

## Design of Glycerol Etherification Process by Reactive Distillation

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The feasibility of an industrial-scale process for production of glycerol ethers by etherification of glycerol with iso-butene, catalyzed by homogeneous or heterogeneous acid catalyst in a reactive distillation column, is analyzed. Firstly, a conceptual design of the plant is developed containing the reaction section with a kinetic model for the reactive column and a black-box model for separation unit. The influence of *i*-butene excess on reaction selectivity and recycles magnitude is investigated. Analysis of the liquid-liquid equilibrium is used to design the separation section. Finally, a detailed design of the entire plant is performed using AspenPlus.

### 1. Introduction

Directive 2003/30/EC of the European Parliament requires that, by the end of the year 2010, traffic fuels should contain 5.25 % of components produced from renewable sources. In biodiesel production (Dimian and Bildea, 2008), glycerol is produced in amounts equivalent to 10 % wt. of the main product. As a result to the increasing availability, the market price of glycerol has dropped. Therefore, new uses for glycerol need to be found. Di- and tri-ethers of glycerol are compounds soluble in diesel and biodiesel, improving the quality of the fuel (Karinen and Krause, 2006). They diminish the emissions of particulate matter, carbon oxide and carbonyl compounds. Moreover, they decrease the cloud point of the fuel when combined with biodiesel (Noureddini, 2000). Therefore, ethers of glycerol are interesting alternatives to commercial oxygenate additives such as MTBE or TAME.

Ethers of glycerol can be obtained by etherification with alcohols and olefins (Figure 1) such as *i*-butene and *i*-butanol or by trans-etherification with another ether such as methyl-tert-butyl ether (Gupta, 1995; Versteeg et al., 2009).

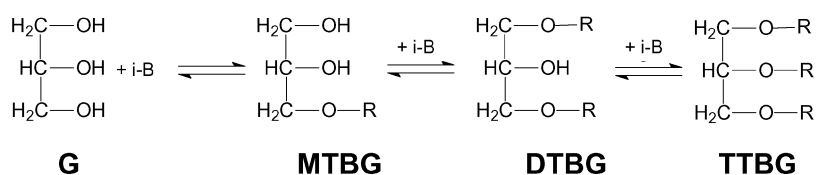


Figure 1: Etherification of glycerol with *i*-butene. *G* – glycerol; *i-B* – *i*-butene; *MTBG* – mono-ether; *DTBG* – di-ether; *TTBG* – tri-ether

Reaction of *i*-butene with glycerol in presence of homogeneous (Behr and Obendorf, 2003) or heterogeneous (Klepacova et al., 2005, 2007; Lee et al., 2010) acid catalysts yields a mono-, di-, and tri-*tert*-butyl glycerol ethers mixture. The processes described in literature which could be used to perform this transformation differ in the way the reaction and products separation are performed. The reaction can be carried on in pressurized reactors operated continuously (Behr and Obendorf, 2003; Vlad et al., 2010) or in batches (Karinen and Krause, 2006; Klepacova et al., 2005, 2007). The separation of products can be achieved by flash, extraction and / or rectification operations.

This paper presents a glycerol etherification process employing reactive distillation (RD). Firstly, the conceptual design is achieved by using a rigorous model of the RD column and a simplified model for the product purification and recycles. Details of the purification are obtained later, after consideration of the liquid-liquid phase equilibrium. Thus, the structure of the flowsheet and the main operating conditions are obtained. Finally, the complete design of the plant is performed.

## 2. Conceptual Process Design

### 2.1 The reactive distillation column

The feasibility of glycerol etherification by reactive distillation is investigated by considering a column fed with 10 kmol/h of glycerol heated at 100 °C and 40 kmol/h of vaporized *i*-butene (Figure 2a). The column has 20 trays and a diameter of 0.3 m. The tray liquid holdup is 10 L. The bottom effluent is fed to a liquid-liquid separator. The column is simulated in AspenPlus (AspenTechnology, 2009). The kinetics is taken from Behr and Obendorf (2003). The vapour-liquid equilibrium is modeled by UNIFAC-Dortmund. The NRTL model with parameters determined by Behr and Obendorf (2003) is used for the liquid-liquid separation. The product stream contains 5.4 kmol/h of MTBG, 3.05 kmol/h of DTBG and 0.2 kmol/h of TTBG. Despite the high conversion of glycerol, recycle is necessary because of the low selectivity in di- and tri-ethers.

Figure 2b presents a conceptual flowsheet where the glycerol and mono-ether are separated and recycled. The behavior of the RD column – separation – recycle system is investigated by sensitivity analysis. The main results are presented in Figure 3.

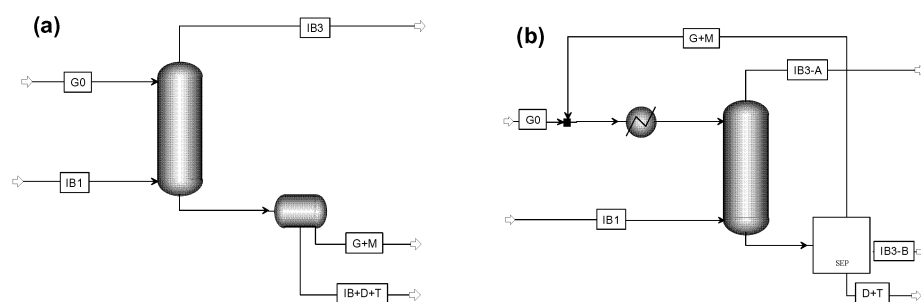


Figure 2: Glycerol etherification by reactive distillation. (a) Single column; (b) RD column – separation - recycle

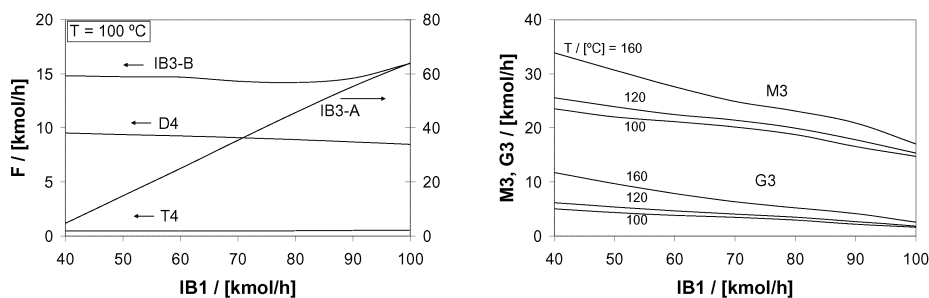


Figure 3: RD column – separation – recycle: Sensitivity with respect i-butene feed rate.

Figure 3 shows the influence of the i-butene feed rate (IB1) on the product and recycle rates. The left diagram indicates that a large excess of i-butene leads to a large recycle, but without improving the di- and tri-ether selectivity. The right diagram shows that a lower temperature of the glycerol feed decreases the amount of mono-ether that is formed. At 100 °C, a limited sensitivity of glycerol and mono-ether recycles (M3, G3) with respect to i-butene excess is observed. Therefore, we opt for a glycerol feed temperature of 100 °C and i-butene feed rate of 40 kmol/h.

## 2.2 Separation section

Depending on the temperature and composition, a mixture of glycerol, i-butene and glycerol ethers can exist in a single or two different liquid phases. Figure 4 analyzes the liquid-liquid equilibrium at 25 °C. Assuming that i-butene can be easily separated by a simple flash, the composition of the RD column bottom stream (Figure 4a, point M+D+G) falls in the single-phase region. This happens because the large amount of mono-ether increases the miscibility of glycerol and di-ether. However the immiscibility can be exploited for separating the reactants from products by mixing, in the L-L separator, the fresh glycerol with the RD column bottom product. The mixture (point L) separates into a glycerol-rich phase (L1) and a DTBG-rich phase (L2). However, the DTBG-rich phase L2 contains significant amounts of MTBG.

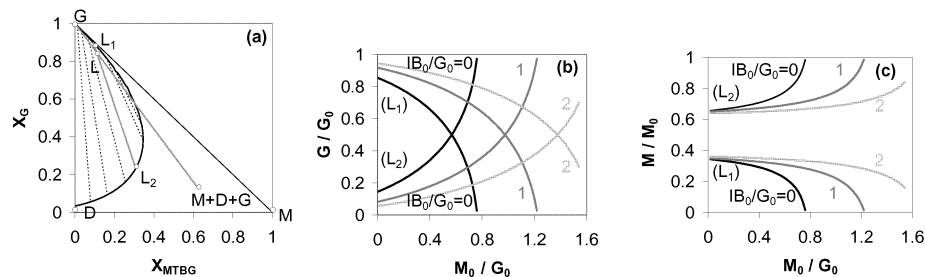


Figure 4: Liquid-liquid equilibrium (a) Liquid-liquid immiscibility occurs when the column bottom stream is mixed with fresh glycerol. (b) and (c) Addition of i-butene improves the separation of glycerol and MTBG from DTBG

Figure 4(b) and Figure 4(c) show the influence of adding *i*-butene to a mixture containing glycerol and DTBG in an equimolar ratio and varying amounts of MTBG. It can be observed that *i*-butene has a favorable effect on the L-L equilibrium because it decreases the solubility of glycerol and MTBG in the DTBG-rich phase. In conclusion, the separation of *i*-butene from the reaction mixture should be done after the liquid-liquid split.

### 3. Detailed Design

#### 3.1 Process description

This section presents the detailed design of the glycerol etherification process. The flowsheeting software ASPEN Plus version V7.0 was used (AspenTechnology, 2009). The physical properties of glycerol and *i*-butene are available in AspenPlus databank. The properties of the ethers were calculated using group contribution methods. The liquid-liquid separation was modeled using NRTL model with interaction parameters of pairs involving ethers and glycerol or *i*-butene taken from the study of Behr and Obendorf (2003). The other unknown interaction parameters were estimated using UNIFAC-Dortmund. Figure 5 presents the flowsheet. In the rest of this section, details concerning the processing units will be given.

The etherification of glycerol with *i*-butene takes place in reactive distillation column with 20 trays and 0.3 m diameter. The column is fed with a mixture of glycerol and recycled mono-ether (stream “G1+M1”) and vapour *i*-butene (“IB1”). The top stream “IB3-A” containing a part of the excess *i*-butene, is recycled to the *i*-butene evaporator. The RD-column bottom product is mixed with fresh glycerol and cooled to 25 °C, when L-L splitting occurs. The stream “G+M”, containing glycerol and MTBG, is recycled. The stream “IB+D+T” containing *i*-butene and high ethers is fed to a flash, where the temperature is increased to 110 °C and the pressure is reduced to 1 bar. The liquid product stream “PROD” is obtained, while the stream “IB3-B” containing *i*-butene is compressed and recycled.

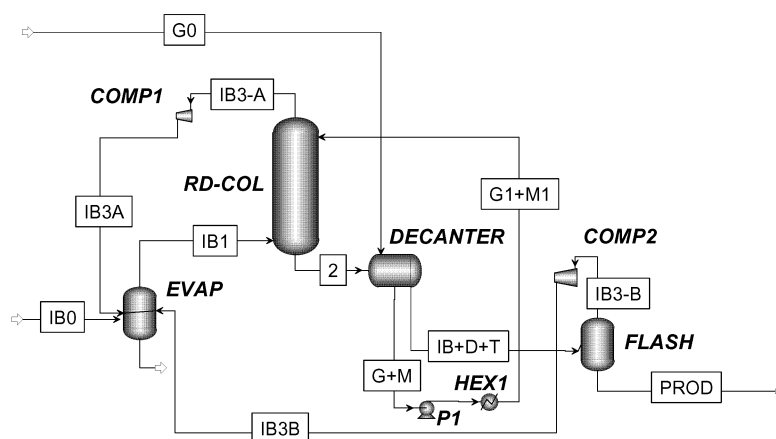


Figure 5: Flowsheet of the glycerol etherification plant

### 3.2 Results

Figure 6 presents the reaction rate and the liquid concentration profiles along the RD column. The reaction mainly takes place in the upper part of the column. MTBG is formed on the first 6 stages, being consumed on the next 4 stages. The maximum DTBG production is observed on stage 7. The reaction rates are also high on the last 3 stages, due to large concentration of i-butene in the liquid phase.

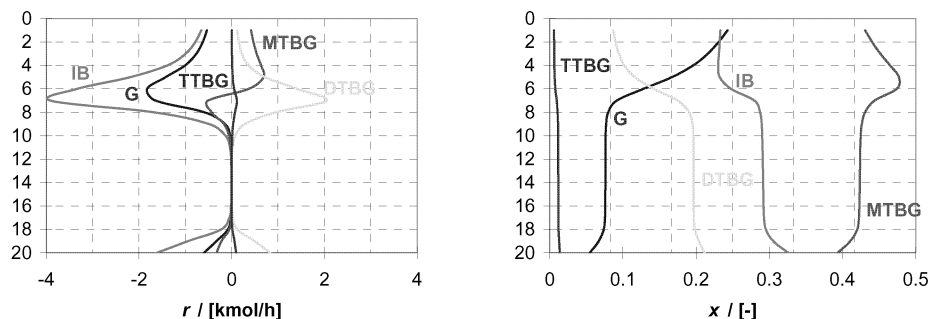


Figure 6: Reaction rate and composition profiles

A detailed stream report is presented in Table 1. The molar ratio between the fresh reactants i-butene / glycerol is 2. The glycerol conversion reaches 80 %. Streams “IB3-A” and “IB3-B” recover 99 % of i-butene. The i-butene recycles are small. Glycerol and MTBG recycle is fairly large because of the sizable amount of MTBG formed during etherification reaction. The product stream “PROD” contains 80 % DTBG, 7 % TTBG, 10 % MTBG and small amounts of glycerol and i-butene. More TTBG could be obtained by working at a higher pressure, allowing for a larger residence time by more trays or larger holdup, or increasing the rate of fresh i-butene. However, this is not necessary because DTBG is a suitable (bio)diesel additive.

Table 1: Stream table

	G0	IB0	IB1	G+M	2	IB3-A	IB+D+T	IB3-B	PROD
Flow rate [kmol/h]	10.00	20.76	40.06	43.98	57.36	8.20	23.38	13.21	10.17
Flow rate [kg/h]	920.9	1164.6	2257.5	5578	7372.8	462.9	2715.5	801.7	1913.8
T / [°C]	90.0	20.0	100.6	25.0	146.3	101.2	25.0	110.0	110.0
P / [bar]	14.00	15.00	15.00	14.00	14.23	14.00	14.00	1.00	1.00
Mass fractions									
G	1	0	$3.8 \times 10^{-5}$	0.211	0.039	$4.9 \times 10^{-5}$	0.012	$3.4 \times 10^{-4}$	0.018
i-B	0	1	0.994	0.054	0.142	0.992	0.276	0.897	0.015
MTBG	0	0	$5.5 \times 10^{-5}$	0.566	0.454	$4.4 \times 10^{-4}$	0.070	$1.5 \times 10^{-3}$	0.099
DTBG	0	0	$4.7810^{-3}$	0.156	0.336	$3.5 \times 10^{-3}$	0.593	0.083	0.807
TTBG	0	0	$9.6 \times 10^{-4}$	0.014	0.028	$3.5 \times 10^{-3}$	0.048	0.018	0.061

#### 4. Conclusions

Production of glycerol ethers by etherification of glycerol with i-butene by reactive distillation, catalyzed by homogeneous or heterogeneous acid catalysts, is feasible. The column is fed with glycerol and i-butene in a molar ratio 1:4. The reactants conversion is high (80 % for glycerol, 50 % for i-butene). The large amount of MTBG formed is recycled together with glycerol, in order to achieve high selectivity in di- and tri-ethers. Separation of MTBG and TTBG (products) from glycerol, MTBG and i-butene (recycled reactants) can be achieved by liquid-liquid split followed by a simple flash. Adding the fresh glycerol directly to the decanter and recovering the excess of i-butene after the liquid-liquid split improves the separation.

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