Comparing Microwave and Classical Synthesis of Oxymethylene Dimethyl Ethers

Patrick Endres, Stefan Zechel, Andreas Winter, Martin D. Hager, and Ulrich S. Schubert*

Polyoxymethylene dimethyl ethers (OME_n) are considered as substituents or additives for fossil diesel fuel. Efficiency of the synthesis is crucial for the development of industrial scale production plants. Therefore, the design of suitable catalysts and the efficient heating play important roles in OME fuel synthesis. In this work, microwave-assisted synthesis (MAS) is carried out and compared to a classical approach using standard thermal heating. Different polymeric materials, e.g., Amerlyst15, are utilized as catalysts, and screened for the catalytic synthesis of OME. Within this approach, the kinetics of the reaction are analyzed in detail.

1. Introduction

The man-made climate change increasingly impacts our society, economics and environment.[1] Hence, the reduction of greenhouse gas emissions represents one of the major challenges of the 21st century.[2] According to the German government, the total greenhouse gas emissions of Germany were reduced by 6.3% from 2018 to 2019.[3] However, in the transportation sector an increase of about 0.7% can be observed at the same time.[3] The main share of the emissions from the transportation sector originates from cars and commercial vehicles (≈94% in 2019).[4] Synthetic fuels, which are based on power-to-liquid (PtL) technologies, represent a possible key contribution to the aim of reducing CO_2-emissions in this sector. These PtL technologies basically rely on CO_2 as carbon source.[5,6] By reaction of CO_2 with hydrogen, obtained from the electrolysis of water, e.g., powered by wind or solar power, a number of different possible carbon neutral PtL fuels can be generated.[7,8] In this respect, poly(oxymethylene dimethyl ethers) (OME_n) represent, besides methanol, Fischer–Tropsch fuels and others, a highly promising class.[8,9] Due to their properties similar to conventional Diesel fuel, short-chain OMEs (i.e., $n = 3$–5) have attracted considerable interest as drop-in fuel or complete substitute to conventional Diesel fuel.[10–13] Furthermore, OME fuels even show higher cetane numbers and lower soot formation compared to conventional Diesel.[14,15]

For the synthesis of OMEs, a formaldehyde source, such as paraformaldehyde (pFA) or trioxane (TRI), as well as a methyl group provider, such as methanol or dimethoxymethane (DMM or OME_1), is required.[16] Afterward, an acid-catalyzed reaction can result in the formation of OME. This acid-catalyzed reaction can follow different routes. In the first one, which is the aqueous route, pFA is reacted with MeOH. Nevertheless, this method also produces water and, thus, the formation of side products, such as glycols or hemiformals, is increased.[17,18] The second approach is performed in a nonaqueous environment and commonly uses trioxane in combination with DMM. The main advantage of this procedure is—due to the absence of water—the significantly reduced side-product formation and, consequently, higher product selectivity.[19–21]

As acidic catalysts, different types of solid and liquid acids have already been investigated. As homogeneous catalysts, strong liquid mineral or organic acids have been applied, e.g., sulfuric acid.[22] These catalysts feature a high catalytic activity; however, several disadvantages, in particular corrosion and the high purification costs, have also to be named. Heterogeneous catalysis is, thus, preferable regarding industrial-scale applications due to the simple separation of the catalyst from the reaction mixture. In particular, zeolites[21,23,24] or polymeric catalysts, such as sulfonated ion-exchange resins,[17,25–27] seem to be highly suitable. Beside cross-linked polystyrene-based catalysts, poly(ionic liquid)s are also known to be macromolecular catalysts for OME synthesis.[28]

Under acidic conditions, the OME fuel synthesis leads to a product mixture, in which the fractions of the components follow a Schulz-Flory-distribution. The distribution is known from polymerization reactions and results from the statistical probability of chain growth.[16] Additionally, the development of the product distribution of the liquid phase can be divided into two parts. In the first part, the change of the components is fast followed by a state, in which only small changes of the molar mass can be observed. This state is called "quasi-equilibrium" state.

P. Endres, S. Zechel, A. Winter, M. D. Hager, U. S. Schubert
Laboratory of Organic and Macromolecular Chemistry (IOMC)
Friedrich Schiller University Jena
Humboldtstr. 10, 07743 Jena, Germany
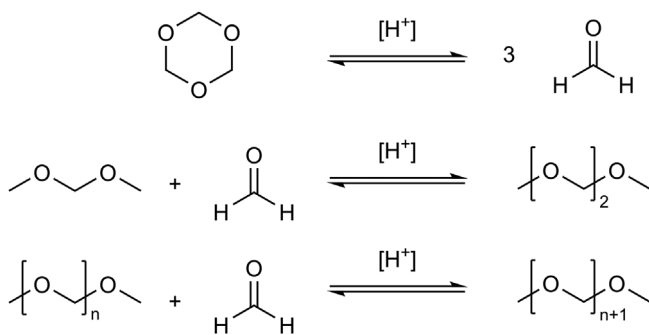E-mail: ulrich.schubert@uni-jena.de
P. Endres, S. Zechel, A. Winter, M. D. Hager, U. S. Schubert
Jena Center for Soft Matter (JCSM)
Friedrich Schiller University Jena
Philosophenweg 7, 07743 Jena, Germany
M. D. Hager, U. S. Schubert
Center for Energy and Environmental Chemistry Jena (CEEC Jena)
Philosophenweg 7a, 07743 Jena, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/macp.202200020

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Scheme 1. Schematic representation of the general route of OME fuel synthesis via trioxane and dimethoxymethane.

Besides the choice of reactants and catalysts, reaction control represents an important parameter for the synthesis. In this context, the use of MAS may bear several advantages in comparison to "classical" thermal heating.[29] MAS often allows more facile and precise reaction control in terms of pressure, temperature and time. Possible implementation into an automated workflow in combination with the well-known, high reproducibility of microwave-assisted reactions leads to the ability to perform a screening of different reaction conditions and catalytic materials.[30] Furthermore, MAS is known to increase the reaction rate, making this type of heating an alternative to the classic method, which could, e.g., be shown for the polymerization of oxazolines.[31] Furthermore, it has been demonstrated that MAS can also be very energy efficient.[32]

In the current study, a microwave-assisted synthesis of OME fuels based on trioxane and dimethoxymethane, as the starting materials, using different commercially available polymeric catalysts, is performed. The optimum reaction conditions in the microwave setup in terms of temperature and time are analyzed. Furthermore, the performance of microwave and thermal heating in OME fuel synthesis is analyzed and compared in detail.

2. Results and Discussion

2.1. Concept of the Study

As already mentioned, the OME fuel synthesis was performed with trioxane and dimethoxymethane, as the starting materials. The reaction leads to an OME mixture consisting of oligomers with different chain lengths, as can be seen in **Scheme 1**.

As catalysts different polymeric acidic ion-exchange resins, as listed in **Table 1**, were used for the screening.

Gas-chromatographic (GC) analysis was utilized for the determination of the composition. Selectivity and conversion were calculated based on the weight percentages (wt%) of the different components of the reaction mixture. Following Equation (1), the conversion of components was calculated

$$X_i = \frac{[A]_0 - [A]_x}{[A]_o} \times 100 \tag{1}$$

Selectivity of OMEs was calculated using Equation (2)

$$S_i = \frac{[OME]_i}{\sum_{i=1}^{10} [OME]_i} \times 100 \tag{2}$$

2.2. Determination of Optimum Reaction Conditions
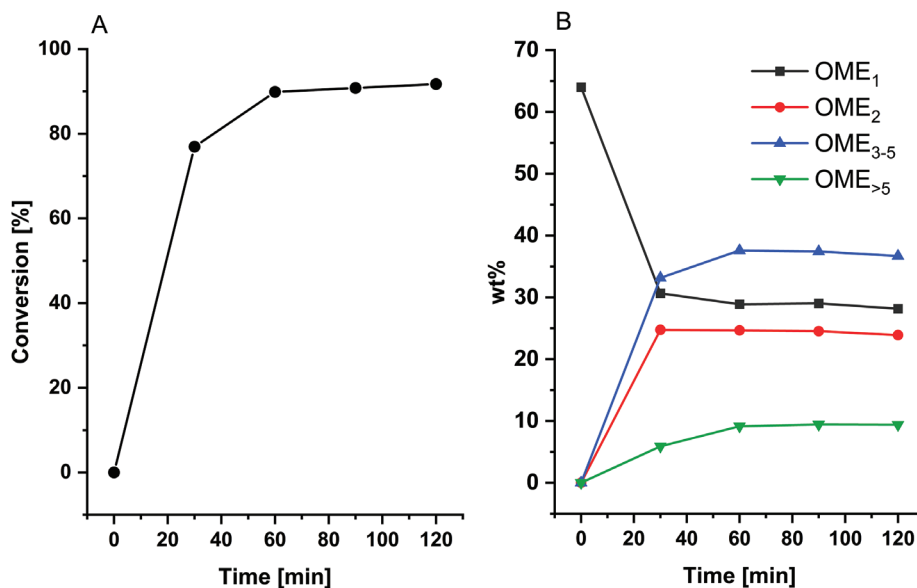
2.2.1. Time

In the first part of this study, the necessary parameters for this reaction under microwave conditions were investigated. To do so, the maximum amount of time required to reach the "quasi-equilibrium" state was evaluated at room temperature.

In the first step, the reaction kinetics were investigated. For this purpose, Amberlyst15 was utilized as catalyst. The synthesis was performed in microwave vials and the mixture was stirred at room temperature. The conversion of trioxane increased significantly to a value of about 90% after 60 min (**Figure 1**). Afterward, only a small increase was detected indicating that the reaction has slowed down and the liquid phase of the reaction mixture reached the "quasi-equilibrium" state, in which no major changes of the product distribution could be detected.

This result was further confirmed by the investigation of the mass fractions of the different OMEs. As depicted in Figure 1, OME_1 is mainly consumed within the first 60 min followed by a slowdown of the reaction rate. The fraction of $OME_{>1}$ in contrary increases with a total share of OME_{3-5} between 35 and 40 wt% after 1 h. Afterward, just slight changes below 5 wt% over the next hour could be observed. Consequently, a reaction time of 1 h seems to be sufficient for the investigation of the product distribution in the quasi-equilibrium state, since this state is also obtained at RT.

2.2.2. Microwave-Assisted Catalytic Reaction

After determination of the reaction time required to reach the quasi-equilibrium composition (at RT), the influence

Table 1. Overview of the utilized polymeric catalysts and their properties.

Polymeric catalysts	Conc. of acid sites [meq g^{-1}]	Particle diameter [µm]	Matrix	Active group
Amberlyst15	≥4.7	300–425	Styrene/DVB	Sulfonic acid
Amberlyst36	≥5.4	550–700	Styrene/DVB	Sulfonic acid
Dowex50Wx2	≥0.8	75–149	Styrene/DVB	Sulfonic acid
Dowex50Wx4	≥1.4	75–149	Styrene/DVB	Sulfonic acid
Nafion	≥0.8	3 × 4 mm	Tetrafluoroethene	Sulfonic acid

Note: DVB, divinylbenzene.

Figure 1. A) Time-dependent trioxane conversion and B) time-dependent development of OME fractions at room temperature with Amberlyst15 as catalyst.
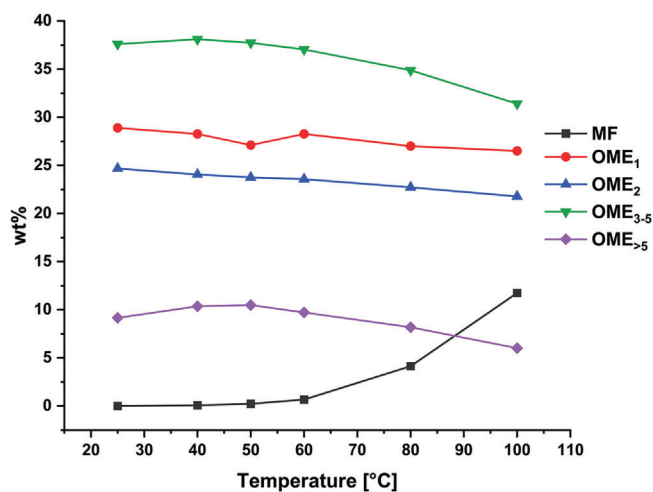
Figure 2. Temperature dependency of the product fractions after 1 h with Amberlyst15 as catalyst (side product MF = methyl formate) (MAS).

of temperature on the product distribution after 1 h under microwave-assisted heating was investigated. For this purpose, the reaction catalyzed by Amberlyst15 was screened at different temperatures, while keeping the reaction time constant at 1 h (**Figure 2**). The portion of OME_{3-5}, which is regarded as the target fraction due to the superior properties in terms of application as alternative fuel,[33,34] increased slightly to about 38 wt% for a reaction performed at 40 °C. A further temperature increase resulted in a decrease to 31 wt% at 100 °C. A similar behavior of the system was also observed for higher oligomers $OME_{>5}$, whilst the portions of OME_1 and OME_2 were just marginally lower at 100 °C. These results are in accordance with literature reports, in which analogous results at higher temperatures for different liquid and polysiloxane-based solid catalysts were reported.[20]

Another important aspect is the formation of methyl formate as a side product. The content of methyl formate is considerably increasing with temperatures above 60 °C and reached a maximum value of ≈12 wt% at 100 °C. This side reaction is irreversible and, thus, should be avoided as otherwise formaldehyde is continuously removed from the OME equilibrium.

This is also in accordance with literature experiments under nonmicrowave-assisted conditions, in which elongated reaction times and higher temperatures led to increased formation of undesired products.[35] Consequently, microwave-assisted synthesis of OME fuels shows a similar behavior in terms of side-product formation as thermal heating. Hence, higher temperatures (≥60 °C) can be identified as unsuitable for OME fuel production under these conditions. To further investigate the influence of temperature on the equilibrium developed after 1 h the Schulz-Flory distribution was analyzed. For this purpose, the selectivity for the different OMEs, based on the weight percentages of the respective fractions, was considered, as a high amount of side product formation at increased temperatures was observed influencing the weight fractions of the different OMEs. The difference between the Schulz-Flory distributions obtained by microwave-assisted synthesis at 40 °C and 100 °C can be seen in **Figure 3**. Higher temperatures lead to a larger fraction of OMEs with shorter chain lengths. Accordingly, $OME_{>5}$ shares are increased at lower temperatures. As OME_{3-5} is seen as the desired product fraction, higher temperatures should also be avoided due to the lower selectivity to OME_{3-5}.

To confirm the results obtained by the Amberlyst15-catalyzed reaction, the temperature dependency of OME fuel formation catalyzed by the polymeric catalyst Nafion was studied. This catalyst was screened analogous to Amberlyst15 at different temperatures and at a reaction time of 1 h, as can be seen in **Figure 4**. The development of the product distribution established by Nafion at temperatures of ≥50 °C was similar to the compositions observed with Amberlyst15. However, the main difference can be found in
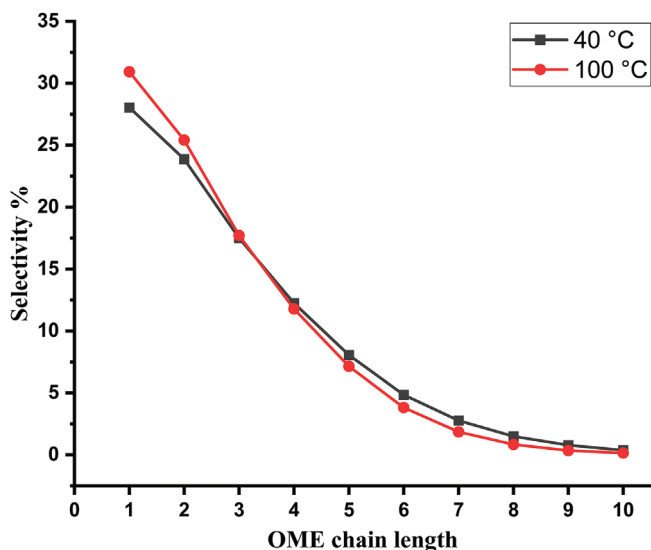
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Figure 3. Schulz-Flory distribution obtained after 1 h reaction time at 40 °C and 100 °C with Amberlyst15 as catalyst (MAS).
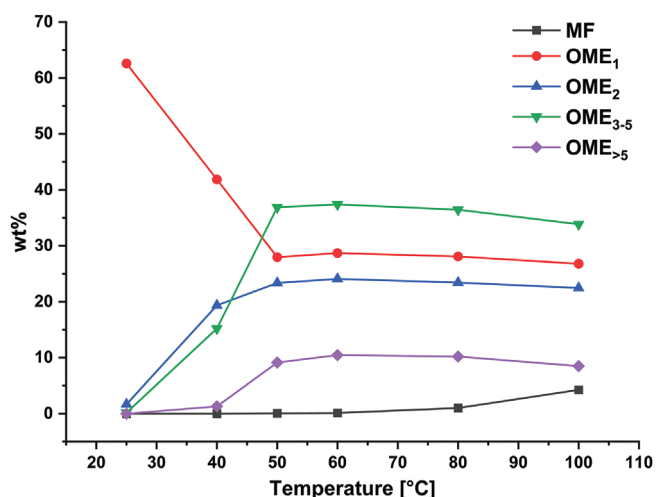

Figure 4. Temperature dependency of the product fractions after 1 h with Nafion as catalyst (MAS).

the suppressed methyl formate formation at 100 °C, which was only just slightly above 4 wt% compared to almost 12 wt% for Amberlyst15. Nevertheless, in contrast to the prior reported reaction, the one catalyzed by Nafion did not reach the quasi-equilibrium state within 1 h at room temperature. After the reaction, an OME_1 content of about 62 wt% and a cumulated share of $OME_{>1}$ below 5 wt% was detected, concluding that almost no conversion of the starting materials occurred. By increasing the temperature to 40 °C the reaction was not sufficiently accelerated to reach the desired state within 1 h. It was found that 50 °C is the lowest temperature, at which the reaction speed can be considered fast enough to reach the quasi-equilibrium state within the desired time. Therefore, 50 °C for 1 h were taken as standard conditions for the screening of possible catalysts. This is justified by the significant acceleration of the reaction at this temperature and by the suppressed side-product formation.

2.3. Equilibrium Compositions of Different Polymeric Catalysts

Following the successful screening of Nafion and Amberlyst15, various other polymeric catalysts were evaluated using the established procedure. As mentioned above, 50 °C and 1 h were chosen as the preferred conditions for the microwave-assisted synthesis of OME_{3-5}. In industrial applications the required mass of the corresponding catalyst represents a crucial parameter. Therefore, the same mass was utilized for all experiments, if not mentioned differently an approach, which is well established in literature.[28] As summarized in **Figure 5**A, similar results in terms of OME fractions, were obtained for each catalyst, taking the standard deviation of the triplicate reaction into account. This effect is in accordance with the proposed transacetalization reaction of OMEs, which was previously described in literature.[36] According to this, an OME, which was formed preferentially during the reaction, will undergo a transacetalization process. As a result, a Schulz-Flory-type distribution—mainly determined by the reaction conditions (e.g., temperature, pressure and ratio of starting materials)—is obtained. This leads also to the conclusion that all catalysts were able to reach the quasi-equilibrium state under the standard microwave conditions. In terms of side-product formation, all catalysts revealed low yields of methyl formate as it can be seen in Figure 5B. Interestingly, the different catalysts performed differently with respect to the methyl-formate formation. Amberlyst15 and Amberlyst36 showed the highest fraction of about 0.21 wt%. Dowex50Wx4 and Dowex50Wx2 formed about half of the amount with about 0.12 wt% and during the Nafion catalyzed reaction the lowest amount of MF with about 0.05 wt% was detected.

To ensure, the different methyl formate contents do not arise from the varying amount of acidic sites of the different catalysts, the reaction was performed with a molar equivalent of Nafion in terms of acid concentration compared to Amberlyst15. Furthermore, the two catalysts were compared after 1 h at 40 °C and 50 °C as depicted in **Figure 6**, since the temperature plays an important role in terms of methyl formate formation. Nafion revealed no detectable MF fraction at 40 °C whilst containing about 0.04 wt% at 50 °C, which is in a comparable range to the measurements at 50 °C with a constant mass of catalyst (Figure 5B). Interestingly the reactions performed with Amberlyst15 showed a significantly higher share of MF at both temperatures indicating the influence of the polymer matrix on the side product formation. Additionally, an influence on the overall reaction can also be detected as a lower OME_{3-5} and $OME_{>5}$ and higher OME_1 and TRI content was observed leading to the conclusion that the polymeric support also influences the reaction rate.

2.4. Kinetic Investigations

After the screening of different polymeric catalysts, the influence of microwave-assisted heating on the reaction rate in comparison to thermal heating was investigated. For this purpose, the optimum reaction temperature was chosen and the development of the product distribution was monitored over time. For this purpose, in the first step a reaction kinetic at 50 °C with thermal heating and, second, with microwave-assisted heating was
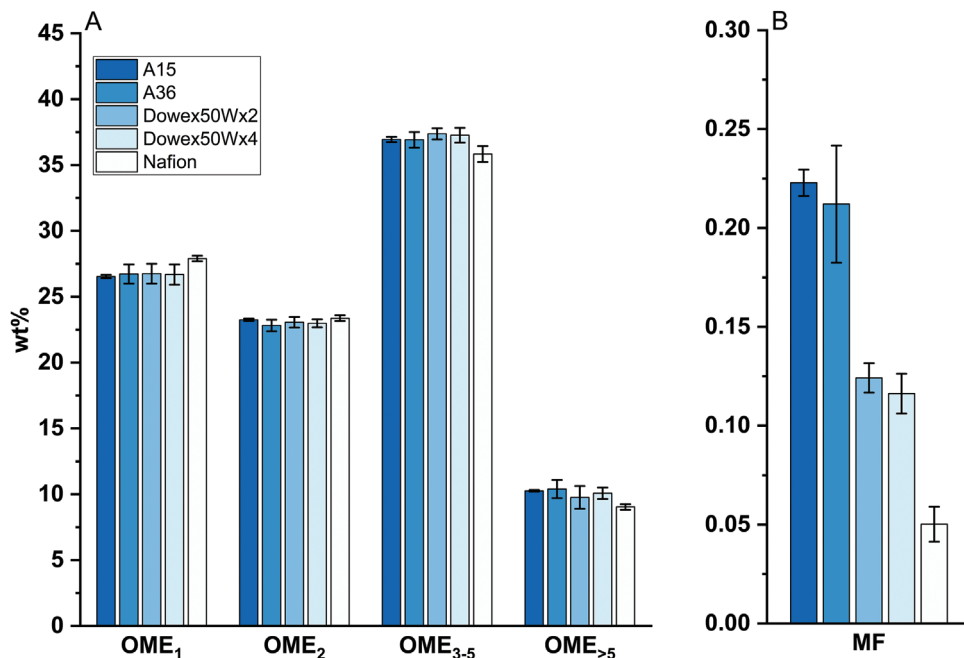
Figure 5. A) OME fractions obtained by different catalysts after 1 h and 50 °C (MAS). B) Methyl formate (MF) fractions after 1 h and 50 °C with different catalysts (MAS).

performed and compared. For comparability microwave vials were used in both experiments.
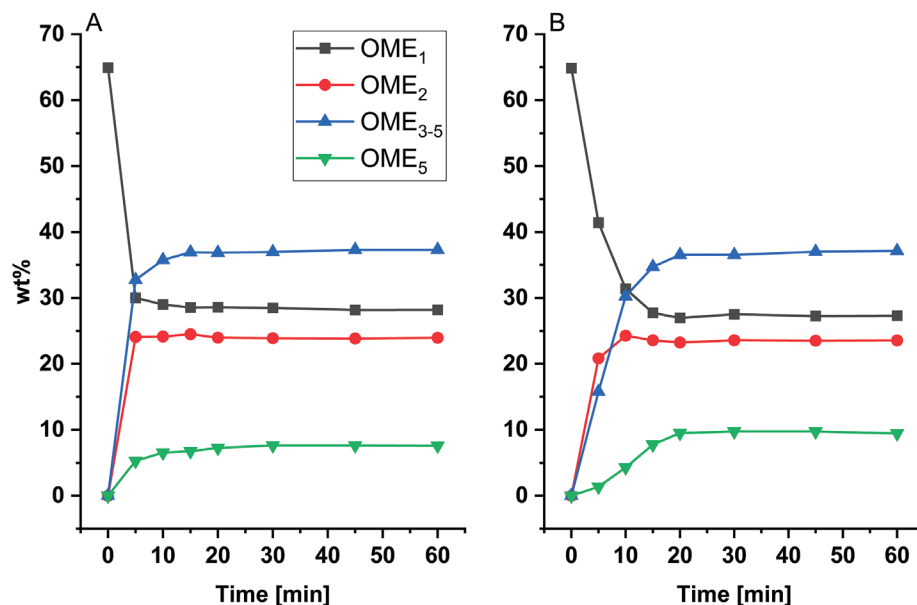
2.4.1. Thermal Heating

Under thermal heating, an acceleration in comparison to the kinetics at room temperature (see Section 2.2) was detected, as depicted in **Figure 7**. After 20 min, the product distribution reached the quasi-equilibrium state reducing the reaction time to one third in comparison to room temperature. The amount of time needed in microwave vials is in accordance with the literature values obtained during OME synthesis in a stainless-steel batch reactor.[37] The OME_{3-5} fraction reached about 37 wt%, which is comparable to the equilibrium measurements performed before.
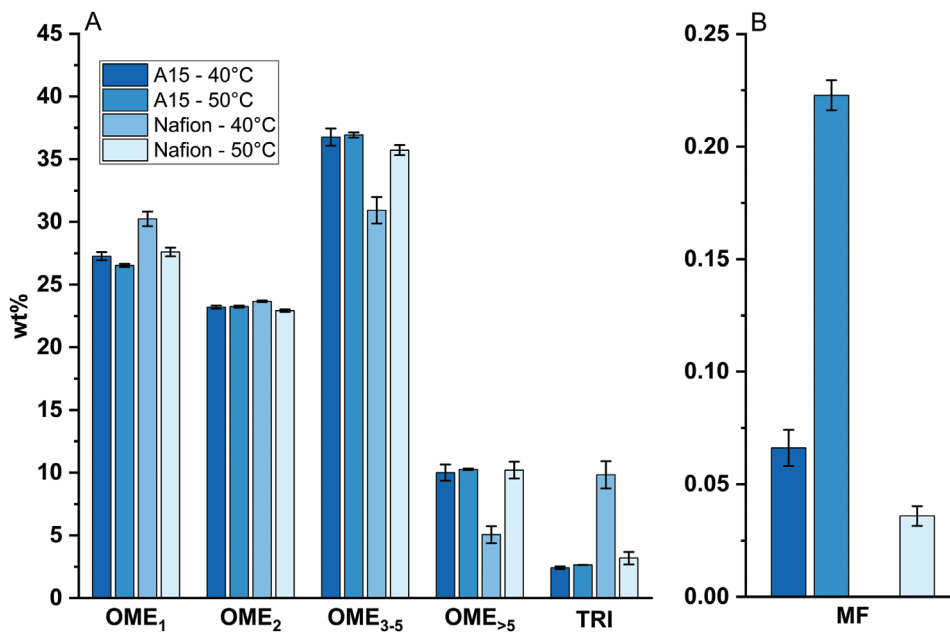
Figure 6. A) OME and trioxane fractions obtained by Nafion and Amberlyt15 after 1 h in equimolar amounts of the acidic groups (MAS); B) methyl formate (MF) fractions after 1 h with Amberlyst15 and Nafion in equimolar amounts of the acidic groups (MAS).

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Figure 7. A) Evolution of OME fractions over time at 50 °C via microwave-assisted heating and B) thermal heating with Amberlyst15 as catalyst.

2.4.2. Microwave-Assisted Synthesis

The same reaction was performed under microwave-assisted heating (Figure 7). In comparison to the thermal reaction, microwave-assisted synthesis increased the reaction rate. Under these conditions, the quasi-equilibrium state was already reached after 10 min, making MAS twice as fast as the classical reaction. Reasons for this might be seen in the more efficient way of heating. During the microwave-assisted synthesis, the reaction temperature was reached and held. Under thermal conditions the direct measurement of the internal temperature was not possible. Nonetheless, it can be assumed that a longer time was required to reach the desired reaction temperature. Furthermore, a temperature difference between the external measured and the internal actual temperature cannot be excluded. In which the latter is expected to be lower. As it can be seen in Figure 7 the difference of the mass fractions during the reaction is most significant after 5 min. Afterward, under both ways of heating the quasi-equilibrium is reached, in which just minor changes occur. Interestingly, the fraction of $OME_{>5}$ in equilibrium, is about 9.48 ± 0.16 wt% for thermal and 7.59 ± 0.07 wt% for microwave-assisted heating. This may be caused by the difference of the average temperatures during the reaction. As mentioned above, higher temperatures would lead to higher shares of short chain OME. Consequently, as the heating process during MAS is faster and the internal temperature was directly measured, a higher average temperature can be assumed, leading to the observed shift of product distribution.

3. Conclusion

The new method of producing OME fuels by microwave-assisted synthesis and the application of polymeric catalysts was successfully introduced. First, the required time to reach the quasi-equilibrium state of oligomeric OMEs was determined. After-

ward, the influence of temperature under microwave conditions was investigated for different polymeric catalysts and the resulting values were compared. Based on this data, the most suitable conditions for catalyst screening could be concluded. Afterward, different polymeric catalysts were screened and evaluated in terms of product distribution as well as side-product formation revealing the lowest amount of side product for Nafion as catalyst. Additionally, kinetic investigations were performed under microwave-assisted and thermal heating to 50 °C. The reaction speed was accelerated by a factor of approximately two when microwave-assisted heating was applied. A more efficient heating, reducing the time required for reaching the desired reaction temperature, and more accurate monitoring of the internal temperature was assumed to be the main reason for this effect.

Further studies may include the influence of catalyst loading on the reaction kinetics during microwave-assisted OME fuel synthesis. Additionally, screening experiments regarding the side product formation in dependence of the used catalyst will be performed.

4. Experimental Section

Materials and Methods: Trioxane, dimethoxymethane (dry, stored over molecular sieves), tetrahydrofuran (HPLC grade), and the analytical standards of dodecane, methanol, and methyl formate were obtained from Sigma-Aldrich and used as delivered. Analytical standards of OME_n ($n = 1$, 2, 3, 4, 5) were purchased from ASG Analytik Service Gesellschaft. Amberlyst15 and Nafion-NR50 were purchased from Sigma-Aldrich and used as received. Amberlyst36, Dowex50Wx2, and Dowex50Wx4 were obtained in wet form and dried in vacuo for 3 d at 40 °C prior to use. For drying, a Hettlab IR-Dancer 300 was utilized. Microwave-assisted reactions were performed in capped microwave vials (2–5 mL) using a Biotage Initiator-8 microwave synthesizer (max. power of 400 W, working frequency of 4.45 GHz). The GC analysis was carried out using a Shimadzu GC-2010 system comprised of an AOC-20s autosampler, AOC-20i injector and a FID detector. Helium was used as carrier gas, a Carl Roth, RotiTMCap-5

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MS column with 30 m length, 0.25 mm ID, and 0.25 µm thickness was utilized for compound separation. GC was performed using the following program: 5 min 35 °C, heating with 15 °K min^{-1}, 10 min at 280 °C, FID temperature 320 °C.

General Procedure for OME Fuel Synthesis: The screening experiments were performed by preparation of a stock solution of trioxane in DMM. For this purpose, trioxane (10 g) was deposited in a microwave vial, which was subsequently flushed with nitrogen followed by addition of dry dimethoxymethane (20 mL). The mixture was stirred until all trioxane was dissolved. For the OME synthesis, the corresponding catalyst (masses are listed in the Supporting Information) was deposited in a microwave vial (2–5 mL). The sealed vial was purged with nitrogen for 5 min, followed by the addition of the stock solution (5 mL).

For reactions performed under thermal heating and at room temperature the vials containing the freshly prepared stock solution were deposited in a preheated oil bath at the respective temperature. Samples were taken after the desired amount of time, filtrated to remove the catalyst and diluted with THF (0.8 mL) in a vial. Dodecane (5 µL) was added as an internal standard. The mass of the sample, as reference for determining the recovery rate, was measured by weighing before and after the sampling procedure. Every reaction was performed three times and the average of the results was utilized.

Reactions performed under microwave-assisted heating to determine the equilibrium compositions at different temperatures were deposited in the microwave system via the autosampler of the Biotage system. All reactions were carried out at the respective temperature with a pre-stirring time of 2 s. Temperature and pressure in the vial were monitored constantly. After the reaction, the mixture was automatically cooled to 30 °C by external flushing with nitrogen. Microwave-assisted kinetic experiments were performed identically but without pre-stirring and without cooling after the reaction. Samples were taken after the release of the vial by the Biotage system, filtrated to remove the catalyst and diluted with THF (0.8–1 mL) in a vial. Dodecane (5 µL) was added as an internal standard. The mass of the sample, as reference for determining the recovery rate, was measured by weighing before and after the sampling. Every reaction was performed three times, except the equimolar experiment with Nafion at 40 °C, and the average of the results was utilized. All results are shown in the Supporting Information.

Analytical Procedure: Quantification of the products in the reaction mixtures was performed using relative response factors (RRF), obtained by measuring well-defined standard solutions of the OME$_n$ ($n = 1, 2, 3, 4, 5$), methyl formate, methanol and trioxane with dodecane as internal standard. For OME$_n$ ($n = 6, 7, 8, 9, 10$) the values of the measured OME were extrapolated by exponential asymptotic fitting in Origin, version 9.7.5.184. The repeatability of the RRF values of OME$_n$ ($n = 2, 3, 4, 5$) had a relative standard deviation (RSD) of ≤1%. For OME$_1$ the corresponding value was 1.7% and for methanol and methyl formate ≤1.1%. Trioxane revealed a RSD-value of 5.4%. For accuracy, each sample was measured at least three times. The standard deviation in between the results of the three reactions was below 3 wt% for each compound except for the reaction of Nafion at 40 °C for which the values were ≤7.1 wt%. The standard deviation of the masses calculated from the repetitive measurements was below 2 wt%, except for a single case, in which the deviation was in the range of 2–3 wt%. For all measurements, the recovery rate was higher than 96 wt%. For comparability reasons the sum of the weight fractions was normalized to one.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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