Pertanika J. Sci. & Technol. 26 (2): 707 - 718 (2018)

PERTANIKA JOURNALS

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

# Simulation and Optimisation of Bioethanol Purification using Extractive Distillation with Additive Solvent

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## ABSTRACT

In this study, simulation and optimisation of the purification of bioethanol from an azeotropic mixture was done using the Aspen HYSYS and the Response Surface Methodology (RSM), respectively, to achieve an acceptable bioethanol content with minimal energy use. The objective of this study is to develop the simulation process of bioethanol production from a fermentation effluent. Additionally, the effects of parameters such as solvent temperature, number of entrainer feed stage, mass flow rate and third components of the process for production of bioethanol were studied. As bioethanol is a product of biofuel production, the main challenge facing bioethanol production is the separation of high purity ethanol. However, the separation of ethanol and water can be achieved with the addition of a suitable solvent such as 1,3-butylene glycol (13C4Diol), mixture 13C4Diol and ethylene glycol (EGlycol) and mixture 13C4Diol and glycol ethyl ether (DEG) in the extractive distillation process. For the 13C4Diol mixture, the temperature of entrainer is 90°C with 1500 kg/hr of entrainer rate, while the number of entrainer feed stage is one. The optimum conditions for mixture 13C4Diol and EGlycol require a temperature of entrainer of 90.77°C with an entrainer rate of 1500 kg/hr, while the number of entrainer feed stage is one. Lastly, for optimum conditions for the mixture 13C4Diol and DEG, the temperature of entrainer should be 90°C with an entrainer rate of 1564.04 kg/hr, while the number of entrainer feed stage is one. This study shows that process simulation and optimisation can enhance the removal of water from an azeotropic mixture.

*Keywords:* Bioethanol purification, extractive distillation, fermenter effluent, HYSYS simulation, Response Surface Methodology (RSM)

*Article history:*
Received: 25 May 2017
Accepted: 5 December 2017

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## INTRODUCTION

The high demand of fuel by a population is predicted to increase by 25% in the next 20 years, with most of the growth in countries

ISSN: 0128-7680 

with emerging economies. Due to this significant energy demand, alternative energy sources are required to sustain future needs. Biofuel is one such alternative. Bioethanol is a biofuel that is commonly used nowadays. According to Szulczyk et al. (2010), worldwide bioethanol demand has grown rapidly due to government mandates such as the Energy Independence and Security Act of 2007 and environmental regulations forbidding the use of *methyl tert-butyl ether* (MTBE) as fuel oxygenate. Bioethanol production represented 4% of total gasoline consumed around the world (2007), and worldwide production may increase to 125 billion litres by 2020 (Balat & Balat, 2009; Flatch et al., 2015).

Distillation is the most common and recognised industrial purification technique for ethanol. Extractive distillation is the partial vaporisation process that occurs in the presence of a miscible entrainer that alters the relative volatilities of the components present in the mixture to be separated (García-Herreros & Gómez, 2011). Extractive distillation is used more often than azeotropic distillation. It is because extractive distillation produces low energy consumption and flexible selection of solvent. Extractive distillation of bioethanol purification is used with ethylene glycol or tetraethylene glycol as entrainer. Ravagnani et al. (2010) pointed out the toxicity of ethylene glycol. However, reports indicated that tetraethylene glycol as entainer had high energy consumption. Gil et al. (2012) reported a design of the extractive distillation process to produce ethanol using glycerol as entrainer. This study hoped to show that glycerol can be used in the production of high purity ethanol by taking advantage of its low cost and high availability. According to Segovia-Hernandez et al. (2014), the analysis of the study reported that the theoretical control properties of complex distillation sequences can be improved by using glycerol as entrainer. Besides that, Bauer and Hulteberg (2013) claimed that the use of glycerol as entractive agent can be increased for the foreseeable future due to the availability at low cost of this chemical compound as co-product of bioethanol production. Zhao et al. (2006) reported the use of several ionic liquids, including 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride for the separation of the mixture, ethanol-water. This is because ionic liquids are considered green solvents that have more advantages, for example, low vapour pressure, low toxicity and high decomposition temperature. Ionic liquids are better in the distillation process when using high concentrations, but ionic liquids are very expensive in contrast to ethylene. In the literature, simulation tools such as Aspen Plus® simulator version 11.1 and Aspen Hysis were used for bioethanol separation (Gil et al., 2008; Pla-Franco et al., 2014)

The aim of this study was to optimise bioethanol purification via additive solvent in a multicomponent distillation system. The third additive that was used to optimise bioethanol production was a mixture of 1,3-butylene glycol (13C4Diol), mixture 13C4Diol and ethylene glycol (EGlycol) and mixture 13C4Diol and glycol ethyl ether (DEG). The process was designed using Aspen HYSYS to study the effect of the entrainer in distillation and to investigate the effect of parameters to optimise the purification of bioethanol.

## MATERIALS AND METHOD

### Materials

In the extractive distillation process, 13C4Diol, mixture 13C4Diol and EGlycol, mixture 13C4Diol and DEG were used as solvents. Tables 1 and 2 show the process parameters and main components of the fermentor effluent, respectively.

Table 1
*Process parameters during the ethanol dehydration experiments*

| Parameter | Unit | Variation range |
|---|---|---|
| Temperature | $^{o}$C | 90-110 |
| Pressure | kPa | 101.3 |
| Mass flow rate | kg/hr | 1500-3400 |
| Number of stages | tray | 1-20 |
| Product ethanol | wt% | 80-100 |

Source: (Niemistö et al., 2013)

Table 2
*Main components in fermenter effluent*

| Component | Composition, % |
|---|---|
| Ethanol | 10 |
| Water | 83 |
| Sucrose | 4 |
| Carbon | 3 |

Source: (Batista et al., 2012)

This mixture was selected based on the literature, in which most of the components were yeast, sucrose, ethanol and water (Habaki et al., 2015; Langston et al., 2005; Navarrete-Contreras et al., 2014). Theoretically, carbohydrate can be converted to 75-95% with about 10-16% of the final ethanol concentration entering into the distillation column. By taking the composition of dissolved carbohydrate from molasses and 10% of ethanol production, presumably, the water content would be 83% and 25% and unconverted sugar consisting of sucrose, glucose and fructose would be 4%. The remaining percentage was assumed to be the amount of yeast. The components were set according to their name in HYSYS except for yeast, which was named as carbon. Carbon serves the same function as yeast that would settle in the hydrocyclone.

### HYSYS Simulation

The suggested process consisted of the removal of solids using hydrocyclone, separation of non-volatile material using a separator and distillation using a distillation column.

**Hydrocyclone.** The fermentation state contains a carbon particle, which was removed using hydrocyclone. The fermentation component was fed into the hydrocyclone in order to remove the solid carbon particle as solid particles cannot remain in extractive distillation. The outlet of the upper stream was in liquid form and the outlet of the bottom stream was the solid carbon particle.

**Separator.** The sucrose had to be separated from ethanol and water to ensure the impurities would not affect the final product. The component was fed into a two-phase separator to separate the liquid and vapour components in the fermented mixture. The inlet stream of the fermented mixture passed through the valve and heater to maintain the pressure drop and increase the temperature of the fermented mixture before entering the two-phase separator and the fermented mixture consisted of vapour and liquid. The components in the fermented stream evaporated due to the processing and was released together with the vapour stream. The fermented mixture was collected at the bottom stream.

**Distillation column.** In order to achieve a high concentration of ethanol, an ethanol-water mixture was added to the purification process during the extractive distillation stage. The third chemical component was also added in this process. Three units of the distillation column were used and simulated. The first distillation column was used to separate the water and solvent from the ethanol. However, since there was still a small amount of water and solvent, the second and third distillation columns were used in order to achieve ethanol concentration higher than 99% mol. For the second and third columns, another solvent stream was added. The temperature of the solvent that was produced at the bottom of the distillation column was reduced using three units of coolers and then mixed in order to recycle it back to the fed solvent stream.

## Response Surface Methodology (RSM)

The HYSYS design simulation data was used for fitting the model to find the best polynomial equation. This data was analysed using Design Expert version 7.0.0. The three main analytical steps were analysis of variance (ANOVA), a regression analysis and the plotting of a response surface. These steps were performed to find an optimal condition for the yield of bioethanol production. The experiment data that was obtained using the optimal conditions established from the mathematical model developed were used as the validating set and these were compared with the predicted values. The fitted quadratic response model is given as:

$$\boldsymbol{Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i<j}^{k} b_{ij} X_i X_j + e} \quad (1)$$

where, Y = response variable, which is yield of bioethanol, $b_0$ = is the intercept value, $b_i$ (i=1,2…k) is the first-order model coefficient, $b_{ij}$ = the interaction effect, $b_{ii}$ = the quadratic coefficients of $X_i$, $X_i$ and $X_j$ = the input variable that influenced the response variable, e = the random error. An effect that exceeded the vertical line (p=0.05) may be considered significant.

## RESULTS AND DISCUSSION

### Data Output

Table 3, 4 and 5 show the removal of solids, non-volatile compounds and operating condition composition in the fractional distillation process, respectively.

Table 3 shows that the amount of solid particles removed from the fermenter effluent was 4% (w/w). It was completely removed from the mixture because the other equipment would not have been able to run if there had been solid particles.

Table 3
*Removal of solids*

| Stream | Temperature, °C | Pressure, kPa | Mass Flow Rate, kg/h | Composition |
|---|---|---|---|---|
| Feed | 25 | 101.3 | 1200 | 0.03 |
| Out 1 | 25 | 101.2 | 5527 | 0.00 |
| Out 2 | 25 | 101.2 | 2763 | 0.04 |

Table 4 shows that the amount of non-volatile compound decreased from 4 to 13% (w/w). Before entering the two-phase separator, the fermenter was heated to 100°C to form a two-phase mixture. The vapour phases consisted of an azeotropic mixture, while the liquid phase consisted of a sucrose. Since sucrose is a non-volatile compound, it cannot enter the distillation process. Therefore, it had to be removed completely.

Table 4
*Non-volatile compound*

| Stream | Temperature, °C | Pressure, kPa | Mass Flow Rate, kg/h | Composition |
|---|---|---|---|---|
| Feed | 100 | 101.2 | 5527 | 0.04 |
| Out 1 | 100 | 101.2 | 2425 | 0.00 |
| Out 2 | 100 | 101.2 | 3102 | 0.13 |

Table 5 shows the results of the fractional distillation process; the amount of water and ethanol was 86% (w/w) and 14% (w/w), respectively. In this process, the most volatile component, ethanol, was concentrated to a greater degree in the vapour, left in the liquid, while the water flows downward through the column as the bottom product of the column.

Table 5
*Operating condition and composition in fractional distillation process*

| Stream | Temperature, °C | Pressure, kPa | Mass Flow Rate, kg/h | Composition | |
|---|---|---|---|---|---|
| | | | | Ethanol | Water |
| Feed | 78.1 | 101.2 | 2425 | 0.14 | 0.86 |
| Out 1 | 78.61 | 99.3 | 15.7 | 0.60 | 0.40 |
| Out 2 | 84.27 | 100.3 | 2409 | 0.14 | 0.86 |

## Optimisation

The flowsheet for the distillation sequence simulated in Aspen Plus is shown in Figure 1. This distillation contains two distillation columns, the extractive distillation column and the entrainer recovery column. In this process, the bottom product from the extractive distillation column contained ethanol, with $p<0.05$ (excluding separating agent). The entrainer recovered high purity ethanol through the second column. The recovery column separated the azeotropic mixture from the entrainer and recycled it back to the initial feed.

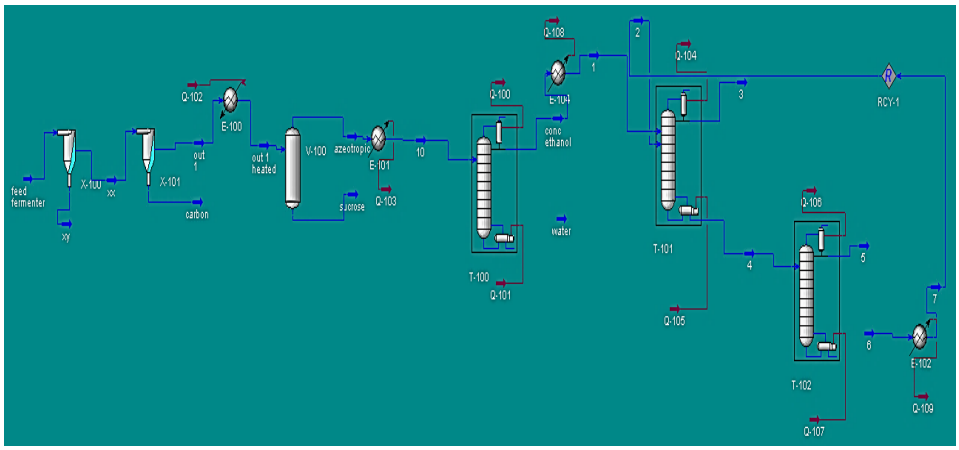



*Figure 1*. Hysys process simulation

Table 6 shows the material balance for the three separating agents that were used for bioethanol production. The three separating agents underwent the same process flow but gave a different balance. This is because their properties were not the same. Therefore, they adjusted their condition to produce more bioethanol and were efficient in water removal.

Table 6
*Material balance for extractive distillation process*

| **Entrainer: 13C4Diol** | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Stream** | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
| Temperature, °C | 25.00 | 90.00 | 78.20 | 176.50 | 84.80 | 182.20 | 90.00 |
| Pressure, kPa | 99.30 | 101.30 | 99.00 | 99.10 | 101.30 | 101.30 | 101.30 |
| Ethanol, kmol/hr | 0.60 | 0.01 | 0.86 | 0.02 | 0.43 | 0.01 | 0.01 |
| Water, kmol/hr | 0.40 | 0.03 | 0.12 | 0.03 | 0.31 | 0.03 | 0.03 |
| 13C4Diol | - | 0.96 | 0.03 | 0.95 | 0.18 | 0.96 | 0.96 |
| Mass Flow Rate, kg/hr | 15.70 | 3039 | 5.00 | 3050 | 17.26 | 3032 | 3032 |
| **Entrainer: 13C4Diol and EGlycol** | | | | | | | |
| **Stream** | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
| Temperature, °C | 25.00 | 90.00 | 78.23 | 178.00 | 85.94 | 188.50 | 90.00 |
| Pressure, kPa | 99.30 | 101.30 | 99.00 | 99.10 | 101.30 | 101.30 | 101.30 |
| Ethanol, kmol/hr | 0.60 | 0.06 | 0.87 | 0.01 | 0.38 | 0.01 | 0.01 |
| Water, kmol/hr | 0.40 | 0.02 | 0.10 | 0.03 | 0.41 | 0.02 | 0.02 |
| 13C4Diol, kmol/hr | - | 0.71 | 0.02 | 0.70 | 0.11 | 0.71 | 0.71 |
| Eglycol, kmol/hr | - | 0.26 | 0.06 | 0.26 | 0.10 | 0.26 | 0.26 |
| Mass Flow Rate, kg/hr | 15.70 | 1564 | 6.00 | 1574 | 17.24 | 1556 | 1556 |

Table 6 (*continue*)

| Entrainer: 13C4Diol and DEG | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Stream** | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
| Temperature, °C | 25.00 | 90.77 | 77.74 | 202.60 | 84.52 | 241.80 | 90.77 |
| Pressure, kPa | 99.30 | 101.30 | 99.00 | 99.10 | 101.30 | 101.30 | 101.30 |
| Ethanol, kmol/hr | 0.60 | - | 0.89 | 0.01 | 0.42 | - | - |
| Water, kmol/hr | 0.40 | - | 0.10 | 0.01 | 0.42 | - | - |
| 13C4Diol, kmol/hr | - | 0.04 | 0.00 | 0.04 | 0.04 | 0.04 | 0.04 |
| DEG, kmol/hr | - | 0.96 | 0.01 | 0.94 | 0.12 | 0.96 | 0.96 |
| Mass Flow Rate, kg/hr | 15.70 | 1500 | 5 | 1511 | 17.30 | 1493 | 1493 |

## Effect of Separating Agent

To analyse the effect of the separating agent in water removal for an azeotropic mixture, the process of extractive distillation was simulated in Aspen Properties v7.1, developed by AspenTech. Table 7 shows that 13C4Diol, 13C4Diol and EGlycol and 13C4Diol and DEG were used as separating agents in the extractive distillation process. The three agents yielded more than 80% of ethanol compared to other separating agents such glycerol and ethylene glycol, which yielded more than 98%. This study investigated other separating agents that could be used in the extractive distillation process. Even though the separating agent could not give release a high amount ethanol, it was highly efficient in water removal. The yield of bioethanol was higher at 88.49% (w/w) with the 13C4Diol and DEG as separating agents. Others separating agents like 13C4Diol had 84.86% (w/w) yield, while 13C4Diol and Eglycol yielded 85.60% (w/w) of bioethanol. The values do not show a significant difference in bioethanol production. This can be improved by adding a suitable component to the mixture.

Table 7
*Yield of bioethanol in different separating agent*

| Entrainer: 13C4Diol | | | | |
|---|---|---|---|---|
| **Condition** | **Temperature, °C** | **No. of Feed of Entrainer** | **Mass Flow Rate, kg/hr** | **Yield of Ethanol, %** |
| Maximum | 108.56 | 5 | 3400 | 77.27 |
| Optimum | 90.00 | 1 | 1500 | 84.86 |
| Minimum | 90.00 | 1 | 3039.29 | 85.32 |
| **Entrainer: 13C4Diol and EGlycol** | | | | |
| **Condition** | **Temperature, °C** | **No. of Feed of Entrainer** | **Mass Flow Rate, kg/hr** | **Yield of Ethanol, %** |
| Maximum | 110.00 | 20 | 3398.12 | 76.38 |
| Optimum | 90.00 | 1 | 1564.04 | 85.60 |
| Minimum | 90.00 | 1 | 1564.04 | 85.60 |
| **Entrainer: 13C4Diol and DEG** | | | | |
| **Condition** | **Temperature, °C** | **No. of Feed of Entrainer** | **Mass Flow Rate, kg/hr** | **Yield of Ethanol, %** |
| Maximum | 108.36 | 20 | 3399.99 | 74.89 |
| Optimum | 90.77 | 1 | 1500.02 | 88.49 |
| Minimum | 90.00 | 1 | 1500 | 88.49 |

## Effect of Parameters on Separating Agent

In order to obtain higher bioethanol production in the extractive distillation process, the parameter analysis was carried out. The analysed parameters were:

1) Temperature of entrainer
2) Number of entrainer feed stage
3) Molar flow rate of entrainer

The feed conditions of the binary mixture and the entrainer are given in Table 8.

Table 8
*Parameter of simulation process*

| Stream | Feed of azeotropic mixture | 13C4Diol | 13C4Diol and EGlycol | 13C4Diol and DEG |
|---|---|---|---|---|
| Temperature, °C | 25.00 | 90.00 | 90.00 | 90.77 |
| Pressure, kPa | 99.30 | 101.30 | 101.30 | 101.30 |
| Ethanol, kmol/hr | 0.60 | 0.01 | 0.01 | - |
| Water, kmol/hr | 0.40 | 0.03 | 0.02 | - |
| 13C4Diol, kmol/hr | - | 0.96 | 0.71 | 0.04 |
| Eglycol, kmol/hr | - | - | 0.26 | - |
| DEG, kmol/hr | - | - | - | 0.96 |
| Mass Flow Rate, kg/hr | 15.70 | 3039 | 1564 | 1500 |

## Effect of Temperature in Entrainer

Temperature of entrainer has an important effect on the distillate composition and the reboiler energy consumption. Several authors have recommended considering temperature as a design variable and operating 5-15°C below the top temperature of the extractive distillation column (Mulia-Soto & Flores-Tlacuahuac, 2011). It can be observed that using a high entrainer feed temperature yielded less bioethanol (Figure 2) because higher temperature demands a high reflux ratio to reach a specified separation. The increase in temperature causes water present in this stage to vapourise, thus increasing the content of water in the distillate and decreasing its purity. By using the standard reflux ratio, a higher yield is produced in optimum temperature. The least energy demand corresponds to a low entrainer feed temperature and a low reflux ratio.

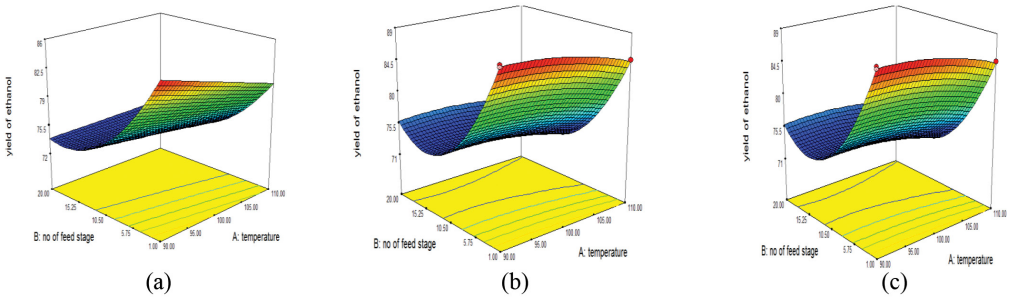
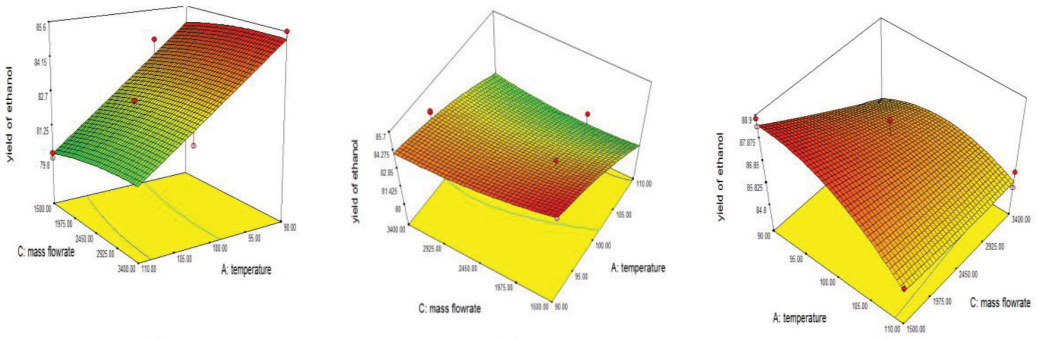



*Figure 2.* Effect of temperature and no. of feed stage on yield of ethanol (a) 13C4Diol (b) 13C4Diol and EGlycol (c) 13C4Diol and DEG

## Effect of Mass Flow Rate

The effect in molar flow rate is different for pure and mixture solvents. Figure 3 shows that pure components like 13C4Diol have a high molar flow rate for high efficiency in order to remove water from ethanol, while mixture components have a lower mass flow rate to obtain high ethanol production. This indicates that mixture components have a lower mass flow rate because the mixture components react together to remove water from ethanol. Pure components have a high mass flow rate because they have to react by themselves in the extractive distillation process.

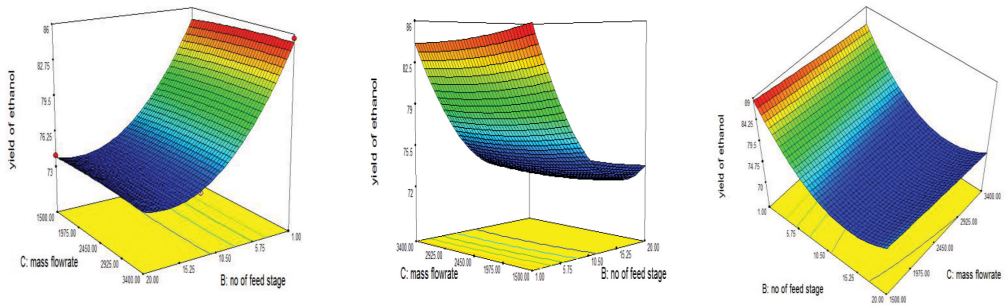



(a) (b) (c)

*Figure 3.* Effect of temperature and mass flow rate on yield of ethanol (a) 13C4Diol (b) 13C4Diol and EGlycol (c) 13C4Diol and DEG

## Effect of Number of Stages for Feed Entrainer

Another parameter affecting the yield is the number of feed entrainers in the stages. The distillation column is operated at semi-batch fashion when the azeotropic mixture is introduced in the reboiler and the entrainer feed is continuous in other stages. Figure 4 presents the result for different feed stages and it can be seen in comparison to the yield of bioethanol production. For the specified number of stages, there is a best mixture feed stage, at which a higher yield of ethanol can be obtained. The separation is improved as more ethanol can be obtained in a longer period because the entrainer feed is close to the top of the distillation column and has greater contact with the ethanol-water mixture. However, when the feed stage is close to the bottom, the numbers of stages in the stripping section are not enough to extract the ethanol from an azeotropic mixture, and the ethanol in the bottom product does not achieve the specific value. This can cause a decrease in the composition distilled according to the mass balance. The reboiler has the same propose as the molar composition of ethanol in the distillate, so that the energy consumption increases when high ethanol concentration in the distillate is obtained.




(a) (b) (c)

*Figure 4.* Effect of mass flow rate and no. of feed stage on yield of ethanol (a) 13C4Diol (b) 13C4Diol and EGlycol (c) 13C4Diol and DEG

## CONCLUSION

In this study, the primary focus was to study the optimal operating parameters for production of bioethanol process. 13C4Diol, 13C4Diol and EGlycol and 13C4Diol and DEG were proposed as entrainers for the separation of an azeotropic mixture by extractive distillation with three columns to produce bioethanol. The operation process was investigated by simulation using the Aspen HYSYS v 7.0.0 software. In order to purify the bioethanol using a fermenter effluent, other compounds such as solid particles had to be removed besides water and ethanol. Therefore, an RSM design was employed to analyse the process variable, including the temperature of entrainer, number of entrainer feed stages and molar flowrate of entrainer. The optimum conditions for entrainer were identified. For the 13C4Diol, the temperature of the entrainer was 90$^{o}$C with 1500 kg/hr as the entrainer flow rate, while the number of entrainer feed stage was one. Next, the optimum conditions for a mixture of 13C4Diol and EGlycol, the temperature of the entrainer was 90.77$^{o}$C, with 1500 kg/hr as the entrainer rate and the number of entrainer feed stage was one. Lastly, the optimum conditions for a mixture of 13C4Diol and DEG needed a temperature of 90$^{o}$C for the entrainer, with 1564.04 kg/hr as the entrainer rate, while the number of entrainer feed stage was one.

## REFERENCES

Balat, M., & Balat, H. (2009). Recent trends in global production and utilization of bio-ethanol fuel. *Applied Energy*, *86*(11), 2273–2282.

Batista, F. R. M., Follegatti-Romero, L. A., Bessa, L. C. B. A., & Meirelles, A. J. A. (2012). Computational simulation applied to the investigation of industrial plants for bioethanol distillation. *Computers and Chemical Engineering*, *46*, 1–16.

Bauer, F., & Hulteberg, C. (2013). Is there a future in glycerol as a feedstock in the production of biofuels and biochemicals? *Biofuels, Bioproducts and Biorefining, 7*(1), 43–51.

Flach, B., Lieberz, S., Rondon, M., Williams, B., & Teiken C. (2015). *EU Biofuels Annual 2015* (pp. 1-42). Global Agriculture Information Network.

García-Herreros P., & Gomez, J. M. (2011). Optimization of the design and operation of an extractive distillation system for the production of fuel grade ethanol using glycerol as entrainer. *Industrial and Engineering Chemistry Research, 50*(7), 3977–3985.

Gil, I. D., Gómez, J. M., & Rodríguez, G. (2012). Control of an extractive distillation process to dehydrate ethanol using glycerol as entrainer. *Computers and Chemical Engineering*, *39*, 129–142.

Gil, I. D., Uyazan, A. M., Aguilar, J. L., Rodríguez, G., & Caicedo, L. A. (2008). Separation of ethanol and water by extractive distillation with salt and solvent as entrainer: Process simulation. *Brazilian Journal of Chemical Engineering, 35(1)*, 207–215.

Habaki, H., Hu, H., & Egashira, R. (2015). Liquid-liquid equilibrium extraction of ethanol with mixed solvent for bioethanol concentration. *Chinese Journal of Chemical Engineering, 24*(2), 253–258.

Langston, P., Hilal, N., Shingfield, S., & Webb, S. (2005). Simulation and optimisation of extractive distillation with water as solvent. *Chemical Engineering and Processing: Process Intensification*, *44*(3), 345–351.

Mulia-Soto, J. F., & Flores-Tlacuahuac, A. (2011). Modeling, simulation and control of an internally heat integrated pressure-swing distillation process for bioethanol separation. *Computers & Chemical Engineering*, *35*(8), 1532–1546.

Navarrete-Contreras, S., Sánchez-Ibarra, M., Barroso-Muñoz, F. O., Hernández, S., & Castro-Montoya, A. J. (2014). Use of glycerol as entrainer in the dehydration of bioethanol using extractive batch distillation: Simulation and experimental studies. *Chemical Engineering and Processing: Process Intensification*, *77*, 38–41.

Niemistö, J., Pasanen, A., Hirvelä, K., Myllykoski, L., Muurinen, E., & Keiski, R. L. (2013). Pilot study of bioethanol dehydration with polyvinyl alcohol membranes. *Journal of Membrane Science*, *447*, 119–127.

Pla-Franco, J., Lladosa , E., Loras S., & Montón , J. B. (2014) Thermodynamic analysis and process simulation of ethanol dehydration via heterogeneous azeotropic distillation. *Industrial and Engineering Chemistry Research, 53*(14), 6084–6093.

Segovia-Hernandez, J. G., Vázquez-Ojeda, M., Gómez-Castro, F. I., Ramírez-Márquez, C., Errico, M., Tronci, S., & Rong, B.-G. (2014). Process control analysis for intensified bioethanol separation systems. *Chemical Engineering and Processing: Process Intensification*, *75*, 119–125.

Szulczyk, K. R., McCarl, B. A., & Cornforth, G. (2010). Market penetration of ethanol. *Renewable and Sustainable Energy Reviews*, *14*(1), 394–403.

Ravagnani, M. A. S. S., Reis, M. H. M., Filho, R. M., & Wolf-Maciel, M. R. (2010). Anhydrous ethanol production by extractive distillation: A solvent case study. *Process Safety and Environmental Protection*, *88*(1), 67–73.

Zhao, J., Dong, C. C., Li, C. X., Meng, H., & Wang, Z. H. (2006). Isobaric vapor–liquid equilibria for ethanol-water system containing different ionic liquids at atmospheric pressure. *Fluid Phase Equilibria*, *242*(2), 147–153.