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UNIVERSITÄT
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TECHNISCHE FAKULTÄT

Synthesis of OME$_{5-7}$

Short Report

CBI Project Course 10/2019

Partner: hubergroup Deutschland GmbH

www.crt.cbi.uni-erlangen.de

Outline

The project course is organized by the *Department Chemie- und Bioingenieurwesen* (CBI) of *Friedrich-Alexander-Universität Erlangen-Nürnberg* (FAU) in cooperation with an industrial partner. It represents a curriculum event with no commercial interest. The industrial partner of the CBI project course in autumn 2019 is the hubergroup Deutschland GmbH, located in Munich, Germany. The company is one of the leading **printing ink producers** worldwide and was founded in 1765.

This year's topic of the project course is the development of a production plant for **1000 ton per annum OME_{5-7}** (polyoxymethylenedimethylethers with chain lengths of 5 to 7) at a site in Germany. Therefore**, two different synthesis routes**, an aqueous and an anhydrous route, are designed and engineered. In the aqueous route, the OME_{5-7} can be synthesized by reacting aqueous formaldehyde with methanol whereas for the anhydrous route trioxane and methylal (OME_1) are being used (see Figure 1).

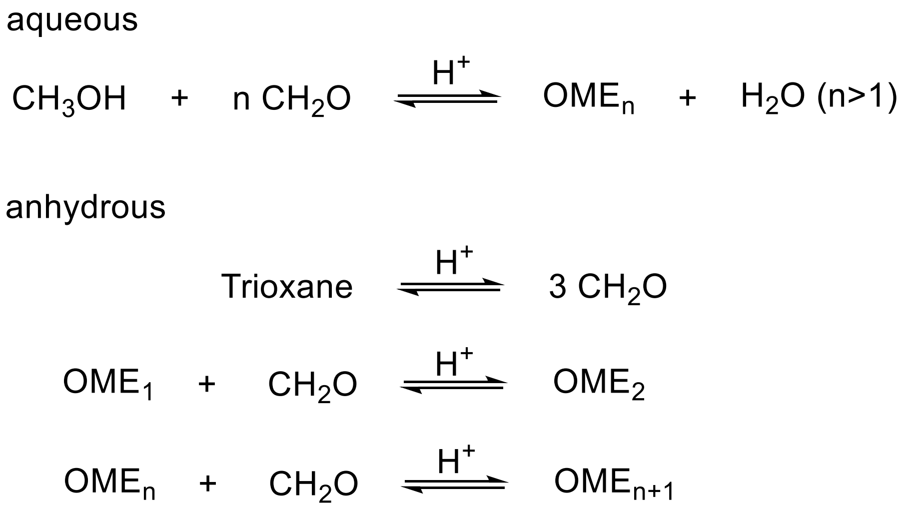

Figure 1. Simplified reaction scheme for the production of OME_n from methanol/formaldehyde (aqueous route, top) or methylal/trioxane (anhydrous route, bottom).

The product has to be separated and **purified to 97 %** after the production process, so that it can be used as an **alternative solvent for ink production**, replacing conventional solvents like mineral or linseed oil.

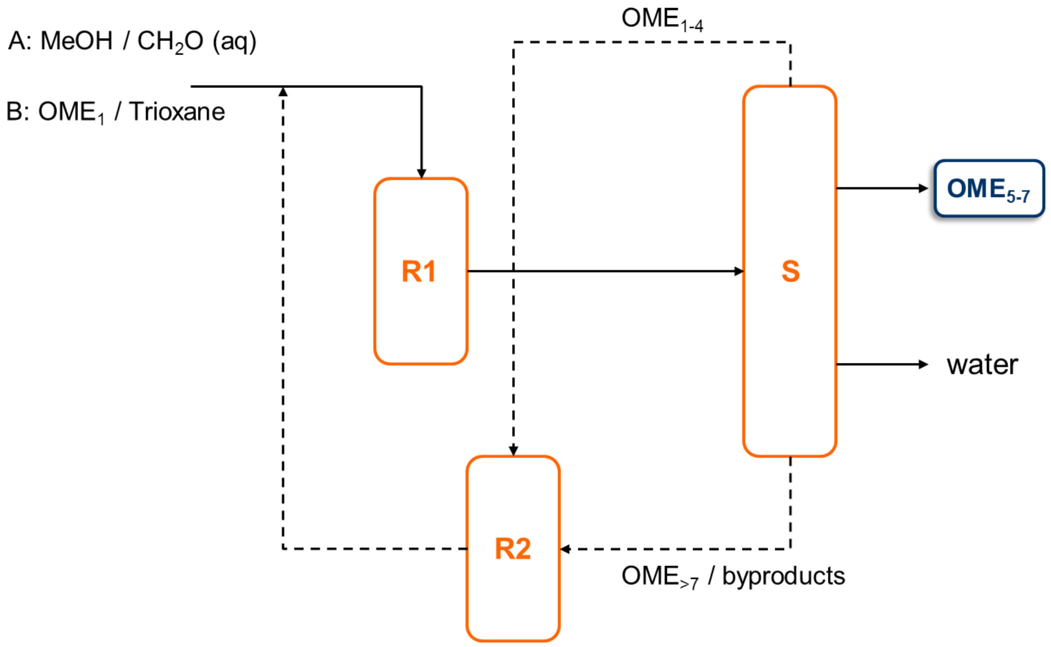

Figure 2. Overall block flow scheme of the OME$_{5-7}$ production process. Both possible routes require a reactor (R1), a separation section (S) and a recycling unit (R2).

The overall layout of the designed process is shown in Figure 2, including **specialized tasks** (e.g. reaction, separation, recycling) and more **general tasks** (e.g. heat, piping, safety, costs). In addition, given the possible application scenario of the OME based inks in food packaging, eco-toxicity and diffusion through cardboard has been estimated.

Results

The results section is structure according to the block scheme shown in Figure 2. First, both routes will be discussed with respect to reaction, separation and recycling, followed by details of apparatus, piping heat management and automation. Finally, safety, toxicity and costs are presented.

Aqueous OME$_{5-7}$ Production

For the aqueous route, the ion exchange resin catalyst **Amberlyst 46** is used because the reactions are **acidic catalyzed** (see Figure 1). After initial estimations of the reactor type and size, the process is simulated for chosen assumptions (feed flow, pipe length, and diameter). A **multi-tubular reactor design** was chosen to avoid high mechanical stress on the catalyst. The reaction zone is divided into two sections. In the first one, a static mixer disperses the emulsion. In the subsequent catalyst bed, the chain growth reaction takes place according to a Schulz-Flory distribution. Important, the non-converted reaction compounds have to be recycled to increase the overall yield as shown in Figure 3.

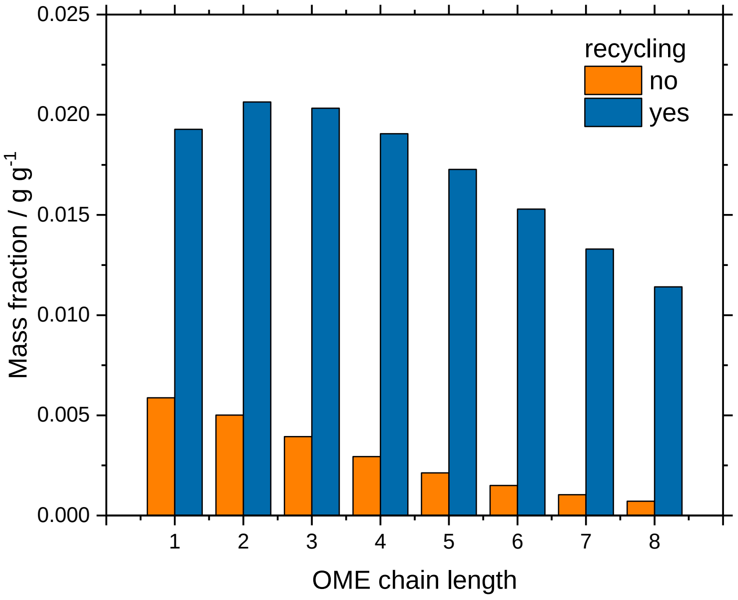

Figure 3. Simulation results for aqueous OME synthesis with and without recycling of unreacted compounds. Note that the majority of reaction mixture contains water.

The feed, consisting of 37 wt.-% formalin solution, additional methanol and the large recycle stream, is delivered via pumps which simultaneously serve for flow control. The feed has an **inlet temperature of 90 °C** and **6 bar absolute pressure**. Places for measuring and control technology are determined. The final setup for the multi tubular reactor consists of a total number of **32 tubes** with an equal **diameter of 5 cm** and a **tube length of 8 m each**. The amount of catalyst required is 5.65 kg per tube and, respectively, **181 kg in total**. The reactor is set up to produce **125 kg h^{-1} of OME_{5-7}** in a stationary process. The **space time yield** amounts to **250 kg m^{-3} h^{-1}**.

The **separation and purification** of the product stream from the reactor is achieved by **four unit-operation steps**. Since the water content of this mixture is relatively high and there are **azeotropes** of water and some reaction components, water has to be separated nearly completely as a first step. Only a small part of the water has to remain in the mixture to stabilize the formaldehyde. Furthermore, the pipes have to be as short as possible in order to stay in a turbulent area and thus avoid a phase separation of the liquid/liquid two-phase system. The **equilibrium of the reaction** is also a challenge that has been considered. After every separation step, a reaction balance is set in presence of the reactants. Since the boiling points of the by-products are in a same range as the ones for the desired product, they are quite hard to remove. To realize the separation of water, **pervaporation** was chosen with a membrane called PERVAP 4101 from DeltaMem AG. A **total membrane area of 310 m²** is required, separated into seven modules. Between all the modules a heat exchanger is arranged to reheat the cooled retentate up to the desired inlet temperature of 100 °C. The pressure on the feed and retentate side is **5 bar** while the **vacuum on the permeate side**, which is needed to force the water to evaporate, is at 0.1 bar. As a result of the pervaporation **99 wt.-% of the water**, which is **433.8 kg h^{-1}** in total, was separated. Afterwards, the remaining mixture has to be separated to obtain the desired product of OME_{5-7}. Three **distillation columns** have been designed to receive the final product of OME_{5-7} overhead of the third column with a **purity of 97.6 %**. The **total mass flow** is **128.5 kg h^{-1}** corresponding to **1028 t a^{-1}**.

The possible **by-products** of the reactions are HF_n (poly(oxymethylene) hemiformals), MG_1 (poly(oxymethylene) glycols), OME_{1-4}, $OME_{n>8}$ (polyoxymethylene dimethyl ether), DME (dimethyl ether) and MEFO (methyl formate). HF_n is recycled as it can be reused as a reactant in the following reaction. MG_1 and HF_1 decay easily into the reactants (FA and methanol) in equilibrium. Using the Amberlyst 46 for the OME synthesis shows no detectable formation of MEFO and DME. OME_{1-4} can further react to OME_{5-7}, the target product. Accumulation of $OME_{n>8}$ is prevented by feeding $OME_{n>8}$ back into the reactor. Therefore, **all by-products** and the unreacted raw materials (FA and methanol), will be **separated** and **sent back to the reactor directly**. 99% of water will be removed during the separation process.

Anhydrous OME_{5-7} Production

For the anhydrous reaction of trioxane (TRI) with methylal (OME_1), the acidic ionic liquid 1-butylsulfonyl-3-methylimidazolium hydrogen sulfate as a **biphasic homogeneous catalyst** has been chosen. For suitable reaction design, the equilibrium reaction based on the kinetic data has been used and implemented in ASPEN Plus. In cooperation with other groups, such parameters as residence time, pressure, substrate-feed-ratio (OME_1/TRI), and recycling have been varied. Compared to literature, the desired **product content in the reactor outlet could be doubled** by varying the reaction parameters and including the recycling stream (see Figure 4).

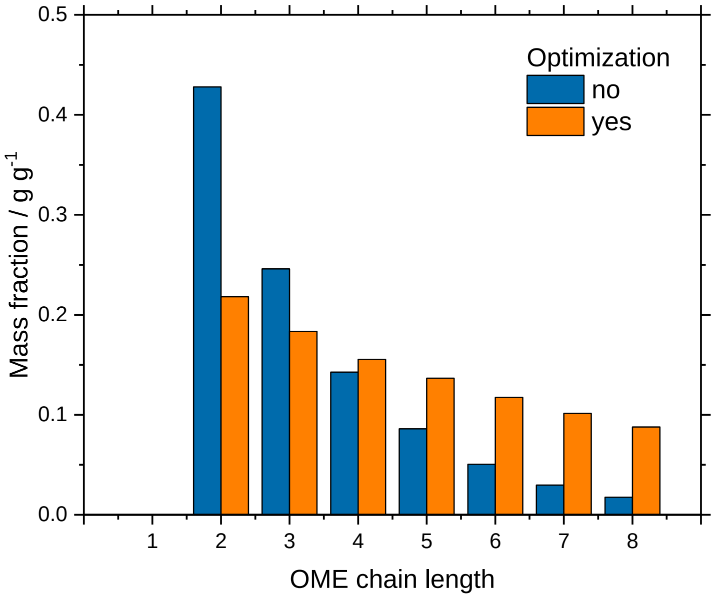

Figure 4. Simulation results for anhydrous OME synthesis. Optimization includes reaction parameter variations and recycling of unconverted feed.

To achieve these results a feed-ratio of OME_1/TRI of 1/1.67, a temperature of 115 °C, 5 bar_{abs} and a residence time of 6800 s have been chosen. In terms of process engineering, the reaction system was implemented in a **continuously stirred tank reactor (CSTR)**. For this purpose, reactor dimensions, agitator and heat management were designed. Process design parameters can be found in the apparatus section. The results show a very controllable**, low risk reactor system** due to a very low reaction heat duty.

For separation of the reaction mixture, a **four-step separation** process was developed. In a first step, the ionic liquid is separated with a tubular centrifuge in a two-phase separation. The separation of the denser ionic liquid is assumed to be ideal. Afterwards the product mixture is **distilled** three times. All fractionating columns are packing columns and were simulated with ASPEN. The total mass flow of the **product stream is 128 kg h^{-1}** with a composition of 33.7 wt.% OME_5, 33.4 wt.% OME_6, 32.7 wt.% OME_7 and a rest of 0.02 wt.%. The required **purity of 97 %** and production capacity are matched.

The only **possible by-products** in this process are OME_{2-4}, OME_8, FA and remaining reactants. For OME_{1-4} and $OME_{n>8}$, the same method is applied as for the aqueous route. FA can be used as reactant propagating the chain growth of OME. Trioxane is reversibly decomposed into FA (reaction 5). Therefore Trioxane can be returned to the reactor and participate in the wanted synthesis reaction. As a result, all by-products and the unreacted raw materials TRI and OME_1 will be r**ecycled by returning them into the reactor** without extra processing.

Process Simulation

The major task of the **process simulation** group is the implementation and validation of reaction kinetics. Provided by reaction specialist groups, kinetic parameters were implemented, and a suitable reactor type is selected. As the kinetic data is obtained from batch experiments reported in the scientific literature, a validation of underlying parameters is inevitable. After the reaction equilibrium of batch experiments from literature could be reproduced under identical conditions within the software, the parameters were assumed to be valid and **different feed composition** were simulated. A last aspect of process simulation comprises the **implementation of separation units**. The choice and design of all apparatuses is performed by respective specialist groups.

Table 1. Summary of ASPEN Plus simulation results for both OME production routes.

Parameter	Aqueous route	Anhydrous route
OME_{5-7} production / kg annum^{-1}	1,028,000	1,000,000
Space-time-yield / kg m^{-3} h^{-1}	250	138
$OME_{>8}$ / kg h^{-1}	82	41
Water / kg h^{-1}	431	-
Purge / kg h^{-1}	118	11
Recycle / kg h^{-1}	2025	209
Purity / %	97.6	99.8
Separation	Distillation (3) Pervaporation (1)	Distillation (3) Centrifugation (1)

As a direct rigorous modeling of thermal separation units is difficult, the process simulation group provides ASPEN Plus **short-cut models** for distillation columns, which can support rigorous simulation via the Fenske-Underwood-Gilliland method, a state-of-the-art process. For this project, the **two different routes** were successfully implemented.

Whenever it is possible, reactors and separation units were based on literature data, complemented by additional simulated data for rigorous calculation. **Recycle loops** and **purge streams** were successfully implemented. As summarized in Table 1, the simulations deliver stream data, such as flow rate, composition, temperature and pressure data from mass and energy balance. **Direct recycling of $OME_{n>8}$** to inhibiting the equilibrium reaction of forming longer chain OME seems to be a more efficient and economical option than a decomposition reactor even with increased recycle current.

Apparatus Design and Construction

The designed apparatuses have to withstand certain properties like corrosive chemicals, induced pressure or specific temperatures. Therefore, the AD – leaflet 2000 B0 - B9 determines the wall thickness of a reactor dependent if a nozzle is attached to the apparatus or not. So, the wall thickness of an apparatus without a nozzle is calculated via the Kettle formula and extended for an added nozzle with the reduction factor. Wounded to the nozzles are flanges, that were constructed in accordance with DIN 2628 – 2632 depending on the pressure in the reactor. An apparatus also consists of torispherical heads that were calculated via specific equations according to DIN 28011. Because of the corrosive medium stainless steel in both routes is the chosen material. Based on the results of the reactor and separation design in the aqueous and anhydrous route, the **main apparatuses** were constructed. These are a **multi tubular reactor**, the **pervaporation** and three **distillation columns** in the aqueous route. The 1724.00 kg heavy multi tubular reactor (see Figure 5) has a wall thickness of 6 mm, because the cooling medium flows with a high pressure in the 10.5 m long reactor.

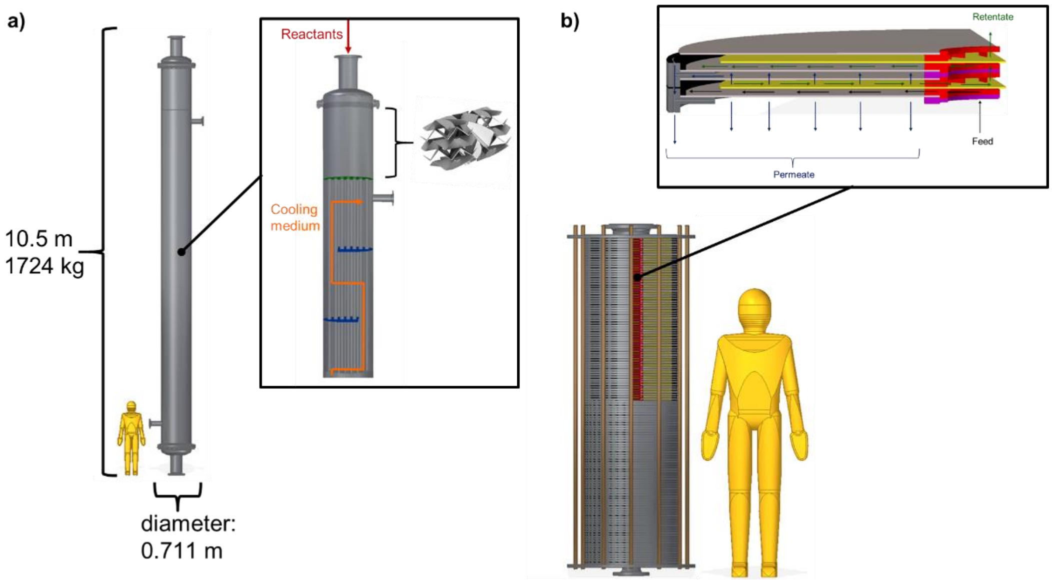

Figure 5. Finalized design for a) the multi tubular reactor and b) the pervaporation unit.

The inner valves have a wall thickness of 2 mm dependent on the inner and outer pressure that they are in direct contact with. Afterwards a pervaporation with seven modules and 133 plates is attached. The height is 2 m with a diameter of 0.71 m. The total weight is 970.15 kg. To distillate the product, three distillation columns are necessary. The product is separated from the sump in the columns with total heights between 16.50 m and 20.50 m. All three distillation columns have a wall thickness of 2 mm.

In the anhydrous route the **CSTR** has, because of the induced pressure and temperature, a wall thickness of 3 mm that comes along with a height of 2.60 m, a diameter of 1.12 m and a total weight of 924.68 kg (see Figure 6 for details). Followed by three distillation columns with heights between 6.00 m and 6.50 m and diameters between 273.00 mm and 355.6 mm. The wall thicknesses of the columns are 2 mm.

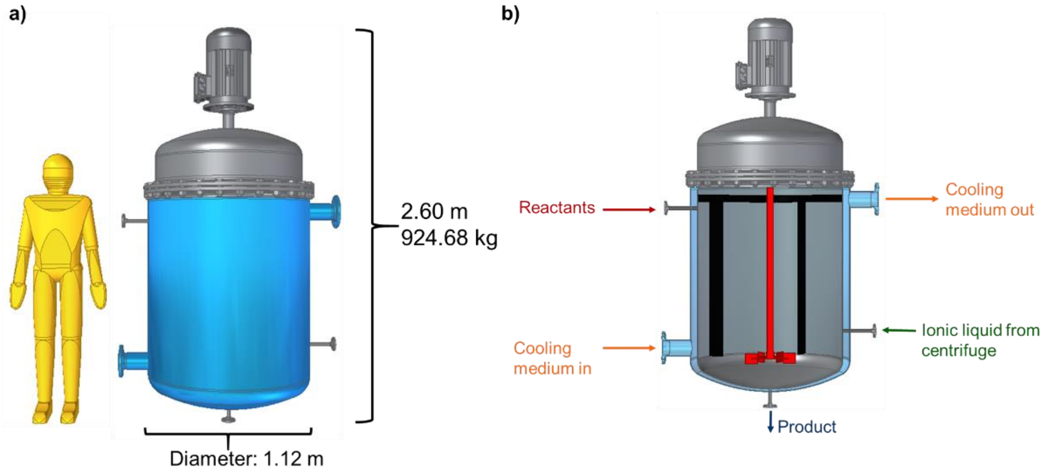

Figure 6. Finalized design for the continuously stirred tank reactor.

To store the chemicals, tanks are necessary. The different volumes, sizes and wall thicknesses are derived from DIN 6616. The wall thicknesses are between 5 and 9 mm depending on the volume.

Plant Layout and Piping Design

The Piping & Sites group used the 3D design software "SketchUp" to build **models** for both routes **based on the minimum safety distance** between each unit. Blue tanks represent feed tanks, red columns are reactors, green columns show separation columns, and yellow tanks exemplify product tanks. The arrangement plan of both routes can be seen in Figure 7. The additional task of the group was the **dimensioning** as well as the material choice of the pipes. The **material of pipes** should work safely up to the temperature of 654 K and the pressure of 25 bar, which are the critical conditions in the production process. Besides, by choosing pipe materials, corrosion resistance is also an important criterion.

Most of the **pipes** in both routes are out of **stainless steel 1.4307 [X2CrNi18-9]** due to its low price and high corrosion resistance.

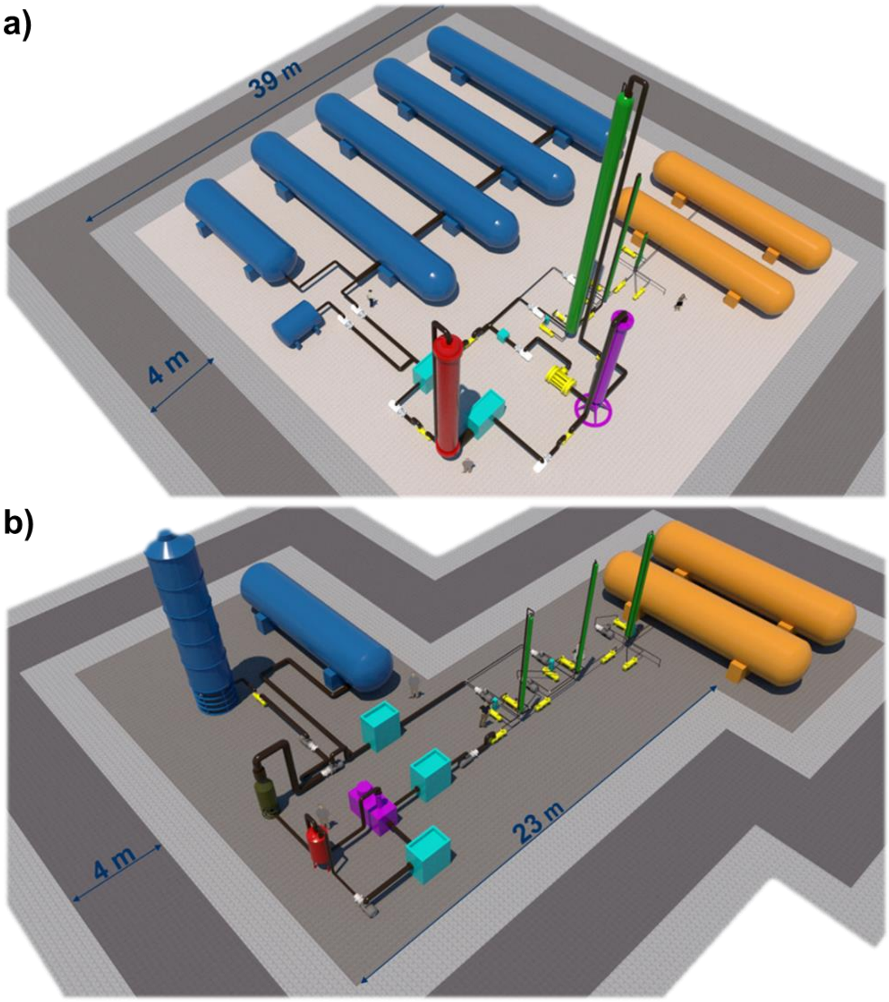

Figure 7. Installation plan for a) aqueous and b) anhydrous OME production.

By calculating the pressure drop of each pipe, it was possible to give information whether pumps are necessary for pressure compensation. Based on the 3D model of each route, the length of the pipes and the thermal expansion of each pipe could be determined. The **maximum pressure loss** of each route is **extremely low**, that no actions are needed for pressure loss compensation. The **thermal expansion** can be compensated by an expansion loop or expansion joint.

Heat management

A compromise between the best possible energy efficiency and the lowest possible investment costs is one of the main tasks in plant development. In order to save energy, the heating process has to be optimized, e.g. **by heat integration**. A tool for **increasing efficiency regarding energy and costs** in the process is the so-called **pinch analysis.**

The pinch analysis can be used to determine the optimum heat exchanger network taking into account all heat flows occurring in the process. After defining the load values, heat flows can be integrated. Based on the results of heat integration it is possible to determine the heat exchange surface and the number of heat exchangers. The energy costs can be calculated considering the payload and the required heat exchangers. Table 2 summarizes the required heating steam, cooling water and costs, by comparing the non-integrated and integrated systems.

Table 2. Summary for aqueous and anhydrous route

	Aqueous		Anhydrous	
	/wo	w/	/wo	w/
Hot utility / kW	774	466	90	77
Steam / kg h^{-1}	2138	1562	269	259
Cold utility / kW	463	120	111	97
Cold water / kg h^{-1}	7521	2625	8449	8213
Investment / k€	715	714	435	434
Energy cost / k€	493	355	76	73

/wo = without heat integration, w/ = with heat integration.

The results are showing that the efficiency of heating and cooling capacity and the investment for heat exchangers with heat integration is higher than without integration. In conclusion, heat integration is a difficult process, but can save a lot of energy and costs.

Process Automatization

For each route a **detailed control scheme** was developed. In the following, the three representative examples for process steps are described: the **reactor of the aqueous route**, the second **distillation column of the anhydrous route** and the **storage of the product**. In the aqueous route a multi tubular reactor is used. For the starting procedure the reactor is flushed with hot water. After pressurizing and tempering the feed is added to the water stream until the stationary point is reached. Then the valve of the waste stream is closed and the valve to the separation is opened slowly as well as simultaneously. During usual operation the inlet temperature is adjusted by a heat exchanger before the reactor. A pump generates the necessary pressure, which is controlled by a pressure control at the beginning of the tube reactor. In addition, the pressure difference in the reactor is measured to ensure that this difference does not exceed a threshold. If the outlet temperature rises above a threshold, an **emergency cooling of the reactor** is initiated. These two emergency procedures are important to prevent the catalyst of decomposition.

For the second distillation of the anhydrous route a vacuum column is used. Therefore, there is a vacuum pump, which is controlled by a pressure control in the top section of the column. In order to preserve a constant temperature, the feed temperature is conditioned. Because our product is in the sump of the column there is a **temperature control at the bottom**. There is a level control connected with the sump-outlet to prevent the distillation column from draining or spilling. Another important parameter is the reflux, which is regulated by a flow control unit. After the column a buffer tank is installed to ensure a constant inlet flow for the next stage. After the last distillation column in each route the product is conveyed into two tanks. Based on the fact that the product is collected monthly two storage tanks are required. There is a level control in order to fill the first tank and afterwards the second one. Since the product must remain liquid the tanks are heated and equipped with temperature instruments. Hence, the automation schemes provide measurements as well as control units for save and efficient operation of each process route.

Location, Legal and Safety Aspects of the Plant

The plant for the OME-synthesis is to be designed as a solvent production plant in the *industrial park Höchst* in the west of Frankfurt (Main). In comparison of building a plant on a green-field site the location in the *industrial park Höchst* comes with several benefits like media supply and required services for the production of OME_{5-7}. For the **establishment and commissioning** of the planned industrial plant several laws have to be considered. Firstly, the plant has to be approved by the authorities according to the *"Bundesimmissionsschutzgesetz (BImSchG)"* because of the handling with dangerous substances. Next to the *BImSchG*, the law of *"Umweltverträglichkeitsprüfung (UVP)"* is relevant as well. According to the attachment 1 of the "*Umweltverträglichkeitsprüfungsgesetz (§*1 Absatz *1 Satz 1)"* a general preliminary test *(§7 Absatz 1 Satz 1*) has to be performed. It can be expected that the results of the preliminary test will show that UVP will not be mandatory due to the small amount of the product per year and the size of the plant. The cost for the whole approval is approximated at 100,000 €.

The **plant safety** is another important aspect. Therefore, it is important to take several precautions against possible incidents. At first the handling of the reactants has to be designed as safe as possible due to their chemical behaviour. Methanol, trioxane and OME_1 are considered as slightly hazardous to water *(Wassergefährdungsklasse 1 / WGK1)* while formalin constitutes a strong danger to water *(WGK3*). Also, methanol and trioxane show explosive behaviour and the reactant OME_1 and the products OME_{5-7} are flammable. As a result, it had to be dealt with the storage of chemicals according to the "*Gefahrenstoffverordnung*" and the usage of retention basins and ATEX execution of apparatuses for transporting the substances inside the facility. Another **precaution measure** is the positioning of the storages, which implies a minimum distance of 10 meters between the storage tanks and buildings. Further **safety measures** are provided by the operator of the chemical park which offers a centralized alarm system to prevent extensive dangers and a local fire department.

Diffusion and eco-toxicity of OME_{5-7}

The colors on food packages are required to meet certain restrictions. These don't only depend on the printing process itself but also on the ink and the transport properties of its components through the material. These are of special importance to ensure the consumer's safety. The aim was to evaluate the **diffusion properties of OMEs** to check whether or not they can safely be used for food packaging. Therefore, a thin film model was applied in order to study the diffusion properties of the OMEs. The model is based on a thin film of paint, with a liquid residue of OMEs that is printed on a carton package (e.g. cereal package). The amount of residual OME was 200 ppm, which is equivalent to the residue amount in dried pharmaceuticals. The residue diffuses through the paint film, the cardboard and later dissolves in the air inside of the package. Thermophyiscal calculations are based on model substances with similar properties. The diffusion through the paint film, which is modeled by a silica gel, and the cardboard is determined using Fick´s first law. Water was taken as a model substance. The partial pressure of OME in air was calculated applying Henry's law. The model substance was an alcohol with similar thermophysical properties and the equivalent molar mass as OME_5, namely 1,2,3,4,5,6-Hexahydroxyheptan ($C_7H_{16}O_6$). In the model, the concentration gradient will decrease over time due to a molar flux from high to low concentration, hence the system reaches an equilibrium state after a given time (2 seconds). The partial pressure of OME in air is $2\ 10^{-24}$ Pa and the amount of OME that diffuses through 0.1 m^2 of cardboard in this time span is 44 µg. Due to the fact that both, the partial pressure in air and the diffused amount of OME are very small, one can **assume no possible health risks** for consumers, hence OME based colors are a fit for printing on food packages.

Not all compounds could be clearly described for **eco-toxicological assessment**. Especially some of the OME-polymers with the chain length of 2-7 and higher could not be characterized since they have not been preregistered according to the REACH requirements. However, researches indicate that due to the low- /non-toxicity of OME1 and POM the assumption can be made that **oligomeric OME** are also **non-toxic for humans or animals**. Methanol is well known for its human and aquatic toxicity and has to be treated with precaution to prevent further damage.

Cost calculation of OME Production

The cost calculation of both processes serves the comparison of the different routes to evaluate profitability. The entire costs are divided into **capital investment** and **manufacturing costs**. Specifically, capital investment includes the costs for purchasing and installing entire process components, the catalyst, planning and approval procedures. Manufacturing costs are calculated by estimating yearly expenses based on a production of 1,000 t OME_{5-7}. This includes rental of the manufacturing site, personnel, reactants, waste management, maintenance and utilities. The number of employees, installation costs and maintenance costs are estimated from the literature. The remaining costs are provided from respective suppliers, mostly estimations and partly specific offers. The calculation yields a capital investment of approximately **1,984,000 €** in case of the aqueous and **1,238,000 €** for the anhydrous route.

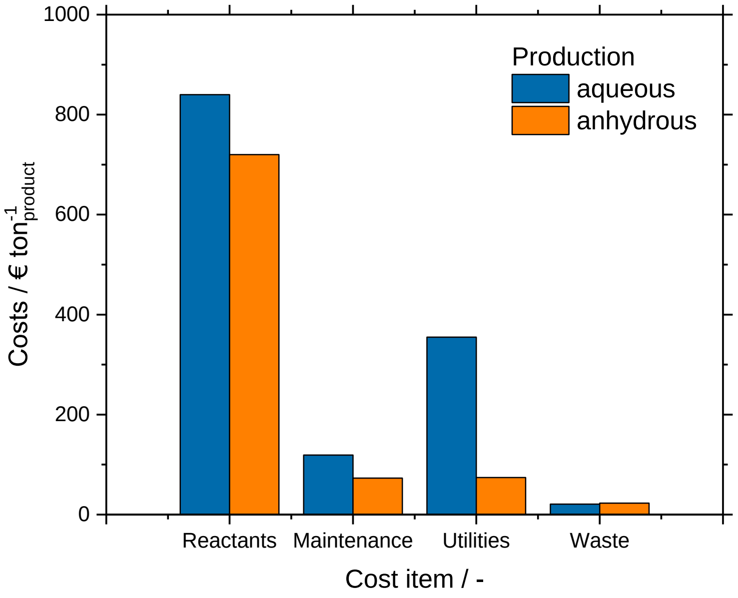

Figure 8. Comparison between the major cost items of the aqueous and anhydrous production routes for OME_{5-7}.

The anhydrous route has more expensive tanks, mainly due to trioxane as reactant, but it is overall the more economical process. On the one hand, reactor, columns and piping for the aqueous route are more complicated and expensive. On the other hand, the heat management for the anhydrous route is notably cheaper, which is mainly due to the huge recycling flow.

Calculating the annual manufacturing costs results in **1,850,000 €** for the aqueous route and **1,405,000 €** for the water-free process. One reason for that difference is the larger amount of reactant, which is needed because of the huge recycle flow in case of the aqueous process. Related to this are also higher costs for heat management (utilities) as shown in Figure 8. Under the assumption of a maximum product revenue of 1,900 € per ton this calculation results in a **break-even point** after roughly **40 years for the aqueous route** and **3 years for the anhydrous route**. This comparison shows that the anhydrous route is considerably more profitable.

Resumé

Two different OME_{5-7}-synthesis routes were developed during the project course. Although the aqueous route, starting from cheaper raw materials methanol and formaldehyde, could be optimized by ASPEN Plus simulation, the much larger recycle stream and the huge water load makes this process economically unattractive. The anhydrous route requires more expensive starting materials (methylal and trioxane), but allows a simple reactor design (CSTR) and lower recycling stream. As a result, the process can reach break-even after 3 years already. As a location site the industrial park in Höchst is chosen due to its benefits regarding media supply and infrastructure for the production.

Since the OME serves as solvent for food packaging ink products, the toxic properties become important. In combination with a diffusion model, it can be determined that the product is non-toxic for humans. The above-mentioned plant designs are the results of a three-week project course and should only be seen as first feasibility study for the OME_{5-7}-synthesis.

Imprint

Synthesis of OME_{5-7}

New solvents for inks –

Partner project hubergroup Deutschland GmbH

Authors/Students

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Erlangen, October 2019