Simulation and parametric study of the innovated process to purify bioethanol with ethylene oxide hydration as an auxiliary reaction

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Abstract. By the conventional process, to purify bioethanol from fermentation reactor or bioreactor is relatively high cost, since the purity of bioethanol in the bioreactor output is very low (just around 8-14%) and there are azeotropes between bioethanol with water. Therefore, in the conventional process, a combination of distillation-adsorption, distillation-pervaporation, or extractive distillation is needed in order to get bioethanol with purity of 99.6% or above. In this research, an innovative process to purify bioethanol in a reactive distillation column with an auxiliary reaction of ethylene oxide hydration was proposed. The auxiliary reaction broke the water/bioethanol azeotrope. Impacts of the reflux ratio and the bottoms rate were investigated by simulating the process in Aspen Plus software. The results revealed that the innovated bioethanol purifying process theoretically could produce bioethanol with a purity of 99.9%.

1. Introduction

Bioethanol is one of promising biofuels that is obtained from renewable sources, namely, biomass and is environmentally friendly [1]. Bioethanol is produced by fermentation of starch from biomass. However, the purity of bioethanol in the bioreactor output is very low (just around 8-14%), because above this concentration, inhibition of yeasts may occur that reduces their activity [1]. Meanwhile, based on PN A 79521 standard, bioethanol as fuel must have minimum purity of 99.6% [2]. Therefore, the bioethanol purification step after the fermentation process is an important issue.

The main components in the output stream of bioreactor/fermentation process are bioethanol and water. There is azeotrope between these components as shown in Table 1. This azeotrope makes the separation of them difficult. In the conventional process, several methods can be used to separate bioethanol from water, such as the combination of distillation-adsorption, distillation-pervaporation, or extractive distillation [3]. However, the cost of these methods is relatively high since they need at least two columns and the addition of adsorbent, membrane, or solvent. Therefore, in this research, an innovative process to separate bioethanol from water in a single column of reactive distillation was proposed. The idea of this innovative process was to remove water by an auxiliary reaction of ethylene oxide hydration.

Ethylene oxide (EO) could be reacted with water and produce ethylene glycol (EG) as

\[ C_2H_4O + H_2O \rightarrow (CH_2OH)_2 \]  

(1)
The present of this auxiliary reaction is worthwhile, because the product, EG, is also a valuable chemical which is used as an antifreeze and coolant, in hydraulic fluids, and in the manufacture of low-freezing dynamites and resins [4]. There is also no azeotrope between EG and bioethanol (EtOH) as shown in Table 1, so the separation process is relatively easy and could be conducted in a single column of reactive distillation.

| Table 1. System azeotrope |
|---------------------------|
| Temp (°C) | EtOH | Water | EO | EG |
| 78.15 | 0.8952 | 0.1048 | 0 | 0 |

This study is a part of research about innovated bioethanol purification. In this study, the innovated bioethanol purification was simulated using Aspen Plus to investigate its feasibility and to study the effects of the process parameters in a steady-state condition. Based on the result of this study, the next parts of the research, which are about process design optimization, dynamic behavior, and process control, can be conducted.

2. Base Simulation

2.1. Kinetic model
The auxiliary reaction of EO hydration may also produce an unwanted by-product of diethylene glycol and triethylene glycol. However, the rate of the side reaction is much lower than that of the main reaction and consequently, the effect of this side reaction can be neglected [5]. The kinetic model of EG production from EO hydration is adapted as follows [5]

\[ r(\text{mol. cm}^{-3}.\text{s}^{-1}) = 3.15 \times 10^9 \exp \left(-\frac{9547}{T}\right)x_{\text{EO}}x_{\text{water}} \] (2)

2.2. Process simulation
Innovated bioethanol purification was simulated in ASPEN Plus software, using a reactive distillation (RD) column as shown in Figure 1. The properties method that was used in this study was NRTL (Non-Random Two Liquid), which has been confirmed to be accurate in simulating a system containing EtOH, water, EO, and EG [5, 6].

![Figure 1. Reactive distillation for innovated bioethanol production](image)

The process variables that were examined were reflux ratio and bottoms rate. The method of examination was by manipulating these two variables simultaneously with the range of 16-20 for reflux ratio and 6.6-8.6 kmol/h for bottoms rate. Other variables besides these two variables were set to constant at the initial condition of simulation. The initial conditions of simulation are shown in Table 2.

Reflux ratio and bottoms rate were examined their effects on the reaction, separation, and economic aspects of the process. The EO conversion was used to quantitatively describe the reaction aspect,
while the economic aspect was described quantitatively by the reboiler duty, since it is connected to the operational cost. To describe separation aspect, two variables were used. They were the purity of EtOH in distillate stream and the purity of EG in bottom stream.

3. Results and Discussion

3.1. The effect of reflux ratio and bottoms rate to the EO conversion

The simulation results from aspen were transferred to Matlab software to make a graph as shown in Figure 2. From the graph, it can be seen that when the reflux ratio was low, the increase in bottoms rate from 6.6 to around 8.1 kmol/h also increased the EO conversion. This was because the increase in bottoms rate forced much more EG to leave the column via bottom stream and maintained the water fraction in the column high. As can be seen in equation (4), the higher water fraction in the column increased the EO hydration rate. Therefore, the EO conversion was also increased.

Table 2. Initial conditions of simulation

| Parameters | Feed 1 (BIOETH) | Feed 2 (EO) | RD Column |
|------------|----------------|-------------|-----------|
| EtOH mole-flow | 1.4 kmol/h | 8.6 kmol/h | Enriching stages |
| Water mole-flow | 8.6 kmol/h | Temperature 25 °C |
| Temperature | 25 °C | Reactive stages 5-35 |
| Stripping stages | 36-40 | - |

Note that the initial conditions are not the optimum conditions. The optimum conditions will be covered in the next study.
However, if the bottoms rate was increased above 8.1 kmol/h when the reflux ratio was low, the EO conversion was decreased. This was because when the reflux ratio was low, there was less water that being returned into the column, resulting in the depletion of EO conversion or EG formation. The EG formation at this condition did not catch up with the value of bottoms rate that was 8.1 kmol/h or above. Therefore, water as the second heaviest component was also forced to leave the column with the EG via bottom stream. This phenomenon decreased the fraction of the water in the column, resulting in the further depletion of EO conversion.

At the higher reflux ratio, when the bottoms rate was increased, the EO conversion was also increased. When both of the reflux ratio and the bottoms rate were high, there was much water that being returned into the column and almost all EG was forced out from the column without dragged the water. This made the EO conversion became higher. The highest EO conversion (almost 100%) was achieved when the reflux ratio was 20 and the bottoms rate was 8.6 kmol/h.

3.2. The effect of reflux ratio and bottoms rate to the EG purity
It can be seen from Figure 3, that most of the variations in reflux ratio and bottoms rate made the EG purity reached 100%. This was because EG was the heaviest component in the system so it was naturally forced down to the bottom without dragged any other components, except when the reflux ratio was lower than 17 and the bottoms rate above 8.1 kmol/h.
As explained in the previous discussion of EO conversion, at the lower reflux ratio, the EG formation was also low and did not catch up with the value of bottoms rate that was 8.1 kmol/h or above. Therefore, water as the second heaviest component was also forced to leave the column with the EG via bottom stream, resulting in the depletion of EG purity in the bottom.

### 3.3. The effect of reflux ratio and bottoms rate to the EtOH purity

As shown in Figure 4, the reflux ratio did not significantly affect the EtOH purity in distillate, because EtOH was the second lightest component in the system, so even the reflux ratio was increased, the EtOH was evaporated again before it reached the bottom and came out as distillate product. This result was synchronous with the result in Figure 5, where the molar flow rate of EtOH at any variations of the reflux ratio and bottoms rate reached the value of 1.4 kmol/h. The EtOH in the feed stream also had a flow rate of 1.4 kmol/h. Therefore, it could be concluded that at any variations of the reflux ratio and bottoms rate, all of EtOH came out from the column via distillate stream.

In addition, within the range of variations, EO conversion reached above 99%, resulting in only small amount of EO that came out with the EtOH in distillate. Therefore, the EtOH purity in distillate was not affected by reflux ratio.
Figure 4. The effect of reflux ratio and bottoms rate to the EtOH purity in distillate

The EtOH purity was significantly affected by the bottoms rate. It can be seen in Figure 6, the decrease in the bottoms rate made some amount of EG was forced out from the column via distillate stream. This phenomenon decreased EtOH purity in distillate as it can be seen in Figure 4.

Figure 5. The effect of reflux ratio and bottoms rate to the EtOH molar flow rate in distillate

3.4. The effect of reflux ratio and bottoms rate to the reboiler duty
It can be seen in Figure 7, the increase in reflux ratio increased reboiler duty. This was because when the reflux ratio was increased, there was much more liquid that being returned into the column. Therefore, much more reboiler duty was needed to boil the liquid.
Figure 6. The effect of reflux ratio and bottoms rate to the EG molar flow rate in distillate

Meanwhile, the increase in bottoms rate decreased reboiler duty. This was because when the bottoms rate was increased, there was a less amount of liquid that needs to be boiled up. Therefore, the reboiler duty also decreased.

Figure 7. The effect of reflux ratio and bottoms rate to the reboiler duty

Based on the result in Figure 7, the best operating condition for this process was the reflux ratio of 20 and the bottoms rate of 8.6 kmol/h, because it gave the lowest reboiler duty, EO conversion of almost 100% and EtOH purity of 99.9%.
4. Conclusions
The simulation results revealed that the innovated bioethanol purification with auxiliary reaction of EO hydration in RD column is highly prospective. It gives very high hydration conversion (almost 100%) and very high purity of bioethanol (up to 99.9%). These results are achieved when the reflux ratio is 20 and the bottoms rate is 8.6 kmol/h.

5. References
[1] Vohra M, Manwar J, Manmode R, Padgilwar S and Patil S 2014 J. Environ. Chem. Eng. 2 573-84
[2] Rutz D and Janssen R 2006 Overview and Recommendations on Biofuel Standards for Transport in the EU (Munchen: WIP Renewable Energy) p 8
[3] Frolkova A K and Raeva V M 2010 Theoretical Foundations of Chemical Engineering 44 545-56
[4] National Center for Biotechnology Information PubChem Database 1,2-Ethanediol, CID=174 Available from: https://pubchem.ncbi.nlm.nih.gov/compound/174 (accessed on Mar. 26, 2019)
[5] Tavan Y, Behbahani R M and Hosseini S H 2013 Chem. Eng. Process. Process Intensif. 73 81-6
[6] Nabgan W, Saeh I, Abdullah T A T, Nabgan B and Mat R 2016 International Journal of Environmental Research & Clean Energy 1 1-3
[7] Luyben W L and Yu C C 2008 Reactive Distillation Design And Control (Hoboken: John Wiley & Sons, Inc.) p 2-11
[8] Altioskka M R and Akyalcin S 2009 Ind. Eng. Chem. Res. 48 10840-4
[9] Ali S H and Merchant S Q 2006 Int. J. Chem. Kinet. 38 593-612
[10] Kumar A and Daoutidis P 2004 AIChE. J. 45 51-68