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Study of Polymeric Membranes Potential for Eugenol Purification from Crude Clove leaf Oil

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Clove oil is an agricultural commodity with economic value. This essential oil can be obtained from flowers, stems, and leaves of clove plants. The quality of clove oil can be evaluated from eugenol levels in oil. An increase in eugenol levels from 70% to 98% can increase oil prices by up to 3 times. Oil obtained from clove leaves has a low eugenol content of 60-70%, therefore the purification is needed to improve the quality of oil. Membrane based separation for eugenol purification was suggested in this paper as new concept in essential oils purification processes. This study aimed to explore the suitable polymer as membrane material for eugenol purification. PES, PA, CA and PI were used in this study, where the membranes were prepared via NIPS technique using manual casting knife to form flat sheet membranes. The membranes were immersed in eugenol to evaluate the solubility. The insoluble membrane was used for purification performance test in membrane filtration cell. The results show that PES and PA membranes were completely dissolved in eugenol in less than 1 minute, while PI and CA membranes were insoluble in eugenol. However, the PI membrane has much lower solvent permeability than CA membrane. The thermal annealed PES membrane for 3 h at 180°C dissolved in eugenol in 30 minutes for complete dissolution. It is concluded that PI and CA membranes can be used as membrane material for eugenol purification but CA more favorable, while PES membrane has a potential for similar purposes after being thermal annealed. However, these findings can offer an important reference for the application of polymeric membranes for clove oil purification through an effective and efficient process.

Keywords : Clove oil, dead-end filtration, Eugenol, Polymeric Membrane, Purification

INTRODUCTION

Clove plant (*Eugenia aromaticum*) is one of plantation crops that can be used as a producer of essential oils that are very useful (Widayat, et al. 2014a). The essential oil of clove plant can be obtained from flowers, stems, and leaves of clove plants. The oil which is obtained from clove leaf distillation is called clove leaf oil. Essential oils, including clove leaf oils, contain a broad range of high value chemical species, many of which have valued organoleptic properties that are used in the food and beverage industry, and the flavour and fragrance industry for example (Kusworo et al., 2018a). In many applications the removal of certain natural and synthetic impurities are the key part of processing the crude essential oil (Vaisali et al., 2015). Natural impurities include components that form solid "wax" material either after extended period of standing or when the oil is cooled, these include but are not limited to high molecular weight hydrocarbons or esters, coumarins, sterols, flavonoids, etc (Chaieb et al., 2007). Furthermore, synthetic impurities that may be present in the crude oil and these include but are not limited to organic compounds extracted from packaging materials (e.g. phthalates) and agrochemicals (e.g. insecticides, fungicides, etc.) (Suarya, 2008).

The quality of clove oil can be evaluated from eugenol levels in oil. An increase in eugenol levels from 70% to 98% can increase oil prices by up to 3 times (Marwati, et al. 2005). Oil obtained from clove leaves has a low eugenol content of 60-70%, therefore the purification is needed to improve the quality of oil (Hidayati, 2003). Clove leaf oil is produced from clove plant materials through three main routes, distillation, extraction with a suitable hydrophobic solvent and expression (physical crushing) depending on the location of the oil within the plant material and the inherent properties of the oil (Guan et al., 2007; Raseem and Nour, 2016). In all cases the production technique generates a solution containing a mixture of compounds. In many cases the essential oil must be removed from a second aqueous phase that is present as a result of the production process. Furthermore, the valuable components of the oil must often be further separated from unwanted materials present in produced oil to generate the final desired product.

The recent technologies for clove oil purification are physical method (e.g distillation and adsorption) and chemical method (using strong alkali and chelating agents). Widayat et al. (2014b) developed vacuum fractionation distillation to obtain high purity eugenol. They achieved the purity of eugenol up to 90%. The chemical method using NaOH produced an eugenol content of 83% while the combination of zeolite adsorption and citric acid addition as chelating agent produced the eugenol content of 86%. The combination process of fractionation distillation and adsorption successfully achieved higher concentration of eugenol up to 98%. However, the recent technology such as distillation needs high energy consumption while chemical methods produced chemical waste that needs further complex treatment before being disposed. Current separation technology that has most attention by researchers is membrane technology (Nasution, et al. 2013; Kusworo et al., 2017a).

Membrane is a selective barrier which has many advantages include membrane processes can separate at the molecular scale up to a scale at which particles can actually be seen, this implies that a very large number of separation needs might actually be met by membrane processes (Kusworo et al., 2017b), Membrane processes generally do not require a phase change to make a separation (with the exception of pervaporation). As a result, energy requirements will be low unless a great deal of energy needs to be expended to increase the pressure of a feed stream in order to drive the permeating component(s) across the membrane, Membranes can be produced with extremely high selectivities for the components to be separated, very large number of polymers and inorganic media can be used as membranes, there can be a great deal of control over separation selectivities, potentially better for the environment since the membrane approach require the use of relatively simple and non-harmful materials, membrane is modular and easy to be scaled-up, and most of membrane operations are carried out in ambient temperature and mild condition (Boam, et al. 2013). However, membrane has some disadvantages such as fouling of the membranes while processing some type of feed streams, chemical incompatibilities with process solutions, and membrane modules often cannot operate at much above room temperature.

The use of membranes to concentrate the valuable essential oil components are very few. Peev et al (2011) discloses the use of organic solvent nanofiltration membranes for the concentration of a rosmarinic acid extract from lemon balm. Tylkowski et al. (2011) reported the use of organic solvent nanofiltration membranes to concentrate an aqueous ethanolic extract of propolis. Carlson et al. (2005) disclose the application of reverse osmosis membranes to separate supercritical carbon dioxide from limonene. And Dupuy et al. (2011) also report the application of membranes in the form of membrane contactors to provide emulsion-free extraction of essential oil components from lemon oil into aqueous ethanolic solutions. However, there is very few the literature about eugenol purification from clove leaf oil. In this study, some polymers such as polyethersulfone (PES), polyamide (PA), polyimide (PI), and Cellulose acetate (CA) are investigated. The study aimed to explore the suitable polymer as membrane material for eugenol purification.

MATERIALS AND METHODS

Materials

Polyethersulfone (PES), and Polyimide (PI) were purchased from solvay advanced material, Cellulose acetate (CA) polymer was purchased from Alpha Chemika, India. N-methyl pirrolidone (NMP), dimethylacetoamide (DMAc), and acetone were purchased from Merck. Polyamide (PA) flatsheet membrane was supplied by Membrane Research Center (MER-C), Diponegoro University. Clove leaf oil was purchased from cloves leaf farmer in Gunung Pati, Indonesia.

Fabrication of Polymeric Membranes

PA was supplied in flat sheet membrane form, while PES, PI, and CA were supplied in powder and granularpolymer forms. In this study, the flat sheet membranes were fabricated using dry-wet phase inversion technique (Kusworo et al., 2018b; Moghadassi et al., 2014). Homogenous dope solutions consist of CA 17 wt% concentration in acetone. PES 17 wt% in NMP, and PI 17 wt% in DMAc. The dope solutions were agitated with a stirrer at least 12 hours to ensure complete dissolution of the polymer. After all of the materials mix completely, the dope solution allowed to stand for 24 hours to remove bubbles. The dope solutions were casted over the glass plate with casting knife. The casted membranes were diped into coagulation bath containing aquadest for 24 hours. The membranes were bried in the vacuum oven for 24 hour at 40-50°C.

Membrane Characterization

Membrane characterization with Scanning Electron Microscopy (SEM) JEOL series JSM-6510-LA, Japan was used to determine the cross-sectional and surface morphology of the membrane. The membrane samples were cleaned with filter paper, then fractured in liquid nitrogen and coated with a gold layer by sputtering. The samples were placed in sample holder and scanned.

Membrane Compatibility Test in Eugenol

Membranes can have chemical incompatibilities with process solutions. This is especially the case in typical chemical industry solutions which can contain high concentrations of various organic compounds. Against such solutions, many polymer-based membranes (which comprise the majority of membrane materials used today), can dissolve, or swell, or weaken to the extent that their lifetimes become unacceptably short or their selectivities become unacceptably low. To test the membrane compatibilies, 0.1 gram of flat sheet membranes were weighed and placed in petri disk. 10 mL of eugenol was poured into petri disk containing flat sheet membrane. The membranes were observed if any changes with their structure such as dissolved, swollen, or weaken.

Membrane Swelling Degree Measurement

Measurement of swelling degree was difficult to be measured directly, however the gravimetric method has been developed by Yi and Bae (2017) with several assumption for simplification. The analysis was carried out by preparing the samples of membranes (5 cm x 5 cm) and were dried in oven at 50°C temperature for 1 h then weighed as dry membrane weight (W_0). The membrane samples were then immersed in eugenol and then weighed every 1 h for 4 h to obtain a mass of swollen membrane (W_i). The degree of swelling was expressed as the ratio of membrane volume changes as expressed by equation 1:

$$\frac{V_i}{V_0} = \frac{(W_0/\rho_{mem}) \times \left[(W_i - W_0)/\rho_{eug}\right]}{W_0/\rho_0} \tag{1}$$

V_i and V_0 were the membrane volumes under swelling conditions and initial conditions. W0 and Wi were the mass of dry membrane and swollen membrane with solvent. ρ_{mem}, ρ_{eug}, and ρ_0 were membrane densities of swollen membrane without solvent, eugenol, and dry membrane. In this study, ρ_{mem} and ρ_0 were assumed to be the same.

Solvent Permeability and Membrane Performance Tests

Only the membranes with good compatibility which were tested for solvent permeability. Membrane samples were mounted on the membrane holder in dead-end filtration cell (Figure 1). The cylinder for feed chamber was placed correctly over the membrane holder and thightenned. 100 mL of n-hexane solvent was filled in the cylinder chamber. The upstream membrane was pressurized using inert gas (N_2) at 2 bar-gauge. The volume of solvent permeates are measured and the permeate fluxes were calculated using Equation 2. For membrane performance test, the n-hexane solvent was replaced with clove oil sample after being mixed with n-hexane (25 wt-%).

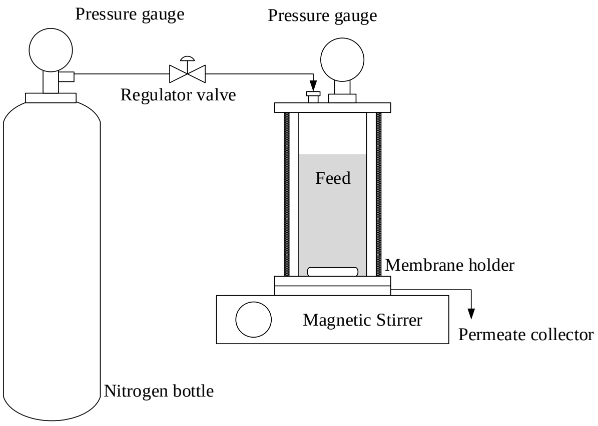


Fig. 1: Dead-end membrane filtration cell

$$J = \frac{V}{P.A.t} \qquad (2)$$

Determination of Total Eugenol Content

Eugenol is phenolic compound, it will react with strong alkali to form phenolat. The other components (impurities) such as beta caryophillene is non-phenolic compound which doesn't react with alkali (Ayoola et al., 2008). 5 mL eugenol was measured thoroughly and filled into test tube. 10 mL of KOH 4% was added into the test tube containing clove oil sample. The mixture was heated in hot water bath for 10 minutes and then mixed. The top layer was removed and then 10 mL of HCl 1 N was added into test tube. The top layer of solution was removed, the remaining liquid was measured as eugenol volume. The eugenol content was calculated using Eq. 2. To obtain the information about membrane selectivity performance, the eugenol contents of feed and permeate were analyzed.

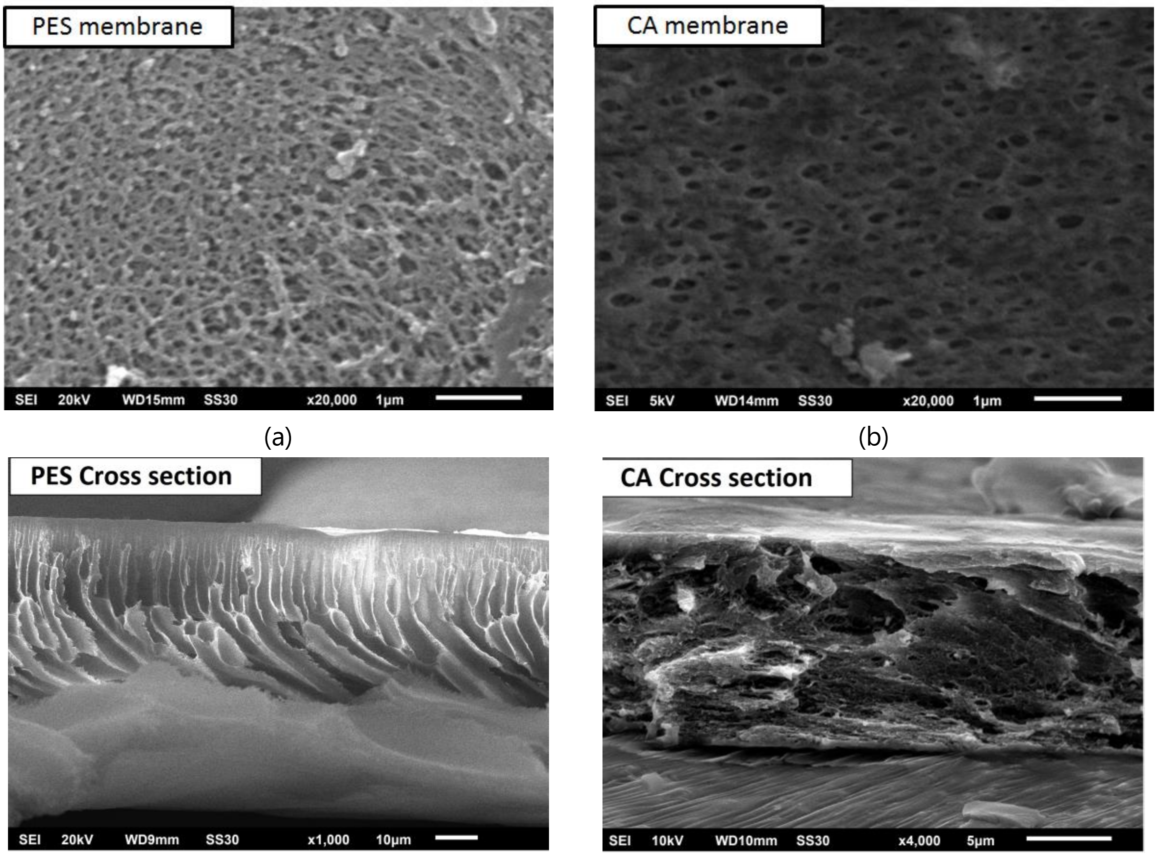
$$Eugenol\ (\%) = \frac{vol.eugenol\ (mL)}{vol.sample\ (mL)} x100\% \qquad (3)$$

RESULTS AND DISCUSSIONS

Membrane Characterization Results

The morphology of CA and PES membranes can be known through analysis using SEM (Scanning Electron Microscopy). The use of SEM analysis makes it possible to know the surface appearance of the membrane and its transverse appearance. The result of SEM membrane analysis with the effect of polymer concentration is shown in Figure 2.

From Figure 2, the surface appearance of membranes with magnification 20,000 times, membrane b (17% cellulose acetate) has fewer pores than membrane a (17% polyethersulfone). This reinforces the phenomena occurring in flux and rejection, as has been previously



(a) (b)

(c) (d)

Fig. 2: SEM images of (a) PES membrane surface, (b) CA membrane surface, (c) PES membrane cross section, and (d) CA membrane cross section

discussed. Increased polymer concentration will increase the thickness of the top layer and decrease membrane porosity as well as pore connectivity, so that macrovoid formation will be reduced.

In Figure 2.b it appears to have a larger pore size. This is because the dope solution has a lower viscosity. After solidification of the polymer phase, low viscosity will result in rapid pore formation (Van de Witte et al., 1996). Rapid internal pore growth leads to the formation of larger pore sizes. With a decrease in polymer concentration, the overall porosity will increase. As shown in sub Figure 2.c, the cross sectional image of PES membrane shows the finger-like structure while in Figure 2.d, sponge-like structure was dominant. The formation of void structure on sub layer of membrane was caused by the physical properties of dope solution and the thermodynamic equilibrium during phase separation process.

Polymeric Membrane Compability in Eugenol

Generally PES, PA, PI and CA polymers are used for treating water, so the possibility of polymer dissolution is very small because the polymers are insoluble in water. Unlike the case in this study, where the material to be processed is clove oil with the main content is eugenol. Eugenol is a non-polar organic compound. The compability test in this study was carried out by observing the posibility of dissolution, swelling, or weaken. Therefore it is necessary to test the membrane resistance to eugenol by soaking the membrane in clove oil while observed changes that occur. The results of compability test are presented in Table 1.

Table 1. Membrane compatibility test in eugenol

No.	Polymers	Observation
1.	PES	Completely dissolve in 1 minute
2.	Thermal annealed PES	Completely dissolve in 30 minutes
3.	PI	Insoluble
4.	PA	Dissolved instantly
5.	CA	Insoluble

Based on Table 1, the membranes materials such as polyethersulfone (PES) and polyamide (PA) are not suitable for use as membrane material for processing of clove oil due to its considerable solubility in eugenol. However, there is a phenomenon with the thermal treatment of the membrane material that can prolong the solubility of the polymer, ie for the PES membrane after the heat treatment treatment at 180°C for 3 hours showed a change. The heated polymer becomes slightly insoluble in eugenol, this is due to the heat effect on the membrane structure. As for membrane materials such as polyimide (PI) and cellulose acetate (CA) are quite potential as membrane material as needed in this study because they showed the insolubility in eugenol. For further research, the membranes to be used for next experiments are CA and PI because the meterial membrane shows better resistance over eugenol than other polymers (PES aand PA).

Membrane Swelling Degree

Membrane swelling degree is a volume ration of swollen membrane and initial membrane. Some polymeric membranes have chemical incompatibility if contact with eugenol. Some of the will tend to swell, dissolve, and weaken. Based on compatibility test, the CA membrane is the suitest membrane for clove oil filtration. However, the swelling phenomenon was occur during filtration process using CA membrane. Swelling of the membrane was caused by the penetration of eugenol molecule into polymer chain that make the polymer moves from their intial structure. This interaction could be due to the affinity between polymer and eugenol. The profile of membrane swelling degree was shown in Figure 3.

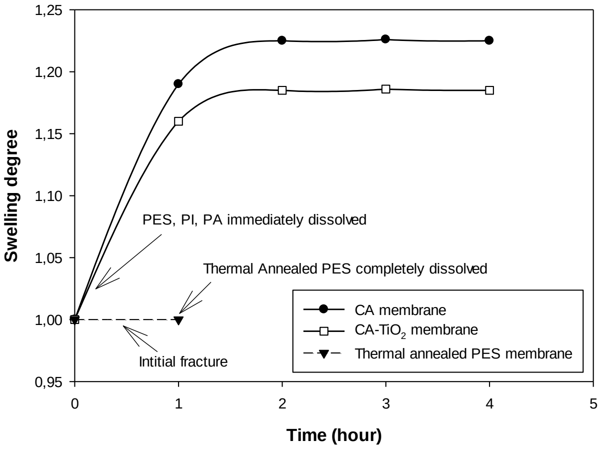


Fig. 3: Profile of membrane swelling degree

As shown in Figure 3, neat PES, PI, and PA immediately dissolved after being immersed in eugenol. The thermal annealed PES needs 30 minute to intiate fracture and completely dissolved in 30 minute. The thermal treatment increase the crystallinity of the membrane which may cause longer dissolution time in eugenol. The neat CA membrane swells about 20% after being immersed in eugenol for an hour, and the swollen membrane slightly changes for more than an hour. CA membrane with nano-TiO_2 loading as much as 1% decreases the swelling degree from 20% into 17%. The introduction of inorganic material shows a significant effect in suppressing the membrane swelling, this phenomenon is accordance with the previous study conducted by Amnuaypanich et al. (2009). The presence of TiO_2 particle restricts the free movement of polymeric chain during immersion process. This result shows that the incorporation of inorganic nano-material supressed the swelling degree of membrane.

Solvent Permeability Test Result

Carrier solvent is a very important factor in membrane applications for organic compunds separation. Clove oil has a high viscosity. A large viscosity will make it difficult to penetrate through the membrane so that a large operating pressure will be required, as large operating pressure will cause the membrane to break easily. Therefore a carrier solvent is required to facilitate the permeation of clove oil components. A good solvent for eugenol is n-hexane, in addition n-hexane is a non-toxic solvent and is widely used in the extraction of foodstuffs other than that it is cheap. Solvent permeation test is important to see the performance of the membrane in this application, because the solvent is hydrophobic while the membrane used (Cellulose acetate) is hydrophilic. Solvent permeation test results using a dead-end filtration cell are shown in Figure 4.

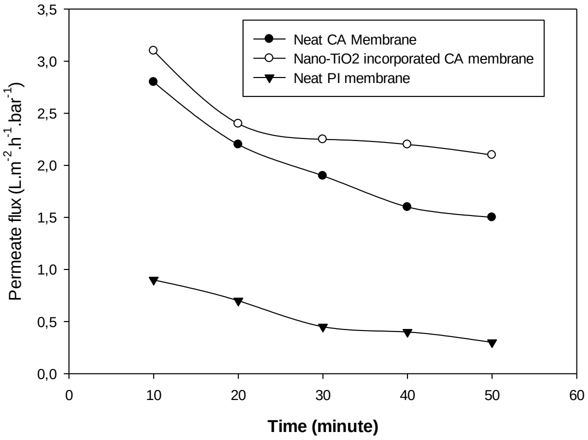


Fig. 4: Flux profile of n-hexane permeate

Based on Figure 4, the permeation of n-hexane in cellulose acetate is quite low because it is influenced by the hydrophilicity of the membrane and solvent hydrophobicity. The cellulose acetate membrane has a hydrophilic property, whereas the n-hexane solvent is hydrophobic, causing a low n-hexane permeation rate. The initial flux of neat CA membrane was 2.8 L.m^{-2}h^{-1}bar^{-1} while in TiO_2 impregenated CA membrane was about 3.1 L.m^{-2}h^{-1}bar^{-1}, slightly higher than neat CA membrane. The flux profile as time funtion showed drastical decline of flux profile due to compaction process during filtration process. The higher flux of TiO_2 impregnated membrane might be due to the presence of nano particle avoided the clogged pores formation. However, the permeation in PI membrane is much lower than CA membrane about 0.9 L.m^{-2}h^{-1}bar^{-1} at initial flux and 0.4 L.m^{-2}h^{-1}bar^{-1} afer 50 minutes operation. The profile of the solvent flux appears to be slightly decreased as a result of the membrane compaction and narrowing the membrane pores. For further experiment, CA membrane is used for clove oil purification due to its higher permeation performance than PI membrane. Moreover, CA membrane is much cheaper than PI membrane.

Membrane Performance in Clove Oil Purification

Performance test of CA membrane for clove oil purification was carried out by applying the membrane in dead-end filtration cell. The clove oil permate flux and eugenol content of feed and permeat are analyzed to evaluate the performance of CA membrane. The permeation profile result is shown in Figure 4 and eugenol content is shown in Figure 5.

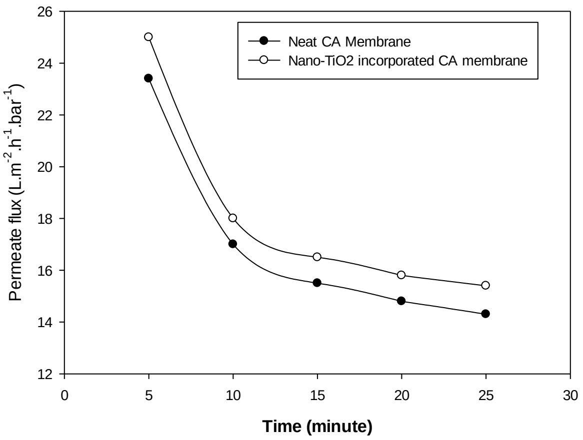


Fig. 5: Clove oil flux profile of CA membrane and CA-TiO2 1.0 wt-% membrane

Figure 5 shows the clove oil flux profile for CA membrane. Flux decreases with filtration time due to compaction and fouling on the membrane surface. The initial flux of clove oil in the CA membrane is 23.4 L.m^{-2}h^{-1}bar^{-1} and then drops drastically to 13 L.m^{-2}h^{-1}bar^{-1} after 25 minutes filtration. Based on permeation experiment, it can be said that CA membrane with 17% polymer concentration gives good enough flux value although it is still relatively low. To improve the membrane performance in terms of flux there needs to be further modification. Filtration operation using CA membranes to purify clove oil causes swelling on the membrane when the process is run for more than 1 hour. This results in decreased selectivity of the membrane. for further research there is an attempt to modify the CA membrane material to reduce the possibility of swelling. The nano-TiO$_2$ impregnated CA membrane shows a better flux profile compared with neat CA membrane. The initial flux was 25 L.m^{-2}h^{-1}bar^{-1} and drastically decreased into 15 L.m^{-2}h^{-1}bar^{-1}.

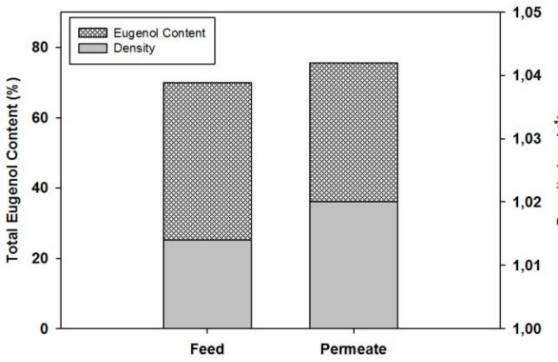


Fig. 6: Eugenol content and density of feed and permeate

Figure 6 shows the eugenol content and density of feed and permeate oil after being filtered using CA membrane. The eugenol content of feed was 70% and the eugenol content of permeate was 75.5%. Filtration process using conventional CA membranes can increase the eugenol content up to 7.8%. It indicates that membrane based separation for clove oil is possible. However, the eugenol content is slightly increase. This separation could be due to beta-caryophyllene molecules were rejected by hydrophilic CA membrane. Eugenol molecule has hydroxyl (OH) group while caryophyllene is satisfied with methyl group. It exhibits that eugenol more hydrophilic than caryophyllene. The density of clove oil also increases after the clove oil being filtered using CA membrane. The density profile corresponds to the content of eugenol in clove oil because the clove oil density depends on the main component contained in clove oil. Although the content of eugenol in clove oil permeate is below acceptable standards, it provides important information that CA membrane is suitable for application in clove oil purification. However, CA membrane will be swollen after 1 h operation, this phenomenon resulted in membrane selectivity decline. This experiment gives the information that among the tested polymeric membrane, CA membrane is the most favorable membrane for clove oil purification as long as the swelling doesn’t occur.

CONCLUSION

The polymeric membrane (PES, PA, PI, and CA) were succesfully fabricated using dry-wet phase inversion. The membrane structure is asymmetric consisting of dense top layer, finger-like porous structure of sublayer. The compability test showed that PI and CA membrane were the suitable membrane for clove oil purification. The permeability test exhibited that CA membrane has better permeate flux than PI membrane. CA membrane showed quite good permeation of clove oil and able to increase the eugenol content in permeat up to 7.8%. however, CA membrane tends to swell after being operated for more than 1 h. The modification is needed for CA membrane to obtained favorable membrane for clove oil purification.

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REFERENCES

1. Amnuaypanich, S., Patthana, J., & Phinyocheep, P. (2009). Mixed matrix membranes prepared from natural rubber/poly (vinyl alcohol) semi-interpenetrating polymer network (NR/PVA semi-IPN) incorporating with zeolite 4A for the pervaporation dehydration of water–ethanol mixtures. Chemical Engineering Science, 64(23), 4908-4918.
2. Ayoola, G. A., Lawore, F. M., Adelowotan, T., Aibinu, I. E., Adenipekun, E., Coker, H. A. B., &

Odugbemi, T. O. (2008). Chemical analysis and antimicrobial activity of the essential oil of Syzigium aromaticum (clove). African Journal of Microbiology Research, 2(7), 162-166.

3. Boam, A. Meniconi, and X. Wu, (2013). Membrane-based processes for selectively fractionating essential oils. WO Patent No. 2013167307 A1.
4. Carlson, L. H. C., Bolzan, A., & Machado, R. A. F. (2005). Separation of d-limonene from supercritical CO_2 by means of membranes. *The Journal of supercritical fluids*, *34*(2), 143-147.
5. Chaieb, K., Hajlaoui, H., Zmantar, T., Kahla-Nakbi, A. B., Rouabhia, M., Mahdouani, K., & Bakhrouf, A. (2007). The chemical composition and biological activity of clove essential oil, Eugenia caryophyllata (Syzigium aromaticum L. Myrtaceae): a short review. *Phytotherapy Research: An International Journal Devoted to Pharmacological and Toxicological Evaluation of Natural Product Derivatives*, 21(6), 501-506.
6. Dupuy, A., Athes, V., Schenk, J., Jenelten, U., & Souchon, I. (2011). Solvent extraction of highly valuable oxygenated terpenes from lemon essential oil using a polypropylene membrane contactor: potential and limitations. *Flavour and fragrance journal*, *26*(3), 192-203.
7. Guan, W., Li, S., Yan, R., Tang, S., & Quan, C. (2007). Comparison of essential oils of clove buds extracted with supercritical carbon dioxide and other three traditional extraction methods. *Food Chemistry*, 101(4), 1558-1564.
8. Hidayati, N. (2003). Ekstraksi eugenol dari minyak daun cengkeh. *Jurnal Teknik Gelagar*, 14(2), 108-114.
9. Kusworo, T. D., Soetrisnanto, D., & Utomo, D. P. (2018a). Development of Nano-hybrid Cellulose Acetate/TiO2 Membrane for Eugenol Purification from Crude Clove Leaf Oil. In *MATEC Web of Conferences* (Vol. 156, p. 08013). EDP Sciences.
10. Kusworo, T. D., Utomo, D. P., & Ramadhan, I. R. (2018b). Enhancement of separation performance of nano hybrid PES–TiO2 membrane using three combination effects of ultraviolet irradiation, ethanol-acetone immersion, and thermal annealing process for CO2 removal. *Journal of Environmental Chemical Engineering*, 6(2), 2865-2873.
11. Kusworo, T. D., Aryanti, N., & Utomo, D. P. (2017a). Effect of ultraviolet on the morphology and performance of PES-nano-silica hybrid membrane for produced water treatment. *Advanced Science Letters*, 23(6), 5744-5747.
12. Kusworo, T. D., Aryanti, N., Anggita, R. A., Setyorini, T. A. D., & Utomo, D. P. (2017b). Surface modification and performance enhancement of polyethersulfone (PES) membrane using combination of ultra violet irradiation and thermal annealing for produced water treatment. *Journal of Environmental Science and Technology*, 10(1), 35-43.
13. Marwati, T., Rusli, M. S., Noor, E., & Mulyono, E. (2005). Peningkatan mutu minyak daun cengkeh melalui proses pemurnian. *Jurnal Penelitian Pascapanen Pertanian*, *2*(2), 45-52.

14. Moghadassi, A. R., Rajabi, Z., Hosseini, S. M., & Mohammadi, M. (2014). Fabrication and modification of cellulose acetate based mixed matrix membrane: Gas separation and physical properties. Journal of Industrial and Engineering Chemistry, 20(3), 1050-1060.
15. Nasution, I. K., Susilo, B., & Nugroho, W. A. (2013). Uji Kinerja Alat Pemurni Minyak Atsiri Daun Cengkeh (Clove Leaf Oil) berbasis Membran Kitosan-Selulosa. *Jurnal Keteknikan Pertanian Tropis dan Biosistem*, *2*(1). 9-14.
16. Peev, G., Penchev, P., Peshev, D., & Angelov, G. (2011). Solvent extraction of rosmarinic acid from lemon balm and concentration of extracts by nanofiltration: Effect of plant pre-treatment by supercritical carbon dioxide. *Chemical Engineering Research and Design*, *89*(11), 2236-2243.
17. Rassem, H. H., & Nour, A. H. (2016). Techniques for extraction of essential oils from plants: a review. *Australian Journal of Basic and Applied Sciences*, 10(16), 117-127.
18. Suarya, P. (2008). Adsorpsi pengotor minyak daun cengkeh oleh lempung teraktivasi asam. *Jurnal kimia*, *2*(1). 19-24
19. Tylkowski, B., I. Tsibranska, R. Kochanov, G. Peev, & M. Giamberini. (2011). Concentration of biologically active compounds extracted from Sideritis ssp. L. by nanofiltration. *Food Bioproducts Processing.*, ***89***(4), 307-314.
20. Vaisali, Chandrasekar, Sampath Charanyaa, Prasanna D. Belur, and I. Regupathi. "Refining of edible oils: a critical appraisal of current and potential technologies." *International Journal of Food Science & Technology* 50, no. 1 (2015): 13-23.
21. Van de Witte, P., Dijkstra, P. J., Van den Berg, J. W. A., & Feijen, J. (1996). Phase separation processes in polymer solutions in relation to membrane formation. *Journal of membrane science*, 117(1-2), 1-31.
22. Widayat, W., Haidar, M. H., Cahyono, B., Ngadiwiyana, N., Nurdiana, L., & Satriadi, H. (2014a). Proses Destilasi Vakum Pada Minyak Cengkeh Pada Tekanan Vakum: Simulasi Dan Eksperimen. In *Prosiding Seminar Nasional Rekayasa Kimia dan Proses 2013,* 17, 1-6. Department of Chemical Engineering, Diponegoro University.
23. Widayat, W., Hadiyanto, H., Cahyono, B., & Ngadiwiyana, N. (2014b). Optimization in Eugenol Production from Clove Oil with Saponification–Neutralization Process by using Response Surface Methods. In *Prosiding International Seminar on Chemical Engineering In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2014* (pp. 729-740). Department of Chemical Engineering Institut Teknologi Bandung Indonesia.
24. Yi, Y.D., and Bae, Y. 2017. Swelling behaviors of proton exchange membranes in alcohols. *Polymer*, 130, 112-123.