Lampung Natural Zeolite Filled Cellulose Acetate Membrane for Pervaporation of Ethanol-Water Mixtures

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Abstract. Pervaporation of ethanol−water can be cost-competitive in the production of renewable biomass ethanol. For the purpose of improving the pervaporation performance of polymeric membranes, we prepared cellulose acetate (CA) filled Lampung Natural Zeolite (LNZ) membranes by incorporating LNZ into CA for pervaporation separation of ethanol-water mixtures. The characteristics and performance of these filled membranes in the varied ratio of CA:LNZ (30:0, 30:5, 30:10, 30: 20, 20:20 and 40:10) wt% were investigated. The prepared membranes were characterized for pervaporation membrane performance such as %water content and membrane swelling degree. Further, the permeation flux and selectivity of membrane were also observed. The results of investigation show that water content of membrane tends to increase with increase of LNZ content. However, the swelling degree of membrane decrease compared than that of CA control membrane. The permeation flux and the selectivity of membranes tend to increase continuously. The CA membrane with ratio of CA:LNZ 30:20 shows the highest selectivity of 80.42 with a permeation flux of 0.986 kg/(m^2 h) and ethanol concentration of 99.08 wt%.

Keywords: Cellulose acetate membrane; Lampung natural zeolite, pervaporation

1. Introduction

Energy is one of the important needs for the global community. The major source of energy comes from fossil fuels. The dominant fossil fuels used today by most industrialized and developing countries are oil, coal, and natural gas. Among these fossil fuels, oil is the most consumed for energy conversion. Along with world population continues to grow and the limited amounts of fossil fuels begin to diminish. Therefore, joint efforts are needed to find alternative energy sources to overcome the energy crisis.

Bioethanol is one of the promising renewable biofuels that continue to be developed as an alternative fuel. However, in order to be used as an alternative fuel, ethanol must have high purity (less than 0.5 wt% water). To achieve high purity, separation techniques such as extractive distillation or azeotropic distillation are required because the ethanol-water mixture forms an azeotrope. However, the ethanol purification process by using conventional distillation followed by extractive distillation is disadvantageous due to the high cost of service (Samanta and Ray, 2015) Therefore, a cheaper alternative of purification process is needed to make ethanol to be applied as fuel.

Currently, the pervaporation technique to purification of bioethanol has attracted considerable attention since its high efficiency and low cost operation. Pervaporation is one of purification method by using membrane like material for separation of mixture of liquids by partial vaporization. Pervaporation has several advantages compared with conventional distillation, such as able to separate the azeotropic mixture, no additives required and relatively low energy consume (Chapman, et al.,2008). Membrane pervaporation technique is used to separate a liquid mixture by partly vaporizing it through a nonporous permselective membrane (Kanse et al., 2015). There are two type of membrane can be applied for ethanol production, namely organophilic membranes for recovery of ethanol from fermentation broth and hydrophilic membranes for dehydration of ethanol near azeotrope point in a hybrid distillation-pervaporation process (Samanta and Ray, 2015**)**.

There are three type of hydrophilic membranes are often used on pervaporation of ethanol-water, such as: (1) polymeric membranes which are based on organic polymer chains that are cross-linked together, (2) inorganic membranes, fabricated from ceramics or zeolites, and (3) composite membranes that are based on an organic polymeric membrane but have inorganic particles dispersed throughout the polymeric structure, these are commonly termed mixed matrix membranes (Chapman et al., 2008). One type of polymeric membrane is widely applied to separate substances in liquid and gas phase is cellulose acetate (CA) (Kanagaraj et al. 2014 and Minhas et al., 2015). CA is widely used as a membrane material because it has several advantages, such as easy to produce and derived from natural renewable substances, low price, moderate chlorine resistance, and it has good biocompatibility (Arthanareeswaran et al., 2008).

However, organic polymer such as CA is not suitable for more aggressive cleaning as it has easily oxidized and low chemical resistances and mechanical strength CA membrane also has several disadvantages, such as its easily oxidized, low chemical and mechanical resistance (Kanagaraj et al., 2014). Therefore, a special treatment is required to improve performance by improving the deficiency of CA properties (Arthanareeswaran et al., 2004; Kanagaraj et al., 2014 and Minhas et al., 2015). Membrane modification is one of the special treatments that can be performed to correct its deficiency properties resulting in increased membrane performance by adding additives such as alumina and silica as fillers to improve the characteristics and improve membrane performance (Huang et al., 2008).

As above mentioned, the performance of the CA membranes can be improved by mixing the additive substance into the membranes. Several researchers have investigated the effect of mixing many CA as organic polymers with inorganic materials such as alumina, silica, titania, and etc [Arthameswaran et al., 2008 and Minhas et al., 2015). The presence of inorganic material able to improve mechanical stability, increasing fouling resistance ability, surface porosity, permeability properties and membrane selectivity in separation processes (Arthameswaran et al., 2008; Dogan and Hilmioglu, 2010; Minhas et al., 2015]. Recently, few researchers have investigated that the blend of zeolite with organic polymer able to improve pervaporation performance of ethanol-water. Ling & Kha, *et al* (2008) had studied the pervaporation separation of ethanol-water mixture using PVA zeolite-clay membranes to investigate the effect of ethanol feed concentration (10%, 30%, 50%, 70% dan 90%) and operation temperature (30, 40, 50, 60, and 70 ^{o}C). Their investigation shows that, when the ethanol concentrations of feed and operation temperature increased, the membrane selectivity increased, on the contrary, the absorption (flux) decreased. Similarly, Zhan, et al., 2009 conducted the investigation of thin-film zeolite-filled silicone/PVDF composite membranes which were fabricated by incorporating zeolite particles into PDMS (poly(dimethylsiloxane)) membranes. The result showed that the increase of zeolite loading from 10% to 30% was increasing the total flux with significantly from 265.0 g/(m^{2}h) into 820.7 g/(m^{2}h) with 5 wt% ethanol feed concentration at 50°C, and the separation factor from 11.3 to 13.7.

In the present study, Lampung Natural Zeolite (LNZ) was added from in 5 to 30 wt % into the casting solution to prepare the new CA/LNZ hybrid membranes. The effects of LNZ addition on prepared membranes were investigated by swelling degree test, and water content. In addition, the pervaporation performance of the membranes such as permeability and selectivity were also evaluated for dehydration of ethanol/water mixture in order to produce ethanol according to fuel specifications.

2. Material and Methods

2.1 Materials

Commercial grade cellulose acetate (Sigma Aldrich, USA) with acetyl content 39 %wt - 41 %wt and Mw 30,000 was used as the matrix polymer membrane. Lampung natural zeolite (LNZ) (200 mesh) which purchased from CV. Minatama, Lampung,Indonesia was used as a filler and N_2 liquid was used as cold trap permeate on pervaporation process.

2.2 Solution Blending and Hybrid Membranes Fabrication

CA filled zeolite membrane were fabricated using the casting solution method by following procedure of Minhas et al. (2015). In this case, CA dissolved in 100 ml of acetone (J.T baker, USA) and stirred until homogen. Afterward, the calculated amounts of LNZ were added into CA solution to making the various ratio of CA : LNZ (30 : 0 ; 30 : 5 ; 30 : 10; 30 : 20; 20 : 20) wt%. The resulting of CA/LNZ slurry was stirred for 24 hours. The resulting CA slurry was set aside for 2 hours to remove air bubbles after 24 hours of stirring. Thus, the CA slurry was casted on a glass plate. The film was then placed in air for 20 seconds to evaporate the solvent, and then dipped in ice water for 20 min to complete the phase separation process. Further, the ice water was replaced with hot water (80 °C) to separate the membranes from the glass surface. For drying purpose, the hybrid membranes underwent to solvent exchange method. Finally, the hybrid membranes were placed in an oven that was maintained at 60 °C for 2 hours.

2.3 Pervaporation test of membrane

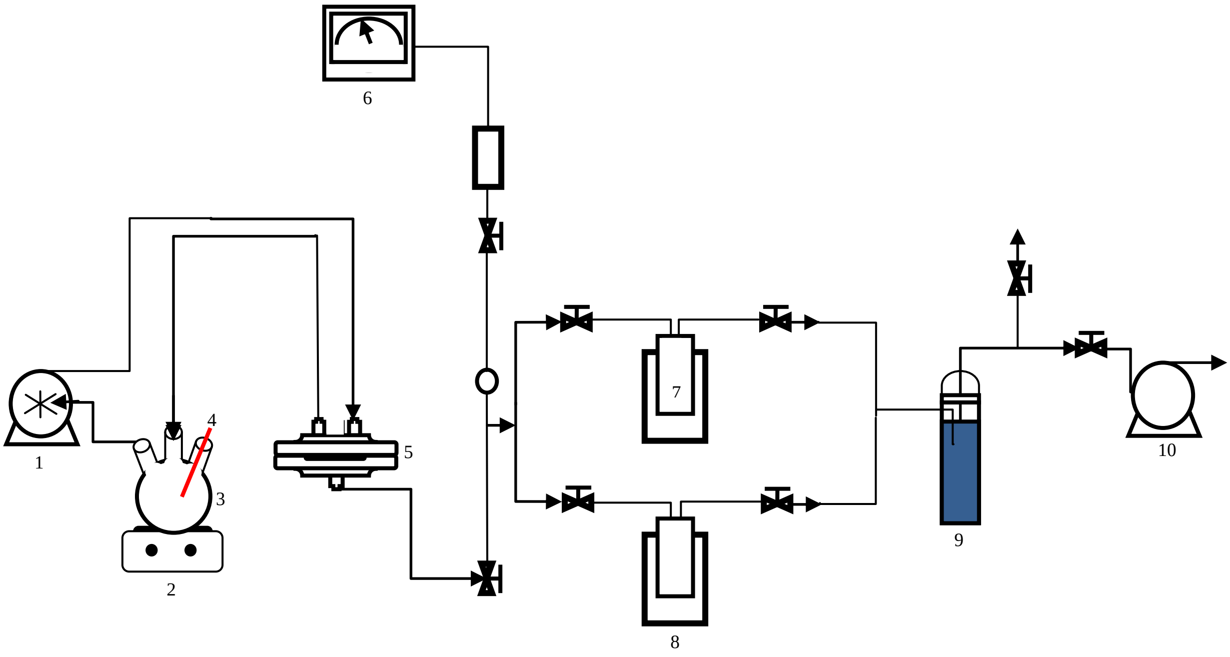
The pervaporation experiments test were conducted by using an apparatus as shown in Figure 1. The prepared CA/LNZ membrane was setted into the membrane cell module in pervaporation apparatus. The diameter of effective membrane area in contact with feed was 12.56 cm^2. First of all, the pervaporation apparatus was setting and tested by run the machine using distilled water to remove unwanted material in the machine. Then, the feed composition was running up to free machine from distilled water. The fed solution with 96 wt-% of ethanol/water mixture was stored in the feed flask and heated into 40 ^{o}C using heater. A perilstatic pump was used to circulate the feed solution from the feed flask into the membrane cell module. The circulation rate was kept high to minimize concentration polarization in the permeation cell and maximize mixing of solution in the feed tank. The vacuum in the downstream side was maintained at about 0,3 mBar kPa using a vacuum pump, and permeate was collected in liquid nitrogen-cold traps. The compositions of the feed remain in the flask and permeate composition were measured using picnometer and gas chromatography to determine the separation factor and total flux. The permeation flux and the separation factor of membrane were determined as equation as follows:

$$J = \frac{1}{\mathrm{A}} \text{ x dm/dt} \qquad (1)$$

Where J is permeate flux (/m^2 h), m is total mass of permeate (gram) collected in t (hours), and *A* (m^2) denotes the effective area of the membrane. The dm/dt is slope which was derived from graph from relations between mass of permeate and time of pervaporation.

$$\alpha = \frac{(Y_W / Y_{eth})}{(X_W / X_{eth})} \qquad (2)$$

Where X_w and X_{eth} are the weight fraction of ethanol and water (wt%) in the feed solution respectively, and Y_w and Y_{eth} represent the weight fraction of ethanol and water (wt%) in the permeate.



1. Peristaltic Pump, 2. Heater, 3. Three neck glass, 4. Thermometer, 5. Module membrane, 6. Manometers, 7. Cold Trap, 8. Condenser, 9. Silica gel, 10. Vacuum Pump

Figure 1 Scematic of pervaporation experiment apparatus

2.4 Membrane characterization test

2.4.1 Swelling Degree

The swelling degree of the membranes was obtained after soaking a known weight of samples in fed solution (ethanol 96 wt%) for 48 h (until equilibrium reached) at room temperature, then removed. The surface of membrane was on swollen samples was blotted by pressing between the folds of filter paper and quickly weighed. The percentage of swelling degree was determined as follows:

$$\text{Swelling Degree (\%)} = \frac{\text{wet sample weight - dry sample weight}}{\text{dry sample weight}} x100\,\% \qquad (3)$$

2.4.2 Water content analysis

The procedure for water content analysis was conducted by following the method of Arthanareeswaran, *et al.* (2004). Water content of the membranes was obtained after soaking a known weight of samples in distilled water for 24 h and the membranes were weighed followed by mopping it with tissue paper. The wet membranes were then dried in vacuum drier at 75 ˚C for 48 h and the dryweights of the membranes were determined. The percent water content was determined by using the equation as follows:

$$\%\mathit{Water\ Content} = \frac{(\text{wet sample weight - dry sample weight})}{\text{wet sample weight}}\, x\, 100\,\% \qquad (4)$$

3. Result and Discussion

3.1 Effect of zeolite addition to swelling degree

The ideal pervaporation membrane should have not easy to swell excessively to maintain its structural selectivity and stability (Pabby et al., 2015). It is observed from Figure 2 that the presence of LNZ as the additive to casting solution decrease membrane swelling degree. The pure 100 wt.% CA membrane was compared with the CA/LNZ ratio of 30:5, 30:10, 30:20, 20:20, and 40:10 wt.%. It was observed that 100 wt.% CA membrane shows almost similar value of swelling degree percentage. In the presence of 10 - 20 wt.% LNZ, the swelling degree percentage showed a lower value than 100 wt % CA membrane. The LNZ presence on casting solution can serve to limit the molecular motions of the polymer chains. Limited molecular motions and a favorable increase in the mean distance between chains can lead to a simultaneous improvement of membrane stability or rigidity and porosity. Thus, it can be concluded that the addition of LNZ into CA gives a significant effect on the swelling degree of the membrane.

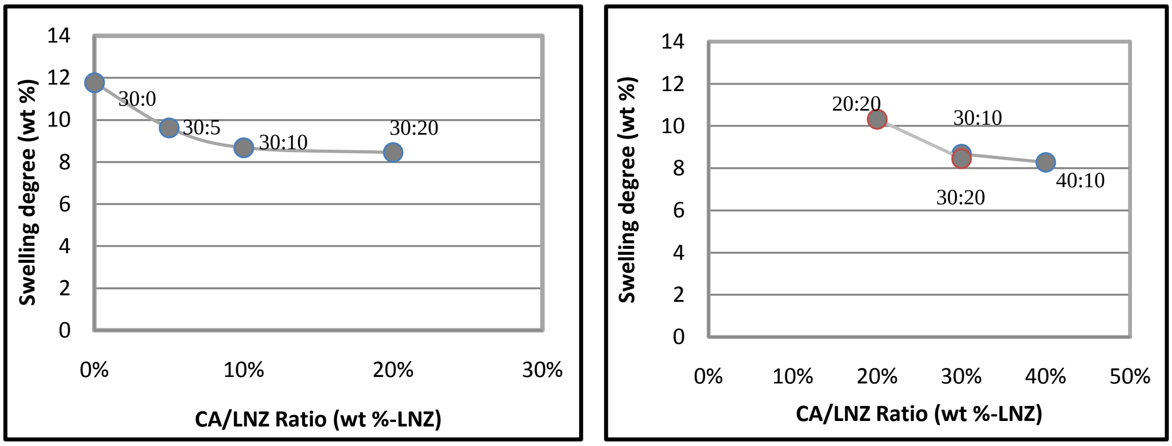


Figure 2. Effect of addition of LNZ into CA solution in varied ratio of CA/LNZ to percentage of swelling degree

3.2 Water Content analysis

Figure 3 shows the effect of LNZ addition into water content of membranes. As can be seen from Figure 3, the percentage water content of 100 wt.% CA membranes are lower than that of the membrane prepared by addition of LNZ. Hydrophilicity properties of the membrane relate to its water content percentage (Sivakumar et al., 2006). The hydrophilicity of the membrane affects the percentage of water content due to water absorbed into the membrane matrix. Similar results were also demonstrated by Arthanareeswaran et al (2014) and Abedini et al., (2011). In their study, it was observed that an addition of polyethylene glycol (PEG 600) and TiO_2 able to increase the membrane water content. The increase of water content possibly due to a presence of TiO_2 as inorganic phase was able to create the spaces in the polymer matrix and make an increase in the mean distance (free volume) between the polymer chains which leads to increasing the water content (Abedini et al., 2011). Moreover, the occurrence of "leached out" or dissolved during the process of gelation leading to the formation of pores, thus, the water molecule is trapped in the pores of the membrane matrix.

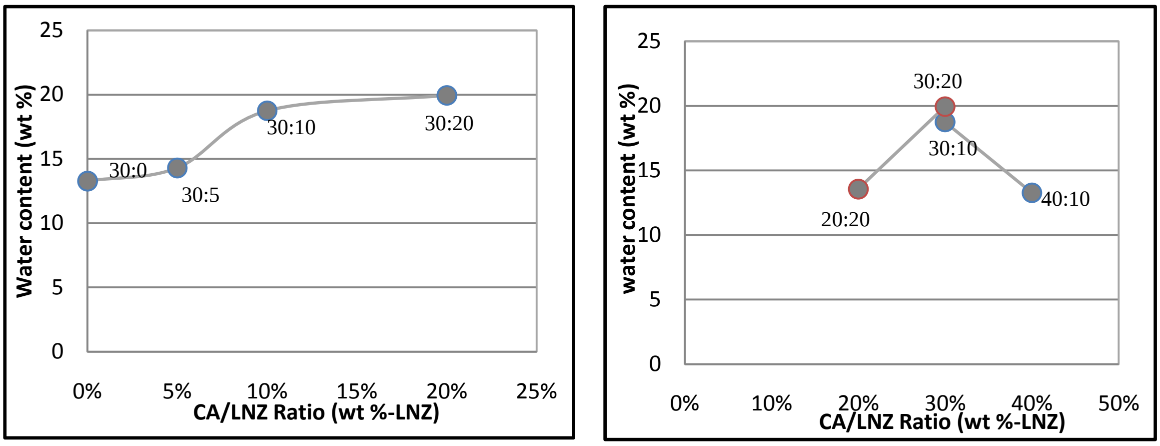


Figure 3 Effect of addition of LNZ into CA solution in varied ratio of CA/LNZ to percentage of water content

3.3 Permeation and selectivity (Separation Factor) of membranes

The results of permeation fluxs test and selectivity of membrane shows in Figure 4 and Table 1. An increase of LNZ addition from 5 to10% resulted an increase of membrane total flux. In contrast to LNZ addition to 20% in the casting solution decreases membrane flux. Similar results were obtain in the ratio of CA/LNZ 20:20 and 40:10. This result occurs due to the thickness of the synthesized membrane were reduced by increasing CA concentration. Increasing CA concentration from 20% to 40% and LNZ loading from 10% to 20% intensifies thermodynamic instability of the cast film solution and thus demixing of this concentrated solution can be performed with less amount of nonsolvent. It also observed from the experiment, viscosity values of the casting solutions are too much and thus it affects diffusivities of ingredients. Increase in the CA concentration 30% to 40% increase in viscosity values and intensive reduction of mutual diffusivities between the nonsolvent (water) and the solvent (acetone) in the system during solidification of the casting solution. Thus, it influence the precipitation process and this leads to preparation of thinner and denser membranes.

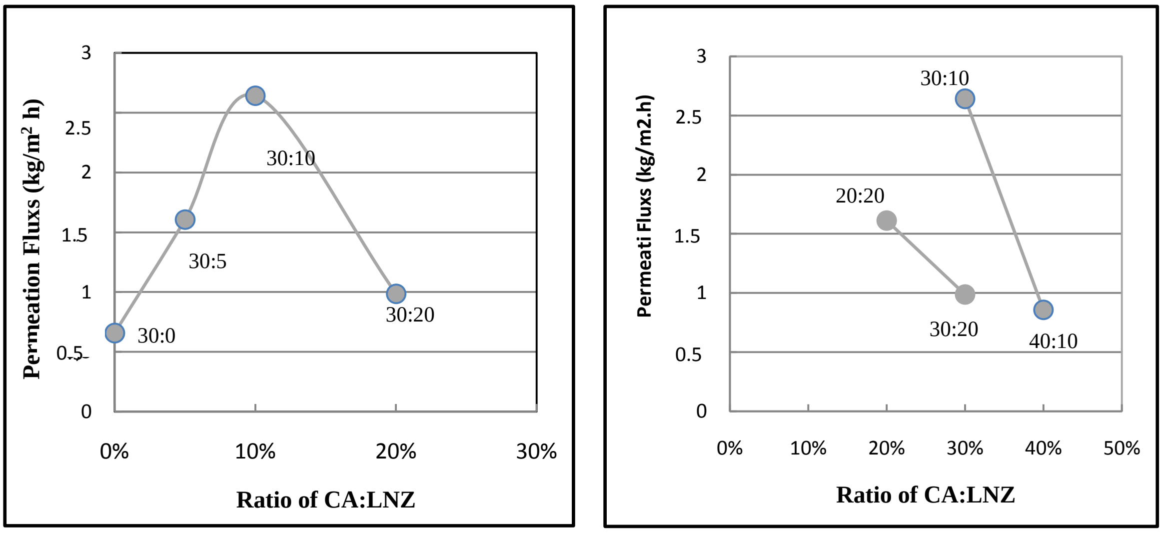


Figure 4 Effect of addition of LNZ into CA solution in varied ratio of CA/LNZ to pervaporation performance of permeation fluxs

Differ with flux permeation value, the selectivity of membrane in ratio of CA/LNZ 30:10 decreases and it was decreasing the dehydration performance of ethanol (97.67%). However, when the ratio of CA/LNZ 30:20 the selectivity of membrane was higher than the separation factor of pure CA and other CA:LNZ ratio. Based on the results, it was observed that increase of LNZ loading into membrane casting solution made hydrophilicity of the membrane changes the membrane morphology in a manner that the flux permeation increase. This can be explained that the transport of ethanol molecules through the CA filled LNZ membranes took place in a straight path through the zeolite pores and led to increase of the separation factor.

Increase in separation factor has achieved when the LNZ content was 20 wt%. The increase in separation factor may have been attributed to the pore size effect of LNZ and a close contact between the polymer and LNZ particles.When excess LNZ was added, more interfacial defects could be generated. Consequently, more ethanol molecules got the opportunity to pass through the membrane. However, the data are shown in the CA / LNZ ratio of 30:10 disagree with the theory or the trend shown by the other data. This is predicted when LNZ mixing in the casting solution causes the viscosity was too high, thus, resulting in an inhomogeneous mixing between CA and LNZ.

Tabel 1 Effect of CA/LNZ Ratio to selectivity and ethanol concentration

Ratio of CA/LNZ	Selectivity (%)	Ethanol Conc. (%)
30 : 0	20,68	97,85
30 : 5	22,15	97,92
30 : 10	17,27	97,67
30 : 20	80,42	99,08
40 : 10	46,88	98,65
20 : 20	31,77	98,28

4. Conclusion

Ratio of CA:NZL affects membrane characteristics and performance. However, the portion of the LNZ added as filler should not be too high, as it may decrease the efficiency of the separation. The best membrane performance was obtained at CA/ZAL ratio 30:20 with flux value 0.986 kg/ m^2.jam, selectivity 80.42 and obtained highest ethanol purity that is equal to 99.081%. Addition of ZAL can improve the hydrophilicity properties of CA membranes.

5. Acknowledgement

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6. References

Abedini R, Mousavi RM, Aminzadeh R 2011 A Novel Cellulose Acetate (CA) Membrane Using TiO_2 Nanoparticles: Preparation, Characterization and Permeation Study, Desalination 277 40–45

Arthanareeswaran G, Thanikaivelan P, Srinivasn K, Mohan D, Rajendran M 2004 Synthesis, Characterization and Thermal Studies on Cellulose Acetate Membranes with Additive, European Polymer Journal 40 2153–2159.

Arthanareeswaran G, Sriyamuna Devi T.K, Raajenthiren M 2008 Effect of Silica Particles on Cellulose Acetate Blend Ultrafiltration Membranes: *Part I*, Separation and Purification Technology 64 38–47

Chapman PD, Oliveirab T, Livingstona AG, Li K 2008 Membranes for the Dehydration of Solvents by Pervaporation, Journal of Membrane Science 318 5–37

Dogan, H and Hilmioglu N D 2010 Chitosan Coated Zeolite Filled Regenerated Cellulose Membrane for Dehydration of Ethylene Glycol/Water Mixtures by Pervaporation, Desalination 258 120–127.

Huang HJ, Ramaswamya S, Tschirner UW, Ramaraob BV 2008 A Review of Separation Technologies in Current and Future Biorefineries, Separation and Purification Technology 62 1–21.

Kanagaraj P, Neelakandan S, Nagendran A 2014 Preparation,Characterization and Performance of Cellulose Acetate Ultrafiltration Membrane Modified by Charged Surface Modifying Macromolecule, India : Korean Journal of Chemical Engineering 31:6 1057-1064.

Kanse NG and Dawande SD 2015 A Review Of Pervaporation Membrane System For The Separation Of Ethanol/Water (Azeotropic Mixture), International Journal Engineering Scince & Research Techology ISSN: 2277-9655 http: // www.ijesrt.com

Ling LK, Ghazali M. Nawawi M, Sadikin AZ 2008 Pervaporation of Ethanol-Water Mixture Using PVA Zeolite-Clay Membranes, Jurnal Teknologi Universitas Teknologi Malaysia, 49(F) 167–177.

Minhas FT, Farrukh S, Hussain A, Mujahid M 2015 Comparison of Silica and Novel Functionalized Silica-Based Cellulose Acetate Hybrid Membrans in Gas Permeation Study, Journal of Polymer Research 22: 63

Mulder M 1996 *Basic Prinsiple of Membran Technology, 2nd edition Dordrecht: Kluwer Academic Publisher*.

Pabby, Anil K., Syed SH, Rizvi, Requena AM 2015 *Handbook of Membran Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications, 2nd edition CRC Press, Taylor & Francis Group*.

Samanta HS and Ray SK 2014 Separation of ethanol from water by pervaporation using mixed matrix copolymer membranes, Separation Purification Technology Journal doi: http://dx.doi.org/10.1016/j.seppur.2015.03.006

Sivakumar, Muthusamy, Mohan D R, Rangarajan R 2006 Studies on Cellulose Acetate Polysulfone Ultrafiltration Membranes II: Effect of Additive Concentration, Journal of Membran Science Volume 268; 2 208–219.

Wang Y, Yang L, Luo G, Dai Y 2009 Preparation of Cellulose Acetate Membrane Filled With Metal Oxide Particles for the Pervaporation Separation of Methanol/Methyl Tert-Butyl Ether Mixtures, Chemical Engineering Journal 146 6–10

Zhan X, Li JD, Chen J, Huang J 2009 Pervaporation of Ethanol/Water Mixtures with High Flux by Zeolite-Filled PDMS/PVDF Composite Membranes, Chinese Journal of Polymer Science 27:6 771−780.