INTEGRATED DESIGN AND CONTROL OF GLYCEROL ETHERIFICATION PROCESSES

BY

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Abstract. The feasibility of an industrial-scale, acid-catalyzed process for etherification of glycerol with i-butene is analyzed. A simplified mass balance of the process is derived using a kinetic model for the reactor and black-box model for the separation section. Degree of freedom analysis is used to suggest plantwide control structures. Sensitivity analysis of the steady state model shows that the system exhibits both state multiplicity and regions where no solution exists. The nominal operating point is chosen to avoid high sensitivity to disturbances and to guarantee feasibility when operation and design parameters change or are uncertain. Detailed design is performed using AspenPlus. The stability and robustness in operation are checked by rigorous dynamic simulation in AspenDynamics.

Key words: glycerol ethers, process design, process control, nonlinear behavior.

1. Introduction

A recent European Union directive 0 requires that, by the end of the year 2010, traffic fuels should contain 5.25% of components produced from renewables. The amount of glycerol obtained as by-product in biodiesel production is equivalent to about 10% wt. of the total product. As a result to the increasing availability, the market price of glycerol has dropped rapidly. Therefore, new uses for glycerol need to be found. Although glycerol could be burnt as a fuel, it could also be processed into more valuable components.

Di- and tri-ethers of glycerol are compounds soluble in diesel and biodiesel, improving the quality of the fuel 0. 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. Therefore,

ethers of glycerol are interesting alternatives to commercial oxygenate additives such as MTBE, ETBE or TAME. Ethers of glycerol can be obtained by etherification with olefins and alcohols (Fig. 1) such as i-butene and i-butanol or by trans-esterification with another ether such as methyl-tert-butyl ether.
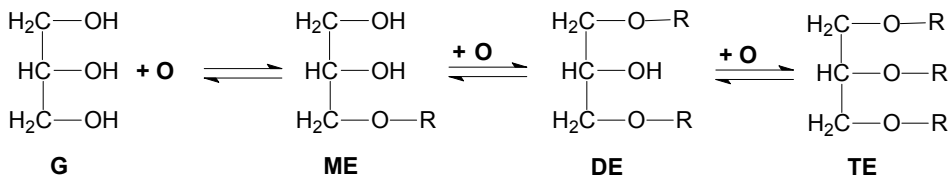

Fig. 1 – Etherification of Glycerol with Olefines. G – glycerol; O – olefin;
ME – mono-ether; DE – di-ether; TE – tri-ether.

Reaction of i-butene with glycerol in presence of homogeneous 0 or heterogeneous 0, 0 acid catalysts yields a mixture of mono-, di-, and tri-tert-butyl glycerol ethers. Conceptual processes which could be used to perform this transformation are described in references 0, 0,…,0.

In this article, we present the detailed design of a glycerol etherification plant processing a nominal flow rate of 2 kmol/h of glycerol, assumed to be the by-product of a 15000 tone/year biodiesel plant. We focus on operating conditions leading to high selectivity in di-ether, 0.9 being a typical value.

2. Mathematical Model

A simplified model of the plant is used to choose a nominal operating point together with the plantwide control structure. Fig. 2 presents the Reactor – Separation – Recycle structure of the plant 0. After the reaction takes place, the reactor effluent enters the Separation section. Here, the di- and tri- ethers are removed from the plant while the glycerol, i-butene and mono-ether are recycled to the reactor, after mixing with fresh reactants.
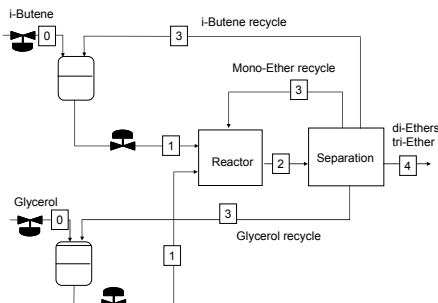

Fig. 2 – Reactor - Separation – Recycle structure of the glycerol etherification plant.

The CSTR is operated at 90ºC. The model of the reactor consists of mass balance equations (1), where the reaction rates are taken from reference 0. Moreover, ideal separation and mixing are assumed.

$$(1) \qquad F_{k,2} - \left(F_{k,1} + V \cdot \sum_{j=1,3} v_{k,j} \cdot r_j \right) = 0 \quad k = G, I, M, D, T$$

The design degrees of freedom represent the variables that must be specified to completely define the process. The control degrees of freedom are the variables that can be manipulated, namely the control valves in the process. For most processes, the number of design degrees of freedom is equal to the number of control degrees of freedom 0. The model of the glycerol etherification plant consists of 23 equations and contains 25 variables (17 flow rates, 5 concentrations and 3 reaction rates). Therefore, 2 degrees of freedom must be fulfilled. This is in agreement with Fig. 2, where two valves must be used for level control, leaving 2 valves available for manipulating flow rates.

3. Steady State Behaviour

The aim of this section is to investigate the steady state behaviour the etherification plant. Three control structures will be considered (Fig. 3). In all control structures the flow rate of fresh glycerol is set to the value $F_{G,0}$. Control structures CS1, CS2 and CS3 differ by the second flow specification: fresh i-butene ($F_{I,0}$), ratio $r_0 = F_{I,0}/F_{G,0}$ and i-butene at reactor inlet ($F_{I,1}$), respectively. For each control structure, the mathematical model is solved using Matlab 0. The conversions of glycerol and i-butene (X_G and X_I, respectively) are plotted versus the flow rate of fresh glycerol ($F_{G,0}$) and conclusion are drawn concerning the sensitivity of the desired operating point when variable flow rates of glycerol must be processed.
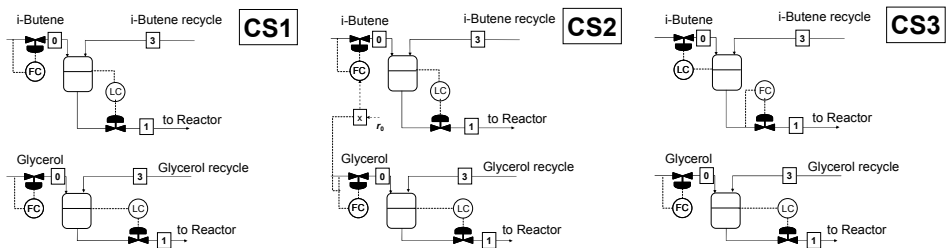

Fig. 3 − Plantwide control structures.

When the control structure CS1 is applied, a closed form solution is available for the product flow rates:

(2)
$$F_{D,4} = 3F_{G,0} - F_{I,0}; \qquad F_{T,4} = F_{I,0} - 2F_{G,0}$$

If follows that, for a fixed value of the fresh i-butene flow rate $F_{I,0}$, the model has a feasible solution (positive flow rates) only for a certain range of the fresh glycerol flow rate $F_{G,0}$.

(3)
$$\frac{F_{I,0}}{3} < F_{G,0}^{\min} < F_{G,0} < F_{G,0}^{\max} = \frac{F_{I,0}}{2}$$

It should be noted that selectivity of the glycerol transformation into di-ether is high when the fresh glycerol flow rate approaches the maximum allowed flow rate $F_{G,0}^{\max}$.

Fig. 4 displays the results obtained when control structure CS1 is applied to two etherification plants employing reactors of volume 1 m³ and 4 m³, respectively. When the flow rate $F_{G,0}$ is set to the upper limit $F_{G,0}^{\max}$, only di-ether is obtained as product. However, both glycerol and i-butene conversions approach zero and the recycle rates become infinite. This limit is independent of the reactor volume. The lower admissible value $F_{G,0}^{\min}$ approaches the theoretical value $F_{I,0}/3$ when the reactor volume V approaches infinity.
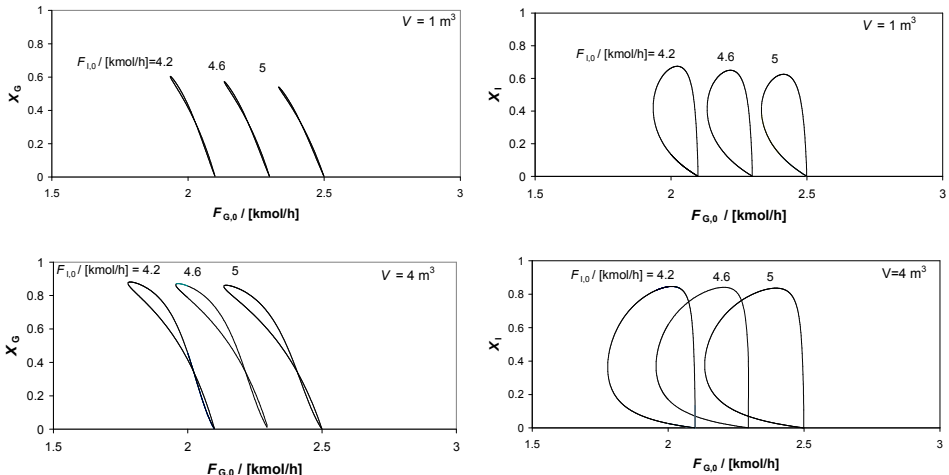

Fig. 4 – Control structure CS1: glycerol and i-butene conversions *vs.* fresh glycerol flow rate, for different values of the fresh i-butene flow rate and reactor volume.

Fig. 4 shows that, for given values of the model parameters, either zero or two steady states are possible. When they exist, the two states are characterized by similar values for the glycerol conversion, but very different values for the conversion of i-butene. Moreover, a very high sensitivity of the i-butene conversion with respect to glycerol flow rate is observed when high selectivity in di-ether is required ($F_{G,0}$ close to $F_{G,0}^{max}$). This implies that small disturbances will lead to large changes of the i-butene recycle rate, known as the "snowball effect" 0, 0. In conclusion, control structure CS1 offers the advantage of easily setting the ratio between the di- and tri-ethers by manipulating the reactants flow rates. However, the operating points of high di-ether selectivity exhibits high sensitivity to disturbances and are dangerously close to the feasibility limit $F_{G,0}^{max}$.

Fig. 5 presents the conversions versus the fresh glycerol flow rate, for different reactor volumes, when control structure CS2 is used. The system exhibits multiple steady states and a region of unfeasibility. On the two solution branches, the values of glycerol conversion are very close to each other. The two steady states extend to zero glycerol flow rate. Compared to control structure CS1, much larger glycerol flow rates can be processed. The same selectivity in di-ether, namely $\sigma_{D/G} = 3 - F_{I,0}/F_{G,0} = 0.9$ is obtained at all operating points depicted in Fig. 5. It appears that the 1 m^3 reactor allows increasing the amount of processed glycerol by 50%.
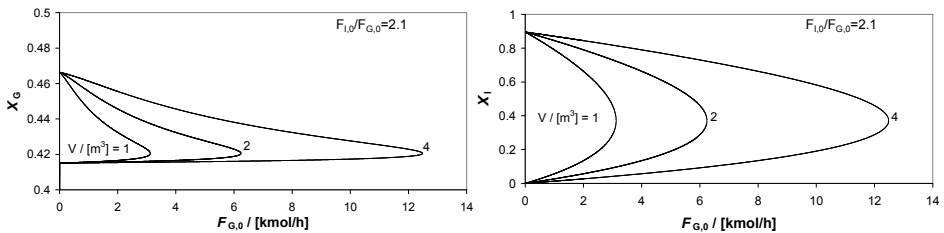

Fig. 5 – Control structure CS2: glycerol and i-butene conversions *vs.* fresh glycerol flow rate, for different values of the reactor volume.

Fig. 6 presents results obtained when the control structure CS3 is used. Again, irrespective of the reactor volume and of the fixed value for the i-butene flow rate at reactor inlet, multiple steady states exist. The high-selectivity operating points are located near the turning points of the conversion – flow rate diagram and, therefore, are dangerously close to the region of unfeasibility. Moreover, a direct relationship between the flow rate $F_{I,1}$ and the selectivity $\sigma_{D/G}$ does not exist. We conclude that control structure CS3 appears to be unsuitable.
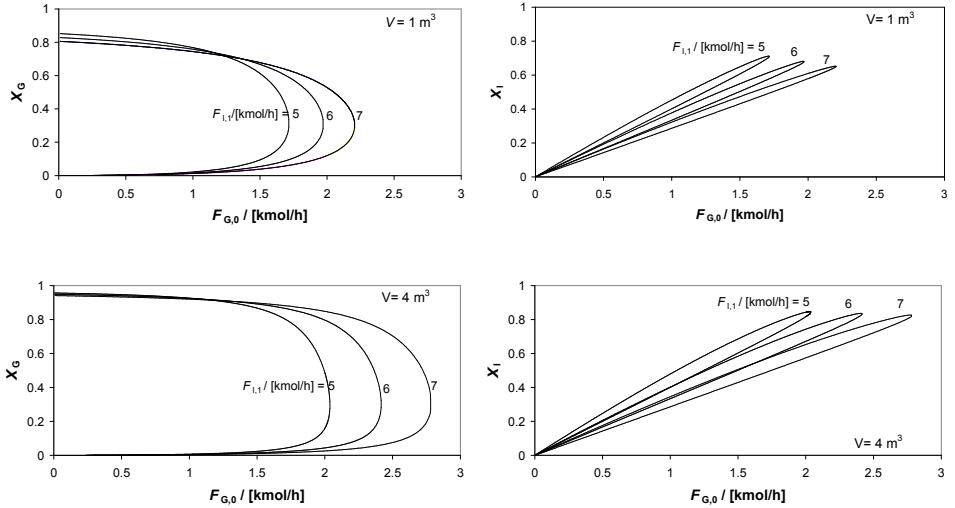
Fig. 6 – Control structure CS3: glycerol and i-butene conversions *vs*. fresh glycerol flow
rate, for different values of the reactor-inlet i-butene flow rate and reactor volume.

4. Detailed Design

This section presents the detailed design of glycerol etherification
process. The flowsheeting software ASPEN Plus version V7.0 0 was used as a
computer aided process engineering tool. Fig. 7 presents the flowsheet. A
detailed stream report is presented in Table 1. In the rest of this section, details
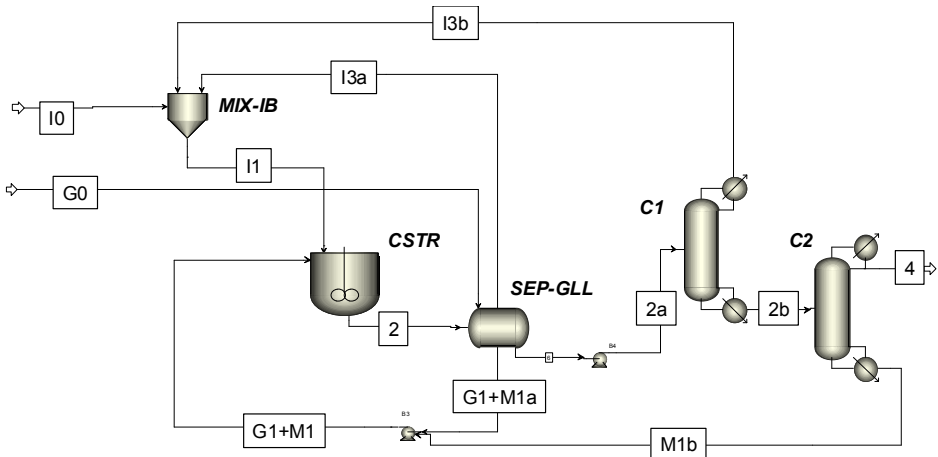concerning the processing units will be given.

Fig. 7 – Flowsheet of the glycerol etherification plant.

Table 1

Stream Report

	G0	I0	I1	G1+M1	2	I3a	G1+M1a	2a	4	I3b	2b	M1b
Flow, [kmol/hr]	2.057	4.063	6.333	8.284	10.55	0.247	7.940	4.429	2.061	2.023	2.406	0.345
Flow, [kg/hr]	189.4	228	355.347	971.8	1327.2	13.876	920.3	582.5	417.4	113.5	469.0	51.6
Temp., [ºC]	90.0	20.0	62.919	61.567	90.0	50.0	50.0	50.0	165.2	−6.6	243.1	244.2
Pressure, [bar]	14.0	14.0	14.0	14.0	14.0	1.0	1.0	1.0	0.2	1.0	1.12	0.73
Vapor Fraction	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0	0.0
Flow, [kmol/hr]												
Glycerol	2.057	0.0	0.0	4.625	2.701	0.0	4.625	0.133	0.133	0.0	0.133	0.0
i-Butene	0.0	4.063	6.333	0.265	2.539	0.247	0.265	2.027	0.004	2.023	0.004	0.0
MTBG	0.0	0.0	0.0	2.947	2.947	0.0	2.611	0.336	0.000	0.0	0.336	0.336
DTBG	0.0	0.0	0.0	0.394	2.106	0.0	0.385	1.721	1.712	0.0	1.721	0.009
TTBG	0.0	0.0	0.0	0.053	0.265	0.0	0.053	0.212	0.212	0.0	0.212	0.0
WATER	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

The physical properties of glycerol, i-butene and water are available in AspenPlus databank. The properties of the ethers were calculated using group contribution methods. The behaviour of the liquid phase was described by the NRTL activity model. The interaction parameters of pairs involving ethers and glycerol or i-butene were taken from 0. The other unknown interaction parameters were estimated using UNIFAC. Ideal mixing was assumed.

Glycerol etherification. The etherification of glycerol with i-butene takes place in a CSTR of 1 m^3. The reaction temperature and pressure are set to 90ºC and 14 bar, respectively, when the reaction mixture is liquid. When the same reactor-inlet flow rates were specified to Matlab and Aspen models, identical results for the reactor-outlet stream were obtained.

G-L-L separation. 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. The composition of the reactor-outlet stream falls in the single-phase region. In order to exploit the immiscibility for separating the reactants from products, the fresh glycerol is fed in the G-L-L separator. The temperature is reduced to 50ºC and the pressure is set to 1 bar. The cooling duty is 27.8 kW. 10% of i-butene is found in the vapour stream "I3a" and recycled. The stream "G1+M1a" contains glycerol and mono-ether and is recycled. The liquid stream "2a" contains i-butene and ethers.

Column C1 separates the i-butene. It has 9 theoretical stages with the feed on stage 3. The column has a partial condenser and is operated at atmospheric pressure. The column diameter is 0.2 m. The reflux ratio is set to 2. The reboiler duty is 79.6 kW and the condenser duty is 25 kW. The entire amount of i-butene is recovered in stream "I3b".

Column C2 separates di- and tri-ether from mono-ether. It has 50 theoretical stages with the feed on stage 25. The column has a total condenser and is operated under vacuum to avoid high temperature in the bottom of the column. The column diameter is 0.8 m. The reflux ratio is set to 4. The reboiler duty is 191 kW and the condenser duty is 209 kW. Stream "M1b" contains 97% mole fraction mono-ether and some of di-ether. Stream "4" contains 83% di-ether and 10.2% tri-ether (mole fractions).

5. Dynamics and Control

From the viewpoint of steady state behaviour, the design performed in the previous sections together with control structure CS2 allow processing the nominal flow rate of glycerol and tolerate rather large disturbances. However, the analysis showed two co-existing steady states, which cannot be simultaneously stable. Moreover, the simplified model used in previous section assumed perfect separation of the products from the un-consumed reactants, which certainly is not the case. Therefore, the dynamics of the plant must be considered in order to prove the stability of the operating point and the resiliency with respect to disturbances. To reach this goal, a dynamic model of the plant was built in AspenDynamics. Besides the control loops of CS2, standard control of the G-L-L separator and distillation columns was used. The controllers were tuned by a simple version of the direct synthesis method 0.
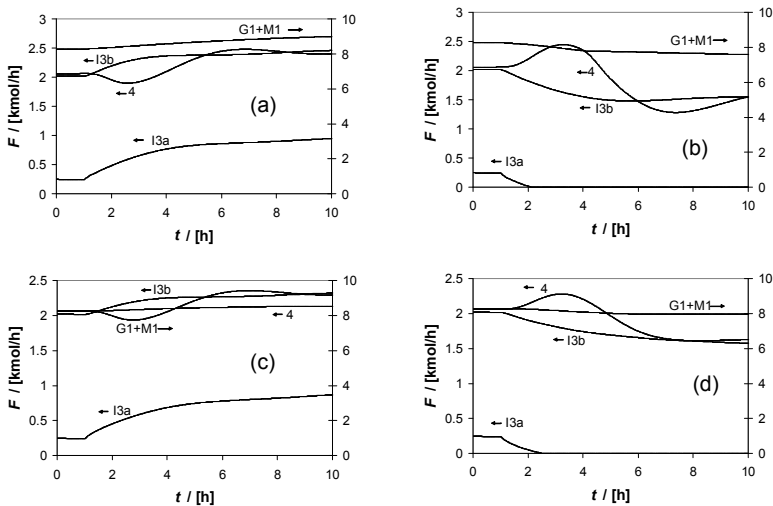

Fig. 8 – Dynamic simulation results.

Fig. 8 presents results of dynamic simulation. Starting from the steady state, several disturbances were introduced at time = 1 h: in simulations a) and

b), the glycerol flow rate was changed from 2 kmol/h to 2.2 kmol/h and 1.8 kmol/h, respectively. In simulations c) and d) the ratio between reactants was changed from the nominal value of 1.2 kg/kg to 1.3 kg/kg and 1.1 kg/kg, respectively. It can be seen that the nominal operating point is stable, and the plant achieves stable operation when disturbances are introduced.

6. Conclusions

Production of glycerol ethers by etherification of glycerol with i-butene catalyzed by homogeneous acid catalysts, such as p-toluene sulfonic acid, is feasible. For a typical glycerol flow rate of 2 kmol/h, the reaction can be carried on in a CSTR of 1 m^3. The reactants conversion is high and small recycles are needed. The separation products - unconsumed reactants can be achieved by a combination of a 3-phase flash and two distillation columns.

When one of the control structures considered in this work is applied, multiple steady states are possible and the flow rate of glycerol that can be processed is limited. For this reason, the behaviour of the plant was investigated by steady state sensitivity analysis. This allowed selecting a robust control structure.

Finally, rigorous dynamic simulation was performed in order to prove that the chosen control structure ensure stable operation when operation and design parameters change or are uncertain.

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INTEGRAREA PROIECTĂRII ŞI REGLĂRII PROCESULUI
DE ETERIFICARE A GLICERINEI

(Rezumat)

Fezabilitatea unui proces industrial de eterificare a glicerinei cu i-butenă, în cataliză omogenă acidă, este investigată. Un model simplificat al bilanţului de masă al procesului este dedus folosind un model cinetic pentru reactor, secţia de separare fiind descrisă printr-un model de tip cutie-neagră. Analiza gradelor de libertate este folosită pentru a dezvolta structuri de reglare a instalaţiei. Analiza de senzitivitate a modelului de regim staţionar arată că sistemul prezintă stări multiple şi regiuni în care nu există soluţii. Punctul nominal de operare este ales astfel încât senzitivitatea faţă de perturbaţii să fie evitată. În plus, fezabilitatea este garantată chiar dacă parametrii de operare se modifică sau sunt incerţi. Proiectarea detaliată a instalaţiei este efectuată folosind AspenPlus. Stabilitatea şi robusteţea în operare sunt verificate prin simulare dinamică riguroasă în AspenDynamics.