Development of Cellulose Acetate – PVP blend membrane and UV irradiation treatment to increase membrane selectivity for clove oil purification

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Abstract. Clove oil obtained from clove leaves and stems has low oil quality. This is caused by the low levels of eugenol which is around 60-80%. The application of membrane technology to purify clove oil is constrained by the almost similar size of the eugenol and caryophyllene molecules. The aim of this study is to improve membrane selectivity by increasing the hydrophilic properties of the membrane. The eugenol will penetrate easily through hydrophilic membrane than caryophyllene. Cellulose acetate membrane was fabricated by dissolving 17 wt-% CA polymer in acetone and then casted via dry-wet phase inversion method. Poly vinyl pyrrolidone (PVP) is added to the dope solution to improve the hydrophilic properties of the membrane. The results of contact angle analysis showed that the addition of PVP by 1% was able to reduce the contact angle from 41° to 32° which means the hydrophilic increased significantly. The combination of PVP addition with nano ZnO incorporation can increase eugenol concentration from 75% to 88% but decrease the permeate flux from 6.78 to 5.33 L.m⁻²h⁻¹bar⁻¹.

1. Introduction
Clove oil is an agricultural commodity with economics value. Clove oil itself is an essential oil produced from clove plants (Eugenia caryophyllata Thunb). This essential oil can be obtained from flowers, trunks, and leaves of clove plants. The quality of the oil is evaluated from the content of phenol, especially eugenol. The quality of clove oil is determined by eugenol [1,2]. Eugenol is one of the main components of essential oils isolated from cloves (Eugenia caryophyllata), which have been widely used as herbal remedies to treat dyspepsia, acute inflammation, and diarrhea [3]. Eugenol also has some potential for the industry, namely in the flavor industry and perfume industry [4]. While β-Caryophyllene is an impurity that must be removed due to its effect that decrease the purity of clove [5].

The Process of Separation and Purification in chemical and petrochemical industries is a very important process. Not only in the production process but also in the determining the energy consumption and the amount of investment in instrument selection. Meanwhile, the process of separation and purification in the chemical industry has not yet reached the thermodynamic minimum separation threshold, up to 70% of the factory cost [5]. Separation technologies such as distillation, extraction and absorption generally require
phase change and solvent removal by heating so that the main weakness in the process is the high energy consumption [6]. Separation processes such as those have been commonly applied in the purification of essential oils such as clove oil, patchouli oil, ginger oil and other essential oils. However, recent separation technologies such as membranes have not been applied in the purification of essential oils.

The limited literature on membrane applications on clove oil purification is due to the ability of eugenol to dissolve the material of membrane. Based on preliminary experiments conducted in October-November 2017 at the Waste Chemical Laboratory at Department of Chemical Engineering of Undip gave the result that from 4 membrane materials (PES, PI, PA, and CA), only CA showed resistance to eugenol. The PES and PA membranes dissolve instantaneously while the PI membrane dissolves after being immersed for more than 3 weeks. Cellulose Acetate (CA) is one of the derivatives of cellulose, where CA is widely used because of its fairly good physical capabilities, including fine and clear porosity in its film, as well as relatively high modulus, also has a high flexibility and tensile strength in its fiber form. CA is also reported as biodegradable materials [11]. So in this study CA membrane is selected to be applied in clove oil purification.

The problem comes from the utilization of CA as membrane material for clove oil purification. The swelling phenomenon occurred during filtration process for long time operation [7]. The addition of nano material such as TiO$_2$ could effectively reduced the swelling phenomenon, however the agglomeration on the membrane surface decreased the membrane selectivity significantly [8].

In this study, the addition of PVP (Polivinylpirolidone) was added to reduce the unequal distribution of ZnO in high polymer concentrations. The choice of PVP is performed as a pore forming material, and dispersants for nanoparticles in the membrane [9], this is used so that when ZnO adds up considerably, aggregation does not occur. However, in that experiment, it has not been explained the optimum amount of PVP addition in membrane fabrication.

2. Materials and methods

2.1. Materials

Clove oil was obtained from clove oil farmers in Semarang, Central Java. Cellulose acetate (CA) with 50% acetic content was supplied from Alpha Chemika, India. The acetone and polyvinyl pirolidone (PVP) were purchased from Merck. The Industrial grade nitrogen gas was purchased from Aneka Gas, Ltd., Semarang.

2.2. Nano-hybrid membrane fabrication

Cellulose Acetate (CA) was grinded and sieved with 150 mesh sieving machines. CA membrane was fabricated by preparing dope solution of CA polymer, additives, and acetone as solvent [10]. An appropriate amount of nano ZnO was filled in beaker glass which contains acetone solvent and followed by adding the PVP to the mixture. The nano particles mixture was ultrasonicated for an hour to obtain homogeneous solution. An appropriate amount of CA polymer was then added to the nano particles dispersion and the stirred for 24 h. To remove the bubbling, the solution is left to set for 1 hour. The casting solution was then poured onto a glass plate, and spread with a casting knife to be as thin as 150 μm. Then, the glass plate was immediately immersed in distilled water bath to complete the phase separation, where the solvent (acetone) and the non-solvent (water) were exchanged. Then, The flat sheet neat CA membrane was dried at room temperature.

2.3. Scanning Electron Microscope

The morphology of nanohybrid CA-nano ZnO membranes with and without PVP addition were characterized by Scanning electron microscopy (SEM) JEOL series JSM-6510-LA,
Japan. A piece of flat sheet fabricated membranes was first immersed in liquid nitrogen and fractured using tweezers, and then sputter coated with gold for SEM examination [11]. Through this analysis, it can be seen the active surface (20000x) and porous (1,000x) morphology of the membrane with a certain magnification.

2.4. Water contact angle
Water contact angle of the membrane that has been made needs to be analyzed even though the membrane is not used in water treatment. Analyzing the contact angle is useful for viewing membrane hydrophilicity. The membrane hydrophilicity properties determine the efficiency of separation between eugenol and β-caryophyllene. Measurement of water contact angles on the surface of the object was introduced by Letey [12]. Ion-free water is used as a probe liquid and when ion free water is dripped over the membrane surface, water contact angles are measured immediately using a water contact angle meter on three or five left and right-side points.

2.5. Filtration test for clove oil purification
Flux determination was performed with a dead-end filtration instrument. The membrane dead-end filtration system was shown in Figure 1. In the nanofiltration instrument which has been membrane installed inside was flowed with a mixture of Clove Oil and n-Hexane 25 wt-%. After the feed was mounted in the cylindrical chamber, the N₂ gas was streamed to the membrane module to give trans-membrane pressure. The upstream pressure was regulated by maintaining the regulator valve. Permeate flux was calculated using equation 1 bellow:

\[ J = \frac{V}{P \cdot A \cdot t} \]  

With, \( J \) is Flux (L.m⁻².h⁻¹.bar⁻¹), \( V \) is volume ( L), \( A \) is membrane’s Area (m²), \( t \) is Time (hr), and \( P \) is trans-membrane pressure (bar)

![Figure 1. Simplified schematic of dead-end filtration system](image)

3. Results and discussions
3.1. Membrane morphology
Membrane morphology can be observed by analyzing under Scanning Electron Microscope (SEM). Membrane morphology is importance to be characterized because it has an important role in providing membrane separation properties [13]. There are two kinds of prepared membranes in this analysis, including 17 wt-% CA-nano ZnO membrane and 17 wt-% CA-nano ZnO 0.5% with PVP doping. The SEM images of the membranes are displayed in Figure 2.
Figure 2 shows SEM images of membrane surface of nano ZnO incorporated CA membrane with and without PVP. Figure 2.A is nano hybrid membrane without PVP as additive, it can be seen that the nano particles formed agglomeration and macro-void between nano-particles and membrane matrix [14]. This phenomenon occurred due to the de-attachment of particle surface to polymer matrix. This condition is not preferred because the selectivity of the membrane decrease significantly. As shown in Figure 2.B, the membrane surface is smooth and no void is observed at this magnification. The particles are spread well over the membrane surface and no agglomeration of particles is found. The addition of PVP could help the distribution of nano-particles as dispersant [15]. The PVP molecule covered the nano ZnO particles and repaired the adhesiveness of particles. As a result, the particles are spread evenly on the membrane surface and the membrane selectivity could be maintained.

3.2. Water contact angle
Measurement of water contact angles on membrane surfaces has become a commonly used method of membrane characterization. It is useful in determining the surface tension of the membrane. Surface tension on the membrane is related to membrane hydrophilicity and relative roughness of the membrane. The value of the contact angle is obtained by dropping the deionized water on the membrane surface and measuring the droplet angle. The results of measurements of water contact angles on the surface of the prepared membrane are presented in Figure 3.
Figure 3 shows that all the membranes are hydrophilic as the water contact angle values are less than 90°. The addition of 0.5 wt-% of nano-ZnO particles in dope solution decreased the prepared membrane contact angle from 40.33° to 39.80°. The result indicates that the addition of nano-ZnO could significantly increase the hydrophilicity of the CA membrane. This phenomenon was accordance with the previous works [16]-[18] that the incorporation of nano ZnO enhanced membrane hydrophilicity. The addition of PVP in dope polymer solution sharply decreased the water contact angle of the membrane to 32.67°, it revealed that the addition of PVP could be a dispersant and hydrophilicity enhancer. The improvement of hydrophilicity of membrane surface provides benefit in separation properties of the membrane. The separation mechanism is expected to occur by solution-diffusion mechanism with the different affinity as the main factor of separation driving force between eugenol and caryophyllene. Therefore, the more hydrophilic membrane surface can allow the eugenol to pass through the membrane barrier and repels the caryophyllene which has very hydrophobic properties.

3.3. Membrane Performance in Purifying Crude Clove Oil

The result presented in Figure 4 shows the total cumulative permeate flux from batch dead-end membrane filtration for an hour operation process. The addition of nano ZnO particles and PVP in dope solution influenced the total cumulative permeate flux. The permeate flux in CA neat membrane was 4.38 L.m⁻²h⁻¹bar⁻¹ with trans-membrane pressure of 5 bar gauge. The higher permeate flux 6.78 L.m⁻²h⁻¹bar⁻¹ was achieved by membrane with 0.5 wt-% ZnO incorporation. The addition of PVP decrease the permeate flux to 5.33 L.m⁻²h⁻¹bar⁻¹ in the purification of crude clove oil.
The addition of nano-ZnO provided the highest permeate flux value due to the formation of macro-void on the membrane surface as a result of particles agglomeration. As shown in SEM images (Figure 2) the membrane surface of CA-nano ZnO membrane has so many macro-voids on the surface which let the clove oil pass through the membrane barrier massively. The addition of PVP in dope solution help the particle spreading over the membrane, however it decreased the permeate flux 21.37%. the addition of PVP repaired the defect in nano hybrid membrane so that the macro-void could be removed. Even the membrane surface was repaired, the permeate flux of the membrane still higher than neat CA membrane, this could be due to the enhancement of membrane hydrophilicity as the result of PVP addition. As mentioned by previous research study [19]-[20] that the enhancement of membrane hydrophilicity significantly increased the permeate flux.

The eugenol concentration of each permeate were evaluated to understand the membrane selectivity performance. Figure 5 shows the concentration of eugenol in permeate from prepared membranes. Eugenol concentration of permeate from neat CA membrane was 75% higher than eugenol concentration of feed that was 69%. The addition of ZnO on membrane matrix decreased the concentration of eugenol into level 70%. It indicates that in the membrane with nano ZnO incorporation doesn’t occur any separation between eugenol and caryophyllene. The addition of PVP to the dope solution reached the highest eugenol content up to 88%.
Clove oil purification using CA membrane can increase the concentration of eugenol from 69% to 75%. It was a significant result that caryophyllene can be separated from eugenol using membrane, however the results still below the Indonesian National Standard of clove oil. The low separation efficiency could be due to the hydrophilicity of neat CA membrane is low and the neat membrane is susceptible to be swollen [7]. In the nano hybrid CA/PVP membrane, the concentration of eugenol increased sharply into 88%. It indicates that the addition of ZnO could mitigate the swelling phenomena so that the solution-diffusion separation process was maintained. The addition of PVP also play important role as particle dispersant and enhanced membrane hydrophilicity.

4. Conclusion
The nano hybrid CA membranes were fabricated successfully and can be used to purify clove oil, with further modification using ZnO nanoparticles and also PVP as an additive. As shown in SEM image, the addition of 0.5 wt-% nano ZnO could form agglomeration and nano-void on the membrane surface. The addition of PVP in dope solution significantly help the dispersion of nano ZnO in the whole membrane matrix. The PVP addition successfully increased the eugenol concentration in permeate from 75% to 88%. However, the permeate flux are lower than CA membrane without PVP that is 5.33 L.m⁻².h⁻¹.bar⁻¹.

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