Synthesis and Characterization of Microfiltration Ceramic Membrane Based on Fly Ash and Clay Mixture Using Sintering Method

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Abstract. Ceramic membranes made from low-cost materials have increasingly been developed. Fly ash is a waste from cement industries, while clay is a natural resource that can be easily found to be used as economical mixed materials in the production of ceramic membrane. The manufacture of microfiltration ceramic membrane from fly ash - clay mixture has been carried out using the sintering method for 4 hours at low sintering temperatures variations at 750 °C (M1), 800 °C (M2), 850 °C (M3) and 900 °C (M4), respectively. The results showed that the ceramic membrane that was sintered at a temperature of 900 °C (M4) had the optimum characteristics with a porosity of 40.82%, a density of 1.0026 gr/cm³. From scanning electron microscopy (SEM) analysis showed that the M4 membrane was classified as a microfiltration membrane with an average pore size of 0.64 μm. The energy dispersive x-ray (EDX) analysis showed that the composition of the M4 membrane was dominated by elements O, Si, and Al. Moreover, the x-ray diffraction (XRD) analysis showed that the fraction patterns of the membranes (M1, M2, M3, M4) were dominated by the quartz phase (SiO₂) and illite phase ((KH₃O)Al₂Si₃AlO₁₀(OH)₂).

1. Introduction
Currently, ceramic membrane applications for microfiltration processes have been increasingly developed and applied due to the excellent thermal, chemical, and mechanical stability of ceramic membranes and due to high separation efficiency compared to polymer membranes [1-2]. Ceramic membranes are generally made from various expensive, inorganic materials such as silica, alumina, titania, and zirconia. Therefore, a development is made in form of natural ceramic materials with abundant material availability and fabrication techniques with sintering temperatures below 1000 °C to produce ceramic membranes at an economical price [3-4]. Fly ash, which is a waste from cement industry, and clay, which is widely available in nature, can be used as a basic material for making ceramic membranes at an economical price. Furthermore, the characteristics of fly ash and clay which have particle sizes of 1μm - 20μm are also very suitable for microfiltration processes [5].

Research on the manufacture of ceramic membranes made from fly ash and clay using sintering methods have been carried out in recent years. However, those researches were conducted at temperatures above 1000 °C, causing the cost of making ceramic membranes to increase. Jedidi, et.al [6] used fly ash as an economical material for the manufacture of ceramic membranes at a sintering temperature of 1125 °C and produced ceramic membranes with a pore diameter of 4.5 μm and porosity of 51%. Belibi, et.al [7] have succeeded in making a clay-based membrane at a sintering temperature of 1100 °C with a porosity value of 42%. Rekik, et.al [8] produced a ceramic membrane made of clay at a sintering temperature of 1250 °C with a porosity value of 27% and a pore diameter of 0.73 μm. The need for cheap materials and low sintering temperatures pose a new challenge in reducing the cost of...
making ceramic membranes while still producing the best-quality ceramic membranes. The purpose of this research is to find out about the effect of sintering at low temperatures with variations in temperature of 800 °C, 850 °C, 900 °C, and 950 °C, on the porosity, density, permeability, pore size, and morphology of ceramic membranes made from fly ash and clay mixture.

2. Research Method

2.1. Material
Fly ash and clay with a particle size of 120 μm were used as the main component for making membranes. Fly ash samples which have been produced as waste in cement manufacturing was collected from PT. Solusi Bangun Andalas Indonesia, Banda Aceh, while the clay was purchased from PT. Rudang Jaya, Medan, Indonesia. Polyvinyl Alcohol (PVA) was purchased from Sigma, Aldrich.

2.2. Synthesis of Fly Ash-Clay Microfiltration Ceramic Membranes
A total of 900 grams of fly ash and clay mixture with at a composition of 65% - 35% were put into a beaker glass and then added 4% Polyvinyl Alcohol (PVA). Then, as much as 700 ml of water was added to it gradually, while being stirred until a paste was formed. The membrane was then molded by pouring the paste into a mold. It was needed to make sure that no air was trapped in it by pressing slowly until using a membrane press tool. The membrane was removed from the mold and dried at room temperature for 7 x 24 hours. The membrane was then continued through sintering process at 750 °C, 800 °C, 850 °C and 900 °C for 4 hours.

2.3. Characterization of Fly Ash-Clay Microfiltration Ceramic Membranes
The density of ceramic membranes is obtained by weighing each membrane weight, measuring the diameter and thickness of the membrane, so that the membrane mass and volume of the membrane are obtained. Then the membrane density is calculated based on the following equation:

\[
\rho = \frac{M (g)}{V (cm^3)}
\]

where \( \rho \) represents the density of membrane (gr/cm³), \( M \) represents the mass of membrane (gr), \( V \) represents the volume of membrane (cm³). The porosity of each membrane is measured using the Archimedes method as follows:

\[
\varepsilon(\%) = \frac{W_1 - W_2}{W_3 - W_2}
\]

where \( W_1 \) represents the weight of dry membrane, \( W_2 \) represents the weight of the wet membrane measured in water, and \( W_3 \) represents the weight of the membrane that was filled with water for 48 hours.

The structure and pore size of membrane were analyzed using scanning electron microscope (SEM, ZEISS2074, Center Laboratory, UM, Malaysia). The elements of the membrane were analyzed using energy dispersive x-ray (EDX, ZEISS2074, Center Laboratory, UM, Malaysia). The phase compositions of the membranes were measured using x-ray diffraction (XRD, Analysis Lab, PNL, Indonesia).

The water flux of ceramic membrane was tested using crossflow filtration system with variation operating pressure from 0.25-1.25 bar. The water flux \( J, \frac{L}{m^2\cdot hr} \) for each pressure variation was calculated using Eq. (3), as follows:

\[
J = \frac{V}{At}
\]
where $V$ represents the volume of the permeate (L), $A$ represents the effective area of the membrane surface (m$^2$), and $t$ represents the filtration time (h).

3. Result and Discussion

3.1. Porosity and Density of Fly Ash-Clay Ceramic Membrane

Sintering process is a process of compacting powder material by forming bond boundaries between the constituent powders/particles. Bonding between items occurs due to thermal treatment with or without pressure and the sintering temperature is set below the melting point temperature of the constituent particles. The thermal treatment contained in this process causes diffusion between the constituent particles where the particles will come in contact with each other, making an increase in the density of the constituent particles and bettering the contact area between the particles [9].

Figure 1 presents the sintering temperature effects on porosity and density of the membrane. The largest porosity was owned by the membrane which was sintered at 750 °C (48.85%), while the porosity decreased to 40.82% at a sintering temperature of 900 °C. The decrease in porosity of the membrane was caused by the increasing sintering temperature. The increase in temperature caused the contact area between the particles becoming wider and made the structure of the porosity becoming smoother, so that the empty space for porosity was also getting smaller [10].

The porosity of the membrane that is formed also affects the density of the membrane. From figure 2, it can be seen that the membrane density increases with the increasing temperature. The increase in sintering temperature affects the growth and compaction process of the particle where the higher the sintering temperature, the higher the percentage of particle density [11]. Therefore, the largest density is owned by the membrane which is sintered at a temperature of 900 °C, equaling to 1.0026 gr/cm$^3$.

![Figure 1. Porosity of Membrane](image1.png)  ![Figure 2. Density of Membrane](image2.png)

3.2. Morphology of Fly Ash-Clay Microfiltration Ceramic Membrane

The structure and pore size of membrane were analyzed using SEM (Scanning Electron Microscope). SEM observations were made on the membrane which was sintered at 750 °C, 800 °C, 850 °C and 900 °C. Figure 3 presents the comparison of the membrane surface structure at different sintering temperatures. At the sintering temperature of 750 °C, the membrane surface was still not homogeneous and the porosity formed still dominated the surface of membrane (figure 3a). The membrane surface
was increasingly seen to be more homogeneous at a sintering temperature of 900 °C (figure 3d). The increase in sintering temperature at 900 °C caused the fly ash - clay mixture particles to melt, forming the neck of the sintering and bind to each other [12]. Thus, the porosity that was formed was reduced and the pore size of the membrane also shrank by 0.64μm (figure 4).

Figure 3. The SEM image of membranes at different sintering temperature: (a) 750°C, (b) 800°C, (c) 850°C, and (d) 900°C

Figure 4. The Pore Size of Membrane

Membrane elements analysis was carried out using Energy Dispersive X-Ray (EDX) to the membrane that had the smallest pore size. It was the M4 membrane which had sintering at 900°C. From figure 5, it can be determined that the main elements of the membrane consisted by O, Si, and Al.
3.3. Effect of Sintering Temperature on Membrane Phase Composition.
The membrane phase composition in this study was analyzed using XRD. Figure 6 presents the XRD patterns of the ceramic membrane with various sintering temperature. It is known that the fraction pattern of all membranes is dominated by quartz (SiO2) and illite ((KH3O) Al2Si3AlO10 (OH) 2) phases. At a sintering temperature of 850 °C, diffraction patterns from the gypsum (CaSO4.2H2O) and graphite (C) phases are formed. At a sintering temperature of 900 °C the graphite phase (C) does not form anymore. The process of mixing materials consisting of fly ash, clay, and PVA causes a deviation in decreasing the melting point, so that at a temperature of 900 °C the graphite phase disappeared.

3.4. The Flux of Fly Ash-Clay Microfiltration Ceramic Membrane
Figure 7 presents the raising of flux value which increases along with the increasing of the pressure and the sintering temperature. The separation occurred because of the driving force caused by the different of input and output pressure of the membrane module [13]. The highest flux value was gained at the pressure of 1.25 bar and sintering temperature of 750 °C. The increasing the the flux is caused by the increasing of the pressure which resulted to the increasing of the propulsive force given to the solution to pass the ceramic membrane so a big amount of feed solution can pass the ceramic membrane and this process will minimize the effect of concentration polarization. The increase in sintering temperature affects the diffusion process between membrane particles, making it wider, and ultimately affects the structure of the shrinking membrane porosity. Low membrane porosity causes the value of flux and membrane permeability to be low as well [11].

Figure 5. The EDX Analysis
4. Conclusion

Microfiltration ceramic membrane with fly ash - clay mixture material has been successfully made with various sintering temperatures. Ceramic membrane that was sintered at a temperature of 900 °C had a porosity of 40.82%, a density of 1.0026 gr/cm³, and water flux at a pressure of 1.25 bar of 192.358 Lm⁻²h⁻¹. Based on the analysis using Scanning Electron Microscopy (SEM), the membranes can be classified as a microfiltration membrane with an average pore size of 0.64 μm.

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