**Performance of Sodium Alginate Membrane with Hydrophilic Activated Carbon Filler for Bioethanol Dehydration**

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**Abstract.** Bioethanol is one of the biofuels that is important to develop as it can reduce the energy crisis. The process of purifying bioethanol via ethanol dehydration pervaporation is an effective way for increasing the concentration of bioethanol, making it suitable for use as fuel. The study focused on investigating the impact of including 0.8 wt% hydrophilic activated carbon (HAC) fillers on the performance of sodium alginate (SA) membranes in bioethanol purification via pervaporation. The morphology, structure, mechanical strength, and thermal stability properties of the membranes were characterized. The incorporation of HAC affected the microstructure of the membranes. The Young’s modulus of the SA/HAC membrane was enhanced by 65% compared to SA pure membrane. The addition of HAC filler in the membrane matrix increased the hydrophilicity of the SA membrane with a decrease of the water contact angle. The ethanol dehydration performance showed the HAC filler enhanced the permeation flux and separation factor. In bioethanol/water (90/10 wt%) solution at 70 °C, the permeation flux of SA/HAC membrane was 553,6 g/m2 h and separation factor was 2191.88. Moreover, the SA/HAC membrane exhibited good long-term operation stability.

# INTRODUCTION

Bioethanol is a type of alcohol used in various fields such as fuel, industry, and pharmaceuticals. The bioethanol produced from various generations still has low concentration values for use in these fields. Bioethanol produced from corn stover is 80.1% 1, while bioethanol produced from rice straw is 67.3% 2. On the other hand, bioethanol produced from sugarcane bagasse has a bioethanol concentration of 91%. Therefore, purification methods are needed to increase the concentration of bioethanol for use in various fields.

Pervaporation is one of the purification methods used to separate solution mixtures above their azeotropic point. Pervaporation with membranes is a type of separation or purification process using membranes for solvent dehydration and organic mixture separation. The bioethanol purification process on feed with high ethanol concentration is referred to as bioethanol dehydration 3. High-performance membranes for bioethanol dehydration are determined by the selection of hydrophilic membrane materials. Hydrophilic membranes, which are most commonly used for ethanol dehydration, have the advantages of easy film formation, flexibility, and economic benefits 4.

One of the polymers widely used is sodium alginate. This polymer has selective absorption of water due to its functional polar groups, caused by ion-dipole, dipole-dipole, and hydrogen bond interactions between water molecules and the membrane surface 5. Several studies on pervaporation with sodium alginate membranes for ethanol dehydration have shown high permeation flux performance and separation factors compared to other polymer membranes 6,7.

One way to improve membrane performance is by adding fillers to the membrane. The addition of inorganic fillers to polymer membranes can also enhance the selectivity of membranes in the ethanol dehydration process. Among the materials commonly used as fillers for pervaporation membranes, carbon is the easiest to synthesize compared to others. Carbon itself is often modified to exhibit hydrophilic properties for ethanol dehydration, which can increase the permeation rate of the membrane. Several carbon materials with hydrophilic properties, such as graphene 8, graphene oxide (GO) 9, carbon nanotube (CNT) 10, fullerenol 11, and graphitic carbon nitride (g-C3N4) 12 have been used in ethanol dehydration pervaporation. Activated and hydrophilically modified carbon also has the potential to be used in ethanol pervaporation because it can increase surface area and generate hydrophilic groups 13, allowing for uniform dispersion in the polymer matrix when used as a filler. In our previous research, hydrophilic activated carbon synthesized from graphite using sodium hydroxide and ammonium persulfate demonstrated good performance in water treatment applications 14. The active sites of the carbon play a crucial role in the separation process. The incorporation of hydrophilic activated carbon into a sodium alginate matrix for pervaporation membranes in ethanol/water separation has not been explored before. Therefore, in this study, sodium alginate membranes with hydrophilic activated carbon fillers are used to achieve high membrane performance.

# MATERIALS AND METHODS

## Materials

The materials used for this work were synthesized hydrophilic activated carbon (HAC), sodium alginate (Himedia), demineralized water, hydrochloric acid 37% (HCl, Sigma-Aldrich), isopropyl alcohol (SAP), glutaraldehyde (GA, SAP), calcium chloride dihydrate (CaCl2·2H2O, SAP). The pervaporation test used 96% bioethanol (extra neutral ethanol, PT. Energi Agro Nusantara).

## Membrane Preparation

The SA dope membrane solution was prepared using the evaporation method. Sodium alginate was dissolved in distilled water until a homogeneous solution of 2.5 wt% polymer was obtained. Once homogeneous, the dope solution was subjected to ultrasonication for 1 hour to remove bubbles. Then, the dope solution was cast onto a glass plate. The membrane cast on the glass plate was dried at room temperature for 24 hours. The dried membrane was then crosslinked with a 5% (w/v) CaCl2 solution for 1 hour at room temperature. After that, the membrane was rinsed with distilled water and dried again at room temperature for 24 hours.

The preparation of the SA/HAC membrane was carried out by dispersing HAC in distilled water with a composition variation of 0.8% (w/w). The HAC dispersed in distilled water was subjected to ultrasonication for 30 minutes. Then, 2.5 wt% sodium alginate was added to the HAC dispersed in water and stirred until homogeneous. The dope solution was then cast onto a glass plate using a roller tube and dried at room temperature for 24 hours. The dried membrane was crosslinked with isopropanol-water (90/10, v/v) and a 5% (w/v) glutaraldehyde (GA) solution, along with 1% (w/v) HCl as an initiator for 30 minutes at room temperature. After that, the membrane was rinsed with distilled water. The crosslinked membrane was then dried again at room temperature for 24 hours.

## Membrane Characterization

The SA and SA/HAC membranes were characterized using Fourier Transform Infrared (FTIR, Thermo Scientific Nicolet iS10) to identify the functional groups present in the membranes by adding potassium bromide (KBr) to the membrane at a ratio of 1:10 (membrane to KBr) and molding it into pellets The membranes were also characterized using Scanning Electron Microscopy (SEM, Hitachi FlexSEM 1000) to examine the membrane morphology began by attaching double-sided carbon tape to the sample, followed by coating it with a 25 nm layer of gold for 15 minutes using a Hummer Sputter Coater. Contact angle analysis was performed using a 3D Optical Microscope. Contact angle measurement was performed using the droplet technique on the carbon surface. A total of 10 μL of water was dropped onto the carbon surface. Thermal stability analysis of the membranes was carried out using a Thermogravimetric Analyzer (TGA, Mettler Toledo). The testing began with weighing the membrane to less than 10 mg. The membrane sample was then folded and placed in a crucible. The measurement was carried out under a nitrogen atmosphere. Additionally, characterization was performed using a Universal Testing Machine (UTM) to determine the mechanical strength of the membranes. The membrane sample was prepared by cutting it into a rectangular shape. The sample was then clamped, and the physical resistance of the membrane was measured until it broke on both sides under tension.

## Pervaporation Experiments

The pervaporation experiments of SA and SA/HAC membranes for bioethanol/water dehydration were performed. The 90 wt% bioethanol feed solution was pumped across the membrane surface with an effective surface area of 25 cm² at a flow rate of 60 L/h. The ethanol dehydration test was performed at a temperature of 70°C. A vacuum pump was used to maintain the pressure on the permeate side at 0.3 kPa. The permeate vapor was collected by cooling in the condenser every hour after equilibrium was reached. The permeation flux (J, kg/(m²·h)) was obtained using Equation (1):

|  | (1) |
| --- | --- |

where Q (g) is the mass of the permeate during the pervaporation time t (hours), and A (m²) is the effective surface area of the membrane. The composition of the feed and permeate was analyzed using the Go Direct Ethanol Vapor Sensor. The membrane separation factor (α) was calculated using Equation (2):

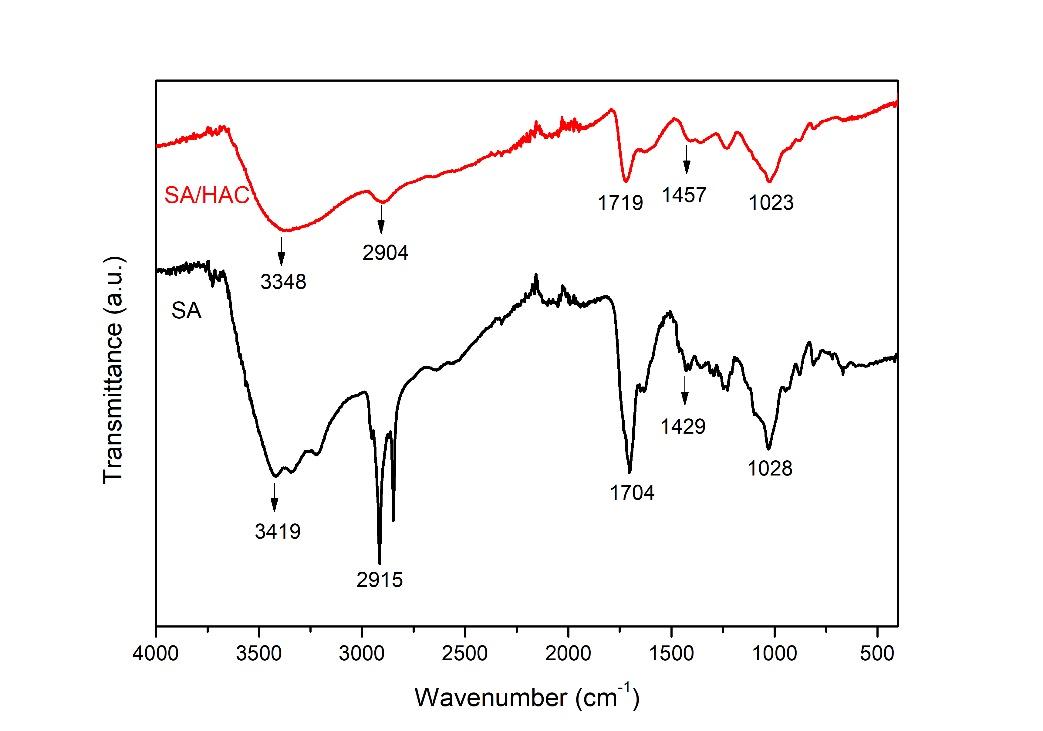
|  | (2) |
| --- | --- |

where P and F represent the mass fractions of water (W) or ethanol (E) in the permeate and feed, respectively.

# RESULTS AND DISCUSSION

## Chemical Structure of Membranes

The SA and SA/HAC membranes have similar IR spectra (Figure 1). Characteristic peak of alginate was observed at 2904-2915 cm⁻¹, which were associated with the stretching vibrations of asymmetrical C-H bond. Meanwhile, the absorption peaks at 1429-1457 cm⁻¹ and 3348-3419 cm⁻¹ represent the O-H (hydroxyl) groups characteristic of hydrophilic activated carbon and sodium alginate 15,16. Additionally, the absorption peak at 1704-1719 cm⁻¹ is characteristic of aldehydes, which is related to the crosslinking reaction by glutaraldehyde. The absorption peak at 1023-1028 cm⁻¹ also shows the characteristic C-O-C ring of sodium alginate 17.



**FIGURE 1.** FTIR spectra of SA neat and SA/HAC membrane

## Morphology of Membranes

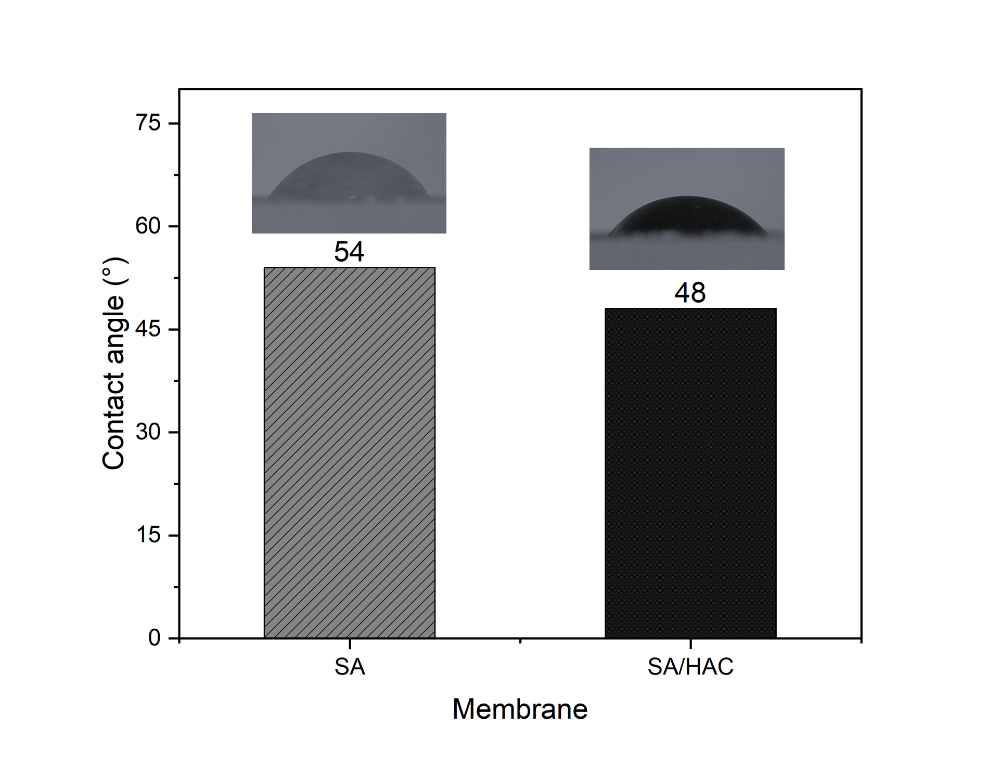
The pure SA membrane displays a smooth surface morphology as shown in Figure 2a. Figure 2b shows the SA membrane with HAC filler has a fibrous surface morphology. The cross-sectional image of the SA membrane (Figure 2c) shows a dense structure 12. In contrast, Figure 2d shows the SA/HAC membrane shows voids on some sides with HAC fillers filling the SA polymer matrix. Although there are some voids, the presence of dispersed HAC within the SA polymer layer can contribute to enhancing the performance of SA in ethanol/water separation 18.



**FIGURE 2.** SEM results of (a) SA, (b) SA/HAC membrane surface and (c) SA, (d) SA/HAC membrane cross-section

## Water Contact Angle of Membranes

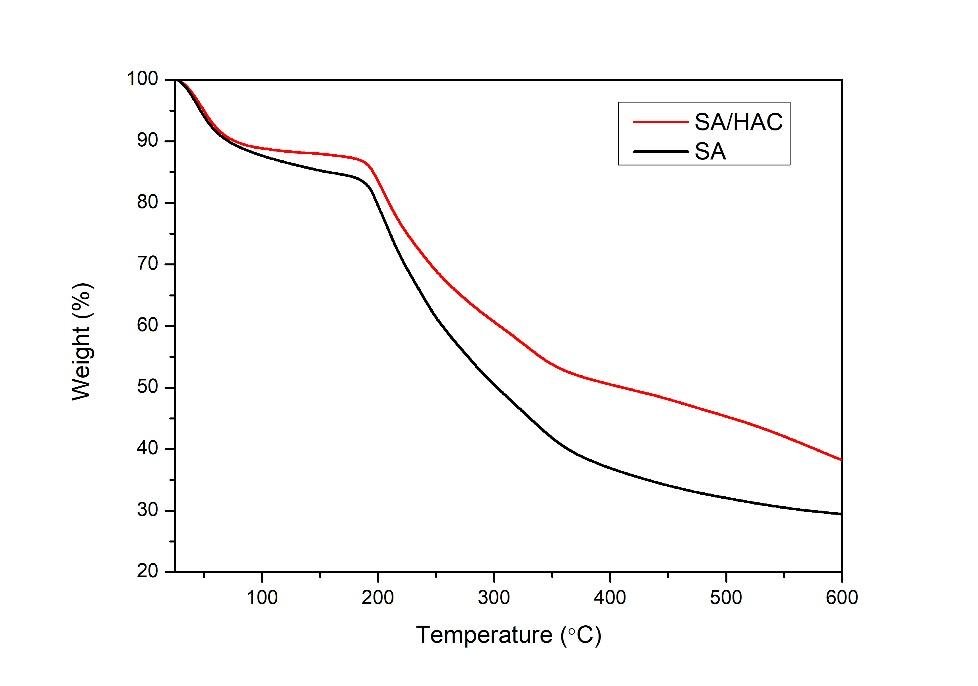
The addition of HAC can affect the water contact angle value of the SA membrane. Figure 3 shows a decrease in the water contact angle value with the addition of 0.8 wt% HAC filler. This decrease in water contact angle value indicates that the SA membrane with HAC filler has more hydrophilic properties compared to the pure SA membrane. Cao et al. 9 and Wang et al. 19 also added carbon fillers to SA membranes, resulting in increased hydrophilicity. The hydrophilicity of this membrane plays a crucial role in its performance for bioethanol dehydration 20.



**FIGURE 3.** Water contact angle of SA neat and SA/HAC membrane

## Thermal and Mechanical Stability of Membranes

Thermal stability analysis of the SA and SA/HAC membranes shows significant differences. As shown in Figure 4, three stages are observed in the thermal mass loss process. The first stage below 200°C represents thermal mass loss due to water vapor decomposition, the second stage between 200 and 360°C indicates functional group decomposition in SA, and the third stage in the range of 360 to 600°C shows degradation of the main SA chain 12. These results demonstrate that membranes with added carbon fillers exhibit improved thermal stability compared to pure SA membranes. The thermal stability of SA/HAC is beneficial in bioethanol dehydration pervaporation processes because the ethanol/water separation process relies on temperature as the driving force, with optimal separation occurring at high temperatures 21.



**FIGURE 4.** TGA curves of SA neat and SA/HAC membrane

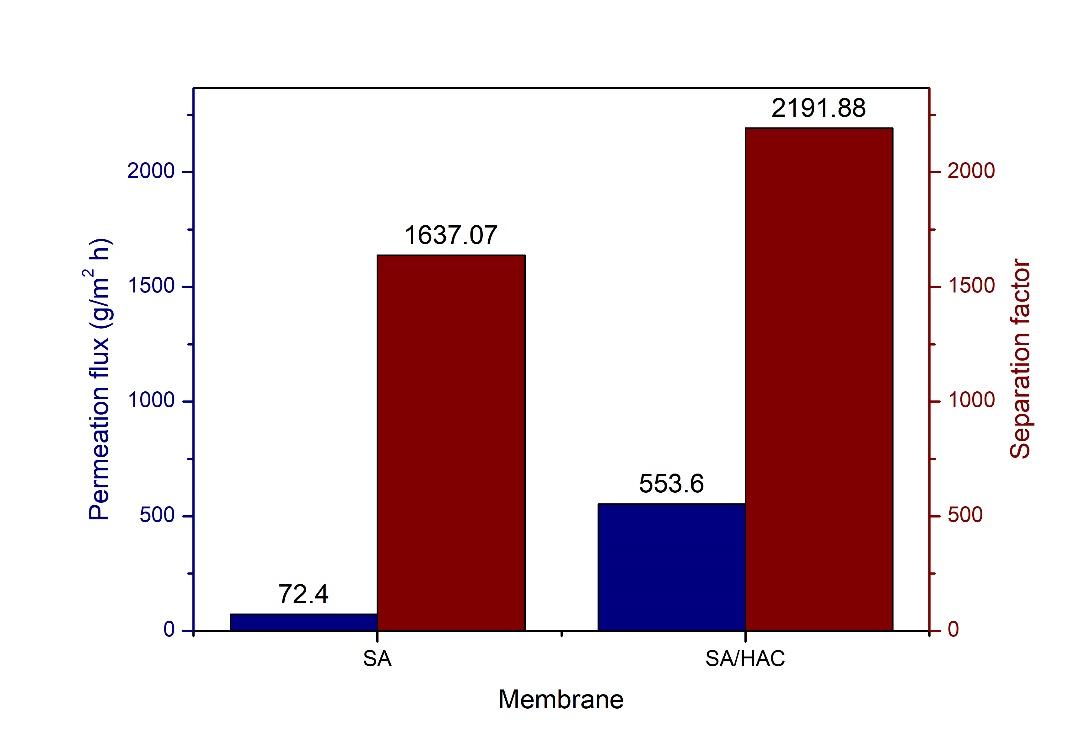
The tensile strength results in Table 1 show different mechanical properties between the SA and SA/HAC membranes. The SA membrane with 0.8 wt% carbon addition exhibits higher mechanical properties compared to the other membranes. This improvement is attributed to the physical architecture and interfacial interactions that can facilitate effective load transfer 9. Specifically, the tensile strength and tensile modulus of SA/HAC increased by 44% and 65%, respectively. The high tensile strength significantly affects the membrane's resistance when subjected to pressure during the pervaporation process 12.

**TABLE 1.** Mechanical properties of SA neat and SA/HAC membrane

| **Membrane** | **Tensile Strength (MPa)** | **Young’s Modulus (MPa)** |
| --- | --- | --- |
| SA neat | 3.31 | 51.69 |
| SA/HAC | 4.76 | 85.96 |

## Performance of Membrane for Bioethanol Dehydration by Pervaporation

SA membranes have been widely used for ethanol dehydration pervaporation due to their hydrophilic properties and ease of modification. In this study, the SA membrane exhibited a flux value of 72.4 g/m2·h and a separation factor of 1637.07 at 70°C. Meanwhile, the SA/HAC 0.8% membrane at the same temperature showed a flux value of 553.6 g/m2·h and a separation factor of 2191.88. There is an improvement in the performance of ethanol dehydration process after adding HAC filler (Figure 5). The increased hydrophilic properties of the membrane contribute to enhancing its performance in pervaporation in accordance with the contact angle results discussed in the previous section 3. The membrane performance results are also confirmed by SEM analysis, showing that the presence of HAC fillers dispersed within sodium alginate naturally enhances permeation flux due to the interaction between water molecules and the mixed membrane matrix, allowing more water molecules to be retained within the membrane pores. Additionally, the molecular sieving effect of HAC within the SA matrix further contributes to improving the membrane's separation factor 18.



# CONCLUSION

The addition of 0.8 wt% HAC filler to SA polymer enhanced membrane performance in ethanol dehydration pervaporation. The flux and separation factor of the membrane modified with HAC increased from 72.4 g/m²·h to 553.6 g/m²·h and 1637.07 to 2191.88, respectively. The improved membrane performance was supported by increased hydrophilic properties indicated by the decreased contact angle value of the membrane with HAC. The increase in hydrophilicity occurred due to the presence of hydrophilic groups, such as hydroxyl and carboxyl groups, in HAC that were incorporated into the SA polymer matrix. Additionally, SA membrane with HAC modification also exhibits better thermal and mechanical stability compared to the pure SA membrane. Based on the results obtained, SA/HAC demonstrated good properties and performance in bioethanol dehydration applications.

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