

Purification Simulation With Vapor Permeation and Distillation-Adsorption In Bioethanol Plant

Misri Gozan^{1*}, Mia Sari Setiawan¹, and Kenny Lischer²

1. Biorefinery Engineering Group, Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok 16424, Indonesia

2. Nara Institute of Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

*e-mail: mrgozan@gmail.com

Abstract

High purity of Bioethanol is required in biofuel mixing with gasoline (EXX). In bioethanol production line, the azeotropic property of ethanol-water becomes the barrier for purification process. This study examined two bioethanol separation processes by support of simulation tools, Superpro Designer 9.0 software. Ethanol purity and a low cost-economical process were the major considerations. Purification method of vapor permeation membrane technology was compared with distillation-adsorption method. Data from previous lab experiments and some literatures were used. The results showed that distillation-adsorption method is more economical compared to vapor permeation technology. Payback period of the simulation is 3.9 years and 4.3 years to distillation adsorption and vapor permeation respectively with each IRR value is 20.23% and 17.89%. Initial investment value of vapor permeation is 9.6% higher than distillation method. Significant difference observed in operating costs, since more units involved in vapor permeation require more labors to operate.

Abstrak.

Simulasi Pemurnian Dengan Permeasi Uap Dan Distilasi-Adsorpsi Pada Pabrik Bioetanol. Bioetanol dengan kemurnian tinggi diperlukan dalam pencampuran biofuel dengan bensin (EXX). Pada proses produksi bioetanol, sifat azeotropik etanol-air menjadi penghalang untuk proses pemurnian. Penelitian ini mengkaji dua proses pemisahan bioetanol dengan bantuan piranti simulasi, Superpro Designer 9.0. Kemurnian etanol dan biaya proses ekonomis rendah menjadi variabel utama. Tulisan ini membandingkan metode pemurnian teknologi membran permeasi uap dengan metode distilasi-adsorpsi. Data yang digunakan untuk simulasi berasal dari percobaan laboratorium sebelumnya dan studi pustaka. Hasil penelitian menunjukkan bahwa metode distilasi-adsorpsi lebih ekonomis dibandingkan dengan teknologi permeasi uap. *Payback Period* dari simulasi ini adalah 3,9 tahun dan 4,3 tahun untuk distilasi adsorpsi dan permeasi uap, secara berurutan. Nilai masing-masing IRR adalah 20,23% dan 17,89%. Nilai investasi awal permeasi uap lebih tinggi dibandingkan dengan metode distilasi yaitu 9,6%. Perbedaan signifikan diamati dalam biaya operasi, karena lebih banyak unit yang terlibat dalam permeasi uap memerlukan lebih banyak tenaga kerja untuk beroperasi.

Kata kunci: Bioetanol; distilasi adsorpsi; simulasi; permeasi uap.

1. Introduction

The use of bioethanol has many advantages, e.g. reducing greenhouse effect, emission of CO gas, as well as reducing global warming. In first generation, production of bioethanol was encouraged from food resources, such as from cassava, maize, sweet potatoes, and sugar cane. Besides, bioethanol can be made from lignocellulose-based materials or better known as second generation bioethanol. As one of the largest palm oil producer in the world, Indonesia's waste of empty fruit bunches

from crude palm oil (CPO) production is abundant. CPO industry generates waste of Empty Fruit Bunches (EFB) as much as 1.1 tons for every ton of CPO produced. Main components of EFB are composed of 37.62% cellulose, 14.62% hemicellulose, and 31.68% lignin, the rest are extractives and ashes [1]. Since EFB is rich in cellulose, it can be utilized as a substrate for bioethanol fermentation process.

Bioethanol production process from EFB basically comprises of pretreatment, fermentation, and purification

steps. Initial pretreatment liberates cellulose from lignocellulose structured, followed by breaking down the cellulose into monomeric sugars. Fermentation of sugars resulted in 6 to 12% ethanol [2]. Ethanol purification by distillation usually had maximum 96% purity due to azeotropic characteristic [3]. Advance purification method is addition of solvents, involving a complex process, and requiring addition of chemical compounds making it less economical to be applied in large scale production. Zeolite particles, with small enough diameter pores which have an affinity for water, can selectively separate water from ethanol-water mixture. Bioethanol purity increased by using modified natural zeolite with purity more than 99% but with lower yield [4,5].

Economic factor is a crucial aspect in bioethanol mass-production as a biofuel [6]. Process simulation helps to analyze economic value of the bioethanol production processes. Some simulation processes had done by using distillation, such as bioethanol production using distillation at industrial plants [7], azeotropic distillation for anhydrous bioethanol [8], nonequilibrium stage model of distillation [9], and using batch distillation [10]. There is lack of study on simulation based on vapor permeation process. This study shows comparison

of simulation of ethanol purification by vapor permeation and distillation-adsorption method.

2. Methods

Process Model Description. Bioethanol production process was arranged and adjusted in Superpro Designer 9.0 worksheet that shown in Figure 1 (a and b).

Pretreatment to Fermentation. Empty Fruit Bunches (EFB) as raw material was pretreated first. EFB was grinded to 3 mm size and then transported to acidification tank. Grinded EPFB fibers were inserted into blending tank to be reacted with sulphuric acid 0.5% v/v in order to break down lignin structure within the fiber and hydrolyze cellulose and hemicellulose become glucose and xylose monomers respectively. The operating condition was cheaper compared with using enzyme by using acid as reactant. Eq. 1 and 2 are the reaction of hydrolysis.



After the hydrolysis reaction was done, the pH of hydrolyzed mixture was neutralized into 5 in alkali tank to reach optimum pH to execute fermentation [11].

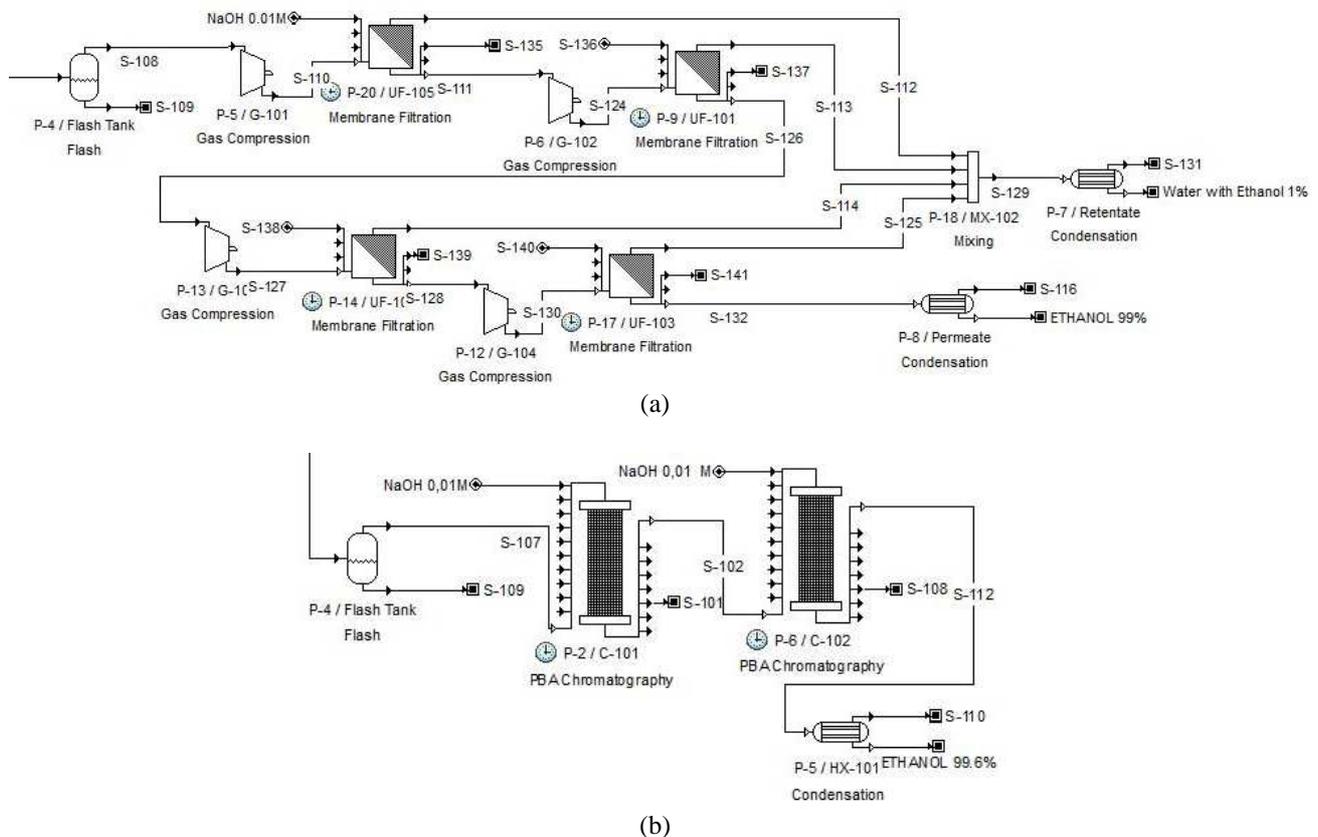


Figure 1. Superpro Simulation of VP (a) Separation Process and (b) Distillation-Adsorption Separation Process

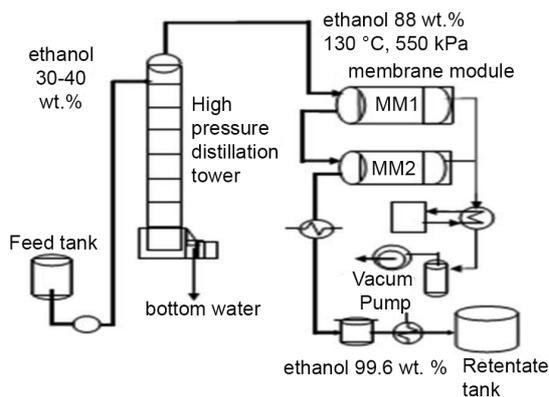


Figure 2. Vapor Permeation Unit Scheme [12]

Fermentation. This step was done in a fermenter. The temperature and pH value was kept at 37 °C and within 4.5-5.0 respectively. Alcohol level produced is within 8%. Fermented broth will be purified to recover the ethanol.

Distillation. Broth from distillation process was then transported into distillation unit. The ethanol which was the output of distillation had 92-94% purity in isotropic condition. Therefore, an advanced dehydration method is required to gain ethanol content until 99%. Water content was further dehydrated using vapor permeation method utilizing ceramic NaA-Ze membrane and distillation-adsorption method.

The distillation was done in several different four columns in order to separate ethanol from water, fuel oil, and aldehyde content. Degasifying column eliminated solute gas and impurities with low boiling point. Temperature condition in reboiler and condenser was 80 °C and 73 °C. Mash column separated wet cake left in fermented broth. Aldehyde column eliminated impurities with low boiling points which was concentrated in the top of the column. Product from aldehyde column was classified as technical ethanol. Temperature condition in reboiler and condenser was 63 °C and 42 °C. Rectifying Column concentrated ethanol content until 96% v/v and eliminated impurity such as methanol. Temperature condition in reboiler and condenser was 73 °C and 45 °C.

Vapor Permeation Process Model. Bioethanol from distillation entered dehydration process to produce biofuel grade bioethanol. In dehydration process, distillate which was hydrate bioethanol was vaporized and separated between ethanol and water by its selectivity in the membrane. Based on performance of permeation process, effective temperature of Perforation and Vapor Permeation (VP) is 323-418 K and water content is 1-10%. Based on research by Sato in 2007, temperature in VP process was 130 °C. Figure 2 described the scheme of vapor permeation model.

Adsorption. Adsorption method used column technology and zeolite molecule to adsorb water content from ethanol-water azeotrope mixture. High temperature vapor of hydrate ethanol was transported vertically through two columns which utilized in parallel. The method used pressure swing adsorption in principle. Zeolite molecule used was type 3A alumina silicate. Two columns processed in parallel as a cycle [12].

Operating Data Sources. In this simulation, data of operation condition for each unit operation were obtained from journals and production process from industry itself. The data include input and output stream composition, preparation condition of each production unit, and constraint in each operating unit.

Simulation Validation. Data of design process simulation compared with data derived from experimental results which had been done. Variables which validated in bioethanol production were yield of fermented bioethanol, yield of bioethanol produced after final separation using vapor permeation method, and yield of bioethanol produced after final separation using distillation-adsorption method.

Economical Analysis. After simulation result was validated, the economy report which was calculated by Superpro Designer simulator was then compared between vapor permeation and adsorption method. Payback period and IRR value was determined in each process.

3. Results and Discussion

In the simulation, overall operation mode was set in continuous, but for process units other than distillation performed in batch system. The operation time and amount of product was calculated in a year basis. Bioethanol purification was set in continuous system because it will be more economical since the system can exchange heat with other streams. However, in this simulation the feature did not support backflow operation. Therefore heat exchange was not able to be executed in this simulation.

Pretreatment. The 232 kg/hr EPFB feed which consist whole fiber was grinded until 3 mm and was then transported with belt conveyor with specific loading rate of 1410 kg/hr.m toward acidification tank to perform hydrolysis. Sulphuric acid 0.5% v/v was mixed with EPFB with ratio of 20% for 30 minutes [11]. The needed capacity of the tank was 27500 L. Hydrolysis reaction was simulated by stoichiometric equation, which for each molecule of cellulose was assumed to produce 10 molecules of glucose. Solids derived from hydrolysis process not be used in further process therefore a unit of plate and frame filtration with filter area of 7.18 m² and maximum cake

thickness of 19.44 cm was utilized to separate the solid. Sugar rich hydrolyzed was then neutralized in blending tank which containing NaOH with tank capacity of 2855 L. Molar equation from acid-base neutralization reaction was used for this reaction process.

Fermentation. Batch fermenter unit was filled with hydrolyzed liquid, and then was cooled to ambient temperature before yeast insertion as much as 10% v/v of total fermentation volume. The fermenter capacity is 24000 L. Reaction was performed stoichiometric ally resulting amount of CO₂ emission for 39 kg/hr (in assumption all reactant reacts perfectly).

Distillation Unit. Unit used shortcut rigorous distillation. Relative volatility value was set based on boiling point difference. The component, e.g. ethanol and water and also all solids and other heavy components were assumed eliminated in mash column. Stream was vaporized using flash tank with capacity of 4.89 L for the stream before to the next step.

Vapor Permeation. Ethanol-water mixture as distillate was separated by utilizing zeolite active site of ceramic NaA-Ze membrane surface which is selective to water. The pore of the NaA-Ze membrane is an arrangement of polycrystalline molecules, which contains of zeolite pores and non-zeolite pore [13]. This non-zeolite pore structure is grain boundary which is generated throughout the membrane's zeolite pore. Dehydration was performed with 4 modules of ceramic membrane continuously at 120 °C with vapor flow rate of 11 kg/hr. Ethanol concentration of the retentate stream as product and the permeate flux was adjusted with experiment result done by Sato et al (2007) as can be seen in Table 1.

According to the final ethanol purity and permeate flux, the total surface area of four membranes are 0.878 m². After ethanol was separated, product was recovered in liquid form therefore condenser was occupied. Transfer heat area which needed for this method is 0.22 m² for both permeate and retentate streams.

Distillation-Adsorption. Adsorption column was resembled by packed bed adsorption (PBA) Chromatography (Detailed) in Flow-Through Mode. Two operation units were performed, which are for adsorption and stripping

Table 1. Separation Result Using Vapor Permeation Unit

Module	Concentration (%)	Permeate Flux (kg/hr)
1	97.29	18.36
2	98.97	6.88
3	99.51	3.15
4	99.69	1.94

to regenerate exhausted zeolite molecules to its initial condition. Before entering adsorption column, entered stream must be prepared by vaporizing the stream so condensation was not able to occur in the column. Operation condition used in simulation was according to pressure swing distillation method in large scale. Hiltz et al analyzed that zeolite molecule of type 3A had hydrophilic character to make bond with water molecules by Van der Waals bond [12].

Adsorption unit in Superpro Designer simulator was chromatography using chamber system. This unit was less similar as the unit desired therefore the sizing was less accurate and had high cost. Therefore, the simulator calculated the dimension manually according to literature data. Although adsorption capacity per zeolite molecules was 20% kg water/kg adsorbent, but it was recommended by ZEOCHEM that the calculation used half of that value, which is 10% kg water/kg adsorbent (ZEOCHEM 2007-2008) (Table 2).

Column diameter must be determined as smallest as possible so the zeolite molecules would not be damaged and able to be operated in turbulent stream as desired. Gas maximum rate can be determined from the equation derived from ZEOCHEM.

$$V \left(\text{down flow, } \frac{ft}{\text{min}} \right) = 61.5 / \sqrt{\rho_{\text{gas}} \left(\frac{lbs}{ft^3} \right)} \quad (3)$$

The gas maximum flow rate was determined as 0.697 m/s so that the column diameter was 0.17 m. Based on breakthrough curve modeling data, adsorption time for column with 3.5 m height was 23.9 minutes. The transfer heat area needed for condenser unit was 0.22 m².

Cost Determination. Table 3 consist value of some parameters that used in economy analysis.

Simulation Validation. Simulation validation occurred by comparing with experiments data using same raw material (second generation bioethanol). In Samsuri's research in 2008, yield of bioethanol produced was 19.7%

Table 2. ZEOCHEM® Z3-03 Specification

	Unit	Value
Tapped bulk density, EN ISO787-11	kg/m ³	750
Bead size	mm	2.5-5
Crush strength	N	70
Water adsorption capacity inequilibrium at 20 °C, 50%RH in 24 hours	%	20
Residual water content, 550 °C	%	1.5
Adsorption heat	kJ/kg water	4200
Specific heat	kJ/kg°C	1.07

Source: ZEOCHEM (2007-2008)

with basis of raw materials amount. Deviation value of the data obtained from simulation was 9.1%, which is still tolerable because EPFB has less cellulose content compared to sugarcane waste.

For vapor permeation method, validation of separation performance graph was done by comparing to the previous experiments using the unit by Banu in 2013. With input of 90%w of technical ethanol, the output obtained was 96% purity. Based on calculation method, the result of the simulation was 96.61% with error value of 0.6%.

Distillation-adsorption method was compared to articles data of anhydrate bioethanol production by Jeon et al in 2013. Distillate result at 93.7% purity can be purified resulting 99.63% purity using feed/purge ratio at 7/3.

Based on the simulation result, the bioethanol purity reached 99.6% purity from distillate purity at 92.04%.

Simulation Economical Analysis. Economic analysis report was calculated by Superpro Designer that can be seen in Table 4. Economical calculation shows that both projects are appropriate to be run, shown by the relative short payback period and high IRR value. This value is used to build an anhydrate bioethanol plant with ± 303 ton in annual production capacity and with total revenues are ± 10 million US\$/year.

Vapor permeation method is less economical than distillation-adsorption method with NPV value difference at 11.8%. Difference in both costs can be seen in detailed capital investment and operating cost which shown that operating cost play a significant role giving a high cost for vapor permeation method with difference of 7.8% per annum. This cost is caused by more units

Table 3. Value of Parameters for Economy Analysis

Raw Material	Price (\$)	Information
EPFB	1.5/ton	Without addition of transportation cost
Water	1/m ³	Based on PAM cost
Sulphuric Acid	0.025/kg	From www.icis.com
Yeast	0.05/kg	
NaA-Ze Membrane	120/m ²	replaced every 2 years
Zeolite molecules	0.3/kg	replaced every 3 months
Bioethanol Price	0.73/kg	according to index from ESALQ
Labor Cost	1.35/hr	minimum paid salary domestically
Project Period	20 years	
Site construction period	30 months	
Income Tax	5%	

Table 4 Details of Cost Differences between Bioethanol Production Process with Distillation-Adsorption Method and Vapor Permeation Method

Economy Analysis	Distillation-Adsorption	Vapor Permeation
Payback Period	3.9 year	4.3 year
IRR	20.23%	17.89%
Total Capital Inv.	\$ 21,413,000	\$ 23,474,000
NPV (interest 7.0%)	\$19,159,000	\$ 16,901,000
EquipmentCost	\$ 3,481,000	\$ 3,749,000
Utility	\$ 2,014,105/yr	\$ 2,062,516/yr
Labor cost	\$417,904/yr	\$531,499/yr
Consumables	\$ 1,504/yr	\$ 262/yr
Total Annual Op. Cost	\$ 4,703,000/yr	\$ 5,068,000/yr

and labor sare needed to operate. Meanwhile, the utility consumed was also bigger.

However, in vapor permeation unit, there are utility that can be omitted so that the utility can reach same value under distillation-adsorption method. This is because in vapor permeation unit, each feed stream entering the membrane filter must be cooled first to be recognized as substrate, while after separated the stream was heated again to reach 120 °C. The filter was not able to process input stream in vapor form so this unnecessary heating and cooling must be performed in order to be able run the simulation, but this condition was neglected the real operation condition.

4. Conclusion

Based on simulation result, bioethanol production process with distillation-adsorption method and vapor permeation give payback period at 3.9 and 4.3 years respectively with IRR reached at 20.23% and 17.89% for distillation-adsorption method and vapor permeation. Based on the result, it is concluded that vapor permeation method is less economical than distillation-adsorption method, however, we believe with right operation conditions, utility usage can be suppressed, and therefore this can significantly decrease operation cost of vapor permeation method.

Acknowledgement

The authors gratitude the funding by the Indonesian National Ministry of Education and Culture with the scheme Competence Research Grant (No. 2245/H2.R1/HKP.05.00/2014).

References

- [1] Shinoj, R Visvanathan, S Panigrahi, M Kochu babu, Ind. Crops Prod. 33 (2011) 7.

- [2] C. Xingkai, Z. Xuebing, Z. Jing, KL. Soh, MC. Yuen, L. Dehua, *Bioresour. Technol.* 166 (2014) 584.
- [3] T. Yadollah, H.H. Seyyed, *Separ. Purif. Technol.* 118 (2013) 455.
- [4] K.W. Satriyo, Hernawan, K. Anis, T. Silvester, A. Haznan, *Energ. Proced.*, 47 (2014) 263.
- [5] Q. Liu, R.D. Noble, J.L. Falconer, H.H. Funke, *J. Membr. Sci.* 117 (1996) 163.
- [6] Bernardina, *Energ. Pol.* 69 (2014) 227.
- [7] R.M.B. Fabio, A.F.R. Luis, L.C.B.A. Bessa, J.A.M. Antonio, *Comp. Chem. Eng.* 46 (2012) 1.
- [8] L.J. Tassia, O.S.D. Marina, M.F. Rubens, R.W.M. Maria, E.V.R. Carlos, *Comp. Aid Chem. Eng.* 27 (2009) 1143.
- [9] L.J. Tassia, M.F. Rubens, R.W.M. Maria, *Comp. Aid Chem. Eng.* 27 (2009) 735.
- [10] N.C. Salomon, S.I. Mauricio, O.B.M. Fabricio, H. Salvador, J.C.M. Agustin, *Chem. Eng. Proc.* 77 (2014) 38.
- [11] M. Samsuri, Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, 2008. [In Indonesian]
- [12] J. Hiltz, Z. Taylor, M. Bajer, Department of Chemical Engineering University of Saskatchewan, 2008.
- [13] K. Sato, T. Nakae, *J. Membr. Sci.* 301 (2007) 151.