



Reactive Distillation - a Viable Solution for Etherification of Glycerol with *tert*-Butyl Alcohol

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Two different alternatives for etherification of glycerol (G) with *tert*-butyl alcohol (TBA) are developed and analyzed. The conventional reaction - separation - recycle system uses a plug-flow reactor to perform the reaction in liquid phase, in the presence of a heterogeneous catalyst (Amberlyst 15). The separation of the products from reactants is achieved by two distillation columns where pure glycerol ethers (GTBE) are obtained, and a section involving extractive distillation with 1,4-butanediol as solvent, which separates TBA from the TBA/water azeotrope. Due to large number of units involved, the total annual cost (TAC) is very high. The second alternative employs a reactive distillation column, where TBA is fed as vapour below the reactive zone, while glycerol enters as liquid above the reactive zone. High purity water and glycerol ethers are obtained as distillate and bottoms, respectively. Because multiple steady states are detected, sensitivity analysis is used to choose a safe operating point. Finally, the controllability of reactive distillation setup is proved by dynamic simulation.

1. Introduction

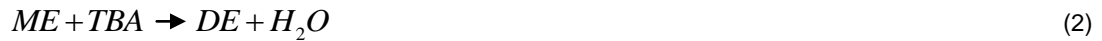
Large amounts of glycerol are obtained as by-product of biodiesel production. Due to the increasing availability, the market price of glycerol has dropped rapidly. Therefore, transformation of glycerol into more valuable components has an important role in the economic efficiency of biodiesel processes.

Di- and tri-ethers of glycerol are interesting alternatives to commercial oxygenate fuel additives, because they diminish the emissions and decrease the cloud point. Ethers of glycerol can be obtained by etherification with alcohols and olefins such as *i*-butene and *tert*-butyl alcohol or by transesterification with another ester such as methyl-*t*-butyl ether.

Reaction of *i*-butene with glycerol in presence of homogeneous or heterogeneous acid catalysts yields a mixture of glycerol ethers. Conceptual processes which could be used to perform this transformation are described by Behr and Obendorf (2003), Versteeg et al. (2009), Gupta (1995) and Nouredini (2000).

All these processes require a nearby source of high-purity isobutene, in order to avoid large transportation costs. The high pressure (14 bar) at which the reaction takes place, necessary for keeping the *i*-butene in liquid phase, is another drawback of the process. Moreover, from the separation section, *i*-butene is obtained as a vapour stream and must be re-compressed before being recycled.

As an alternative, the etherification reaction can be performed at lower pressure using *tert*-butyl alcohol as reactant (Klepáčová et al., 2005, 2006) and ion exchange resins (Amberlyst 15) as catalyst. The equilibrium reactions lead to a mixture of mono-, di-, and tri-*tert*-butyl glycerol ethers (ME, DE, TE). Small amounts of *i*-butene (IB) are obtained in a secondary reaction:



An autoclave reactor (Kiatkittipong et al., 2011) was used to develop several kinetic models of the glycerol - TBA etherification. Then, feasibility of performing the reaction in a reactive distillation column was proved. However, the distillate stream contained a mixture of water and TBA, while the bottom stream consisted of TBA, glycerol, and mono-, di- and tri-ether. Therefore, separation of reactants and products from the column-outlet streams was still necessary.

In this contribution, two different alternatives for etherification of glycerol with *tert*-butyl alcohol are developed and analyzed: a conventional reaction - separation - recycle (RSR) system and by reactive distillation. Although high purity ethers can be obtained in the RSR system while efficiently using the raw materials, the large number of distillation columns necessary for products/reactants separation leads in a very large Total Annual Cost of the plant. In contrast, reactive distillation delivers similar performance at a much smaller cost. The reactive distillation column is controllable, as proved by dynamic simulation.

2. Reaction - Separation - Recycle

The process proposed performs the reaction between glycerol and TBA in liquid phase, in a plug flow reactor, in the presence of a heterogeneous catalyst (Amberlyst 15). Figure 1 presents the flowsheet. A selection of stream results for 2.25 kmol/h GTBE plant is presented in Table 1.

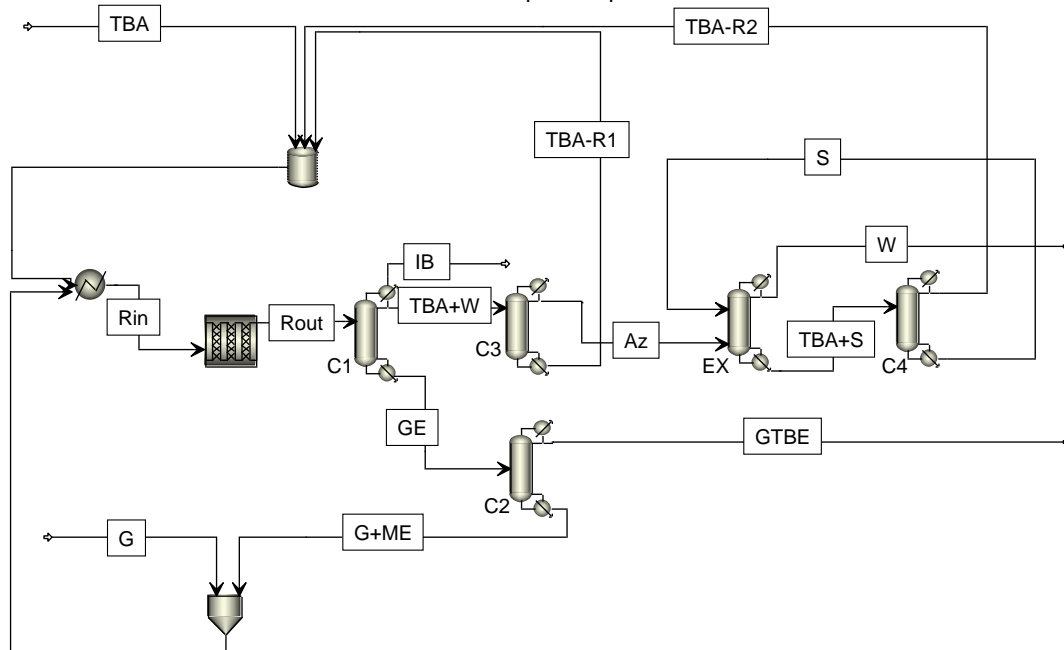


Figure 1: Etherification of glycerol with TBA by Reaction - Separation- Recycle

The fresh reactants are mixed with the recycle streams and sent to the reactor. From the reactor effluent, the first distillation column (C1, 6 trays, reflux ratio 0.32, reboiler duty $Q_W = 517$ kW) separates the water, TBA and IB from glycerol and ethers. The di-ether is obtained, together with small amounts of tri-ether, as the distillate of column C2 (15 trays, reflux ratio 3.2, $Q_W = 189$ kW). The bottom stream containing mostly glycerol and mono-ether is recycled. Distillation column C3 (40 trays, reflux ratio 4, $Q_W = 615$ kW) delivers TBA and TBA-water azeotrope, which is further separated by extractive distillation using 1,4 butanediol as solvent (columns EX, 30 trays, $Q_W = 469$ kW and C4, 7 trays, $Q_W = 344$ kW).

The capital cost includes the costs of reactor, distillation columns, trays and heat exchangers. The energy cost includes the costs of cooling water and steam.

$$TAC = \frac{\text{capital cost}}{\text{payback period}} + \text{energy cost} \quad (5)$$

For a payback period of 3 years, the total annual cost of the plant of 2.25 kmol/h capacity is $TAC = 1.954 \times 10^3$ USD, from which 1.178×10^3 USD is the energy cost.

Table 1: Stream table for etherification of glycerol with TBA by reaction - separation - recycle

Stream name	G	TBA	Rin	Rout	G+ME	GTBE	W	TBA-R1	TBA-R2
Flow / [kmol / h]	2.25	4.84	39.13	39.18	3.04	2.25	3.55	12.03	6.08
Flow / [kg / h]	207.2	358.7	3139.6	3139.6	424.2	457.03	65.72	841	445.8
Temp. / [°C]	20	20	70	70	185.1	136.7	45	81.2	82.1
Pressure / [bar]	1	1	5	5	0.1	0.1	1	1	1
Flow / [kmol / h]									
G	2.25	4.84	2.73	0.49	0.486	0.0015	0	0	0
TBA	0	0	33.83	29.3	Trace	0.006	0.029	11.13	5.93
IB	0	0	Trace	0.05	0	0	0	0	0
ME	0	0	2.54	2.54	2.537	0.0025	Trace	0	0
DE	0	0	0.011	2.25	0.011	2.226	0	0	0
TE	0	0	Trace	0.004	Trace	0.004	0	0	0
Water	0	0	Trace	4.54	Trace	0.0045	3.52	0.9	0.1

In conclusion, glycerol etherification in a conventional reaction - separation - recycle system is economically un-attractive due costly separation of the water - TBA azeotrope. In the following section we will show that reactive distillation is a viable alternative.

3. Reactive distillation

3.1 Design

Figure 2 (left) shows the reactive distillation column performing the etherification of glycerol with TBA. The column has a diameter of 0.3 m and 30 trays. There are 10 reactive stages, each having a holdup of 40 L (40 kg of catalyst). The column is fed with 2.25 kmol/h of glycerol heated at 150 °C and with 4.51 kmol/h of vapor TBA. The reboiler duty is 93.4 kW, while are 86 kW are necessary for reactant pre-heating. The top product contains water and small amounts of GTBE and TBA. A fraction of the condensate is recycled (reflux ratio = 0.5). The rest is sent to a liquid-liquid separator, where the organic phase is recycled and the aqueous phase is removed as product. The bottom product contains DE with small amounts of TE and traces of glycerol. The right diagrams present temperature, reaction rate and the liquid concentration profiles along the RD column, obtained from simulation in AspenPlus. The reaction takes place in the reactive part of the column (trays 10 to 20), where GTBE are formed. The maximum concentration of GTBE and water are observed on stage 30 and 1.

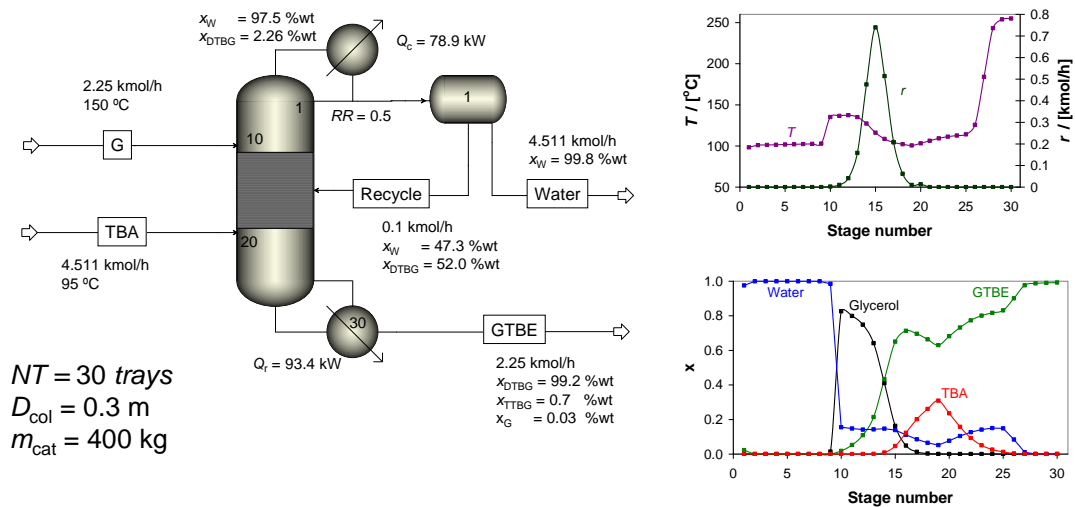


Figure 2: Etherification of glycerol with TBA by reactive distillation. Flowsheet (left) and temperature, reaction rate and liquid mass fraction profiles (right).

Figure 3 (left) presents the influence of reflux ratio (RR) on the product purity, for different values of the TBA / glycerol feed rate. Although higher purity can be achieved at reflux ratios around $RR = 0.35$, multiple steady states exist in this region, which could lead to operating difficulties. Therefore, the reflux ratio was set to $RR = 0.5$, for which a single steady state exists. A small excess of TBA is necessary for high purity of the GTBE product. The right diagram shows the influence of the amount of catalyst on each tray. As expected, higher purity is obtained when more catalyst is used. Above 40 kg/tray, the amount of catalyst has a small influence on product purity.

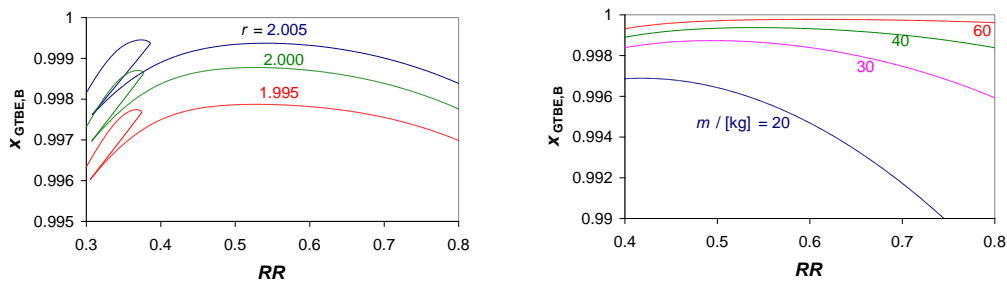


Figure 3: Etherification of glycerol with TBA by reactive distillation. Mass fraction of GTBE in product versus the reflux ratio, for different TBA : glycerol ratio (left) and amount of catalyst on each reactive stage (right).

3.2 Dynamics and control

Figure 4 shows the control of the reactive distillation column. The pressure and levels are controlled by conventional loops. The reflux ratio is kept constant at the design value. The reboiler duty is ratioed to the glycerol feed rate. Sensitivity analysis (Figure 3) shows that feeding the reactants in the stoichiometric ratio is necessary to ensure high product purity. However, a simple feed-forward scheme would not work because of unavoidable measurement and implementation errors (Al-Arfaj and Luyben, 2000). Therefore, concentration controller XC provides the necessary feedback.

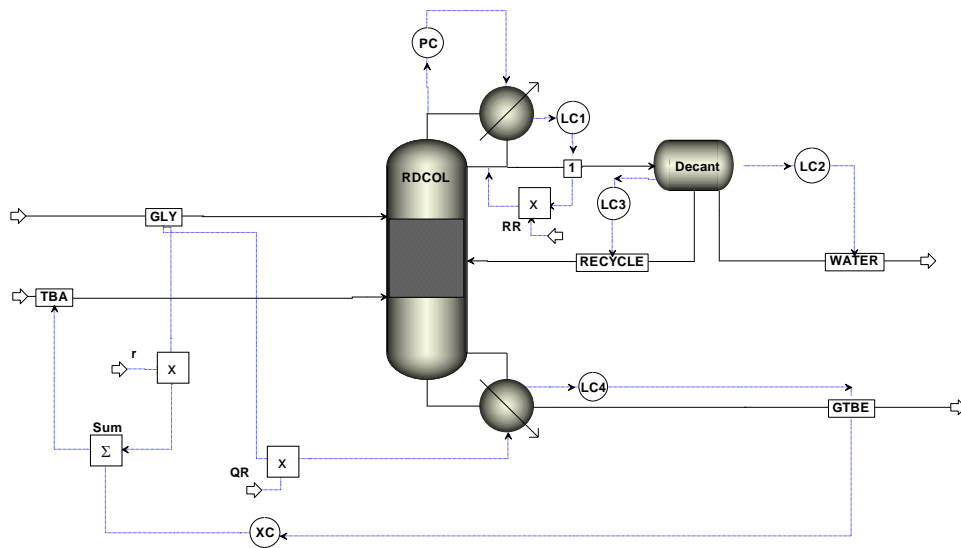


Figure 4: Control structure of glycerol etherification process by reactive distillation.

Figure 5 presents the results of dynamic simulation. The simulation starts from the nominal steady state, which is maintained for the first hour. Then, a disturbance in column feed was introduced: at time $t = 1$ h, the glycerol feed rate was increased from 2.25 kmol/h to 2.5 kmol/h (left). The TBA flow rate is adjusted to the required stoichiometric ratio. Consequently, the GTBE flow rate increases, while the products purity remains constant. A new steady state is established in about 1 hour. The right diagrams show the effect of a $\pm 10\%$ error in glycerol flow rate measurement occurring at time $t = 1$ h and $t = 10$ h, respectively. Small fluctuations on GTBE and TBA flow rates and on products purity are observed. However, the purity of GTBE remains high and the degradation of water purity is very small.

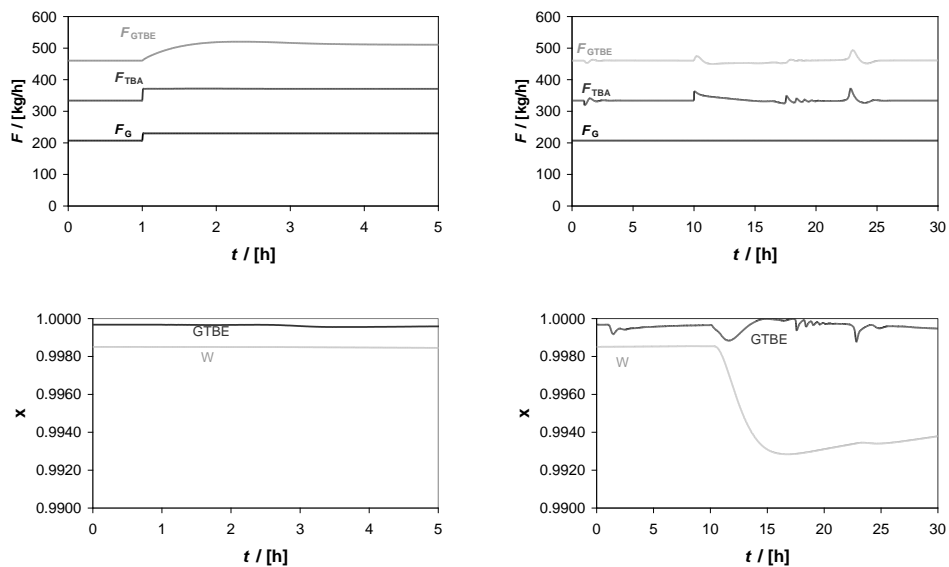


Figure 5: Dynamic simulation results. Feed and product flow rates and product purity (mass fraction) for 10% increase of the production rate (left) and glycerol flow rate inaccuracy (right).

4. Conclusions

Etherification of glycerol with tert-butyl alcohol in a conventional reaction - separation - recycle system, using a catalytic plug-flow reactor, is feasible. However, due to large number of units required for product separation, the total annual cost of the plant is very high (TAC = 1954×10^3 USD/y, from which $1,178 \times 10^3$ USD/y utilities). The alternative of reactive distillation column allows obtaining high purity glycerol ethers and water, at a greatly reduced cost (TAC = 116×10^3 USD/year, utilities cost = 33×10^3 USD/y). The reactive distillation shows multiple steady states, which should be avoided for safe operation. The reactive distillation alternative is well controllable, as proved by rigorous dynamic simulation.

Acknowledgement

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