E-fuels for the Energy Transition in the Transport Sector – Properties and Application: Current State of Research

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Summery

The defossilization of the transport sector is of crucial importance to reduce climate effects, while emissions of soot particles and NO_x are harmful to environment and human health. Sustainable fuels offer the chance of addressing both: Reducing climate impact and improving local air quality. Among alternative fuels, E-fuels are considered to become a game player. Using Power-to-Liquid (PtL) technologies they will be produced from CO_2 and green hydrogen based on (excess) renewable energy, such as wind or solar power. This study provides an overview on the variety of E-fuels, including OME, DME, and methanol as well as synthetic gasoline, diesel, and kerosene produced via Fischer-Tropsch synthesis. Important fuel properties are analyzed to assess the technical applicability as well as their usage as drop-in and neat fuels by considering fuel regulations and the compatibility with existing technology. This study is part of our ongoing work within “Begleitforschung Energiewende im Verkehr” (BEniVer), a research project accompanying the funding initiative “Energy transition in transport” of the German Federal Ministry of Economic Affairs and Energy (BMWi).

1. Introduction

Carbon dioxide (CO_2) is the main anthropogenic greenhouse gas causing global warming [1]. The emissions originate from energy supply, transport and industrial processes. According to the report of the Intergovernmental Panel on Climate Change (IPCC), human made global warming reached an increase of 1 °C in 2017 compared to the pre-industrial period increasing currently by about 0.2 °C per decade [1]. Consequences of climate change are observed all over the world with drastic impacts on human and environment: Extreme heat (waves not only) in summer, aridity, forest fires, more heavy storms, floods, hurricanes, glacier melting, and raising sea level, besides others. To reduce impacts from climate change, the Paris Agreement was adopted by the United Nations in 2015 [2] with the aim to keep global warming well below 2 °C and step up efforts to keep the limit to 1.5 °C. To achieve this goal within the European Union, the European Climate Law was proposed with the target of net zero greenhouse gas emissions by 2050 [3]. On the path to climate-neutrality, the greenhouse gas emissions shall be reduced to at least 55 % by 2030 compared to 1990 [4]. In Germany, the updated climate change act aims for a CO_2 reduction of 65 % by 2030 and climate-neutrality in 2045 [5].

As part of the European 2030 Climate Target Plan, the share of renewable energy should increase to 24 % in the transport sector [6]. Here, *advanced biofuels* and *low carbon fuels* are named as central pillars, among others, to reach this goal. Besides the reduction of CO_2 emissions, the deployment of sustainable (advanced, low-carbon) fuels aims to reduce further also the emissions of nitrogen oxides (NO_x) and soot particles since they are harmful to human health and the environment.

Among sustainable fuels, E-fuels became of high importance within the past few years, with the focus put on research, besides of application aspects. They can be produced based on the Power-to-Liquid (PtL) technology using renewable energy such as wind or solar power as illustrated in Figure 1. First, hydrogen (H_2) is produced via electrolysis of water whereas CO_2 originating from industrial processes, direct air capture (DAC), or biogas is converted into carbon monoxide (CO). Biomass can be used as carbon source as well. The specific composition of the resulting syngas, i.e. a mixture of H_2 and CO, in detail the specific ratio between H_2 and CO, depends on the further process chain. For the fuel production from syngas, two main paths are considered within this study: (I) direct fuel synthesis via the Fischer-Tropsch (FT) process, and (II) synthesis of methanol (CH_3OH) being further converted to the fuel of interest.

Based on the design of the production process, different types of fuels can be produced which then can be applied across the different transport sectors: Road, rail, aviation as well as maritime shipping. Whereas the variety of sustainable aviation fuels (SAFs) is limited due to strong global regulation and requirements [7-9], the road, rail, and maritime sectors offer more possibilities for the usage of alternative fuels.

Within this work, the technical applicability and capability for the usage as drop-in or neat fuel is evaluated for different kinds of synthetic fuels based on their chemical and physical properties. This includes the characterization of E-fuels, a comparison of selected fuel properties of E-fuels with fossil fuels (depending on the considered sector), the analyses of combustion properties and emissions, as well as the preparation of an overview on the current state of research. This study is part of our ongoing work within BEniVer (*Begleitforschung Energiewende im Verkehr*), the accompanying research on the funding initiative "Energy transition in transport" of the German Federal Ministry of Economic Affairs and Energy (BMWi).

2. Classification of alternative fuels

This study distinguishes the following classes of alternative fuels: (I) Synthetic diesel, (II) synthetic gasoline, (III) synthetic kerosene, (IV) dimethyl ether and oxymethylene ethers, (V) methanol and higher alcohols, (VI) further oxygenated fuels, and (VII) methane and hydrogen. Table 1 gives an overview of the different alternative fuels as studied within the research initiative "Energy transition in transport" (methane and hydrogen are leave out in Tab. 1 since they are not comparable to the other fuels). Here, these E-fuels are primarily considered as alternatives in road transport; however, they are, in general, possible candidates for the substitution of conventional maritime fuels as well. In addition, Tab. 1 includes synthetic kerosene for application in the aviation sector. The table illustrates relevant fuel properties and existing standards. Moreover, it summarizes their possibility to use as neat fuel or blend component and drop-in fuel or near-drop-in fuel.

Figure 1 illustrates the classification of the different kinds of E-fuels according to their production route via the FT process or methanol path. The FT process yields a mixture of mainly linear hydrocarbons (known as paraffins) differing in the number of carbon (C-) atoms and separated by distillation according to their boiling range. Gasoline contains the lightest hydrocarbons with carbon chains of about C_5 to C_{10}. Next, kerosene covers a C-number-range from C_8 to C_{16}. The heaviest fuel is diesel with C_{10} to C_{20} or even longer.

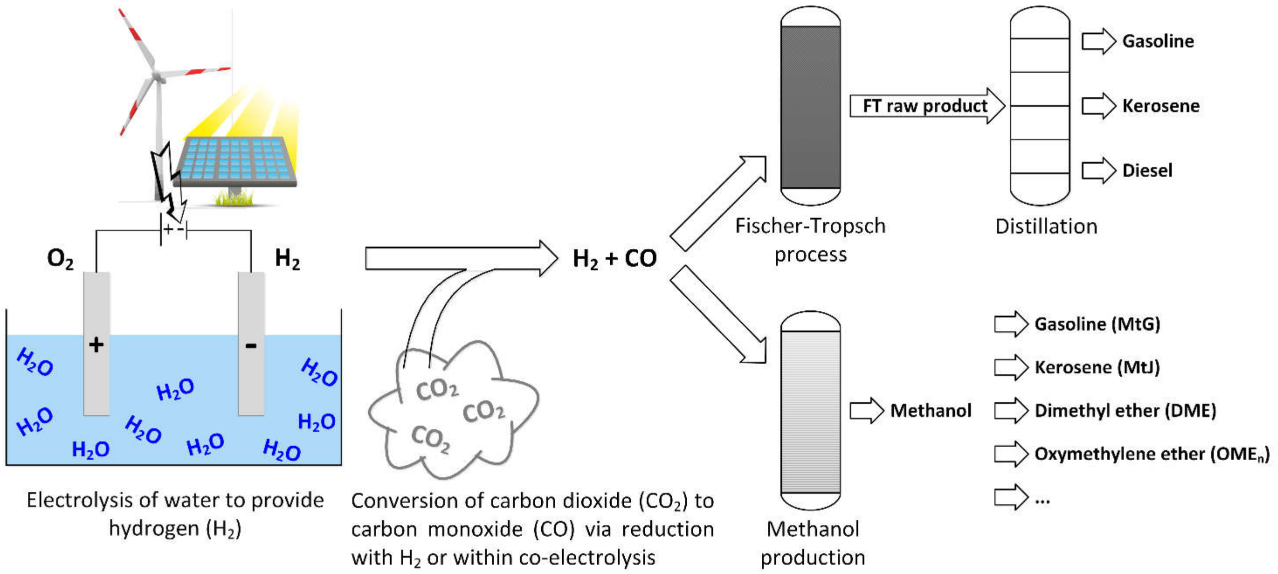

Fig. 1 Illustration of E-fuel production via the Power-to-Liquid (PtL) process including (I) water electrolysis, (II) syngas production, and (III) fuel production via the Fischer-Tropsch (FT) process or methanol production. Methanol can be processed to further sustainable fuels. Abbreviations: MtG – Methanol-to-Gasoline, MtJ – Methanol-to-Jet

Tab. 1 Overview of alternative fuels considered within BEniVer. Abbreviations: (I) Fuels: DMC – dimethyl carbonate, DME – dimethyl ether, FT – Fischer-Tropsch, MeFo – methyl formiate, MtG – Methanol-to-Gasoline, MtJ – Methanol-to-Jet, $OME_{2\text{-}5}$ – oxymethylene ether (for explanation of the subscript “2-5” the reader is referred to section 3); (II) properties: CN – cetane number, FBP – final boiling point, FP – flash point, H_u – lower heating value, (M/R)ON – (motor/research) octane number, T_b – boiling temperature, T_f – freezing point, ρ – liquid density at 15 °C and 1 bar.

	Synthetic diesel	**Synthetic gasoline**		**Synthetic kerosene**		**Ether**		**Alcohol**		**Other oxygenated fuels**	
	FT diesel	**FT gasoline**	**MtG**	**FT kerosene**	**MtJ**	**DME**	**$OME_{2\text{-}5}$**	**methanol**	**higher alcohol**	**DMC**	**MeFo**
	Neat fuel	Neat fuel		Blend		Neat fuel	Neat fuel, Blend	Neat fuel, Blend	Blend	Blend	
	Drop-in	Drop-in		Drop-in up to 50 %(v/v)		Near-Drop-in		Near-Drop-in	Drop-in up to 50 %(v/v)[a]	Near-Drop-in	
standard	EN 15940 (EN 590)	EN 228		ASTM D7566	--	ISO 16861[b]	--	ASTM D5797[c]	ASTM D7862[c),d]	--	--
T_b (°C)	85...360[e]	210[e] (FBP)		205...300[e]	[g]	-24.8[e]	105...280[h]	65[f]	99.5...117.7[d),e]	90[f]	32[f]
T_f (°C)	-40...6[f]	-90.5...-95.4[f]		≤ -40[e]	[g]	≈ -140[h]	-70...48[h]	-98[f]	-89.5...-114.7[d),e]	5[f]	-100[f]
ρ (kg/m³)	765-810[e] (800-845[e])	720-775[e]		730-770[e]	[g]	gas	961-1100[h]	792[h]	801-810[d),e),j]	1007[f] (20 °C)	970[f] (20 °C)
FP (°C)	≥ 55[e]	≤ -35[f]		≥ 38[e]	[g]	-42.2[f]	54-115[h]	9[f]	24...35[d),e]	14[f]	-27[f]
CN	≥ 51[e]	--		--	--	> 55[e]	63-100[h]	5[h]	17-25[d),h]	--	--
ON	--	≥ 95[e] (RON) ≥ 85[e] (MON)		--	--	--	--	109[i] (RON) 89[i] (MON)	96-113[d),e] (RON) 78-94[d),e] (MON)	--	--
H_u (MJ/kg)	≈ 44[h]	--		≥ 42.8[e]	[g]	27.60[h]	17.5-20.3[h]	--	--	--	--
H_u (MJ/l)	--	30-33[i]		--	[g]	18.44[h]	19.5-19.7[h]	15.8[i]	26-27[d),i] 31.1[a),i]	--	--

a) refers to 1-octanol (n-octanol)
b) deals with physical properties and does not give any requirements for application
c) US standard being not valid in Germany or the European Union
d) refers to 1-butanol (n-butanol), 2-butanol (sec-butanol), and 2-methyl-1-propanol (iso-butanol)
e) taken from standard mentioned in table
f) taken from [18]
g) no information available but properties expected to be similar with FT kerosene
h) from [19]
i) from [20]
j) temperature not specified in ASTM D7862 [16]

2.1. Neat fuel vs. blend / Drop-in vs. Near-Drop-in

As written in Tab. 1, the E-fuels considered in this study can be used both as neat fuels and as blend components. This depends on various aspects, including fuel composition, compatibility with current vehicle technology as well as regulations and standards, the modification or further development of power unit concepts, and the sector being of interest for specific fuel application.
The differentiation between drop-in and near-drop-in fuels describes originally the compatibility of synthetic blend components with (addition to) fossil fuels. In theory, blending of drop-in or near-drop-in fuels with synthetic fuels, being identical with fossil fuels, would be possible as well. Drop-in / near-drop-in fuels differ in the need of (minor) modifications of the (engine) components or of the used material. Classical neat fuels are pure gasoline and diesel, for example, whereas the typically used fuels E10 and B7 are blends containing 10 %(v/v) ethanol and 7 %(v/v) fatty acid methyl ester, respectively. With the advanced development of engine technology, also oxygenated fuels (having O atoms, besides H and C atoms) such as methanol and dimethyl ether (DME), being different from fossil fuels, became of interest as 'new' neat fuels.
Thus, the differentiation between drop-in and near-drop-in fuels is applied to neat fuels as well. In general, fuels being compatible with the existing technology (no modifications necessary) and directly usable in transport are defined as drop-in fuels. For the use of near-drop-in fuels, modifications or even new motor components are necessary.
Regarding higher alcohols, the limit of max. 50 %(v/v) (see Tab. 1) relates to the *technical compatibility* of the admixture of 1-octanol to diesel [10]. However, the resulting fuel mixture does not meet today's requirements as defined in the *relevant standard*, here EN 590 for diesel [11], i.e. using 1-octanol in road transport diesel is currently not allowed. The technical limit of alcohols as possible blending components for gasoline is likewise lower, e.g., for 2-butanol it amounts to about 15 %(v/v).
The 50 %(v/v) limit of blending synthetic kerosene is defined by the standard ASTM D7566 [9]. Note that depending on the type of a specific SAF, the technical compatibility would allow the usage higher blends up to the usage of SAF as neat fuel [12].

2.2. Regulations and standards

The fuel standards listed in Tab. 1 specify the requirements existing for the use of those E-Fuels considered in this study. Of these standards, EN 228 for gasoline [13], EN 590 for diesel [11], and EN 15940 for paraffinic diesel [14] are valid in the European Union. EN 228 and EN 590 define the requirements as well as fuel properties for gasoline and diesel for their usage in road transport. According to these specifications, synthetic fuels can be added to the fossil ones as long as the properties of the "final" fuel meets the requirements [11,13]. Currently, EN 15940 is the only standard defining a fully synthetic fuel, i.e. allowing its use as 100 % neat fuel. Due to its composition, paraffinic diesel has a lower density compared to fossil diesel. Therefore, paraffinic diesel is not identical with fossil diesel as defined within EN 590. As a result, synthetic diesel can be blended up to 30 %(v/v) with fossil diesel and according to EN 15940 [14] used as neat paraffinic diesel in automobiles approved by the manufacturer.
The ASTM D5797 standard for the use of methanol as blend component for gasoline between 51 %(v/v) and 85 %(v/v) [15] as well as ASTM D7862 for butanol as gasoline component up to 12.5 %(v/v) [16] are not valid in Europe.
Since aviation is a global business the standard specification for synthetic kerosene ASTM D7566 is valid almost all over the world. Here, different types of SAFs are defined as blending components for fossil-based kerosene (Jet A-1) up to 50 %(v/v) [9]. Whereas FT-based kerosene is certified as SAF, the Methanol-to-Jet route has no approval yet. Alcohol-to-Jet (AtJ) is a specific SAF already certified which is produced using ethanol or isobutanol.
In contrast to the regulations mentioned before, the standard ISO 16861 for DME specifies solely fuel properties [17] and made no requirements regarding the use as alternative fuel for the transport sector.
To sell synthetic fuels in Germany it is also required that the trade with the fuel is permitted by law, in detail by the 10^{th} Federal Emission Control Directive (10. BImSchV) [21]. This directive contains requirements not only on road transport fuels but also on maritime fuels and heating oil.

3. E-Fuels in transport

3.1. Synthetic diesel

The synthetic diesel studied within projects as part of the funding initiative "Energy transition in transport" (EiV) is produced almost exclusively via Fischer-Tropsch (FT) processes from syngas yielding FT-diesel. A further production process uses esters and fatty acids from vegetable or used cooking oils. According to the raw material, the product is called HVO (hydrogenated vegetable oil) or HEFA (hydrogenated esters and fatty acids). In contrast to FT-diesel, the production of HVO has already reached industrial scale being available in the U.S. and Europe, with Neste as largest producer [22,23].
The product of both process routes is a pure paraffinic diesel being suitable as drop-in fuel in diesel engines of light- and heavy-duty vehicles as well as of ships. At present, paraffinic diesel is the only synthetic fuel with a European standard (EN 15940) [14] for the (neat) use in the automobile sector. Indeed, most of the fuel properties are nearly identical with fossil diesel. However, the density of synthetic diesel is lower than the density of its fossil counterpart (see Tab. 2), which is due to the absence of aromatic compounds. Therefore, the manufacturer has to prove if the motor vehicle can be, fueled up with neat paraffinic diesel, i.e. without any drawbacks [14]. For

blending paraffinic diesel with fossil diesel, EN 590 defines no percentage limit but requires that the properties of the mixture have to comply with all the requirements being specified in the standard [11].

On the other hand, the absence of aromatic compounds has a positive effect on the emissions of particulate matter. In general, aromatic compounds are precursors for the formation of soot. Indeed, soot is formed during combustion of synthetic diesel as well – but without aromatics, the emissions of soot and particulate matter, respectively, are considerably reduced. This offers the additional possibility that the exhaust catalyst can reduce NO_x emissions more effectively.

3.2. Synthetic gasoline

As presented in Tab. 1 there are two different kinds of synthetic gasoline being processed via the PtL technology. The first, FT gasoline, will be produced together with diesel and kerosene (see section 3.3) from syngas. Following the synthesis unit, the FT product is separated via distillation. Apart from gaseous products, the lightest fraction contains hydrocarbons with a carbon size distribution similar to the one of gasoline (components). The raw product from the FT synthesis are mainly linear paraffins, being beneficial for a diesel fuel since the cetane number of linear hydrocarbons is higher than the ones of branched hydrocarbons. To achieve a high octane number, as required for gasoline, further refinement processes like isomerization and alkylation are necessary within the upgrading of the FT crude oil.

The production of the second type of a synthetic gasoline considered, the Methanol-to-Gasoline (MtG), is based on syngas, too. Due to the gasoline production from methanol, the extent of additional refinement processes depends on the used catalyst and the process control.

Independent of the production route, the development of synthetic gasoline generally tends to meet the requirements specified in EN 228. This means, synthetic gasoline can be used as neat fuel without any adjustments of the engine, engine components, or materials. Regarding the usage, synthetic gasoline differs from synthetic diesel or oxygenated fuels, both being of interest in different transport sectors. Since diesel engines dominate heavy-duty transport, including the maritime sector, the development of synthetic gasoline focuses on the application in passenger cars.

3.3. Synthetic kerosene

As of May 2021, a total of seven different alternative jet fuels have been approved for the usage as drop-in fuel in blends with fossil jet fuel, up to 50 %(v/v) [9]. The mixing limit results not only from the specification of fuel properties but also from the share of aromatics being natural (historic) fuel components due to their occurrence in fossil oil. Without using any aromatization and cyclization processes, specific SAFs consist of linear and / or branched paraffins only. However, the aromatics lead to the appropriate swelling of seals, i.e. without aromatics in the jet fuel the risk of leakages cannot totally be ruled out. Hence, a number of aromatics of min. 8 %(v/v) [9] is required within the specification; therefore, blending with fossil jet fuel is unavoidable at present. Nevertheless, test flights with 100 % SAF have recently demonstrated that also the use of neat paraffinic kerosene is feasible [12]. As a consequence, it is not to be excluded that future specifications might allow the use of completely non-aromatic jet fuels. Thus, additional benefits in terms of reducing non-CO_2 effects might be realized due to the reduced emission of particles.

Paraffinic FT kerosene belongs to the certified SAFs and is called FT-SPK (synthetic paraffinic kerosene). As mentioned earlier, the raw FT product can be separated in three different fractions – gasoline, diesel, and kerosene being in the middle distillation range compared to the other fuels.

A new synthetic kerosene under development, thus being not yet approved as SAF, is Methanol-to-Jet (MtJ). MtJ is produced by the oligomerization of methanol, similar to MtG, leading likewise to a paraffinic kerosene, without any aromatics. Even though at present not included in ASTM D7566, the MtJ kerosene resembles the certified Alcohol-to-Jet (AtJ) being produced from ethanol or iso-butanol.

In contrast to road transport and maritime fuels, oxygenated fuels are out of question for the use as SAFs since C-O bonds are expected to come along with a lower storage stability and an increased risk of water contamination due to hygroscopicity. Therefore, a drastic reduction of soot emissions is only achievable by keeping the amount of aromatics within the jet fuel as low as possible.

3.4. Dimethyl ether and oxymethylene ethers

Dimethyl ether (DME, H_3COCH_3) and oxymethylene ether (OME_n: $H_3CO(H_2CO)_nCH_3$ with $n \geq 1$) are of high importance as alternative fuel compounds for diesel engines in road transport as well as maritime shipping for several reasons. (I) Due to the absence of any C-C bonds within the fuel, even fuel rich mixtures show nearly no soot formation – compared not only to fossil diesel but also to synthetic diesel or other oxygenated fuels like alcohols or even to conventional biodiesel, consisting of fatty acid methyl esters. Hence, the use of DME or OME_n as a near-drop-in fuel not only promises a substantially stronger reduction of soot emission but, even more, an escape from the trade-off between soot and nitrogen oxides (NO_x). (II) DME and OME_n can be produced from renewable sources using methanol as the intermediate product – either via the Power-to-Liquid (PtL) process but also from sustainable resources (biomass) via gasification or fermentation. This means, the use of DME or OME_n will help to achieve CO_2 neutrality. (III) Although OME_n do not have any C-C bonds, they are fully miscible with conventional hydrocarbon fuels; especially higher OME_n ($n \geq 2$) are in line with important diesel fuel properties like cetane number, boiling temperature, freezing point (besides OME_5), and flash point, as shown in Tab. 2.

On the other hand, the liquid density as well as the viscosity, both properties characterizing the fluidity of a fuel, are outside of the parameter range for a diesel fuel. The high oxygen content of these fuels has a beneficial effect on reduced soot and NO_x emissions; but, on the other hand, this may cause increased emissions of new harmful substances like aldehydes and ketones, lead to a reduced heating value, and might also adhere the risk of material incompatibility. For these reasons, adjustments or even new developments of the engine system are unavoidable in case neat DME or OME_n is fueled [24,25]. For the use in blends with diesel, the degree of modifications depends on the amount of OME_n in the fuel mixture. According to Avolio et al. [26] even mixtures up to 15 %(v/v) might be compatible with the current vehicle technology. On the other hand, OME_n requires different sealing materials due to the oxygen in the molecule [25] to ensure that even the use of blends with small amounts of OMEn may not lead to leakages in long-term use.
Concerning the effect of OME_n on the combustion behavior when blended in diesel, it was found that 30 %(m/m) could be added without any significant change in the laminar burning velocity, being an important fundamental combustion property and a measure for heat release as well as reactivity of any fuel. Figure 2 shows the comparison of the laminar burning velocity of: (I) neat OME_4, (II) a diesel surrogate (50 %(n/n) n-dodecane + 30 %(n/n) farnesane (2,6,10-trimethyldodecane) + 20 %(n/n) 1-methylnaphthalene), and (III) a mixture of the diesel surrogate + 30 %(m/m) OME_4; all data were reported at 200 °C and 1 bar. With a maximum of about 108 cm/s, OME_4 yields a distinctly higher laminar burning velocity than the diesel surrogate with a maximum of about 83 cm/s. Interestingly, the mixture of the diesel surrogate + 30 %(m/m) OME_4 shows a maximum being only slightly higher than the pure diesel surrogate. According to these results, OME_4 can be added to diesel in high amounts without having any influence on heat release or reactivity [27]. This is assumed to be true for OME_n in general as well.

Tab. 2 Overview of important physical properties of dimethyl ether (DME) and oxymethylene ethers (OME_n) compared to fossil diesel. Abbreviations: CN – cetane number, FP – flash point, H_u – lower heating value, T_b – boiling temperature, T_f – freezing point, ν – viscosity, ρ – liquid density (at 1 bar).

	Diesel	**DME**	**Oxymethylene ether (OME_n)**				
			OME_1	**OME_2**	**OME_3**	**OME_4**	**OME_5**
T_b (°C)	85...360 a)	-24.8 e)	42 f)	105 f)	156 f)	201 f)	242 f)
T_f (°C)	-40...6 b)	≈ -140 f)	-105 f)	-70...-65 f)	-43...-41 f)	-10...-7 f)	≈ 18.4 f)
ρ (kg/m³)$_{15°C}$	820-845 a) 800-840 a),c)	gas	850-867 f)	961 f)	1021 f)	1059 f)	1100 f)
ν (mm²/s)$_{40°C}$	2.0-4.5 a) 1.5-4.0 a),c)	gas	0.32-0.33 f)	0.64 f)	1.05 f)	1.75 f)	2.63 f),g)
FP (°C)	≥ 55 a)	-42.2 b)	-32 f)	12 h)	54 f)	88 f)	115 f)
CN	≥ 51 a)	> 55 e)	29-37.6 f)	63 f)	70-78 f)	90 f)	100 f)
H_u (MJ/kg)	≈ 43 f)	27.60 f)	22.44 f)	20.32 f)	19.14 f)	18.38 f)	17.86 f)
H_u (MJ/l)	≈ 35 f)	18.44 f)	19.30 f)	19.53 f)	19.54 f)	19.47 f)	19.64 f)

a) data taken from [11]
b) data taken from [18]
c) values belong to winter diesel
d) data taken from [20]
e) data taken from [17]
f) data taken from [19]
g) at 25 °C
h) data taken from [24]

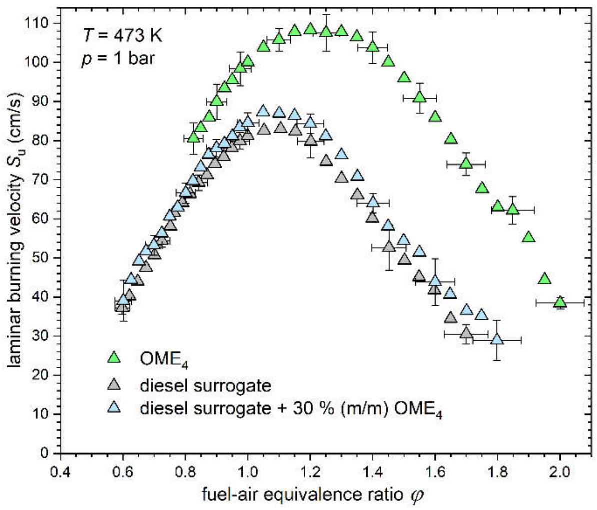

Fig. 2 Comparison of experimentally determined laminar burning velocities of: (I) neat OME_4, (II) a diesel surrogate (50 %(n/n) n-dodecane + 30 %(n/n) farnesane (2,6,10-trimethyldodecane) + 20 %(n/n) 1-methylnaphthalene), and (III) a mixture of the diesel surrogate + 30 %(m/m) OME_4. All data are measured at 200 °C and 1 bar [27].

3.5. Methanol and higher alcohols

For the energy transition in the transport sector, methanol is a key molecule due to several reasons: (I) As already mentioned previously, methanol is a platform molecule as it is an important intermediate product for the production of several specific E-fuels. (II) Methanol offers the possibility for a flexible usage since it is of interest as alternative fuel for light- and heavy-duty vehicles as well as for the maritime sector. (III) Current research activities focus on the usage of methanol both as neat fuel and as blending component.

Regarding dominant relevant fuel properties (see Tab. 3) methanol is an ideal blending component for gasoline with the benefit to increase the octane number. In the USA methanol gasoline blends are specified for the use in spark-ignition engines according to ASTM D5797 [15]. Here, the amount of methanol ranges from 51 %(v/v) to 85 %(v/v). The oxygen content leads to a cleaner combustion regarding soot emissions. In transport sectors (heavy-duty loading and shipping), where diesel engines are dominant, this advantage is of high importance within the consideration for the application. However, due to several unfavorable properties of methanol compared to diesel fuel (e.g., density, cetane number, and heating vale are (too) low), modifications of the engine, components, and / or material are to be expected for the use in blends and, to an even larger extent, for the use as neat fuel.

The higher alcohols being in focus within the energy transition are 2-butanol (also named sec-butanol) and 1-octanol (n-octanol). For the sake of completeness, in Tab. 3 are also listed ethanol, 1-butanol (n-butanol), and tert-butanol. Ethanol is already a standard blending component for gasoline (depending on percentage of admixture named as E5 and E10) being not produced via the PtL-path but from fermentation ("bioethanol").

Regarding the C_4-alcohols, not only 2-butanol might be considered as synthetic fuel component for gasoline but also 1-butanol and iso-butanol. Even though their densities are higher, their boiling temperatures and octane numbers are within the specification for gasoline and, compared to ethanol, the heating values are closer to gasoline as well. Similar to methanol, these butanols are specified as blending components up to 12.5 %(v/v) in the USA following the standard ASTM D7862 [16]. The fourth mentioned C_4 alcohol, tert-butanol, is out of consideration due to its physical properties such as the high melting point of about 26 °C.

Based on the physical properties, 1-octanol appears as an ideal blending component to diesel fuel aiming for the reduction of the emissions of soot and particulate matter, respectively. Although not yet specified as fuel component, it was already shown by Zubel et al. [10] that an admixture of up to 50 %(v/v) is feasible from a technical perspective. In contrast to other E-fuels considered for the application in diesel engines of road transport vehicles as well as maritime shipping, 1-octanaol is currently only of interest for light-duty vehicles.

3.6. Further oxygenated fuels

Further oxygenated E-fuels considered (Tab. 1) are dimethyl carbonate (DMC, H_3C-COO-CH_3) and methyl formiate (MeFo, HCOO-CH_3) both being produced from methanol; they are of interest for the usage in spark-ignition engines due to their high octane numbers [28]. Similar to DME or OME_n no C-C bonds exist within the molecular structures, i.e. the emission of soot is significantly reduced when burned in blends with gasoline. Even if the boiling temperature is within the range of gasoline, the density is distinctly higher. For these reasons, modifications on the engine and / or engine components are assumed to be required.

3.7. Methane and hydrogen

As gaseous E-fuels, renewably produced methane (CH_4) and mixtures of renewable methane and hydrogen (H_2) are considered. Whereas H_2 stems directly from electrolysis, CH_4 is produced from syngas similar to the FT fuels. In road transport as well as in shipping, gas engines using methane as fuel are well-established. Irrespective of whether the engine runs on CNG (compressed natural gas) or LNG (liquified natural gas), the PtL based methane can be used directly with almost no modifications. According to the specification EN 16723-2 [29], the amount of H_2 is limited to 2 %(v/v) in natural gas vehicles while it is mentioned that a H_2 content of 10 %(v/v) could be applicable in gas engines with an advanced control system. Besides the currently existing regulations, also the technology has to be adjusted for the use of CH_4 + H_2 mixtures. For example, due to the low gas density of about 0.084 kg/m³ for H_2 (at 15 °C and 1 bar) compared to 0.671 kg/m³ for CH_4 [18], higher pressures in the fuel tank (for storage) and the engine (during operation) are necessary. What comes along is the small size of the hydrogen molecule as well as the hydrogen embrittlement, important regarding material compatibility. In detail, the diffusivity of H_2 and the degradation of the material due to embrittlement have to be respected. Furthermore, H_2 leads to higher combustion temperatures causing higher NO_x emissions. On the other hand, H_2 shows higher burning velocities which enables the combustion of lean mixtures. This offers the possibility to reduce the fuel consumption as well as the combustion temperature and therefore the NO_x emissions. Due to these reasons, the engine design and materials used require modifications respectively when the amount of H_2 exceeds 25 %(v/v) [30].

Besides in transport, the gaseous fuels are of interest in the energy sector as well. Here, the PtL based CH_4 is usable without difficulty. The use of mixtures with H_2 is possible in modern gas turbines up to 15 %(v/v) H_2.

Tab. 3 Overview of important physical properties of different alcohols compared to fossil diesel and gasoline. Abbreviations: CN – cetane number, FP – flash point, H_u – lower heating value, (M/R)ON – (motor/research) octane number, T_b – boiling temperature, T_f – freezing point, v – viscosity (at 40 °C), ρ – liquid density (at 15 °C and 1 bar).

	Diesel	Gasoline	Alcohols						
			Methanol	Ethanol	1-Butanol	2-Butanol	iso-Butanol	tert-Butanol	1-Octanol
	$C_{14}H_{30}$ g)	C_8H_{15} g)	CH_3OH	C_2H_5OH	nC_4H_9OH	sC_4H_9OH	iC_4H_9OH	tC_4H_9OH	$nC_8H_{17}OH$
T_b (°C)	85...360 a)	210 e) (FBP)	65 b)	78 f)	117.7 h)	99.5 h)	108 h)	83 b)	195 b)
T_f (°C)	-40...6 b)	-90.5... -95.4 b)	-98 b)	-114 b)	-89.5 h)	-114.7 h)	-108 h)	26 b)	-16 b)
ρ (kg/m³)	820-845 a) 800-840 a),c)	720-775 e)	792 d)	785 d)	810 d)	806.3 h),i)	801.8 h),i)	790 b) (20 °C)	830 b) (20 °C)
v (mm²/s)	2.0-4.5 a) 1.5-4.0 a),c)		0.75 d)	1.5 d)	2.63-3.7 d)				
FP (°C)	≥ 55 a)	≤ -35 b)	9 b)	12 b)	35 h)	24 h)	28 h)	11 b)	84 b)
CN	≥ 51 a)	--	5 d)	8 d)	17-25 d)	--	--	--	--
RON	--	≥ 95 e)	109 f)	109 f)	96 h) 98 f)	101 h) 105 f)	113 h) 105 f)	107 f)	28 i)
MON	--	≥ 85 e)	89 f)	90 f)	78 h) 85 f)	82 h) 93 f)	94 h) 90 f)	94 f)	27 f)
H_u (MJ/l)	≈ 35 d)	30-33 f)	15.8 f)	21.4 f)	26.9 f)	26.7 f)	26.6 f)	25.7 f)	31.1 f)

a) data taken from [11]
b) data taken from [18]
c) values belong to winter diesel
d) data taken from [19]
e) data taken from [13]
f) data taken from [20]
g) average formula, taken from [20]
h) data taken from ASTM D7862 [16]
i) temperature not specified in ASTM D7862 [16]

4. Conclusions

This paper provides an overview on a range of E-fuels being of interest for the energy transition in the transport sector. Based on syngas stemming from electrolysis, hydrocarbon fuels (gasolines, diesel, kerosene) and oxygenated fuels (like alcohols or ethers) as well as gaseous fuels can be produced. Besides synthetic methane, being applicable like natural gas, synthetic gasoline, diesel and kerosene can be used as long as the required fuel properties comply with the corresponding standards. From a technical point of view, the oxygenated fuels are usable in blends with small or even no modifications to engine, engine components and / or materials. However, specifications and standards being valid in Europe are still missing.

Despite many research and development projects in progress, the PtL technology has not yet reached an industrial scale. To achieve CO_2 neutrality by 2045 in Germany, not only the PtL technology has to be promoted in order to become mature and vivid; in addition, further CO_2 saving technologies need to be implemented as well as the optimization of combustion engines regarding their efficiency and infrastructures.

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