Development of Nano-hybrid Cellulose Acetate/TiO_2 Membrane for Eugenol Purification from Crude Clove Leaf Oil

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Abstract. Chemical separation and purification are the important part of the chemical industry which consumes up to 70% energy cost. The separation technology such as distillation and absorption are well known in essential oil purification. The purification of clove leaf oil needs an attention because the current technology still consumes high energy and produces chemical wastes. The employment of membrane separation for clove leaf purification is a novel concept that needs many improvements. The main problem of polymeric membrane utilization is eugenol ability to dissolve the polymer membrane. Cellulose acetate is one of membrane polymers that is insoluble in eugenol. This paper reveals the performance of nanohybrid CA/TiO_2 membrane for eugenol purification. The stability of produced membrane as an organic solvent nanofiltration (OSN) is evaluated in this study. The SEM image result shows that fabricated membrane has an asymmetric structure of membrane sub-layer. The different nano-particles loading shows the variation of permeate fluxes, the increase of nano-particles in polymer blend tends to increase the permeability. Thus, this study provides an overview of the potential CA/TiO_2 for OSN development by incorporating inorganic nano-particles in membrane polymers for eugenol purification that can be integrated in upstream separation process.

1 Introduction

Chemical separation and purification are the important part of the chemical industry which specify the quality of the product. Generally, the separation process consumes up to 70% of energy costs for a chemical plant [1]. The separation technology such as distillation and absorption which requires a solvent removal by heating process are highly applied for essentials oils purification for example crude clove leaf purification [2]. The crude clove leaf oil is produced from leaves and twigs of the clove tree through distilation process. Crude clove leaf oil has lower quality than clove bud oil due to its eugenol content is bellow the quality standard of clove oil. The eugenol concentration in crude clove leaf oil ranged from 60 – 70% and needs to be purified to increase the economic value [3]. However, the recent technologies for crude clove leaf oil purification inflict the other problem such as high energy consumption, chemical waste generation, and needs a certain condition e.g vacuum, high temperature, etc [4]. Membrane separation technology can be proposed as an alternative separation technology because it is currently known as an inexpensive technology, low energy consumption, can be conducted in a mild operating condition, and easily to be scaled up [5].

Membrane separation is well used in the separation of gasses, water, proteins, and viruses. Several membranes have been developed for organic chamicals separation that is also known as an Organic Solvent Nanofiltration (OSN) membrane [6]. The field of OSN membranes refers to the separations of chemicals with molecular weights from 100 to 2,000 $g.mol^{-1}$ [7]. The main concerns in this study are developing the membrane material which is suitable for crude leaf oil purification and determining the best operating condition. The quality of clove leaf oil is defined by the content of eugenol and the main impurity of the crude clove leaf oil is Caryophyllene [3]. These chemicals are challenging to be separated using a membrane due to very few literature which reports about this separation concept.

Eugenol has molecular weight of 164 $g.mol^{-1}$ while the caryophyllene has a higher molecular weight of 204 $g.mol^{-1}$. Figure 1 shows the molecular structure of eugenol and caryophyllene, where there is a difference in their chemical potentials. Eugenol has hydroxyl and ether group which refer a hydrophilic properties, while caryophyllene has only methyl group. These different properties indicates that eugenol and caryophyllene are potential to be separated using membrane. Nasution et al. studied the purification of the clove oil using cellulose-

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chitosan membrane in a dead-end membrane filtration cell [8]. They found that the highest flux and eugenol quality of the permeate are 0.239 $L.m^{-2}.s^{-1}$ and 58.21% respectively. However, the concentration of eugenol in the permeate product is far bellow the desired standard and also there is not enough scienctific approach in the separation process. In the WO Patent that was invented by Boam et al. they disclosured in general relates to a process for reducing impurities present in an essential oil using selective membrane [9]. They reported that the membrane should gave MWCO at least 400 – 1500 $g.mol^{-1}$ and the essential oil should be dissolved in organic solvent before being filtrated using selective membrane. In their invention, there are no information about the specification of the selective membrane and opertaing condition for this purpose.

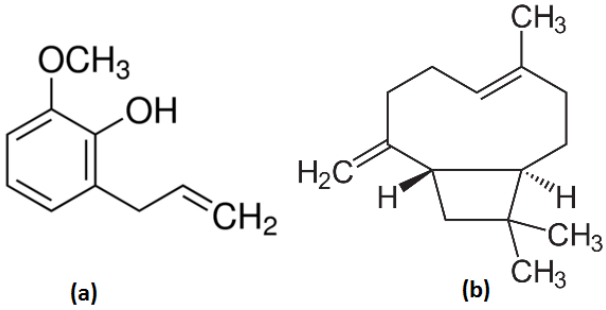

Fig. 1. Molecular structure of (a) eugenol, (b) caryophyllene

In this study, cellulose acetate (CA) polymer is used as membrane material due to its insolubility in eugenol. Other polymeric membrane such as polyethersulfone (PES), polyamide (PA), and polysulfone (PSf), can be used in this application because they are highly soluble in eugenol. The nano-TiO_2 is incorporated as an inorganic nanomaterial filler in the CA membrane fabrication to enhance its mechanical strength. The performance of CA/nano-TiO_2 membranes are discussed in this study and the final product quality of clove oil permeate are also reported.

2 Materials and Methods

2.1. Materials

Cellulose acetate (CA) polymer was purchased from Alpha Chemika, Mumbai, India. The polymer average molecular weight was 30 kDa and the acetic content was 53-56%. Acetone as polymer solvent was purchased from Merck. Nano-TiO2 was supplied by Nano Center Indonesia with average particles diameter were 128 nm. Original crude clove leaf oil was purchased from clove farmers in Semarang, Indonesia. The characteristics of crude clove leaf oil sample was shown in Table 1.

2.2 Fabrication of Nanohybrid CA/nano-TiO_2 Membrane

Flatsheet cellulose acetate (CA) membranes were fabricated by preparing the dope solution containing polymer CA (17 wt-%), nano-TiO_2 (1 and 2 wt-%), and

Table.1 Characteristics of crude clove leaf oil

No.	Parameter	Value
1.	Color and odor	Yellow brownish and typical clove
2.	Density 20ºC ($g.mL^{-1}$)	1.014
4.	Solubility in 70% Alcohol	Completely soluble
5.	Eugenol content (% v/v)	69.23 ± 0.71

acetone as solvent. An appropriate amount of nano-TiO_2 was poured into the acetone and then agitated for 1 h. Subsquently, the nano-TiO_2 mixture was added with powdered CA polymer gradually to avoid polymer aggregation The polymer mixture was mixed for 24 h. The CA dope solution was allowed to stand for another 24 h with gentle mixing to remove air bubbles and to prevent the precipitaion of nano-TiO_2. The membranes were casted using dry-wet phase inversion method. The CA dope solution was poured on the flat glass plate and then was casted using mechanic casting knife. The casted film was immediately soaked in distilled water for demixing process. The membranes were handled in storing tank containing distilled water at 30 ± 2°C for 24 h. Wet membranes were dried in the drying chamber at 40-50°C for 24 h [10].

2.3 Membrane characterization

The surface and cross-sectional structure images were analyzed using Scanning Electron Microscope (SEM) JEOL JSM-6510-LA. The membrane sample was immersed in liquid nitrogen and then fractured. The sample was sputtered with a gold layer before analyzing and then scanned at certain magnification.

The molecular weight cut-off (MWCO) of the membrane was determined to estimate the size of pore radius. The determination was performed in a dead-end filtration cell by applying the solution containing PEG with different molecular weight (400; 600; 1,000; 4,000; 6,000; and 10,000 Da), the permeate sample was analyzed using visual handheld refractometer (Atago). The MWCO was determined at 90% of solute rejection. The value of MWCO was used to estimate the pore size radius using Eq. 1 [11].

$$r_m(cm) = 16.73 \times 10^{-10}(MWCO)^{0.557} \quad (1)$$

Porosity of the membrane was performed by weighing the dried membrane and wetted membrane. The different weight of the membrane was assumed as void fraction. The porosity of membrane was calculated using Eq. 2.

$$\varepsilon = \frac{wt_0 - wt_i}{\rho_{water} A.l} \quad (2)$$

Where, ε is the membrane porosity, wt0 and wti are the membrane weights before and after drying, respectively. A is the membrane surface area, l is the membrane thickness and ρwater is water density. While water contact angle of membrane was determined to observe the hydrophilicity and the surface tension of membrane. Distilled water was used as a probe liquid and then dropped on the membrane surface. The water contact angle was immadiately average measured thress times at two points of positions.

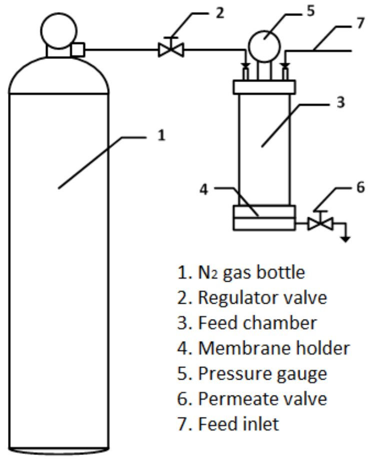

Fig. 2. Dead-end membrane filtration cell

2.4 Performance test of fabricated membrane

The performance test of fabricated membranes were carried out in a dead-end membrane filtration cell (Figure 2). The membrane with effective filtration area pf 12.56 cm^2 was conditioned in hexane solvent for 3 h and then mounted on membrane holder. Clove leaf oil sample was poured in filtration chamber with capacity of ± 100 mL. N_2 gas was streamed into filtration chamber as a gas suppressor and the pressure was maintained at 2 bar-gauge. The permeate flux was determined using Eq. 3. The permeate and consentrate of clove leaf oil were analyzed according to the quality parameter i.e density, and total eugenol content. The analysis methods refer to Indonesian National Standard (SNI 06-2387-2006) [12].

$$J = \frac{V}{t.A.P} \quad (3)$$

Where J is permeate flux ($L.h^{-1}m^{-2}bar^{-1}$), V is permeate solume at certain operation time (L), t is operation time (h), A is effective area of membrane (m^2), and P is pressure given to membrane (bar).

3 Results and Discussions

3.1 Membrane characterization results

Figure 3 shows the SEM image of CA membrane and CA/nano-TiO2 membrane both of surface and cross-section. The surface image of CA membrane is shown in Figure 3.a, the surface is flat and smooth, there is not observed any void at 20,000x magnification. It indicates that the membrane pores are in nanoscale. Figure 3.b displays the surface image of CA/TiO2 membrane, the polymer matrix is well attached on the nanoparticles surface. The cross-sectional SEM images (Figure 3.c and 3.d) show assymetric structure of membrane consists of dense layer and support layer of finger-like pore structure. Dense layer contributes on the membrane selectivity and the finger-like pore structure plays on the permeation performance.

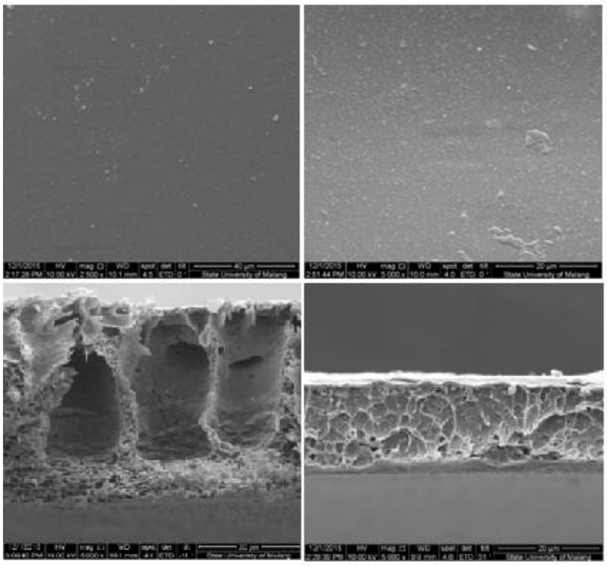

Fig. 3. SEM image of fabricated membrane

Table. 2 Characteristics of fabricated membrane

Membranes	MWCO (Da)	pore radius (nm)
CA	4839 ± 147	1.89 ± 0.27
CA/TiO_2 1%	4387 ± 298	1.79 ± 0.40
CA/TiO_2 2%	4253 ± 185	1.76 ± 0.31

Membranes	Porosity	Contact angle (θ°)
CA	0.51 ± 0.06	67.43 ± 1.2
CA/TiO_2 1%	0.43 ± 0.08	59.77 ± 1.5
CA/TiO_2 2%	0.39 ± 0.11	53.21 ± 1.1

Table 2. shows the characteristics of fabricated membrane which play important role in membrane performance. MWCO indicates the molecular weight of solute which is 90% rejected by membrane, it relates with pore size diameter. The increase in nano-TiO_2 loading concentration will decrease the MWCO value and pore diameter. This is due to the nano-particles fill the nano-voids in the membrane structure. Porosity of the membrane also decrease with the increase of nano-TiO_2 loading. The nano-fillers devide thelarge void into smaller voids without creating any dead-end void. The contact angle represents the hydrophilicity and surface tension of membrane. The lower contact angle of membrane indicates more hydrophilic membrane. The addition nano-TiO_2 in the membrane matrix increase significantly the hydrophilicity of the membrane. This properties is very usefull to enhance the caryophyllene rejection.

3.2 Clove oil permeation of prepared membrane

The permeation tests of clove oil through fabricated membrane were performed in dead-end filtration cell. Figure 4. shows the flux profiles of clove oil for each fabricated membrane. The flux declines with the filtration time due to membrane compaction and fouling. The initial flux of clove oil in CA membrane is 23.4 $L.m^{-2}h^{-1}bar^{-1}$ and then sharply declines until 13 $L.m^{-2}h^{-1}bar^{-1}$ after 25 minutes filtration. CA/nano-TiO_2 membranes show higher permeate fluxes with the initial fluxes are 30 and 34 $L.m^{-2}h^{-1}bar^{-1}$ for nano-TiO_2 concentration 1 wt-% and 2 wt-% respectively. The incorporated membranes are able to achieve higher fluxes because the nano-fillers are avoiding dead-end pores formation and maintain the structure of membrane from compaction as the result of pressure-driven filtration process. This indicates that CA/nano-TiO_2 membrane is a favorable structure for this process. This work revealed that 2% incorporated nano-TiO_2 in CA membrane enhances the permeate flux up to 52% compared with conventional CA membrane.

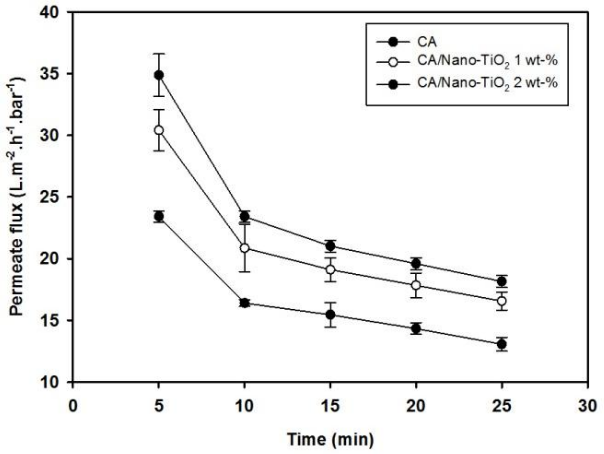

Fig. 4. Flux profiles of clove leaf oil permeate for each membrane

3.3 Separation performance of membrane and permeate product quality

Selectivity of the membrane is representing the separation performance of membrane. In this work the separation efficiency between eugenol and caryophyllene is studied. To observe the separation performance, the eugenol content and clove oil density of feed and permeate are analyzed. The density of pure eugenol and caryophyllene are 1.060 $g.mL^{-1}$ and 0.905 $g.mL^{-1}$, respectively. In other words the density of clove oil will increase as the increase of eugenol content in clove oil. Figure 5 shows the eugenol content and density of clove oil as feed and permeate of each membrane.

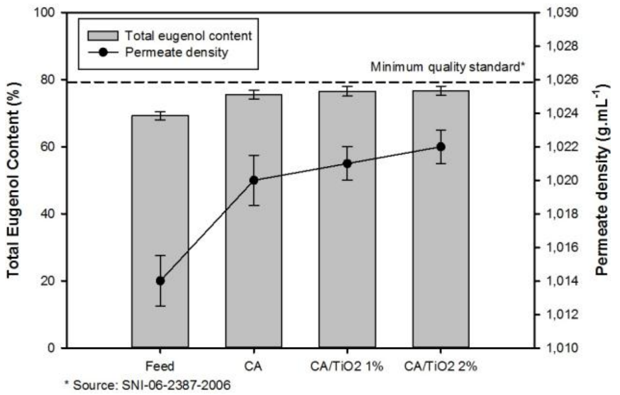

Fig. 5. Eugenol content and density of feed and permeates clove leaf oils

Figure 5 shows that eugenol content of feed is 70% and the eugenol content of clove oil permeate of CA, CA/nano-TiO_2 1%, and CA/nano-TiO_2 2% membranes are 75.5%, 76.4%, and 76.6% respectively. The filtration using conventional CA membrane is able to increase the eugenol content up tp 7.8%, while the nanohybrid membranes of CA/nano-TIO_2 are able to increase the eugenol content up to 9.1 – 9.4%. Nanohybrid membrane exhibits higher separation efficiency than conventional CA membrane. This could be due to the membrane hydrophilicity is enhanced by incorporating the nano-TiO_2 in the membrane matrix. Caryophyllene molecule will be rejected more when a very hydrophilic membrane is employed. The density of clove oil permeates also increase as the increase of nano-TiO_2 loading in membrane matrix. The density profile corresponds with eugenol content in clove oil since the density of clove oil depends on the major component contained in clove oil. Even though the eugenol content in clove oil permeate is bellow the accepted standard, however these results give important information that nanohybrid CA/nano-TiO_2 is suitable to be applied in crude clove leaf oil purification.

4 Conclusion

Nanohybrid CA/nano-TiO_2 flat sheet membranes are successfully fabricated using dry-wet phase inversion method. The MWCO values of fabricated membrane ranging from 4200 – 4800 Da which are equivalent with 1.7 – 1.9 nm of pore radius. The incorporation of nano-TiO_2 in CA membrans are proven to improve the hydrophilicity of membrane, where the 2 wt-% loading in membrane polymer is able to decrease the contact angle from 67.43° to 53.21°. The conventional 17 wt-% CA membrane has been observed capable to increase the eugenol content up to 7.8%, while 2 wt-% nano-TiO_2 loading in CA membrane gives 9.4% eugenol content enhancement. The nanohybrid CA/TiO_2 2 wt-% exhibits the flux enhancement up to 52%. These results inform the potential of CA membrane for crude clove leaf oil purification and nano-TiO_2 incorporated CA membrane is more favorable for this work.

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References

1. C. Gilmer and N. B. Bowden, ACS Appl. Mater. Interfaces. **8**, 1-30 (2016)
2. J. L. N. R. D. Falconer and D. P. Sperry, Marcel Dekker, (1993).
3. Widayat, M. Hilman, B. Bagus, and A. Rahmawan, Simposium Nasional RAPI XIII, (2014)
4. T. Marwati, M. Syahbanna, E. Noor, and E. Mulyono, J. Pascapanen, **2**, 45-52 (2005).
5. T. D. Kusworo, N. Aryanti, R. A. Anggita, T. A. D. Setyorini, and D. P. Utomo, J. Environ. Sci. Technol. **10,** 35-43 (2017)
6. K. Werth, P. Kaupenjohan, and M. Skiborowski, Sep. Pur. Technol. **182,** 185-196 (2017).
7. H. Siddique, E. Rundquist, Y. Bhole, L.G. Peeva, and A. G. Livingston, J. Membr. Sci. **452**, 354-366 (2014).
8. I. K. Nasution, B. Susilo, and W. A. Nugroho, J. Keteknikan Pertanian Tropis dan Biosistem, **2**, 9-14 (2014).
9. A. Boam, A. Meniconi, and X. Wu, WO Patent No. 2013167307 A1, (2013).
10. T. D. Kusworo, H. Hadiyanto, D. Deariska, and L. Nugraha. Chem. Ind. Chem. Eng. Q. **23**, (2017).
11. C. J. Davey, Z. X. Low, R. H. Wirawan, and D. A. Patterson, J. Membr. Sci. **526**, 221-228 (2017).
12. Indonesia Nastional Standard (SNI), No. 06-2387-2006, (2006)