

A Novel Process Design for Biobutanol Purification from ABE Fermentation

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The decrease in the oil supply and increasing environmental concerns boost the demand for alternative biofuels. In this context, biobutanol production from acetone-butanol-ethanol (ABE) fermentation comes forward as a remarkable process alternative. The main drawback of this alternative is the production of dilute fermentation broth which results in very energy demanding separation steps. Thus, several hybrid separation techniques have been studied combining extraction and distillation technologies to develop energy efficient separation processes. However, these techniques bring their own disadvantages, while they are solving the well-known drawbacks. In this study, a novel process including reactive distillation columns is proposed to purify biobutanol from acetone-butanol-ethanol (ABE) fermentation. The results indicate that there is a significant decrease in the reboiler heat duties. In addition, a co-product (ethylene glycol) is obtained as the result of the reaction taking place in the process besides the purification of butanol, ethanol and acetone.

1. Introduction

There is an increasing interest to biofuels because of the problems related to economic and environmental concerns like global warming and climate change. Although bioethanol is currently the most used biofuel, biobutanol has several advantages over bioethanol such as higher energy content, lower volatility, less flammability, and the possibility of blending it with gasoline in any percentage without any engine modification. Because of all these properties, biobutanol production based on ABE fermentation is considered as a prominent process alternative (Ezedi et al., 2007).

However, ABE fermentation has an important disadvantage in terms of engineering; butanol toxicity to microorganisms results in a dilute product with a very low concentration. Thus, biobutanol production with desired purity requires very energy intensive separation and purification steps. Besides, the presence of azeotropes in the mixture (homogeneous ethanol-water and heterogeneous butanol-water) makes the separation more difficult.

For this reason, development of energy efficient separation processes for biobutanol comes into question. Although there are several techniques suggested in the literature such as gas stripping, liquid-liquid extraction, reverse osmosis, adsorption, perstraction and pervaporation (Abdehagh et al., 2014, Kujawska et al., 2015), most of the recent studies focus on hybrid separation technologies. Among them, processes consisting of extraction and distillation are the most widely used methods in case of large scale production of biobutanol.

Kraemer et al. (2011) suggested a hybrid extraction-distillation process using mesitylene as the solvent. Another study suggested by van der Merwe et al. (2013) includes centrifugation, liquid-liquid extraction (with 2-ethyl-1-hexanol as extractant agent) and steam stripping distillation columns. Sanchez-Ramirez et al. (2015) compared different process flowsheets where one of them is consisted of a liquid-liquid extraction (using hexyl acetate as extractant agent) column followed by steam stripping distillation columns. Results of these studies showed that the total annualized cost of the suggested processes is considerably lower than the cost of pure distillation processes. Errico et al. (2016) compared thermally coupled or thermodynamic equivalent configurations of these hybrid processes, and suggested that the flowsheet including two thermal couplings improves the total annual cost and eco-indicator as objective functions of the problem.

However, this hybrid extraction-distillation process still presents relatively high energy cost, since the large content of water should be removed from the process and the solvent used in the system should be

recovered. Thus, recently, a new process based on the combination of a decanter and a distillation sequence is proposed in the literature (Patraşcu et al., 2017). However, this process has a big drawback, since it includes large recycle streams with azeotropic mixtures which increase the capital and operating costs. The aim of this study is designing a novel biobutanol separation process including reactive distillation columns to achieve economically efficient biobutanol from fermentation broth. In the reactive distillation columns, ethylene oxide reacts with water to produce ethylene glycol. Thus, the consumption of water in the reaction results in a serious reduction in the amount of water which should be removed from the process or recycled in the system. In addition, removal of water by the reaction breaks the azeotropes, which helps biobutanol to be purified without any need for separation agents and recycle streams. Also, high purity ethylene glycol is produced as a co-product besides the main products of the process.

2. Problem statement

Figure 1 illustrates the flowsheet of the recently suggested decanter-distillation process. Decanter is the first unit of the process where butanol rich organic phase is separated from the aqueous phase rich in water. Organic phase is fed to the first stripping column to separate butanol as bottoms product, while the water rich top stream is recycled to the decanter. Aqueous phase is first fed to a stripping column to remove a large amount of water from the system. Top stream of this column is fed to a distillation column where acetone-ethanol rich mixture is taken from the distillate stream, while the bottoms stream including mainly butanol-water mixture is recycled back to the decanter. Finally, the distillate stream is fed to the fourth distillation column to separate ethanol and acetone.

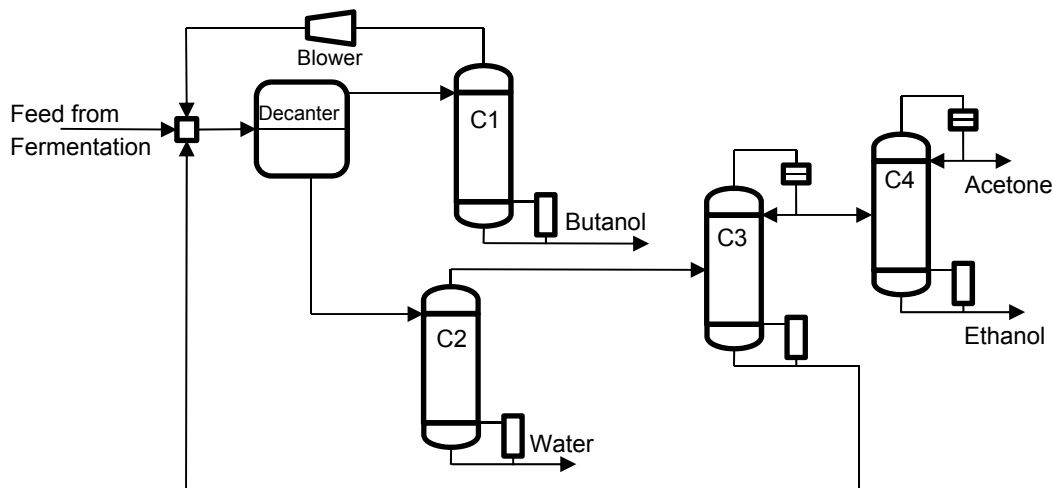


Figure 1: Flowsheet of the decanter-distillation process in the literature (Patraşcu et al., 2017)

The design parameters of the configuration given in the literature are reported in Table 1. Because of the recycle streams mixed with fresh feed stream, a large amount of liquid, mainly water, cycles in the process, and this results in an increase in the equipment sizing (diameter) and energy requirements.

Table 1: Design parameters of the decanter-distillation process in the literature (Patruşcu et al., 2017)

	C1	C2	C3	C4
Number of stages	37	8	24	30
Feed stage locations	1	1	19	25
Pressure (atm)	1	1	1	1
Reflux ratio (molar)	-	-	14.18	12.56
Diameter (m)	1.3	1.3	1.4	1.3
Reboiler duty (kW)	2527	5459	1001	2409
Total duty (kW)	11396			

3. Process studied

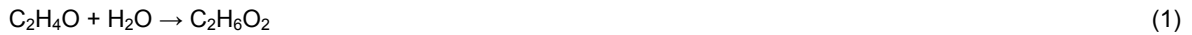
A fermentation broth with a flowrate of 26945 kg/h, which corresponds to a plant capacity of 40 ktpy butanol, is fed to the process. Feed properties are given in Table 2. Products are obtained with purities of 99.5 mole% butanol, 99.5 mole% ethanol and 98.5 mole% acetone. The steady-state simulations have been performed by

the process simulator Aspen Plus. The NRTL method that is most suitable for the components and process conditions is chosen as property model. The binary interaction parameters for this property model are present in the component databank of the simulator. Reactive distillation columns are designed using the rigorous RadFrac model in Aspen Plus. The conventional distillation columns are designed starting with DSTWU shortcut model, and then using rigorous RadFrac model.

Table 2: Properties of feed stream

Components	Mass fraction
Acetone	0.045
Butanol	0.185
Ethanol	0.010
Water	0.760

Figure 2 shows the novel process proposed in this study to overcome the drawbacks of the process given in the literature. Fresh feed is the only stream fed to the decanter. The butanol rich organic phase (including a significant amount of water) of the decanter is fed to a reactive distillation column. The second feed stream of the reactive distillation consists of ethylene oxide. Water and ethylene oxide reacts irreversibly to produce high purity ethylene glycol. The kinetic data for the uncatalyzed reaction is obtained from Tavan and Hosseini (2013),



$$r(\text{kmol m}^{-3} \text{ s}^{-1}) = 3.15 \times 10^{12} \exp[-9547/T] X_{\text{EO}} X_{\text{Water}} \quad (2)$$

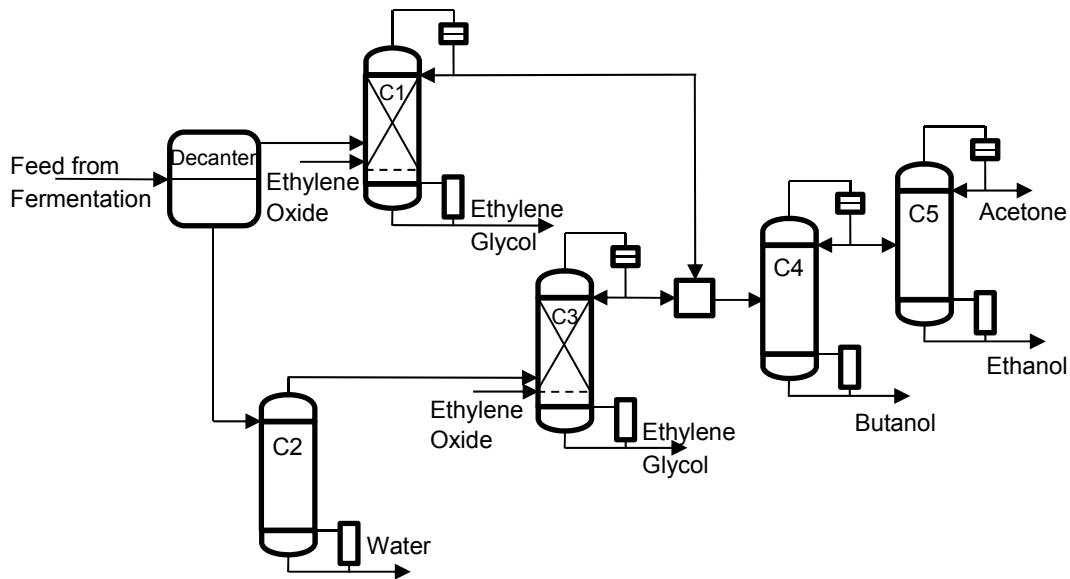


Figure 2: Flowsheet of the novel process

Ethylene glycol is removed from the bottoms of column while the acetone-butanol-ethanol mixture leaves the column from the distillate. Aqueous phase is first fed to a stripping column to remove some of the water from the system. Top stream of this column is fed to another reactive distillation column where the second feed is the ethylene oxide. The same reaction occurs in this column, and ethylene glycol, the product of the reaction, is taken from the bottoms of the column. The top stream including mainly acetone-butanol-ethanol mixture is mixed with the top stream of the first reactive distillation column, and fed to a distillation column to separate butanol from the bottoms with a desired purity. Acetone-ethanol mixture including a small amount of unconverted ethylene oxide and water leaves the column from the distillate, and fed to the final distillation column to separate acetone and ethanol from the top and bottoms, respectively.

4. Results and discussion

4.1 Effect of reflux ratio and number of reactive trays on conversion of reactants

Figure 3 shows the effects of the reflux ratio on the conversion of water and purity of ethylene glycol in the bottoms of the first reactive distillation column operating at 1 atm pressure. Flowrate of distillate stream, number of reactive trays, number of stripping trays, and feed tray locations are fixed at 44.5 kmol/h, 33, 4 and 29, respectively. The results show that the conversion of water has a maximum of ~ 0.975 at a reflux ratio of 2. Since this maximum value of conversion is far from the 99.5 mole% conversion, a big amount of reactants, which are water and ethylene oxide, leaves the system from the distillate stream. Thus, a part of the butanol moves down the column and leaves the system from the bottoms, which results in a decrease in the purity of ethylene glycol.

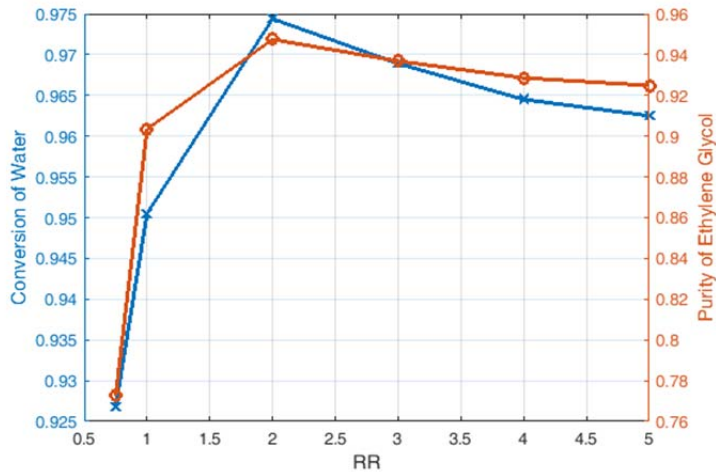


Figure 3: Effect of reflux ratio on conversion of water and purity of ethylene glycol

Effects of reactive tray numbers on the conversion of water and purity of ethylene glycol in the bottoms of the first reactive distillation column are given in Figure 4. Flowrate of distillate stream, number of stripping trays, and molar reflux ratio are fixed at 44.5 kmol/h, 4 and 2, respectively. The results show that the increase in the number of reactive trays increases both the conversion and purity. However, the magnitude of changes in conversion and purity is smaller than the changes in the number of reactive trays which brings a big capital cost to the system. It is easily seen that even with 59 reactive trays, the conversion is far from the 99.5 mole% conversion.

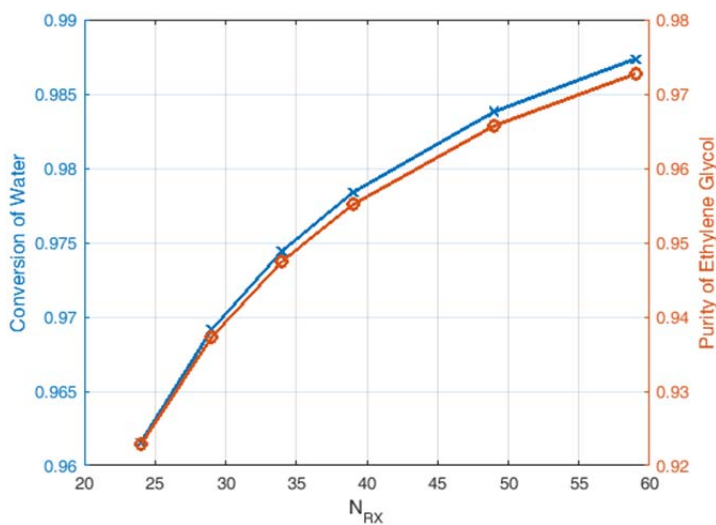


Figure 4: Effect of reactive tray numbers on conversion of water and purity of ethylene glycol

These results indicate that reactive distillation columns operating at 1 atm cannot totally convert the reactants. This is because of the low concentration of reactants in the reactive distillation column as given in Figure 5, which directly effects the reaction rate. Besides the purity of ethylene glycol removed from the bottoms of reactive distillation columns, the unconverted reactants leaving the reactive distillation columns from the distillate stream also effect the purities of butanol, acetone and ethanol which are purified in the following steps of the distillation sequence. To overcome this problem and obtain higher conversion, reactive distillation columns should operate at higher pressures.

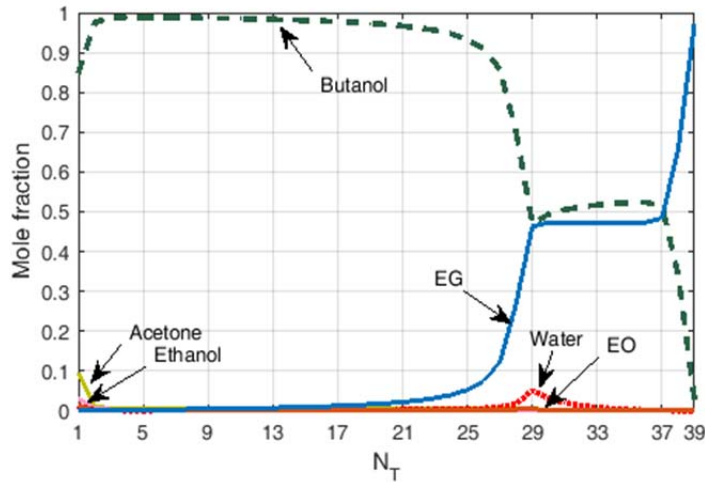


Figure 5: Composition profile in reactive distillation column (C1)

4.2 Effect of operating pressure on conversion of reactants

Effects of operating pressure on the conversion of water and purity of ethylene glycol in the bottoms of the first reactive distillation column are illustrated in Figure 6. Flowrate of distillate stream, molar reflux ratio, number of reactive trays, number of stripping trays, and feed tray locations are fixed at 44.5 kmol/h, 2, 33, 4 and 29, respectively. It is seen that the increase in the pressure dramatically improves the conversion, and the conversion of reactants exceeds 99.9 mole% at the operating pressure of 5 atm. As a result of the high conversion, the amount of reactants running away from the distillate decreases significantly, and ethylene glycol with more than 99.5 mole% purity can be obtained.

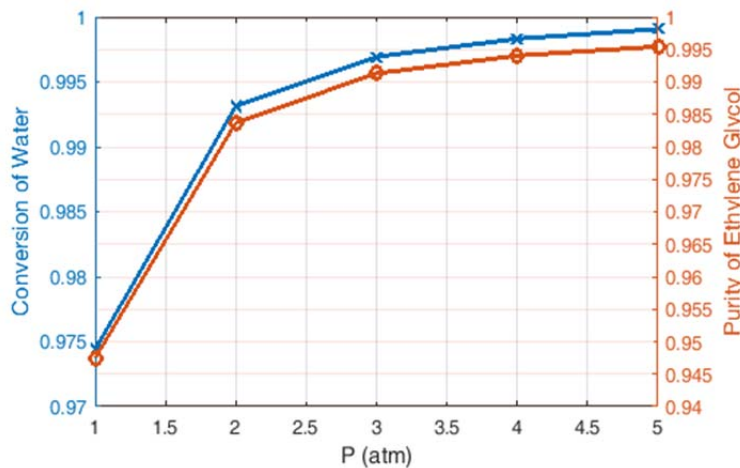


Figure 6: Effect of operating pressure on conversion of water and purity of ethylene glycol

The design parameters of the novel process are given in Table 3. Reactive distillation columns (C1 and C3) have 3 stripping trays. Although no detailed economic analysis has been done yet, some general comparison between processes proposed here and in the literature by Patruşcu et. al. (2017) is possible based on the results given in Table 1 and Table 3. First of all, the results show that this process decreases the total reboiler

duty by more than 40% compared to the configuration in the literature. Since there is an extra distillation column in the novel process, there might be an increase in the capital cost. On the other hand, the diameters of first and second columns shrink significantly because of the decrease in the molar holdup passing through the process as the result of the consumption of water in the reactive columns. Thus, the decrease in the capital cost because of the shrinking of diameters might compensate the increase coming from the extra distillation column.

Table 3: Design parameters of the novel process

	C1	C2	C3	C4	C5
Number of stages	37	8	29	18	30
Feed stage locations	28-28	1	20-20	10	21
Pressure (atm)	5	1	5	1	1
Reflux ratio (molar)	2.26	-	6.69	2.25	8.62
Diameter (m)	0.74	0.83	1.23	0.69	1.10
Reboiler duty (kW)	801	1929	1850	324	1677
Total duty (kW)	6581				

5. Conclusions

In this study, a novel process is proposed for biobutanol purification from ABE fermentation. Distinctly from the processes widely studied in the literature, this process does not include any extraction unit. Instead, it includes reactive distillation columns to consume water recycling in the process. Results of the simulation show that the proposed process significantly (~40%) decreases the reboiler heat duty necessary for the purification. In addition, ethylene glycol, which is a co-product for the whole process besides butanol, acetone and ethanol, is obtained as the result of the reaction. However, there is a slight decrease in the purity of acetone, because the small amount of unreacted ethylene oxide leaves the system from the distillate of the last column as the main impurity.

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