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Production process for diesel fuel components poly(oxymethylene) dimethyl ethers from methane-based products by hierarchical optimization with varying model depth

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ABSTRACT

Poly(oxymethylene) dimethyl ethers (OMEs) are attractive components for tailoring diesel fuels. They belong to the group of oxygenates that reduce soot formation in the combustion when added to diesel fuels and can be produced on a large scale from methane-based products. This opens a new route for gas-to-liquid technology. The present work deals with a particularly favorable route for the large scale production in which OMEs are formed from methylal and trioxane. An OME process based on these educts is designed using two process models of varying depth. In a hierarchical optimization, in which the optimum obtained with a reduced model is used as a starting point for the optimization with the detailed model, an optimal design is found. The resulting design is further adopted to practical needs including a possibility of side-product purge. This work shows that OME production from methylal and trioxane is feasible with technology that could be used in very large scales. The physical property model that is required for the design of the OME process is described in the present work. It is based on literature data on thermo-physical properties and reaction data from previous work of our group. That database is complemented in the present work by measurements of the density of pure OMEs and the vapor–liquid equilibrium in the system (dioxymethylene dimethyl ether + trioxane).

Keywords: Poly(oxymethylene) dimethyl ether; Process design; Hierarchical optimization; Reduced model; Physical property model; fuel additives

1. Introduction

It is well known that diesel engines have revolutionized transportation due to their high thermal efficiency. Environmental and linked regulatory issues have driven the development of low emission diesel engines. Still, even in modern high performance diesel engines, the formation of soot during the combustion remains a problem. Oxygenated compounds (molecules that contain oxygen in their structure) such as methanol or dimethyl ether (DME), are known to reduce soot formation during the combustion, when added to diesel fuels (Natarajan et al., 2001).

Promising oxygenates for the use as diesel fuel additives are poly(oxymethylene) dimethyl ethers (OMEs). In contrast to methanol or DME, their physical properties enable usage in modern diesel engines without significant change of the engine's infrastructure (Burger et al., 2010; Lumpp et al., 2011). OMEs can be produced from the sole feedstock methane, i.e. with gas-to-liquid technology (Burger et al., 2010). We recently proposed a production process for OMEs from the intermediates methylal (dimethoxy methane) and trioxane (Burger et al., 2010; Schelling et al., 2006). Methylal can be produced on a large scale by a pressure-swing process from formaldehyde and methanol (Drunsel, 2012).

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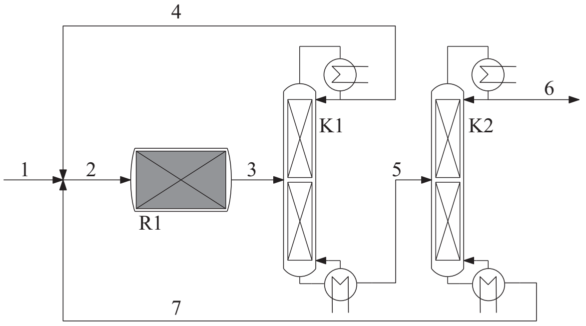

Fig. 1 – Flowsheet of the basic OME process.

The present paper demonstrates the feasibility of the process described in Burger et al. (2010) by simulation and describes the optimization of the process design. The process consists of a fixed bed reactor that contains an acidic catalyst and two distillation columns (cf. Fig. 1). One important characteristic of the OME process design problem is that the product composition is not known a priori. Due to physical properties OMEs of chain length between $n = 3$–5 are preferred (Burger et al., 2010). The optimal ratio of these three components depends on the combustion characteristics, but also on the process technology. From a process engineering standpoint it is desirable to specify the product composition in a way, so that the production costs are minimal. In earlier work (Burger, 2012) we solved this problem of finding the unknown product specification using ∞/∞-analysis (Bekiaris and Morari, 1996; Petlyuk and Aventyan, 1971; Serafimov et al., 1971). To achieve this a reduced model was employed for which a multi-objective optimization problem was solved. That solution also yielded an optimal product specification. The reactor was modeled using a kinetic model derived in our group based on extensive own experiments (Burger et al., 2012; Burger, 2012). The model reduction is based on the assumption of perfectly sharp separations in the distillation columns which, however, respect the boiling sequence.

This reduced representation does not provide any information on process temperatures or pressures. Nothing can be stated about meeting technically feasible operation ranges. Further, the model cannot be used for apparatus sizing or cost estimation. The present work, therefore, extends the reduced model to a more detailed process model that allows the design and optimization of the distillation columns and provides information on energy demands and apparatus sizes, i.e. it allows estimating the CAPEX and OPEX of the process. The optimal design point determined by the reduced model serves as a starting point for optimization using the detailed model. Thus, a hierarchical optimization with varying model depth is carried out here for the OME process.

In the first part of the paper the physico-chemical property model is described which is required for the process simulation. It is based on literature data on thermo-physical properties and reaction data from previous work of our group. This data basis is complemented in the present work by measurements of the density of pure OMEs and the vapor–liquid equilibrium in the system (dioxymethylene dimethyl ether + trioxane). In the second part of the paper an optimization using the detailed process model is described which is based on the design point obtained by the reduced model. In the third part it is shown that the process requires an extension to purge the side-product methyl formate that could not been considered by the reduced model. A flowsheet option for the side-product purge is proposed. Thereby, the optimized process of the detailed model serves as starting point for a final optimization.

2. Chemical model

2.1. *Chemical system*

Poly(oxymethylene) dimethyl ethers (OME_n) have the general structure $H_3C–O–(CH_2–O)_n–CH_3$ and are oligomers of the monomer formaldehyde (FA, structure $O{=}CH_2$). The simplest OME is methylal ($n = 1$, MAL, often also referred as dimethoxy methane or DMM). In neutral environment the OMEs are chemically stable. Up to $n = 6$ they are liquids at ambient conditions.

In the sequel reactions taking place in the liquid phase are described. In acidic environment MAL and OMEs react with monomeric formaldehyde.

$$\mathrm{MAL} + \mathrm{FA} \overset{H^+}{\rightleftharpoons} \mathrm{OME}_2 \tag{Ia}$$

$$\mathrm{OME}_{n-1} + \mathrm{FA} \overset{H^+}{\rightleftharpoons} \mathrm{OME}_n; \quad n > 2 \tag{Ib}$$

Reactions (Ia) and (Ib) are reversible and lead to an equilibrium chain distribution which mainly depends on the overall formaldehyde concentration in the solution (Burger et al., 2010). Increasing the formaldehyde concentration shifts the distribution to longer chains. In this work, formaldehyde is provided by trioxane (TRI, $(CH_2O)_3^{\mathrm{cyc}}$), a cyclic, anhydrous form of formaldehyde. At ambient conditions trioxane is a chemically stable solid. The trioxane breakup is described as the acid-catalyzed, reversible formation of three monomeric formaldehyde segments.

$$\mathrm{TRI} \overset{H^+}{\rightleftharpoons} 3\mathrm{FA} \tag{II}$$

With the catalyst Amberlyst 46, used in the process of the present work, and operation at mild temperatures of about 340 K side-product formation is efficiently suppressed (Burger, 2012). Only methyl formate (MEFO, $HCOOCH_3$) is found in traces after the reaction. This side-product is formed in acidic environment from formaldehyde in a Tischenko reaction (Burger, 2012).

$$2\mathrm{FA} \overset{H^+}{\rightarrow} \mathrm{MEFO} \tag{III}$$

Methyl formate may accumulate through recycles and must be purged from the process. The educt should contain no water to avoid the occurrence of oligomerization reactions in the system (formaldehyde + water) and the triggering of side-reactions forming other products like methanol or DME (Burger et al., 2012; Burger, 2012).

2.2. *Reaction kinetic model*

The reaction kinetic model used in the present work was adopted from previous work in our group (Burger et al., 2012). It is based on comprehensive experimental studies of the OME synthesis from methylal and trioxane in a batch reactor using the catalyst Amberlyst 46. The model is adsorption-based and uses a modified Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach, in that the sorption processes are the rate determining steps. It is formulated on a mole fraction basis