Oxygenated Transport Fuels from Carbon Dioxide

Driving towards Net Zero

Peter Styring*, George R. M. Dowson

UK Centre for Carbon Dioxide Utilisation, Department of Chemical & Biological Engineering, Sir Robert Hadfield Building, The University of Sheffield, Sheffield, S1 3JD, UK

*Email: p.styring@sheffield.ac.uk

The restructuring of the economy post-COVID-19 coupled to the drive towards Net Zero carbon dioxide emissions means we must rethink the way we use transport fuels. Fossil-carbon based fuels are ubiquitous in the transport sector, however there are alternative synthetic fuels that could be used as drop-in or replacement fuels. The main hurdles to achieving a transition to synthetic fuels are the limited availability of low-cost carbon dioxide at an appropriate purity, the availability of renewable hydrogen and, in the case of hydrocarbons, catalysts that are selective for small and particular chain lengths. In this paper we will consider some of the alternative fuels and methods that could reduce cost, both economically and environmentally. We recommend that increased effort in the rapid development of these fuels should be a priority in order to accelerate the possibility of achieving Net Zero without costly infrastructure changes. As ground transportation offers a more straightforward approach legislatively, we will look at oxygenated organic fuels as an alternative drop-in replacement for hydrocarbons.

Introduction

The concepts of carbon dioxide utilisation (CDU) and carbon capture and utilisation (CCU) are not new [1]. The first recorded example of a CCU process dates back to the 18th century when Joseph Priestly recorded the capture of 'fixed air' (CO_2) from Leeds Brewery 1768 [2]. The process was so successful that Priestly sold what would be now known as the intellectual property (IP) to Jacob Schweppe. To this day the Schweppes Tonic Water labels contain the strapline "creator of bubbles since 1783". Salicylic acid, a precursor to aspirin was first synthesised from CO_2 in 1898. However, it is the synthesis of urea fertiliser from CO_2 and ammonia (**Figure 1**) that highlights a major issue in CCU. If we look at the complete supply chain in reverse, we need ammonia to react with CO_2. The ammonia comes from the catalytic reduction of nitrogen using hydrogen, which typically comes from steam methane reforming (SMR). In the SMR reaction, methane reacts with water at high temperature and pressure, over a catalyst, to give hydrogen and CO_2 as shown in Equation (i):

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \text{(i)}$$

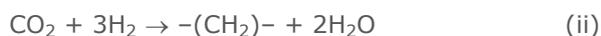Fig. 1. Synthesis of ammonia using Haber-Bosch and Bosch-Meisner chemistry

If we consider the synthesis of transport fuels from CO_2 then the same problem exists: we need hydrogen to reverse the combustion process. If we consider the synthesis of hydrocarbons (3) built from multiple methylene groups, then the stoichiometry is shown in Equation (ii):

$$CO_2 + 3H_2 \rightarrow -(CH_2)- + 2H_2O \qquad \text{(ii)}$$

As the chain length increases, so does the total hydrogen requirement and this also highlights another important issue. While three equivalents of hydrogen are required to reduce each CO_2 molecule, only one equivalent is incorporated in the fuels while two equivalents produce water. If we consider diesel to be $C_{18}H_{38}$, then a total of 55 equivalents of hydrogen are required for each diesel molecule, also resulting in 36 molecules of water being produced. While synthetic hydrocarbons will become an essential component in the transition of aviation jet fuel from fossil-based to synthetic (4), engines used in ground transportation are more tolerant to a more diverse range of chemical species and are less stringently legislated. Of particular interest are oxygenated fuels such as alcohols and ethers (5). As the energy of a fuel is directly related to the hydrogen content, and so for hydrocarbons the number of C–H bonds, addition of heteroatoms such as oxygen will result in a dilution of the energy density (**Table I**). However, there is a balance between the relative energy density and the number of carbons, and consequently hydrogen, in the fuel.

In this paper we consider the energy-carbon balance using methanol, butanol and oxymethylene ethers as exemplars. We consider the pros and cons and suggest avenues for future research where catalysis lies at the centre.

Oxygenated Synthetic Transport Fuels

Methanol Synthesis

The direct transformation of CO_2 to methanol requires the addition of three equivalents of hydrogen to generate methanol and water from CO_2. This can be performed at moderate temperatures and pressures (220–250°C and 10–30 bar) over heterogeneous metal oxide catalysts, particularly copper and zinc oxides with alumina (CZA, $Cu/ZnO/Al_2O_3$), which are based on catalysts that date back to the 1930s (8, 9). This process is now being carried out commercially by Carbon Recycling International, producing 4000 tonnes a year of sustainable methanol from Icelandic geological CO_2 and geothermal energy (10).

For this direct conversion, heterogeneous copper-based catalysts are the most extensively studied with catalyst performance thought to be generally dependent on the structure of the copper surface and also possibly the interface between the copper and the other transition metal components, most commonly zinc, zirconium or their oxides (11). Further weight is also given to the degree of dispersion of the copper within the catalyst structure, with increasing copper dispersion and thus copper surface area correlating directly with increased methanol yield (12).

Computational studies have suggested that CO_2 reactions on the stepped and close-packed Cu(211) representative surface gives the primary low-temperature reaction pathway *via* both formic acid and formaldehyde, the route *via* CO being an alternative and potentially competitive route (13). This CO, generated by the reverse water gas shift reaction (RWGS) can be problematic, particularly

Table I Specific Energy and Energy Density of Selected Fuels that are Derived from Fossil Oil or Can Be Synthesised from CO_2 or Other Waste or Bio-Based Carbon Sources (6, 7)			
Fuel	**Reference**	**Specific energy, MJ kg^{-1}**	**Energy density, MJ l^{-1}**
Heavy fuel oil	(6)	41.8	41.0
LPG	(7)	50.2	25.4
Diesel	(7)	45.6	38.6
Gasoline	(6)	46.4	34.2
Jet-A	(7)	46.4	36.7
Methanol	(6)	23.0	18.2
DME	(7)	31.7	21.0
Butanol	(6)	37.3	30.2

at higher temperatures, where excess carbon monoxide is generated from CO_2 and hydrogen (see **Figure 2**).

Both the CO and the byproduct water can limit the selectivity to and yield of the desired methanol product, especially where carbon monoxide side production increases and the RWGS reaction dominates (14). While the water that is inevitably generated while the reaction proceeds can sinter and degrade the catalyst alone, high CO and H_2 concentrations from the RWGS reaction have also been shown to overly reduce these copper surfaces, making sintering happen more easily (15, 16). Additionally, the excess CO production typically promotes hydrocarbon and also higher-alcohol generation *via* well-understood Fischer-Tropsch chemistry, further increasing hydrogen consumption and complicating product purification (17, 18). However, as discussed in the later section of this article, the production of higher alcohols and other products directly from CO_2 by taking advantage of the greater propensity for CO to form new C–C bonds on these catalyst surfaces might be a way to generate CO_2 fuels more effectively than individual production of methanol and then carrying out subsequent dimethyl ether (DME), methanol to gasoline (MTG) or methanol to olefins (MTO) processes, thereby avoiding multiple individual processes (19).

One method used to avoid CO production and to generally promote milder reaction conditions is the use of precious metal catalysts such as palladium or platinum instead of, or in addition to, the traditional copper as these help to reduce the required temperature for the reaction and therefore increases reaction selectivity as the RWGS reaction is less favourable (20, 21). In addition, these catalysts can promote the hydrogenation of any CO to methanol, further reducing the $CO:CO_2$ ratio within the reaction mixture (22). However, these catalysts typically show poor CO_2 conversion, thought to be due to the lower strength of the bonding between the CO_2 and metal surface (23). Yet another approach is to use copper encapsulated in metal organic framework (MOF) catalysts which further promote the exclusion of water from the catalyst surface, increasing the catalyst turnover number. The frameworks can also increase the effective surface area of the active copper species by limiting the growth of the metal surface, a result that can also be achieved by using a hydrotalcite-like compound as the catalyst precursor (24).

For the indirect production of methanol, the RWGS reaction can alternatively be harnessed to generate CO as an intermediate that can then be used to create a sustainable synthesis gas (syngas). This syngas can then be used for methanol production separately. Using CO in this way has the benefit of very high selectivity (over 99.5%) and high yield, facilitated by the absence of water byproduction (which in this case would be removed during CO formation) and the fact that CO is a more reactive starting material than CO_2 (25). In some cases, when producing methanol from CO, the product methanol solution could even be used for further product generation without additional purification or drying (26). It is due to these advantages that general industrial (non-sustainable) methanol production typically uses this syngas route, and it supplies the overwhelming majority of the global methanol demand, which was 83 million tonnes in 2019 (27). The routes for creating the CO starting material from CO_2 are numerous, including classic hydrogenation (RWGS), disproportionation
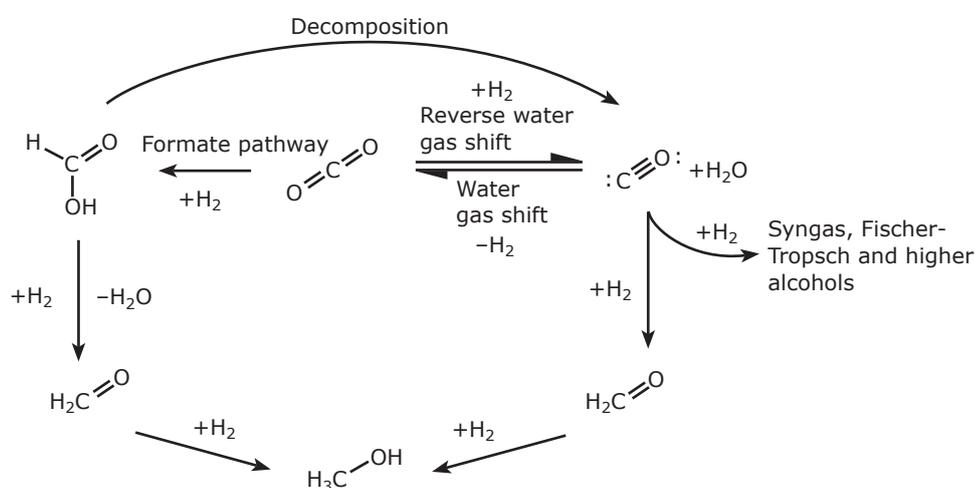

Fig. 2. A generalised scheme showing the various routes for production of methanol from CO_2

reactions with biochar (where elemental carbon reacts with carbon dioxide to form two equivalents of CO), electrochemical and even plasmolytic routes (28–31).

Butanol Synthesis

Compared with methanol, producing the four-carbon chain butanol from CO_2 is a far more challenging synthesis. However, butanol is a valuable potential 'drop-in' replacement for petrol as a liquid transport fuel and is compatible with existing fuel infrastructures. It can even be used alone as fuel for unmodified vehicles, with an octane number of 96 (32). It is hydrophobic enough to prevent water and salt corrosion in modern engines, which is a major drawback when using high ethanol content in road vehicle fuel in much of the world (33). Butanol in standard petrol engines has also been shown to have similar or even superior fuel economy than the petrol it replaces, despite having approximately 11% less energy density. This is due to its nature as a single-component fuel, rather than the wildly diverse mixture of compounds that make up fossil fuels, with the entirety of the fuel burning at the optimum rate. Unlike both methanol and ethanol, butanol can also be blended with aviation fuels in limited amounts and its corresponding diester, butyl butyrate, shows good compatibility with aviation kerosene (34). This may be crucial for decarbonisation of the aviation industry as major industrial nations move towards net zero CO_2 emissions in the coming decades.

While there are biological routes for the creation of sustainable butanol from carbon dioxide, particularly acetone–butanol–ethanol (ABE) fermentation, separation of low-concentration butanol from water is challenging due to the low volatility of the butanol and the fact that high concentrations of butanol are toxic to microorganisms, limiting the extent of the fermentation for butanol synthesis (35). One method to avoid these issues is to instead dimerise easily manufactured bioethanol *via* borrowed hydrogen or Guerbet chemistry (36) (see **Figure 3**).

As with the biological routes above, most potential methods to synthesise butanol from CO_2 will similarly involve a multistep process. For example, the Guerbet route could also be appropriate for a CO_2 to fuels approach, by first carrying out the conversion of CO_2 to ethanol and then using the ethanol as a feedstock for the generation of butanol or other higher alcohols. This can be carried out using conventional transition metal catalysis, with
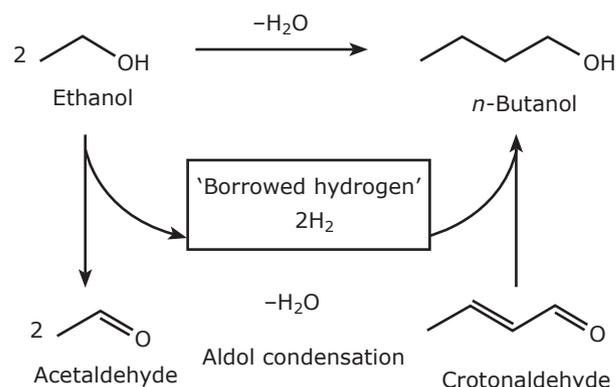

Fig. 3. Scheme showing borrowed hydrogen/ Guerbet condensation of ethanol to produce butanol (higher alcohols can also be produced by further condensation of butanol)

reduction being combined with methylation of the absorbed and partially reduced CO_2 to generate the C_2 alcohol. The chemical stability of ethanol, a quirk of its structure, allows this process to be carried out under surprisingly mild conditions and with high selectivity. Catalysts that have shown good activity have included palladium-copper nanoparticles and cobalt-alumina catalysts, both have been able to produce ethanol at over 90% selectivity under 200°C, with the palladium-copper nanoparticles achieving production of over 100 mmol ethanol per gram catalyst per hour (37). Interestingly however, the cobalt-alumina catalysts, while less active for ethanol production, showed trace production of butanol directly, suggesting that a direct conversion of CO_2 to butanol may be possible with the development of the right catalyst and conditions (38).

CO_2-to-ethanol has also been carried out using both atomically divided copper and traditional Cu/ ZnO/Al_2O_3 catalysts, used for methanol synthesis, with electrochemical or plasma assistance. The former has recently been carried out with a Faradaic efficiency of over 90% at –0.7V, although both routes showed very low turnover rates (39, 40). Once again, the fact that butanol has also recently been generated directly from CO_2 by copper electrocatalysis in low yield is worthy of note: in this case, it is thought that the acetaldehyde intermediate has undergone *in situ* condensation, as found in Guerbet chemistry (41).

An alternative method to convert CO_2 to butanol, using Grignard chemistry, has been demonstrated by the authors (**Figure 4**). First methylmagnesium bromide is synthesised, which can be generated
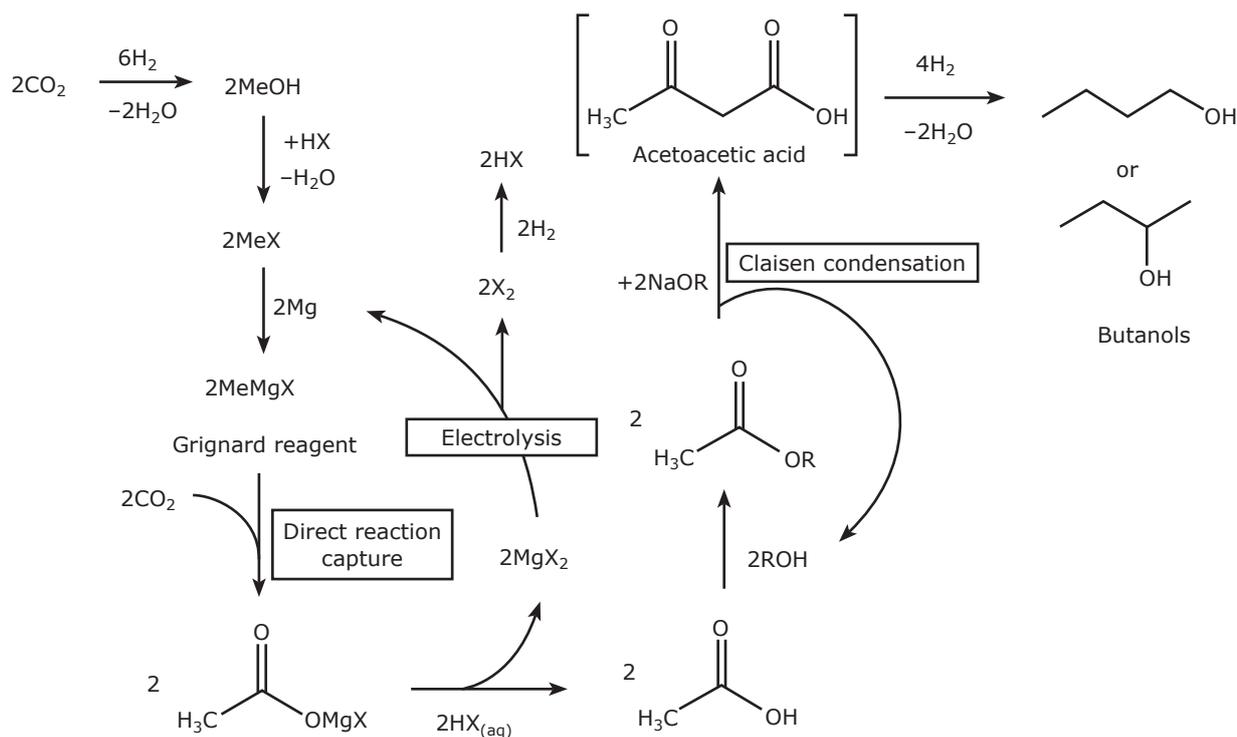
Fig. 4. A CO_2 to butanol route involving Grignard chemistry (with the Grignard generated from CO_2 methanol) and Claisen condensation and subsequent hydrogenation of the Grignard product to produce butanol from CO_2 and H_2 with all other components regenerated by electrolysis

by the reaction of methyl bromide, produced from CO_2-derived methanol, with magnesium. This then can be reacted with dilute gas phase CO_2 at room temperature and atmospheric pressure to generate acetic acid, thus incorporating the CO_2 capture process itself into the fuel generation. This acetic acid was then dimerised *via* Claisen condensation and reduced using copper on zinc oxide and hydrogen to form a mixture of alcohols including butanol. In principle the magnesium halide byproduct could then be recycled by high efficiency electrolysis, also allowing for the creation of further methyl halide and an overall electrosynthesis-by-proxy route (42). The magnesium can be regenerated in existing electrolysis processes and returned to the process, an example of stoichiometric metal looping. As the electrolysis process is routinely used to produce magnesium from sea water, additional magnesium halide in the process will increase the efficiency of the metal production.

As a nascent part of the CO_2-to-fuels research field, other routes could yet be discovered. Some of these routes could include a selective MTO process to produce either butenes or ethylene from CO_2-derived methanol. After dimerisation (if ethylene is used) the resulting butenes can be simply hydrated

to produce (primarily) 2-butanol, which is the main industrial manufacturing method for 2-butanol, and also the preferred butanol isomer for transport fuels (43). Finally, butanol can be synthesised directly from sustainable synthesis gas by Cr/ZnO catalysts, although as might be anticipated, selectivity and yield to butanol by this route has so far been low (44).

Dimethyl Ether and Oxymethylene Ethers

Synthetic transport fuels will be in increasing demand as fossil-based fuels are phased out. The initial focus in this paper has been on methanol, however internal combustion engines need to be modified because of the corrosivity of high concentration methanol fuels (these are generally limited to below 18% of the fuel as a consequence) as discussed previously. Drop-in hydrocarbons such as synthetic diesel and kerosene have been developed, however these are expensive approaches and require considerable quantities of dihydrogen as a major byproduct of the reduction process is water. Recent developments have focused on DME, formed by the condensation
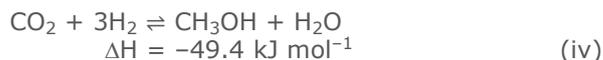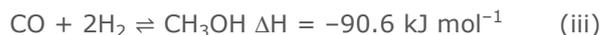
of CO_2-derived methanol (45). Indeed, Volvo (46) and Ford (47) trucks in North America have developed DME vehicles that have been deployed in commercial environments. DME has a lower energy density than diesel but, unlike lower alcohols, is a direct drop-in fuel at 100% concentration. As it contains no C–C bonds it has much lower (approaching zero) particulate emissions than diesel (5) and as it is not fossil-derived it has no SO_x emissions. DME (CH_3OCH_3) has less hydrogen than diesel ($C_{18}H_{38}$) and so becomes a more economical proposition as less dihydrogen needs to be produced in order to reduce the CO_2. One major challenge will be to produce DME in a single-step process from CO_2 and dihydrogen, or preferably water. Photocatalysis may offer a viable route to achieve this sustainably.

In many countries, governments are proposing a transition to electric vehicles (EVs) as a means to defossilise road transport. However, while there are advantages such as zero tailpipe greenhouse gas emissions, there are also many problems. For a true picture of environmental impact, comparative 'well to wheel' and 'weather to wheel' technologies should be compared and the latter should be based solely on low carbon energy as a changing grid mix will lead to different carbon intensities (48) with the actual emissions being transferred to point source emitters; power stations. Furthermore, we will need fuels that are compatible with existing internal combustion (IC) engines for the foreseeable future if we wish to avoid the risk of creating a social transport underclass; restricting the use of older spark injection (SI) and compression injection (CI) vehicles.

Ford in Aachen, Germany announced the world's first original equipment manufacturer (OEM)-built DME passenger vehicle, a Ford Mondeo, at the DME Sustainable Mobility Workshop at Landesvertretung NRW in Berlin in 2019 (49). Ford has claimed that the well-to-wheel CO_2 emissions for a DME powered CI engine could be as low as 5 g km^{-1}, compared to a conventional diesel fuel value of 116 g km^{-1} (4). A technoeconomic analysis (TEA) of DME derived from CO_2 has shown that DME can be produced at a 740 tonnes per day scale with a minimum selling price of €2193 per tonne, which compares well with fossil-derived DME of around US\$3000 per tonne (50).

Conventional DME synthesis relies on the formation of methanol from natural gas or syngas, the latter being an exothermic process as shown in Equation (iii). Direct hydrogenation (Equations (iv) and (v)) can also be achieved catalytically as discussed previously, with the enthalpy of reaction being less than that of CO.

$$CO + 2H_2 \rightleftharpoons CH_3OH \ \Delta H = -90.6 \ \text{kJ mol}^{-1} \quad \text{(iii)}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$
$$\Delta H = -49.4 \ \text{kJ mol}^{-1} \quad \text{(iv)}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \ \Delta H = +41.2 \ \text{kJ mol}^{-1} \quad \text{(v)}$$

Acid catalysed dehydration in the condensation of two molecules of methanol gives DME in an exothermic reaction (Equation (vi)). In order for this be considered a sustainable process, the methanol should be produced from captured CO_2 or from biogenic methanol. Both of these approaches have been applied to the commercial synthesis of DME by Oberon Fuels (51). The provenance of the supply has led to the DME gaining Renewable Fuel Standard approval from the US Environmental Protection Agency.

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$
$$\Delta H = -23.4 \ \text{kJ mol}^{-1} \quad \text{(vi)}$$
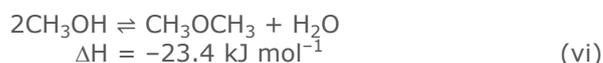
Recently, considerable effort has been directed to the direct synthesis of DME from captured CO_2 and hydrogen (Equation (vii)). The advantages include a single process operation and a highly exothermic reaction. However, there is still an issue that of the six equivalents of hydrogen consumed, half end up in the water byproduct.

$$2CO_2 + 6H_2 \rightleftharpoons CH_3OCH_3 + 3H_2O$$
$$\Delta H = -122.2 \ \text{kJ mol}^{-1} \quad \text{(vii)}$$
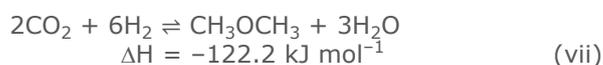
It has been shown that DME can be produced by the direct reduction of CO_2, however a more exothermic process is the direct hydrogenation of CO in the form of syngas in a 1:1 stoichiometry (Equation (viii)) (52, 53).

$$3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2$$
$$\Delta H = -244.9 \ \text{kJ mol}^{-1} \quad \text{(viii)}$$
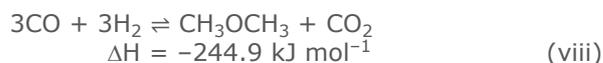
A benefit of this process is that all the hydrogen is retained in the DME product, however the byproduct is one equivalent of CO_2. There is of course the opportunity to separate the CO_2 and feed it into a second reactor to produce more DME using the processes described in the following discussions. This offers an opportunity to utilise waste gases from iron and steel industries which contain high concentrations of CO and CO_2 as well as hydrogen in the furnace off-gas (54).

Bifunctional catalysts, such as Cu-In-Zr-O with SAPO-34 zeolite (CIZO-SAPO) have been reported (55) for the direct conversion of CO_2 to

DME at 250°C and 30 bar. While the selectivity to DME is good (64%) the conversion of CO_2 is disappointing at 4.2%.

Polierer *et al.* (56) have reported a direct synthesis of DME from CO_2 using a mixed catalyst system based on $Cu/ZnO/ZrO_2$ produced by continuous precipitation. The catalyst combines methanol synthesis with subsequent dehydration using CO/CO_2 mixtures at 230°C and 50 bar. DME synthesis was enhanced when CO_2-rich gas feeds were used.

The use of a hybrid $Cu/ZnO/ZrO_2$-ferrite (CZZ(C)-FER) catalyst to produce DME directly from CO_2 has been reported (57). A mechanism was proposed in which hydrogen is adsorbed onto the copper atom and CO_2 onto the Zn-Zr-FER surface. Formation of formate on the surface is achieved by hydrogen transfer which then undergoes dehydration through further hydrogen transfer to give the surface bound methoxide. Two methoxides then combine to give DME, completing the dehydration step.

Modak *et al.* (58) have recently reviewed the catalytic reduction of CO_2 to give amongst other things methanol and DME and have included the use of hydrides and carbon instead of hydrogen as the reducing agent. An optimised reactor has been used for the direct synthesis of DME from CO_2 (59) using $CuO/ZnO/Al_2O_3$ and γ-Al_2O_3 as the catalyst system.

In common with many reports, Kornas *et al.* (60) have reported the Cu-ZrO_2 system as an active catalyst for DME direct synthesis from CO_2, modified using a heteropolyacid, montmorillonite K10 as the acidic motif.

The energy density (MJ l^{-1}) of DME is only 54% that of diesel, and 60% of its specific energy (MJ kg^{-1}). However, it also contains significantly less carbon and so when it burns in air or oxygen it follows the following stoichiometric reaction, Equation (ix):

$$C_2H_6O + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad (ix)$$
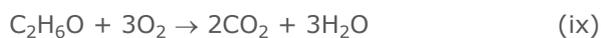
By contrast, the combustion of diesel can be generalised as follows, Equation (x):

$$C_{18}H_{38} + 27\tfrac{1}{2}O_2 \rightarrow 18CO_2 + 19H_2O \qquad (x)$$

It has been shown that despite the lower energy density and specific energy, in a conventional compression engine, DME demonstrates lower well-to-wheel emissions when compared to fossil-oil derived diesel (61).

DME is a gas under ambient conditions so needs to be stored under slightly pressurised conditions (5.1 bar at 20°C), but considerably lower than the pressures required for hydrogen. In the vehicle, the DME must be pressurised to 12–30 bar to ensure the material is in the liquid phase (62). Oxymethylene ethers (OME_x) may ultimately be a better option as those with more than three carbons (OME_1 and higher) are liquids that can be stored in conventional tanks. However, the emissions reductions decrease as the value of x increases as while the density becomes similar to diesel the energy density does not increase proportionately. Furthermore, as x increases so do the production costs.

A one-pot synthesis of OME_1 by hydrogenation of CO_2 in methanol using a 3% ruthenium catalyst over the high silica zeolite BEA has been reported (63) to give good selectivity at 150°C (Equation (xi)). A mechanistic study also suggests that the reaction proceeds *via* a bound formate species.

$$CO_{2(MeOH)} + 2H_{2(MeOH)} + 2CH_3OH_{(l)}$$
$$\rightleftharpoons CH_3OCH_2OCH_{3(l)} + 2H_2O_{(l)} \qquad (xi)$$
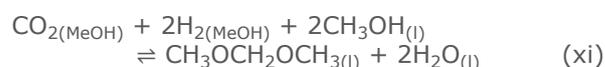
Conclusions

While there is a drive towards electrification of the road transport system, there will still be a need for fuels to power internal combustion engines for the foreseeable future. This is because there will still be legacy vehicles in use if a social underclass is to be avoided and also where high energy density is required, for example in long-distance road haulage. While there has been considerable acceleration in synthetic hydrocarbon production, there is also an emerging market for oxygenated fuels with lower emissions. These include methanol, butanol and methylene ethers such as DME and OME_x. Of these, perhaps the greatest promise is shown for DME due to soot emissions approaching zero and reduced well-to-wheel CO_2 emissions even when compared to EVs depending on the source of the electricity. The challenge lies in the synthesis of methylene ethers through selective oligomerisation (64) and directly for CO_2 using mild reaction conditions and catalysts based on sustainable elements, such as iron, nickel and copper. There also needs to be policy interventions to aid the transition from fossil-based fuels to synthetic carbon-based fuels while servicing existing engine architectures until a new vehicle norm is established.

The challenge is truly interdisciplinary taking expertise from chemistry, engineering and the social sciences. The transition will also need sustainable finance in order to accelerate deployment. However, perhaps the greatest need is for a high level of creative thinking to allow paradigm

shifts in technology rather than slow incremental development. Whatever happens, catalysis will be at the centre of these activities.

A range of methodologies have been discussed for the production of oxygenated synthetic transport fuels. Each is at a different level of maturity or technology readiness level (TRL). These range from the synthesis of butanol from Grignard agents (TRL3) to the commercial production of DME (TRL9) which is being deployed at scale through a recent marketing opportunity between Oberon Fuels and Suburban Propane in the USA. It is important that the environmental sustainability of the new materials is fully evaluated using robust and open life cycle assessment (LCA), however this should be carried out in the context of TEA so that the commercial viability of the process is also considered. Readers are therefore recommended to consider recent publications that highlight the need for harmonisation of such approaches with respect to carbon dioxide utilisation technologies (50, 56, 65, 66).

Acknowledgements

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The Authors

Peter Styring is Professor of Chemical Engineering & Chemistry at The University of Sheffield, UK. He is a former Head of the Chemistry Department. His expertise lies in carbon dioxide capture and utilisation with particular interests in catalysis and the production of low-carbon synthetic transport fuels and fertilisers.

George Dowson is a Postdoctoral Research Associate in the Styring Group at The University of Sheffield. His expertise lies in catalysis, novel carbon capture approaches and creation of sustainable synthetic fuels.