

# Processes to provide methanolic formaldehyde solutions for the production of synthetic fuels OME

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Formaldehyde solutions are an important intermediate for the production of numerous chemical compounds. Currently mostly aqueous solutions of formaldehyde are produced; the demand for methanolic formaldehyde solutions is rather low. This may change because these solutions are a feedstock in the production of the synthetic fuels poly(oxymethylene) dimethyl ethers (OME) (Schmitz et al., 2017). Presently, there is no process commercially available to produce such methanolic formaldehyde solutions with high selectivity, i.e. without producing substantial amounts of aqueous formaldehyde solution on the side. The present work investigates processes for the selective production of methanolic formaldehyde solutions. An overview of the concepts described in the patent and academic literature is presented. Among the proposed concepts are rectification, extractive distillation, fast evaporation, as well as chemical- and membrane-based separations of aqueous formaldehyde solutions. The proposed concepts are assessed using process simulation. Material and energy balances are calculated and optimized by heat integration via a steam cycle. A techno-economic analysis is performed. The concepts are compared using a set of partly conflicting key performance indicators. Recommendations for the selection of concept in different application scenarios (purity of the methanolic solution, acceptable production rate of side product, energy prices etc.) are derived.

## 1. Introduction

Polyoxymethylene dimethyl ethers (OME) are oligomers of the structure  $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{CH}_3$ . The OME with chain length  $n$  between 3 and 5 are diesel fuels which suppress soot formation during combustion in internal combustion engines (Burger et al., 2010, Härtl et al., 2015). They can be produced from various feedstocks including biomass, natural gas, and  $\text{CO}_2$  (when hydrogen is added to provide energy). In any case, methanol is formed as intermediate. From methanol, there are several routes to OME. All of them involve a step in which formaldehyde - the monomer of the OME oligomers - is produced from methanol.

OME are ultimately synthesized from two types of educts: a) formaldehyde or formaldehyde-containing substances like trioxane, and b) methanol, dimethylether or methylal. The most direct route uses methanolic formaldehyde solutions as feed for the OME synthesis (Schmitz et al., 2017).

Aqueous and/or methanolic solutions of formaldehyde are reactive mixtures. Understanding the involved reactions is important for process design and operation, since the reactive mixtures have a complex behaviour in reactors and separation units. In aqueous solutions, formaldehyde (FA,  $\text{CH}_2\text{O}$ ) and water (WA,  $\text{H}_2\text{O}$ ) form poly(oxymethylene) glycols ( $\text{MG}_n$ ,  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ ) according to:



In presence of methanol (ME,  $\text{CH}_3\text{OH}$ ), formaldehyde forms poly(oxymethylene) hemiformals ( $\text{HF}_n$ ,  $\text{HO}(\text{CH}_2\text{O})_n\text{CH}_3$ ):





All Reactions (1) - (4) have appreciable rates at all pH values and do not require any catalyst to occur. The chemical equilibrium of Reactions (1) - (4) is far on the product side, i.e. the amount of monomeric formaldehyde in aqueous and methanolic solutions is small.

In OME synthesis, methanol and poly(oxymethylene) hemiformals undergo etherification under the presence of an acidic catalyst:



The yield in an OME reactor is limited by the chemical equilibrium of Reactions (1)-(5). In this equilibrium, three types of oligomers ( $\text{MG}_n$ ,  $\text{HF}_n$ ,  $\text{OME}_n$ ) are competing for formaldehyde. To maximize the yield, the water content in the formaldehyde solution used as feedstock for the OME reactor feed should be as low as possible. Since water is formed as stoichiometric side product in Reaction (5), it is however not necessary (i.e. not economical) to separate water completely from the feedstock.

Methanolic formaldehyde solutions with low water content will be called OME feedstock in the following. Most industrial formaldehyde processes produce aqueous solutions as main product. A few of them also provide side streams of methanolic formaldehyde solution. For fuel applications, the production rate of OME would however be large and a lot of OME feedstock would be needed. Simply scaling the present industrial formaldehyde processes would lead to a massive overproduction of aqueous formaldehyde solutions. Instead, dedicated processes are needed that produce methanolic formaldehyde solutions with high selectivity i.e. without producing substantial amounts of aqueous formaldehyde solution on the side. The aim of the present work is to provide a systematic overview of these processes and compare them with respect to their yield, energetic efficiency and economic performance.

## 2. Methodology

### 2.1 Scope

We investigate processes that can provide a methanolic formaldehyde solution that serves directly as feedstock for OME synthesis (OME feedstock). The OME feedstock should have a FA/ME mass ratio of 1.647 and a maximum water content of 0.1 g/g (Schmitz et al., 2017). The processes shall produce the OME feedstock from 2000 kg/h of pure methanol and any desired amount of water and air (21 vol% O<sub>2</sub>, 79 vol% N<sub>2</sub>). These educts enter the process at 25 °C. All side products shall be ideally recycled to increase the yield, or at least separated into pure components. The processes are selected from the existing literature and trimmed toward the task. Process simulation is used to obtain material and energy balances. Key performance indicators (both economic and technical) are defined and evaluated for a conclusive comparison.

### 2.2 Considered routes

Several patents describe production processes for methanolic or water-lean formaldehyde solutions. We have arranged them into seven different routes toward OME feedstock as shown in Figure 1. The Routes 1-6 combine a process for formaldehyde synthesis with a process for water removal. The Route 7 integrates both tasks into one process.

Two processes for formaldehyde synthesis are considered: Process I is based on complete conversion of ME in one pass through the reactor (e.g. Formox processes, off-gas recycle processes). Thus, the reactor delivers a mixture of FA and WA with very little ME (0-2%). As a literature reference we chose the BASF process (Reuss et al. 2012), it provides an aqueous 0.5 g/g FA solution. Process II is based on incomplete conversion of ME in one pass. Thus, the reactor delivers mixtures of FA, ME, and WA, however with a distinctly higher FA/WA mass ratio than in Process I. As a literature reference we chose the process described in the patents by Kloepper et al. (1961).

In Routes 1-6, water has to be removed after formaldehyde production to obtain the OME feedstock. Three different options are considered: Process III is a fast evaporation, i.e. the partial evaporation with short residence time, e.g. in a thin-film evaporator (Gruetzner et al., 2003). Process IV is a membrane separation. In the considered reference (Schmitz et al., 2018), a pervaporation process is considered. Process V is an extractive distillation with the goal of obtaining a highly-concentrated gaseous formaldehyde stream from aqueous formaldehyde (Morishita et al., 1989). Process VI is a fast condensation, i.e. the partial condensation with short residence time (Kloepper et al., 1961).

Finally, Route 7 represents a reference process (Masamoto et al., 1989) that integrates formaldehyde production and concentration. It is based on reacting formaldehyde to the intermediate methylal from which water is separated before it is converted back to formaldehyde.

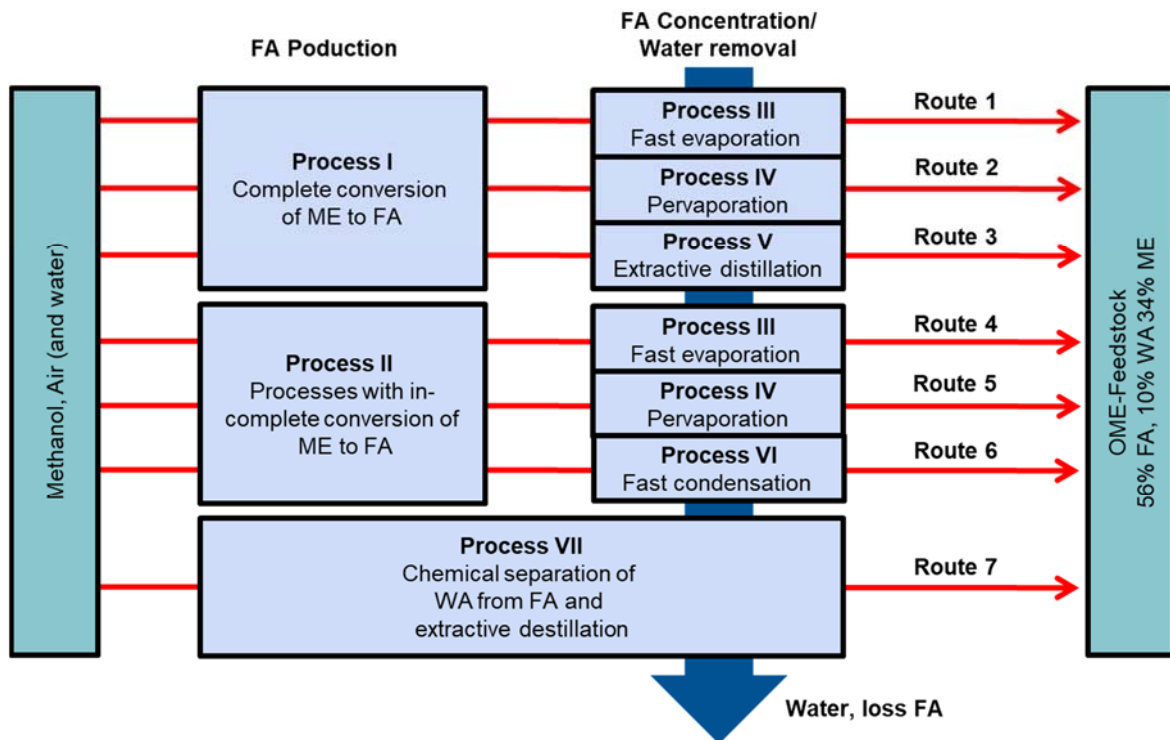


Fig. 1 Overview of the considered routes in the present work. Reference literature as follows. I: (Reuss et al. 2012). II: (Klopper et al., 1961), (Eek Vancells, 1990). III (Gruetzner et al., 2003), (Eek Vancells, 1990). IV: (Schmitz et al., 2018). V: (Morishita et al., 1989). VI: (Klopper et al., 1961). VII: (Masamoto et al., 1989).

In the Routes 4 and 6, methanolic FA solution and aqueous FA Solution are formed simultaneously. As stated above, this might be a disadvantage when the large-scale production of OME is considered. Thus, we have considered the respective losses using a key performance indicator, cf. below.

It should be noted that there are also conceivable routes in which formaldehyde is isolated in a rather pure and solid form (e.g. paraformaldehyde or trioxane) and afterwards dissolved in methanol. We have excluded them for practical considerations (avoidance of solid handling) in the comparison.

### 2.3 Process modeling and simulation

The flowsheets of the processes I-VII were adopted from the mentioned literature references. If not already given in the source, the mass flowrates of all streams were estimated from the information on composition, reactor yields and selectivities. Using these mass flowrates as inputs, process simulations were done to obtain results for apparatus dimensions, heat demand and power demand.

For the simulations, a property model was created by combining correlations for vapour pressures, enthalpies of vaporization and heat capacities from the literature (Kuhnert et al., 2006, Albert, 1999, Thermophysical Properties Laboratory Project 801, 2009). A UNIFAC activity model for the liquid phase that is tailored for formaldehyde systems, was taken from Kuhnert et al., (2006). The gases  $N_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$  and  $H_2$ , were considered as non-dissolvable inert gases.

### 2.4 Optimization by heat integration (HI)

An optimization by heat integration (HI) is done over all processes along each route between methanol and OME feedstock. HI is realized using a steam cycle operating at three pressure levels: 40 bar (290 °C), 20 bar (220 °C) and 4 bar (150°C). The minimum temperature difference is chosen to 10 K. Cooling is done with cooling water.

### 2.5 Process economics

Capital expenditure (CAPEX) and operational expenditure (OPEX) are estimated for all considered routes using an equipment-factor method with an accuracy of -30% to +30% (Christensen and Dysert, 2005). For the raw material cost, a methanol price of 329 €/t is assumed. The purchased cost is calculated for the year 2018 by accounting for inflation using the Chemical Engineering Plant Cost Index (CEPCI). An exchange rate of 0.85 €/€ and a location factor of 1.11 (Germany) are assumed. For standard equipment, cost correlation are taken

from Towler and Sinnott (2012) and Peters et al. (2003). Factors accounting for additional costs (e.g. installation, power supply, engineering and indirect OPEX) costs are taken from Peters et al. (2003).

## 2.6 Key performance indicators (KPI)

The following key performance indicators (KPI) are defined for all routes.

$$\text{Total yield} = \frac{\dot{n}_{\text{FA}}^{\text{all products}} + \dot{n}_{\text{ME}}^{\text{all products}}}{\dot{n}_{\text{ME}}^{\text{in}}} \quad (6)$$

$$\text{Product yield} = \frac{\dot{n}_{\text{FA}}^{\text{OME Feedstock}} + \dot{n}_{\text{ME}}^{\text{OME Feedstock}}}{\dot{n}_{\text{ME}}^{\text{in}}} \quad (7)$$

While the total yield also includes aqueous formaldehyde solutions, the product yield considers only the yield of OME feedstock. Energetic KPIs are the total heat demand after HI and the total power demand. Economic KPIs are the absolute CAPEX and OPEX (for processing 2000 kg/h methanol). The technology readiness level (TRL) is used as KPI to reflect the maturity of the investigated technologies. It is estimated from the information in the literature.

## 3. Results & Discussion

### 3.1 Energy balance

The energy balance of all routes is visualized in Figure 2. Differentiated are high temperature (HT) heat demands and excesses, low temperature (LT) heat demands and excesses, and power demands. High temperature heat demands and excesses are the ones over 150 °C. High temperature heat excess is heat taken out by producing high-pressure steam at 150 °C to 290 °C. Excess is displayed as negative bar, demand as positive bar. For each route, results before (left bar) and after HI (right bar) are shown.

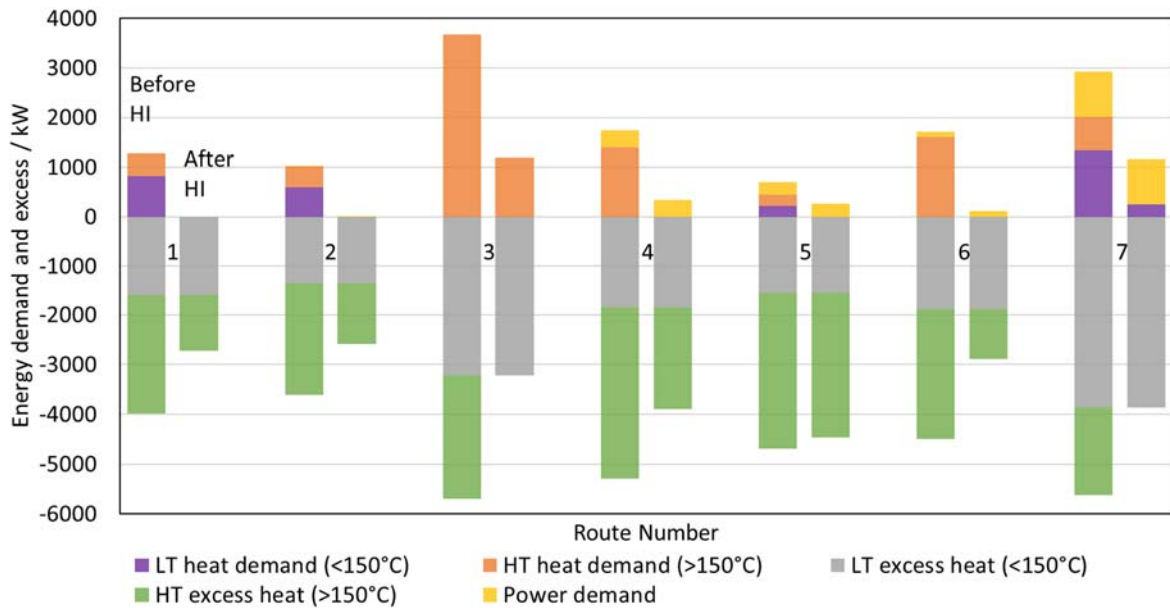


Fig. 2 Energy demand and excess of all considered routes for a plant processing 2000 kg/h methanol. Excess is negative, demand positive. Left bar: before heat integration (HI), right bar: after HI.

Due to the exothermic formation of formaldehyde from methanol at high temperatures, all routes provide large amounts of excess heat. For Routes 1, 2, 4, 5 and 6, this excess heat covers all heat demands after heat integration. There is even significant left over excess heat to be used elsewhere or sold. Routes 4, 5 and 7 are the only routes with significant power demand due to compression of major gas streams.

### 3.2 Key performance indicators

Table 1 shows the best and worst result of the individual KPIs when comparing all routes. For visualization of the trade-offs between the individual KPIs, they are normalized using a best-worst normalization:

$$KPI_{Norm} = \frac{KPI - KPI_{Worst}}{KPI_{Best} - KPI_{Worst}} \quad (8)$$

After normalization, the route with the best (worst) original KPI has a normalized KPI of 1 (0). Figure 3 shows the normalized KPI plotted as a radar chart.

The routes perform quite different regarding product yield, while the total yield is always above 74 %. Routes 4 and 6 produce additional aqueous FA solution. Therefore, they have a lower product yield. The lowest total losses occur in Routes 2, 6 and 7. This achievement is paid by a high heat demand (Route 7), a low TRL (Route 2) and low product yield (Route 6).

Route 7 has by far the highest CAPEX and OPEX. This is due to a complex process with many units and chemical conversion steps. The lowest OPEX results from Route 1, followed by Route 4, both routes use fast evaporation. Generally, pervaporation (Routes 2 and 5) results in a rather low energy demand with reasonable yields at fair costs. The low TRL indicates however that the technology is not yet market ready. Route 3 has a high TRL, a low power demand and low capital costs, but it performs quite poor in all other aspects.

Table 1: Best and worst key performance indicators over all routes. Values are given for a plant processing 2000 kg/h methanol.

Performance indicator	Target	Best value	Worst value
Product yield / (mol/mol)	Maximize	0.93	0.47
Total yield / (mol/mol)	Maximize	0.93	0.74
Total heat demand / kW	Minimize	0	1211
Total power demand / kW	Minimize	0	928
Capital expenditure / Mio €	Minimize	6.6	12.4
Operational expenditure / Mio € / a	Minimize	7.2	9.5
TRL	Maximize	9	5

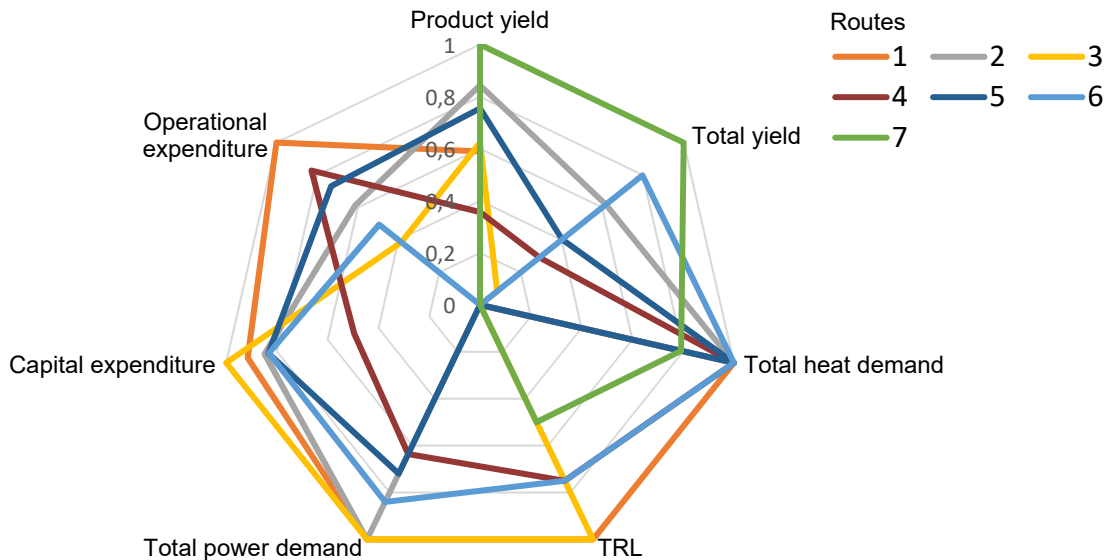


Fig. 3 Comparison of multiple performance indicators using best-worst normalization to transform all indicators to a value between 0 and 1. The value 1 (0) refers to the best (worst) performing process in its category, 0 to the worst.

### 4. Conclusions

The production of methanolic formaldehyde solution as feedstock for OME production was investigated using a comprehensive review of possible process routes. Seven routes have been identified and analysed using process simulation to obtain material and energy balances. Heat integration has been considered via a steam

cycle. The performance of the individual routes were compared using indicators for yield, energy, economics and technical readiness levels. It is found that water removal by evaporation/condensation with short residence times, e.g. in a thin film evaporator, has superior economics at good product yield, no matter whether the formaldehyde synthesis is run with or without methanol excess. Water removal by pervaporation can achieve high yields and low energy demands, however has a lower TRL at the moment. Other options - including extractive distillation and chemical formaldehyde concentration via the intermediate methylal - are not competitive.

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