

# Conceptual Design of a Novel Process for the Production of OME Fuels

Niklas Schmitz<sup>a,c</sup>, Christian Breitzkreuz<sup>a,c</sup>, Eckhard Ströfer<sup>a,c</sup>, Jakob Burger<sup>b,c,\*</sup>, Hans Hasse<sup>a,c</sup>

<sup>a</sup>Laboratory of Engineering Thermodynamics (LTD), TU Kaiserslautern, Germany

<sup>b</sup>Chair of Chemical Process Engineering, Technical University of Munich, Campus Straubing, Germany

<sup>c</sup>OME Technologies GmbH, Kaiserslautern, Germany  
 burger@tum.de

Poly(oxyethylene) dimethyl ethers (OME) are oxygenates of the general structure  $\text{H}_3\text{C-O-(CH}_2\text{O)}_n\text{-CH}_3$  with  $n \geq 2$ . OME are synthetic diesel fuels, which strongly reduce the soot formation and indirectly also the NO<sub>x</sub> formation in diesel engines. This work presents the conceptual design of a novel OME process, which employs aqueous solutions of formaldehyde and methanol as feedstock. Process-relevant data on physico-chemical properties are determined experimentally and models for their description are developed. This includes describing the chemical equilibrium and the vapor-liquid-liquid equilibrium in the system (formaldehyde + water + methanol + methylal + OME). The models are used for determining thermodynamic limits of the process like chemical equilibria and distillation boundaries. Based on that knowledge the novel OME process is designed. It consists of a reactor, two distillation columns, and a pervaporation unit. The first column is a reactive distillation in which OME with  $n \geq 3$  are separated from a complex reactive multicomponent mixture with more than 30 components. All critical units, including the reactive distillation and the pervaporation are tested in lab-scale experiments. The column profiles of the distillation experiments are well described by simulations using the equilibrium-stage model.

## 1. Introduction

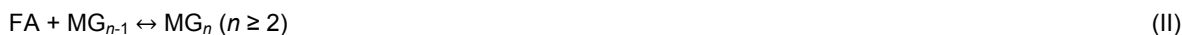
Poly(oxyethylene) dimethyl ethers (OME) are oxygenates of the structure  $\text{H}_3\text{C-O-(CH}_2\text{O)}_n\text{-CH}_3$  with  $n \geq 2$ . OME are environmentally benign synthetic fuels which strongly reduce the soot formation and indirectly also the NO<sub>x</sub> formation in diesel engines (Burger et al. 2010, Härtl et al. 2015). When used as fuels, OME of chain lengths  $n = 3 - 5$  are favorable (Burger et al. 2010, Härtl et al. 2015). OME are obtained from the methanol / synthesis gas route, which enables a flexible use both traditional (coal, natural gas) and renewable (biomass, CO<sub>2</sub>) raw materials. This makes OME one of the most attractive alternative fuels. Presently, processes for the production of OME require the use of expensive intermediates as feedstock, such as methylal and trioxane. This contribution presents the conceptual design of a novel OME production process, which employs a cheaper feedstock, namely aqueous solutions of formaldehyde and methanol. In this process, OME of the desired chain lengths  $n = 3 - 5$ , and water are separated from the inherently reactive multicomponent mixture (formaldehyde + water + methanol + methylal + OME), which features a liquid phase split and several reactive and non-reactive azeotropes.

In state-of-the art OME production, OME<sub>3-5</sub> are produced from expensive intermediates, such as methylal and trioxane (Burger et al. 2010, Burger et al. 2013). Both, methylal and trioxane are produced from formaldehyde and methanol in additional process steps (Masamoto et al. 1993, Grützner et al. 2007, Weidert et al. 2017). The production costs of OME fuel via the methylal / trioxane route are in the order of the production costs of classical diesel fuel (Schmitz et al. 2016a). However, an integrated OME production process starting directly from formaldehyde and methanol would make OME production even more competitive. It is thus highly desirable, in particular with regard to reducing the investment and the energy costs of OME production. In the present work the conceptual design of such process is described highlighting the thermodynamics, the process concept and lab-scale distillation and pervaporation experiments.

## 2. Chemical system

### 2.1 Reactions

Formaldehyde (FA, CH<sub>2</sub>O) reacts with water (H<sub>2</sub>O) and methanol (MeOH, CH<sub>3</sub>OH) to poly(oxymethylene) glycols (MG<sub>n</sub>, HO-(CH<sub>2</sub>O)<sub>n</sub>-H) and poly(oxymethylene) hemiformals (HF<sub>n</sub>, HO-(CH<sub>2</sub>O)<sub>n</sub>-CH<sub>3</sub>), respectively, according to reactions (I) to (IV). Reactions (I) to (IV) occur without the addition of any catalyst and the chemical equilibrium is far on the side of the products (Hahnenstein et al. 1995).



The formation methylal (MAL, H<sub>3</sub>C-O-(CH<sub>2</sub>O)-CH<sub>3</sub>) and OME of various chain lengths, reactions (V) to (VIII), requires an acidic catalyst. OME of chain lengths  $n \geq 2$  are formed either by an acetalization of methanol and poly(oxymethylene) hemiformals of corresponding chain length, reaction (VI), or by a sequential growth mechanism by addition of monomeric formaldehyde, c.f. reactions (VII) and (VIII).



All reactions (I) to (VIII) are reversible. Thus, poly(oxymethylene) glycols, poly(oxymethylene) hemiformals and OME of undesired chain lengths can be recycled in the process, whereas OME of the desired chain lengths  $n = 3 - 5$  and the coupled product water need to be separated from the reactor outlet.

### 2.2 True composition and overall composition

In systems containing formaldehyde, water, and methanol two different ways of describing the composition are used, the true and the overall composition, respectively. The true concentrations quantify all poly(oxymethylene) glycols and poly(oxymethylene) hemiformals, whereas the overall concentrations are found when the unstable poly(oxymethylene) glycols and poly(oxymethylene) hemiformals hypothetically decompose back to formaldehyde, methanol, and water.

## 3. Physico-chemical properties

### 3.1 Reaction model

Mole-fraction based chemical equilibrium constants of reactions (I) to (IV) were determined by Hahnenstein et al. (Hahnenstein et al. 1995) and those of reactions (V) to (VIII) were determined by Schmitz et al. (Schmitz et al. 2015a; Schmitz et al. 2015b). From the chemical equilibrium constants, the overall and the true composition in chemical equilibrium are calculated. This is shown in Figure 1 for a typical reactor outlet at 60 °C. Figure 1 shows that there is a good agreement between the calculated and the measured overall composition in chemical equilibrium. The mole fractions-based model of the chemical equilibrium was consistently extended to a model for describing the reaction kinetics (Schmitz et al. 2015a) and can thus be used for reactor sizing.

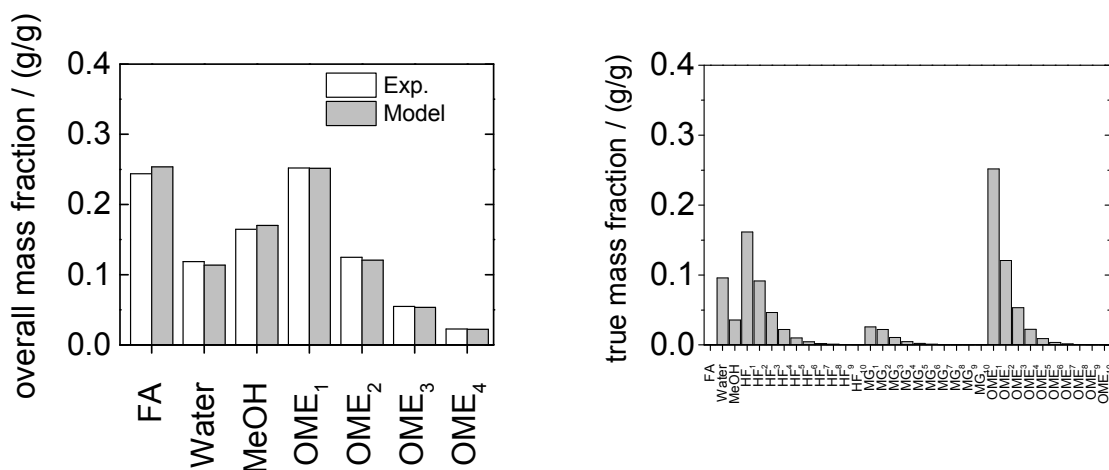


Figure 1: Overall composition (left) and true composition (right) in chemical equilibrium at 60 °C. Overall composition of reactant mixture: 0.48 g/g formaldehyde, 0.02 g/g water and 0.50 g/g methanol. Amberlyst 46 was used as heterogeneous acidic catalyst. The calculations were carried out using a mole fractions-based model of the chemical equilibrium (Schmitz et al. 2015b).

### 3.2 Vapor-liquid-liquid equilibrium

Figure 2 shows a scheme of the reactive vapor-liquid-liquid equilibrium in the system (formaldehyde + water + methanol + methylal + OME) in a non-acidic environment (Kuhnert et al. 2006; Schmitz et al. 2016b; Schmitz et al. 2017). The model explicitly accounts for the chemical reactions (I) to (IV), which have to be considered not only in the acid-catalyzed reactor, but in all process steps.

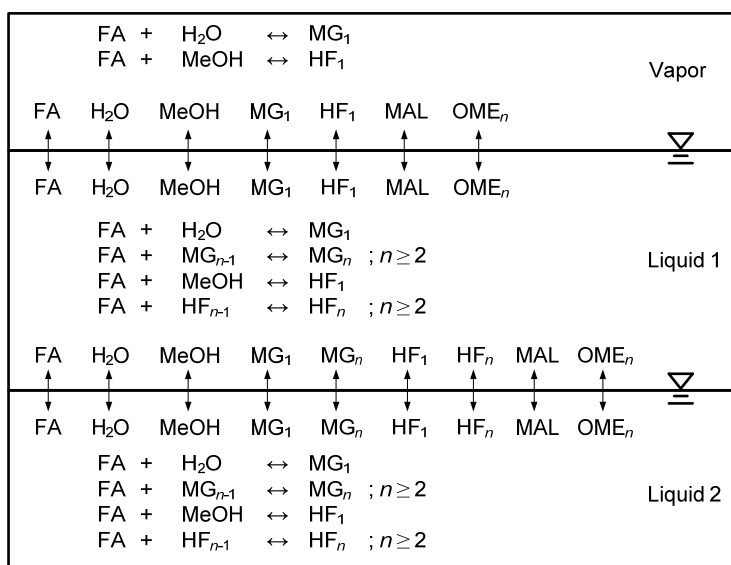


Figure 2: Scheme of the reactive vapor-liquid-liquid equilibrium in the system (formaldehyde + water + methanol + methylal + OME) (Kuhnert et al. 2006; Schmitz et al. 2016b; Schmitz et al. 2017).

### 3.3 Reactive distillation boundaries

Exemplarily for the full system, reactive distillation boundaries in the subsystems (formaldehyde + methanol + OME<sub>2</sub>) and (formaldehyde + methanol + OME<sub>3</sub>) are shown in Figure 3 at 1 bar. The distillation boundaries are reactive in the way that the chemical reactions (I) to (IV) are considered. Figure 3 shows that the region in which OME can be obtained as a pure bottom product drastically increases from OME<sub>2</sub> to OME<sub>3</sub>. By the calculation of multicomponent distillation lines for all components of the reactor outlet, it can be shown

that OME of chain lengths  $n \geq 3$  can be separated with good yield from the reactor outlet (Schmitz et al. 2017). The separation of the coupled product water is, however, not straightforwardly solved by distillation.

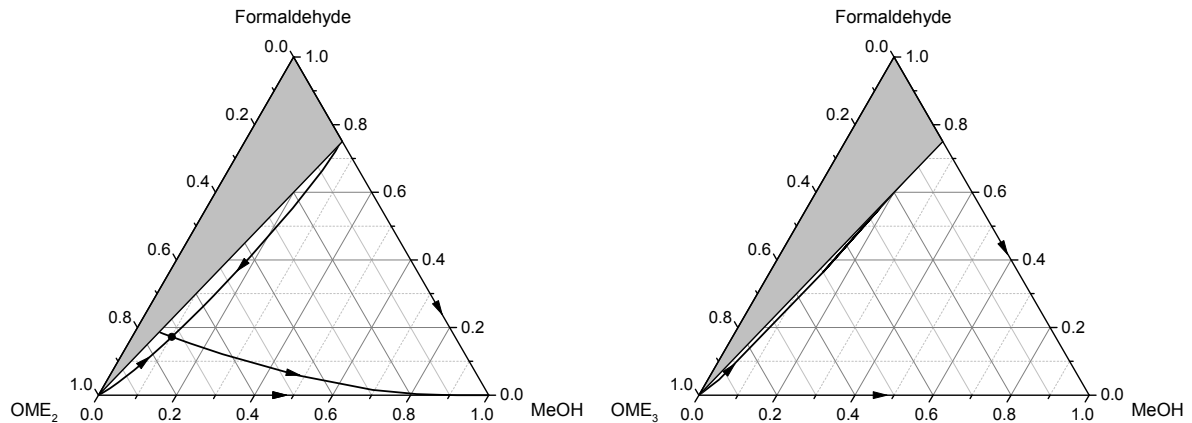


Figure 3: Solid lines: reactive distillation boundaries in the systems (formaldehyde + methanol +  $\text{OME}_2$ ) and (formaldehyde + methanol +  $\text{OME}_3$ ) at 1 bar. Shaded area: formaldehyde precipitation (qualitatively). Overall concentrations in g/g. (Schmitz et al. 2017)

#### 4. The OME Technologies process

Figure 4 shows a flowsheet of the novel OME process (Schmitz et al. 2017), named the OME Technologies process. The feed stream 1 comprises formaldehyde and methanol and may contain water. The feed stream is mixed with the two recycle streams 7 and 9 and fed into the heterogeneously acid-catalyzed reactor to obtain a stream comprising formaldehyde, water, methanol, methylal, and OME of various chain lengths (stream 3). The separation of the desired product fraction  $\text{OME}_{3-5}$  is carried out in two distillation columns C1 and C2. The first distillation column C1 separates OME of chain lengths  $n \geq 3$  as bottom product (stream 5) from the reactor outlet. The second distillation column C2 separates the product fraction  $\text{OME}_{3-5}$  as overhead product from OME of longer chain lengths  $n \geq 6$  which are recycled back to the reactor (stream 7). The separation of water is carried out using a membrane process, such as pervaporation using hydrophilic membrane materials.

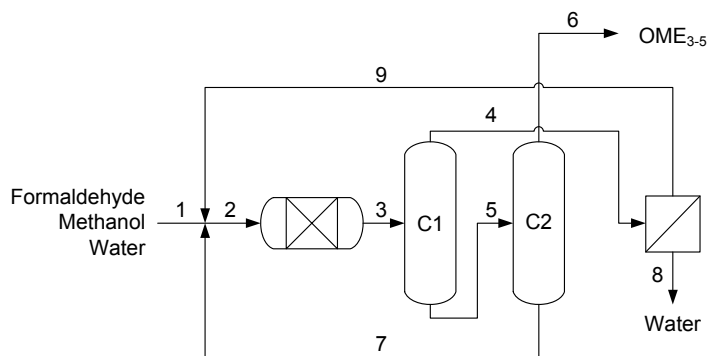


Figure 4: Flowsheet of the novel OME production process. (Schmitz et al. 2017)

#### 5. Experimental validation

##### 5.1 Distillation

Figure 5 shows the overall liquid phase concentration profiles and the temperature profile of a distillation experiment, in which the separation in column C1 was investigated in a continuous DN 50 distillation column equipped with the structured packing Sulzer CY. Note again, that the investigated system is a complex reactive system, in which the chemical reactions (I) to (IV) must be considered for the simulation of the column profiles. Here, an equilibrium stage model was used for the simulation of the column profiles, in which the chemical reactions (I) to (IV) were modelled to be in equilibrium on every stage.

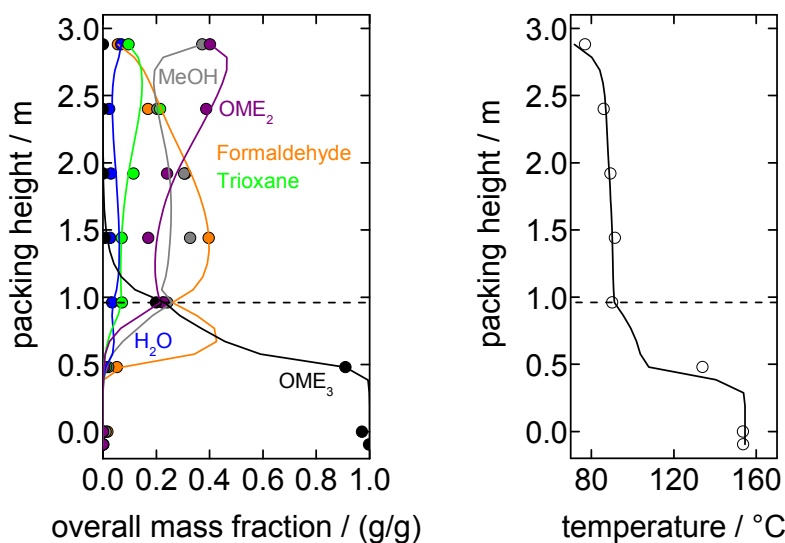


Figure 5: Overall liquid phase concentration profiles and temperature profile of a distillation experiment, in which OME<sub>3</sub> was separated as bottom product from the residual components of the system. This separation occurs in column C1 in the novel OME process, c.f. Figure 4. Symbols: Exp. data. Lines: Simulation using the equilibrium stage model, for which besides the feed composition and temperature, the overall mass fraction of formaldehyde at 1.44 m and the overall mass fraction of OME<sub>3</sub> at 0.48 m packing height were specified. Dashed line: Feed position.

Figure 5 shows that there is good agreement between the experiments and the simulations. Furthermore, it is shown that OME<sub>3</sub> (and therefore also OME with  $n > 3$ ) can be separated as bottom product from the other components of the system.

## 5.2 Pervaporation

Figure 6 shows the experimentally measured water fluxes and overall mass fractions of water in the permeate, in which a mixture containing the components formaldehyde, water, methanol, methylal, and OME<sub>2</sub> was dehydrated using the commercial PVA-based polymeric membrane PERVAP<sup>TM</sup> 4100. It was found that the membrane separation is generally feasible. The membrane is stable in a reproduction measurement. Preliminary stability tests showed no significant degradation of the membrane in three days of operation at 80 °C. Further tests would be necessary to confirm this.

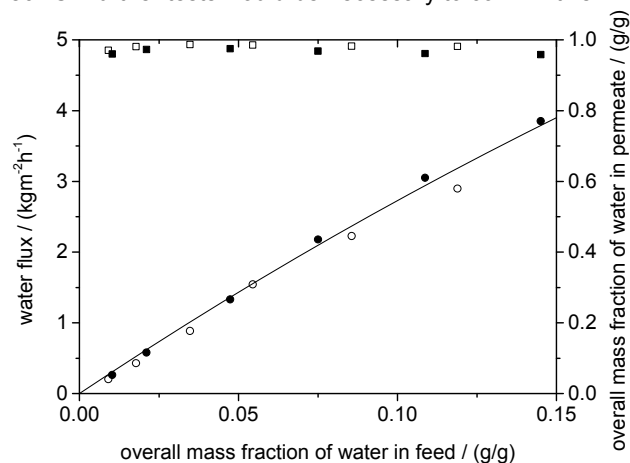


Figure 6: Experimental water fluxes (●,○) and overall mass fractions of water in the permeate (■,□) for the pervaporation of a mixture containing initially 0.175 g/g formaldehyde, 0.137 g/g methanol, 0.347 g/g methylal, 0.201 g/g OME<sub>2</sub>, and 0.141 g/g water (overall composition). The membrane PERVAP<sup>TM</sup> 4100 was used. Open symbols: new membrane. Filled symbols: reproduction with used membrane. Line: Empirical Correlation of the water flux. The temperature is 80 °C, the volumetric flow rate is 80 l/h, and the permeate pressure is 2 mbar.

## 6. Conclusion

A novel process for the production of OME fuels was developed. Relevant physico-chemical properties were measured and thermodynamic models for their description were developed. This includes the chemical equilibria, the reaction kinetics, and the vapor-liquid-liquid equilibrium. The models are used for determining thermodynamic limits pertinent to the process design like distillation boundaries. Based on that knowledge the novel OME process is developed. Lab-scale distillation and pervaporation experiments are used to validate the simulation results and prove the feasibility of the novel OME process. The novel OME process substantially reduces the production costs of OME and makes it one of the most promising synthetic fuels. The novel OME process thereby significantly contributes to the market integration of OME.

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