

Energy Storage Via Carbon-Neutral Fuels Made From CO₂, Water, and Renewable Energy

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Abstract—Fossil fuels are renewable only over geological time scales. The oxidation, via combustion, of considerable amounts of carbonaceous fuels since the dawn of the industrial revolution has led to a rapid accumulation of CO₂ in the atmosphere leading to an anthropogenic influence on the Earth's climate. We highlight here that a versatile energy carrier can be produced by re-cycling CO₂ and combining it chemically with a substance of high chemical bond energy created from renewable energy. If CO₂ is taken from the atmosphere a closed-loop production process for carbon-neutral fuels is possible providing an energy-dense and easily distributed storage medium for renewable energy.

The rationale for reduced carbon or carbon-neutral energy carriers made from re-cycled CO₂ is described, focussing on, for transport applications, their manifestation as energy-dense carbonaceous liquid fuels. Techniques for the separation of CO₂ directly from the atmosphere are reviewed, and the challenges and advantages relative to flue-gas capture are discussed. Pathways for the production of carbonaceous fuels from CO₂ are discussed. An integrated system is proposed where renewable energy is stored in the form of synthetic methane in the gas

grid for supply to the power generation and heat sectors while methanol and drop-in hydrocarbon fuels are supplied to the transport sector.

The use of atmospheric CO₂ and water as feed stocks for renewable energy carriers raises the important prospect of alleviating a dependency on imported fossil energy with the associated large financial transfers. Their application in the transport sector yields a high-value end product. The synthesis and storage of carbon-neutral liquid fuels offers the possibility of decarbonising transport without the paradigm shifts required by either electrification of the vehicle fleet or conversion to a hydrogen economy. They can be supplied either as drop-in hydrocarbon fuels for existing reciprocating and turbine-powered combustion engines or, at lower energetic cost and using simpler chemical plant, in the form of low-carbon-number alcohols which can be burnt at high efficiency levels in optimized internal combustion engines. The suitability of these fuels for conventional engines enables the continued provision of globally compatible, affordable vehicles.

Index Terms—BPMED, CO₂, electrofuel, fuel, internal combustion engine, methane, methanol, transport.

Nomenclature—

AEM	anion exchange membrane
AFR	air:fuel ratio (by mass)
BEV	battery electric vehicle
BPM	bipolar membrane
BPMED	bipolar membrane electro dialysis
CNG	compressed natural gas
DME	dimethyl ether
EREV	extended range electric vehicle
EU	European Union
EXX	blend of XX% by volume of ethanol in gasoline
FC	fuel cell
FFV	flex-fuel vehicle
FT	Fischer-Tropsch
G	Gibbs free energy
GEM	gasoline, ethanol, and methanol
GHG	greenhouse gas
HHV	higher heating value
ICE	internal combustion engine

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LCOE	levelized cost of energy
LHV	lower heating value
LNG	liquefied natural gas
LPG	liquefied petroleum gas
MTG	methanol-to-gasoline
MtSynfuels	methanol-to-synfuels
MXX	blend of XX% by volume of methanol in gasoline
\dot{N}	molar flow rate
NEDC	New European Drive Cycle
ppm	parts per million
PHEV	plug-in hybrid electric vehicle
PEM	polymer electrolyte membrane
RON	research octane number
S	entropy
SoC	state of charge
SOFT	Sustainable Organic Fuels for Transport
T	temperature
TTW	tank-to-wheel
\dot{W}	power
WTT	well (wind)-to-tank
WTW	well (wind)-to-wheel
x	mole fraction
ZEV	zero emission vehicle

I. INTRODUCTION

Tidal and geothermal energy, together with solar energy in its various manifestations, including heat, photoelectric, wind, and wave energy, are the only true primary resources on Earth. Fossil fuels are naturally occurring energy carriers and as such are regarded as the corresponding primary energy resources. One can regard such resources as simply solar energy stores in the form of carbon sinks created over geological time scales. The rate of mining and combustion of these energy stores has been extremely rapid compared with their rate of natural replenishment and this is causing a significant accumulation of CO₂ in the atmosphere. There is now consensus that this CO₂ accumulation is causing an anthropogenic influence on the climate of the Earth [1].

The continual depletion of fossil fuel reserves, the burgeoning human population, which increased by a factor of 6 during the 20th Century, and the rapid growth in energy consumption per capita, which increased by a factor of over 13 during the 20th Century [2], is now gradually conspiring to create a disturbing supply – demand discrepancy which favours a serious consideration of the economics of harvesting renewable energy and feed stocks.

The escalation of fossil fuel prices [3] has been accelerated, for oil in particular, by the reduced geographical diversity of reserves. Up to the early 1970s Western investor-owned oil companies controlled -

directly or indirectly - almost all of the world's oil production and reserves. In 2006 companies owned or claimed by their national governments controlled 80% of global oil reserves, with a further 14% controlled by Russian companies and joint ventures between Western and national oil companies. Western investor-owned companies controlled only the remaining 6% outright [4]. The trading of oil currently transfers vast quantities of wealth from countries with high consumption-to-reserves ratios to those with comparatively low ratios. With prices averaging close to \$100/barrel over the year in 2008 both the EU and the US each paid approximately 450×10^9 to import oil [5]. The rapidly growing economies of China and India are also heavily dependent on imported oil and, in particular the former, will begin to incur costs of a similar magnitude in the medium term. Conversely the 13 countries comprising OPEC in 2008 collectively received approximately 1×10^{12} [5]. This lack of control over feed stock supply and prices has led to legislation such as the recent US Energy Independence and Security Act, mandating increased supply of alcohol fuels [6].

Increasing the amount of renewable energy has the combined benefits of reducing the accumulation of CO₂ in the atmosphere whilst also improving energy independence through the use of sustainable resources. The use of large amounts of renewable energy in transport requires either the expansion of the biofuels industry or the removal of significant technical and economic obstacles preventing widespread adoption of electric or hydrogen fuel cell vehicles. These are discussed in Section III.

Overall there has been a gradual shift toward deliberately reducing the fossil carbon-intensity of the energy used by mankind. As the use of alternative energy carriers has evolved historically the average hydrogen / carbon (H/C) ratios have increased from 0.1 for wood, to 1 for coal, to about 1.8 for the refined crude oil products gasoline and diesel, and to 4 for methane. The introduction of renewable energy brings a potentially carbon-free (infinite H/C ratio) resource into the mix, usually in the form of electricity, but the intermittent nature of almost all renewable energy sources and the independently varying consumer demand necessitates viable storage options.

II. STORAGE OPTIONS

Prime on-shore wind energy is claimed to be cost competitive with coal, with a levelized cost of energy (LCOE) as low as \$45/MWhr [7] in areas of high wind penetration in the US. Over the past 15 years wind energy has sustained a global growth rate of 22%/yr, however future growth is likely to be constrained by the increased difficulties of dealing with off-peak energy generation. Deployment of large-scale energy storage systems could

ameliorate the situation by enabling the transfer of abundant low-value off-peak energy to markets and sectors where demand is strong and the value of the energy is permanently high [7].

Doty [8] points out that, in the US, the proportion of 'clean' (reduced- or zero-carbon) energy on the grid in off-peak times can be over 90% compared with around 25% at peak times, thus limiting the impact of high cycle storage options such as flywheels, lithium ion batteries, and ultracapacitors. Storage times of 12 hours or more are required for significant impact on greenhouse gas (GHG) emissions and load shifting. Most conventional energy storage approaches have limited economic viability for the purposes of progressing wind energy penetration [8] – the necessity to bridge perhaps two week periods of low or absent wind speeds requires large long-term storage options. It is not the purpose of this paper to review all such options – other contributions to this volume will cover some of the alternatives. Remarks will be made here on batteries however, since they are relevant to the discussion in the following section.

For dedicated grid storage applications, carbon-lead-acid or conventional lead-acid batteries may have significant potential due to their relatively low cost [9]. Advanced batteries developed for automotive applications are likely to prove too expensive since, for dedicated immobile grid storage, their relatively high gravimetric and volumetric energy storage densities (see Section III) which are crucial for transport applications have limited value for immobile storage options. The batteries of vehicles carrying all (BEVs) or a substantial proportion (EREVs/PHEVs) of their energy in the form of electricity could potentially offer a form of grid storage while they are stationary [10]. These so-called 'vehicle-to-grid' schemes will have to surmount significant practical and logistical barriers in addition to offering only a short-period storage solution. A recent projection by an independent automotive analyst estimated the fraction of new car sales in the US by 2020 represented by BEVs as 0.6% (about 110000 vehicles) [11]¹. If the average battery capacity of these vehicles is 24 kWh and the maximum battery depth of discharge is 75% (including reserve for regenerative braking) then this number of vehicles (sold in this single year) offers a potential storage reservoir of about 1.6 GWh (including discharge losses). A similar number of PHEVs makes a much smaller additional contribution of about 0.44 GWh due to their smaller batteries and lower depth of discharge (to ensure acceptable battery life with the higher rate of cycling encountered by EREVs in service).

¹ The main barrier to increased BEV and PHEV sales was deemed to be high battery cost – see Section III.

In fact grid operators require a minimum power supply capability of about 1 MW in the US. Clearly a contract will not be formed with the owner of individual vehicles. Coalitions requiring the simultaneous availability of about 350 vehicles will be required at 3 kW discharge rates or about 50 vehicles using 240V/80A power lines [10], so in practice the realistic storage capacity is significantly lower than the values given above. The monitoring and co-ordination of individual vehicles within such a coalition will be a formidable task, as indeed will be the formation of the coalitions themselves [10]. The potential impact of additional charge cycling on the life of the most expensive component in the vehicle (see Section III) may compromise the financial rewards of coalition membership to the vehicle owner, especially at high rates of discharge. Additionally, the simultaneous energy demand of the owner needing to use the vehicle to get to their place of work or transport children to school just as the grid demand ramps up may limit the amount of available vehicles (or require very large coalitions).

A simpler option, once the off-peak electricity is on-board the vehicle, is simply to use it for vehicle propulsion without the complication of selling it back to the grid. This does not directly assist with the grid storage problem but if the energy can be sold at a higher value in the transport sector it can finance the further expansion of renewable generating capacity and the inter-connection of resources distributed over a wide geographical area. Currently, however, there are no schemes which charge a premium for electricity used in transport applications and the demand may be constrained by the limited number of vehicles in the fleet [11].

Chemical energy storage systems, based on the conversion of renewable energy into a liquid or gaseous energy carrier, enable the stored energy to be either re-used for power generation or transferred to other energy sectors such as transport, where the de-carbonization issue is more problematic, and there is an ever-present demand to supply a high-value energy carrier. In the case of liquid fuels the vehicle demand is already in place.

In principle the use of hydrogen for this purpose preserves the carbon-free nature of the renewable energy² in the supply and use chain. Unfortunately, in practice, its low volumetric energy density combined with the technical difficulties in providing a safe, low loss, energy-efficient infrastructure at an acceptable cost are major challenges and limit the appeal of hydrogen as an energy vector [12]. Minz et al. [13] estimated the cost of providing a hydrogen infrastructure in the USA capable of re-fuelling 100 million fuel cell vehicles (40% of the US light duty vehicle fleet) as up to $\$650 \times 10^9$. Moreover, in

² Note that hydrogen can only serve as an energy carrier as its reactivity ensures that it is not found naturally on Earth in significant quantities in its molecular state.

the transition period to a hydrogen-based energy economy, a dual infrastructure must be maintained and vehicles with two incompatible fuel systems must be produced (assuming a dual fuel gasoline-hydrogen internal combustion engine). In addition the use of hydrogen (or electricity) directly in the transport sector implies significant increases in vehicle cost above current levels: this will be discussed in Section III. There is currently negligible vehicle demand for molecular hydrogen as a fuel in the transport sector.

In this paper an alternative approach is described in which the renewable energy is first stored in hydrogen via the electrolysis of water but then, for an additional small energy penalty, this hydrogen is reacted with CO₂ to form an infrastructure-compatible hydrocarbon fuel. In this way hydrogen is used *in* the fuel rather than *as* the fuel. Importantly, if all processes are powered with carbon-free energy and the CO₂ used to make the fuel is captured directly from the atmosphere, then the combustion of this fuel would result in zero net increase in the atmospheric CO₂ concentration.

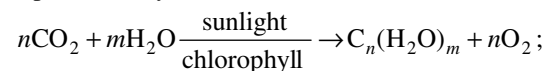
Methane can be made in this way using surplus renewable energy and fed into the gas grid producing a large buffer with essentially no time limits for storage using existing infrastructure in developed countries. This concept, which integrates the gas and electricity grids, is called Renewable Power Methane by Sterner [14] and is utilized in the scheme proposed in Section VI. For example, the combined existing storage and pipeline capacity of the German natural gas network is about 200 TWh_{th}, enough to satisfy consumption for several months, compared with the existing pumped hydro storage capacity of 0.04 TWh_{th} in the power grid [14].

Energy-dense liquid fuels can also be synthesized by this approach, resulting in an energy carrier which is easy to store, distribute, and utilize in other sectors. In the form of liquid hydrocarbon fuels they can be used in the transport sector and can supplement or extend the use of biofuels as described in Section III. Methanol, with its H/C ratio of 4, is particularly well suited to this task, being the simplest organic³ hydrogen carrier which is liquid at normal ambient conditions. Gasoline, diesel, and kerosene can also be synthesized as drop-in fuels at a higher energy penalty and using more complex plant than that required for methanol production.

The concept of synthesizing fuel from feed stocks of CO₂ and water was first proposed in the 1970s by Steinberg [15] and there have been many other proposals in the meantime [16]-[26]. Three broad generic schemes for incorporating CO₂ into fuels can be envisaged as shown in Fig. 1. Olah et al. [21],[27] provide a wealth of information on the conversion of CO₂ to fuels, and in

particular, methanol. They make a compelling case for the use of methanol as the basis of an 'anthropogenic chemical carbon cycle' which they term the 'Methanol Economy'. In it methanol would replace the functions currently provided by petroleum. Similarly, Mikkelsen et al. [28] provide a concise perspective on the use of CO₂ as chemical feedstock and commodity, together with approaches to its capture and storage.

The most familiar manifestation of renewable liquid fuels is in the form of biofuels, depicted in Fig. 1(a). 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 [29]. Biofuels recycle CO₂ by extracting it from the atmosphere as part of the photosynthesis process which forms plants, algae, or cyanobacteria. This process is referred to as carbon fixation and is a redox reaction. The feed stocks are CO₂ and H₂O which are combined using chlorophyll to absorb the energy in sunlight and transform it, by rearrangement of the atoms of the reactants, into chemical energy (chemical availability) in the form of carbohydrates in the resulting biomass material. The process can be represented by the overall reaction



$$\Delta H_{298}^0 = +470 \text{ kJ}/(\text{mol. carbohydrate}), \quad (1)$$

where ΔH_{298}^0 is the standard enthalpy of reaction. The theoretical maximum photosynthetic energy conversion efficiency to biomass is approximately 6% [29]. A plant contains between 0.1-3.7% (typically 1%) of the original solar energy which is incident upon it during its growth [29],[30]. Since the solar energy reaching the earth's surface is on average about 290 Wm⁻² [1] this low conversion efficiency requires large allocations of land for energy crops.

The oxidation of the carbohydrate either by natural processes or, in the case shown in Fig. 1(a), following suitable processing, by anthropogenically contrived combustion, releases energy. This returns the participating atoms to compounds in lower chemical availability states, in the course of regenerating the carbon dioxide and water⁴. The re-growth of an equivalent amount of vegetation ensures renewability and that theoretically there is no net accumulation of CO₂. Indeed 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 CO₂ which was converted to biomass or animal matter and accumulated via fossilization in a hydrocarbon store over a period of millions of years.

Fig. 1(b) represents a generic open-cycle process in which CO₂ is captured from the flue gases of industrial

³ In this context 'organic' is used to mean 'carbon containing'.

⁴ Figure 1 omits the accompanying water cycles.

plant, e.g. power stations, aluminium plants, or cement factories, and is combined with renewable hydrogen to synthesize fuel. The fuel production process is discussed in greater detail in Section V. Here it is sufficient to say that by combining the hydrogen with CO₂ it is effectively chemically liquefied into a high energy density hydrocarbon fuel. Clearly, if the captured CO₂ stems from the combustion of fossil energy resources this approach is not renewable and will still result in an increase in atmospheric CO₂ concentration. Rather than a re-cycling process it amounts to CO₂ re-use and offers the potential of a notional reduction in emissions of approximately 50% [26]. Such schemes have been advocated by several researchers [7],[8],[31]-[33]. An interesting variant of this cycle uses CO₂ resulting from the exploitation of geothermal energy sources [34].

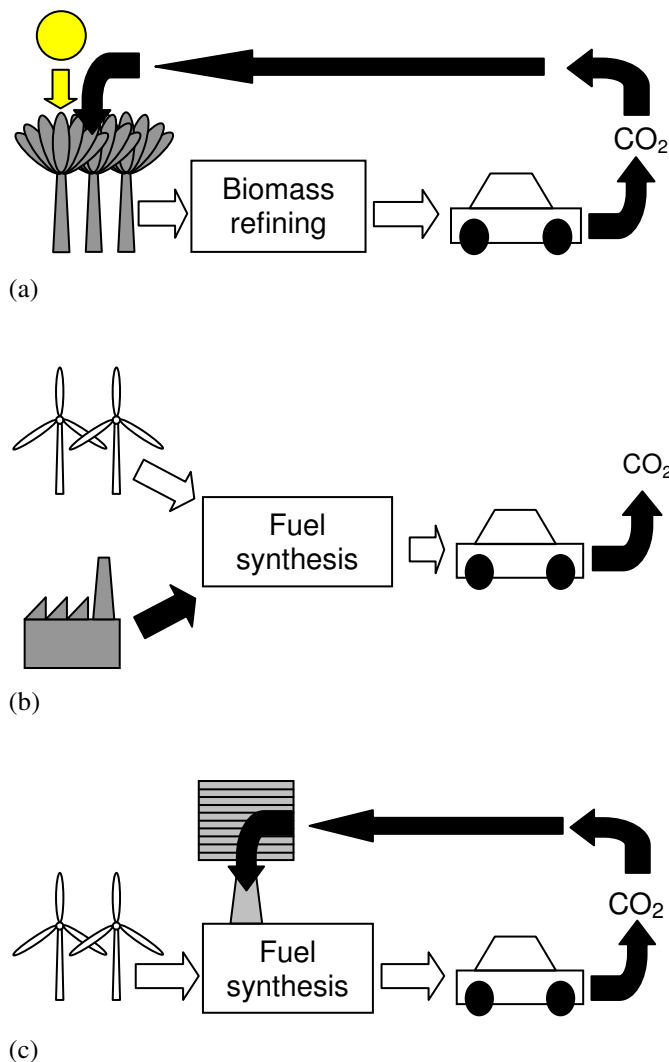


Fig. 1. Generic schemes for the incorporation of CO₂ in fuels (Adapted from Graves [26]).

Zeman and Keith [35] consider several options including the production of hydrogen thermochemically

from fossil resources (using energy input from the same fossil sources) where the resulting CO₂ is sequestered. A carbon-neutral liquid hydrocarbon fuel is produced by substituting the fossil carbon with carbon from atmospherically re-cycled CO₂. Although the use of CO₂ re-cycling in this way enables the application of fossil hydrocarbon resources in a carbon-neutral manner to the transport sector, with its many mobile emitters, it places more constraints on the materials transfer (fossil resource and CO₂) infrastructure compared with the option of using fossil fuels directly with atmospheric CO₂ capture and sequestration. The philosophy of swapping carbon bound in the fossil fuel in an already chemically active state with carbon in a highly oxidized state has also been questioned [26].

From the perspective of sustainability and energy independence for most countries it is ultimately preferable to source and re-cycle the CO₂ by atmospheric extraction. Fig. 1(c) illustrates such a closed-cycle fuel production process in which, ideally, there is no net release of CO₂. The hydrogen generation process in both Figs 1(b) and 1(c) is likely to be via the electrolysis of water and this represents by far the greatest energy input to the process, as shown later. For this reason the fuels produced in this way may be referred to as 'electrofuels' as they are essentially vectors for the storage and distribution of electricity generated from renewable energy.

When the feed stocks are water and CO₂ from the atmosphere the fuel production and use cycle is materially closed and therefore sustainable. Such a cycle also offers security of feed stock supply on a par with that of the 'hydrogen economy' since the time scale for mixing of CO₂ in the atmosphere is sufficiently short to ensure a homogeneous distribution. With access to sufficient water and renewable energy, the process has the potential to provide fuel from indigenous resources and can ultimately be financed by the elimination of the wealth transfer involved in the purchase of oil.

Fig. 2 shows a closed carbon cycle for the production of methanol as an electrofuel. Clearly there is an analogous closed hydrogen cycle involving its oxidation to water. Methanol is an attractive transport fuel in its own right (see Section III) and its production from CO₂ is well established. Indeed, in the US, some of the industrial methanol plants operating in the 1920s and 1930s used carbon dioxide from processes such as fermentation as a feed stock [33]. It is also possible, with increased energy requirements and plant complexity, to go on from methanol to synthesize gasoline, kerosene and diesel [36].

An additional feature of the cycle is to provide a route to synthesizing replacements for petrochemicals via the ready manufacture of olefins from methanol [21,31]. This aspect of sustainability is often over-looked by those focusing on the energy sector. The synthesis of plastics, paints and other synthetic materials in this way could

effectively sequester carbon allowing the continued exploitation of some remaining fossil fuel reserves without causing a net accumulation of CO₂ in the atmosphere.

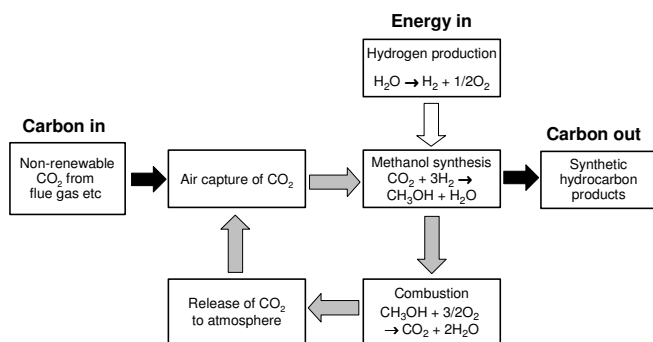


Fig. 2. Cycle for sustainable methanol production and use. (Adapted from 21.)

III. SUBSTITUTION OF FOSSIL FUELS IN THE TRANSPORT SECTOR

Globally the transport sector has the fastest growing CO₂ emissions. In the EU it was the only sector in which CO₂ emissions grew between 1990 and 2005 (at a rate of 30% [37]) however a target for 60% reduction in GHG emissions in transport has been put forward as part of the strategy to reduce GHG emissions overall by 80% by 2050 [38]. A global growth in the consumption of liquid fuels in transport is predicted by 2035 [39]. While the growth in consumption in OECD countries is estimated at about 8%, that in non-OECD countries is projected to be almost 105% [39]. This burgeoning demand will be driven by their rapidly developing economies and the increasing availability of high-quality low cost vehicles.

Transport, particularly the air, marine and road sub-sectors, is very difficult to decarbonize due to its large number of mobile emitters and its strong dependence on fossil fuels (96% in the EU [38]). Burning 1 litre of gasoline, weighing about 0.75 kg, creates 2.33 kg of CO₂, through the addition of two atoms of oxygen from the atmosphere replacing approximately (in a long chain hydrocarbon) two atoms of hydrogen in the fuel. Hence every 50 litre tank refill signifies the release of 116.5 kg of CO₂ into the atmosphere. After 11 refuelling stops of this type a 1250 kg vehicle will have emitted more than its own mass in CO₂ emissions. A vehicle with a fuel consumption of 7 litres / 100 km (about 40 miles / UK gall.) will emit almost 40 tonnes of CO₂ in its lifetime (assuming 240,000 km). The 116.5 kg of CO₂ represents about 20% of the 550 kg of all gas emitted from the vehicle in consuming a 50 litre tank of gasoline fuel; the rest is about 10% water and 70% nitrogen, the latter passing through the engine essentially unchanged. The high rate of mass accumulation, largely via the atmospheric nitrogen, makes it implausible to capture and store all the exhaust gas on-board a vehicle for subsequent

separation and sequestration of the CO₂. On board separation of the CO₂ would require the packaging of a large, heavy, complex, and expensive chemical plant on the vehicle which is capable of removing a high proportion of the CO₂ from the exhaust gas in a single pass at the rate at which it is generated. For similar reasons, removing and releasing the nitrogen from the air before the combustion process (as in so-called 'oxyfuel' combustion) is not practical.

The difficulty of preventing CO₂ emission from vehicles with internal combustion engines (ICEs) burning fossil fuels immediately suggests the option of using a fuel or energy carrier such as hydrogen or electricity which does not release CO₂. Clearly the use of fuels which recycle CO₂ aims to achieve a similar effect so that rather than causing an atmospheric accumulation of greenhouse gas, no net increase is produced.

Commercial air transport has no realistic alternative but to retain the use of energy dense liquid fuels. Large ships may be able to incorporate alternative forms of energy storage, perhaps including hydrogen (but not electricity), for use in large ICEs with some sacrifice in payload (some LNG tankers use the gas which they carry as a fuel). However, as the low-cost bunker fuels which they currently use have few other applications, very high fiscal penalties on non-renewable GHG emissions would be required to incentivize the use of alternatives. The EU has expressed the desire for the penetration of low-carbon sustainable fuels in aviation to reach 40% by 2050 and for the reduction of CO₂ emissions from maritime bunker fuels by 40% in the same time scale [38]. Although the infrastructure costs are high, trains can be powered effectively by electricity because they do not need to store and carry the energy on-board. Heavy-duty road transport will continue to require energy dense liquid fuels in order to achieve acceptable range without compromising payloads, but in Europe the longer term directive is to move toward cleaner fuels in this subsector [38].

In the light-duty commercial and automotive sub-sectors vehicles capable of using a wide range of alternatives to liquid hydrocarbons from fossil resources are being developed by many manufacturers. In the EU the primary driver for this activity is the imminent imposition of severe fiscal penalties based on tail-pipe, or tank-to-wheel (TTW), CO₂ emissions [40]. In 2010 proposals for national GHG emissions standards for light-duty vehicles were proposed for the first time by the EPA, which were accompanied by new Corporate Average Fuel Economy standards issued by NHTSA [41]. In the European Union system, battery electric vehicles (BEVs) count as zero emission vehicles (ZEVs) and, for a limited time, each vehicle with lower than 50 gCO₂/km counts 3.5 times when the sales-weighted CO₂ emissions of the manufacturer are calculated. There is therefore considerable opportunity to subsidize such products from

the savings in CO₂ penalties they will facilitate. In the same way that the carbon intensity of the electricity to charge BEVs (well-to-tank (WTT) emissions) is not considered in relation to vehicle usage in current EU CO₂ legislation, hydrogen fuel cell vehicles also count as CO₂-ZEVs, irrespective of the source of the hydrogen.

A more sophisticated but perhaps more equitable system might be one based on setting propulsion efficiency targets for vehicles (energy used per unit distance travelled) on the TTW side, and non-renewable carbon intensity targets for the fuels / energy carriers which they use on the WTT side. The product of the two parameters would be mass of CO₂ emission per unit distance travelled. Resolving the emissions in this way avoids conflating the sources of the GHG emissions originating in different branches of the transport sector. Thus, the industries responsible for the respective contributions could take more direct control of their targets. The clarity that this approach brings to assessing the impact of each component of the production and use chain will become increasingly important as the portfolio of fuels and energy carriers increases. Indeed, the logical extension of this ‘well-to-wheels’ (WTW) analysis is full life-cycle analysis of both the vehicles and the fuels where the CO₂ released and the energy used in the vehicle manufacturing process is included in the accounting procedure [42].

The three usual contenders as alternative fuels / energy carriers for the eventual decarbonising of transport are: (a) electricity, (b) hydrogen, and (c) biofuels. Fig. 3 shows that in 2008, of the 4.2% of US transportation energy consumption which did not derive from petroleum sources, biofuels in the form of ethanol in ‘gasohol’⁵, E85⁶, and biodiesel, accounted for 95% of the share [43]. In fact ethanol in gasohol (up to E10) dwarfed all other contributions, providing 89.5% of the alternative energy forms used [43]. The inset shows that, even though E85 comprised less than 1% of the 4.2% share of transportation energy which was not petroleum-derived, its contribution was 12 times larger than that of electricity and 535 times that of hydrogen. It could be argued that these differentials are in part due to the relative subsidies allocated to the various fuels, or that they were related to the degree of technology maturity resulting from the age of the devices employed in exploiting the various energy sources. It is posited here that the driving forces are more closely linked to fundamental physical, electrochemical, and economic principles.

⁵ A blend of ethanol at low concentration (mostly at 10% by volume) with gasoline. From 2011 EPA has approved ethanol in gasohol at 15% for vehicles made in or after 2001.

⁶ A blend of up to 85% ethanol and 15% gasoline by volume – the concentration of ethanol may be lowered to perhaps 70% by volume in winter to assist cold starting.

A. Electrification of Transport

Electrification of the vehicle fleet has the thermodynamic attraction that the majority of the various sources of renewable energy are most conveniently converted to electricity and utilizing this in the grid directly to power electric vehicles removes the conversion losses involved in manufacturing a chemical energy carrier. Over an unaggressive drive cycle such as the NEDC, BEVs have a TTW efficiency of about 75%, compared with about 20% for a modern gasoline-fuelled vehicle. 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, the transmission lines required to convey the renewable electricity from the remote locations in which the resource may be located to the regions in which the demand is located are often not readily available and would be extremely expensive to install. There is also the issue of storage, discussed in Section II.

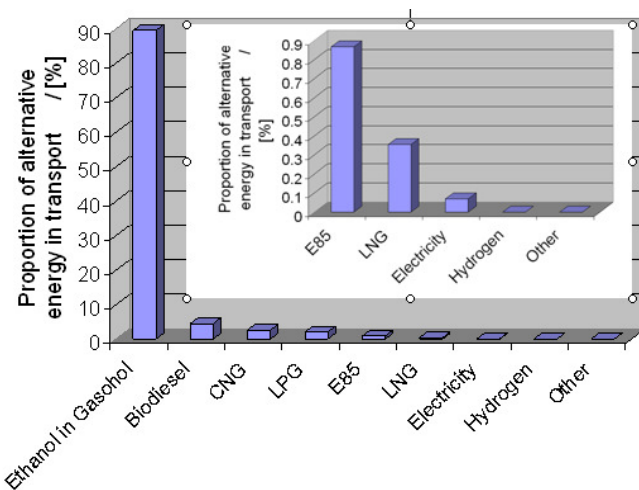


Fig. 3. Proportion of alternative energy in the US transport sector (2008). Based on data in [43].

As energy carriers, batteries are fundamentally limited by the electrical potential available from the elements used in the construction of the cells and by carrying the oxidant in addition to the reductant (analogous to oxygen in the air, and the fuel, respectively, in a combustion reaction). At the upper levels available using lithium-ion chemistries, cell potentials for stable batteries appear to be close to their limit. While advances in metal-air batteries, where oxygen from the ambient air is drawn through a porous cathode, have recently been made using ionic liquid electrolytes, these developments are presently only at the laboratory stage [44].

Vehicles for personal transport require high density storage of on-board energy. The very low net⁷ gravimetric and volumetric energy densities of current technology

⁷ Including the mass / volume of the fuel / energy containment system.

batteries are shown for lead-acid, nickel-metal hydride, and lithium ion chemistries in Fig. 4. To match the range of a conventional gasoline vehicle with a 50 litre fuel tank would require a useable battery capacity of approximately a 100 kWh, accounting for the greater TTW efficiency of an electric vehicle. A fuel tank containing 50 litres of gasoline would weigh about 46 kg; a 100 kWh lithium ion battery would weigh 700-900 kg, depending on the technology and the permissible depth of discharge. It is interesting to note that an ICE vehicle would have to transport about 545 kg of air to combust 50 litres of gasoline if it had to carry its oxidant as well as its fuel, taking the mass of fuel and oxidant to almost 600 kg.

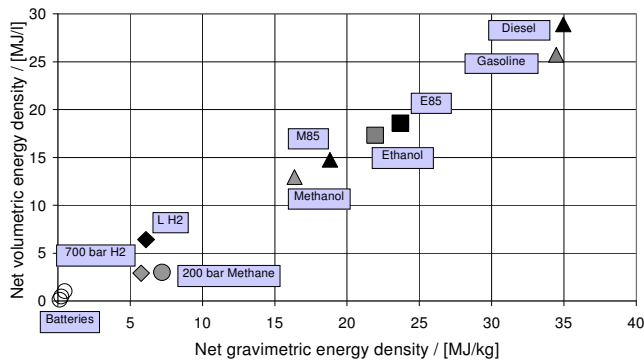


Fig. 4. Net system volumetric and gravimetric energy densities for various on-board energy carriers (based on lower heating values).

The largest barrier to the widespread adoption of electric vehicles is their high cost. Fig. 5 compares the vehicle bill of material costs for a variety of alternative fuel vehicles with a conventional vehicle powered by an ICE. A fixed ‘glider’⁸ cost is assumed for all options. The battery cost assumed, for volume production levels, is \$750/kWh (slightly better than current prices). For the BEVs a minimum state of charge (SoC) of 15% has been assumed; for the EREV⁹ and PEM FC options a minimum SoC of 35% has been assumed. It is clear that, for a range-equivalent vehicle, the cost of the battery makes the BEV unaffordable to most customers. Reducing the vehicle range to 150 km from 550 km brings the costs down to a more accessible level but this significantly range-compromised vehicle is still about 2.5 times more expensive than a conventional vehicle with a much higher utility level. This presents the customer with a very large negative price-performance differential. The EREV option, which enables lower capacity batteries to be used but requires both an electric motor and a fuel converter / generator (ICE assumed in this case), has a similar cost premium but is not encumbered by range compromise.

⁸ Vehicle rolling chassis including the body.

⁹ An extended range electric vehicle (EREV) can be thought of as a plug-in hybrid electric vehicle (PHEV) with a significant electric-only range. For EREVs the strategy is often to try to size the battery so that a large portion of the distance travelled by the vehicle can be done in EV mode.

Recent work published in the UK shows that 80% of trips are made by individuals travelling less than 65 km per day, however these trips only account for 44% of the total daily distance driven [45] and a similar portion of the CO₂ emissions. Including the effects of range anxiety may require pure EVs to have a maximum technical range of 400 km to enable drivers to cover 75% of the total annual car-km driven in EV mode, leading back to very high vehicle costs as shown in Fig. 5. Due to the elimination of the effects of range anxiety EREVs with an 80 km EV range have been shown to be capable of having the same impact on the CO₂ emissions of the vehicle parc [45]. This is due to users of EREVs driving the first 80 km of much longer journeys, which would not be attempted by users of pure EVs (BEVs), in EV mode. Whilst optimistic assessments of future battery technology development have been made [46], no convincing projections are available showing that the cost of advanced batteries is likely to drop below \$500/kWh including the systems for battery energy management and temperature regulation.

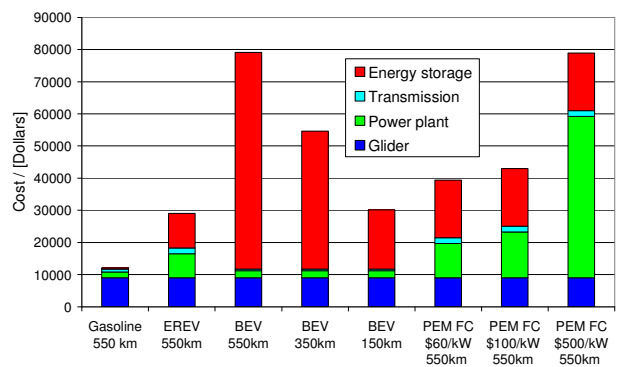


Fig. 5. Cost comparison of alternative energy vehicles.

The European Union has stated a desire to allow only vehicles with a zero emissions mode to be used in cities by 2050 [36]. For the reasons of cost and utility described above (notwithstanding those relating to fundamental limits of electrochemistry) it is possible that vehicles carrying only electricity for their motive power may never become dominant. If widespread electrification is mandated it is likely that, without significant mode switching, EREVs will be the pragmatic solution to personal transport, avoiding the requirement for a family to own a portfolio of (expensive) vehicles suited to different purposes. In this case there will still be strong demand for carbon-neutral liquid fuels as a high energy density storage medium to power the vehicle when its minimum battery SoC is reached. This would offer possibilities for energy storage in both networked vehicle batteries and synthetic liquid fuels.

B. Hydrogen

Hydrogen in its molecular form is held back on two major fronts: (i) the technical obstacles and cost of supplying a safe energy-efficient distribution infrastructure

are major obstacles, as discussed in Section II and summarized well by Bossel [12]; (ii) the costs of fuel-cell vehicles (although hydrogen can be used as a fuel for ICEs as described elsewhere in this volume). A significant portion of the high cost premium of a hydrogen-fuelled vehicle, including an ICE-based vehicle, is the cost of the hydrogen storage system. Estimates for the volume manufacture of the carbon-fibre wound pressure vessels required for 700 bar hydrogen storage range from the proposed target of €2000 [47] to €10000 [48] for systems capable of storing around 10 kg of hydrogen. In Fig. 5 a cost of €5000 has been assumed for the polymer electrolyte fuel cell (PEM FC) vehicle. Cryogenic storage systems, which store hydrogen in its liquid state at -253 °C, are significantly more complex and therefore expensive; they also have to manage boil-off losses effectively.

In Fig. 5 the total energy storage system costs for the PEM FC option include both the hydrogen storage costs and those of a 14 kWh battery (the same as the EREV) which is necessary to hybridize the fuel cell in order to exploit its potential high efficiency levels (theoretically around 50% over the NEDC). The costs of hydrogen fuel cell vehicles are very sensitive to the assumed cost per kW of the fuel cell itself (included in the 'power plant' costs in Fig. 5). Leaving aside the potential vehicle cost at volume production levels of between 3 and 6.5 times that of a conventional vehicle, the expense and basic incompatibility of the fuel-distribution infrastructure, described in Section II, is the biggest obstacle to the adoption of hydrogen as an energy vector in transport.

C. Biofuels

As discussed in Section II biomass is essentially solar energy stored in a chemical form in plant matter by combining carbon dioxide and water to form carbohydrates. That they supply the vast majority of the alternative energy used in the transport sector is due to the compatibility, in low level blends, with current vehicles and the fuelling infrastructure of liquid biofuels. Fig. 4 shows that although the net energy density of ethanol and, particularly methanol, is significantly lower than diesel and gasoline, the values are much higher than electricity and hydrogen, even if the higher TTW efficiencies of BEVs and PEM FC vehicles are included.

The inclusion of biofuels in transport energy has been mandated in the European Union and the United States: the former at a level of 5.75% (energy-based) by 2010 [49] and subsequently via the requirement that the share of energy from renewable sources in all forms of transport is at least 10% in 2020 [50], 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 [51]. The EU have set GHG reduction targets for the use of such fuels as 35% (current

and 60% for biofuels produced in installations in which production started on or after 1 January 2017 [50]. California has initiated carbon intensity targets for all fuels, including biofuels [52].

In the US blends of up to 10% by volume of ethanol in gasoline (E10) have been allowed for use in light-duty vehicles since 1979. The EPA has recently granted a partial waiver on the use of E15 in light-duty vehicles of model year 2001 or more recent [53]. Flex-fuel vehicles (FFVs) are capable of running on ethanol concentrations of up to 85% by volume in gasoline. As of July 2009 there were more than 7 million such vehicles on US roads [54]. Although many such vehicles seldom use E85 they represent a potentially large market for alcohol fuels.

Additional costs of manufacturing new vehicles which are E15 compatible are practically negligible and those for an FFV are perhaps \$200-\$300 for the increased specification fuel system materials and an alcohol concentration sensor in the fuel line. Thus the cost of an FFV would appear very similar to that of the gasoline-fuelled vehicle shown in Fig. 5. The beneficial properties of alcohols as fuels for internal combustion engines are summarized by Pearson and Turner [55]. In low concentration blends these are minor. Although E85 gives around a 5% increase in engine efficiency and a concomitant reduction in CO₂ emissions compared with gasoline on the NEDC, it can give around 25% improvement in efficiency at high load (up to 35% for E100) where its high octane index, high heat of vaporization, and low combustion temperatures are a significant benefit, particularly in high-specific output pressure-charged engines. The efficiency of the engines of FFVs is compromised by the requirement to run on high concentrations of gasoline as well as ethanol. In spark-ignition engines optimized for high concentration ethanol or methanol blends using high compression ratios, higher levels of *peak* thermal efficiency than automotive diesel engines (>42%) can be achieved [56]. Clearly the alcohol-fuelled engines would not match the low-part-load efficiency of the diesel engine but the trend toward heavily downsized spark-ignition engines is reducing the part-load efficiency differential.

D. The Biomass Limit

The sustainable potential of biogenic wastes and residues world-wide has been estimated at approximately 50 EJ¹⁰/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 retaining biodiversity. The total sustainable technical potential of bioenergy in 2050 is thus projected to be between 80-170 EJ/year [55]. The mid-point value of this range, 125 EJ, is around one quarter of the current global energy use (about 500

¹⁰ 1 EJ = 1×10¹⁸ J

EJ/year) and less than one tenth of the projected global energy use in 2050 [57]. The global transport energy demand in 2007 was about 100 EJ [39] and is projected to grow to about 170 EJ in 2050¹¹. Assuming that half the available sustainable biomass energy was available for biofuel production at a conversion efficiency of 50% [17] limits the substitution potential of biofuels to about 20% of the 2050 energy demand. A slightly more optimistic position is adopted by the IEA with a prediction that 32 EJ of biofuels will be used globally in 2050, providing 27% of transport fuel [58]. Clearly the biomass potential could be significantly higher or lower for individual countries, depending on their population densities and sustainable agricultural potential, considering the impact of land use change.

A further limiting factor is the requirement to feed the burgeoning population of the Earth, with its increasingly westernized diet demanding much greater amounts of land and water than previously [59], and to avoid the accelerated escalation of feed stock prices. These issues, together with the consideration of balancing security of energy supply with that of food supply may constrain biofuel production to the use of the wastes and residues quantified above.

E. Beyond the Biomass Limit – Sustainable Organic Fuels for Transport (SOFT)

For transport applications the internal combustion engine has already won the technical and commercial battle against vehicles propelled by battery-driven electric motors or fuel cells¹². This is because it can be easily mass produced using low-cost processes from abundant and therefore cheap materials which are easy to re-cycle, and because it is capable of operating on a wide variety of energy-dense fuels. The ICE is not, however, tied to fuels containing non-renewable carbon.

Biofuels present the dichotomy that they are easily integrated into the transport energy supply and use structure due to their miscibility with current fossil fuels while being ultimately constrained in the extent to which they can displace the latter. Because biofuels alone will not be capable of completely decarbonising the transport sector they are in danger of being regarded merely as a technical and commercial dead end. A lifeline is provided by the electrofuels described in Section II, where energy carriers are synthesized from CO₂ and water using renewable energy as shown in Fig. 2. Drop-in fuels such as gasoline, diesel, and kerosene can be produced in this way but the simplest and most energetically efficient liquid fuel to make is methanol.

Ethanol is currently the most familiar alcohol fuel used in the transport sector but there is also much experience of

methanol [60][55] and it has been successfully used in large-scale fleet trials over a period of 15 years [61]. To aid the transition to electrofuels based on methanol, ultimately fuelling optimized spark-ignition engines using high compression ratios, as described above, it is possible to make a relatively conventional vehicle operate on any combination of methanol, ethanol, and gasoline with the aid of an alcohol fuel sensor and modified engine management software [62]. An immediate application for methanol is in blends of up to 3% by volume in European gasoline. Additionally, it is possible to formulate ternary blends of methanol, ethanol, and gasoline which have the same stoichiometric air-fuel ratio and volumetric energy concentration as any binary ethanol-gasoline blend. In the form of E85 substitutes, these ternary blends can act as drop-in fuels for FFVs [63] and, in addition to serving as a market pull for methanol synthesized from CO₂, can act to extend the use of the limited amount of ethanol produced as a sustainable biofuel. Initial tests on blends formulated in this way also reveal almost identical octane numbers to E85 [63].

Fig. 6 shows that, starting with E85 on the left, ethanol can be removed by the addition of methanol and more gasoline to maintain the same volumetric energy content and stoichiometric air-fuel ratio (AFR). The displaced ethanol can be used to produce additional fuel blends. The overall effect is also to displace gasoline. For example, the ethanol in 1 gallon of E85 can be used to make 4 gallons of Blend C in Fig. 6. The 2.16 gallons of gasoline which would, together with the 0.15 gallons of gasoline in 1 gallon of E85, give the same delivered energy as 4 gallons of Blend C, represents an additional 36% gasoline displaced.

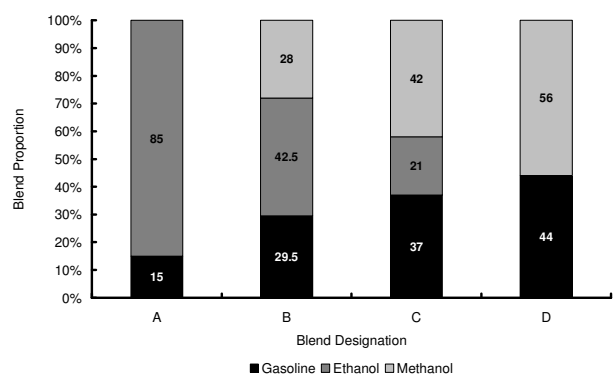


Fig. 6. Volumetric proportions of ternary GEM blends with the same stoichiometric AFR and volumetric energy content as E85.

Equivalent ternary blends to E10 or E15, for example, can also be formulated. In this way a ‘soft start’ is possible to an alternative transport energy economy, in which the majority of the fuel is eventually synthesized from CO₂, water, and renewable energy. Thus, biofuels need not be viewed as a dead end. This concept, where the biofuels store solar energy, the electrofuels store all economic

¹¹ Extrapolating the EIA value of 143 EJ for liquid fuels 2035 [38].

¹² Batteries, electric motors, and fuel cells are all older inventions than the internal combustion engine.

forms of renewable energy, and both embody recycled CO₂ and water as feed stocks, is referred to here as Sustainable Organic Fuels for Transport (SOFT). It is possible that, in the long term, the production of biofuels may be phased out to increase the amount of biomass available to balance fluctuations in renewable power generation and stabilize supply or to provide feed stock for a replacement to the petrochemical industry.

The three steps required to synthesize sustainable organic fuels are: CO₂ separation, hydrogen generation, and fuel reaction. Some of the individual processes which could be used are briefly described in Sections IV and V and efficiency estimates for the overall cycles are given.

IV. CO₂ RE-CYCLING

In order for the SOFT process outlined in Sections II and III to emit zero net CO₂ (over a full cycle of storage of renewable energy into liquid fuel and the subsequent conversion of that fuel into work), two things are essential: (i) all processes must be powered by carbon-free energy; (ii) the CO₂ that is incorporated into the fuel must be captured directly from the atmosphere, a process sometimes referred to as "direct air capture". It is important to note that using only flue gas CO₂ separated from power plants, as shown in Fig. 1b, would not create a carbon-neutral fuel because the CO₂ emitted upon combustion of the synthetic fuel could not be re-separated for a subsequent fuel synthesis and combustion cycle.

Although direct air capture of CO₂ is less developed than flue-gas capture, research in this area has increased rapidly in the last 10 years and much progress has been made [17]-[19],[64]-[79]. Direct air capture has been shown to be technically feasible, and much of the discussion now centers on whether this technology will prove sufficiently cost-effective to enter the market [80]-[82]. It is important to note that the cost threshold depends on the specific application; for example, without policy intervention, the cost of direct air capture would likely need to be much lower for deployment as a sequestration technology than for deployment as part of a fuel-synthesis process for making a value-added product like gasoline. In this section the status of direct air capture of CO₂ is reviewed, specifically in the context of the SOFT process.

A. Thermodynamic minimum energy of separation

Although the concentration of CO₂ in the atmosphere (about 386 ppm in 2009, rising at a rate of about 1.9 ppm per year [83]) is about 260 times less than the concentration of CO₂ in flue gas (about 10%), the logarithmic scaling of the thermodynamic minimum energy (in the form of work) of separation means that the minimum energy required to separate CO₂ from air is only 2.6 - 2.9 times greater than the minimum energy required to separate CO₂ from flue gas.

The energy required, in the form of thermodynamic work, to separate a mixed-gas stream of CO₂ and other molecules into two separate gas streams, one with an increased concentration of CO₂ relative to the input stream and one with decreased concentration of CO₂ relative to the input stream, is equal to the difference in the well-known energy of mixing [84] between the output streams and the input streams. At constant temperature and pressure, the change in Gibbs free energy of mixing ($\Delta G = G_{\text{out}} - G_{\text{in}}$) between the output and input streams is directly proportional to the entropy of mixing (ΔS), and is given by

$$\Delta G = -T\Delta S. \quad (1)$$

For the general case of an input stream that is separated into two output streams, the minimum power \dot{W} that must be input to the system to enable the separation is given by:

$$\dot{W} = R_{\text{mol}} T \left[\sum_{i=1}^2 \left\{ \dot{N}_{\text{out } i} \sum_j (x_{\text{out } i, j} \ln x_{\text{out } i, j}) \right\} - \dot{N}_{\text{in}} \sum_j (x_{\text{in } j} \ln x_{\text{in } j}) \right] \quad (2)$$

where R_{mol} is the universal gas constant, T is the temperature, \dot{N}_i is the molar flow rate in stream i , and $x_{i,j}$ is the mole fraction of molecule j in gas stream i . Using this formula, the minimum energy required to separate CO₂ directly from the atmosphere can be calculated and compared to the energy required for flue-gas capture.

TABLE I

THERMODYNAMIC MINIMUM WORK AT 20 °C.

Fraction of CO ₂ captured for direct air capture	Thermodynamic min. work for air capture (kJ/mol.CO ₂)	(Min. air-capture energy) / (Min. flue-gas capture energy with 90% capture)
1.0	21.6	2.95
0.8	20.6	2.82
0.6	20.1	2.75
0.4	19.7	2.70
0.2	19.4	2.66
Limit → 0	19.2	2.62

Table 1 shows the theoretical minimum energy required in the form of thermodynamic work for air capture with CO₂ capture fractions ranging from the limit as the capture fraction approaches zero to 1 (complete capture), as well as the ratio of this minimum air-capture energy to the minimum energy required to capture 90% of the CO₂ in the flue gas stream (7.3 kJ/mol.CO₂). Since the capture fraction for direct air capture can be varied to optimize several metrics, various capture fractions for air capture are examined, whereas the capture fraction is typically

fixed at 0.9 for flue-gas capture. From Table 1, it can be seen that although the concentration of CO₂ in the atmosphere is 260 times less than the concentration of CO₂ in flue gas, the minimum energy required for capture directly from the atmosphere only requires 2.6 - 2.9 times the minimum energy required for capture from flue gas. Note that the data in Table 1 assumes both air capture and flue-gas capture at 20°C. More realistically, air capture can be carried out at 20°C, but flue gas capture will be performed at about 50°C. These temperature differences would modify the range of energy ratios in column 3 of Table 1 to 2.38, in the limit of zero capture, to 2.68 for complete capture.

B. Direct air capture technologies

The separation of CO₂ generally involves two steps: capture and desorption / regeneration. In the capture step, CO₂ is absorbed or adsorbed into a solid or liquid by contacting the CO₂ source with the absorber or adsorber. In the desorption / regeneration step, CO₂ is selectively desorbed from the absorber / adsorber, resulting in a flow of pure CO₂ gas, and the original capture solvent / adsorber is regenerated.

Over the last ten years, many research groups around the world have been pursuing a variety of strategies for the separation of CO₂ directly from the atmosphere [17]-[19],[64]-[79]. In this section we give an overview of the various approaches and progress in the field.

In addition to the increased energy required for capture from dilute sources like the atmosphere when compared to flue gas capture, other challenges must also be considered, including a smaller absorption flux of CO₂ into the capture solvent, and smaller loading of CO₂ into the capture solvent when compared to capture from flue gas. The smaller flux means that a larger capture unit volume is required to fix an equivalent amount of CO₂, while the smaller loading, and specifically the smaller gap between rich loading immediately after capture and lean loading immediately after desorption/regeneration, requires a larger volumetric flow rate of capture solvent to separate an equivalent amount of CO₂ [82]. Due to these challenges most studies of air capture have not used the industry standard flue-gas capture solvent monoethanolamine (MEA) [85], but rather have focused on caustic solvents such as sodium hydroxide [66],[69]-[74], potassium hydroxide [17]-[19],[66],[73],[77]-[79], or calcium hydroxide [64],[65],[67],[68],[75],[76] that demonstrate better performance than amines for capture from dilute gas streams like the atmosphere. Capture of CO₂ into hydroxides (e.g., NaOH, KOH, and Ca(OH)₂) results in carbonates (Na₂CO₃, K₂CO₃, and CaCO₃, respectively).

In order to complete the cycle and produce a pure stream of gas, CO₂ must be desorbed from these carbonates, and the original capture solvent (NaOH, KOH, and Ca(OH)₂, respectively) regenerated. Because the binding energies of these carbonates are relatively high, care must be taken to

minimize the energy of desorption/regeneration. One common approach is to use thermal/chemical cycles to desorb the CO₂ and recover the original capture solvent. When CO₂ is captured into Ca(OH)₂ to form CaCO₃, desorption can be accomplished by a calcination reaction (CaCO₃ → CaO + CO₂) to liberate the CO₂, followed by the hydration of CaO (CaO + H₂O → Ca(OH)₂) to recover Ca(OH)₂ for a subsequent capture-regeneration cycle [64],[65],[67],[68],[75],[76]. In the case where CO₂ is captured into NaOH or KOH to form Na₂CO₃ or K₂CO₃, the process often is designed to produce a post-capture solution in which not all of the NaOH or KOH is converted to Na₂CO₃ or K₂CO₃ so that the reaction kinetics remain favorable. In this case, the carbonate can be precipitated out with Ca(OH)₂ (Na₂CO₃ + Ca(OH)₂ → 2NaOH + CaCO₃), followed by the calcination and hydration reactions described above to liberate the CO₂, and recover the Ca(OH)₂ [69],[70]. Also, for capture into hydroxides to form carbonates and bicarbonates, CO₂ and capture solvent regeneration can be accomplished by the thermal decomposition of the carbonates and bicarbonates followed by the hydrolysis of the decomposition products to recover the capture solvent [72]. Finally, a sodium titanate regeneration cycle (7Na₂CO₃ + 5(Na₂O.3TiO₂) → 3(4Na₂O.5TiO₂) + 7CO₂ and 3(4Na₂O.5TiO₂) + 7H₂O → 5(Na₂O.3TiO₂) + 14NaOH) has also been investigated [73],[74].

An alternative to these thermal/chemical desorption/regeneration cycles is the electrochemical regeneration of CO₂ from post-capture solutions, usually in the form of electro dialysis [17]-[19],[66],[77]-[79]. This approach is typically used for the regeneration of Na₂CO₃ and K₂CO₃, but not CaCO₃ due to the challenges of preventing scaling with divalent cations like Ca²⁺. The electro dialytic regeneration of CO₂ is illustrated in Fig. 7. On the left side of the figure, a solution of KOH is converted to K₂CO₃ via the capture of CO₂ (and depending on the process conditions, the K₂CO₃ is itself converted to KHCO₃ by the additional capture of CO₂). This post-capture solution of KOH/K₂CO₃/KHCO₃ is then fed into a bipolar membrane electro dialysis (BPMED) unit for the regeneration of CO₂ and the recovery of the KOH capture solution.

The BPMED unit consists of an alternating series of bipolar membranes (BPMs) and anion exchange membranes (AEMs) between two electrodes. This unit separates the KOH/K₂CO₃/KHCO₃ post-capture solution into an acid and a base by applying a voltage across an alternating stack of ion-selective AEMs and water-dissociating BPMs. CO₂ is transported (via CO₃²⁻ or HCO₃⁻ transport) from the post-capture solution across AEMs into the adjacent solution that is acidified by H⁺ ions transported out of the BPM. The acidic solution converts the transported CO₃²⁻ or HCO₃⁻ into CO₂ gas, and the low solubility of total dissolved CO₂ in the acidic solution results in CO₂ gas evolution. The CO₃²⁻ and HCO₃⁻ ions removed from the post-capture solution are

replaced with OH^- ions from the BPM, thus regenerating the capture solution, which can then be fed back to the capture unit for an additional capture cycle.

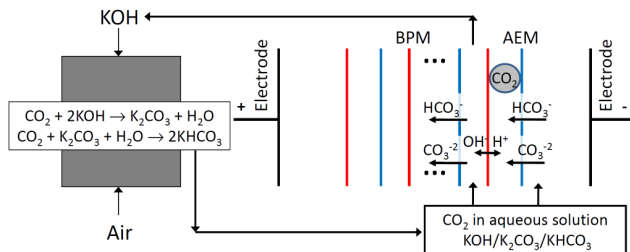


Fig. 7. Schematic of capture and regeneration cycle using electrodiolytic regeneration [77]. BPM = bipolar membrane, AEM = anion exchange membrane.

At ambient pressure for 0.5M KHCO_3 in a seven-cell electrodiolysis unit, the CO_2 regeneration energy ranges from 150 kJ/mol. CO_2 at a current density of 5 mA/cm² to 325 kJ/mol. CO_2 at 80 mA/cm². For a seven-cell lab-scale unit, about 30% of this energy is the contribution from the electrodes. Commercial-scale systems typically have over 100 cells per unit, resulting in a negligible contribution of the electrodes to the total energy consumption. This suggests that a commercial scale unit would consume 100 kJ/mol. CO_2 (at 5 mA/cm²) - 219 kJ/mol. CO_2 (at 80 mA/cm²) for CO_2 regeneration from a 0.5M KHCO_3 solution. The regeneration energy for 0.5M K_2CO_3 is observed to be about twice that of 0.5M KHCO_3 , due to the fact that for each CO_2 molecule regenerated, two charges must be transported across the membranes for CO_3^{2-} , compared to one charge per CO_2 for HCO_3^- [77].

When a BPMED-based CO_2 regeneration system is operated at ambient pressure and sufficiently high current density, CO_2 gas can evolve out of the solution inside the membrane stack. This can lead to gas bubbles trapped in the membrane stack on the surfaces of the membranes which reduces the effective area of the membranes, leading to increased resistance, voltage, and energy consumption for ion transport. The irregularity of the electrolyte distribution in the presence of effervescent CO_2 can also lead to localized hot-spots of high current density on the membranes (referred to as "current crowding") that can lead to membrane damage and reduced lifetime.

By pressurizing the membrane stack to 10 atm, the CO_2 can be kept in solution until the pressure is released downstream of the membrane stack. This eliminates the increased resistance due to the bubbles in the membrane stack, thus decreasing the voltage and energy for a given current density. Specifically, at a current density of 139 mA/cm², the energy required at pressures greater than 6 atm (333 kJ/mol. CO_2) is 29% less than the energy required at 1.5 atm (471 kJ/mol. CO_2). This energy represents the CO_2 regeneration energy required for a seven-cell lab-scale electrodiolysis unit, and as mentioned

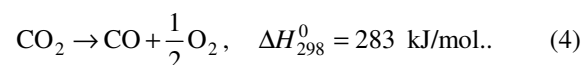
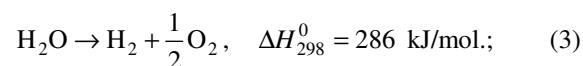
above, the energy required for a commercial unit with over 100 cells per unit would likely be about 30% lower than these values [78],[79].

From this description, it is clear that electrodiolytic separation, in contrast to the thermal/chemical regeneration cycles described earlier, performs work only on the specific molecules that contain the CO_2 . This electrochemical work comes in two forms: the work required to transport the CO_3^{2-} and HCO_3^- ions across the AEMs, and the work required to dissociate water into H^+ and OH^- across the BPMs. Because the electrodiolytic approach does not require heating the entire solvent mass to extract the CO_2 , electrodiolytic regeneration has an increasing advantage, compared to thermal/chemical regeneration, for solvent/gas stream combinations with high binding energies and low CO_2 loading.

V. FUEL SYNTHESIS

Carbon dioxide is a highly stable molecule as reflected by its large standard Gibbs free energy of formation (-394.4 kJ/mol.), with the main contribution to the $\Delta_f G^\circ$ value coming from an enthalpy of formation of $\Delta_f H^\circ = -393.5$ kJ/mol. The carbon-oxygen bonds are strong and substantial energy must be input for their cleavage in order to achieve ultimate reduction of the carbon. Optimized reaction conditions and active catalysts are also required for any chemical conversion of CO_2 to a carbonaceous fuel. Since chemical reactions are driven by differences between the Gibbs free energy of the reactants and products, the CO_2 can be combined with another reactant with a higher Gibbs free energy which gives up some of its intrinsic chemical energy to promote the formation of a more convenient energy carrier. This is the critical central role of hydrogen in the present discussion. Since the long-term objective is to produce a fully renewable cycle for fuel synthesis and energy storage, the generation of hydrogen from water in a closed hydrogen cycle (analogous to the closed carbon cycle for the CO_2 feed stock) is required in order to synthesize hydrocarbon-based energy carriers.

Carbon dioxide and water require very similar minimum energy levels for their dissociation according to the reactions [26]



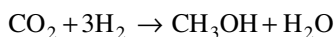
These mechanisms represent the largest energy inputs to the synthetic fuel production process. A comprehensive overview of the options for the production of sustainable hydrocarbon fuels via this route is given by Graves [26]. Thermolysis (direct thermal decomposition), thermochemical (thermally driven chemical reactions at

lower temperature), electrolytic (low and high temperature) and photoelectrolytic processes are described [26]. In the present work attention is focussed on the direct hydrogenation of CO₂ to form methanol and only the dissociation of H₂O using low temperature electrolysis is discussed as this is commercially available ‘off-the shelf’ technology (COTS) which operates at large-scale in industrial environments. The process steps based on these approaches are explained to demonstrate the feasibility of the technologies. Developments in hydrogen generation via water electrolysis are also covered in depth in another contribution to this volume.

Commercial alkaline electrolyzers are typically operated at voltages in the range 1.8-2 V and current densities of 0.2-0.5 A/cm². This gives higher heating value efficiencies in the range 70-80% depending on whether the device is run at peak efficiency or peak load, with 73% being a typical value when balancing amortization of capital costs, cell lifetime, and capacity factor [26]. The capital cost of an alkaline electrolyser is in the range \$7.5-9/GJ of hydrogen produced at a capacity factor of close to 100% [26] [86]. Capital costs are increased significantly by intermittent operation due to the use of renewable energy but durability is thought not to be an issue [26]. Operating lifetimes of 10-20 years are typical at close to 100% capacity factor [26]. Seawater can be electrolysed effectively using alkaline electrolyzers with modified anode materials but desalination can supply water at \$1/m³ which adds a fraction of 1 cent to the cost of a gallon of synthetic fuel [26].

Fig. 8 shows a schematic representation of the various chemical reactions and processes involving CO₂, hydrogen, oxygen, methanol, and carbonates. CO₂ is, with water, the end product of any combustion process involving materials containing carbon and hydrogen. Further reactions to form carbonates are exothermic processes. The capture of CO₂ in inorganic carbonates is described in Section IV.

Once hydrogen and CO₂ are available the simplest and most direct route to producing a high quality liquid fuel is the catalytic hydrogenation of CO₂ to methanol via the reaction



$$\Delta H_{298}^0 = -49.9 \text{ kJ}/(\text{mol. methanol}) \quad (5)$$

This reaction was used commercially in the 1920s and 1930s but was displaced by the development of syngas-based (a mixture of CO and H₂) production techniques [21],[33]. Despite the fact that this is an exothermic reaction a significant activation energy barrier prevents the methanol synthesis from carbon dioxide without an energy input and a selective catalyst (Fig. 8). Modern developments in catalysts based on Cu/ZnO/Al₂O₃ have improved conversion efficiencies, operating at pressures of 50-100 bar and temperatures of 200-300°C. More

recent approaches have been based on developments with ZrO₂ modified Al₂O₃ catalysts, zeolite membrane reactors [26] and the use of organometallic complexes which exploit the important activation of H₂ by so-called frustrated Lewis pairs [87]. Photocatalytic CO₂ conversion into methanol has also been extensively studied using various photocatalysts. However, the low efficiency of the process requires much more work to bring it to practical large scale applications [25].

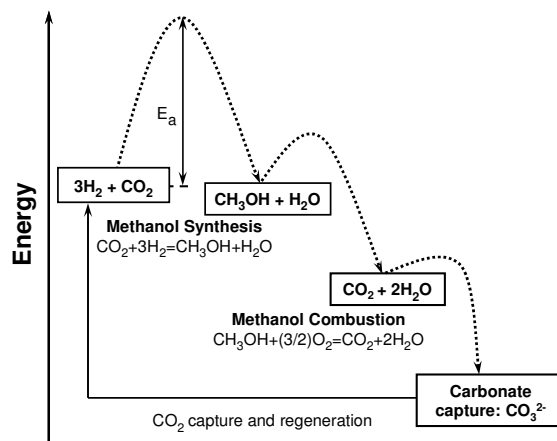


Fig. 8. Schematic representation of a potential energy profile for methanol synthesis, methanol combustion and capture of CO₂ to form carbonates.

Fig. 9 shows that, in producing methanol via the direct hydrogenation of CO₂, by far the largest component of the process energy requirement is the hydrogen production. This is true of any electrofuel using hydrogen as an intermediate or final energy carrier. An 80% electrolyser efficiency has been assumed together with a nominal CO₂ extraction energy of 250 kJ/mol.CO₂ (representing about a 10% rational thermodynamic efficiency relative to the minimum Gibbs free energy / thermodynamic work requirement). This gives a HHV ‘electricity-to-liquid’ efficiency of 46%, including multi-pass synthesis of the methanol and re-compression of the unconverted reactants. 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.

Fig. 10 shows the estimated sensitivity of the process efficiency to the energy requirement for CO₂ extraction. Almost 15 years ago Specht et al. [20],[88] measured total-process CO₂ capture energy levels of 430 kJ/mol. in a demonstration plant using an electro dialysis process to recover the absorbed CO₂. This represents a rational efficiency of less than 5% using the values shown in Table 1. The measured overall fuel production efficiency of 38.1% matches well with the corresponding value given by the simplified analysis shown in Fig. 10. Stucki et al. [18] also measured a very similar value for the overall fuel production efficiency using a lab-scale demonstration

plant. The analysis of Zeman [69],[70] indicates that a value of 350-440 kJ/mol. CO₂ might be reasonably expected for the overall energy requirement from a causticization and thermal calcination approach based on the use of mainly thermal energy inputs. About 90 kJ/mol. CO₂ are due to air contactor / capture system with about 20 kJ/mol. CO₂ being required for the compression process, giving a total of about 110 kJ/mol. CO₂ required in the form of direct mechanical work.

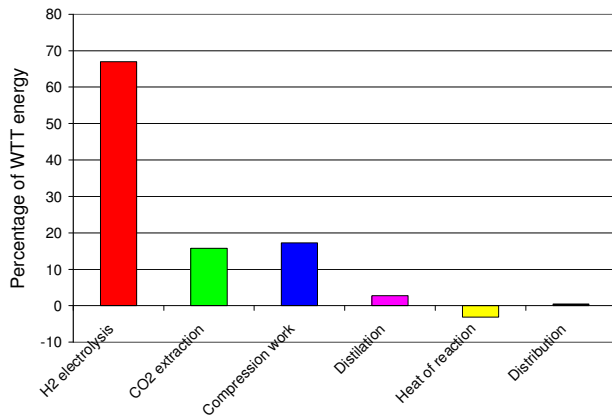
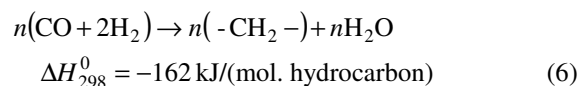


Fig. 9. Process energy requirements for synthesis of methanol from atmospheric CO₂ and renewable hydrogen.

Mahmoudkhani et al. [73,74] propose a process based on the use of sodium tri-titanate in the causticization step which reduces the high-grade heat energy requirement of this step by 50%. In contrast, MEA-based flue gas scrubbing techniques require between 180 and 140 kJ/mol. CO₂ [69]. Since the largest component (60-65% depending on the efficiencies of the other steps) of the fuel production process energy requirement is that of the electricity input used for the electrolysis step the sensitivity of the overall efficiency to the CO₂ capture process, and whether the energy is required in the form of electricity or heat, is relatively low.

In addition to being attractively simple to synthesize, methanol ultimately offers high potential for efficiency improvements in spark-ignition engines. For applications where vehicle range is of paramount importance, further processing to kerosene and diesel can produce high energy density drop-in fuels (with a concomitant decrease in overall process efficiency and with a significant increase in plant complexity and cost). The Fischer-Tropsch (FT) synthesis of general hydrocarbon fuels proceeds from the availability of syngas via the mechanism



Bandi and Specht [37] describe processes for FT synthesis of gasoline and diesel from both CO and CO₂ with hydrogen; they also give details of the Methanol-to-Gasoline (MTG) and Methanol-to-Synfuels (MtSynfuels) processes which have been developed to commercial

readiness. In the MTG process [21],[37] the methanol is first converted to DME from which light olefins are produced; these are eventually converted to heavier olefins, paraffins, and aromatics following the route

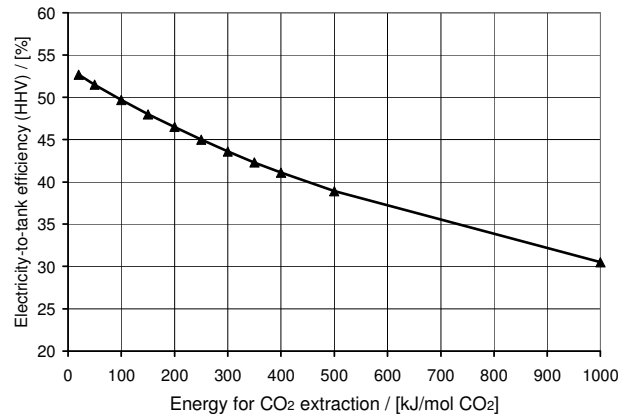
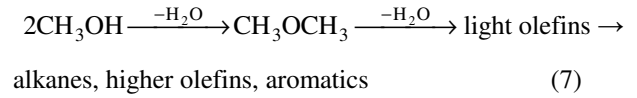


Fig. 10. Sensitivity of methanol electrofuel synthesis to energy required for CO₂ extraction and concentration.

A 14000-barrel-per-day MTG plant, using technology developed by Exxon Mobil, was built in New Zealand in the early 1980s and plants employing second-generation versions of this technology have recently been commissioned in China and embarked upon in the US [89]. 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 small plants synthesizing methanol from atmospheric CO₂ 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 [36].

Without policy intervention the intermittent use of alkaline electrolyzers, due to their limited current densities, is likely to be too expensive [26] to produce fuel under present market economics. Improvements on this technology are at an advanced state of development [26],[90] and other promising technologies are emerging. Graves [26] describes the use of high temperature co-electrolysis of CO₂ and H₂O giving close to 100% electricity-to-syngas efficiency for use in conventional FT reactors. This ultra-efficient high temperature electrolysis process using solid oxide cells combined with a claimed CO₂ capture energy (from atmospheric air) as low as 50 kJ/mol. [91] leads to a prediction of an electricity-to-liquid efficiency of 70% (HHV basis). Using this high overall efficiency enables the price of electricity required to produce synthetic gasoline at \$2/gallon (\$0.53/litre) to be as low as \$0.02-0.003/kWh [26]. Doty [7] states that

off-peak wind energy in areas of high wind penetration in the US averaged \$0.0164/kWh in 2009 and the lowest 6 hours of the day averaged \$0.0071/kWh.

VI. ENERGY STORAGE

To achieve a fully integrated system based on the use of renewable energy requires large-scale storage of an energy carrier which can be readily accessed for power generation. To provide long term energy storage capable of covering the contingency of extreme meteorological events a system based on the integration of the electricity and gas infrastructure would be a key component. Such a system could be based on the synthesis of renewable methane as an energy vector from CO_2 and H_2 (using the Sabatier process) and in many countries could use the capacity of the existing gas network for storage and subsequent re-use in the power generation and heat sectors. The synthesized and stored methane is thus readily retrievable to smooth out the supply of renewable energy. Sterner [14] describes such a concept in detail and has modelled its operation within a renewable energy system based on wind, solar, and biomass over a period of 1 week on a 1 hour resolution based on a winter load demand. The renewable-power-to-methane efficiency, is predicted to be 48% [14] using measured energy values for capture and concentration of CO_2 from air of 430 kJ/mol. [88].

The production of renewable electricity and renewable methane for power generation back up and use in the heat sector could be integrated with the synthesis of liquid fuels for use directly in transport. A schematic representation of such a system combining the power, heat, and transport sectors is shown in Fig. 11 where the renewable liquid

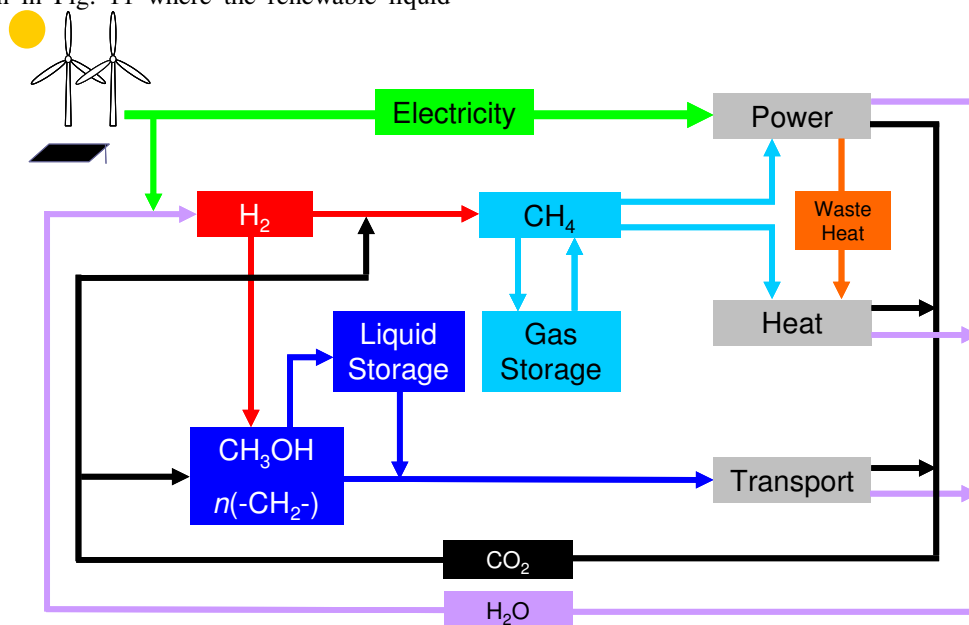


Fig. 11. Integrated power, heat, and transport system combining renewable methane and liquid fuels.

fuels are represented by methanol (CH_3OH) and drop-in hydrocarbon fuels ($n(-\text{CH}_2-)$). The production of liquid fuels also offers an energy storage option. The use of stored energy for transport via this route gives a similar efficiency to the 'round-trip' efficiency of producing renewable methane and reconverting it for use in charging electric vehicles but allows the use of significantly cheaper vehicles.

When electricity from wind and other renewables is less than the demand, renewable methane could be used for fuelling gas-fired power stations. Additional renewable methane could displace natural gas used for heating, so reducing the emissions of GHG [14]. However the electrolytic production of hydrogen and the synthesis of renewable methane and of Sustainable Organic Fuels for Transport (SOFT), together with the production of electricity in gas-fired power stations, would produce large amounts of reject heat. This could be used in district heating networks to displace much more natural gas. In developed countries, the final energy demand is about 20% electricity, 30% transport fuels and 50% heat while both fuel synthesis and power generation have efficiencies of about 50%. Assuming that half of the electricity is produced via renewable methane then the reject heat available would be about 30%, while the production of SOFT would also produce about 30%. So even with some losses, reject heat could meet all the demand for heat and, compared with using renewable methane, would reduce the input energy required for heat by about 50%. Thus the input energy for meeting all the final demands – the Primary Energy Factor - would be reduced from about 210% to about 110%.

VI. CONCLUSIONS

The fundamentals of physics and electrochemistry dictate that the energy densities of batteries and molecular hydrogen are 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. Additionally, there are many technical and logistical difficulties in using the batteries of electric vehicles as an integrated storage system.

The production of carbon-neutral liquid fuels is proposed as a route to the continued provision of compatible, affordable, and sustainable transport. This approach retains the use of low-cost internal combustion engines and liquid fuel systems. These powertrain systems have high power densities, energy storage densities, and low embedded manufacturing and materials extraction energies. They also have considerable potential for further efficiency improvement, especially using highly boosted small ('down-sized') engines exploiting the superior qualities of alcohol fuels.

The replacement of fossil fuels with carbon-neutral liquid fuels would not compromise current levels of mobility and would enable transport to remain globally compatible. Low-carbon number alcohols can be used for personal mobility and light-duty applications, and synthetic hydrocarbons for applications where maximum energy density is crucial. The technology to enable the transition from the current vehicle fleet to equivalent-cost vehicles capable of using sustainable methanol has been described. This takes the form of either tri-flex-fuel vehicles capable of running on any combination of gasoline, ethanol, or methanol, or current flex-fuel vehicles which can run on specific pre-blended mixtures of these three fuels. All transport energy can be supplied using biofuels up to the biomass limit, and beyond it using carbon-neutral liquid fuels made using renewable energy and CO₂ from the atmosphere. The role of biofuels in this transitional route and end-game prevents them being regarded as a dead-end by vehicle manufacturers.

In addition to minimizing the environmental impact of the rapid growth of transport-related CO₂ emissions, the use of atmospheric CO₂ and water as feed stocks for renewable energy carriers offers potential freedom from dependency on imported oil and a concomitant reduction in associated financial transfers.

A broader integrated system is proposed here where renewable energy is stored in the form of synthetic methane in the gas grid for supply to the power generation and heat sectors while carbon-neutral methanol and drop-in hydrocarbon fuels are supplied to the high-value transport fuel sector which is difficult to de-carbonize. The liquid fuels also

offer an energy storage option, increasing the flexibility of the system. In this scenario both the gaseous energy storage medium and the liquid fuel energy carriers are compatible with existing infrastructures, enabling a soft start to their adoption.

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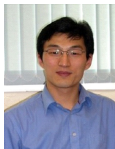


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