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Synthetic Fuels Based on Dimethyl Ether as a Future Non-Fossil Fuel for Road Transport From Sustainable Feedstocks

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In this review we consider the important future of the synthetic fuel, dimethyl ether (DME). We compare DME to two alternatives [oxymethylene ether (OME_x) and synthetic diesel through Fischer-Tropsch (FT) reactions]. Finally, we explore a range of methodologies and processes for the synthesis of DME.

DME is an alternative diesel fuel for use in compression ignition (CI) engines and may be produced from a range of waste feedstocks, thereby avoiding new fossil carbon from entering the supply chain. DME is characterised by low CO₂, low NO_x and low particulate matter (PM) emissions. Its high cetane number means it can be used in CI engines with minimal modifications. The key to creating a circular fuels economy is integrating multiple waste streams into an economically and environmentally sustainable supply chain. Therefore, we also consider the availability and nature of low-carbon fuels and hydrogen production. Reliable carbon dioxide sources are also essential if CO₂ utilisation processes are to become commercially viable. The location of DME plants will depend on the local ecosystems and ideally should be co-located on or near waste emitters and low-carbon energy sources. Alternative liquid fuels are considered interesting in the medium term, while renewable electricity and hydrogen are considered as reliable long-term solutions for the future transport sector. DME may be considered as a circular hydrogen carrier which will also be able to store energy for use at times of low renewable power generation.

The chemistry of the individual steps within the supply chain is generally well known and usually relies on the use of cheap and Earth-abundant metal catalysts. The thermodynamics of these processes are also well-characterised. So overcoming the challenge now relies on the expertise of chemical engineers to put the fundamentals into commercial practice. It is important that a whole systems approach is adopted as interventions can have detrimental unintended consequences unless close monitoring is applied. This review shows that while DME production has been achieved and shows great promise, there is considerable effort needed if we are to reach true net zero emissions in the transport sector, particularly long-haul road use, in the require timescales.

Keywords: dimethyl ether, diesel, net zero carbon, de-fossilise, synthetic fuel, e-fuels

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INTRODUCTION

The drive towards 'net zero' policies in the United Kingdom, and indeed globally, has led to a re-evaluation of energy policies. While the obvious sectors needed to maximise emissions reductions are electricity and heating, a considerable quantity of energy is consumed by the transportation sector, including road, rail, aviation and maritime. The urgent need to decarbonise, or more correctly, de-fossilise, the transport sector is a huge challenge. Internal combustion engines (ICEs) have been developed and optimised over many decades and represent the most abundant form of mobility powertrains. While there has been a governmental drive in the United Kingdom to replace ICEs with electric vehicles (EVs), a recent report by the Royal Society (Royal Society, 2019) has also considered policies surrounding a migration to synthetic transport fuels. The reason is partly because a transition to an EV infrastructure would require a complete overhaul of the electricity supply chain and economics. While plug-in battery electric vehicles (BEVs) provide zero tailpipe emissions, the energy required to power them needs to be generated elsewhere.

In the current electrical energy grid mix the amount of renewable power available is dependent on many factors including weather and demand. In the United Kingdom, low carbon energy (including nuclear) accounts for 55% of the electricity generated on average across a year (2019 figures, UK Department for Business, Energy and Industrial Strategy, 2020). This means that nearly half of the electricity remains fossil-derived and so the emissions for BEVs are deferred to the power generator. Therefore, BEVs cannot truly be considered as zero-emissions vehicles if a complete life cycle is carried out to include deferred electricity generation within the system boundaries. Furthermore, it is also necessary to include the battery manufacture and disposal of end-of-life units in the environmental analyses (Wang and Yu, 2021).

In a transition to net zero emissions, due to the economic inertia of the existing supply infrastructure and logistics, it is well-worth considering a graduated transition rather than attempting a step change. For example, in compression ignition vehicles (CIVs) such as diesel, it is not the engine that is the problem but the fuels. Rather than significantly redesigning the engine, can we instead redesign the fuels? In the case of diesel replacement, one fuel that is attracting considerable attention is dimethyl ether (DME) and the family of oxymethylene ethers (OME_x) where DME is equivalent to OME₀ and x is the number of additional oxymethylene units (-CH₂-O-) within the molecule. Alternative liquid fuels are interesting in the medium term, while renewable electricity and hydrogen are considered as reliable long-term solutions for the future transport sector. DME may be considered as a circular hydrogen carrier which will also be able to store energy for use at times of low renewable power generation.

Work by Willems at Ford has shown that in engine tests, not only is there zero SO_x emissions associated with DME fuels (because the fuel is not fossil-derived) but due to the reduced carbon content in the molecules compared to diesel, CO₂ emissions can be as low as 3 g/km, compared to EU 2020 standard diesel car emissions of 95 g/km (European Council

directive, 443/2009; European Council directive, 443/2009). Furthermore, as less air is needed and the flame temperature is lower there are practically zero NO_x emissions, and because there are no C-C bonds in the ether molecules particulate matter (PM or soot) is also practically zero (Lee et al., 2016). Therefore, compared to current electricity grid mixes and emissions in power generation for EVs, the full scope life cycle emissions for DME-CIVs could be considerably lower.

We recently published a review on the synthesis of oxygenated transport fuels from carbon dioxide (Styring and Dowson, 2021), including DME which prompted us to consider expanding the range of feedstocks to include other materials considered to be waste. Unilever have recently announced their ambitions to remove fossil-based carbon materials from their supply chain by using waste materials described by Unilever as a 'Carbon Rainbow' (Unilever, 2020). This includes 'Purple' carbon (CO₂), 'Green' carbons (bio-based), 'Blue' carbons (marine based) and 'Grey' carbons (general waste including plastics). Using these principles, we present an up-to-date analysis of routes to DME/OME_x using waste feedstocks to eliminate fossil-carbon from the fuels supply chain.

This paper aims to show that DME is a useful mobility fuel that can be used as a diesel drop-in fuel that requires only slight modifications to existing combustion engines. This will allow low-emissions fuels to be used in legacy combustion engines while the industry and society transitions to electric vehicles in the mid- to long-term. Comparisons are made to FT and OME ethers which may also be used as drop-in fuels. We consider the technology available, and the feedstocks needed to assure a just and economically viable move to synthetic fuels.

CARBON NEUTRAL FUELLING OPTIONS

Carbon neutrality, or the aim to reach a net zero state, refers to the balance between reducing carbon dioxide emissions as far as possible and removing the remaining of carbon dioxide from the atmosphere. The European Union has committed to climate neutrality by 2050 which includes the goal of being a society with net-zero greenhouse gases. This commitment is also in line with the legally binding Paris agreement as signed by 190 parties (United Nations, 2015).

Transport is fundamental to modern living and is a key stimulator for societal improvement and economic growth. However, the negative externalities surrounding the emissions caused by transport indicate that it is a key sector for improvement to reach a net zero state.

In order to create carbon neutral transport, a multitude of options need to be considered for the many different forms of transport. The breakdown of global CO₂ emissions per transport division can be seen in **Figure 1** (Our World in Data, 2020).

Some transport sectors have already been optimised to reduce CO₂ emissions. For example, the majority of passenger rail links across the globe have been, or are in the process of being, electrified (IEA, 2019). Thus, rail emissions only contribute to 1% of the global CO₂ emissions from transport (Our World in Data, 2020).

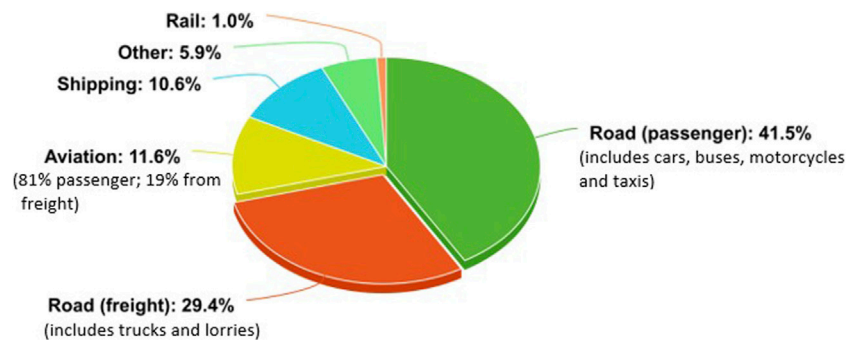


FIGURE 1 | Breakdown of global CO₂ emissions per transport division.

When looking at electrification and carbon neutrality, again it is important to recognise that in order to be truly carbon neutral the electricity source must also be made in a carbon sustainable manner. Carbon sustainable electricity sources include renewables such as energy retrieved from solar and wind farms, or energy options from sources such as nuclear which has a negligible direct production of CO₂ (IEA, 2020a). Concentrating on road transport which dominates an estimated 71% of the transport CO₂ emissions, there are two key sectors, passenger and freight. In order to reach net zero, carbon neutral fuel options need to be considered and implemented in both these sectors. However, the same methods can not necessarily be used for each sector, due to their different working requirements.

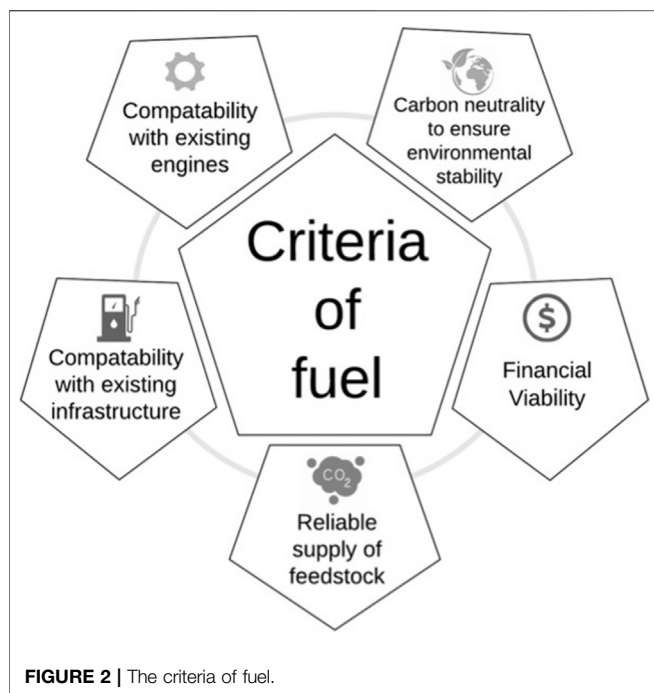
The main driving force in United Kingdom passenger transport is the electrification of the vehicle fleet, with the United Kingdom government promising to ban the sale of new combustion-engine vehicles by 2030 (Johnson, 2020). This United Kingdom policy however does not cover freight and heavy goods vehicles (HGVs) as there are many issues surrounding their electrification. The barriers that would need to be overcome by an advance in battery technology in order to electrify the HGV fleet include the long charging time and limited driving range of existing batteries. An increase in the size of the battery to solve these problems, rather than an increase in efficiency, would lead to the weight and size of the battery being too much to make it a viable and cost-effective option (Sia Partners, 2016). Current research on using BEVs to support large heavy goods vehicles over 15 tonnes, shows low feasibility for a conventional vehicle configuration due to their increased loads and the longer trip distances required. The possibility of BEVs supporting lighter medium goods vehicles (3.5–7.5 tonnes) and smaller heavy goods vehicles (7.5–15 tonnes) would require multiple charging events a day which would decrease sector efficiency and require a massive infrastructure change (Forrest et al., 2020). While fast charging of large battery-powered goods vehicles may be possible in principle, this will require enormous electrical power availability at major recharging stations (such as motorway services), especially when multiple heavy goods vehicles will need to be charged simultaneously. We have calculated that to allow fast charging (1 h charge) of upcoming battery goods vehicles such as the Freightliner eCascadia or the

Tesla Semi (long range), power supplies between 0.56–0.68 and 1.12–1.36 megawatts per vehicle respectively would need to be made available at recharging stations. This is based on battery sizes of 500 and 1,000 kWh in these vehicles and a 64–88% charging efficiency (Apostolaki-Isofidou et al., 2017), which may be lower when fast charging such large batteries (Michaelides, 2020). Note that a single full charge of the larger battery, enough for a truck to drive for a full 9-hour day (approximately 500 miles), requires around a third of the electricity the average United Kingdom household will use in a year (O'Mahoney, 2020). Indeed, the scale of challenges facing electrification of larger heavy goods vehicles by using batteries has promoted the alternative concept of electrification by use of overhead cables and cabin-mounted pantographs in the United Kingdom and abroad (Ainalis et al., 2020), eliminating much of the battery weight.

Other on-board storage strategies include hydrogen fuel cell technology. However, there is still a lack of the technology and supply infrastructure that would be required to allow for widespread adoption of this technology. Depending on the production method used, the cost of producing hydrogen is up to seven times more than that of petrol and diesel (Abbasi and Abbasi, 2011). Furthermore, introducing hydrogen fuel cell technology would also require a mass investment in and restructure of fuelling infrastructure due to the necessity for new fuelling stations and pipelines (Popov et al., 2018).

As alternative on-board power sources (such as hydrogen fuel cell technology) require entirely new fleets of vehicles together with significant and very costly infrastructure changes, there is a gap in the market for synthetic fuels or biofuels, particularly those which can be fed into the existing supply infrastructure. Furthermore, synthetic fuels such as DME are circular hydrogen carriers and utilise hydrogen as a method of storing energy in a vector form that can be transported and stored with more ease and safety than using hydrogen as the singular fuel source (Catizzone et al., 2021).

Biofuels are fossil replacement transport fuels made directly from biomass, instead of from fossil-based carbon sources. The most widely used biofuels for transport are bioethanol and biodiesel. Bioethanol can be produced from first generation feedstock e.g. sugarcane as well as second generation feedstock such as lignocellulose. The complexity of the process increases



CRITERIA OF THE FUEL

For a synthetic liquid fuel to be the best option to move freight vehicles to a carbon neutral transport source, it needs to fulfil the ‘fuel criteria’. This includes the environmental cost, referring primarily to whether it can be made sustainably in order to make it carbon neutral, but also other environmental factors (such as resource depletion, water use and generation of other pollutants) which must be considered in detailed life cycle assessment. It also refers to whether the fuel itself can be made in a financially viable manner so that the industry can continue to work profitably without continued reliance on substantial government subsidies. Additional criteria include the supply and scope of the new fuel and the reliability of supply. Compatibility with the existing global infrastructure and combustion engines is also essential. Finally, it would be advantageous if it were possible to mix the new fuel with existing fuels. This would allow immediate introduction of the new fuel and therefore an immediate transition towards carbon neutrality. This has the added advantage that it would either comply with existing legislation or fall within the scope of realistically foreseeable future legislation. These criteria are illustrated in **Figure 2**.

Synthetic liquid fuels in this setting work from the principle of defossilisation rather than decarbonisation. This is due to the fuel still being a carbon combustion source. The feedstock material being captured carbon dioxide which is utilised (CCU) or other sustainable carbon resource to synthesise the fuels (Global Alliance Powerfuels, 2020). Defossilisation acknowledges that it is not just carbon atoms being present in the atmosphere which cause dangerous climate change but rather the increase in the overall concentration of the carbon atoms. Thus, it is the carbon atoms derived from fossil sources that need to be prevented from reaching the atmosphere (ETIP PV, 2020). Although during the use phase of using synthetic liquid fuels carbon will be a factored emission in such forms as CO₂ and lesser so carbon particulates within the life cycle of the fuel, the circular nature of CO₂ being both the initial feedstock and final product in the forms of emissions, leads the fuel to have similar inclusive carbon emissions as carbon free fuels such as hydrogen and ammonia. This minimises the environmental concerns. Further environmental concerns coming from conventional fuels can also be diminished. This is because certain liquid synthetic fuels can reduce other emissions such as NO_x, whereas carbon-free fuels currently being researched in a dual-fuel capacity show high NO_x emissions and unburnt ammonia due to the fuel-bound nitrogen (Dimitriou and Javaid, 2020).

In order to maintain a carbon neutral fuel source, the carbon atoms that are taken away from the atmosphere in the form of the material feedstock need to be equal in number to the carbon atoms released when the fuel is burnt, with no additional fossil carbon used. Subsequently, the energy-intensive processes of synthesising the fuels need to be powered by renewable energy sources, such as wind, solar and hydro. Nuclear fuel, although not considered renewable, is a low-carbon source of energy suitable for clean electricity provision for the production of synthetic fuels. It should also be noted that recent research considered extracting uranium from seawater, making nuclear power a

as you go from 1st → 2nd → 3rd generation, however the movement away from 1st generation feedstock avoids a key barrier for the production of biofuels, namely the food vs fuel argument (Prasad and Ingle, 2019). Biodiesel manufactured mainly in the EU is produced by the transesterification and esterification of vegetable oils or animal fats with alcohols such as methanol (Brito Cruz et al., 2014). Although regarded as one of the most viable options for the reduction of CO₂ in transport, biofuels only acquired around a 3% share of total global transport fuel demand in 2018 (IEA, 2020b) due to limitations such as raw material supply insufficiency, the low mitigation of CO₂ and low-cost competitiveness (Oh et al., 2018). In order for biofuels to cope with the increasing demand for carbon neutral fuelling options, development in advanced biofuels using inedible biomass looks to be a promising solution.

It is clear that there is no single “silver bullet” solution to decarbonisation of existing transport modes, including long haul transport, aviation and maritime transport, that does not, in turn, have further issues in terms of either public or private financing, raw material availability or technology readiness. While conventional fossil diesel fuel may be eventually banned, starting with the elimination of new diesel passenger vehicles in the United Kingdom in 2030 (Johnson, 2020), engines that currently burn diesel and kerosene are still very likely to be used and needed much further into the future. Indeed, the legacy vehicles purchased before 2030 will still require fuels until they reach their end of life. While this could be fossil-based petrol and diesel, there is an opportunity to introduce alternative fossil-free fuels such as DME to accelerate the de-fossilisation of the passenger transport fleet while EVs become more established.

significantly more sustainable and egalitarian energy source (Parker et al., 2018). It has also been suggested that as there is growing demand for renewable energy sources and as the sources are not always constant, the use of excess-energy during low periods of demand can be used to produce synthetic fuels (Luo et al., 2015) rather than being “wasted” by curtailment. In this way the liquid fuels acts as an energy vector that can be stored using existing facilities and infrastructure. This could boost the financial value of the renewable energy source. To determine and demonstrate the true carbon neutrality of a fuel an environmental lifecycle assessment can be used (Zimmermann et al., 2020).

A viable synthetic fuel also needs to a financially sound investment. Here, the variables that contribute into the cost of the fuel are the feedstock materials, production costs and the fuel-to-vehicle transport, otherwise known as the fuelling infrastructure. As previously mentioned, for a synthetic liquid fuel to be financially viable in comparison to other fuelling methods, one main component is that the fuel would be compatible with current pipelines, infrastructure and combustion engines (Willems, 2018).

To be financially viable, the synthesis route also needs to be cost-effective. This may differ depending on the country in which country the fuel is produced. For example, the cost of producing electricity in France is low due to the high use of low-cost nuclear energy sources (Nuclear Power in France | French Nuclear Energy - World-nuclear.org, 2020). If the low cost of nuclear electricity production could be exploited, it could be more realistic for France to use the energy intensive hydrolysis method of hydrogen production. The specific route for the generation of the fuel from sustainable carbon and how that carbon is acquired or captured will be compared in a later section.

Finally, to be the answer to the carbon neutral fuelling crisis, ideally the synthetic fuel would be compatible with current combustion engines as this would mean that current trucks and HGVs could be made carbon neutral by just changing the fuelling source instead of changing the engine or having to build a new fleet of HGVs entirely. This would give an enormous advantage because of the existing fuelling infrastructure. If this is the case, and the new fuel can be mixed with conventional fuels, this allows a gradual transition towards higher concentrations of the low carbon fuel whilst the supply line is developed and ramped in scale sufficiently to replace the current supply demands. However, mixing of fuels and using different fuels in existing engines and within existing infrastructure may encounter legislation restrictions which may need to be changed in order to make a smooth and complete legal shift (European Council directive 2018/2001). this will depend on a variety of factors from the degree of blending and the nature of the new fuel to the intended use of the fuel.

TYPE OF SYNTHETIC FUEL CONSIDERED

For the reasons explained above we are interested in fuels that have a possibility of being “drop-in” compatible with diesel combustion engines (the most common in goods vehicles) and

which would only require limited retrofitting of existing engines (such as replacing the fuel tank) rather than the development of a completely new engine. Accordingly, we have not focussed on hydrogen directly as a synthetic fuel, because an additional fuel cell or significant change to HGVs’ internal combustion engines would be required.

The fuels that best meet most or all of these criteria are dimethyl ether (DME), oxymethylene ether (OME_x) and potentially synthetic diesel through Fischer-Tropsch (FT) reactions. These are considered individually below.

Dimethyl Ether

DME is a liquefied gas that has been identified as a potential diesel fuel replacement. It has a chemical formula of CH₃OCH₃. Its structure is illustrated in **Figure 3**.

Using DME as a fuel significantly reduces NO_x output in comparison to conventional diesel engines due to lower flame temperatures and more efficient combustion. Additionally, DME combustion produces far less particulate matter (Pélerin et al., 2020), which is a significant concern in major cities around the world. The lack of particulate matter is due to the absence of C-C bonds in DME, this results in the clean burning and the shorter ignition delay compared to diesel (Kajitani et al., 1997). Rather than C-C bonds, the abundance of C-O bonds leads to a vast reduction in unburnt hydrocarbon fuel exhaust. This is because the extra presence of oxygen in the combustion leads to complete combustion and results in less carbon monoxide and unburnt carbon (soot) being produced. The additional oxygen in the molecular structure also reduces the amount of air required for the same energy output in the engine, which further reduces NO_x generation. The particulate yields for DME are 0.013% compared to that of regular diesel (0.026%) or biodiesel engines (0.51%) (Sidhu et al., 2001).

The liquefied gas has a boiling point of -25.05°C . This, in combination with the differences in other physical properties, such as the viscosity and calorific value, means that some changes to a vehicle would be required to make DME a suitable replacement for diesel (Willems et al., 2020). In order to retrofit existing diesel HGVs either low level retrofitting (replacing the tank for on-board blending) or high-level retrofitting (low level plus the additional replacement of the injection system and air path modification) is required; these come at an estimated additional cost to consumers of ≈ 4 k€/truck or ≈ 7 k€/truck respectively (INERIS, 2020).

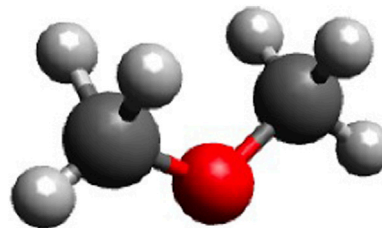


FIGURE 3 | The structure of DME (built in Avogadro, 2021).

TABLE 1 | The comparison between the properties of DME, diesel and methanol can be seen in (Arcoumanis et al., 2008), (Worldwide Fuel Charter Committee, 2019), (Wang et al., 2020), (US department of energy, 2021):

Property (unit/condition)	Unit	Diesel	DME	Methanol
Chemical structure		Av. C ₁₅ H ₂₈ Range C ₁₂ –C ₂₀	CH ₃ –O–CH ₃	CH ₃ OH
Oxygen content	Mass%	0	34.8	50
Final boiling point	°C	365	–25.05	64.7
Density at 15°C	kg/m ³	815–850	667	797
Cetane number		>51	>55	5.0
Lower heating value	MJ/kg	43.8	27.6	22.7
Volume required for diesel equivalence	m ³ /m ³	1	1.8	2.2

As shown in **Table 1**, DME has a higher cetane number than diesel. This allows it to perform well as a fuel alternative since the low auto-ignition temperature in combination with the low boiling point means that the fuel, once injected into the system, vaporises almost instantly leading to reduced ignition delay and good cold-starting properties (Teng et al., 2001).

However, a consideration for fuel substitution is that due to the lower heating value (LHV) of DME in comparison with diesel, the equivalent fuel volume of DME to diesel is 1:1.8 L proficiently (McKone et al., 2015). Thus, larger fuel tanks are needed to fulfil the same distance requirements, and these fuel tanks must be designed to handle the gaseous fuel. This, along with other vehicle changes such as timing, air fuel mixture ratios and alternative lubrication methods encompass most of the modest modifications required to allow conventional diesel engines to run using DME.

However, while pure DME is not compatible with gasoline or petrol engines that use spark ignition, it can be used in a 30% DME/70% liquified petroleum gas (LPG) ratio, potentially also allowing some non-diesel vehicles to run up to 30% cleaner in terms of CO₂ emissions (IDA Fact Sheet No. 2, 2010).

Although a gas at room temperature, DME has a comparable vapour-pressure interaction to LPG which forms a liquid phase above 0.5 MPa (5 bar). Therefore, DME has similar characteristics to LPG, which is widely transported (Verbeek and Van der Weide, 1997) and so would be compatible with existing transport infrastructure. Additionally, DME can be used as a carbon neutral feedstock for production of olefins using a zeolite catalyst. This provides an innovative mechanism for making carbon neutral polymers and other products that are usually derived from petrochemicals (Galanova et al., 2021).

The colourless DME gas has no negative health effects. Even at high vapour concentrations the human reaction is only that of a

small narcotic response (Arcoumanis et al., 2008). Due to historical usage of DME as an aerosol propellant, the safety aspects of DME exposure have been evaluated extensively (McKone et al., 2015).

Dimethyl Ether Efficiency

The basic cycle of carbon-based greenhouses gases and other sustainable carbon sources to produce DME fuels follows CO₂/CH₄ capture and storage from a variety of sources including, but not limited to, power, steel, cement and other industrial plants, landfill sites, waste to gas by anaerobic digestion and potentially air-captured CO₂. The well-to-miles or well-to-wheel cost compares different fuelling solutions and their impact on climate change through greenhouse gas emissions (Semelsberger et al., 2006). DME has shown high well-to-wheel efficiency, demonstrated using a fleet of DME-fuelled Volvo vehicles operating on sustainable feedstocks (IDA Fact Sheet No. 2, 2010). Well-to-tank efficiencies have varying values from various sources as this is dependent on the designation of affecting variables. The higher values of well-to-tank efficiencies come with the assumption of total vehicle efficiency of 40%, with the well-to-tank portion calculated at 27%, whereas a well-to-wheel efficiency of 18% was calculated using conventional technology (Semelsberger et al., 2006). The efficiencies will also change depending on the source of the carbon dioxide.

‘Well-to-miles’ calculations show a 2% overall change when comparing air as a carbon dioxide source in comparison to biogas in passenger vehicles (Hänggi et al., 2019). Although the well-to-miles efficiency is lower than that in conventional diesel and petrol engines due to the high well-to-tank efficiency of these established processes, DME fuel has an equivalent or higher efficiency than all other alternative transport fuels in the study (Semelsberger et al., 2006). If DME becomes a conventional feedstock, the well-to-tank efficiency would increase as technology is developed and perfected.

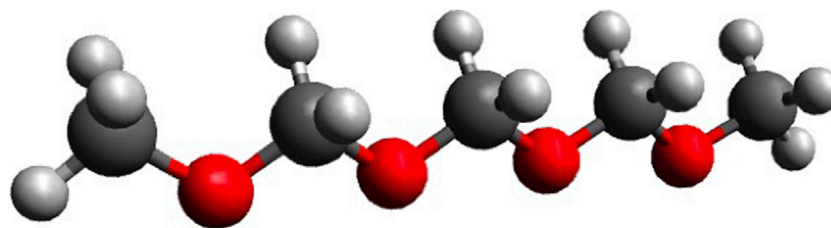


FIGURE 4 | The structure of OME₃ (built in Avogadro, 2021).

TABLE 2 | Comparison of OME_x and diesel properties.

Property (unit/condition)	Unit	Diesel	OME ₁	OME ₂	OME ₃	OME ₄	OME ₅
Chemical structure		Av. C ₁₅ H ₂₈ Range C ₁₂ –C ₂₀	C ₃ H ₆ O ₂	C ₄ H ₁₀ O ₃	C ₅ H ₁₂ O ₄	C ₆ H ₁₄ O ₄	C ₇ H ₁₆ O ₆
Oxygen content	Mass%	0	42.1	45.2	47	48.1	48.9
Final boiling point	°C	365	42	105	156	202	242
Density at 15°C	kg/m ³	815–850	860	980	1,030	1,070	1,110
Cetane number		>51	29	63	67	76	90
Lower heating value	MJ/kg	43.8	22.4	20.6	19.4	18.7	18.1
Volume required for diesel equivalence	m ³ /m ³	1	1.77	1.75	1.7	1.7	1.7

Oxymethylene Ethers (OME_x/OME_n)

OME_x are related to DME with the chemical formula of CH₃O-(CH₂O)_x-CH₃, x = 1–8 (Ouda et al., 2018). OME_x as DME derivatives have similar properties but a higher molecular mass and boiling points. An example of the chemical structure of an OME₃ molecule is illustrated in (Figure 4).

The oligomer length of the OME has a significant effect on the physical properties of the fuel. However, due to the increased length and higher boiling point in comparison to DME, the fuel acts similarly to LPG but has physical, chemical and fuel-properties similar to conventional diesel (Deutsch et al., 2017). The similarities allow conventional diesel supply structures to be used without significant alterations (Oestreich et al., 2018). This allows OME to be a direct replacement for fossil fuels as an immediate “drop in” replacement (Deutz et al., 2018).

OME_x also have no C-C bonds so are clean burning as discussed above in relation to DME. Similarly, precursors for soot such as C₂H₂ are inhibited in the combustion cycles (Sun et al., 2017). Another advantage of minimal particulate matter production is that there is a reduction in fouling in engine parts such as in the exhaust gas recirculation system (Härtl et al., 2017).

As the oligomer lengths affect the fuel properties, the compatibility and suitability of OME_x as a diesel replacement is dependent on oligomer length. Properties of different oligomer length OMEs and a comparison to diesel properties are shown in Table 2 (Worldwide Fuel Charter Committee, 2019), (Härtl et al., 2017).

The operating efficiency of a modern diesel engine will decrease if the cetane number is not higher than 51. Therefore, OME₁ is not a viable candidate as a replacement for diesel fuels.

An increase in the length of the oligomer sees a decrease in the lower heating value. The lower heating value determines the rate of flow of fuel required into the engine needed for the defined output energy from the engine. If a fuel has a lower heating value a high volume of fuel is required to meet the same energy output. The increase in density with oligomer length does help combat this issue. The volume of fuel needed for fuel equivalence is 1.7x that of diesel m³/m³.

Fischer-Tropsch Diesel

Fischer-Tropsch (FT) diesel is produced from syngas condensation (CO/H₂) and post-processing to create a synthetic fuel that has a similar long chain hydrocarbon

structure to conventional diesel. However, the fuel properties can vary from batch to batch due to the changing of process temperatures, catalysts and feedstock quality (Alleman and McCormick, 2003) with variations that can be used to tailor the fuels to the end-users needs (Gill et al., 2011).

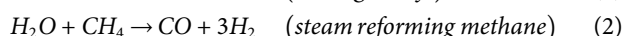
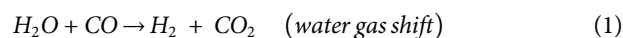
Although very similar to conventional diesel, FT diesel has virtually no sulfur or aromatic hydrocarbons (Abu-Jrai et al., 2006). Although this decreases emissions such as SO_x, the sulphur and aromatic contents of conventional diesel provide it with natural lubricity, which is absent in FT diesel. However, this can be rectified by commercial additives (Rodríguez-Fernández et al., 2019). The high cetane number of fuels that can be derived from the F-T process also show a high potential for reducing the NO_x/PM trade-off seen in conventional diesel engines (Rounce et al., 2009).

SYNTHESIS ROUTES

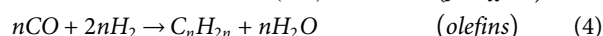
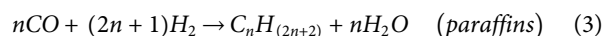
Fischer-Tropsch Diesel

FT synthesis is classified into high temperature (310–340°C) and low temperature (210–260°C) reactions (Leckel, 2009). The low temperature and high temperature methods give different compositional outcomes. Low temperature provides a higher cetane number and paraffinic compounds more suitable as diesel fuels. High temperature FT is more suitable as a gasoline substitute. One draw-back to the low temperature product is the lower density than conventional diesel which may lead to a need to reconfigure the fuel injection strategy and hardware (Larsson and Denbratt, 2007). The catalytic FT process to produce diesel fuels is shown in the following reactions:

Syngas production



FT Process



The complete diesel production process, including post-production, is complex with numerous reactors and processes required. This is because direct FT products are a range of carbon numbers requiring upgrading to reach the desired carbon number

for a homogenous fuel. This is less of an issue for OME_x fuels due to their limited range of products and even less of an issue for DME production as a single component fuel, which requires a simple distillation.

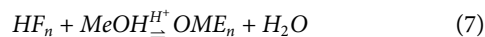
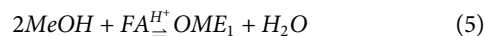
According to (Becker et al., 2012) and (Hänggi et al., 2019) it takes 80 kJ/mol of electrical energy to transform 1 mol of CO into the desired diesel product. Although only 85% of the initial FT products can be formulated into the desired diesel product (Oscar et al., 2009), the other 15% can be burnt as a heat source for processes such as distillation or the water gas shift reaction. The excess heat provided also provides the thermal requirements for the diesel production process (Hänggi et al., 2019). Due to the additional refining processes in FT synthesis, the well-to-miles efficiency is lower than for DME production. The energy consumed in the production is approximately 25% more (Hänggi et al., 2019) than that of DME (Oscar et al., 2009). On the other hand, FT fuels benefit from the lack of changes to the IC engine and the diesel supply infrastructure. However, these may not be significant enough to establish FT diesel as a more promising fuel for the decarbonisation of HGVs than DME.

Oxymethylene Ether Synthesis

From DME or methanol there are a variety of different synthesis pathways to OME as shown in Figure 5 (inspired by Baranowski, et al., 2017).

The most common synthesis pathway uses formaldehyde, as shown. However, the additional step required to synthesise formaldehyde, while it can be produced sustainably through partial oxidation of the MeOH (Ouda et al., 2017), decreases the well-to-wheel efficiency. The efficiency and economic viability of the process, no matter what route is taken, is also significantly reduced due to the many energy intensive fractional distillation

processes required to separate the OMEs in order to make a fuel of equivalent compositions (Lautenschütz et al., 2016).



Due to the increased complexity of the process and due to the required separation processes, OME synthesis has a lower exergy efficiency and a lower total fuel energy obtained from the same amount of CO₂ and H₂ in comparison to other synthetic fuels such as DME. However, it is comparable on this basis to that of FT diesel (Burre et al., 2019). Thus, unless and until further research and development leads to increased efficiency of the precursor of OME, DME appears to be a more efficient energy source.

Dimethyl Ether Synthesis

Dimethyl Ether From CO₂

DME can be synthesised from CO₂ via two main routes. By Route 1 it can be synthesised through the formation of syngas in the reverse water gas shift reaction (RWGSR) where it is then converted to DME through direct or indirect synthesis. Route 2 involves the synthesis of DME directly from CO₂. Figure 6 shows a selection of potential routes to produce sustainable DME from a variety of sustainable carbon sources, with the key ‘steppingstones’ of most pathways, namely syngas and methanol, highlighted in green. This gives considerable scope for process development and new chemistries.

The Korean institute of Science and Technology developed a reactor sequence using the formation of syngas. It claimed that the reduction in the size of the methanol synthesis reactor

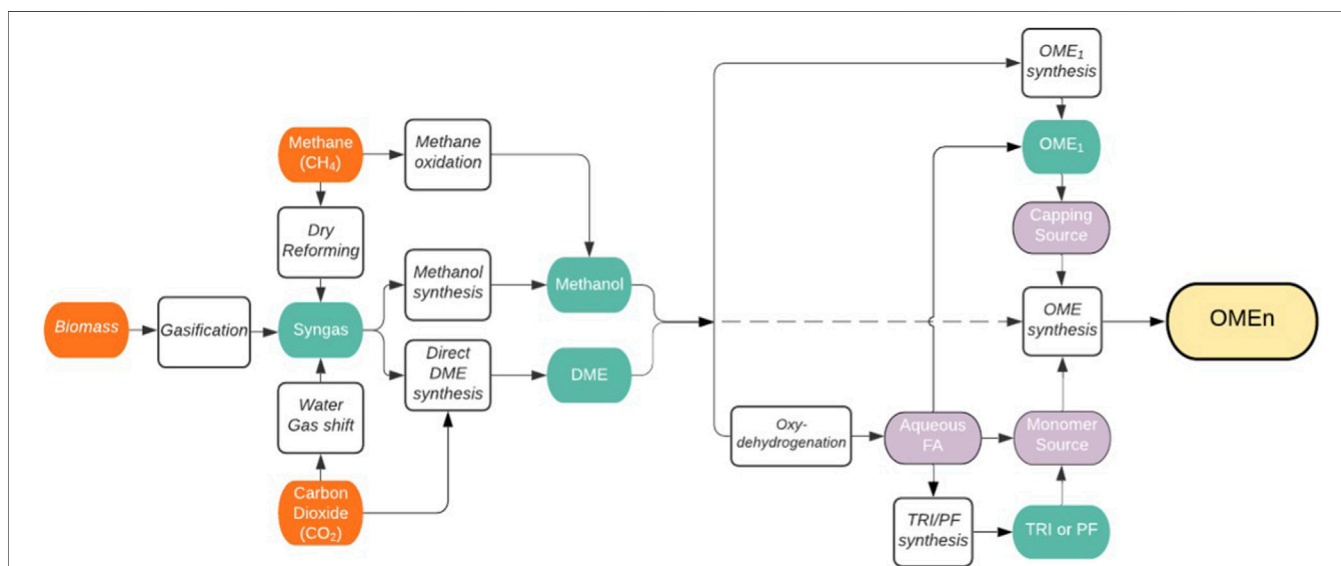
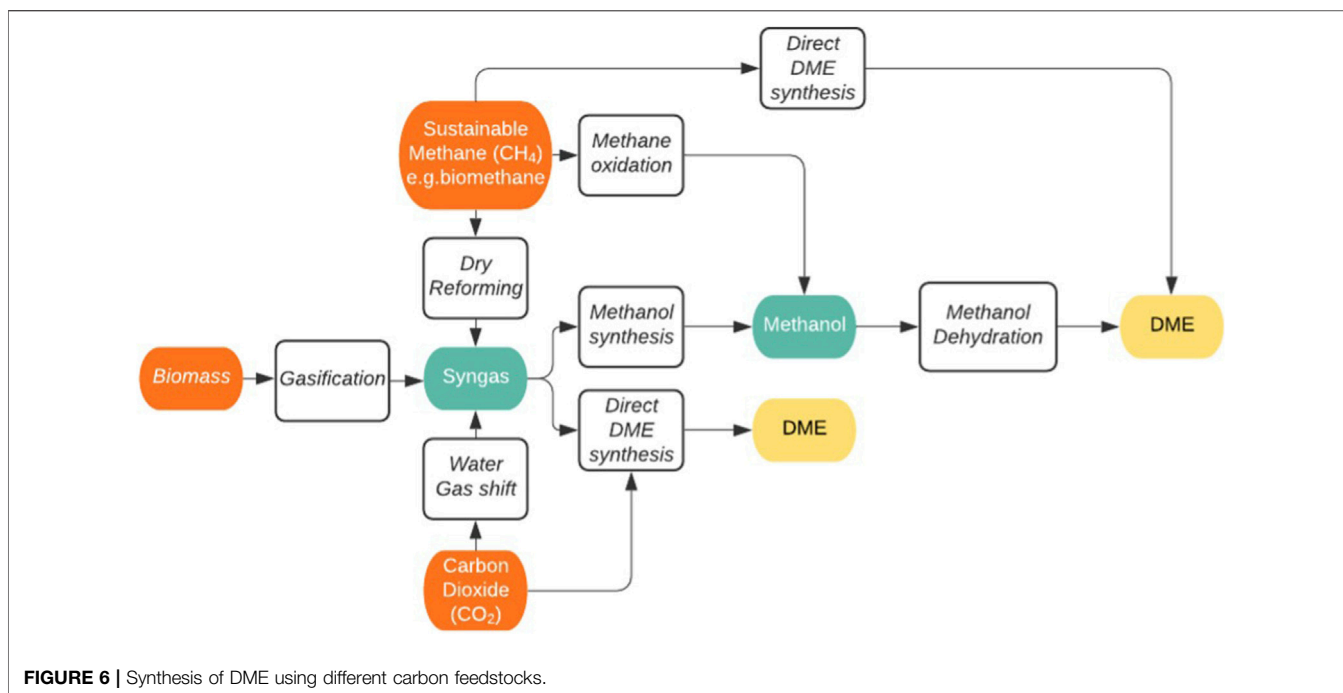
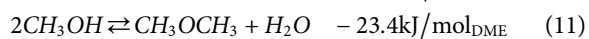
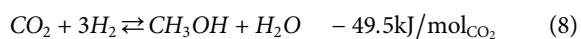


FIGURE 5 | Liquid phase synthesis of polyoxymethylene dimethyl ethers (OME) via methanol (derived from various sources) and DME. The depicted routes and reactants have been reported to be used for the production of OME_n with n > 1: OME₁ = dimethoxymethane, TRI = trioxane, PF = paraformaldehyde, FA = formaldehyde, DME = dimethyl ether.

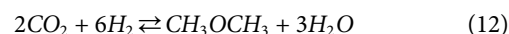


and the increased efficiency in the production of methanol in this reactor led to the two-step procedure being the optimal method (Joo et al., 1999; Goepfert et al., 2014). Although the water produced during CO_2 hydrogenation limited the formation and dehydration of methanol, thus resulting in a lower DME yield in comparison to CO (Azizi et al., 2014), more recent studies show that the higher oxidation power of CO_2 in comparison to CO positively affects the active state of the catalyst for methanol formation, thus increasing the methanol yield, making it an equally viable pathway (Centi and Perathoner, 2013).

Evaluation of intermediate syngas production is not within the scope of this review. However, DME synthesis from CO_2 without syngas can also be categorised into a single-step process (direct synthesis) or a two-step process (indirect synthesis) (Asthana et al., 2016). The basic principle of DME formation from CO_2 is hydrogenation of CO_2 to form methanol then the dehydration of methanol to form DME. In the indirect process two reactors and two catalysts are used, whereas in the direct process a single reactor and a bifunctional catalyst is used; the bi-functional catalyst carries two active sites, one for methanol formation and one for dehydration (Álvarez et al., 2017). The reactions for the formation of DME from CO_2 are the hydrogenation of CO_2 , the reverse water gas shift reaction and the dehydration of methanol:



The combination gives the overall reaction:



In indirect synthesis, as methanol is synthesised separately and requires purification before the DME synthesis in a separate reactor, the economic viability of methanol production compared to DME is the main issue (Takeishi and Akaike, 2016). The dehydration/condensation of methanol to produce DME as a distinct step is discussed later. For the direct synthesis of DME using a ‘one-pot’ method, referring to simultaneous CO_2 hydrogenation and methanol dehydration, the bifunctional catalyst requires a redox function to catalyse the CO_2 and an acidic function to convert methanol to DME (Álvarez et al., 2017). The direct synthesis is theoretically more efficient and economical than the indirect method due to the reduction in process complexity and the thermodynamic equilibrium limitation of methanol synthesis decreasing by the consumption of methanol in the dehydration reaction. This moves the equilibrium in the forward direction (Vakili et al., 2011; Catizzone et al., 2017). As a result, the methanol purification unit required by indirect synthesis can be discarded as only one reactor is required in direct synthesis (Mollavali et al., 2008) and higher DME selectivity can be achieved (Aguayo et al., 2007).

The bifunctional catalyst historically used for DME synthesis is made up of $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ (CZA) for the CO_2 hydrogenation and has been proven to be highly active (Ali et al., 2015) working alongside a solid acid catalyst HZSM-5 or $\gamma\text{-Al}_2\text{O}_3$ for the methanol dehydration to DME (Ren et al., 2019). As one of the key features that limits the effectiveness of bifunctional catalysts is the water production from the use of CO_2 instead of CO, recent research has been conducted to improve the stability of the hydrogenation catalyst. Zirconium modified

CZA catalysts (Ren et al., 2020) and zeolite surface interaction with CuO-ZnO-ZrO₂ (Bonura et al., 2020) have both been shown to increase the stability of the catalysts with significant improvements on catalytic stabilities being recorded.

Thermodynamic Considerations

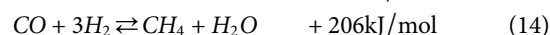
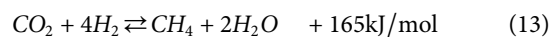
According to Le Chatelier's principle and equations, using a lower temperature and higher pressure should promote the formation of the desired products as the exothermic nature of both methanol and DME production favour lower temperatures, whilst the endothermic nature of the reverse water gas shift reaction favours higher temperatures and is independent of pressure. As DME is synthesised with methanol as an intermediary product, the thermodynamic profiles are closely related with, as previously mentioned, the limitation of the CO₂ conversion being removed by carrying out the methanol dehydration within the same catalytic system. Although the formation of olefins is possible in the production of DME from CO₂, these can be minimised by optimising the catalysts (Catizzone et al., 2017) and shortening the residence time in the reactor (Moulijn et al., 2013) and therefore are not taken into thermodynamic consideration.

Thermodynamic profiling by (Shen et al., 2000) show that the combination of methanol synthesis and dehydration to DME indeed gave a consistently higher CO₂ equilibrium conversion than the singular CO₂ hydrogenation to methanol process. Kinetic modelling of this process (Aguayo et al., 2007; Qin et al., 2015) concluded, that the rate-determining step in DME synthesis was the methanol synthesis. Use of a Gibbs free energy minimisation approach verified this and supported Le Chatelier's principle, concluding that CO₂ conversion and DME selectivity also increases with increasing total pressure (Ahmad and Upadhyayula, 2018). Although CO₂ conversion increases with temperature above 350°C, this signifies the move from equilibrium to kinetics controlling state of reaction completion. As a result of these competing influences, complete conversion to DME is close to impossible and there will always be a mixture of methanol and DME at equilibrium, meaning a separation process will always be required (Stangeland et al., 2018).

Dimethyl Ether From Methane

Rather than using CO₂ as the direct source of the carbon for the DME, sustainably derived methane can alternatively be reformed or oxidized to form syngas or methanol respectively as shown previously in **Figure 6**. Either product can then be used to derive the DME fuel. The sustainably derived methane is generated by two main routes, anaerobic digestion or the Sabatier reaction of waste organic material, which will naturally in turn have been generated from photosynthetic air-captured CO₂ at some point in the past. The Sabatier route involves the gasification of carbon-rich resources to generate pyrolysis gases; CO₂, CO, H₂, CH₄ and hydrocarbons, that can be further converted to commercially useful grades of methane using hydrogen and nickel-based catalysts (Sabatier and Senderens, 1902). The reactions are typically carried out at elevated temperatures and pressures (400°C and 30 bar) and

proceed *via* complete hydrogenation of the carbon-species present:



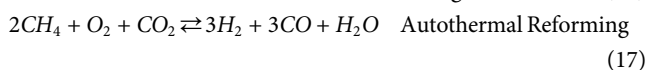
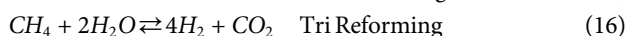
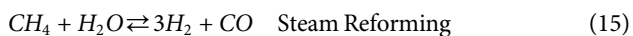
Side reactions typically include the generation of short hydrocarbon chains and elemental carbon.

A small number of plants using this principle have been operating for decades, converting coal into synthetic natural gas. Nevertheless, only one remains (in Beulah North Dakota) as low-cost shale gas has grown to dominate the non-sustainable fossil fuel market for natural gas (Kopyscinski et al., 2010; De Simio et al., 2013). New opportunities in this area remain, such as the possibility of using sustainable waste carbon resources like woodchip and other biomass which allow for the generation of renewable natural gas as a distinct product that can be immediately injected into the local national grid (Uchida and Harada, 2019; Vogt et al., 2019). By contrast, methane production from anaerobic digestion is widespread and typically carried out in individual small-scale digesters and on-site generation in suitable locations, particularly landfill sites. In the US in 2020, the total production of renewable natural gas via anaerobic digestion reached approximately 1.2 Mt (Mintz and Voss, 2020). The methane produced through anaerobic digestion, by contrast to that produced in the Sabatier reaction, is typically mixed with significant quantities of CO₂ and has a high water content. However, biogas drying and sweetening either by removal of this (originally biogenic) CO₂ (Aepli et al., 2020) or by further conversion of that CO₂ to more methane using renewable energy sources (Cave, 2020) is a developing industry.

While it may initially seem to be a circuitous route to generate DME from CO₂-derived methane, given that methane is in a lower oxidation state than the DME, the potential benefit of using methane as an intermediate may be practical. For example, methane is readily transported by the existing natural gas pipeline networks in most developed economies. Furthermore, existing, highly developed and commercialised processes such as those used for drying natural gas, can be used directly. The initial cost-savings of being able to use this existing infrastructure have been discussed previously and it holds significant benefit, avoiding the necessity of the generation of a new fuel transport infrastructure. The sustainable methane, delivered *via* pipeline, could then be converted into DME at the desired site, allowing flexible development of the technology by separation of the direct or indirect CO₂ utilisation from the fuel production. Once there is a supply of sustainable methane, it may be partially oxidized to methanol or syngas and then converted into DME as detailed previously, or even directly converted into DME by other means. For either partial oxidation route, selectivity to the desired product can be controlled by the reaction temperature. High reaction temperatures favour the production of syngas, whereas lower reaction temperatures promote the formation of methanol (Khirsariya and Mewada, 2013). However, the low reactivity of methane also makes the activation of the selective oxidation route challenging at low temperatures, resulting in a trade-off between

reaction rate and selectivity to methanol. Supported copper-based catalysts have however shown promise, especially with water included or even used as the oxidant (Shi et al., 2018; Koishybay and Shantz, 2020).

Once the methanol is obtained, the formation of DME is carried out over a variety of acidic solid catalysts at 200–300°C and typically gives DME in high yield and selectivity through methanol dehydration. Example catalysts include supported iron and copper oxides and copper/zinc/zirconia catalysts, typically used in CO₂ hydrogenation to methanol (Armenta et al., 2020). These catalysts can approach the maximum theoretical yields and selectivities for the reaction, which are limited by the presence of water (Migliori et al., 2020). Methane partial oxidation or reforming into syngas is a highly active area of research, both for hydrogen production and for further chemical synthesis, *via* syngas, from methane sources. The former is usually carried out by steam reforming, generating three molar equivalents of hydrogen per molecule of methane, with an additional molecule of hydrogen available from RWGS in tri-reforming. The latter route, where syngas with a lower hydrogen concentration is desired, can be achieved through dry autothermal reforming, which uses further carbon dioxide with the methane at high temperatures to generate 1:1 syngas.



This is carried out using a wide variety of catalysts, typically including supported nickel but also iron, calcium, zinc and cerium-based catalysts (Gao et al., 2020a; Ugwu et al., 2020; Dang et al., 2021; Shah et al., 2021) among others. Along with this variety of catalysts, a wide variety of conditions are also used with temperatures ranging from 550°C to 2,000°C, however very high yields (>95%) and selectivities (>95%) are typically achieved. The subsequent conversion of syngas to DME proceeds as detailed in the previous section on the direct route for DME from CO₂.

Finally, it is also possible to use methane as a direct precursor, rather than as a syngas or methanol source. This involves the activation of methane using a halogen radical to generate the methyl halide, followed by a precious-metal catalysed hydration-dimerisation process. Of note here is the potential for a low-temperature route to DME, with the hydration-dimerisation of methyl bromide to DME shown to occur with good yield and selectivity at just 150–180°C using a simple ruthenium catalyst (Xu et al., 2005). While the initial bromination step in that research required temperatures of 530–560°C, which were achieved through self-heating by partial methane combustion, the dimerization process could also be fuelled by low temperature methane halogenation through photochemical, electrochemical or even mechanochemical means, where a chlorine-rich substrate is milled in the presence of methane to selectively generate methyl chloride at temperatures below 150°C (Bilke, et al., 2019). Indeed, this route has been recently demonstrated for an electrochemical

methane-to-methanol conversion at 130°C and 46.5 bar CH₄ over platinum which proceeds *via* a methyl chloride intermediate in a similar fashion (Kim and Surendranath, 2019).

HYDROGEN SOURCES

In order for these synthetic routes to be truly carbon neutral, the hydrogen sources also need to be derived from non-fossil sources. These sources include thermochemical water decomposition (Mehrpooya and Habibi, 2020), water electrolysis and biomass gasification (Badwal et al., 2014) as shown in **Figure 7**. As mentioned earlier, any energy required in the production of hydrogen and the synthesis of the DME must also be derived from non-fossil, renewable energy sources. The synthesis of DME from CO₂ requires the addition of hydrogen, as six hydrogen molecules are required for every two molecules of CO₂ to produce one molecule of DME. The highest heating value for H₂ is 142 MJ/kg (Chen et al., 2011), which compares well with other known fuels and is why it is seen as not only a feedstock for making other synthetic fuels but as a potential fuel itself.

As mentioned previously, in order to ensure that the DME produced is carbon neutral the source of the hydrogen and any electricity/heat energy used in the production must come from renewable sources (Kothari et al., 2008). This means that conventional hydrogen production from heavy hydrocarbons, coal gasification and fossil natural gas steam reforming cannot be considered, as CO₂ is the largest emission from the process (Kothari et al., 2004). With only 5% of hydrogen currently being produced by sources other than natural gas and coal (IRENA, 2019) and the leading practice being electrolysis of water, which is also the most energy consuming route (Holladay et al., 2009), it is necessary to look at other methods such as producing hydrogen from biomass and to compare their efficiencies.

It can be seen that water is always crucial for hydrogen generation, however, in many of these cases a very high purity of water is required for good conversion yields (Gandia, et al., 2013). Since globally clean water is an ‘under-pressure resource’, especially in arid areas which also contain solar primary energy resources (Saleth and Dinar, 2004), the location and distribution of any putative large scale sustainable hydrogen production requires serious consideration.

Hydrogen From Water

Water splitting or cracking to produce hydrogen is completed through three predominant methods; electrolysis, thermolysis and photo-electrolysis. The simple base principle is water is divided into its individual components; oxygen and hydrogen—requiring either free energy or high temperatures (Kothari et al., 2004). The basis of water electrolysis is the movement of ions promoted by an external circuit through an electrolyte to promote the splitting of water in an electrolysis cell (electrolyser) (**Eq. 20**) (Bhandari et al., 2014). In the electrolyser,

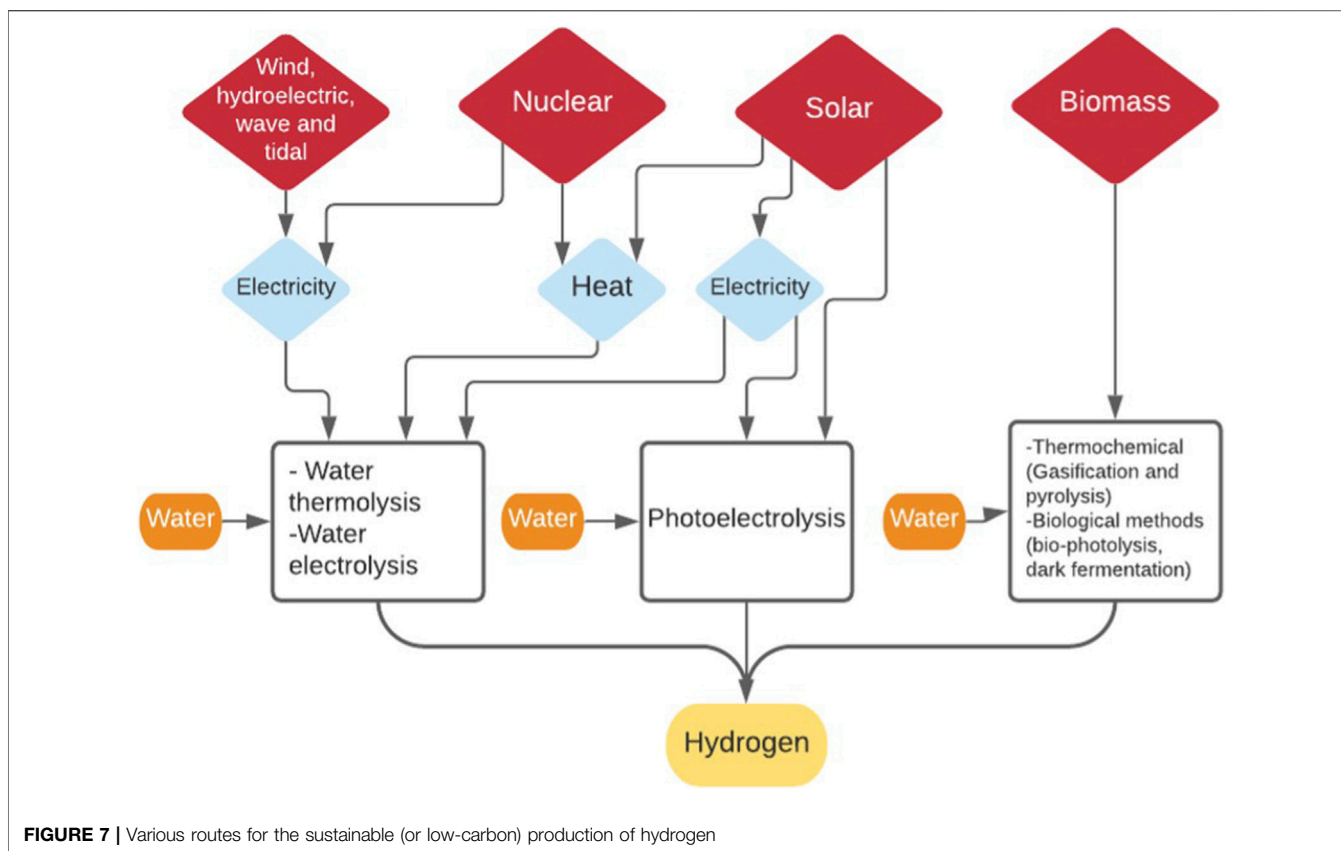
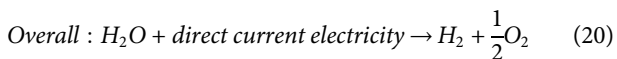
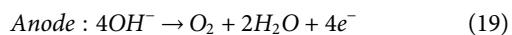
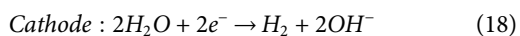


FIGURE 7 | Various routes for the sustainable (or low-carbon) production of hydrogen

two electrodes are placed in the water thus facilitating the external circuit and the formation of ions/electrons on either electrode:

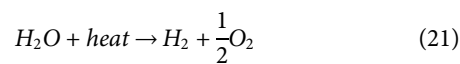


There are different types of electrolysis cells, such as polymeric electrolyte membrane electrolyzers, alkaline electrolyzers and solid oxide electrolyzers among those in production and development. Although similar in their goal they use slightly different methods, catalysts and materials to try to formulate the most efficient and cheapest process, whilst also achieving the purity of hydrogen required. As low-temperature water electrolysis can take advantage of relatively low space requirements and exploiting the existing infrastructure for the electricity and water use, it can rapidly be added to an existing plant (FreedomCAR and Fuel Partnership, 2009). The downside of water electrolysis is its efficiency of 60–80% (Shiva Kumar and Himabindu, 2019) and the high capital cost due to catalyst/membrane poisoning depending on the water source and the low hydrogen evolution rate compared to the high energy consumption, especially prevalent if sea water is used (Shi et al., 2020). This means its economic compatibility is low. The energetic efficiency (energy obtained from the hydrogen fuel per unit of electrical energy required) is around 56–73% (Turner et al., 2008). In 2008, the cost of producing sustainable hydrogen to reach an equivalent fuel price to that of fossil-derived

hydrogen required access to electricity prices as low as \$0.045–\$0.055 kWh⁻¹ (Turner et al., 2008), no transportation of energy costs to be included, and the hydrogen being produced at a local wind power site as the primary energy source.

Water electrolysis requires 47.99 kWh per kg H₂ (Martínez-Rodríguez and Abánades, 2020). This is around four times higher than the energy required to produce hydrogen through steam reforming. Although research and development are leading to more energy efficient electrolyzers, this still proves a barrier to an economically viable production method.

Thermolysis is the direct one-step method of decomposing water into its constituent molecules governed by homogenous kinetic mechanisms (da Silva Veras et al., 2017).

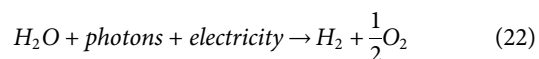


In order to achieve the thermal decomposition, the temperature needs to reach over 2,500 K (Dincer and Acar, 2015), which theoretically allows a >4% dissociation level at atmospheric pressure (Baykara, 2004). This increases at even higher temperatures, with 64% dissociation achieved at 3,000 K and 1 bar, (Dincer and Acar, 2015). As this is a reversible reaction, the recombination of the end products needs to be avoided. Common methods include rapid cooling of the gaseous mixture through direct contact with cold fluid (Lede et al., 1982). Having temperatures in both extremes increases the running cost of the facility thus increasing the cost of the hydrogen produced. In order not to require extreme cooling, the use of palladium

membranes can be used to avoid the recombination of H₂ and O₂ (Dincer and Acar, 2015).

In order to obtain the high temperature required for this process, the renewable energy sources need to be evaluated. However, the scaling up of the process is believed to increase thermal efficiency (Holladay et al., 2009). The only renewable energy or low carbon sources currently generally capable of producing the heat required for this process are nuclear energy and concentrated solar power providing high temperature steam (Dincer and Acar, 2015; Dincer and Safari, 2020). The overall efficiency of the process is dependent on the renewable energy source and can vary between 17–45%, with a nuclear heat source providing a higher overall efficiency than a solar heat source (Nikolaidis and Poullikkas, 2017). As heat energy and electrical energy are not equivalent, with 1 J of electrical energy being equal to around 4 J of heat energy a kWh per kg H₂, comparison is not effective. However, comparisons based on cost of the hydrogen produced can be made at 2.17–2.63 United States \$ per kg H₂. If it were decided to incorporate a hydrogen production plant into the DME production plant instead of outsourcing the hydrogen production, the excess heat released from the exothermic DME synthesis reactions could, in principle, contribute towards the heat require for thermolysis.

Photo-electrolysis or the photoelectrochemical (PEC) splitting of water, uses the absorption of photons from sunlight to directly decompose water on irradiation, using semiconductors. An advantage of the PEC cell is that it combines the water electrolysis and solar energy absorption into a single monolithic device (Chaubey et al., 2013; Dincer and Safari 2020).



The basis of PEC is that a photoelectrode absorbs photons from solar irradiation with enough energy to excite the electrons from the valence shell to the conduction band (Yang et al., 2017). The semiconductor is immersed in a water-based electrolyte where the energy released when the electrons return to the valence band is used to energise the water and facilitate the hydrogen production as water is split on the semiconductor surface (Turner et al., 2008). Depending on the conductor material, the density of the electric current produced varies between 10 and 30 mA cm² of the semiconductor. This facilitates a lower voltage requirement that leads to higher efficiencies (Christopher and Dimitrios, 2012). A minimum energy of 1.36 eV is required to split a water molecule and, including the electron transfer induced losses, a photon of 1.6–2.4 eV is required to be absorbed for effective photo-electrolysis (Roger, Shipman and Symes, 2017). This corresponds to wavelengths within the visible light spectrum, thus providing a potentially reliable energy feedstock and electrolysis efficiency levels reaching 91% (Christopher and Dimitrios, 2012). The overall hydrogen production efficiency of 10–12.4% (Turner et al., 2008; Christopher and Dimitrios, 2012) is promising for future production possibilities, with this efficiency level in 2007 corresponding to only requiring 4,000 square miles of photoreceptors for the entire United States vehicle fleet.

Hydrogen From Biomass

The two major categories of hydrogen production from biomass are thermochemical technology routes [which include gasification and pyrolysis (Zhang, 2010; Sanna, 2013)] and biological treatments [which includes bio-photolysis and fermentation (non-exclusively) (Levin, 2004)]. The thermochemical conversion of biomass to hydrogen is the most advanced and established technological production method (Lepage et al., 2021). Lignocellulosic biomass is the main feedstock for these processes, although it is currently expensive to produce, thus contributing to the higher production cost of hydrogen from thermochemical biomass. There is an indication that these prices will reduce in the future as a result of the environmental policy price impact on fossil resources (Fiorese et al., 2014). As the hydrogen content of biomass is only 6–6.5% depending on the feedstock, in comparison to 25% in natural gas (Kothari, et al., 2004), previously there has not been economic reason to make the swap to biomass. However, reduction in net CO₂ makes this a feasible production option.

Biomass gasification is a mature technology which adopts the same principles as coal gasification. Gasification and pyrolysis are related processes where the thermochemical conversion of solid biomass fuel into syngas uses steam, oxygen or air as a medium for gas generation at a level lower than that required for full stoichiometric combustion (Holladay et al., 2009; Sansaniwal et al., 2017). Gasification is a highly endothermic process, operating at temperatures between 500–1,400°C and from atmospheric pressure up to 33 bar depending on plant scale, type of reactor, initial feedstock material and the function of the syngas produced (Iribarren et al., 2014). Within biomass gasification, the biomass mass goes through three phases: drying, pyrolysis and reduction (Lepage et al., 2021). The gasification reaction can be achieved using air, oxygen and oxygen enriched air.

It is possible for a biorefinery to stop processing the biomass after pyrolysis producing three products; syngas, bio-oils and char. This allows the products to be separated and used for multiple end products such as such as the products of light olefins from the catalytic cracking of bio-oil (Arregi et al., 2018). However, as the required output is the hydrogen, for maximum biomass to hydrogen efficiency, full gasification must take place. Although hydrogen is a direct product of gasification, in order for the maximum hydrogen content to be extracted from this process, thus making it more efficient, the syngas received from gasification then goes through a water gas shift reactor to obtain the maximum hydrogen possible (Holladay et al., 2009).

Any excess products can be burnt as a cheap source of electricity or heat. This contributes to the lower cost of hydrogen production of 1.21–3.5 United States \$/kg H₂ (Lepage et al., 2021), depending on the feedstock, scale of production, catalyst and methods used. Efficiencies can vary from 30–70% based on the LHV (Binder et al., 2018).

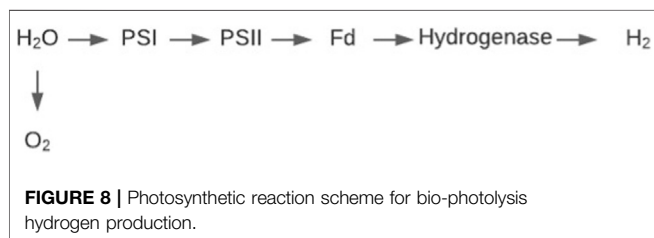
Biological treatments or processes are methods to produce hydrogen which depends on the use of enzymes to catalyse hydrogen formation (Levin, 2004). The biological treatments can be split into the biological splitting of water (direct and

indirect bio-photolysis) and the fermentation of biomass to produce hydrogen. In comparison to the thermochemical biological methods to produce hydrogen, biological treatments tend to operate at atmospheric pressure and temperatures between 30–60°C (Lepage et al., 2021). Taking account of the ability of the microorganism to be regenerated by replication (Henstra et al., 2007) reduces the catalyst turnover resulting from degradation in high temperatures through thermochemical processes.

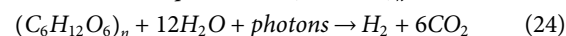
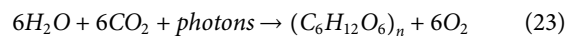
Bio-photolysis

Bio-photolysis utilises the photosynthetic abilities in green algae or cyanobacteria in a method adapted for the generation of hydrogen gas instead of carbon containing biomass (Kothari et al., 2004). The process is split into two methods direct and indirect photolysis. Direct bio-photolysis is the process of green algae splitting water via photosynthesis into a hydrogen ion and oxygen, using the ability of the algae to transform solar energy into chemical energy (Melis et al., 2000). The reaction is governed by two photosynthetic systems PS I and PS II (Figure 8). These systems harvest light energy under anaerobic conditions, transferring H₂O electrons to ferredoxin (Kim and Kim, 2011). The hydrogenase enzyme then catalyses the reaction of the reduced ferredoxin acting as an electron donor providing an electron to the hydrogen ion, forming hydrogen gas (Eroglu and Melis, 2011). This can be categorised in the following reaction scheme (Bičáková and Straka, 2012):

The major disadvantage of this system for producing hydrogen is that in order for the hydrogenase to function efficiently, anaerobic conditions are required as it is very sensitive to oxygen (Prince and Kheshgi, 2005). However, the reaction also produces oxygen as a product so maintaining complete anaerobic conditions is a priority for researchers. Research is on-going to increase the yield of hydrogen by depleting the production of oxygen, however current methods such as the addition of a sulphate solution also suppresses hydrogen production (Williams and Bees, 2013). Progress has been made with recent research leading to an increase in light utilisation energy from 5 to 15%, with further room for improvement possible by increasing the scale of the algal bioreactors (Show et al., 2011). As the process does not require vast amounts of electricity, the price of the hydrogen produced is around 2.13 \$/kg H₂ (Hallenbeck and Benemann, 2002; Kayfeci et al., 2019) this is comparable to some fossil-based methods, however production on a large scale remains a barrier to mass rollout.



Indirect bio-photolysis is sometimes also referred to as aerobic dark fermentation as it consists of two major steps. The first comprises of the photosynthesis of cyanobacteria to produce glucose in a conventional manor. The second, involves the aerobic dark fermentation of the glucose to produce hydrogen as seen in Eqs 23, 24 (Chaubey et al., 2013):



The reactions are catalysed by both hydrogenase and nitrogenase, as cyanobacteria are capable of fixing atmospheric nitrogen (Benemann, 2000). Cyanobacteria are the ideal candidates for this process with a maximum of 16.35% light efficiency (Prince and Kheshgi, 2005), however in practice efficiency is only 1–2%, so further development is required before this process can become commercially viable (Chaubey et al., 2013). Although the low efficiency leaves this method in its conceptual phase, calculations have been carried out which place the price of hydrogen needed to make the processes economically viable at 1.42 \$/kg of H₂ (Hallenbeck and Benemann, 2002; Kayfeci et al., 2019).

Dark Fermentation

Dark fermentation is the process of producing hydrogen through anaerobic bacteria being grown on carbohydrate rich substrates without accesses to light (Levin, 2004; Ghavam et al., 2021). It requires temperatures between 25°C and 80°C (Lepage et al., 2021) depending on the strains. The products of this process are mostly CO₂ and H₂ with other gas products being released such as CH₄ and H₂S. The combination of products and their ratios depends on the quality of the substrate used. Due to the production of other products, the H₂ yield is lower than that of bio-photolysis, thus contributing to the lower efficiency of the process (Soares et al., 2020). Glucose could be an ideal feedstock, however due to its high price it makes the process uneconomical. Lignocellulosic biomass has been identified as a promising feedstock although the requirement of pre-treatment increases the price of the hydrogen required to make the process economically viable (Soares et al., 2020). The amount of hydrogen produced also depends on the pH of the fermentation atmosphere with the maximum hydrogen yields occurring at a pH of 5–6 (Fang and Liu, 2002).

Dark fermentation has significant advantages such as being a light independent. It does not require large land use (such as those depending on solar energy), it can capitalise on being able to use a multitude of different feedstocks and it has high rates of hydrogen production unsurpassed by other biological processes (Chaubey et al., 2013; Soares et al., 2020) with values ranging from 184 to 2,710 ml hydrogen L⁻¹h⁻¹ reported (Turner et al., 2008). Dark fermentation has a biomass conversion efficiency of 60–80% assuming that the maximum yield of glucose as a feedstock is catabolised (Kovacs et al., 2006), which contributes to a hydrogen cost of 2.57 \$/kg Nikolaidis and Poullikkas, 2017).

The optimal hydrogen source for DME production will vary depending on the location of the plant, the availability of the feedstock and the price and availability of the primary energy source. This can change depending on location, for example (as

TABLE 3 | Hydrogen cost as a function of different processes (Kayfeci et al., 2019; Nikolaidis and Poullikkas, 2017; Kayfeci et al., 2019 and Lepage et al., 2021).

Process	Energy source	Feedstock	Hydrogen cost \$/hg
Water electrolysis	Wind	Water	5.89–6.03
	Nuclear	Water	2.35–7.0
Thermolysis	Solar	Water	2.17–2.63
	Nuclear	Water	7.98–8.40
Photo electrolysis	Solar	Water	10.36
Biomass gasification	Internally generated steam	Biomass	1.21–3.5
Direct bio-photolysis	Solar	Algal biomass + water	2.13
Indirect bio-photolysis	Solar	Algal biomass + water	1.42
Dark fermentation		Organic biomass	2.37–2.80

explained above) France produces a lot of low-carbon electricity due to their vast nuclear programme. Producing hydrogen through water electrolysis from a nuclear source will be cheaper as the sustainable electricity is cheaper. The hydrogen sources discussed in this review are non-exhaustive and are meant to provide a brief overview. Comparisons can be seen in **Table 3**.

CARBON CAPTURE AND UTILISATION TECHNOLOGIES

In order to access CO₂, vital as the required feedstock for DME synthesis, it initially needs to be captured, compressed and transported from CO₂ point sources. As global political pressure regarding CO₂ output has increased on energy and industrial processes, there has been increased research and implementation of carbon capture and storage (CCS) technologies. This involves the selective removal of CO₂ from gas streams, after which it is then compressed and transported to geological storage solutions such as exhausted natural gas reservoirs and saline aquifers, where in principle the CO₂ can be stored for geological periods, instead of adding to the growing atmospheric concentration (Al-Mamoori et al., 2017). However, in spite of government subsidies, the high costs of CCS (with 75% of the total cost coming from the primary capture and compression of the CO₂) have inhibited large scale industrial roll-out. Therefore, Carbon Capture and Utilisation (CCU), where the CO₂ is used as a feedstock after capture and possibly compression and can be used by the industrial and energy sector as a valuable product instead of an expensive waste; a concept that make it a much more attractive alternative (Styring et al., 2011; Styring et al., 2014; North and Styring, 2019a; North and Styring, 2019b).

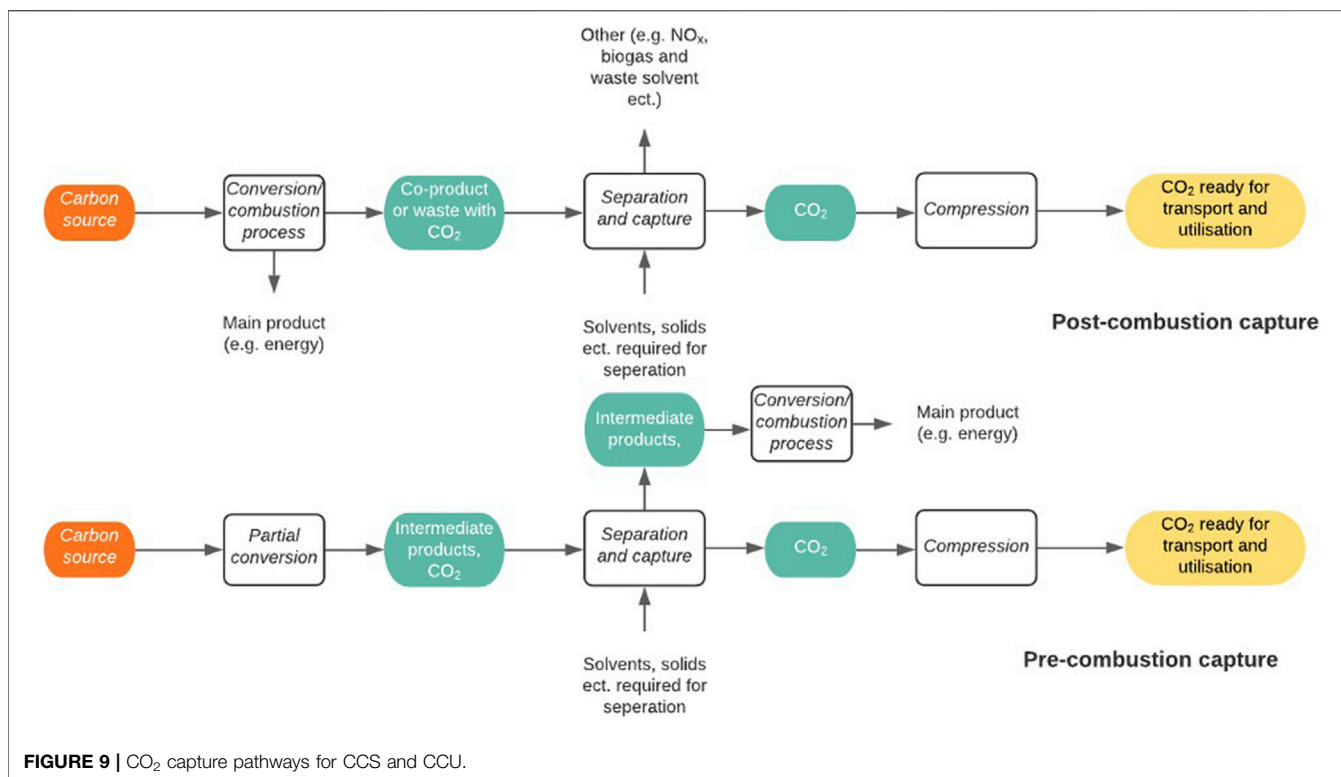
The industrial sector accounted for almost 40% of global CO₂ emissions in 2018 (after allocating electricity and heat emissions across final sectors) (IEA, 2020a). This makes the industrial sector the prime location to install CCU technologies for the production of CO₂ as a valuable feedstock, along with fossil-fuel power plants (Markewitz et al., 2012). As well as offsetting CO₂ emissions by utilising the CO₂ for chemical synthesis of other products, in this case DME, it has been suggested that CCU can further reduce the emissions by forgoing conventional production strategies. For example, the use of 1 kg CO₂ for the production of CO₂-based polymers can overall reduce emissions totalling 3 kg CO₂ when

compared to the non-CCU route (von der Assen and Bardow, 2014; Kätelhön et al., 2019). Michailos et al. (2019) have also considered the techno-economics of integrated carbon capture and DME production in the context of a positive life cycle impact.

Generally, there are three main methods for CO₂ capture from industry; pre-conversion/combustion, post-conversion/combustion and oxy-fuel combustion (Kanniche et al., 2010). These can be seen in **Figure 9**, adapted from Cuéllar-Franca and Azapagic, (2015):

Post-combustion carbon capture involves the separation of CO₂ from the waste gas stream after the combustion of the carbon source, or conversion of the carbon source in the formation of the target product, e.g. energy or steel. When used in power plants, the process is known as post-combustion capture, however when used in industrial plants it can be referred to as post-conversion capture. Post-conversion CCU requires the least amount of retrofitting to the existing facilities and is typically regarded as the most efficient strategy (Gao et al., 2020b). Using aqueous amine solution to capture CO₂ through absorption is the current industrial standard for post-combustion carbon capture (Nwaoha et al., 2017). However, as the solution has a high heat capacity and results in significant material losses, it causes elevated costs leading to a need for a more economical system (Patel, Byun and Yavuz, 2017). Many other post combustion methods have been developed as alternatives to amine solution separation such as absorption in other solvents, adsorption by solid sorbents (Patel, Byun and Yavuz, 2017), separation via membranes and cryogenic separations. The optimum overall strategy will depend on available energy at the CO₂ source. For example, the energy requirement needed for monoethanolamine (MEA) absorption can be met to facilitate lower energy costs if the plant has a combined heat and production feature. However, this is not the case in some industrial processes such as cement plants, as insufficient heat is produced (Kuramochi et al., 2012). An issue that needs to be addressed is that the separation processes can be challenging due to the low partial pressure of CO₂ in flue gas resulting in a low CO₂ driving force and a large volume of gas to be treated (Zhang et al., 2019). For the process to be truly carbon neutral, the energy required for CCU either needs to come from the process itself in the form of waste heat or from a renewable energy source.

Pre-combustion/conversion carbon capture purifies CO₂ generated during an intermediate process, resulting in the production of less end-CO₂. Examples include the gasification



of coal, reforming of natural gas and the production of ammonia (Jansen et al., 2015). As the majority of pre-combustion carbon capture involves the removal of CO₂ from syngas, the prime separation method will be dependent on the partial pressure of CO₂ in the treated gas. An example of industrial utilisation is the separation of CO₂ from H₂ before it can be used in ammonia synthesis. This usually occurs with the use of MEA as the absorption mechanism (Global Carbon Capture and Storage Institute, 2012). However, these methods are similarly disadvantaged to post-conversion/combustion technologies in that the regeneration of chemical solvents such as MEA cause an incurred energy penalty to the system, thus decreasing the overall efficiency (Cuéllar-Franca and Azapagic, 2015). The use of physical solvents decreases the energy required for the CO₂ capture. It is therefore the primary method for integrated gasification in combined cycle plants, which are being used to produce 'clean coal', where the physical solvents such as Selexol and Rectisol are used (Porter et al., 2017). For all CCU methods, it needs to be noted that any energy being supplied to the system to aid in the carbon capture needs to be renewable and therefore not be a process that itself produces CO₂.

Oxy-fuel combustion does not have a conversion alternative as it can only be applied to processes involving combustion. The principle uses pure oxygen for the combustion instead of air. This avoids the dilution of the flue gas with other gasses such as nitrogen, resulting in an exhaust gas with a significantly increased partial pressure of CO₂ (Borgert and Rubin, 2017). Partial recycling of the flue gas into the boiler is required to moderate the flame temperature which would otherwise burn excessively high as a result of burning in pure oxygen (Porter et al., 2017).

Although the CO₂ does have a much higher partial pressure in the exhaust gas, there are still traces of water vapour, particulate matter and other pollution gases, which require a separation process before the CO₂ can be dried and compressed for transport (Najera et al., 2011). In order to retrofit a plant for oxy-fuel combustion carbon capture, it requires an air separation unit (which is often cryogenic) to provide pure oxygen from air and a CO₂ compression and separation unit and an exhaust gas recycle (Porter et al., 2017).

Although these three methods are not the only methods to capture CO₂ for utilisation, they are the main methods used from industrial and energy producing sources. Other sources include the CO₂ produced from biological processes and brewing sources, however these come with their barriers for the making of synthetic fuels. Biological sources of CO₂ come with more sulfur and a higher moisture content than energy and industrial sources (Thema et al., 2019). There is competition for the high purity of CO₂ produced from brewing for use in the fizzy drink industry, driving up the price of the CO₂, making this CO₂ not economically viable for synthetic fuel production. Porter et al. (2017) produced a comparative report of the cost and performance of carbon capture methods based on the three methods discussed in this review.

Once the CO₂ has been compressed and purified to the specification required by the consumer, in this case to produce DME, the CO₂ must be transported to the synthetic fuel plant. As any transportation of CO₂ will incur costs, the most economical option would be to synthesise the DME on the same site as the CO₂ is captured. This approach can also take advantage of the economies of scale of the existing plant where

the CO₂ is being captured, as well as any excess heat from the plant, recycled where necessary in the DME synthesis process. If the CO₂ does need to be transported, a pipeline infrastructure is required, and currently there is no CO₂ infrastructure in the United Kingdom for CO₂ from industrial flue gases (Ecofys, 2017). However, CO₂ transportation plans exist in Europe and retrofitting of existing infrastructure by repurposing oil and gas pipelines is being considered. This approach represents a cost of around 1–10% of the cost of building an entirely new CO₂ pipeline (IOGP, 2019). While implanting CCU decreases the overall plant efficiency for the initial product, the addition of CCU creates another valued product whilst complying with strict government regulation imposed to reduce the level of CO₂ emissions to the atmosphere.

CONCLUSION

Dimethyl ether (DME) is discussed in this review as a future fuel that can help facilitate the transition from a fossil-fuel based economy to a net zero economy. DME is a single molecule fuel (unlike fossil fuels which are complex mixtures) and while having half the energy density of diesel it has several benefits.

- It contains only two carbon atoms and so burns almost completely, so NO_x emissions are low.
- As the fuel is non-fossil-based there are also no SO_x emissions.
- Because there are no carbon-carbon (C-C) bonds, only carbon-oxygen (C-O) bonds, there is no soot formation and so low PM emissions.
- Furthermore, due to its favourable cetane number it can be used directly in CI engines.
- Some fuel delivery modifications are needed as DME is a gas, but the interventions are similar to those already available for LPG fuels.
- Oxymethylene ethers (OMEx) are higher homologues where x represents additional oxymethylene (-CH₂O-) groups, and where $x = 3-5$ possess liquid properties similar to diesel.

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DME can be produced from carbon dioxide and other carbon-containing waste materials. However, it also needs additional resources such as electricity, water and ultimately hydrogen, which must be sustainably obtained. Strategies to produce hydrogen from low-carbon energy sources were therefore reviewed. The processes that facilitate DME from waste feedstocks have been presented and the routes considered over the complete system. DME and OMEx production and properties have been put into a synthetic fuel context through comparison to the production of Fisher-Tropsch synthetic diesel. The ether route represents a low hydrogen and so lower overall energy route to a useful synthetic fuel. While we do not consider the use of DME as a silver bullet in a transport energy transition, we do not consider that any single solution technology will provide the answer. The clue lies in the word transition. We need to move away from fossil fuels in a way that is sustainable environmentally, financially, and socially. Whatever technology or suite of technologies are used, this needs to be introduced sensitively and must avoid creating transport fuel poverty where members of society are denied mobility as a consequence of a fuel ideology. This review demonstrates that in spite of the need for further innovation and development, DME has an important role to play in this transition as an energy vector, with the availability to store surplus or curtailed renewable energy over seasons.

AUTHOR CONTRIBUTIONS

Each author contributed to the literature review and analysis and to the writing of the paper. IOT was a Master's student who led the data acquisition and analysis and produced the first draft of the manuscript. PS was the research supervisor and GRMD Postdoctoral Research Associate and project co-supervisor.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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