

# Alternative Liquid Fuels from Renewable Resources

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Recent progress regarding the production of alternative liquid fuels is described with a focus on catalyst development. Fuels for spark ignition engines as well as diesel fuels are considered and their potentials regarding the reduction of harmful emissions are addressed. Two main strategies are described. The first implies production of synthesis gas from renewables or CO<sub>2</sub> and subsequent synthesis of methanol or dimethyl ether. Both can be further converted to a series of valuable fuels, e.g., high-quality gasoline or oxymethylene ethers. The second strategy comprises the production of ethanol and its conversion to gasoline.

**Keywords:** Dimethyl ether, Emission reduction, Fuel composition, Fuel production, Oxymethylene ethers

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## 1 Introduction

In 2009, the leaders of the EU and the G8 announced at the 35th G8 summit to limit global warming below 2 °C compared to the preindustrial level. The objective to reduce greenhouse gas emissions until 2050 by 80 % compared to 1990 was set. In the same year, the EU decided to set a target of 95 g<sub>CO<sub>2</sub></sub>km<sup>-1</sup> for new cars registered in the 28 EU countries (EU-28) [1] and a 10-% target of renewable energies for the transport sector by 2021, phased in from 2020 [2]. The European Climate Foundation (ECF) states the challenges on the way to decarbonization of the transport sector in the *Roadmap 2050* [3]. The goal is an overall emission reduction of at least 80 % CO<sub>2</sub> compared to 1990, which requires a 95 % reduction for the road transport sector, according to the estimates of the study. At the UN climate conference 2015 in Paris, it was agreed to keep global warming below 2 °C and this agreement was signed by 175 states in 2016. To reach this ambitious goal, the greenhouse gas emissions must be reduced completely to zero.

In addition to the greenhouse gas issue, the improvement of air quality, especially in large cities, is a great challenge. The European Environmental Agency (EEA) reports 436 000 premature deaths (4 668 000 years of life lost, YLL) by fine particulate matter (PM, particulate diameter 2.5 μm or less, PM<sub>2.5</sub>), 68 000 premature deaths (723 000 YLL) by NO<sub>2</sub> and 16 000 premature deaths (179 000 YLL) by O<sub>3</sub> in the EU-28 in 2016 [4]. According to the report, the transport sector contributed 15 % of total PM<sub>2.5</sub> primary emissions (approximately 22 % non-exhaust emissions) and was the

largest contributor regarding emissions of nitrogen oxides (NO<sub>x</sub>), with 46 % of total EU-28 emissions in 2014. The emission legislation in Europe is regulated by the Euro standards, which were introduced in 1992 with the Euro 1 regulation, followed by successively stricter standards up to Euro 6 which is valid today. CO<sub>2</sub> and PM emissions have been considered for a long time as the main issues and the legislation has been designed accordingly. For example, the limits for PM emissions have been reduced by 97 % from Euro 1 to Euro 6. Studies in the last years have shown a mismatch between official measurements within a test stand and the performance under real driving conditions. The latest Euro 6 diesel vehicles emit up to seven times more NO<sub>x</sub> in real-world conditions than in official tests [5]. To close this gap, the United Nations Economic Commission for Europe (UN-ECE) started to work on the development of an updated procedure, the world-harmonized light-duty vehicle test procedure (WLTP). This test cycle reflects the real driving behavior and closes the loopholes of the current cycles.

Furthermore, the European Union introduced a real driving emission (RDE) test for cars and vans with the legal validity of the Euro 6d-TEMP in September 2017. This makes the EU the

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first region in the world with on-road emissions testing methods for legal compliance purposes. The challenging demands of the legislators cause tremendous efforts to develop new technologies. Exhaust emissions can be reduced by complex aftertreatment systems. However, a holistic solution, that can reduce both global CO<sub>2</sub> and local exhaust emissions, is highly desirable and, in this context, the development of alternative fuels is imperative. These should lead to a closed CO<sub>2</sub> cycle, if production is based on regenerative resources, and their properties can be adapted in such a way, that combustion is almost complete, without significant exhaust emissions.

Within this work, some promising concepts for the production of alternative fuels from renewable resources are described. Fuels for spark ignition engines as well as diesel fuels are considered and their physicochemical as well as fuel properties indicate significant advantages compared to their counterparts obtained from fossil resources. Two main strategies are described: processes which proceed via methanol or dimethyl ether (DME) and processes with ethanol as key element (Scheme 1). The former are based on synthesis gas which can be obtained from renewables or CO<sub>2</sub>, employing different gasification technologies or, in the case of CO<sub>2</sub>, chemical reduction. Synthesis gas can be converted to methanol or DME and both can serve for the production of several fuels like gasoline (with and without aromatics) and, regarding diesel fuels, so-called oxymethylene ethers (OMEs). Combustion of OMEs is almost soot- and NO<sub>x</sub>-free, and thus, this article focusses on this class of promising diesel substitutes. The second main strategy is the fermentative production of ethanol, ideally from cellulose to minimize interferences with the nutrition sector. Ethanol can be used directly as fuel or it can be converted to ethyl *tert*-butyl ether (ETBE) which is used on a large scale as octane enhancer. Another option is the conversion of ethanol to gasoline via dehydration to ethylene followed by oligomerization and hydrogenation. The resulting gasoline is free of aromatics and, during combustion, formation of harmful emissions is strongly reduced.

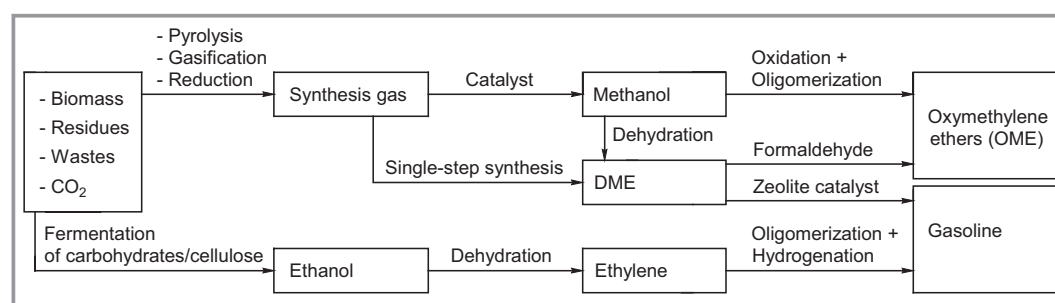
## 2 Synthesis of Gasoline from Renewable Resources

Exhaust emission legislation is getting stricter both in Europe and the United States in the next years. The Califor-

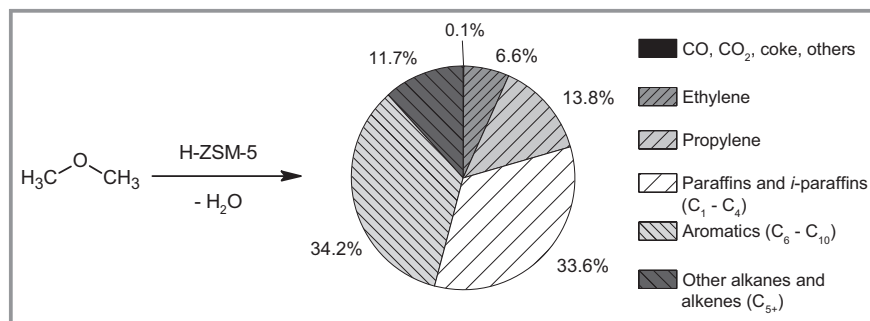
nia Air Resources Board (CARB) leads the way with an intensification of the particulate matter emission limits from 3 mg mile<sup>-1</sup> in 2017 to 1 mg mile<sup>-1</sup> in 2025 [6]. In Europe, the current valid Euro 6d-temp standard restricts the maximum PM emissions to 4.5 mg km<sup>-1</sup> [7]. To be able to compete with locally emission-free electric motors, the formation of emissions during combustion of liquid fuels has to be reduced drastically. This is not only an issue for diesel engines, vehicles with Otto engines are affected as well. The EU intensified its efforts for PM reduction with the compulsive launch of a gasoline particulate filter (GPF) in 2018, for vehicles which are not able to reach the PM limits during RDE tests [8]. However, exhaust aftertreatment is expensive. Thus, a promising approach to force PM reduction is to lower the formation of PM during combustion. In the following, different concepts for the production of gasoline with beneficial combustion properties are outlined.

### 2.1 Synthesis of Gasoline from Dimethyl Ether Using Hierarchical ZSM-5 Catalysts

Besides being a promising intermediate for the production of alternative diesel fuels as described in Sect. 3.2, DME can also be used as feedstock for the generation of liquid gasoline-range hydrocarbons (DME-to-gasoline, DTG). Similar to the well-established methanol-to-gasoline (MTG) process [9], this approach employs zeolite catalysts for the production of gasoline fractions with relatively high contents of aromatic components, as shown, e.g., in Fig. 1 [10,11]. These products can be used as blendstocks to increase octane numbers of gasoline fuels without adding to the oxygen content [12–15]. However, the DTG process has several advantages over MTG technology. These include the potential for higher space time yields of liquid products due to stoichiometry and thermodynamic reasons, such as a lower heat of reaction and higher equilibrium conversion, as well as a simplified process design because of the obviated need for a methanol dehydration reactor up-stream to the gasoline synthesis step [16–18]. However, the microporous H-ZSM-5 catalysts commonly used in MTG and DTG processes often undergo rapid deactivation under reaction conditions due to internal and external coking [19]. This issue can be addressed by the use of so-called hierarchical



**Scheme 1.** Strategies for the production of fuels from renewable resources.



**Figure 1.** Reaction scheme of the DTG process. As an example for typical product yields, values are given in wt % as reported in [10] for the conversion of methanol over nano-ZSM-5. Process conditions: reactor  $\varnothing_i = 17$  mm;  $L = 250$  mm;  $T = 370$  °C;  $p = 1$  atm; 500 mg zeolite + 5 g quartz sand + soda glass beads + quartz glass; methanol partial pressure, 0.21 atm in  $N_2$ ;  $\Delta T \leq 1$  K in axial direction;  $WHSV = 2.6$  g<sub>Methanol</sub>/g<sub>Catalyst</sub> h<sup>-1</sup>; modified residence time  $\tau_{mod,0} = 1.3$  g h mol<sup>-1</sup>,  $TOS = 10$  h.

H-ZSM-5 catalysts which incorporate a complementary meso- and/or macroporous structure. These kinds of materials can be generated using a variety of techniques, including postsynthetic modification or aggregation, and template-assisted synthesis [20, 21]. When used for MTG and DTG applications, hierarchical zeolite catalysts can promote the reduction of mass transport limitations [22], utilization of catalyst crystal volume [23], and improvement of long-term stability, conversion capacity, and selectivity to liquid products in the gasoline range [24–26].

The postsynthetic modification of microporous ZSM-5 by leaching of framework Si with bases, such as aqueous solutions of NaOH (desilication), to generate additional mesoporosity is a thoroughly investigated method that can readily be transferred to the industrial scale [27–33]. In previous publications [26, 34], the preparation, characterization, and application of hierarchical H-ZSM-5 catalysts in powdered form generated by desilication of commercially available H-ZSM-5 for the DTG conversion was detailed. The catalysts were tested in a laboratory-scale plant with a down-flow tubular fixed-bed reactor at 375 °C, 1 bar, and a weight hourly space velocity (WHSV) of 3.3 g<sub>DME</sub>/g<sub>Cat</sub> h<sup>-1</sup>. Relative to their untreated parent materials, the hierarchical zeolite catalysts showed 1.5- to almost 7-fold increase in conversion capacity for the DTG process with partially over 200 h of full DME conversion under the employed conditions (Fig. 2). In addition, increased selectivity to hydrocarbons in the gasoline range was also evident. This significant improvement in long-term stability and lifetime yield of gasoline-range products can mainly be attributed to decreased deactivation rates found for H-ZSM-5 catalysts with a hierarchical pore structure when compared to the purely microporous materials.

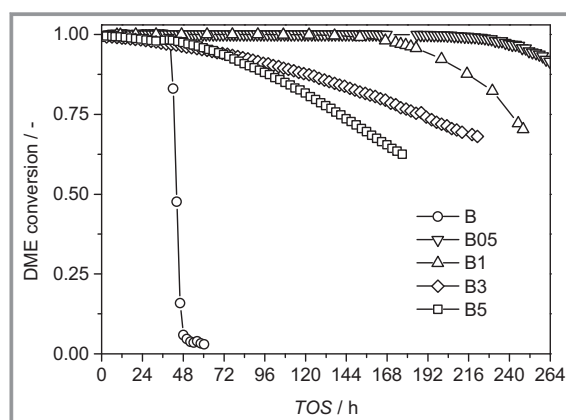
This demonstrates that hierarchical zeolites generated by desilication are beneficial catalysts for the application in gasoline synthesis from dimethyl ether. In comparison to conventional H-ZSM-5, these materials show improved catalytic performance, both in terms of increased conversion capacity of DME as well as in terms of enhanced selectivity towards gaso-

line components. Based on these auspicious results, ongoing work focuses on generating shaped catalyst bodies, such as cylindrical extrudates, using hierarchical zeolite powders and various ceramic binders like alumina and silica. This is done with the aim of applying hierarchical ZSM-5 catalysts for the DTG process on an industrially relevant scale. However, establishing a comprehensive understanding of catalyst and binder characteristics, such as the types and distribution of acid sites or porous topology as well as interactions and catalytic impacts of these properties, remains a challenge for these investigations.

## 2.2 Synthesis of Gasoline without Aromatics

Aromatics are known to be precursors of soot formation in the engine combustion chamber [35]. Furthermore, recent studies show negative interactions between aromatics and ethanol regarding PM formation [36]. The vaporization of the aromatic fraction in the gasoline is hindered with increasing ethanol content, which leads to incomplete evaporation and mixing of the fuel in the combustion chamber, resulting in increased PM formation. A medical study from 2013 states aromatic hydrocarbons, emitted from gasoline-powered vehicles, as a major source of PM<sub>2.5</sub> in the atmosphere and predicts about 3800 premature mortalities and a total social cost of \$28.2 billion caused by aromatics across the contiguous U.S. for the baseline year 2006 [37].

Current legislation allows a maximum aromatics content of 35 vol % in automotive fuels (DIN EN 228 [38]). Due to



**Figure 2.** DME conversion as function of TOS for hierarchical H-ZSM-5 catalysts B05, B1, B3, B5, and purely microporous catalyst B modified from [26]. Process conditions: reactor ( $V_4A$  steel)  $\varnothing_i = 8$  mm;  $L = 80$  mm;  $T = 375$  °C;  $p = 1$  bar; 200 mg zeolite + 3 g SiC; 4.4 % DME in Ar (140 mL min<sup>-1</sup>);  $\Delta T \leq 4$  K in axial direction;  $WHSV = 3.3$  g<sub>DME</sub>/g<sub>Catalyst</sub> h<sup>-1</sup>;  $\tau_{mod,0} = 0.51$  g h mol<sup>-1</sup>.

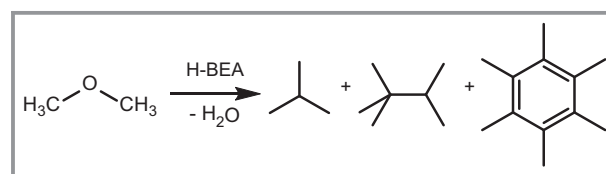
their high octane numbers, aromatics are used to improve the knock resistance of the fuel [39]. With technical applied biomass-to-liquids (BTL) methods for the production of synthetic gasoline, like the MTG or the DTG process, 30 vol % aromatics or even more are formed [10, 11]. Particularly problematic in this case is the formation of heavy aromatics ( $C_{9+}$ ) with boiling points above 160 °C. The most problematic species is durene (1,2,4,5-tetramethylbenzene) with its high melting point of 79 °C. Durene has to be removed completely from the gasoline because it can clog the fuel injection system after crystallization. Heavy gasoline treatment (HGT) processes are used in MTG/DTG plants to reduce the durene content of the product. The following reactions occur in HGT units: isomerization, disproportionation, transalkylation, ring saturation, dealkylation, and cracking [15]. However, there is still a large  $C_{9+}$  fraction in the product after HGT. An approach to convert the  $C_{9+}$  aromatics to branched alkanes by hydrogenation, ring opening, and isomerization would be complicated and impractical to realize on a large scale, due to the many required reaction steps. Each step is limited by conversion and selectivity which leads to undesirable loss of product. Compared to aromatics, branched alkanes have the advantage of high octane numbers and improved reactivity during combustion.

A far more elegant solution is the direct production of gasoline free of aromatic components. An interesting approach in this regard is a BTL process for the production of branched alkanes like triptane (2,2,3-trimethylbutane) and *iso*-butane (2-methylpropane). Thereby, two urgent environmental problems of our time can be solved in parallel. Global  $CO_2$  emissions can be reduced by using regenerative feedstocks and PM emissions can be lowered by low-emission combustion. Halide catalysts like  $ZnI_2$  or  $InI_3$  produce triptane with high selectivity from methanol or DME in homogeneous processes, but the conversion is inhibited by  $H_2O$  which is formed by dehydration of the educt [40–44].

This article will focus on continuous heterogeneous synthesis routes. A promising catalyst in this regard is zeolite beta (H-BEA). Zeolite beta is a 3D 12-ring pore system with diameters of  $5.5 \times 5.5$  and  $6.4 \times 7.6$  Å [45]. First investigations of methanol-to-hydrocarbons (MTH) reactions over zeolite beta at typical MTG/DTG temperatures (approx. 370–400 °C) showed a high selectivity for the formation of *iso*-butane [46]. With increasing time on stream (TOS) and associated deactivation, the ratio of hexamethyl benzene (HMB) in the reaction product rises [47]. In MTH processes, hydrocarbons and  $H_2O$  are formed by methylation of olefins and aromatics in a dual catalytic cycle, as reported by Ilias et al. [48, 49]. Catalysts without steric restrictions tend to form polymethylated benzenes in hydrogen-deficient reactions [12].

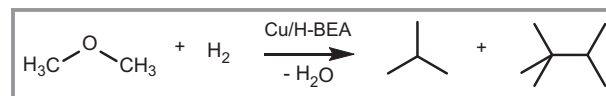
Iglesia and co-workers [50, 51] investigated the conversion of DME over several acidic zeolites. They showed that triptane and *iso*-butene can be selectively produced at lower reaction temperatures (180–220 °C) and DME pressures (60–250 kPa) compared to established MTH processes.

Ferrierite (H-FER), mordenite (H-MOR), ZSM-5 (H-MFI), Y (H-FAU; USY) and beta (H-BEA) zeolite catalysts were tested, whereof H-BEA showed a high selectivity towards *iso*-butyl and triptyl species and the highest formation rates among all tested materials. In a subsequent work, the authors investigated the chain growth mechanism of the DME homologation to triptane over H-BEA [52]. The chain growth is controlled decisively by the stability of carbenium ion transition states, leading to the formation of molecules with four-carbon backbone structures, which terminate preferentially as triptane. *iso*-butane is formed by isomerization and  $\beta$ -scission, when the chain growth exceeds triptane. However, DME homologation into branched alkanes and water as described so far is still a hydrogen-deficient reaction, leading to the formation of HMB as exemplary shown in Scheme 2.



**Scheme 2.** Simplified conversion of DME to hydrocarbons catalyzed by zeolite H-BEA.

Simonetti et al. [53] used adamantane as hydride transfer co-catalyst. Thereby, a decrease in HMB formation relative to alkanes could be observed, but, unfortunately, the selectivity to triptyl isomers decreased as well by hydrogenation of surface alkoxide intermediates. Schaidle et al. [54] enhanced the process by adding copper as hydrogenation component on the H-BEA catalyst and  $H_2$  to the DME educt feed. The Cu-modified H-BEA catalyst can incorporate the added hydrogen into the reaction products and shifts selectivity towards branched alkanes instead of undesired aromatics as exemplary shown in Scheme 3.



**Scheme 3.** Simplified conversion of DME to branched aliphatics catalyzed by Cu/H-BEA.

Furthermore, the Cu/H-BEA catalyst shows an increased activity compared to pure H-BEA. The *iso*-butyl species formed in the reaction can be fed back into the reactor and react further to branched alkanes like *iso*-octane with olefins, which are formed as intermediates during DME homologation [53]. A problem that could not be solved by the addition of copper is the rapid deactivation of the catalyst. Better understanding of the deactivation mechanisms is an important issue for future research on the way to a highly selective process for the synthesis of branched alkanes with improved long-term stability.

### 2.3 Production of Gasoline from Ethylene

Because of their high power-to-weight ratio, simple construction, and the ability to be used position-independent, small two-stroke combustion engines are used to drive handheld gardening tools [55]. However, the two-stroke design involves disadvantages. Due to the use of a fuel-oil mixture for lubricating and incomplete combustion, exhaust emissions can contain harmful components like aromatics, naphthenes, and polycyclic aromatic hydrocarbons [56]. These emissions are easily inhaled by the operator of these handheld tools. It is reported that the use of alkylate-type fuels can reduce the amount of harmful components emitted from two-stroke engines [57, 58]. This reduction is attributable to the composition of the alkylate fuel which consists of isoparaffins [58, 59]. Its naming is derived from the production process via alkylation, i.e., the reaction between alkenes and alkanes [60].

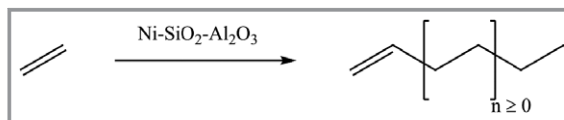
However, such fuels are produced from fossil feedstocks and no processes are established to produce them from renewables. One feasible approach is to use biomass-derived olefins as starting materials (Scheme 4). First, the biomass-derived olefins are oligomerized to olefins with a higher molecular weight. After oligomerization, products within the desired gasoline boiling range are separated and hydrogenated. Thus, a tailored fuel for two-stroke engines can be produced and its properties can be adjusted by tuning catalysts and reaction parameters.

In 1935, Universal Oil Products (UOP) commercialized the so-called catalytic condensation process, which is also known as the UOP Catpolly process [61]. Applying this process enables enhancement of fuel production by using the olefinic by-products of thermal cracking plants. Typically, a solid phosphoric acid catalyst is used to oligomerize a mixture of propenes and butenes to gasoline and distillate-range fuels. In 1980, Mobil developed the Mobil olefins to gasoline/distillate (MOGD) process which uses a zeolite catalyst to convert light olefins to liquid fuels [62].

To obtain light olefins from renewables, several routes are described in the literature [63–65]. The main route is catalytic cracking of vegetable or pyrolysis oils. An easier approach to obtain olefins from biomass is the dehydration of alcohols like ethanol or butanol, which are obtained by fermentation. Ethylene production from renewable ethanol is already commercialized in some countries, e.g., in Brazil [66]. Because of the good availability of biomass-derived ethanol, several attempts have been made to use ethylene as starting material for the synthesis of paraffinic gasoline.

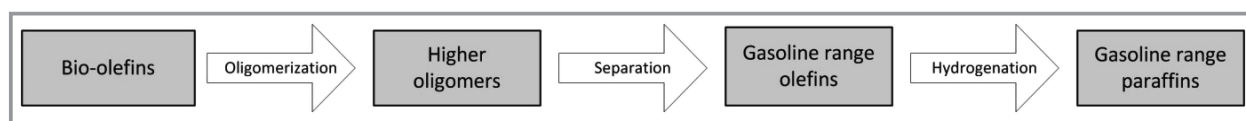
The aforementioned processes for olefin oligomerization utilize acidic catalysts. However, activity of these catalysts is

not very high regarding ethylene oligomerization, in particular at moderate reaction temperatures [67]. At higher temperatures, several side reactions take place, leading also to the formation of aromatics [68]. Considering ethylene oligomerization in homogeneous phase, transition metal complexes based on nickel and titanium are predominantly used as catalysts. In the heterogeneously catalyzed oligomerization of ethylene, nickel on acidic supports exhibits high activity (Scheme 5).



**Scheme 5.** Reaction scheme for the oligomerization of ethylene to higher olefins.

The most widely used supports can be assigned to three classes: silica aluminas [67, 69, 70], zeolites [71–73], and mesoporous aluminosilicates [74, 75]. Such systems catalyze the oligomerization reaction even at low temperatures around 120 °C and pressures up to 50 bar, reaching ethylene conversions above 90%. At these temperatures, the reaction products mainly consist of even-numbered olefins with up to 14 carbon atoms. Very low quantities of odd-numbered hydrocarbons are formed, indicating that cracking reactions are negligible under these conditions. Regarding the chain length distribution of the oligomers, different observations have been described in the literature. In some cases, the produced oligomers follow a Schulz-Flory distribution [76, 77], while other distributions with an emphasis on octenes in the C<sub>4+</sub> fraction have been published [67, 71]. It has been suggested, that dimerization of previously formed C<sub>4</sub> oligomers on the acid sites of the catalysts contributes to the deviation in the chain length distribution. With increasing chain length, the ratio of branched to linear oligomers increases [67, 71]. Dependent on the applied catalyst, the C<sub>8</sub> fraction consists mainly of single- or double-branched octenes. Recently, Moussa et al. compared three different types of catalysts and showed that there is a correlation between the acidic properties of the catalyst support and the degree of branching as well as the quantity of branched isomers [78]. The catalyst lifetime strongly depends on the catalyst type. Microporous materials like Ni-zeolite-Y or Ni-MCM-22 showed fast deactivation due to pore blockage by large oligomers [72, 74], while mesoporous catalyst systems exhibited higher lifetimes. Heveling et al. reported a time-on-stream of more than 100 days for a Ni-silica-alumina catalyst without severe deactivation [67].



**Scheme 4.** Process chain for the production of gasoline from bio-based starting materials.

The aim of ongoing research is the production of high-quality gasoline blending components by using ethylene as starting material. The heterogeneously catalyzed oligomerization of ethylene is the key step in such a production process. A high selectivity to branched products and a long catalyst lifetime are crucial. To realize this, current research concentrates on Ni species supported on silica aluminas, since promising results have been obtained with such catalyst systems.

### 3 Oxymethylene Dimethyl Ethers as Alternative Diesel Fuels

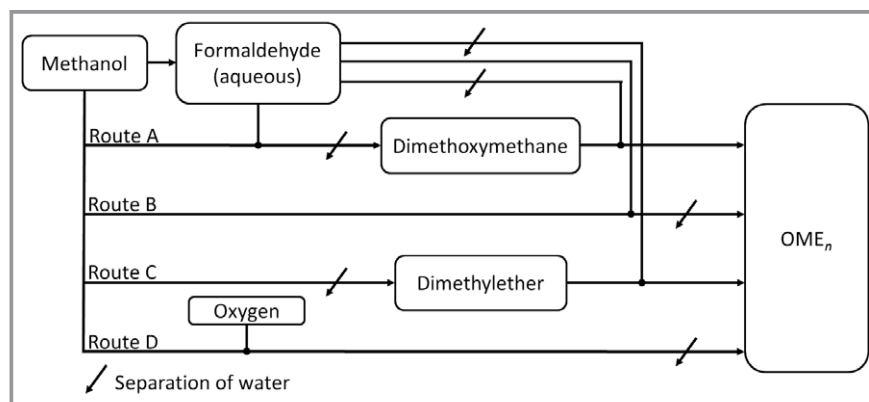
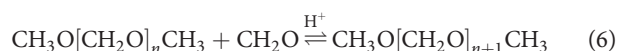
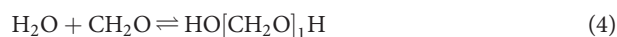
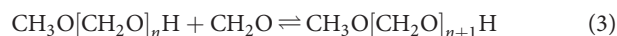
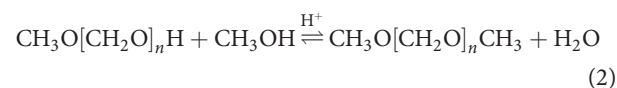
Regarding self-igniting internal combustion engines, future emission standards for soot and NO<sub>x</sub> will lead to additional complexity and costs for exhaust gas treatment. The use of oxymethylene dimethyl ethers (OMEs) as alternative diesel fuels enables to overcome this obstacle. These oligomeric compounds with the molecular structure CH<sub>3</sub>O(CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> (OME<sub>n</sub>) exhibit advantageous combustion properties [79, 80] and good accordance with current diesel standards [81, 82]. In general, OMEs can be produced from fossil or renewable resources [83] by reactions of methanol or methanol derivatives with formaldehyde. Formaldehyde is obtained by partial oxidation of methanol and is commercially available as aqueous solution (formalin) or in dry state (paraformaldehyde, trioxane) [84]. Several synthesis routes are outlined in Scheme 6. Herein, route A is the current state of the art for OME production. Routes B–D are comparatively new synthesis strategies and current research concentrates on these pathways.

According to route A, methanol and formaldehyde are converted to dimethoxymethane (OME<sub>1</sub>) first. Afterwards, OME<sub>1</sub> and the water-free intermediate trioxane are used to synthesize OMEs in a nonaqueous procedure. This route has been investigated in detail [85–87] and optimized to a large extent [88, 89]. Theoretical studies on this approach provided considerable insight into the mechanism of OME formation [90]. Route B implies OME synthesis from methanol and

formaldehyde in aqueous reaction systems. The presence of water leads to the formation of by-products and necessitates a sophisticated separation process to isolate the OMEs. Details on the reaction network and catalytic activities for this system are outlined in Sect. 3.1. Within route C, OMEs are synthesized from DME and a nonaqueous formaldehyde source. Compared to the other routes, this strategy is significantly less explored and the use of DME as starting material is discussed in Sect. 3.2. According to route D, OME<sub>1</sub> is produced by selective oxidation of methanol with oxygen and higher OMEs are formed subsequently, preferably in the gas phase. While OME<sub>1</sub> formation is already in an advanced stage of development, formation of higher OMEs is still a major challenge. A comprehensive discussion on catalysts and reaction parameters is presented in Sect. 3.3.

#### 3.1 Synthesis of Oxymethylene Dimethylethers from Methanol and Formaldehyde

Using methanol and formaldehyde as reactants in the synthesis of OMEs (Scheme 6, route B), enables OME production from inexpensive standard chemicals. The reaction network can be subdivided into the following reactions (Eqs. (1)–(6)) [83, 91–93].



Scheme 6. Synthesis routes for OMEs.

At the beginning, methanol reacts with formaldehyde to the corresponding hemiformal (Eq. (1)) followed by either acetalization with methanol to OME (Eq. (2)) or by incorporation of formaldehyde monomers to form higher hemiformals (Eq. (3)). The variable *n* refers to the number of formaldehyde units in the molecules. Due to the by-product water, which is formed in the acetalization reactions, formaldehyde is also converted to methylene glycol (Eq. (4)). Higher glycols and OME<sub>n</sub> occur as well through insertion of

formaldehyde according to Eqs. (5) and (6). All reactions are equilibrium reactions and only the reactions shown in Eqs. (2) and (6) require a catalyst. The reactions in Eqs. (1) and (3) – (5) are much faster than the acetalization reactions (Eq. (2)) and the chain growth reactions (Eq. (6)) [94, 95].

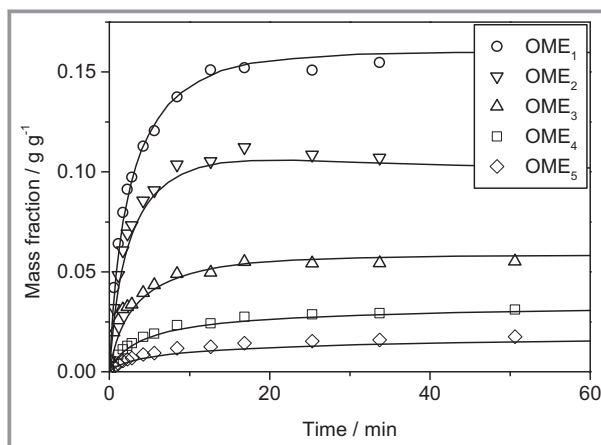
The reaction can be carried out in a batch reactor [93, 95–98] or in a continuously operating laboratory plant [93, 99]. Efficient catalysts are zeolites or ion exchange resins. Activities of different catalysts are compared in Tab. 1. According to Tab. 1, ion exchange resins exhibit the highest activity to form OME<sub>*n*</sub> in aqueous reaction systems. Using 40 wt % of methanol and 60 wt % of paraformaldehyde, the yields of OME<sub>1</sub> to OME<sub>6</sub> in equilibrium (80 °C) are 15.8, 9.9, 5.6, 3.1, 1.6, and 0.8 wt %, respectively [93]. Equilibrium parameters for the reaction of methanol with formaldehyde can be found in [91–93] and [96].

**Table 1.** Catalysts and reaction times for the synthesis of OME<sub>*n*</sub> from methanol and formaldehyde [93].<sup>a)</sup>

Catalyst	Time to reach 99 % of equilibrium [min]
Dowex50Wx2	6.8
Dowex50Wx4	7.0
Dowex50Wx8	8.5
H-BEA 25	20.0
H-MFI 90	23.4
Amberlyst 36	29.5
IR 120	55.4
CBV 720	> 100
H-MFI 400	> 100
H-MOR 30	> 100

<sup>a)</sup> Reaction conditions: 60 g paraformaldehyde, 40 g methanol, 80 °C, 1 wt % catalyst.

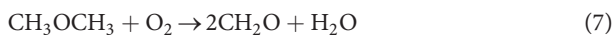
The kinetics of the non-catalytic reactions has already been investigated [92, 94, 100, 101]. Studies on the formation of OME<sub>*n*</sub> in combination with intermediate hemiformals and glycols, are published in [93, 95, 99]. Fig. 3 shows a concentration profile of different OMEs for the highly active catalyst Dowex50Wx2; the kinetic parameters can be found in [93]. The kinetic equations are defined by a hyperbolic approach similar to a Langmuir-Hinshelwood approach. Macroscopic effects like film or pore diffusion could be excluded by using appropriate process parameters. The final product mixture comprises oligomeric OMEs along with unconverted methanol and formaldehyde as well as hemiformals and glycols as by-products. An optimal yield of the desired OMEs with *n* = 3–5 can be achieved by varying the stoichiometric ratio of methanol and formaldehyde. OMEs with inappropriate chain length have to be recycled and can react again to the desired OMEs.



**Figure 3.** OME<sub>1–6</sub> formation vs time. Symbols represent experimental data and the curves correspond to the kinetic model [93]. Reaction conditions: 60 °C, 40 g methanol, 60 g paraformaldehyde, 1 wt % catalyst.

### 3.2 Synthesis of OMEs from Dimethyl Ether and Formaldehyde

A systematic and detailed comparison of different mobility concepts carried out by Maus et al. revealed a remarkable potential of OMEs in terms of a clean and sustainable fuel option [102]. To realize this potential, highly efficient process chains starting from renewable resources have to be designed. In this context, DME is discussed as starting material for sustainable OME production (Scheme 6, route C). OME synthesis by oxidative conversion of DME has been reported by Zhang et al. [103, 104] and Wang et al. [105]. Within these studies, formaldehyde emerges from partial oxidation of DME according to Eq. (7). The formation of OMEs results from subsequent reactions.



Catalysts and reaction conditions are summarized in Tab. 2. The catalyst system reported by Zhang et al. comprised MnCl<sub>2</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> impregnated on a SiO<sub>2</sub> support. Employing this catalyst, the highest yield of OME<sub>1</sub> was 3.4 mol % with a DME conversion of 8.6 mol % at 320 °C, 1 bar, and a gas hourly space velocity (GHSV) of 360 h<sup>-1</sup> [103]. In a subsequent publication, the authors described the use of rhenium and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> on carbon nanotubes for the same reaction [104]. In this case, the OME<sub>1</sub> yield was 4.9 mol %. Regarding OME<sub>2</sub>, a yield of 0.4 mol % was reported for a reaction at 240 °C, 1 bar, and 1800 h<sup>-1</sup> [104]. Wang et al. described OME formation by DME oxidation over a V<sub>2</sub>O<sub>5</sub>/H-BEA catalyst. An OME<sub>1</sub> yield of 6.3 mol % was observed at 200 °C, 1 bar, and 800 h<sup>-1</sup>. The yield of OME<sub>2</sub> was 0.3 mol % under these reaction conditions [105].

During DME oxidation, water is formed and this leads to a complex reaction network (see Sect. 3.1) including the for-

**Table 2.** Literature data on OME synthesis by partial oxidation of DME (molecular ratio of DME/oxygen is 1).

Catalyst	$T$ [°C]	$p$ [bar]	$GHSV$ [h <sup>-1</sup> ]	$Y_{\text{OME}_1}$ [mol %]	$Y_{\text{OME}_{1+}}$ [mol %]	Ref.
MnCl <sub>2</sub> /H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	320	1	360	3.4	n.r. <sup>a)</sup>	[103]
Re/H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /CNTs	240	1	1800	4.9	0.4	[104]
V <sub>2</sub> O <sub>5</sub> /H-BEA	200	1	800	6.3	0.3	[105]

<sup>a)</sup> Not reported.

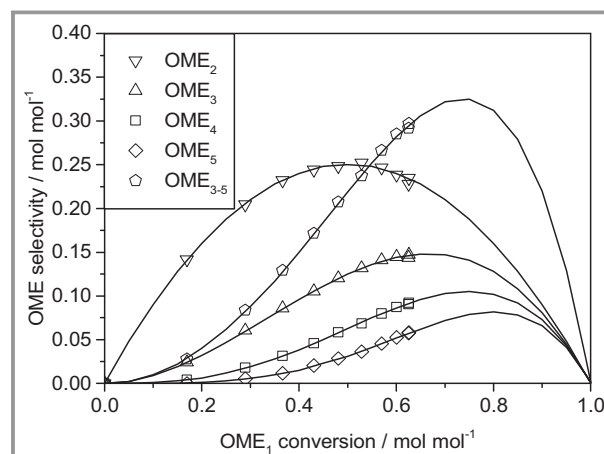
mation of side products. Thus, DME should be converted in nonaqueous reaction systems and suitable formaldehyde sources are needed. These are trioxane or monomeric formaldehyde. Trioxane is a trimer of formaldehyde and a crystalline solid under standard conditions. It is used as reactant in polyoxymethylene production. In 2015, the world capacity of trioxane was above 1.4 Mt a<sup>-1</sup> [84]. A process for the production of OMEs by reaction of DME with trioxane was patented by Ströfer et al. [106]. The experimental examples describe OME preparation procedures using sulfuric acid ( $m_{\text{Trioxane}}/m_{\text{DME}} = 0.48$ ,  $m_{\text{Catalyst}}/m_{\text{Trioxane+DME}} = 0.002$ ) and the ion exchange resin Amberlite IR 120 ( $m_{\text{Trioxane}}/m_{\text{DME}} = 0.85$ ,  $m_{\text{Catalyst}}/m_{\text{Trioxane+DME}} = 0.4$ ) as catalysts at 100 °C for several hours. The obtained product mixtures contain 18 wt % OME<sub>2</sub>, 58 wt % OME<sub>3</sub>, and 16 wt % OME<sub>4</sub> for sulfuric acid and 19 wt % OME<sub>2</sub>, 64 wt % OME<sub>3</sub>, and 1 wt % OME<sub>4</sub> for Amberlyst IR 120.

Production chains for sustainable OME manufacturing need to consider the complexity and energy demand of every process step. Therefore, the use of trioxane in a sustainable OME production appears to be challenging [84]. Monomeric formaldehyde is a highly reactive species and tends to polymerize immediately in the presence of water. On lab scale, it can be synthesized by catalytic decomposition of trioxane [107, 108] or paraformaldehyde [109, 110]. The dehydrogenation of methanol was discussed as a direct and highly efficient synthesis pathway for monomeric formaldehyde. Su et al. [111] and Usachev et al. [112] published comprehensive reviews on the state of the art of catalytic methanol dehydrogenation. Monomeric formaldehyde would be an advantageous reactant but OME synthesis from DME and monomeric formaldehyde has not been demonstrated yet. Ongoing research concentrates on this topic and suitable catalysts for DME activation have been identified recently. This finding is the key for OME production from DME and enables new synthesis strategies. The experimental demonstration of these promising concepts is the scope of ongoing work in our laboratories.

### 3.3 Direct Synthesis of OMEs by Partial Oxidation of Methanol

Common synthesis routes for OMEs are based on formaldehyde sources such as trioxane and paraformaldehyde and endcapping sources such as OME<sub>1</sub> (Scheme 6, route A) or methanol (Scheme 6, route B). Usually, syntheses are carried

out in liquid phase resulting in a product composition which follows the Schulz-Flory distribution [89, 113, 114]. An example for the theoretical calculation of the Schulz-Flory distribution matching experimental results is shown in Fig. 4 [89].



**Figure 4.** OME selectivity as a function of OME<sub>1</sub> conversion for the synthesis of OMEs from OME<sub>1</sub> and trioxane. Symbols represent experimental data and the curves correspond to the calculated Schulz-Flory distribution [89].

Therefore, it is reasonable to search for alternative synthesis routes which can be carried out in the gas phase. Thus, the product spectrum could be influenced by adjusting catalyst systems and reaction parameters such as partial pressures of the reactants and residence times. One possibility for OME synthesis in the gas phase is the reaction of methanol with molecular oxygen (Scheme 6, route D) according to Eq. (8). In principle, it should be possible to direct the reaction towards OME<sub>3-5</sub>, which are the preferred OMEs for fuel applications. In the following, selected studies on the oxidation of methanol with molecular oxygen are discussed with a focus on catalyst systems. In these reactions, predominantly OME<sub>1</sub> is obtained which can be further converted to higher OMEs.



For OME synthesis via methanol oxidation, bifunctional catalysts with moderate contents of redox and acid sites are needed. On the redox sites, methanol is converted to formaldehyde. In the next step, formaldehyde reacts with metha-



nol to yield OME<sub>1</sub>. These acetalization reactions are catalyzed by acid sites.

Iron-molybdenum catalysts (FeMo catalysts) are used for the commercial production of formaldehyde [84, 115]. By varying the partial pressure of methanol, they can also be used to synthesize OME<sub>1</sub>. Gornay et al. investigated a FeMo catalyst with varying feed compositions [116]. In general, a feed rich in methanol is needed for OME<sub>1</sub> synthesis. Under lean conditions, a methanol conversion of 65 % and a OME<sub>1</sub> selectivity of 74 % were observed. Under methanol-rich conditions, OME<sub>1</sub> selectivity reached 90 % at a methanol conversion of 56 %. Thavornprasert et al. reported a methanol conversion of 46 % with an OME<sub>1</sub> selectivity of 85 % using a molar ratio methanol/O<sub>2</sub>/He of 40:13:47 [117]. The optimum molar ratio Fe/Mo in the catalyst was found to be 3.2 and the highest OME<sub>1</sub> yield was 50 %.

Another class of suitable catalysts for this reaction are heteropolyacids. Liu and Iglesia used SiO<sub>2</sub>-supported heteropolyacids with Keggin structures [H<sub>3+n</sub>PV<sub>n</sub>Mo<sub>12-n</sub>O<sub>40</sub>] (*n* = 0–4) and found that the selectivity to OME<sub>1</sub> could be improved by a substitution of molybdenum with vanadium [118]. The best results were obtained with H<sub>4</sub>PVMo<sub>11</sub>O<sub>40</sub>/SiO<sub>2</sub>; here, the OME<sub>1</sub> selectivity reached 58 % at a methanol conversion of 68 %. DME was obtained as a by-product with a selectivity of 31 %. In another study, the heteropolyacid H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> has been supported on zeolite SBA-15 [119]. Thus, the stability of the catalyst could be enhanced and the conversion rate of methanol was 22 % while OME<sub>1</sub> selectivity was 39 %.

Several reports on vanadium-based catalysts have been published [120–126] and exemplarily, three examples will be considered in the following. A mesoporous bifunctional catalyst with the general composition Al-P-V-O has been reported by Chen et al. [121]. It could be shown that there is a synergetic effect of phosphorous and vanadium, which has a significant influence on the redox and acid properties of the catalyst. It has been proposed that the good redox behavior of the catalyst is due to a high mobility of oxygen on the catalyst. The reaction can be described by a Mars-van-Krevelen mechanism and it is assumed that a well-balanced content of redox centers and moderate acid sites contributes to the high catalytic activity for OME<sub>1</sub> synthesis. For the catalyst composition AlP<sub>10</sub>V<sub>15</sub>, a methanol conversion of 47 % and an OME<sub>1</sub> selectivity of 89 % were reported. In another study, a comparison between a V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst and a V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-SiO<sub>2</sub> catalyst has been carried out [124]. Both catalysts have been prepared by a sol-gel method and it has been shown that OME<sub>1</sub> selectivity can be significantly improved by SiO<sub>2</sub> modification. OME<sub>1</sub> selectivity was 89 % in the case of V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> and 99 % in the case of V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>. Methanol conversion reached 43 and 51 %, respectively. It should be noted that several more studies on V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalysts exist [127–131] and V<sub>2</sub>O<sub>5</sub> in combination with TiO<sub>2</sub> is among the best catalyst systems for OME<sub>1</sub> synthesis from methanol. In this context, the influence of sulfate on the catalytic performance of

V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> has been studied [125]. Liu et al. reported an increase in methanol conversion with increasing reaction temperature that accompanies a decrease of OME<sub>1</sub> selectivity. Up to a temperature of 150 °C, high OME<sub>1</sub> selectivities have been observed and a comparison of VO<sub>x</sub>-TiO<sub>2</sub> with a SO<sub>4</sub><sup>2-</sup>/VO<sub>x</sub>-TiO<sub>2</sub> catalyst has been carried out. In the case of the former, methanol conversion was 26 % with an OME<sub>1</sub> selectivity of 45 %, and in the case of the latter, methanol conversion was 57 % with an OME<sub>1</sub> selectivity of 83 %. It has been concluded that the enhanced surface acidity due to the addition of SO<sub>4</sub><sup>2-</sup> is beneficial.

Apart from catalysts, OME formation can be significantly influenced by varying the reaction parameters. Increasing the reaction temperature usually favors the formation of by-products, in particular DME and methyl formate. Furthermore, increased desorption of methoxy groups has been observed which inhibits OME<sub>1</sub> formation [132]. Compared to other catalyst systems, FeMo catalysts are an exception, inasmuch as OME<sub>1</sub> formation is significantly less affected even at comparatively high temperatures [117]. The influence of stoichiometry has also been investigated [115, 116, 133]. In general, a minimum ratio of methanol/O<sub>2</sub> of about 6 is needed for the formation of OME<sub>1</sub> [132]. Additionally, explosion limits for the system methanol/O<sub>2</sub> have to be considered which restrict the operating window [134].

In summary, it can be stated that direct OME<sub>1</sub> synthesis by oxidation of methanol with molecular oxygen is already in an advanced stage of development. Different heterogeneous catalysts are available for this reaction and current activities concentrate on an extension of this reaction to produce also oligomeric OMEs with more than one CH<sub>2</sub>O unit.

## 4 Conclusions

This work describes selected strategies for the production of alternative gasoline and diesel fuels from regenerative resources. These include the development of hierarchical ZSM-5 zeolites by desilication of conventional ZSM-5 and their use as heterogeneous catalysts for the synthesis of gasoline from DME (DTG process). Due to the presence of mesopores, these catalysts exhibit reduced transport limitations and increased catalyst lifetimes compared to pristine ZSM-5 materials, which are solely microporous. Catalytic tests have been carried out using a laboratory plant equipped with an isothermal fixed-bed reactor operating at 375 °C and 1 bar. Thus obtained results are exemplarily discussed. In this context, the ambivalent role of aromatics is addressed. On the one hand, aromatics lead to high octane numbers and on the other hand, aromatics promote the formation of PM emissions. A procedure for the production of gasoline without any aromatics is outlined, which comprises the synthesis of branched aliphatics from DME, and the current state of catalyst development is illustrated. A better

understanding of the catalyst deactivation mechanisms is necessary for a large-scale industrial implementation of such a procedure. Furthermore, in-depth investigations on the long-term stability of the catalysts for continuous process designs are needed. Gasoline without aromatics is an interesting fuel for special motor applications like hand-operated working machines. For this purpose, laboratory investigations on the oligomerization of ethylene with subsequent hydrogenation of liquid products to provide sufficient quantities of gasoline for motor tests are under way. Future experimental work will be performed to determine the optimal synthesis parameters as well as a highly optimized catalyst system. The objective is not only to obtain a high-quality fuel for small two-stroke combustion engines of handheld machines, but also to minimize health impacts on operators.

Regarding diesel fuels, various routes for the synthesis of OMEs are presented. OME production from methanol and formaldehyde has been investigated intensely and an overview of possible catalysts and purification processes for the separation of the products from the reaction mixture is given. The incentive is a comprehensive description of this route, which enables OME production in a pilot plant. OME synthesis from DME, by a non-oxidative process route, has not been described in detail yet. This water-free route is advantageous compared to the known partial oxidation of DME, since the formation of by-products can be avoided. Future work will focus on the activation of DME in combination with a suitable formaldehyde source for OME formation. Finally, the current state of the art regarding the direct synthesis of OME<sub>1</sub> by partial oxidation of methanol, which is already in an advanced stage of development, is reported. Future work in this field will focus, firstly, on the testing of newly developed catalyst systems and their long-term stability in continuous process designs and, secondly, on the optimization of these systems for the synthesis of higher OMEs.

All fuels discussed within this work are characterized by beneficial physicochemical and combustion properties as well as lower overall emissions compared to the corresponding fuels from fossil resources. Thereby, they can contribute to the achievement of European emission and climate change goals. Production processes are steadily optimized and the different strategies are comprehensively evaluated and compared. Besides sustainable and profitable production, a series of other criteria has to be taken into account, e.g., compatibility with established infrastructures and logistics, storage stability, material compatibility, health- and safety-related demands, and customer acceptance. In any case, the major challenge and basic prerequisite for feasibility will be the availability of renewable resources and regenerative energies on a large scale and avoiding competition with established markets.

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From left to right: Ulrich Arnold, Simon Wodarz, Thomas Otto, Dorian Oestreich, Kathrin Hackbarth, Benjamin Niethammer, Matthias Betz (not shown: Philipp Haltenort and Jörg Sauer)

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### Symbols used

$\varnothing_i$	[mm]	internal diameter
GHSV	[h <sup>-1</sup> ]	gas hourly space velocity
$L$	[mm]	length
$m$	[kg]	mass
$p$	[bar]	pressure
$T$	[K]	temperature
TOS	[h]	time on stream
WHSV	[g g <sup>-1</sup> h <sup>-1</sup> ]	weight hourly space velocity
$Y$	[mol %]	yield

## Greek symbol

$\tau_{\text{mod},0}$  [g h mol<sup>-1</sup>] modified residence time

## Abbreviations

BTL	biomass-to-liquids
DME	dimethyl ether
DTG	DME-to-gasoline
ETBE	ethyl <i>tert</i> -butyl ether
GPF	gasoline particulate filter
HGT	heavy-gasoline treatment
HMB	hexamethyl benzene
MOGD	mobil olefin to gasoline/distillate
MTG	methanol-to-gasoline
MTH	methanol-to-hydrocarbons
NO <sub>x</sub>	nitrogen oxides
OME	oxymethylene dimethyl ether
PM	particulate matter
PM <sub>2.5</sub>	particulate matter with a diameter of 2.5 μm or less
RDE	real driving emissions (test procedure)
WLTP	world-harmonized light-duty vehicle test procedure
YLL	years of life lost

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