

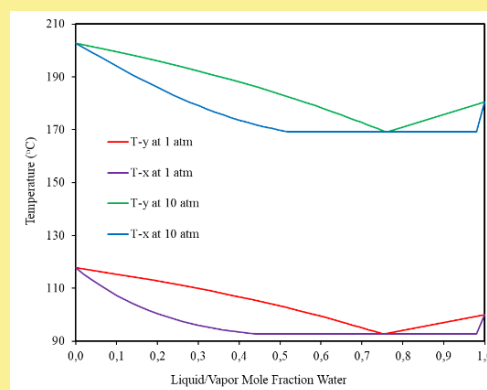
Applied of Phase Equilibrium to Simulate Pressure Swing Distillation of 1-Butanol + Water Mixtures

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Abstract— Butanol as fuel mixtures has been sufficiently proven to be able to reduce NO_x and PM gas emissions. Water is a by-product produced in the butanol production process. The mixture of butanol and water system contains an azeotrope which cannot be separated using conventional distillation. Azeotropic distillation techniques have been developed quite a lot, one of which is Pressure Swing Distillation (PSD). In this study, the computational simulation was performed using commercial software Aspen Plus and thermodynamic model UNIQUAC. The configuration of operating conditions and equipment in the PSD for the 1-butanol and water system has effects on the need for supporting equipment and its techno-economic analysis. From the results of this simulation study, it is obtained that the PSD configuration with a High Pressure (HP) to Low Pressure (LP) design can obtain a 1-butanol product with a purity of 99.98% with a TAC (Total Annual Cost) of 0.64 (10g USD/year) and the cost of separating 1-butanol is 0.085 USD/kg and the cost for energy is 0.03 USD/kg.



Keywords— Azeotrope, Distillation, Phase Equilibrium, Pressure Swing, 1-butanol

I. INTRODUCTION

Butanol is known to be used as a chemical with many uses, one of which is as a fuel. Butanol has better potential value than ethanol because it is non-volatile and has a higher flash point and lower vapor pressure, contains more energy, is not hygroscopic and can be easily mixed with gasoline in any proportion. Additionally, butanol and gasoline have similar energy contents. Butanol can be used directly or mixed with gasoline or diesel [1].

Butanol is used as biofuel to meet EURO emission standards. Previous research by Lapuerta, M. et. al. [2] and Luis Tipanluisa et. al. [3] discussed that the use of a mixture of n-butanol and diesel in diesel engines could reduce exhaust emissions, especially NO_x, CO and PM and increase the engine's thermal efficiency.

Butanol used as a fuel oil mixture has a specification of 99.8% by weight. One of the separation methods to obtain products with high purity is distillation, separating the components in the form of a mixture by boiling and collecting the condensed steam. However, more than 50% of the total energy requirements are used in distillation in

the hope of obtaining a product with a purity of 80-90% to close to 100%. Very large energy consumption due to low thermodynamic efficiency [4].

The mixture of 1-Butanol + Water will form a partially miscible mixture due to the difference in polarity [5]. Due to non-polar and polar interactions, 1-Butanol has limited solubility in water. Because of this, it will form two separate layers, 1-Butanol will be in the top layer because it is more non-polar, while water will be in the bottom layer because it is more polar. In heterogeneous azeotropic conditions, when the incompletely dissolved liquid mixture boils, the vapor formed has a different composition from the liquid mixture, resulting in changes in the properties of the mixture during distillation. In general, heterogeneous azeotropes are more difficult to separate than homogeneous azeotropes due to the compositional differences between the liquid and vapor phases. Therefore, this mixture will form Vapor Liquid-Liquid Equilibrium.

Apart from that, this mixture will also form an azeotrope point so that conventional distillation is not effective to apply because of the large number of theoretical plates and

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the large reflux ratio which will impact equipment investment and operations [6]. One of the Azeotrope distillation technologies is Pressure Swing Distillation which is the answer to separating azeotrope mixtures. The use of simulation software such as ASPEN PLUS has been widely used to obtain optimum results. This type of approach is quite effective as an initial step in determining design [7]. In this research, process simulation and optimization were carried out to obtain the optimum results using the Pressure Swing Distillation method. The effect of pressure on configuration scheme process and its techno-economic value were studied in this study.

II.METHOD

The software used in this research is ASPEN PLUS. The material properties are shown in Table 1. The fluid package used in this study was NRTL thermodynamic model with the parameter interaction obtained from the software databanks shown in Table 2.

TABLE 1.
MATERIAL PROPERTIES

Component	1-Butanol	Water
Specific Gravity at 60°F	0.8138	1
Normal BP (°C)	118.75	100
Pc (bar)	44.14	220.64
Tc (°C)	289.95	373.94
ω	0.588	0.344
Solubility in water 25°C	73 g/L	-
Polarity	Non-Polar	Polar

Determination of feed refers to research by Chakraborty (2015) with the Guebert reaction mechanism with the conversion of 37% ethanol using a nickel catalyst. This approach was also carried out in previous research [8] by taking a 1-Butanol composition of 0.35 (mass fraction). The feed and product specification are listed in Table 3.

TABLE 2.
NRTL MODEL AND PARAMETER INTERACTION OF 1-BUTANOL (1) + WATER (2)

Parameters			
a_{12}	-2.405	b_{12}	763.869
a_{21}	13.1102	b_{21}	3338.95
α	0.3		
Model			
$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right)$			
$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$			
$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$			

TABLE 3.
FEED AND PRODUCT SPECIFICATIONS

Parameter	Specification	
	Feed	Product
1-Butanol mass fraction	0.35	0.998
Water mass fraction	0.65	0.002
Pressure	2 atm	1 atm
Temperature	70°C	25°C

The effect of pressure configuration process was categorized in two cases, that were Case 1, Low Pressure to High Pressure, and Case 2, High Pressure to Low Pressure. The basis design was 100 kmol/h of the feed stream. The high and low operating pressure on PSD were 1 and 10 atm, respectively.

Analysis of economic calculations to predict TAC (Total Annual Cost) [9]. Prices for other equipment such as pumps, decanters and separators are close to APEA (Aspen Process Economic Analyzer). The economic parameters used in this study were shown in Table 4.

TABLE 4.
ECONOMIC EVALUATION PARAMETERS

Condensers		
Heat-transfer coefficient	0.852	kW/(K.m ²)
Typical differential Temperature	13.9	K
Capital Cost	7296(area) ^{0.65}	Area in m ²
Reboilers		
Heat-transfer coefficient	0.568	kW/(K.m ²)
Typical differential Temperature	34.8	K
Capital Cost	7296(area) ^{0.65}	Area in m ²
Column vessel capital cost	17640(D) ^{1.066} (L) ^{0.802}	D and L in meters
Energy Cost		
LP Steam (6 bar, 160°C)	\$7.78 / GJ	
MP Steam (11 bar, 184°C)	\$8.22 / GJ	
HP Steam (42 bar, 254°C)	\$9.88 / GJ	
Electricity	\$16.8/GJ	
TAC	$\frac{\text{Capital Cost}}{\text{Payback Period}} + \text{Energy Cost}$	
Payback Period	3 years	

III. RESULTS AND DISCUSSION

A. Thermodynamic Analysis

A heterogeneous azeotropic mixture will form a VLLE graph which has partially miscible liquid properties as shown Figure 1. The azeotropic was found in homogeneous and heterogeneous type with the classification listed in Table 5.

TABLE 5.
AZEOTROPE ANALYSIS OF THE 1-BUTANOL + WATER SYSTEM AT
DIFFERENT PRESSURES

T (°C)	Type	Azeotrope composition	
		1-Butanol	Water
P = 1 atm			
117.749	Homogeneous	1	0
100.018	Homogeneous	0	1
92.639	Heterogeneous	0.247	0.753
P = 10 atm			
202.77	Homogeneous	1	0
180.549	Homogeneous	0	1
169.139	Heterogeneous	0.238	0.762

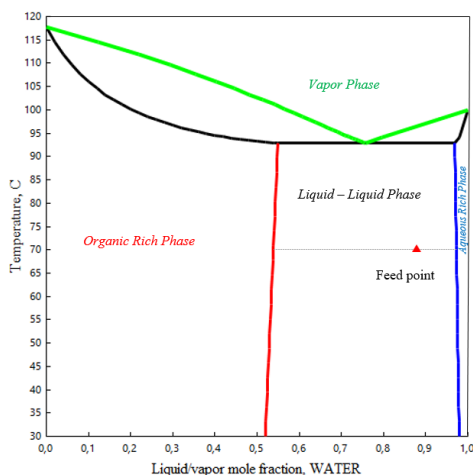


Figure 1. VLLE graphic of 1-Butanol + Water at 101.3 kPa

From the results of the azeotrope analysis obtained from the Figure 2, it can be concluded that increasing the pressure in the system not only changes the composition but also the boiling point of each component. The effect of pressure on azeotrope temperature and composition were shown in Figure 3 and 4, respectively. The small change in the azeotrope composition between 1 and 10 atm clearly illustrates that the Pressure Swing Distillation method is less attractive when applied in this system. Increasing pressure tends to reduce the mole fraction of butanol, although not significantly. This is also explained in previous study [10-11], if a system is sensitive to pressure, there will be a significant change in the composition of the azeotrope. The effect of pressure is very visible on equilibrium temperature as shown in Figure 5. In general, increasing pressure tends to increase the boiling point of

an azeotropic mixture, while decreasing pressure tends to lower it. This can change the distribution of components between the gas and liquid phases, which in turn can affect the composition of the azeotrope.

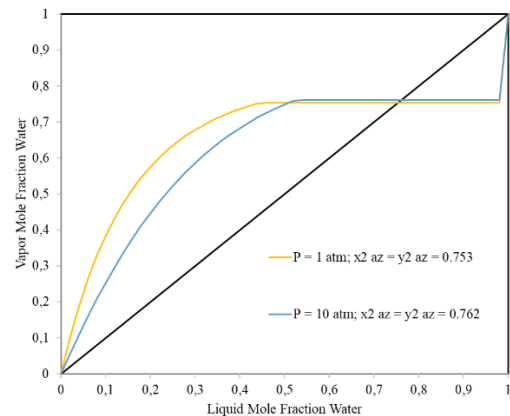


Figure 2. x-y graph for 1-Butanol + Water System with Different Pressures

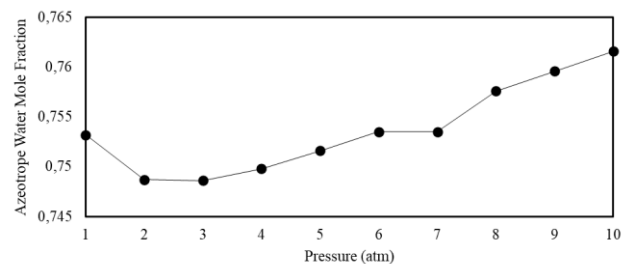


Figure 3. Effect of Pressure on the Azeotrope Composition of 1-Butanol

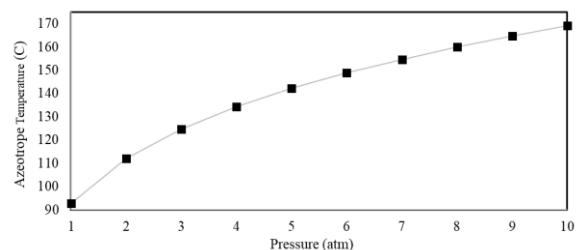


Figure 4. Effect of Pressure on Azeotrope Temperature

B. Pressure Swing Distillation Process Design

The initial flowsheet, Figure 6a and 6b, was simulated to obtain design data using the "Design Specification" feature in Aspen Plus. The column specification was listed in Table 6.

TABLE 6.
PRODUCT SPECIFICATIONS FOR CASE 1 AND 2

Case	Air		1-Butanol	
	Mass fraction	Mass rate (kg/h)	Mass fraction	Mass rate (kg/h)
1	0.998	1051	0.9998	7
2	1	1081	0.9998	26

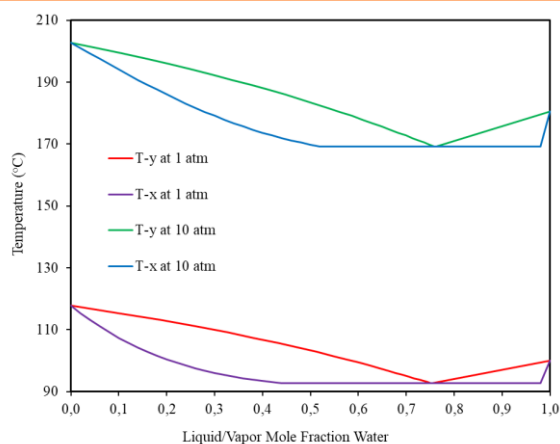


Figure 5. Effect of Pressure on T-x,y diagram of 1-Butanol + Water

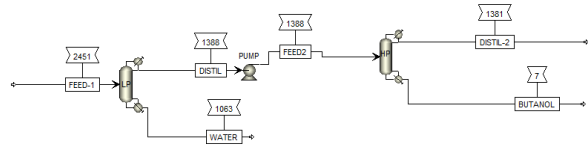


Figure 6a. Case 1 (Low Pressure to High Pressure)

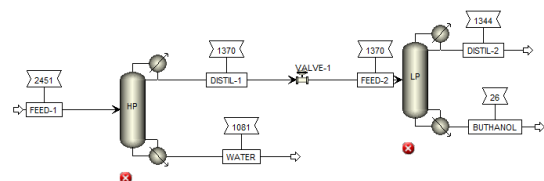


Figure 6b. Case 2 (High Pressure to Low Pressure)

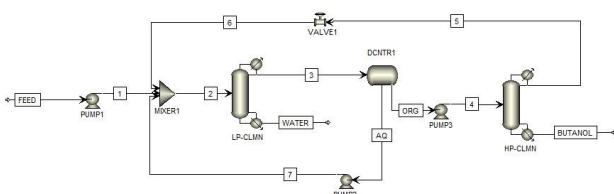


Figure 7. LP to HP configuration equipped with decanter (CASE 1A and 1B)

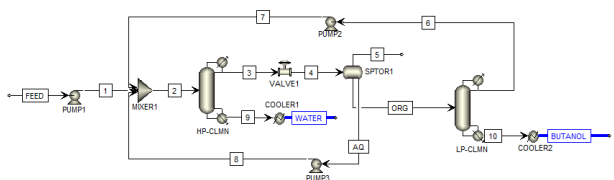


Figure 8. HP to LP configuration equipped with decanter placed after the pressure changer (CASE 2A and 2B)

The product obtained is in accordance with the desired specifications, but the butanol product with the desired purity, the mass rate produced is very low. Hence, several adjustments are needed to improve the butanol product, one of which is the addition of a decanter to separate components with water rich phase and organic rich phase.

C. Design Optimization

The effect of pressure configuration process were categorized in two option, Low Pressure to High Pressure, and, High Pressure to Low Pressure. The process configurations were shown in Figure 7-9. Case 1A and 1B were LP to HP configuration equipped with decanter where Case 1B had less stage than Case 1A. Case 2A and 2B were HP to LP configuration equipped with decanter placed after the pressure changer where Case 2B had less stage than Case 2A. Case 3A and 3B were HP to LP configuration equipped with decanter placed before the pressure changer where Case 3B had less stage than Case 3A. The use of a lesser number of stages is expected to be more economical.

From the results of the simulations, less stage utilization will lead to lesser heat duty for reboiler and condenser requirement. The temperature difference in both the initial design and the final design in the *distillate* and *bottom* is also very small. Similarly, the amount of Butanol products obtained is in the range of 855-857 kg / hour. A recapitulation of the simulation can be seen in Table 7. Case 2B has the least Q_{total} among other cases, with only 1289.891 kW from both columns, it can produce a product with 99.8% mass purity. This can be achieved because the distillate in the second column is recycled and the feed in the first column has the smallest amount among the others, thus impacting the total Q of both columns. The design parameters for Case 2B were listed in Table 8.

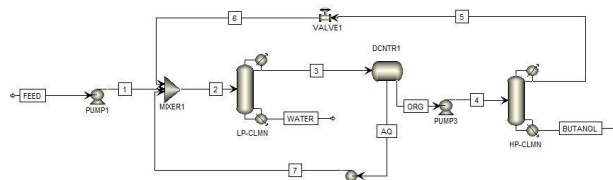


Figure 9. HP to LP configuration equipped with decanter placed before the pressure changer (CASE 3A and 3B)

TABLE 7. EFFICIENCY AND HEAT REQUIREMENTS

Case	Q total (kW)	Efficiency (%)
1A	2815.916	8.45
1B	2577.829	
2A	1372.743	5.38
2B	1298.891	
2C	3122.958	43.11
2D	1776.535	

D. Techno-Economic Evaluation

As shown in Table 8, the Total Annual Cost (TAC) was 0.64 (10⁶ USD/year). The CAPEX value in this study only considers the price of equipment in the simulations that have been carried out. Where details on the price of the tool are completed using the Aspen Process Economic Analyzer. Payback Period taken for three where in the

study did take the average of the existing payback time, the time was also used in other studies that require predictions of TAC. Operating Cost only consists of energy and electricity prices.

TABLE 8.
HP AND LP COLUMN PARAMETERS

Parameter	LP Column	HP Column
Number of stages	13	7
Diameter (m)	0.242	0.308
Height (m)	9.51	5.12
Top Temperature (°C)	91.3	166.9
Bottom Temperature (°C)	117.3	177.5
Q Reboiler (kW)	96.0	774.9
Q Condenser (kW)	60.5	367.5
Mole reflux ratio	0.339	0.15
Optimum feed stage	4	3

TABLE 9.
ECONOMIC ANALYSIS

CAPEX (10 ⁶ USD)	1.244
Operating cost	
Energy (10 ⁶ USD / year)	0.226
Electricity (10 ⁶ USD / year)	0.00142
Payback period	3 years
Total (10 ⁶ USD / year)	0.64

IV. CONCLUSION

From this study, 1-butanol + water mixture can be separated using *Pressure Swing Distillation*, the most effective and efficient configuration is on PC2 > PC1 or from *High Pressure to Low Pressure Column* in Case 2B, although the azeotrope in this system does not change much with pressure changes. From the results of economic analysis, it is estimated that *the TAC* of the process is 0.64 (106 USD / year) with the cost of producing butanol is 0.085 USD / kg and the cost of energy is 0.03 USD / kg.

V. ACKNOWLEDGMENT

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VI. REFERENCES

- [1] M.D. Saquete, A. Font, J. García-Cano and I. Blasco, "Study of the LLE, VLE, and VLLE of the ternary system water+ 1-butanol+ isoamyl alcohol at 101.3 kPa," *J. Chem. Eng. Data*, vol. 63, pp.3733-3743, Sep. 2018.
- [2] M. Lapuerta, J.J. Hernández, J. Rodríguez, J. Barba, A. Ramos and D. Fernández-Rodríguez, "Emission benefits from the use of n-butanol blends in a Euro 6 diesel engine," *Int. J. Engine Res.*, vol. 19, pp.1099-1112, Nov. 2017.
- [3] L. Tipanluisa, N. Fonseca, J. Casanova and J.M. López, "Effect of n-butanol/diesel blends on performance and emissions of a heavy-duty diesel engine tested under the World Harmonised Steady-State cycle," *Fuel*, vol. 302, p.121204, Oct. 2021
- [4] R. Vooradi, V.S. Patnaikuni, A.K. Tula, S.B. Anne, M.R. Eden and R. Gani, "Hybrid Separation Scheme for Azeotropic Mixtures–Sustainable Design Methodology," *Chem. Eng. Trans.*, vol. 69, p.637, Oct. 2018.
- [5] Z. Mužíková, P. Šimáček, M. Pospíšil, and G. Šebor, "Density, viscosity, and water phase stability of 1-butanol-gasoline blends," *J. Fuels*. vol. 2014, p.1, Jan. 2014.
- [6] Y. Guo, and L. Wang, "Research progress on azeotropic distillation technology. *Advances in Chemical Engineering and Science*," vol. 9, p.333, Oct. 2019.
- [7] J. Haydary. "Chemical process design and simulation: Aspen Plus and Aspen Hysys applications," John Wiley & Sons, Jan. 2019.
- [8] H. Gai, K. Lin, Y. Feng, M. Xiao, K. Guo, and H. Song, "Conceptual design of an extractive distillation process for the separation of azeotropic mixture of n-butanol-isobutanol-water," *Chin. J. Chem. Eng.*, vol. 26, pp.2040-2047, Oct. 2018.
- [9] W.L. Luyben, "Distillation design and control using Aspen simulation," John Wiley & Sons, Apr. 2013.
- [10] W.L. Luyben, "Comparison of extractive distillation and pressure-swing distillation for acetone/chloroform separation," *Comput. Chem. Eng.*, vol. 50, p.1-7, Mar. 2013.
- [11] W.L. Luyben, "Importance of pressure-selection in pressure-swing distillation," *Comput. Chem. Eng.*, vol. 149, p.107279, Jun. 2021.