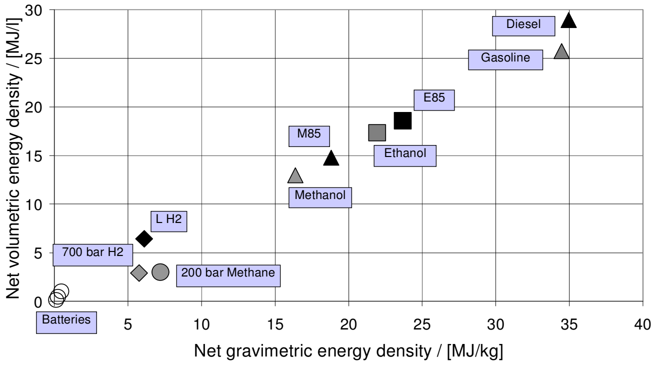

Figure 1: Net system volumetric and gravimetric energy densities for various on-board energy carriers (based on lower heating values).

2.2 Hydrogen

For mobile emitters hydrogen is an appealing energy carrier from the perspective that it can be burnt in an engine or oxidized at high efficiency in a fuel cell with no release of CO_2 in to the atmosphere. Internal combustion engines (as distinct from their fuel systems) and gas turbines require relatively little modification to run on hydrogen, and it is the energy carrier required for most types of low-temperature fuel cell – i.e. those considered most suitable for transport applications. However, the current largest industrial source of hydrogen production is steam reformation of methane which produces 5.5 kg of carbon dioxide for every 1 kg of hydrogen produced; the well-to-wheel GHG production of burning hydrogen, from steam reformation of methane, in an internal combustion engine is significantly worse than if the methane is burnt directly in the engine [10]. This emphasizes the importance of de-carbonizing the upstream energy supply.

Figure 1 shows that, while the net on-board energy density of hydrogen comfortably exceeds that of batteries, it is still very low compared with liquid fuels. The net volumetric energy densities shown in Figure 1 include system package volumes and show the deficiency of even liquid hydrogen as an energy storage medium. Because of the extreme physical conditions required to package hydrogen the bulky system volume becomes a high percentage of the net volumetric energy content. The packaging problems are exacerbated by the constraints on the tank shapes imposed by pressure vessel design considerations and the requirement to minimize heat ingress in cryogenic systems.

Although hydrogen has a very high energy per unit mass (gravimetric energy density) its net packaged value, including the storage system mass, suffers in an even more marked way than the volumetric energy density, as shown in Figure 1. Pressure vessels and cryogenic tanks are extremely heavy: a 700 bar system for automotive use, holding 4.6 kg of hydrogen (the energy equivalent to 17.5 litres of gasoline) is quoted by Eberle [11] as weighing 95 kg, whilst cryogenic systems can weigh around 170 kg and contain only 9 kg of hydrogen (the energy equivalent of about 34 litres of gasoline). In contrast a tank for a liquid hydrocarbon fuel system may weigh around 10 kg. While physical metal hydride storage systems for hydrogen [12,13] achieve similar volumetric energy density to a 700 bar gaseous system, the gravimetric energy content is comparable with lithium-ion batteries. Chemical metal hydrides can achieve superior volumetric hydrogen storage density than 700 bar gas storage or liquid hydrogen but their gravimetric energy density is also worse [14].

Bossel et al. [12,13] state that, if mechanical and electrical losses are also considered, the total energy used for compression of hydrogen to an 800 bar supply pressure may reach 20% of the higher heating value of the hydrogen undergoing the process. The energy efficiency of liquefaction plants is strongly dependent on size. For a large scale plant about 40% of the higher heating value is consumed in liquefaction – this figure can approach or exceed the energy content of the fuel for small-scale systems [12,13]. The high degree of purity required by some hydrogen fuel cells compounds this upstream fuel energy loss as the purification process can involve a ‘distillation’ process in which the hydrogen is evaporated. The effect of boil-off losses during distribution and re-fuelling can lead to unacceptable loss of hydrogen [15].

Figure 2 is based on systems giving the equivalent stored energy of 50 litres of gasoline, where the differences in tank-to-wheel efficiency of the vehicles have been included. A hybridized fuel cell vehicle is considered for the compressed hydrogen fuel option. It can be seen that liquid fuel systems are very cheap compared with systems for containing pressurized gases or battery packs. Eberle [11] quotes 2000 Euros for a 700 bar hydrogen tank capable of storing 6 kg of hydrogen but a figure of 10,000 Euros was deemed more realistic by Jackson [16]; these costs appear prohibitively expensive compared with the intended $2500 price for the Tata Nano [17]. The expense is compounded when the additional cost of a fuel cell is considered as part of the powertrain system. Table 1 shows that current fuel cell costs are prohibitively expensive compared with conventional or hybrid powertrain technologies: a 100 kW fuel cell would currently cost between $50,000 and $100,000 and would require additional bill of material costs due the requirement to hybridize the powertrain. Hybridization is required for fuel-cell vehicles to reach the tank-to-wheels efficiency levels of about 0.5 which are usually assumed over a drive cycle[2].

As noted by Jackson [16], the fuel economy potential of internal combustion engine / hybrid systems may improve significantly at US$50 / kW. The manufacture of internal combustion engines and their fuel systems places low demands on scarce materials – they are made from cheap, abundant raw materials at concomitantly low costs and contain low embedded energy levels.

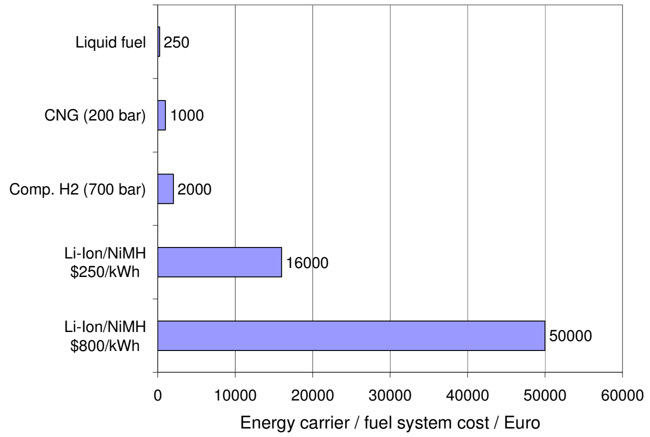

Figure 2:: Fuel / energy carrier system costs for volume production (100,000 units per annum) at projected 2010 costs – based on vehicle range of 50 litres of gasoline. (Data derived partly from Jackson [16] and Eberle [11].)

Clearly the provision of hydrogen production, distribution and re-fuelling facilities will require large investment since a completely new infrastructure capable of dealing safely with a highly explosive gas is needed. Mintz et al. [18] have estimated the cost of providing a hydrogen infrastructure in the USA capable of re-fuelling 100 million fuel cell vehicles (40% of the light-duty vehicle fleet) at up to $650 billion. Moreover, in the transition period to a hydrogen-based energy economy, a dual infrastructure must be maintained and vehicles with two incompatible fuel storage systems must be produced, thereby escalating costs of both appreciably.

Table 1. Estimated powertrain manufacturing costs. (Based on Jackson [16]).

Powertrain System	Cost : US $/kW Current	Cost: US $/kW Medium Term
Gasoline	10-15	15-20
Diesel	15-20	20-30
Hybrid	25-40	20-35
Fuel Cell	500-1000	Target 50

Under the predicate of a decarbonized energy supply, the ostensible attraction of battery-electric vehicles (BEVs) and hydrogen fuel cell vehicles (HFCVs) is their high tank-to-wheels efficiency. Clearly a full life-cycle analysis of energy requirements and greenhouse gas emissions is needed, where not only tank-to-wheel and well-to-tank efficiencies are considered but the fuel and component use over the lifetime of the vehicles and the energy used and GHG emissions released during its manufacture from raw materials are also included. Although analysis based on this type of approach is relatively immature some recent studies have shown that the life-cycle CO_2 emissions for BEVs and HFCVs fuelled with fossil-based energy can be higher, under higher speed driving condiitions, than vehicles powered by gasoline-fuelled internal combustion engines (ICEs) [19,20]. The CO_2 emissions released in the manufacturing processes for BEVs and FCVs are 2-3 times those for ICEs [19,20]. In a scenario where all vehicles are supplied with fuels and energy carriers sourced from renewable energy this overhead provides an opportunity for a concept based on the use of a closed carbon cycle liquid fuel supplying ICE-powered vehicles. In addition to their high cost of ownership, this makes the adoption of BEVs and HFCVs in significant numbers unlikely.

LOW-CARBON-NUMBER ALCOHOLS AS FUELS FOR THE INTERNAL COMBUSTION ENGINE

The potential of alcohols as fuels for the internal combustion engine was noted as early as 1907 in the literature [21]. Because it can be synthesized from a wide range of renewable and alternative fossil-based feed stocks methanol was the subject of many studies during the oil crises of the 1970s and 1980s [22-24]. More recently the focus has shifted to ethanol made from biomass. Both alcohols are liquid fuels which can be stored in low-cost fuel systems. They also have the enormous advantage of being miscible with gasoline so that a single vehicle fuel system can be used and an infrastructure relatively similar to that which exists currently can be used to distribute them. The miscibility

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[2] It should be noted that in many instances quoted fuel cell efficiencies are based on the lower heating value (LHV) of the hydrogen. When calculating the amount of upstream renewable energy required for a given application the higher heating value (HHV) energy carrier is the correct parameter to consider. For hydrogen, using the LHV produces an efficiency over-estimate of about 18% compared with an over estimate of only 6% if efficiencies are based on gasoline LHV. Using HHV-based efficiencies brings the peak efficiencies of internal combustion engines and fuel cells closer together than is often claimed.

of methanol with ethanol and with gasoline means that it may be considered, initially as an ethanol 'extender'; it will be shown in later sections that methanol itself could form the basis of an alternative transport fuel which, in the long term, is carbon-neutral.

3.1 Physico-chemical properties

The presence of the hydroxyl group in alcohol molecules gives rise to local polarity, endowing them with various desirable physico-chemical properties which are much more pronounced in the smaller low carbon-number alcohols such as methanol (CH_3OH) and ethanol (C_2H_5OH) than the higher alcohols such as butanol (C_4H_9OH) and pentanol ($C_5H_{11}OH$). The molecular polarity generates strong inter-molecular forces, known as hydrogen bonds, and these forces give rise to high boiling points (for their molecular mass), high heats of vaporization, and good miscibility with nominally dissimilar substances having strong molecular polarity (e.g. water). This polarity is also the reason for the greater corrosiveness of these fuels toward some materials compared with gasoline. Methanol and ethanol also have much higher octane indices than the higher normal (straight-chain) alcohols.

3.2 Methanol and ethanol as fuels for SI engines

Unusually for 'alternative' fuels, ethanol and methanol have the potential to increase engine performance and efficiency over that achievable with gasoline. This is due to a variety of factors, including their higher octane rating, heat of vaporization, flame speed, energy per unit mass of air, molar ratio of products to reactants, and heat capacity of combustion products due to a high ratio of triatomic to diatomic molecules.

Properties such as octane number and vapour pressure vary non-linearly as fuels are blended. Kar et al. [25] show that the Research Octane Number (RON) of E60[3] is close to that of pure ethanol (E100) using a 95 RON gasoline in the blend. Brinkman, Gallopoulos, and Jackson [26] studied low-level blends of methanol and ethanol in production gasoline engines of the time and concluded that the behaviour of the two alcohols in these blends was similar. Brinkman [27] found a 3-4% improvement in thermal efficiency using ethanol (E100) relative to operation on a control gasoline fuel using a single-cylinder engine with a low compression ratio. Using methanol (M100) Koenig, Lee, and Bernhardt [28] found improvements of around 8% in thermal efficiency over gasoline operating at full-load at 2000 rev/min. with a compression ratio of 8.2:1; a power increase of about 12% was achieved. A thermal efficiency of over 40% was reported when a compression ratio of 12:1 was used.

Recent work on modern multi-cylinder engines has demonstrated significant opportunities for both increasing efficiency and performance. Nakata et al. [29] used a high compression ratio (13:1) naturally aspirated port-fuel injected spark-ignition and found that engine torque increased by 5% and 20% using E100 compared with the operation on 100 RON and 92 RON gasoline respectively. The full improvements in torque due to being able to run MBT ignition timing were apparent for E50. Using E100 a full-load thermal efficiency at 2800 rev/min. of 39.6% was reported, compared with 37.9% and 31.7% using the high and low-octane gasoline respectively. A thermal efficiency improvement of 3% was achieved using E100 over the 100 RON gasoline at the 2000 rev/min / 2 bar BMEP operating point, where the engine was far from the area where knock becomes a limiting factor – this is indicative of the benefits of faster flame speed, higher product specific heat capacity, and lower combustion temperatures (lowering heat losses) of the alcohol fuel. Similar results were reported by Marriott et al. [30] at this operating point; the improvements were attributed to the reduced heat losses when running on E85, established by heat release analysis. Up to 6% benefit was found at other low speed / load points, with CO_2 emissions being reduced by up to 11%, with the additional benefit above the efficiency gain being due to the low CO_2 emissions per unit energy released by combustion of the alcohol fuel.

The higher heats of vaporization of methanol and ethanol, combined with their low values of stoichiometric air:fuel ratio (AFR), lead to high degrees of cooling of the cylinder charge as the fuel evaporates. In addition to increasing intake charge density this has an appreciable effect on reducing the propensity of the engine to knock and is a supplementary effect to that of the high octane numbers of the fuels. This enhanced knock resistance of methanol and ethanol makes them well suited to pressure-charged engines [31] where improvements in fuel economy achieved by 'downsizing' may be compromised when using gasoline by the requirement to use a relatively low compression ratio to avoid excessive knock at high loads. The lower exhaust temperatures obtained using alcohol fuels also reduces the requirement for component protection over-fuelling. The engine used in the Tri-Flex-Fuel vehicle described in Section 6 was modified to realize the benefit of the charge cooling effect at full-load by introducing a portion of the fuel load upstream of the supercharger. The thermal efficiency and performance benefits using E85 fuel in this engine have been described in detail elsewhere [32,33].

Peak torque and power increases of 15% and 10% respectively were obtained by Bergstrom et al. [34,35] using a production ethanol-gasoline flex-fuel engine with port-fuel injection. The lower exhaust gas temperatures experienced when running on E85 allowed the fuel enrichment level at full-load to be reduced to the extent that, for the same limiting peak pressures as those tolerated using gasoline fuel, stoichiometric operation across the engine speed range is possible [35]. Kapus [36] found that for identical engine performance the more favourable combustion phasing when running on E85 leads to less requirement for fuel enrichment giving a 24% reduction in full-load fuel economy compared with operation on 95 RON gasoline. Thermal efficiency improvements at full-load of over 35% relative to 95 RON gasoline have been found using E100 in a direct-

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[3] E60 is a mixture of ethanol and gasoline in the ratio of 60% ethanol and 40% gasoline by volume.

injection, turbocharged spark-ignition engine [37] operating at high BMEP levels.

Direct injection of the fuel into the cylinder increases the possibility to exploit the heat of vaporization of the fuel to good effect. Marriott et al. [30] quote a 13% increase in maximum power when running on E85 fuel relative to 91 RON gasoline in a naturally aspirated engine and show that, of the 11.3% increase in peak torque, 3.1% was due to improved volumetric efficiency, with 3.7% and 4.5% being attributed to improved combustion phasing and reduced heat losses respectively. When the fuelling on E85 was limited to stoichiometric across the speed range peak torque and power were still improved by 8.2% and 10.7% respectively, above the results obtained with enriched operation on the baseline 91 RON gasoline. Compared with 104 RON gasoline fuel, which was not knock limited at maximum torque, the improvement in peak torque was about 7%.

Recent work by Malcolm et al. [38] has shown faster burn rates than iso-octane using commercial E85 fuel at stoichiometric and lean air-fuel ratios but a splash-blended E85/iso-octane mixture gave slightly slower burn rates at lean operation conditions. Several studies have identified that the faster combustion rate experienced using methanol extends the dilution limit relative to gasoline [23,28,39] and Pannone and Johnson [40] employed these characteristics in a lean-burn turbocharged engine.

The greater dilution limit of methanol and ethanol was exploited by Brusstar et al. [41] who converted a base 1.9 litre direct-injection turbocharged diesel engine to run on M100 and E100 by replacing the diesel injectors with spark plugs and fitting a low-pressure alcohol fuel injection system in the intake manifold. Running at the 19.5:1compression ratio of the base diesel engine the PFI methanol variant increased the peak brake thermal efficiency from 40% to 42% while parity with the diesel was achieved using ethanol. Cooled EGR enabled the engine to achieve close to MBT ignition timing at high loads, while high levels of EGR dilution were used to spread the high efficiency regions to extensive areas of the part-load operating map. Emissions of NO_x, CO, and HC were extremely low operating on methanol using a conventional 'three-way' after treatment system. Particulate and aldehyde emissions were not measured due to earlier work [42] which had established the ability to control these to very low levels using a conventional oxidation catalyst. Low-carbon-number alcohols give inherently low particulate emissions, particularly methanol which has no carbon-carbon bonds. Similar results were found by Brusstar and Gray [43] using a 4.5 litre V6 diesel as a base engine. The dilution limits for both fuels were established for throttle-less operation and these also increase with the proportion of alcohol in the fuel so that, for M100, throttle-less operation from a BMEP of 16 bar down to 4 bar is possible.

While the high heat of vaporization and low stoichiometric air-fuel ratio are beneficial from the perspective of engine performance they are also responsible, together with their relatively high boiling points (65 ^{o}C for methanol and 78 ^{o}C for ethanol, at 1 bar), for the additional attention required in order to achieve acceptable cold-start performance using low-carbon-number alcohols. In addition to the performance benefits resulting from the adoption of direct fuel injection, Siewart and Groff [44] have achieved cold start at -29 ^{o}C using charge stratification and late fuel injection. Kapus et al. [36] and Marriott et al. [30] have proposed high pressure late injections, using several split injections to further augment the quality of the start. For port-fuel-injected engines measures such as heating the fuel rail can enable acceptable cold-start performance down to -25 ^{o}C. Bergstrom et al. [34] report acceptable cold starts down to -25 ^{o}C in the absence of additional technology with a PFI engine using Swedish winter standard bioethanol (E75 with Reid vapour pressure = 50).

Mixtures of alcohol and gasoline are non-ideal solutions in that partial vapour pressure of a component (gasoline itself is a mixture of components) is not proportional to its concentration (mole fraction) and its vapour pressure when pure, i.e. they do not obey Raoult's law. Not only is the variation of the vapour pressure non-linear with alcohol concentration, it is not even monotonic. This irregular behaviour is thought to be caused by hydrogen bonding where, for example, methanol forms a 'quasi-super-molecule' known as a cyclic tetramer in which four methanol molecules form a super-structure via hydrogen bonds between the individual molecules. These cyclic tetramers have an effective molecular mass of 128 (four times that of an individual molecule) rendering the vapour pressure of the pure methanol relatively low. The hydrogen bonds are progressively weakened and become less extensive when the alcohol is mixed with increasing quantities of a non-polar solvent such as gasoline, making them behave as low molecular mass components (32 in the case of methanol) which increase the vapour pressure of the mixture. Fuel volatility is also increased because alcohols form low-boiling point azeotropes with some hydrocarbons. Compared with a typical gasoline, the Reid vapour pressures of methanol and ethanol blends with the same gasoline are higher up to concentrations of about 80% and 45% respectively, before dropping steeply [24,25]. In addition to affecting the cold-start performance of an engine this behaviour illustrates how evaporative emissions using methanol and ethanol at high concentration levels can be lower than those of gasoline.

It should be noted that while ethanol and methanol offer some significant advantages over gasoline as fuels for spark-ignition engines (listed at the beginning of this section), the normal-configuration higher alcohols exhibit progressively degraded knock resistance such that propanol could considered only slightly better than gasoline, and *n*-butanol and *n*-pentanol significantly worse. Yacoub, Bata, and Gautum [45] and Gautum and Martins [46] have shown that whether a binary mixture of gasoline and alcohols or multiple-blends are considered (all with controlled oxygen content) methanol and ethanol clearly produce superior fuels to the higher alcohols. The gasoline they used, UTG-96[4] [47], had a research octane number of 96 and so can be considered representative of a premium US gasoline or a regular European one. More recently Cairns et al. [48] have also tested blends of different alcohols in a more modern engine configuration with direct injection and turbocharging, and their full-load results indicate that matched-oxygen-content blends of ethanol or *n*-butanol with gasoline provide better and worse knock resistance than the base 95 RON fuel respectively.

Thus the normal alcohol molecules considered to be beneficial in blends with gasoline are those with up to only two carbon atoms. In general however the alcohols display similar characteristics to the paraffins as the molecule is branched. Popuri and Bata [49] suggest that the branched molecules of isobutanol make it the equal of ethanol and methanol as a blending component but at the expense of considerable extra complication in the manufacturing process over n-butanol, the fuel most readily manufactured and generally used by other researchers (note that Popuri and Bata were using a CFR engine with a carburettor and did not test all of the fuels at exactly the same equivalence ratio [49]).

In summary, for spark-ignition combustion, when blending alcohols with gasoline or considering the alcohols as fuels in their own right, the lower alcohols methanol and ethanol are superior to gasoline, with monotonic degradation in performance from propanol onwards. *n*-Butanol is quantifiably worse than gasoline. In a future transport energy economy where well-to-wheels energy efficiency is a key criterion, the clear benefit of only synthesizing C1 and C2 alcohols is plainly apparent: they will require less energy to create and will provide higher thermal efficiency in use.

3.3 Methanol and ethanol as fuels for CI engines

As a corollary of the low-carbon-number alcohols having high octane numbers they have very low cetane numbers (CN). For methanol the number is so low that it cannot be measured directly. Extrapolation of test data using additives gives a CN of 3 for pure methanol and a CN of 2 for methanol with 10% water [23]. Since CN is a measure of a fuel's auto-ignitibility pure methanol and ethanol are unsuitable for use in conventional compression-ignition engines, however it can be used in conjunction with another fuel which is more auto-ignitable, or with an 'ignition improver'. In the 1980s the Detroit Diesel Company (DDC) and MAN [50] produced modified versions of their compression-ignition engines which ran on 'ignition improved' methanol fuel (the ignition improver constituted about 5% by volume of the fuel). The MAN engine was a four-stroke engine using spark-assisted ignition whilst the DDC engines operated on the two-stroke cycle, controlling the scavenge ratio and using glow plugs to assist ignition [51,52]. Urban [52] showed that the diesel base DDC engine was easily modified to run on ignition-improved methanol and could develop more power at the same level of particulate emissions. These engines ran in service in heavy-duty applications [50,53].

Hikino and Suzuki [54] modified a 9.9 litre 6-cylinder direct-injection diesel engine to run on pure methanol in compression-ignition mode. The engine ran in naturally aspirated form with its compression ratio increased from 17.9:1 to 27:1 in order to achieve auto-ignition and using EGR to increase the intake temperature at low loads. Significant improvement in NOx was achieved as a result of the combustion system employed. Additionally, both ethanol and methanol produce low levels of particulate emissions when used in compression ignition engines due to smaller, or in the case of methanol, lack of, carbon-carbon chains in the fuel. These characteristics show the potential of methanol as a heavy-duty engine fuel against the necessity of reducing pollutant emissions while maintaining high thermal efficiency operation.

BIOMASS, BIOFUELS, AND THE BIOMASS LIMIT

4.1 Biomass and biofuels

Biomass is usually defined as material that is directly or indirectly derived from plant life and that is renewable in time periods of less than about 100 years [55]. Biomass is produced from combining 'feed stocks' which are essentially the products of combustion (CO_2 and H_2O) and effectively have zero chemical availability (exergy), via the process of photosynthesis, to form oxidizable organic matter of higher chemical availability. The oxidizable materials of relevance to biomass energy conversion are carbohydrates and lignin. The photosynthesis process for the production of carbohydrates can be represented by the overall reaction

$$n\mathrm{CO}_2 + m\mathrm{H}_2\mathrm{O} \xrightarrow[\text{chlorophyll}]{\text{sunlight}} \mathrm{C}_n(\mathrm{H}_2\mathrm{O})_m + n\mathrm{O}_2\,;$$

$$\Delta H^0_{298} = +470\,\text{kJ/mol.} \qquad (1)$$

A plant typically contains between 0.1-3.0% of the original solar energy which is incident upon it during its growth [55]. The CO_2 which is taken from the biosphere by the plant may be formed by respiration, biological degradation, or combustion, and is reprocessed by photosynthesis into biomass. The re-growth of an equivalent amount of vegetation ensures renewability and that theoretically there is no net accumulation of CO_2. Clearly the concern over the climatic impact of burning fossil-based fuels is the return to the atmosphere within a few decades of a large amount of CO_2 which was converted to biomass or animal matter and accumulated in a hydrocarbon store over a period of millions of years.

The production methods for biofuels can be broadly classed as extractive, fermentative (biochemical), and thermochemical (mainly gasification). The main biofuels currently in the market are bioethanol and biodiesel, made by fermentative and extractive processes respectively. Biodiesel can be made by trans-

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[4] Unleaded Test Gasoline – 96 (also known as indolene) is supplied by Chevron Phillips and is widely used in the industry. It has a RON of 96.1 and a MON of 87.0.

esterification (using methanol) of plant oils, animal fats, and recycled cooking oils and fats and is classed as a fatty acid methyl ester (FAME). Rapeseed methyl ester (RME) is a widely used form of biodiesel in Europe, with palm oil, and soybean oil being widely-used feed stocks in other regions. Biodiesel can also be made by hydroprocessing in which hydrogen is used to convert bio-oils into a product which can be refined in a conventional refinery [56].

The carbohydrates are either mono- or disaccharides (sugars), or polysaccharides (polymers of sugars). The mono-saccharides ($C_6H_{12}O_6$/$C_5H_{10}O_5$), such as glucose, found in corn and grapes, and fructose, found in other fruits, are fermentable to ethanol. Butanol can also be fermented from sugars but its production is three-fold less efficient than for ethanol production [57].

The disaccharide ($C_{12}H_{22}O_{11}$) sucrose, which is the primary sugar in the sap of plants and is abundant in sugar cane and sugar beet, can be hydrolysed by an enzyme (catalyst) present in yeast to form fermentable monosaccharides. The polysaccharides include starch, hemicellulose, and cellulose, together with the non-carbohydrate lignin. Starch is readily turned into fermentable sugars via enzymatic hydrolysis. An example of the saccharification of starch (maltose) and the subsequent fermentation process to form ethanol can be summarized by the reactions [55]

$$\left(C_6H_{10}\right)_n + \frac{n}{2}H_2O \rightarrow \frac{n}{2}C_{12}H_{22}O_{11} \qquad (2)$$

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6 \rightarrow 4\ C_2H_5OH + 4CO_2 \qquad (3)$$

It can be seen that for every 12 atoms of carbon contained in the original biomass, 4 are converted back to CO_2 during the fermentation process; indeed CO_2 is produced at a molar rate equivalent to that of the ethanol. This is a consequence of the oxygen ratio in the original biomass being higher than that required for the intended alcoholic product. The fermented liquid contains up to 18% ethanol and is fractionated (distilled) in order to concentrate the alcohol up to the required level. Separation of the ethanol is an energy intensive step. Increasing the concentration of ethanol before distillation improves the process efficiency but is constrained by the level which the micro-organisms can tolerate the alcohol.

First-generation biofuels are made from fermentation of plant sugars (bioethanol) or trans-esterification of plant oil (biodiesel). There are significant concerns regarding the production of these first-generation fuels, discussed in the next section, hence the considerable recent effort to develop second-generation biofuels which employ advanced pre-treatment techniques in order to break down ligno-cellulosic biomass into fermentable sugars.

Hemi-cellulose is more resistant than starch to hydrolysis in to fermentable sugars, traditionally requiring the use of dilute alkaline solutions [55], and new approaches to fermenting the pentoses (C_5-sugars) derived from hemi-cellulose are under development [57]. Cellulose, being the main constituent of the cell walls of land plants, is the most abundant naturally-occurring organic substance on earth. As it is a major component of wood, hemp, and straw it has the potential to supply significant quantities of biomass which does not cause conflict with food requirements but it is extremely resistant to traditional enzymatic hydrolysis. Cellulose can be processed by acid-hydrolysis but this is expensive, due to the costly wastewater recovery and treatment, and reduces the yield of sugar. Lignin, which is a polymer of single benzene rings (often phenolic[5]) linked by aliphatic chains, is also formed as a constituent of the walls of woody cells but totally resists hydrolysis and is resistant to microbial degradation [55]. Lignin and its by-products need to be removed before fermentation as they can be toxic to the micro-organisms and enzymes used for hydrolysis. It can be burnt, however, to provide part of the process heat requirements.

The vegetation providing the main source of sugars and ligno-cellulosic compounds useful for biomass energy includes trees, grasses, legumes, grain and sugar crops, and aquatic plants. Wood provides perhaps the greatest potential source of biomass but it contains about two-thirds cellulose and hemicellulose (together known as holocellulose) and one quarter lignin (the remainder being extraneous materials such as resins, gums, tannins, and waxes [55]). Since only the hemicellulose and about one quarter of the cellulose can be readily hydrolysed to fermentable sugars biochemical processes are of limited application in the utilization of woody biomass.

There has been considerable effort recently to develop so-called ‘second generation’ biofuels which employ steam explosion, high-pressure hot water treatments, and advanced enzymatic hydrolysis techniques in order to break down lingo-cellulosic biomass into fermentable sugars but the optimal pre-treatment will be feed-stock-specific [57]. However, most biomass materials can be gasified and the resulting gas may be used for the synthesis of liquid fuels - this is sometimes referred to as thermo-chemical conversion, as opposed to biochemical conversion. Wood, municipal solid waste, gases, and crop residues can be gasified. Biomass materials produce little by-product on gasification, and many of the chars and oils evolved may be recycled until they are eliminated [55]. A large portion of the calorific value of the original biomass material leaves the gasifier in the chemical energy of the resulting carbon monoxide (CO) and hydrogen. The carbon monoxide and hydrogen gas mixture is referred to as synthesis gas, or syn-gas, because it provides the basis for synthesizing fuels in an additional process step. Although direct combustion of the biomass provides a low cost route to converting its energy content the use of biomass to provide heat or electricity has to be balanced against the versatility of producing a liquid fuel for use in the transport sector which is extremely difficult to decarbonize.

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[5] A phenolic compound is one in which a hydroxyl group is attached to the benzene ring.

Gasification is particularly attractive as, with the addition of extra hydrogen, it allows the utilization of all the biomass, i.e. total plant use, and permits the use of a wide variety of biogenic resources, conserving ecological diversity [58,59]. The avoidance of propagating monocultures, since specific enzymes do not have to be tailored to particular crops, enhances security of supply as the feed stock is not then vulnerable to the propagation of a single crop disease.

Fuel production via gasification also enables a wide range of fuels to be produced, if required. Amongst the fuels which can be produced from the syn-gas are methanol, DME, synthetic natural gas (SNG), hydrogen, and synthetic gasoline and diesel. The production of liquid fuels from biomass is sometimes generically referred to as biomass to liquids[6] (BTL). Methanol is most easily produced by this process. The production of the higher alcohols and longer chain hydrocarbons such as the components of synthetic gasoline, diesel, and kerosene, requires Fischer-Tropsch or Methanol-to-Gasoline / Methanol-to-SynFuels [59,60] technology. In these processes the small molecules of the syn-gas are re-assembled into more complex molecules. The plants required are large and complex with significantly higher costs. They give a mixture of products and there is a reduction in the resulting fuel energy supplied (of about 10 per cent).

It should be noted that the chemical composition of biodiesel formed by trans-esterification differs distinctly from fossil-derived diesel, being a mixture of methyl esters, the composition of which differ as the composition of the oils from the plant species differ. Thus blends of various oils may be needed to produce an acceptable product. In contrast biofuels produced from gasification and subsequent carefully controlled synthesis (as well as GTL and CTL fuels) can have properties which are very close to, or better than, their fossil-based counterparts. They are necessarily ‘cleaner’ due to the removal of contaminants in order to avoid poisoning the catalysts used in the synthesis step [57].

In the primary thermo-chemical conversion step the biomass is ideally decomposed into a gas with hydrogen and carbon monoxide as the main components. Air, oxygen, water vapour and hydrogen in any partial mixture usually form the gasification components, with the main challenge being the production of syn-gas of the desired composition which is free of tar, particles, and catalytic poisons, having a low concentration of inert gas and a high concentration of hydrogen [59]. The composition of the syn-gas is often characterized by the stoichiometry factor, *S*, which is defined as

$$S = \frac{\left(p_{\mathrm{H_2}} - p_{\mathrm{CO_2}}\right)}{\left(p_{\mathrm{CO}} + p_{\mathrm{CO_2}}\right)}, \qquad (4)$$

where *p* represents the partial pressure of the species identified by their subscripts.

The simplest reaction involving the syn-gas resulting from gasification leads to the production of methanol via combination of one mole of carbon monoxide with two moles of hydrogen via the path

$$\mathrm{CO} + 2\mathrm{H_2} \Leftrightarrow \mathrm{CH_3OH}\,(l)$$

$$\Delta H^0_{298} = -128.2 \text{ kJ/mol..} \qquad (5)$$

Clearly this reaction requires syn-gas with composition such that *S* = 2, as does the production of Fischer-Tropsch fuels via the reaction

$$n(\mathrm{CO} + 2\mathrm{H_2}) \rightarrow n(-\mathrm{CH_2}-) + n\mathrm{H_2O}$$

$$\Delta H^0_{298} = -162 \text{ kJ/mol. .} \qquad (6)$$

In fact, because part of the biomass carbon is converted to CO_2 in the gasification step, and its subsequent hydrogenation to methanol requires 3 moles of hydrogen according to

$$\mathrm{CO_2} + 3\mathrm{H_2} \Leftrightarrow \mathrm{CH_3OH} + \mathrm{H_2O}$$

$$\Delta H^0_{298} = -49.9 \text{ kJ/mol.,} \qquad (7)$$

the stoichiometry factor, *S*, defined in equation (4), needs to be greater than 2 in order avoid the use of a shift reactor in the plant with a concomitant increase in cost [61]. This can be achieved either by adding hydrogen or removing CO_2, or both. By using renewable energy to electrolyse water, oxygen and steam can be added to the gasifier and the hydrogen can be added to the product from the gasifier to produce methanol with a biomass carbon conversion efficiency of over 80% for the entire crop [61]. Achieving a high level of carbon conversion efficiency is an important aspect of biofuel production due to the factors discussed in Section 4.2 below.

The synthesis of methanol or other fuels via biomass conversion using hydrogen addition requires high investment costs for the electrolysis unit but provides high production rates, together with high energy (over 50%) and carbon conversion efficiency. The cost estimates made by Specht et al. [61] are clearly dependent on the costs of the energy and biomass inputs and the capital costs of the production plant at the time of the study but simple analysis indicates that methanol made in this way would be about 50% more expensive than $65 / barrel gasoline on an equivalent-energy basis.

The gasification and gas cleaning processes involved in the approaches described above still require large scale demonstration but the methanol synthesis and methanol-to-gasoline (MTG) processes are commercially available [59]. Currently there is no commercial bio-methanol plant using gasification of biomass but some use mixed biomass and fossil-based feed stocks [58]. BioMCN have started production of bio-methanol using the glycerine by-product from the biodiesel manufacturing process [62]. Some recently developed processes for ethanol production use a combination of thermochemical (gasification) and biochemical processes to avoid the total reliance on catalysts, which are sensitive to

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[6] Gas-to-Liquids (GTL) and Coal-to-Liquids (CTL) are the equivalent fossil-based synthetic fuels produced from natural gas and coal, respectively.

poisoning, or expensive enzymes, whilst being able to process a wide range of carbon-based feed stocks [3,63].

Gasification is, however, an option for fuel production as most biomass materials can be gasified, including wood, municipal solid waste, gases, and crop residues, and the resulting gas may be used for the synthesis of liquid fuels. A large portion of the calorific value of the original biomass material leaves the gasifier in the chemical energy of the resulting carbon monoxide (CO) and hydrogen 'syn-gas' mixture.

4.2 The Biomass Limit

Biomass-based fuels are being produced today in significant amounts in the form of ethanol and biodiesel from vegetable oil methyl-esters. In 2007 global ethanol and biodiesel production was 40 million tonnes and 8 million tonnes respectively [64]. These apparently low contributions (1.5% of global transport fuels – around 34 Mtoe[7] in 2007 [65]) are nevertheless large compared with other alternative fuels. Of the 4.1 million 'alternative energy' automotive vehicles produced in 2007, 66% were flex-fuel vehicles, 16% hybrids (excluding micro hybrids), 10% CNG fuelled vehicles and 8% LPG-fuelled vehicles [64]. Because of the miscibility of ethanol and biodiesel with gasoline and diesel respectively, biofuels are currently being used in low concentration blends within the conventional infrastructure and vehicles. They are also being used to a lesser extent in high-concentration blends with slightly modified infrastructure and vehicle technology. Flex-fuel E85 / gasoline vehicles are an example of the use of high concentration biofuels in spark-ignition engines.

The presence of biofuels in the market now is driven by their potential to improve energy security and to contribute toward climate change mitigation. Their use has been mandated in the EU and US, the former at a level of 5.75% (energy-based) by 2010 [66] and then 10% by 2020 [67], 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 [68]. 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% carbon emissions saving compared with fossil fuels [69], are being introduced in the EU.

Assessments of reductions in GHG emissions compared with gasoline for biofuels, based on life cycle analysis, range from about 80% for Brazilian sugar cane ethanol to less than 10% for some US maize-based ethanol [57]. Life cycle analyses can produce extremely varied results depending on the assumptions made regarding factors such as feed stocks types and yields, management practices, how to account for co-product credits, nitrous oxide emissions from soil arising from the application of nitrogen-based fertilizer, and land-use changes. For example, ethanol produced from wheat in the UK has been assessed as providing between 10% and 80% reductions in GHG emissions [57]. Most analyses continue to indicate that first generation biofuels (based on conventional fermentative and extractive methods) show a net benefit in terms of GHG emissions reduction and energy balance [70] but recent studies have concluded that in some instances the are significantly over-estimated [71]. Other concerns expressed recently about biofuels are listed below:

- With the exception of sugar cane ethanol, they provide only limited GHG reduction benefits at a relatively high cost ($/tonne CO_2 avoided).
- They compete with food crops and may contribute to increasing food prices.
- They compete for scarce water resources in some regions.
- They may struggle to meet their claimed environmental benefits as the biomass feed stock may not be produced sustainably.
- They may promote monocultures which have a negative impact on biodiversity.
- There is insufficient land area to provide substantial security of energy supply.
- Security of supply may be vulnerable to disease or insect plagues, particularly when monocultures are used as feed stocks.

The cost of reducing GHG emissions using maize-based ethanol and biodiesel from palm oil or soya is mostly in the region of \$150-250/tonne CO_2 [57], (compared with \$40-\$150/tonne for sugar cane ethanol) and this is not expected to reduce in the short-term.

Second-generation biofuels which use ligno-cellulosic feed stocks made from agricultural and forest residues and non-food crops, as described above, ameliorate many of the concerns of first-generation biofuels. On the whole ligno-cellulosic feedstock produced from specialist energy crops will give higher energy yields per unit area of land because of their greater carbon utilization. These crops may also be grown on poorer quality marginal land. With the exception of sugar cane ethanol, this will to lead to gradual replacement of first-generation biofuels by their second-generation counterparts but this is not likely to occur to a significant degree until around 2020. Policies which mandate sustainability and environmental criteria for biofuels, in addition to setting targets for substitution levels, are beginning to materialize and these will incentivize the development of second-generation biofuels.

The issue of land utilization is key to the future development of biofuels due to pressures which will be brought about by the projected growth in world population whose food consumption patterns are increasingly land-intensive, and the increasing demand for land to cultivate industrial feedstock [72]. This increasing population also needs to be housed. In countries with high population densities biofuels are not likely to achieve substantial energy security by exploiting

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[7] Mtoe = millions of tonnes oil equivalent.

indigenous biomass resources. For example, wheat straw ethanol and rapeseed biodiesel would require approximately 45% and 40%, respectively, of the UK arable land area to supply 5% of the UK energy demand by transport in 2001 [73]. These figures reduce to between 10% and 15% of the arable land area for sugar beet ethanol and wood methanol, respectively, but they remain unviable.

In order to quantify the potential of the global biomass resource it has also become increasing clear that assessment of the fuel production process must consider any effects of land-use change. 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 [74,75]. Table 2 shows the impact of these emissions, quantified in terms of 'carbon payback' time, i.e. the time required for the production and use of the biofuels to produce a net positive saving in GHG emissions. It can be seen that the time required to produce a net benefit from some biofuel production chains can be hundreds of years.

Table 2. GHG release from land clearing and time required to re-pay the carbon debt. (Based on [74])

Fuel Chain	Assumed country of origin	Converted eco-system	GHG release / [tons/ha]	Time to re-pay carbon debt / [years]
Palm to biodiesel	Indonesia	Peat forest	3003	423
Soya to biodiesel	Brazil	Rain forest	287	319
Corn bioethanol	US	Grassland	111	93
Palm to biodiesel	Indonesia	Rainforest	611	86
Corn to bioethanol	US	Abandoned cropland	57	48
Soy to biodiesel	Brazil	Grassland	33	37
Sugar cane to bioethanol	Brazil	Cerrado woodland	165	17
Prairie grass	US	Abandoned cropland	6	1

A recent WBGU study [72] estimates the sustainable potential of biogenic wastes and residues world-wide at approximately 50 EJ[8]/year. The estimate of the global sustainable potential of energy crops has a huge spread: between 30 EJ and 120 EJ/year, depending mainly on the assumptions made regarding food security and biodiversity. The total sustainable technical potential of bioenergy in 2050 is thus projected to be between 80-170 EJ/year. This quantity of energy is around one quarter of the current global energy use (about 450 -500 EJ/year) and less than one tenth of the projected global energy use in 2050 [72]. The economically/politically realizable quantity may amount to around one half of the technically sustainable potential, and the amount of this quantity available for transport use a fraction of this number, as the use of biomass for electricity production leads to significantly lower cost and greater yield (tonne of CO_2 avoided per hectare) than its use as a transport fuel.

Currently biofuels for transport amount to only about 2.2% of all bioenergy; the vast majority (almost 90%), amounting to 47 EJ/year (around one tenth of global primary energy use) is accounted for by traditional use, burning wood, charcoal, biogenic residues, or dung on basic open-hearth fires [72]. On top of this, a well-, or field-to-tank energy conversion efficiency of about 50% applies for biomass-to-synfuel conversion [59]. Assuming that ultimately around half of the biomass energy was available for use as transport fuel gives a substitution potential of about 15 EJ/year. With the current global transport energy requirement at between 85 and 90 EJ/year, this represents a global substitution of less than 20%. Bandi and Specht [59] arrived at a level of 27% substitution globally, and 18% for the EU-27, based on transport energy consumptions (for 1999) of 70.2 and 12.0 EJ/year respectively. For Germany around 7% substitution was deemed to be possible.

It is clear that biofuels cannot substitute fossil fuels completely in the transport sector. A biomass limit exists which globally is between 20 and 30% by energy at current usage levels, and is much lower for developed countries with high population densities. Improvements in vehicle fuel efficiency (due to downsizing of powertrains, their optimization to operate on the biofuel, and low mass, low drag/rolling resistance vehicle technology) and 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 with high dependency on biofuels associated with attempting to solve the climate change problem using a technology which is dependent on the climate. Nevertheless, with appropriate sustainability criteria in place which limits the amount of fuel supplied, biofuels are capable of delivering reductions in GHG emissions immediately in a sector in which the emissions are growing and which is extremely difficult to de-carbonize.

BEYOND THE BIOMASS LIMIT – SUSTAINABLE SYNTHETIC METHANOL

Section 4 has described how ethanol and, in particular, methanol and 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, at the level imposed by the biomass limit established in the above section. In this section approaches to synthesizing alcohol and hydrocarbon fuels which are theoretically capable of supplying them in sufficient quantities to meet the entire global transport fuel demand are described.

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[8] 1 EJ = 1×10^{18} J

Biofuels result from producing oxidizable organic matter by combining carbon dioxide and water in a biogenic cycle involving photosynthesis according to equation (1). Equation (7) shows that it is possible to synthesize methanol directly from hydrogen and carbon dioxide: this can be viewed as a mechanism for liquefying chemically the hydrogen using carbon dioxide. The product 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 3. In order for the production and use of methanol in this cycle to be a carbon-neutral process, the energy inputs to the cycle must also be carbon-neutral. Thus, 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. The basic cycle shown in Fig. 3 has been proposed by a number of previous workers over a period of over 30 years [13,76-82].

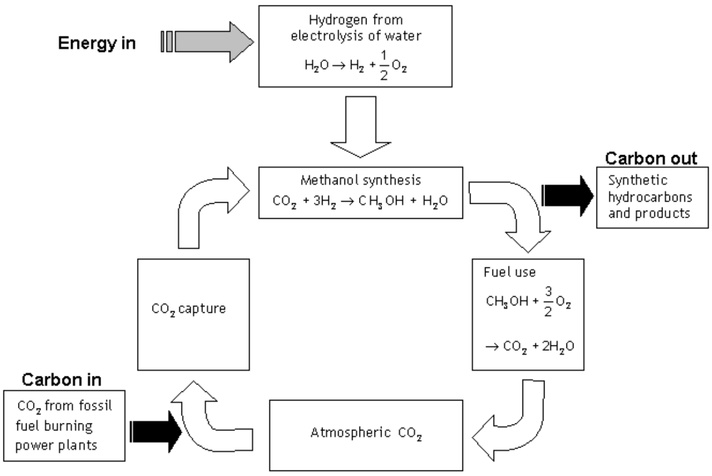


Figure 3: Cycle for sustainable methanol production and use (adapted from Olah et al. [79]).

An additional feature of the cycle is that, by synthesizing chemical feed stocks for the manufacture of plastics and paints, carbon is effectively sequestered such as to allow the continued exploitation of remaining fossil fuel reserves without causing a net accumulation of CO_2 in the atmosphere. This is facilitated by the ready manufacture of olefins from methanol - the so-called methanol-to-olefins (MTO) process [79,82].

The viability of the cycle is predicated on: 1) investment in upstream renewable energy; 2) investment in a CO_2 extraction and regeneration infrastructure. The provision of large quantities of renewable energy is a pre-requisite for any sustainable de-carbonized transport economy. 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 [83]. The extraction of CO_2 from the atmosphere is ostensibly a future technology, but there has already been a significant body of work in the area. References dating back to the 1940s exist [84] but significant interest has arisen in the last 10-15 years [77,78,85-96].

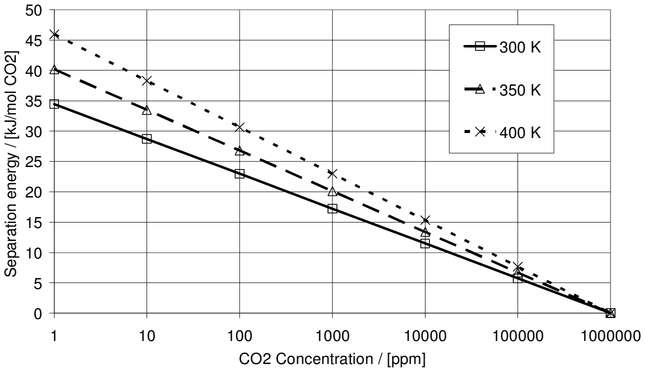
Figure 4 shows the variation of theoretical CO_2 separation energy with concentration, where the free energy for separation is given by

$$\Delta G = R_{\mathrm{mol}} T \ln\left(\frac{p_0}{p}\right). \qquad (8)$$

In equation (8) 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). The logarithmic nature of equation (8) means that the energy to separate atmospheric CO_2 is only 4 times higher than that required for flue gas separation, even though the concentration level is a factor of about 300 times lower. In fact the difference between the energy for flue gas capture and atmospheric capture is lower than the factor of 4 described above due to the requirement for flue gas capture to extract a large percentage of the CO_2 in a single pass so that the energy to capture the marginal concentrations is higher than that for the initial concentrations. Keith et al. [90] put the figure for the theoretical ratio of atmospheric capture to flue gas capture at 1.8.

Although the minimum energy of separation 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.) many of the actual values achieved in practice have been an order of magnitude higher.

Figure 4: Variation of theoretical gas separation energy with concentration.



5.1 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 [84], and NASA developed devices in the 1970s and 1980s capable of removing CO_2 from enclosed cabin air [97-103], the prospect of climate change due to increased atmospheric CO_2 concentrations has caused increased interest over the last decade into cost-effective, energy efficient, high-rate "direct air capture" technologies [77, 78,85-96].

Concentrating CO_2 from atmospheric concentrations to a stream of pure CO_2 typically involves two steps: capture and extraction. First, the atmosphere (containing CO_2 at about 387 ppm) 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 [104,105], chemical and thermal [104,106-108], or electrochemical methods [95,96,77,105], among others [105]. 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.

After first summarizing some of the approaches being pursued by other research groups, an energy-efficient electrochemical approach to CO_2 concentration being developed at the Palo Alto Research Center (PARC) [94-96] will be described.

Most approaches to CO_2 concentration that are currently being pursued accomplish the first step of CO_2 capture by contacting air with a caustic liquid capture solution in a 'wet scrubbing' technique that has been known for several decades [84,109,110]. In the specific case of a sodium hydroxide capture solution, the mechanism is initiated by the absorption of CO_2 in the sodium hydroxide in the reaction [97]

$$2\mathrm{NaOH}_{(aq)} + \mathrm{CO}_{2(g)} \rightarrow \mathrm{Na}_2\mathrm{CO}_{3(aq)} + \mathrm{H}_2\mathrm{O}_{(l)}$$

$$\Delta H^0 = -109.4\,\mathrm{kJ/mol.} \quad (9)$$

While many research groups propose spray tower capture for the first step, they differ in their approach to the subsequent extraction. Keith et al. [91] and Lackner [105] have both investigated capture via a sodium hydroxide solution, followed by regeneration of the sodium hydroxide via the 'causticization' reaction

$$\mathrm{Na}_2\mathrm{CO}_{3(aq)} + \mathrm{Ca(OH)}_{2(s)} \rightarrow 2\mathrm{NaOH}_{(aq)} + \mathrm{CaCO}_{3(s)},$$

$$\Delta H^0 = -5.3\,\mathrm{kJ/mol.} \quad (10)$$

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 CO_2 according to the following reaction

$$\mathrm{CaCO}_{3(s)} \rightarrow \mathrm{CaO}_{(s)} + \mathrm{CO}_{2(g)},$$

$$\Delta H^0 = 179.2\,\mathrm{kJ/mol.} \quad (11)$$

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

$$\mathrm{CaO}_{(s)} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Ca(OH)}_{2(s)},$$

$$\Delta H^0 = -64.5\,\mathrm{kJ/mol.} \quad (12)$$

The sodium and calcium hydroxide are recycled in two separate loops and there are CO_2 emissions associated with their initial production. Steinfeld et al. have also investigated air capture using both Ca-based [106,107] and Na-based [108] capture solutions. Keith et al. [90] and Zeman [91] give the net energy requirement for the above processes as about 350 kJ/(mol. CO_2), and indicate that there is scope for significant further improvements on this figure [104]. Lackner [105] gives a figure of '<250 kJ/(mol. CO_2)'.

Lackner is also pursuing the commercialization of atmospheric CO_2 capture technology through the company Global Research Technologies, LLC [105]. This proprietary technology captures CO_2 by binding it to the surface of an ion exchange sorbent material. Lackner lists a variety of possible regeneration techniques, including pressure swing, temperature swing, water swing (liquid or vapour), or carbonate wash plus electrodialysis [105].

Steinberg [76] and Stucki [77] have proposed combined electrolysis / electrodialysis units for the production of methanol. Stucki [77] 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

$$2\mathrm{H}_2\mathrm{O} + \mathrm{K}_2\mathrm{CO}_3 \rightarrow \mathrm{H}_2 + \frac{1}{2}\mathrm{O}_2 + 2\mathrm{KOH} + \mathrm{CO}_2 \quad (13)$$

which has identical stoichiometry when sodium is used instead of potassium.

Research into atmospheric CO_2 capture at PARC initially focused on a fuel-cell-based approach similar to the technologies investigated by NASA in the 1970s and 1980s [97-103]. While this approach was demonstrated to be energy efficient (< 400 kJ/(mol. CO_2) captured [95]), it proved to be difficult to achieve CO_2 capture at a sufficiently high rate for commercial application. For the last year, CO_2 capture research at PARC has focused on the electrodialytic technique described below.

As shown in Figure 5, this approach involves the capture of CO_2 from the air using a spray tower with KOH capture solution, followed by regeneration of the CO_2 via high-pressure electrodialysis. The goal of this research is to demonstrate energy-efficient and scalable atmospheric CO_2 capture that will enable the generation of renewable liquid hydrocarbon fuels [81,94,95]. 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 CO_2 separation from the atmosphere in a compact, reliable unit [96].

A schematic of the entire CO_2-capture unit as well as a detailed view of the electrodialytic CO_2 separator are shown in Figures 5(a) and 5(b), respectively. Using well-established techniques [111-113], air is first passed through a spray tower consisting of a counter flow of a 10 - 50% aqueous K_2CO_3 solution at ambient conditions. The capture solution, now loaded with CO_2, is then pressurized (10 - 100 atm, depending on conditions) and introduced into the bipolar membrane electrodialysis (BPMED) unit, see Figure 5(b). The bicarbonate is transferred across the anion exchange membrane to the CO_2-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 CO_2. The CO_2 is removed and fed to a reactor for the production of fuel. The now CO_2-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 CO_2, 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.

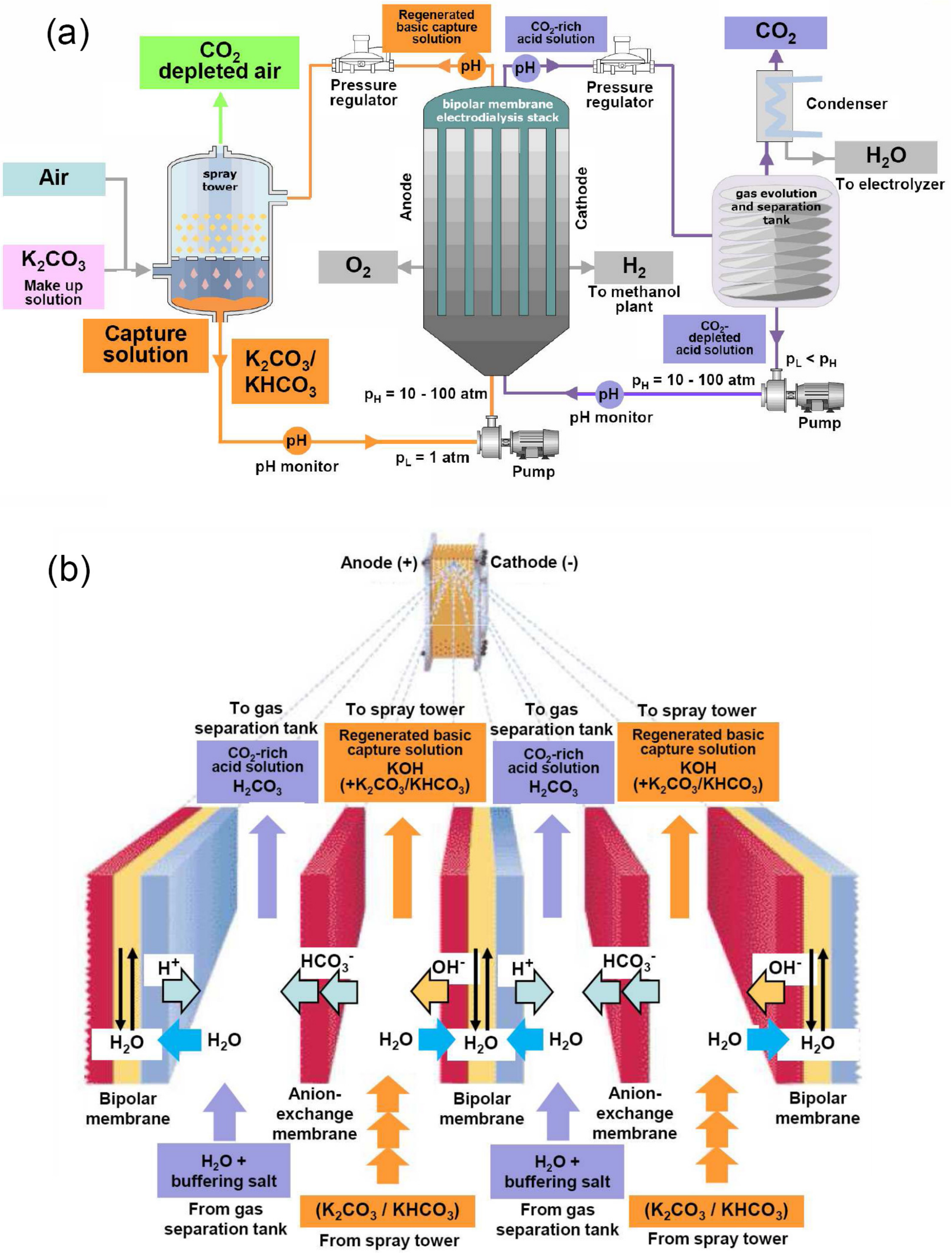


Figure 5: (a) Schematic of atmospheric CO_2 separation using a continuous-flow bipolar membrane electrodialysis (BPMED) system. (b) Detailed view of the BPMED membrane stack. See text for details. Portions of this figure courtesy of Ameridia Corp.

Constant monitoring of the pH of the acid and base streams ensures that the minimum possible electrical potential is used for electrodialysis, thereby maximizing the energy efficiency. It is ultimately envisaged that 100-cell electrodialysis stacks will be used to decrease the fractional energy requirement for H_2 (O_2) gas formation at the cathode (anode) to between 1% and 2%. In parallel to the CO_2 capture, H_2 for fuel production can be produced via electrolysis of water. The separation of the electrodialysis for CO_2 regeneration and electrolysis for H_2 production is in contrast to the approach of Stucki [77], which combines both processes into one unit. Separating the electrodialysis and electrolysis provides more flexibility to operate independently and optimize the two processes.

The technology PARC proposes to use for CO_2 concentration, namely bipolar membrane electrodialysis (BPMED), is a well-established technology for converting aqueous salt solution into acids and bases without the addition of other chemicals [114-116]. BPMED has been successfully deployed in commercial applications ranging from organic and amino acid production to hydrofluoric acid recovery since 1986 [116]. 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/cm^2. A common feature of these commercial systems, however, is that none of the input and output solutions evolve significant quantities of gas inside the membrane stack at ambient pressure. It is worth noting the success of the Soxal™ process for flue gas desulphurization, in which BPMED separates $NaHSO_3$ capture solution, formed from the capture of SO_2 flue gas, into sodium sulfite (Na_2SO_3) and partially saturated sulfurous acid (H_2SO_3). The acid is continuously withdrawn from the BPMED unit and decomposed into water and SO_2 gas in a steam stripper [117-120]. The key to the success of the Soxal™ process is that the gas is evolved from solution in a process that is physically separated from the BPMED system, a similarity to the process proposed here for CO_2 concentration. This avoids problems that occur when gas bubbles out of solution inside the BPMED membrane stack itself.

Regeneration of carbonate/bicarbonate solutions [121-126] and other gas-evolving solutions [126] 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 CO_2 recovery were observed.

PARC proposes to solve these problems associated with gas-evolving solutions by designing, constructing, and testing a BPMED system 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 will allow 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 our goal is to optimize the system for CO_2 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 as described above, we estimate that this system could extract CO_2 gas from the capture solution with an energy consumption of approximately 100-150 kJ/(mol. CO_2). This estimate does not include the energy required for spray tower operation, pumping of fluid, or compression and dehumidification of the extracted CO_2.

Experiments to investigate CO_2 concentration and pH control using ambient-pressure electrodialysis are underway at PARC. Preliminary results from these tests are presented below. Electrodialytic CO_2 concentration at ambient pressure can damage the membranes due to focused spots of high current density at the membrane due to CO_2 gas bubble evolution inside the membrane stack. To avoid this problem, all tests of CO_2 concentration performed on this ambient pressure unit were done either at high current density for very short durations, or for longer durations at low current densities.

CO_2 concentration tests have been performed on a bipolar membrane electrodialysis stack used in the same configuration as shown in Figure 5(b). The stack itself consists of 7 cells, with each membrane having an area of 200 cm^2.

Experiments were performed using K_2CO_3 (10g/l to 100g/l) as input to the base compartment, K_3PO_4 (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 (shown in Figure 6(b)) from the electrodialysis unit were compared to chromatograph analysis of bottled N_2 and CO_2, as well a sample of air (shown in Figure 6(a)). The tests with bottled N_2 and CO_2 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 N_2 peak (for this chromatograph tube, the N_2 and O_2 peaks overlap), whereas no peak is seen at the CO_2 position. For the gas captured from the output of the acid compartment of the electrodialysis stack (Figure 6(b)), a large peak at the CO_2 position (117.4 s) can be seen together with a smaller peak at the N_2/O_2 position (81.1 s). The areas under the peaks indicate that this gas is 84% CO_2 and 16% air. This residual air is likely to be the air present in the electrodialysis stack when idle. It has been observed that the fraction of CO_2 in the acid output gas increases as the electrodialysis unit is run for longer and the air that was in the stack at start-up is flushed out of the system. This comparison confirms that the gas bubbling out of solution at the acid compartment output is CO_2.

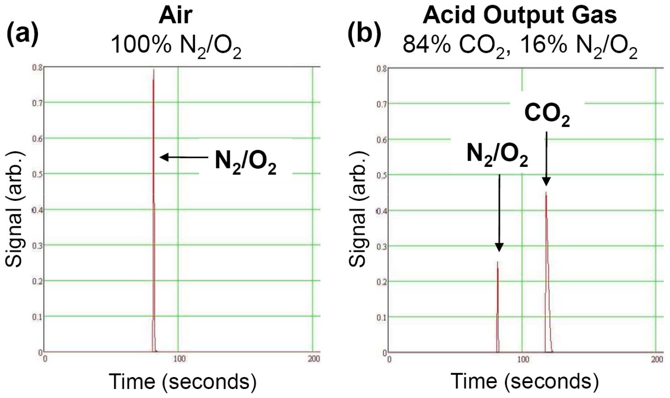


Figure 6: Gas chromatograph data. (a) Sample of air. (b) Sample taken from the gas evolving from the solution exiting the acid compartment.

5.2 Renewable Liquid Fuel from Atmospheric CO_2

In order to produce a stoichiometric mixture for methanol synthesis the hydrogen (see equation (7)) must be supplied using a separate water electrolyser. Higher heating value (HHV) efficiencies (of the stoichiometric gas mixture) for the extraction of CO_2 and the production of a stoichiometric mixture for methanol synthesis were found by Stucki to be over 60% [77]. Steinberg [76] quotes an energy requirement of CO_2 extraction from the atmosphere of about 92 kJ/mol. for a combined electrolysis / electrodialysis approach while Martin and Kubic [127] state a net energy consumption of 55 kJ/(mol. CO_2) for electrolytic stripping after accounting for the supplemental hydrogen production.

Specht et al. [78,128] show that methanol made from atmospheric CO_2 compares favourably with liquid hydrogen as a renewable transport fuel, both in terms of well-to-tank efficiency and cost of production. The lower distribution losses for methanol and absence of a physical liquefaction step offset the energy overhead of separating the CO_2.

Figure 7 shows that by far the largest component of the processes energy requirements for synthesizing methanol is that to produce the hydrogen via electrolysis. An 80% efficiency has been assumed for the electrolyser together with a CO_2 extraction energy of 250 kJ/mol. This gives a HHV 'wind-to-tank' efficiency of 46%, including accounting for multi-pass synthesis and re-compression. 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. This figure compares well with the number measured by Specht et al. [78,128] using an electrodialysis process to recover the absorbed CO_2. An increase of about 8 percentage points in the fuel synthesis efficiency is likely using CO_2 extracted from flue gas [128] and overall efficiencies which are well over 50% are thought to be possible with high temperature electrolysis. Indeed, recent improvements in solid oxide electrolyser cell technology have given electricity to hydrogen efficiencies of 95% [129].

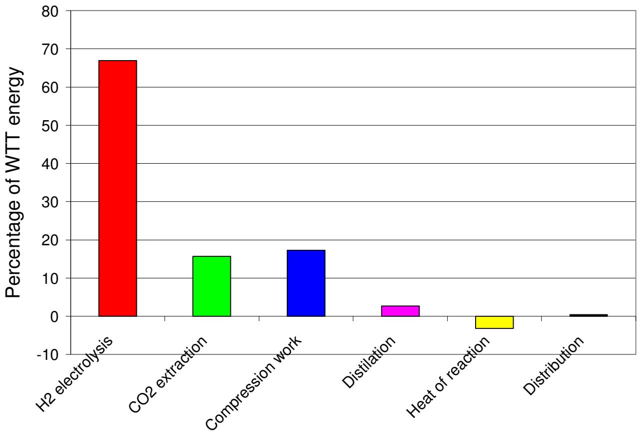


Figure 7: Breakdown of process energy requirements for synthesis of methanol from atmospheric CO_2 and renewable hydrogen.

Lackner [105] claims that large extractors of 60m x 50m dimensions would extract 3kg of CO_2 per second (90,000 tonnes/year), which copes with the emissions rate from 15000 cars; 250,000 such units could deal with all annual anthropogenic CO_2 emissions if sequestration were possible. The use of CO_2 in a closed cycle to produce carbon-neutral liquid fuels obviates the requirement to sequestrate the component of emissions from the transport sector and, since the mixing time in the atmosphere is rapid, there is no geographical concentration of feedstock, ensuring security of supply for the carbon ingredient.

It has been established that a renewable means of synthesizing a low-carbon number alcohol fuel, viz. methanol, is feasible which, with the provision of sufficient upstream renewable energy, enables the continued use of liquid fuels. This synthesized methanol would ultimately form the basis of the bulk of the transport fuel requirement, significantly exceeding the availability of properly sustainable biofuels without the supply constraints implied by the impacts of land use change and other issues discussed in Section 4. The miscibility of methanol with ethanol and gasoline supports the gradual transition toward the use of carbon-neutral liquid fuels with the only feedstock constraints being access to the atmosphere and water. The following section will discuss the ease with which the concept can be implemented on the downstream side.

TECHNOLOGIES TO EXPEDITE THE USE OF METHANOL IN THE VEHICLE FLEET

In an attempt to illustrate the ease with which vehicles capable of supporting the transition to sustainable alcohol fuels can be provided, a production vehicle was taken and modified to operate on standard 95 RON gasoline (its normal fuel), ethanol, methanol, or any combination of these fuels. This was a continuation of a previous project which sought to identify the necessary engine and vehicle modifications required to operate on E85 [32,33]. The vehicle was a Lotus Exige S, which uses a Toyota 2ZZ-GE engine fitted with a supercharger system engineered by Lotus and which uses Lotus's own engine management system. The development of electronic engine control systems over the past 30 years has now enabled practical realization of flex-fuel vehicles which can operate seamlessly on a variety of fuel mixtures. Saab and Ford have shown how the approach can work beneficially within a European architecture, with issues of cold-start addressed down to very low (-25°C) ambient temperatures [34] 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 'Lotus T4e' engine management system using the spare inputs and outputs for the alcohol sensor and the pre-compressor injectors which are specific to this application [32,33]. Starting with the E85 / gasoline flex-fuel system already developed [130], the calibration was evolved to deduce the possible range of AFRs for 'all ethanol' or 'all 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 and pre-compressor-injection duty factor were 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 and this is the route taken by Saab for their BioPower engines [34] but methanol shows a greater propensity towards this phenomenon due to the lower temperature at which it decomposes, advancing the phenomenon into the compression stroke. Fortunately, a significant reduction in the propensity to pre-ignite can be achieved by adopting spark plugs with electrodes made from non-precious metals. Replacing the standard iridium electrodes with copper-cored versions was shown to eliminate the pre-ignition issue up to 100% methanol concentration in the fuel. There were no further hardware modifications necessary.

The aim of the calibration process was to comply with Euro 4 emissions limits on any combination of the three fuels and this was achieved using the standard vehicle catalyst which was formulated primarily for operation on gasoline [131]. The tail-pipe CO_2 emissions are shown in Figure 8 - in general, as the alcohol concentration increases, so the CO_2 emissions reduce. The figure of 210 gCO_2/km represents a total energetic requirement by the vehicle of 2.84 MJ/km to complete the drive cycle. Both ethanol and methanol generate less CO_2 per unit of energy released than gasoline (4.0% and 7.5% respectively). The fuel concentration used in test 3, 88% by volume methanol, should produce 69.61gCO_2/MJ, 94% of the CO_2 emissions when operating on gasoline. The measured results of 199 gCO_2/km correlate well with this expectation. In a more heavily-downsized engine, or when applied to a heavier vehicle, the octane rating of the alcohol component, and its reduced need for component protection fuelling, could be more beneficially exploited in the drive cycle. The tailpipe CO_2 benefit of the alcohol blend over straight gasoline would then be expected to be even greater.

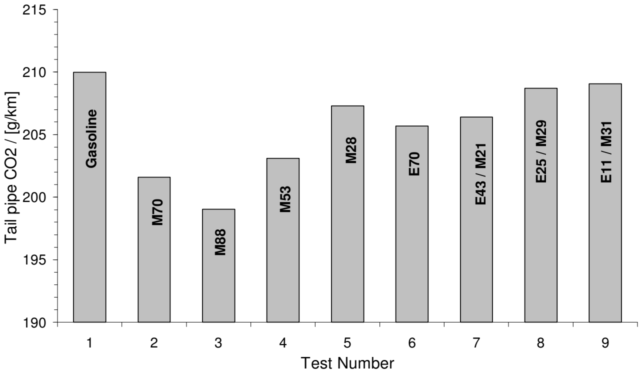


Figure 8: Tailpipe CO_2 emissions of tri-flex-fuel demonstrator vehicle when operating on various mixtures of gasoline, methanol and ethanol on the NEDC.

Figure 9: Lotus Exige 270E tri-flex-fuel demonstrator vehicle.

Using modern control technology the conversion of existing production vehicles to tri-flex-fuel operation on gasoline, ethanol and methanol is therefore straightforward and can be achieved with very low on-cost. The demonstrator vehicle is shown in Figure 9. The ability to continue to produce low-cost, globally compatible vehicles with very low well-to-wheel GHG emissions, for the mass-market, helps ensure the survival of the vehicle manufacturers and secures fuel demand from the fuel / energy providers. From the customer perspective the low 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 life.

6.1 Using Methanol to Extend the Displacement of Gasoline by Ethanol

In addition to the concept of introducing a tri-flex-fuel vehicle as a means of operating vehicles on any combination of the two alcohols and gasoline, it may be possible to introduce methanol in a far more pragmatic manner more quickly and thus accelerate the displacement of fossil energy. 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.

Methanol can be introduced now into gasoline due to standards such as the 'DuPont Waiver' [45,132]. Ethanol is listed as one of the co-solvents required to comply with these standards. However, the resulting mixture is still predominantly a gasoline-based fuel and would thus be suitable for gasoline cars operating at a normal gasoline AFR in the region of 14.7:1.

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 for these cars which the US Energy Independence and Security Act has mandated [68]. 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 and the issues of land usage change, it is desirable to find means of extending the amount of renewable fuel that can be introduced in the short-term. Many vehicles are in the field at the moment which can utilize alcohol fuels and the number is increasing continuously: about 2.7 million of these vehicles were sold world-wide in 2007. The authors have noted that 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 into the 'E85' to produce a 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.

It is intended to describe this concept more fully in a further publication, but an example calculation is included here for illustrative purposes. The tool used for the calculation was the Lotus Fuel Properties Calculator [133]; the fuel properties used in this analysis are listed in Table 3. From the data different blend proportions to achieve the same AFR can be calculated. The results of some of these calculations are given in Table 4.

Table 3: Values used in the AFR calculations.

Fuel Component	Stochiometric AFR (:1)	Gravimetric LHV (MJ/kg)	Density (kg/l)	Molecular Mass (-)
Gasoline	14.53	42.7	0.736	114.6
Ethanol	8.60	26.8	0.789	46
Methanol	6.44	19.9	0.791	32

Table 4: Ternary mixtures of ethanol, gasoline and methanol to yield the same stoichiometric AFR as 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 4 is termed E42.5 G28.8 M28.7 to correspond to the volume fraction of the major blend components in volumetric terms. 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 while, for this ternary blend, the extra 0.675 litres of methanol supplied enables the 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.

Methanol can be made from a wider range of feed stocks more easily using biomass gasification and there is currently significant excess capacity of fossil methanol – these factors could provide the incentive to make available blends such as that described above in order to displace more gasoline and potentially improve the security of energy supply in the transport sector. The ability to do this simply will depend on a variety of other factors and it is intended to discuss more fully the potential of the approach in much more detail in a later publication. The important consideration making this a desirable avenue of investigation is that CAFÉ regulations have given rise to a situation where there are currently significantly more alcohol-compliant vehicles on US roads than can be supplied with renewable fuel, and so introduction of any suitable ternary blend will not be limited by vehicle availability. If the methanol used in the blends is also cheaper on an energetic basis than gasoline, the blends should also be cheaper in the market place, providing a significant consumer pull. The ethanol and methanol lobbies would then have a significant inducement to work together, since both would benefit from the approach. Later publications will consider all of these factors.

A COMPLETE SOLUTION – SUSTAINABLE ORGANIC FUELS FOR TRANSPORT

In the near-term security of energy supply and climate change are driving consideration of alternatives to fossil-based fuels while, in the longer term, sustainability is the motivation. Section 4 established that while biofuels are currently part of the transport fuel mix and, under the correct conditions, can make positive contributions to reducing greenhouse gas emissions and improving security of supply, they are limited in the extent to which they can achieve these goals. Biofuels can thus be part of a complete solution but they cannot supply transport energy in full amounts, necessitating the use of renewable energy to generate hydrogen which is chemically liquefied by combining it with a CO_2 molecule to produce a carbon-neutral liquid fuel.

A lack of global consensus for fuelling transport would lead to the development of vehicle designs which were specific to particular geographic regions and create difficulties when vehicles moved between regions. The question of whether full provision for all types of transport can be ensured also arises. Some suggested alternatives, for example electrification, might suit a portion of the light-duty transport fleet but cannot realistically form the basis for heavy-duty land transport[9], marine or air transport. It is also extremely unlikely that the latter transport mode will be fuelled by molecular hydrogen and clear that electric vehicles are not feasible for use in remote regions with no grid infrastructure. The high energy density of methanol and ethanol relative to non-liquid 'fuel' alternatives makes them suitable for use in light-duty land transport. 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% [59]) and a significant increase in plant cost.

Bandi and Specht [59] and Biedermann et al. [60] describe processes for the Fischer-Tropsch (FT) synthesis of gasoline and diesel from both CO and CO_2 with hydrogen; they also give details of the Methanol-to-Gasoline (MTG) and Methanol-to-Synfuels (MtSynfuels) processes. In the MTG process the methanol is first converted to DME from which light olefins are produced which eventually convert to heavier olefins, paraffins, and aromatics. A 14000-barrel-per-day MTG plant, using technology developed by Exxon Mobil, was built in New Zealand in the early 1980s. The MtSynfuels process was developed by Lurgi and 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 and plants synthesizing methanol from atmospheric CO_2 and renewable hydrogen. 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. It is estimated that the MtSynfuels process is 10% more efficient and requires 10% lower investment costs than a conventional FT plant. Both processes produce fuel of very high quality and provide high versatility for a future transport energy economy underpinned by the synthesis of methanol from atmospheric CO_2. Steinberg [76], Martin and Kubic [127], and Zeman and Keith [81] all propose synthesis of hydrocarbon fuels in this way. In the present work it is proposed only to use the additional synthesis step, with its concomitant energy penalty, to supply the applications requiring the highest on-board energy storage densities possible. It has been established above that low-carbon-number alcohols are superior fuels for internal combustion engines and that their use implies minimal on-cost for new vehicles. It is thus contended here that it is expedient to use methanol in automotive and light-duty transport applications with spark-ignition powertrains, where it can be phased in via the technology described in Section 6, and eventually used in optimized engines with high compression ratios, achieving considerable efficiency improvements over existing gasoline engines. Methanol and ethanol can be phased in as fuels for compression-ignition engines using the technology described in Section 3.3 where relatively small engine modifications are required. Depending on how high the thermal efficiency of spark-ignition engines using methanol with high EGR rates can be raised, it may be expedient to transition toward gradual replacement of CI engines with high efficiency methanol SI engines. In any case, for applications requiring the highest fuel energy density, diesel and kerosene can be synthesized as carbon-neutral liquid fuels at an upstream energy penalty of about 10%.

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 organic*[10] *fuels for transportation*. Figure 7 shows that the energy requirements for the production of these fuels are dominated by the renewable hydrogen requirements and the fuel costs would likewise be dominated (70-80% for methanol) by the costs of making the hydrogen. In this context it should be noted that there is no intrinsically expensive material in the CO_2 extraction and methanol synthesis plant.

Biedermann et al. [60], Aldewereld et al. [134], and Olah et al. [79,82] all point out the synergies possible from the adoption of methanol as the basis of the transport energy economy and its diverse applicability as a base feedstock for the petrochemical industry.

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[9] With the obvious exception of vehicles with predefined paths, e.g. trains, to which the electricity can be supplied externally.

[10] Organic meaning 'carbon containing'.

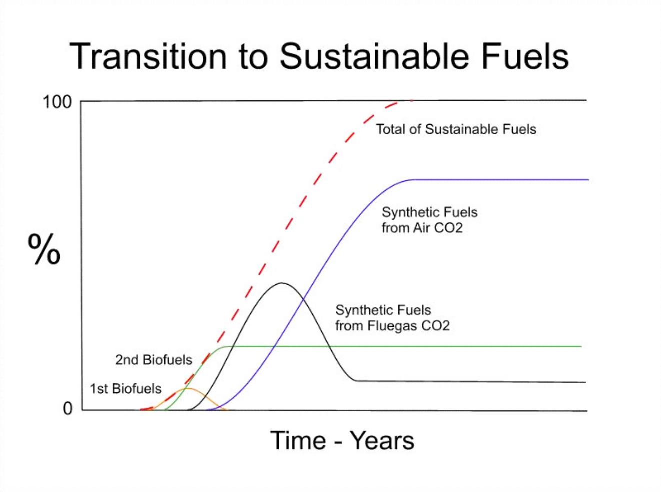

Figure 10: Schematic of possible fuel transition. (Courtesy Gordon Taylor)

Figure 10 shows how the transition to sustainable organic fuels might occur; the dynamics will clearly differ between countries depending on factors such as their state of development, geographical location and population density. 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 between, say, 10-30%. The remaining fuel demand would be provided by synthetic fuel production from atmospheric CO_2 capture and flue gas capture of CO_2 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 adopt or continue with first generation biofuels, the production facilities for which can be developed at relatively low cost to diversify the use of their produce and, where local fuel demand is exceeded, may provide opportunities for export. It is more expedient to export liquid fuels than 'raw' biomass.

A schematic of a CHP+F plant is shown in Figure 11 where the ratio of coal to biomass is dictated by the desired overall CO_2 saving and feedstock availability. The process integration could provide low temperature reject heat for district heating networks in buildings and industrial processes. In addition to the CO_2 capture apparatus, such a plant would house the electrolysers producing hydrogen from low-cost 'surplus' wind electricity. The electricity input and fuel production could be distributed between CHP+F plants to suit their local heat loads.

The ultimate 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 in the system. The current global transport fuel demand is between 85EJ and 90EJ per annum. The upper bound figure represents an average power consumption of 2.85TW – this compares with the world electricity generation in 2006 of 2.06TW [135]. Specht et al. [78] showed that methanol synthesized from atmospheric CO_2 and electrolytic hydrogen requires a slightly lower level of upstream renewable energy than liquid hydrogen when both fuels are used in internal combustion engines. 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, clearly a huge requirement. Although the global wind resource at turbine heights of 72TW [136] may be capable of providing this power in the long term, clearly synergies and process integration such as the CHP+F plant with district heating shown in Figure 11 may be necessary to maximize the efficiency of energy utilization. Fuel synthesis plants using electrolysers may be a practical way to store 'stranded' wind energy in remote locations where installation of an electricity grid is not economic. Such plants would provide ideal interruptible loads for wind turbines, obviating the problem of the intermittent nature of wind energy.

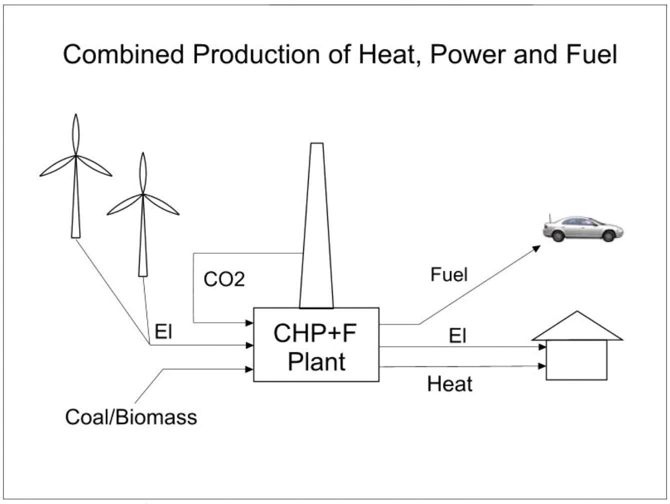

Figure 11: Schematic of combined heat, power, and fuel plant. (Courtesy Gordon Taylor)

Reductions in upstream 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, as described in Section 2. Additionally, full life-cycle analysis of energy requirements have shown that the life-cycle CO_2 emissions for BEVs and HFCVs can be higher, under some operating conditions, than even vehicles powered by gasoline-fuelled internal combustion engines due to the higher emissions in the vehicle production process [19,20]. Initial work by the authors indicated that these high embedded GHG emissions for BEVs and HFCVs translate in to high embedded energy costs which give a substantial overhead to accommodate the construction of the upstream energy supply of carbon-neutral liquid fuels.

The precedents of the large-scale fleet trials conducted in the California and Canada in the 1970s, 1980s and 1990s [24,137-139] show that the implementation of methanol as an automotive fuel is feasible. From the mid-1980s to the late 1990s over 15,000 methanol flex-fuel vehicles were used in California, along with hundreds of methanol-fueled transit and school buses. Over 12 million gallons of methanol were used as transport fuel in the state at the height of the programme in 1993, dispensed at 105 fuel stations which were converted at low cost [139]. A series of initiatives led to the demonstration of 18 different models of methanol-fuelled cars from a dozen US, European, and Asian manufacturers, four of which were produced commercially, including the Ford Taurus which was produced between 1993 and 1998 [140] in both methanol (M85) and ethanol (E85) / gasoline flex-fuel versions. Methanol-fuelled heavy-duty vehicles were demonstrated by many major OEMs for applications such as refuse trucks, dump trucks, school and transit buses, and haulage and delivery trucks, using ignition-improved fuel or spark-assisted ignition [24] described in Section 3.3.

Since 1975, with its National Alcohol Program, Brazil has promoted ethanol made from sugar cane as a fuel. After some severe fluctuations in penetration following those of the oil price the fuel is now well established, to the extent that ‘pure’ gasoline is no longer available as a fuel, the base blend varying between 20% and 25%, depending on the sugar cane harvest. The development of flex-fuel vehicles in the early 1990s has allowed the expansion of ethanol use so that it provided over 50% by volume of the market share of fuel for the gasoline-powered fleet. In 2007 1.72 million passenger cars with flex-fuel capability were manufactured in Brazil (from a total of 2.39 million, including exports).

Outside Brazil several other countries, notably the USA and Sweden, have built up substantial ethanol-gasoline flex-fuel vehicle (FFV) fleets, and fuel production is set to grow, supported by legislation and initiatives (e.g. [66-68]). Many FFVs have been recently developed (eg. [141,142]), some of which offer substantial performance improvements over the equivalent gasoline-fuelled model, particularly in turbocharged form [34,143]. The benefits of low-carbon number alcohol fuels in spark-ignition engines are described in Section 3. GM has over 4 million flex-fuel E100/E85 vehicles in service currently [144] and have pledged that half its model range will be FFVs by 2012; Renault are aiming to achieve a similar target by the end of 2009.

In the heavy-duty field SEKAB is supplying renewable ethanol-based fuel designated ‘E95’ for use in compression ignition engines [145]. In this case, instead of being mixed with 5% gasoline, the 95% ethanol is mixed with 5% ‘ignition improver’. Since 1989 Scania has built around 600 ethanol-fuelled city buses which operate in Swedish cities [146]. The latest engines give 43% peak thermal efficiency compared with 44% for their diesel-fuelled counterparts and meet Euro 5 emissions legislation. Such engines have been demonstrated in fleet trial in Brazil [147], and the technology has been extended to passenger cars with CI-engines [148].

The presence of ethanol-fuelled vehicles in the market in significant numbers (in the case of vehicles with spark-ignition engines), 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 CO_2 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 CO_2 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.

Methanol is currently made in quantities of around 50×10^9 litres a year (compared with gasoline and diesel at about 1.25×10^{12} litres and 1.1×10^{12} litres a year, respectively [149]) as a chemical feedstock, mainly from natural gas and coal, with considerable potential to increase production in the near term. China is now exploiting its abundant coal deposits (it is the world’s largest producer and consumer of coal) and is now the world’s largest producer of methanol [150]. In 2007 China imported 47% of its oil; it is keen to reduce this external dependency but has banned the use of grain for ethanol production in order to ensure food supplies and so has declared coal-based methanol to be a strategic transportation fuel [150]. The wholesale price of methanol in China is about one third that of gasoline making it cheaper per unit energy contained in the fuel. About 3.4×10^9 litres of methanol was blended in gasoline in 2007 [150,151] and many indigenous manufacturers are developing methanol FFVs. National standards for high proportion and low proportion methanol fuels are being put in place and local standards are proliferating [152]. In Shanxi province there are over 2000 M100 taxis and around 400 city buses; 770 methanol fuel stations have been set up [152]. A 100,000 tonne per year methanol-to-gasoline demonstrator plant is being built in this province which will be in service in 2009. The methanol derivative, DME, is also being considered as a diesel substitute; the city of Shanghai had 90 DME buses in operation in 2008 and plans to have 1000 such vehicles running in the city by 2010.

The rapid implementation of methanol as a transport fuel in China demonstrates the ease with which the technology can be applied, the low cost of the vehicles in which the fuel is used, and the low cost of the fuel distribution infrastructure. Unfortunately methanol produced from coal can generate about 2.3 times as much well-to-wheel GHG emissions as gasoline, as shown in Figure 12, whereas the GHG emissions from methanol via natural gas are shown to be 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 atmospheric

CO_2 and renewable hydrogen are extremely low due to the recycling of carbon in the production and use processes [59], making this a pathway to an essentially carbon-neutral liquid fuel.

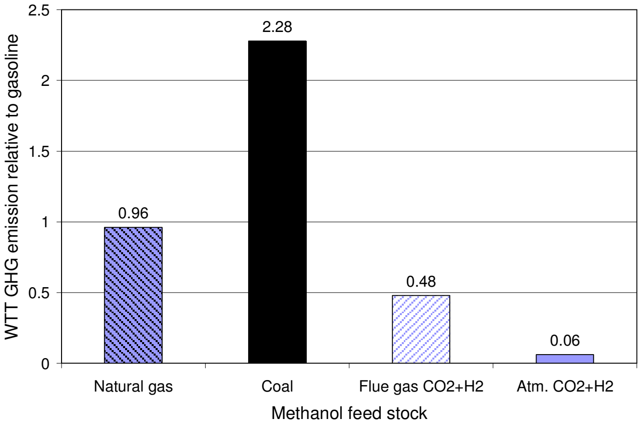

Figure 12: Well-to-wheel GHG emissions (mass-based) for methanol made from different feed stocks relative to gasoline base (=1). Adapted from Bandi and Specht [59].

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. Although the superior tank-to-wheel efficiency of BEVs and, to a lesser extent, HFCVs give notional benefits in minimizing the demand on upstream renewable energy required to decarbonize transport there is also evidence that the life-cycle energy requirements and GHG emissions for these vehicles are very substantially higher - this area is deserving of considerable further study as it is often acknowledged as being potentially of high importance but then excluded from analysis due to lack of data.

The production of sustainable organic liquid fuels for transport 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 and low embedded manufacturing and materials extraction energies. They would be globally compatible due to the ability to supply the fuels in full amounts and make them from widely available feed stocks. They also have considerable potential for further improvement in efficiency. The technology to enable the evolution, not revolution, from the current vehicle fleet to equivalent-cost vehicles capable of using closed carbon cycle fuels has been described in the form of either tri-flex-fuel vehicles capable of running on any combination of gasoline, ethanol, or methanol, or flex-fuel vehicles which can run on pre-blended mixtures of these three fuels. In this way, together with the ability to transcend the biomass limit for biofuels, the technologies proposed can be seen as extending the supply of alcohol fuels. The technology path described avoids leaving vast stranded assets in the automobile industry.

Sustainable organic liquid fuels, comprising low-carbon number alcohols for personal mobility and synthetic hydrocarbons for applications where maximum energy density is crucial, can be supplied from the biosphere up to the biomass limit for each country from biofuels, and beyond the biomass limit from the atmosphere and the oceans using captured CO_2 and hydrogen electrolysed from water. Producing liquid fuels from renewable electricity provides an excellent storage buffer against the intermittency of the energy source and potentially offers a route to ‘shipping’ renewable energy from remote locations which lack grid infrastructure. Significant and exciting progress is being made in the development of low energy, durable CO_2 extraction and concentration technologies which will enable the efficiency of synthetic fuel production to be maximized.

The approach of manufacturing synthetic liquid fuels can be thought of a pragmatic implementation of the hydrogen economy where the hydrogen is effectively liquefied chemically using carbon dioxide or, in the manufacture of hydrocarbon fuels, carbon monoxide. Methanol is the simplest molecule in which the benefits of the high carbon-hydrogen bond energy are manifested in an energy carrier which is a liquid over a wide range of ambient temperatures and pressures. The cost of the atmospheric CO_2 extraction infrastructure required to produce sustainable organic fuels for transport is off-set against the costs necessary to develop a hydrogen fuelling infrastructure. The development of a CO_2 extraction infrastructure also results in a much more powerful tool than simply replacing one fuel distribution infrastructure with another as, with sufficient capacity and the addition of sequestration, it could provide the ability to regulate the CO_2 level in the atmosphere and thereby extend the use of fossil-based fuel feed stocks where they remain economically exploitable.

It is clear that in order to decarbonize transport the GHG intensity of the energy carrier must be addressed, even at target levels of 60-80% GHG reduction. Focusing efforts on tank-to-wheel efficiencies of vehicles is not sufficient. Whilst the importance of well-to-wheel analysis is widely recognized (notwithstanding full life-cycle analysis) targets and fiscal penalties in many regions continue to be based on tailpipe CO_2 emissions. A more rational resolution of the CO_2 emissions total is suggested as a precursor to full life-cycle analysis. Setting vehicle targets in terms of MJ/km and fuel / energy carrier targets in terms of non-renewable gCO_2/MJ inherent in the fuel resolves the tank-to-wheel and well-to-tank emissions so that the legislators for, and originators of, each contribution can focus more effectively on each issue (related concepts are discussed in ref. [153]). This makes vehicle manufacturers responsible for a target over which they have direct control, i.e. producing affordable energy-efficient vehicles which have low pollutant emissions, and puts the responsibility of decarbonizing the fuel/energy carrier on the historically profitable fuel/energy supply business. It is posited that this would therefore accelerate the development of closed-carbon fuel systems.

ACKNOWLEDGMENTS

Anthony Peck of Lotus Engineering carried out the engine calibration work on the Exige 270E tri-flex-fuel vehicle. Many of the ideas developed in this paper have benefited greatly from discussions with Gordon Taylor of GT Systems who has also provided figures as indicated in the captions. 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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ABBREVIATIONS

AFR	air:fuel ratio
atm	atmosphere
BEV	battery electric vehicle
BTL	biomass-to-liquids
CHP+F	combined heat and power plus fuel
CNG	compressed natural gas
CTL	coal-to-liquids
DME	dimethyl ether
EXX	blend of XX% by volume of ethanol in gasoline
EU	European Union
FFV	flex-fuel vehicle
GHG	greenhouse gas
GTL	gas-to-liquids
HFCV	hydrogen fuel cell vehicle
ICE	internal combustion engine
MTG	methanol-to-gasoline
Mtoe	million tonnes of oil equivalent
MtSynfuels	methanol-to-synfuels
MXX	blend of XX% by volume of methanol in gasoline
OPEC	organization of petroleum exporting countries
RON	research octane number
SNG	synthetic natural gas

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