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Simulation of Fermentation Compounds for Bioethanol Production Using Different Separating Agents

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ABSTRACT

This study focuses on the simulation of ethylene glycol $(C_2H_6O_2)$ – glycerol $(C_3H_8O_3)$ and ethylene glycol $(C_2H_6O_2)$ – calcium chloride $(CaCl_2)$ as separating agents in bioethanol production from fermentation effluent. The entire process was simulated using Aspen HYSYS V7.3 software, but the main focus is the extractive distillation where the mixture compounds were utilised. Response Surface Methodology (RSM) was used to optimise the process variables in extractive distillation column with the separating agent ethylene glycol, temperature, solvent to feed molar ratio and reflux ratio. Non-random two-liquid (NRTL) model was used for activity coefficients of mixture from Aspen properties databank. Results show that both mixture compounds values on solvent to feed molar ratio, reflux ratio and reboiler energy consumption were slightly different as separating agent temperature maintained at 80 oC and ethanol composition in distillate was 99.89 mole%. The separating agents show that better ethanol-water separation with lower energy consumption compared with a well-known single compound such as ethylene glycol. Thus, this study is important to improve extractive distillation column operating conditions by studying the effect of mixture compounds as separating agents in bioethanol production.

Keywords: Calcium chloride, extractive distillation, ethylene glycol, glycerol, simulation

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INTRODUCTION

Bioethanol is a promising alternative new energy to ensure adequate supply of low cost fuel that burns completely and without unwanted exhaust emissions (Manivannan and Narendhirakannan, 2015; Govumoni et al., 2013; Nikzad et al., 2012). The current source of bioethanol generation is crop as well as agricultural residues and they serve as a cheap and abundant feedstock to produce bioethanol at reasonable cost (Won et al., 2012; Balat, 2011; Goh et al., 2010; Hii et al., 2010; Fenning et al., 2008; Basiron, 2005). Bioethanol is generated from biomass by hydrolysis process, followed by sugar fermentation process. Biomass contains a complex combination of carbohydrate polymers from plant cell walls known as cellulose, hemi cellulose and lignin. Sugar is extracted from biomass by pre-treating it with acids or enzymes to reduce the particle sizes and to opening up the fibrous structure (Nitayavardhana et al., 2010). The cellulose and hemi cellulose are broken down by enzymes or acids into glucose, and then into bioethanol by anaerobic fermentation (Ajibola et al., 2012).

However, in alcoholic fermentation process, a large quantity of polluted water is generated due to presence of oxygen (Nikzad et al., 2012; Lin et al., 2012). Thus, purification process for final fermented product of bioethanol is required to recover remaining ethanol with the aid of third component, in this case extractive compounds are useful in order to produce dry bioethanol production (Anwar & Neni, 2012; Gil et al., 2008).

There are many alternatives to distillation for recovering ethanol from aqueous solutions, such as membrane permeation, vacuum stripping, gas stripping, solvent extraction, adsorption and various hybrid processes (Offeman et al., 2008). For ethanol dehydration, extractive distillation is commonly used to recover ethanol. Extractive distillation is used to separate azeotropic mixture by applying third solvent, known as entrainer or separating agent to alter the relative volatility of the compounds of the mixture (Gil et al., 2008). However, many studies have been done using a pure component as entrainer to improve the value of bioethanol (Gil et al., 2014; Gil et al., 2012; Llano-Restrepo & Aguilar-Arias, 2003). Hence, the purpose of this work was to investigate the effect of entrainer as solvent in extractive distillation process of bioethanol from fermentation effluent in order to produce high purity bioethanol. Optimisation of ethanol dehydration is also important due to high energy consumption and capital investment cost (Bastidas et al., 2010).

There are three main objectives for this study. First, to develop a simulation process of bioethanol production from fermentation effluent using Aspen HYSYS V7.3 software and the main focus for the simulation is the extractive distillation. Second, to study the effect of process variables in extractive distillation which are separating agents concentration glycerol $(C_3H_8O_3)$ and calcium chloride $(CaCl_2)$ in ethylene-glycol $(C_2H_6O_2)$, feed temperature, solvent to feed molar ratio and reflux ratio (Gil et al., 2008; Gil et al., 2014). The responses are ethanol composition in distillate and energy consumption by reboiler. Third, to design an experiment using response surface methodology (RSM) for analysing the contribution of process variables in order to optimise the extractive distillation column.

METHODS

Process Flow

There are two main steps to obtain dry ethanol: removal of solid and liquid substance from effluent and bioethanol refining. The bioethanol dehydration process is shown in Figure 1.



Figure 1. Process flow diagram of bioethanol production from fermentation effluent

Materials

The fermented feed proposed in this process contains yeast, sucrose, ethanol and water. By taking composition of dissolved carbohydrate from molasses and carbohydrate conversion into ethanol entering distillation column, the proportion of water and ethanol are be 83% and 10% respectively (75% sugar converted) respectively. The rest of the unconverted sugar consists of sucrose (4%), glucose and fructose. The remaining is assumed as the equivalent amount of yeast. To conclude, the compositions are 10% ethanol, 83% water, 4% sucrose and 3% yeast (Amin et al., 2013; Arvinius et al., 2010). The components are set according to their name in HYSYS except for yeast which is named carbon. Carbon serves the same function as yeast that can settle in the rotary drum vacuum filter.

Process Description

Starting from rotary drum vacuum filter, the temperature of the unit is 25°C and yeast is removed from the effluent that leaves ethanol, water and sucrose as the by-product. The stream is feed to flash distillation where the feed temperature is adjusted to 170°C and sucrose is eliminated. Then, ethanol and water are fed to fractional distillation and the feed temperature is lowered to

78.1°C. The column parameters such as number of stages, distillate flow and reflux ratio are 10, 100 kmol/hr and 0.3 respectively and adjusted until 88% ethanol is achieved in the top stream. Lastly, ethanol-water or azeotrope mixture enters the extractive distillation and it is mixed with the separating agent. The feed temperature is maintained at 78.1°C. Other parameters such, as distillate rate, azeotrope molar flow, number of theoretical stages, separating agent stage and azeotrope stage are 86.8 kmol/hr, 100 kmol/hr, 18, 3 and 12 respectively. Table 1 shows the initial process variables for extractive column (Gil et al., 2014; Gil et al., 2008).

Table 1Initial value of process variables for extractive column

Parameter	Initial value
Separating agent concentration in ethylene glycol, mole%	$C_3H_8O_3 = 0.4$; $CaCl_2 = 0.05$
Separating agent temperature, °C	80
Solvent-feed ratio	0.8
Reflux ratio	0.5

Simulation Process

Aspen HYSYS V7.3 software is used to develop simulation for bioethanol production from fermentation effluent, while *non-random two-liquid* (NRTL) thermodynamic model is used to calculate the activity coefficients for the mixture (Llano-Restrepo and Aguilar-Arias, 2003; Gil et al., 2012; Gil et al., 2014; Lars, 2012). Initial data as discussed previously, is used and adjusted in the simulation to satisfy the end result.

Statistical Analysis

In order to study the interaction between e process variables - third component feed temperature, solvent concentration in ethylene glycol ($C_2H_6O_2$) – glycerol ($C_3H_8O_3$) and ethylene glycol ($C_2H_6O_2$) – calcium chloride (CaCl₂), solvent to feed molar ratio and reflux ratio, a statistical analysis is required, and to study the interaction between variables, considering the composition of ethanol in distillate and energy consumption by reboiler in order to optimise the process and to obtain anhydrous ethanol. RSM in Design Expert 7 software is used to perform the process variables relation (Myers & Montgomery, 1995).

RESULTS AND DISCUSSION

Simulation

The simulation is done by parts based on HYSYS and Aspen Properties databank at steady state (Julio, n.d.; Smejkal & Soos, 2002; Seider et al., 1999). The first part is the rotary drum vacuum filter until fractional distillation, the thermodynamic model general NRTL is used in HYSYS. The second part is extractive and recovery distillation column where NRTL is

used to estimate the activity coefficients of mixture from Aspen properties. The reason is that carbon may not be pure component as solid form in Aspen properties. Hence, separation of carbon cannot be done. General NRTL is performed because it analyses the system according to molecular interaction. However, carbon atom is considered as solid. Additionally, the NRTL model is the best fit for ethanol-water system or exhibits phase splitting (Ngema, 2010). Figure 2 shows the simulation process of bioethanol production from fermentation effluent. In Figure 2, the blue line indicates the simulation is working. The red dash line region shows an extractive distillation where ethanol-water separation occurs - the focus of this study. The bottom distillate for recovery column is not recycled into the extractive column in order to maintain the composition and temperature of initial separating agent entering the column as it is studied in a particular range.



Figure 2. Simulation process of bioethanol production from fermentation effluent

In order to study the effect of process variables related to separating agent in extractive distillation process, these variables are set in a range, solvent concentration in $C_2H_6O_2$ for $C_3H_8O_3$ is 0.3 to 0.7; meanwhile CaCl₂ is 0.05 to 0.1. The separating agent temperature, solvent to feed molar ratio and reflux ratio are 60 to 110°C, 0.3 to 1 and 0.3 to 0.8 respectively. As for responding variables, molar fraction of ethanol in distillate and reboiler energy consumption, kJ/kg of ethanol is chosen. The four ranges of process variables are important which are used in Design Expert 7.0 to help in interpretation of the multi-factor to produce comprehensive data (Buxton, 2007; Myers and Montgomery, 1995). The responses values are keyed in based on Aspen HYSYS V7.3 result according to values of factors as shown in Table 2 and 3.

Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2
$C_3H_8O_3$ concentration in $C_2H_6O_2$, mole fraction	Separating agent temperature, °C	Solvent-feed molar ratio	Reflux ratio	Molar fraction of ethanol in distillate	Reboiler energy consumption, (kJ/kg of ethanol)
0.50	110.00	0.65	0.55	0.999	1473.22
0.50	85.00	0.65	0.55	0.9992	1552.91
0.70	60.00	0.30	0.30	0.9807	1218.12
0.30	60.00	0.30	0.30	0.9711	1203.87
0.70	60.00	1.00	0.30	0.9999	1723.93
0.30	110.00	1.00	0.30	0.9956	1361.24
0.30	60.00	0.30	0.80	0.9804	1629.71
0.70	60.00	1.00	0.80	1.0000	2146.29
0.50	85.00	0.65	0.55	0.9992	1551.91
0.50	85.00	0.65	0.55	0.9992	1551.91
0.50	85.00	0.65	0.30	0.9975	1336.84
0.70	110.00	0.30	0.80	0.9864	1571.86
0.50	85.00	0.65	0.55	0.9992	1552.41
0.30	110.00	0.30	0.60	0.9803	1568.10
0.70	110.00	1.00	0.80	0.9999	1898.47
0.30	60.00	1.00	0.30	0.9994	1595.05
0.50	85.00	0.30	0.55	0.9821	1393.68
0.50	85.00	1.00	0.55	0.9999	1752.19
0.50	85.00	0.65	0.80	0.9993	1765.57
0.50	60.00	0.65	0.55	0.9992	1625.97
0.50	85.00	0.65	0.55	0.9992	1552.66
0.70	85.00	0.65	0.55	0.9996	1583.79
0.30	60.00	1.00	0.80	0.9998	2018.76
0.70	60.00	0.30	0.80	0.9863	1648.01
0.30	85.00	0.65	0.55	0.9983	1516.40
0.70	110.00	0.30	0.30	0.9749	1142.97
0.70	110.00	1.00	0.30	0.9994	1473.24
0.50	85.00	0.65	0.55	0.9992	1553.16
0.30	110.00	1.00	0.80	0.9998	1799.40
0.30	110.00	0.30	0.30	0.9658	1135.09

Table 2 Design process variables data for $C_2H_6O_2$ and $C_3H_8O_3$

The tables show that reboiler energy consumption increases as molar fraction of ethanol in distillate increases. The result is analysed to verify the factors of significant effect toward the responses. The analysis is called ANOVA (analysis of variance) used as alternative method to highlight the active factor (Myers & Montgomery, 1995).

Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Separating agent temperature, °C	Solvent-feed molar ratio	Reflux ratio	Molar fraction of ethanol in distillate	Reboiler energy consumption, (kJ/kg of ethanol)
0.08	60.0	0.65	0.55	0.9951	1535.74
0.05	110.00	1.00	0.30	0.9870	1284.96
0.08	85.00	0.30	0.55	0.9689	1372.16
0.10	85.00	0.65	0.55	0.9937	1472.14
0.05	60.00	1.00	0.30	0.9976	1493.49
0.08	85.00	0.65	0.80	0.9962	1687.72
0.05	110.00	1.00	0.80	0.9992	1724.04
0.10	60.00	1.00	0.30	0.9967	1484.72
0.08	85.00	0.65	0.55	0.9943	1474.28
0.08	85.00	0.65	0.55	0.9943	1474.28
0.10	110.00	1.00	0.30	0.9850	1282.54
0.08	85.00	1.00	0.55	0.9985	1610.51
0.05	60.00	0.30	0.30	0.9622	1190.68
0.08	85.00	0.65	0.55	0.9943	1474.28
0.10	60.00	0.30	0.30	0.9594	1192.05
0.10	60.00	1.00	0.80	0.9992	1911.43
0.08	85.00	0.65	0.55	0.9942	1473.29
0.05	60.00	0.30	0.80	0.9742	1620.43
0.10	60.00	0.30	0.80	0.9716	1612.98
0.10	110.00	0.30	0.30	0.9553	1136.25
0.05	110.00	0.30	0.80	0.9737	1561.26
0.05	85.00	0.65	0.55	0.9950	1474.54
0.08	85.00	0.65	0.55	0.9943	1471.77
0.08	85.00	0.65	0.30	0.9845	1255.43
0.05	110.00	0.30	0.30	0.9577	1134.72
0.10	110.00	1.00	0.80	0.9989	1722.22
0.08	85.00	0.65	0.55	0.9942	1472.77
0.10	110.00	0.30	0.80	0.9711	1562.23
0.05	60.00	1.00	0.80	0.9994	1919.94
0.08	110.00	0.65	0.55	0.9928	1408.09

Table 3 Design process variables data for $C_2H_6O_2$ and $CaCl_2$

In ANOVA, if the p-value is less than 0.05, it means the model (or term) is statistically significant. A value of more than 0.10 indicates the model is not significant and if it is in between 0.05 and 0.10, then the model may be significant (Ngema, 2010; Anderson & Whitcomb, 2005). The analysed result is a quadratic model that allows for curvature in the effect of a control on the response (Buxton, 2007; Myers & Montgomery, 1995). Tables 4 shows the ANOVA for response surface quadratic model on both responses.

Source			Response	1				Respo	nse 2	
22 Inoc	Sum of squares	df	Mean square	F value	p-value Prob > F	Sum of squares	df	Mean square	F Value	p-value $Prob > F$
Model	3.012 x 10 ⁻³	14	2.152 x 10 ⁻⁴	139.13	< 0.0001	1.583 x 10 ⁶	14	1.131 x 10 ⁵	17672.78	< 0.0001
A	7.442 x 10 ⁻⁵	1	7.442 x 10 ⁻⁵	48.13	< 0.0001	18499.33		18499.33	2891.49	< 0.0001
В	1.369 x 10 ⁻⁵	1	1.369 x 10 ⁻⁵	8.86	0.0094	1.067×10^{5}		1.067 x 10 ⁵	16683.45	< 0.0001
C	1.916 x 10 ⁻³	1	1.916 x 10 ⁻³	1238.89	< 0.0001	5.894 x 10 ⁵		5.894 x 10 ⁵	92123.70	< 0.0001
D	1.275 x 10 ⁻⁴	1	1.275×10^{-4}	82.43	< 0.0001	8.260 x 10 ⁵	1	8.260 x 10 ⁵	1.291 x 10 ⁵	< 0.0001
AB	5.256 x 10 ⁻⁷	1	5.256 x 10 ⁻⁷	0.34	0.5685	274.31	-	274.31	42.88	< 0.0001
AC	4.258 x 10 ⁻⁵	1	4.258 x 10 ⁻⁵	27.53	< 0.0001	11198.95	1	11198.95	1750.42	< 0.0001
AD	7.156 x 10 ⁻⁶	1	7.156 x 10 ⁻⁶	4.63	0.0482	12.86		12.86	2.01	0.1767
BC	2.806 x 10 ⁻⁶	1	2.806 x 10 ⁻⁶	1.81	0.1980	28054.58		28054.58	4384.99	< 0.0001
BD	1.463 x 10 ⁻⁵	1	1.463 x 10 ⁻⁵	9.46	0.0077	34.51		34.51	5.39	0.0347
CD	7.966 x 10 ⁻⁵	1	7.966 x 10 ⁻⁵	51.51	< 0.0001	4.18		4.18	0.65	0.4314
\mathbf{A}^2	8.243 x 10 ⁻⁷	1	8.243×10^{-7}	0.53	0.4766	0.43	-	0.43	0.067	0.7986
\mathbf{B}^2	$4.441 \text{ x } 10^{-7}$	1	4.441×10^{-7}	0.29	0.5999	9.24	1	9.24	1.47	0.2438
C^2	1.878 x 10 ⁻⁴	1	1.878 x 10 ⁻⁴	121.45	< 0.0001	1189.91		1189.91	185.99	< 0.0001
D^2	3.216 x 10 ⁻⁶	1	3.216 x 10 ⁻⁶	2.08	0.1699	0.23		0.23	0.036	0.8530
Whereb both equ	y, $A = C_3 H_8 O_3 co$ lations	ncentr	ation in C ₂ H ₆ O ₂ ,	mole fracti	on; B = Separating a	igent temperature	°C; C	c = Solvent-feed	l molar ratio and	l D = Reflux ratio for

Table 4 ANOVA for $C_2H_6O_2$ - $C_3H_8O_3$ on responses

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The ANOVA analysis for $C_2H_6O_2$ - $C_3H_8O_3$ of responses with variation of factors is represented by polynomial equations 1 and 2.

 $X = 1 + 2.033 \times 10^{-3} \text{ A} - 8.722 \times 10^{-4} \text{ B} + 0.010 \text{ C} + 2.661 \times 10^{-3} \text{ D} + 1.813 \times 10^{-4} \text{ A} \text{ B} - 1.631 \times 10^{-3} \text{ A} \text{ C} - 6.687 \times 10^{-4} \text{ A} \text{ D} + 4.188 \times 10^{-4} \text{ B} \text{ C} + 9.563 \times 10^{-4} \text{ B} \text{ D} - 2.231 \times 10^{-3} \text{ C} \text{ D} - 5.640 \times 10^{-4} \text{ A}^2 - 4.140 \times 10^{-4} \text{ B} 2 - 8.514 \times 10^{-3} \text{ C}^2 - 1.114 \times 10^{-3} \text{ D}^2$ (1)

 $X = 1552 + 32.06 \text{ A} - 77.01 \text{ B} + 180.95 \text{ C} + 214.21 \text{ D} - 4.14 \text{ A} \text{ B} + 26.46 \text{ A} \text{ C} - 0.90 \text{ A} \text{ D} - 41.87 \text{ B} \text{ C} + 1.47 \text{ B} \text{ D} - 0.51 \text{ C} \text{ D} - 0.41 \text{ A}^2 - 1.91 \text{ B} 2 + 21.43 \text{ C}^2 - 0.30 \text{ D}^2$ (2)

Based on Table 4 for reboiler energy consumption, the four factors show significant p-value that is less than 0.05. In other words, the effects are significant for the response (CAMO Software AS, 2016). As for Table 4 for molar fraction of ethanol in distillate, only separating agent feed temperature is not significant, and it can be concluded that the investigated factor does not affect the response. In contrast, the concentration of calcium chloride in ethylene glycol is not showing significant result for both responses as can be seen in Table 5.

The ANOVA analysis for $C_2H_6O_2$ - $CaCl_2$ of responses with variation of factors is represented by polynomial equations 3 and 4.

 $X = 0.99 - 8.389 \times 10^{-4} \text{ A} - 1.928 \times 10^{-3} \text{ B} + 0.015 \text{ C} + 5.45 \times 10^{-3} \text{ D} - 5 \times 10^{-5} \text{ A} \text{ B} + 4.375 \text{ x}$ $10^{-4} \text{ A} \text{ C} + 1.5 \times 10^{-4} \text{ A} \text{ D} - 8.25 \times 10^{-4} \text{ B} \text{ C} + 1.838 \times 10^{-3} \text{ B} \text{ D} - 1.6 \times 10^{-3} \text{ C} \text{ D} + 3.535 \times 10^{-4} \text{ A}^{-2} - 4.649 \times 10^{-5} \text{ B}^{2} - 0.01 \text{ C}^{2} - 3.646 \times 10^{-3} \text{ D}^{2}$ (3)

 $X = 1473.19 - 1.53 \text{ A} - 63.62 \text{ B} + 113.95 \text{ C} + 214.86 \text{ D} + 1.35 \text{ A} \text{ B} - 1.12 \text{ A} \text{ C} - 0.53 \text{ A} \text{ D} - 35.88 \text{ B} \text{ C} + 1.72 \text{ B} \text{ D} + 1.80 \text{ C} \text{ D} + 0.40 \text{ A}^2 - 1.03 \text{ B}^2 + 18.40 \text{ C}^2 - 1.37 \text{ D}^2$ (4)

Both solvents with the four factors studied has shown a model with significant effect on the response molar fraction of ethanol in distillate and reboiler energy consumption. Then, model graphs can illustrate the relationship between factors and responses in 3D surface. Two variables and one response for three tests are selected to standardise the study on the effect for both mixture compounds as separating agent.

Effect of Separating Agent Concentration in C₂H₆O₂

The effect of separating agent concentration is analysed by fixing two factors at constant such as separating agent temperature, and solvent to feed ratio, 80°C and 0.65 respectively. Figure 3 shows the ethanol in distillate curvature purity increases moderately from the lowest value of reflux ratio and glycerol to the highest. Figure 4 shows a linear behaviour of negative slope when the reflux ratio value decreases at constant glycerol concentration in $C_2H_6O_2$. Meanwhile, increasing the value of concentration of $C_3H_8O_3$ in $C_2H_6O_2$ consumes higher energy in reboiler at constant reflux ratio.

Source			Respoi	nse 1				Respo	nse 2	
221000	Sum of squares	df	Mean square	F value	p-value $Prob > F$	Sum of squares	df	Mean square	F Value	p-value Prob > F
Model	5.902 x 10 ⁻³	14	4.215 x 10 ⁴	411.96	< 0.0001	1.160 x 10 ⁶	14	82885.31	10081.05	< 0.0001
A	1.267×10^{-5}	1	1.267 x 10 ⁻⁵	12.38	0.0031	42.02	1	42.02	5.11	0.0391
В	6.689 x 10 ⁻⁵	1	6.689 x 10 ⁻⁵	65.37	< 0.0001	72854.29	1	72854.29	8861.01	< 0.0001
C	3.972×10^5	1	3.972 x 10 ⁻³	3882.00	< 0.0001	2.337×10^{5}	1	2.337 x 10 ⁵	28427.01	< 0.0001
D	5.346 x 10 ⁻⁴	1	5.346 x 10 ⁴	522.48	< 0.0001	8.309 x 10 ⁵	1	8.309 x 10 ⁵	1.011 x 10 ⁵	< 0.0001
AB	$4 \ge 10^{-8}$	1	$4 \ge 10^{-8}$	0.039	0.8459	29.21	1	29.21	3.55	0.0790
AC	3.063 x 10 ⁻⁶	1	3.063×10^{-7}	2.99	0.1041	20.09	1	20.09	2.44	0.1389
AD	3.6×10^{-7}	1	3.6×10^{-7}	0.35	0.5619	4.53	1	4.53	0.55	0.4692
BC	1.089 x 10 ⁻⁵	1	1.089 x 10 ⁻⁵	10.64	0.0052	20601.88	1	20601.88	2505.74	< 0.0001
BD	5.402 x 10 ⁻⁵	-	5.402 x 10 ⁻⁵	52.79	< 0.0001	47.11	-	47.11	5.73	0.0302
CD	4.096 x 10 ⁻⁵	-	4.096 x 10 ⁻⁵	40.03	< 0.0001	51.60	-	51.60	6.28	0.0243
\mathbf{A}^2	$3.238 \text{ x } 10^{-7}$	1	3.238×10^{-7}	0.32	0.5821	0.41	1	0.41	0.050	0.8260
B^2	5.6 x 10 ⁻⁹	1	5.6 x 10 ⁻⁹	5.473 x 10-3	0.9420	2.74	1	2.74	0.33	0.5724
C^2	2.747 x 10-4	1	2.747×10^{4}	268.43	< 0.0001	876.87	1	876.87	106.65	< 0.0001
D^2	3.445 x 10 ⁻⁵	1	3.445 x 10 ⁻⁵	33.67	< 0.0001	4.86	1	4.86	0.59	0.4541
Whereb	y, $A = CaCl_2 \text{ con}$	centra	ation in $C_2H_6O_2$,	, mole fraction;	B = Separating age	nt temperature, °(C; C =	: Solvent-feed m	nolar ratio; D = I	keflux ratio

Table 5 ANOVA for $C_2H_6O_2$ - $CaCl_2$ on responses

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Figure 3. Effect of C₃H₈O₃ concentration in C₂H₆O₂ and reflux ratio on response 1



Figure 4. Effect of C₃H₈O₃ concentration in C₂H₆O₂ and reflux ratio on response 2

For $C_2H_6O_2$ and $C_3H_8O_3$, the ethanol in distillate purity increases moderately until it reaches the maximum concentration from the lowest value of reflux ratio and $C_3H_8O_3$ concentration until the highest. In terms of energy, it presents a linear behaviour of negative slope when reflux ratio value decreases at constant $C_3H_8O_3$ concentration and increasing value of $C_3H_8O_3$ concentration consumes higher energy at reboiler by constant reflux ratio. The most adequate composition of $C_3H_8O_3$ in $C_2H_6O_2$ is between 40 until 50 mol% of $C_3H_8O_3$. Hence, 40 mol% of $C_3H_8O_3$ is chosen.

The reduction of energy consumption for reboiler is explained by lowering the reflux ratio compared with $C_3H_8O_3$ concentration. Therefore, the most adequate composition of $C_3H_8O_3$ in $C_2H_6O_2$ is between 40 until 50 mol% of glycerol. Hence, 40 mol% of $C_3H_8O_3$ is chosen. This concentration is within the range as reported by Gil et al. (2014) and by setting 60 mol% of

 C_2H6O_2 and 40 mol% of $C_3H_8O_3$, a distillate in steam with 0.999 or higher, molar composition of ethanol can be achieved.

Figures 5 and 6 show the CaCl₂ concentration increases at constant reflux ratio, ethanol in distillate slightly decreases and energy consumption slope almost approaches zero. This pattern of CaCl₂ concentration affecting the distillate purity is also reported by Gil et al., (2008) that distillate purity is higher for the 0.05 and 0.075 g of CaCl₂/mL of C₂H6O₂ compared with 0.075 and 0.1 g of CaCl₂/mL of C₂H6O₂. Energy consumption can be minimised as benefit of salt in solvent that helps to reduce number of theoretical stages needed for the separation, which is lower than only using C₂H6O₂ from previous study. Presence of CaCl₂ combined with low reflux ratio diminishes the amount of energy consumption. Hence, the CaCl₂ concentration is fixed at 0.075 mol% to achieve lower energy utilisation at reboiler.



Figure 5. Effect of CaCl₂ concentration in C₂H₆O₂ and reflux ratio on response 1



Figure 6. Effect of CaCl₂ concentration in C₂H₆O₂ and reflux ratio on response 2

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Effect of Separating Agent Feed Temperature

The initial feed temperature of separating agent has a significant effect on purity of ethanol in distillate and energy utilisation compared with reflux ratio. Increasing the temperature to separate the agent entering the column requires high reflux ratio to reach high ethanol composition in distillate as shown in Figures 7, 8, 9, and 10. This is because as the temperature of separating agent increases, water at the top stage vaporises and it condenses together with ethanol that leads to reduction of ethanol purity (Gil et al., 2008). Thus, higher reflux ratio is needed to balance this effect. For both cases, 80°C was used as the temperature of separating agent.



Figure 7. Effect of C₂H₆O₂-C₃H₈O₃ temperature and reflux ratio on response 1



Figure 8. Effect of C₂H₆O₂-C₃H₈O₃ temperature and reflux ratio on response 2

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Figure 9. Effect of C₂H₆O₂- CaCl₂ temperature and reflux ratio on response 1



Figure 10. Effect of C₂H₆O₂- CaCl₂ temperature and reflux ratio on response 2

Effect of Solvent to Feed Molar Ratio

The concentration of $C_3H_8O_3$ and $CaCl_2$ in $C_2H_6O_2$ was chosen constant at 0.4 mol% and 0.075 mol% respectively and the separating agent temperature was set at 80°C. Based on Gil et al., (2008), solvent to feed ratio causes a direct effect on the distillate purity. In order to evaluate this effect, the solvent to feed molar ratio with a of range 0.3 to 1.0 is analysed. Figures 11, 12, 13, and 14 represent the results of the assessment.



Figure 11. Effect of C₂H₆O₂ -C₃H₈O₃ to feed ratio and reflux ratio on response 1



Figure 12. Effect of C₂H₆O₂ -C₃H₈O₃ to feed ratio and reflux ratio on response 2

Different values of solvent to feed ratio at constant reflux ratio can either increase or reduce energy consumption. In order to maintain the solvent to feed ratio with increasing reflux ratio causes increase in energy consumption. However, by making solvent to feed ratio constant and setting the reflux ratio until targeted distillate is achieved needs more energy in reboiler. For this reason, the reflux ratio must be performed in the lowest value, hence, the solvent to feed ratio can be controlled to obtain desired ethanol purity with low energy consumption.



Figure 13. Effect of C₂H₆O₂-CaCl₂ to feed ratio and reflux ratio on response 1



Figure 14. Effect of C2H6O2-CaCl2 to feed ratio and reflux ratio on response 2

Summary of the Operating Conditions

A summary of the operating conditions achieved for the extractive column using the two mixtures is shown in Table 6. Using only ethylene glycol as solvent in extractive distillation to separate ethanol-water, the amount of energy consumed to produce dry ethanol is 1760 kJ/kg of ethanol (Meirelles et al., 1992). Based on Table 6, the amount of energy required to obtained dry ethanol using proposed mixture is lower than using ethylene glycol as solvent

alone. The relative volatility of ethanol - water when using ethylene glycol mixture with CaCl2 with salt concentration of 0.2 g/ml of solvent is 2.56 rather than only $C_2H_6O_2$ is 1.85 (Lei et al., 2003). This is due to the presence of ions in solid salt for a stronger effect compared with molecules of a liquid agent including both in the strength of attractive forces they can apply on feed component molecules and degree of selectivity applied. In contrast, the strength of using glycerol in $C_2H_6O_2$ is primarily physical force including hydrogen bonding. Using mixture of liquid solvents, the most important criteria is relative volatility. Hence, finding a better additive to increase the relative volatility of ethanol – water leads to decrease in the solvent to feed ratio. Furthermore, the energy consumed at reboiler to reach about 99.9% molar concentration of ethanol in distillate using CaCl₂ is higher compared with glycerol. The difference is due to solvent to feed molar ratio. This is because increasing the reflux ratio leads to the dilution of solvent, reducing its function on relative volatility of the mixture ethanol-water. Thus, high solvent to feed ratio is necessary to offset the condition (Gil et al., 2008).

Parameter		Solvent	
	C ₃ H ₈ O ₃	CaCl ₂	
Azeotrope feed flow (kmol/h)		100	
Separating agent flow (kmol/h)		80	
Distillate flow (kmol/h)		86.8	
Temperature of azeotrope feed (°C)		78.1	
Number of theoretical stages		18	
Pressure (atm)		1	
Separating agent feed stage		3	
Mole % of solvent in ethylene glycol	0.40	0.075	
Solvent to feed ratio	0.74	0.87	
Temperature of separating agent (°C)		80	
Molar reflux ratio	0.4	0.5	
Mole % of ethanol in distillate	99.89	99.89	
Reboiler energy consumption in extractive column (kJ/kg of ethanol)	1470.85	1527.05	

Table 6

Operating condition of extractive column for $C_2H_6O_2$ - $C_3H_8O_3$ and $C_2H_6O_2$ - $CaCl_2$

CONCLUSION

In this study, four parameters which are separating agent concentration in $C_2H_6O_2$, separating agent to feed molar ratio, separating agent feed temperature and reflux ratio are analysed and optimised. It can be concluded that adding a salt and $C_3H_8O_3$ in liquid solvent provide good separation ability to achieve high ethanol in distillate with lower energy consumption compared with liquid solvent alone. Additionally, reflux ratio has shown a significant effect corresponding with energy consumption whereby as reflux ratio increases, energy required in reboiler also increases. So, reflux ratio must be performed at lowest possible value along with fixed additional solvent in $C_2H_6O_2$ and temperature at 80°C. At the same time, solvent to feed

molar ratio has become the manipulating variable for balancing changes in column operating conditions that enables the regulation of the distillate purity and reboiler energy consumption.

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