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CARRAGEENAN AND CHITOSAN MEMBRANES FOR ETHANOL PERVAPORATION

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ABSTRACT

Pervaporation is an energy-efficient membrane-based separation process that effectively separates azeotropic mixtures without requiring additives. Hydrophilic membranes are particularly suitable for ethanol dehydration. This study explores the pervaporation-dehydration of ethanol using a carrageenan-chitosan composite membrane supported by polyethersulfone (PES) and crosslinked with glutaraldehyde. The membrane's hydrophilicity enables selective water permeation, which is evaluated through swelling degree measurements. Results indicate that membranes without chitosan exhibit the highest swelling degree, while increasing chitosan content reduces swelling. Scanning electron microscopy (SEM) reveals distinct structural differences between the carrageenan-chitosan layer and the PES support, with crosslinked membranes displaying compact bonding between layers. Optimal pervaporation performance was achieved with a carrageenan-to-chitosan ratio of 1:1, a glutaraldehyde concentration of 1%, and an immersion time of 2 hours.

KEYWORDS: carrageenan, chitosan, membrane, pervaporation, ethanol

1. INTRODUCTION

The demand for fuel oil continues to rise annually, driven by population growth and increased industrialization, while the availability of global oil reserves continues to decline. This imbalance has led to a surge in fuel prices and heightened concerns over energy security and sustainability. Considering these challenges, the development of alternative energy sources has become a critical global priority. One such alternative is bioethanol, a renewable and environmentally friendly fuel that can be blended with gasoline to reduce dependency on fossil fuels and mitigate greenhouse gas emissions [1].

Ethanol, when used as a gasoline additive, must achieve a purity level exceeding 99.5% to ensure compatibility with combustion engines and optimal performance [2]. However, conventional distillation processes face significant limitations in achieving this level of purity. Due to the formation of an azeotrope at approximately 95% ethanol concentration, further purification using distillation becomes inefficient and energy-intensive [3]. This has driven research into advanced separation techniques capable of overcoming these limitations.

Pervaporation, a membrane-based separation process, offers a promising solution for ethanol purification. Unlike distillation, pervaporation can efficiently separate azeotropic mixtures without the need for chemical additives and with lower energy consumption [4]. This process involves the selective permeation of components through a non-porous membrane, transitioning the liquid feed into a vapor phase driven by a partial pressure difference across the membrane surfaces [5]. Introduced by Kober in 1917, pervaporation has since evolved into a scalable and practical technology known for its energy-saving properties, simple operational requirements, and high separation efficiency [6], [7]. These attributes make it particularly suitable for ethanol-water separation in bioethanol production.

The membrane plays a pivotal role in determining the efficiency and selectivity of the pervaporation process. Serving as a thin, selective barrier, the membrane divides the feed into permeate (components passing through the membrane) and retentate (components retained by the membrane). The development of composite membranes, which combine two or more materials, has emerged as a key strategy to enhance pervaporation performance by integrating the desirable properties of each material [8].

Among potential materials, chitosan and carrageenan have gained attention for their complementary properties. Chitosan-based films are known for their excellent mechanical strength, elasticity, flexibility, and resistance to tearing [9], [10]. Additionally, chitosan exhibits superior film-forming capabilities, strong adhesion, biocompatibility, and high mechanical strength, making it an ideal candidate for membrane applications [11]. Carrageenan, on the other hand, is a hydrophilic polymer with exceptional water-binding capabilities, making it suitable for use as a selective layer in ethanol-water dehydration [12]. However, carrageenan's low mechanical strength can limit its standalone use, necessitating its combination with other materials like chitosan to achieve optimal performance.

Crosslinking agents, such as glutaraldehyde, are often used to enhance the stability and selectivity of composite membranes. Crosslinking introduces covalent bonds between the polymer chains, improving the mechanical properties and reducing excessive swelling during the pervaporation process [13]. The concentration and duration of crosslinking play a crucial role in achieving the desired balance between selectivity and permeability in the membrane [10], [14].

This study aims to investigate the effects of the carrageenan-to-chitosan ratio and the addition of the crosslinking agent glutaraldehyde on the selectivity of ethanol dehydration via pervaporation. Furthermore, the research evaluates the structural and functional characteristics of the resulting composite membrane, with the goal of optimizing its performance for bioethanol purification applications.

2. MATERIALS AND METHODS

2.1 Materials

Chitosan, with a high molecular weight (118.4 cps) and a deacetylation degree of 80.4%, was sourced from Surindo Biotech (Cirebon, Indonesia). Carrageenan was procured from Multi Kimia Raya (Semarang, Indonesia). Additional materials, including glycerol, acetic acid, hydrochloric acid, isopropanol, polyethersulfone (PES), and glutaraldehyde, were supplied by Merck.

2.2 Preparation of composite membrane

The chitosan solution was prepared by dissolving chitosan in a 2% acetic acid solution, while the carrageenan solution was prepared by dissolving carrageenan in a 20% glycerol solution. The chitosan solution was then added to the carrageenan solution and mixed according to the specified ratio while stirring until a homogeneous mixture was obtained. The carrageenan/chitosan mixture was cast onto the PES membrane to a thickness of 0.3 mm and dried at room temperature for 24 hours. After drying, the membrane was immersed in a glutaraldehyde solution at a concentration and duration specified by the experimental variables. Finally, the composite membrane was dried at room temperature and stored in a suitable storage medium.

2.3 Swelling degree analysis

The dried membranes were cut into square shapes with sides measuring 4 cm. Each membrane was weighed and subsequently immersed in a test solution (distilled water, technical ethanol, or pure ethanol) for three hours. After immersion, the membranes were gently wiped on the surface to remove excess liquid and then reweighed. The swelling degree was calculated using Equation 1:

$$SD = \frac{W_o - W_i}{W_i} \quad (1)$$

where, W_i is the weight of the membrane before immersion and W_o is the weight of the membrane after immersion.

2.4 Pervaporation Procedure

The pervaporation experiment was conducted in batch mode. A 1000 mL solution of 95% w/v ethanol was placed in the feed tank and maintained at a constant temperature of 30°C. The ethanol-water feed

was circulated through the membrane module using a pump, while a vacuum pump was used to achieve a pressure of 6 cm Hg on the permeate side. After the specified duration, the permeate and retentate were collected, and their volumes were measured. The ethanol concentration in the retentate was analyzed using HPLC. The experiment was repeated for various experimental conditions based on the specified variables. The selectivity value of the pervaporation membrane can be determined using Equation 2:

$$\alpha = \frac{Y_A/Y_B}{X_A/X_B} = \frac{Y_A/1-Y_A}{X_A/1-X_A} \quad (2)$$

where:

X_A = weight fraction of component ethanol in the feed phase

X_B = weight fraction of component water in the feed phase

Y_A = weight fraction of component ethanol adsorbed in the permeate phase

Y_B = weight fraction of component water adsorbed in the permeate phase

3. RESULTS AND DISCUSSION

This study aims to develop an optimized composite membrane for ethanol-water separation using the pervaporation process at a temperature of 30 °C and a pressure of 6 cmHg. The performance of the pervaporation membrane is evaluated based on its selectivity. A more selective membrane for water results in higher water content in the permeate phase and consequently higher ethanol content in the retentate phase. The effectiveness of the pervaporation process is strongly influenced by the membrane's characteristics [15].

3.1 Characterization of composite membranes

3.1.1 The swelling degree of composite membranes

Swelling degree indicates the absorption capacity of the membrane film to liquids [16]. In this study, membrane swelling degree analysis was carried out on water, 95% ethanol, and pure ethanol. Figure 1 shows the effect of the carrageenan-chitosan ratio on the swelling degree of the membrane.

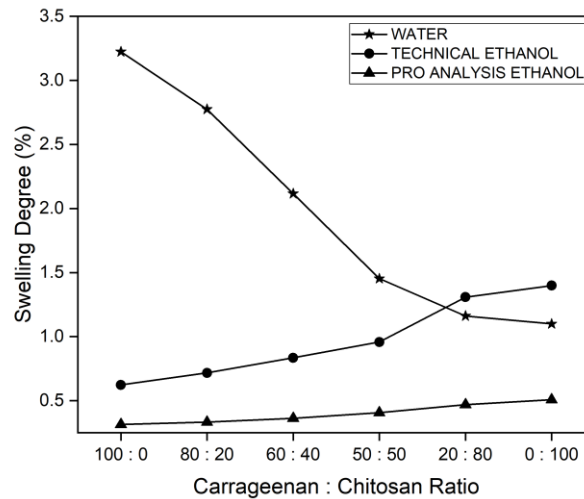


Fig. 1. Effect Carrageenan: Chitosan Ratio on swelling degree in various liquids

An increase in carrageenan concentration leads to higher water absorption [17]. Carrageenan, a sulfated polygalactan, contains approximately 15% to 40% ester-sulfate groups [18]. Kappa-carrageenan, in particular, exhibits a high affinity for water due to the presence of two hydrophilic functional groups: hydroxyl groups and sulfate esters. These properties enable carrageenan to effectively bind water [19].

The swelling degree of the membrane in water decreases as the chitosan content in the composite membrane increases. This is attributed to the chitosan's degree of deacetylation (80.4%), which indicates it still contains hydrophobic acetyl groups. According to Ong et al. (2016), a higher concentration of chitosan, combined with crosslinking treatment using glutaraldehyde, promotes the formation of crosslinks between hydroxyl ($-OH$) and amine ($-NH_2$) groups [20]. This reduces the pore size of the membrane, limiting the liquid absorption capacity and thus lowering the swelling degree. Furthermore, as the chitosan content increases, the hydrophobicity of the membrane also increases, enhancing its ethanol absorption capacity [11]. Consequently, the swelling degree in ethanol increases with higher chitosan concentrations.

Figure 1 also indicates that as the carrageenan content increases, the swelling degree of the membrane in ethanol decreases. Ethanol contains a hydrophobic ethyl group, whereas carrageenan is hydrophilic, making composite membranes with higher carrageenan content less capable of absorbing ethanol. Additionally, as the water content in ethanol decreases, the absorption capacity of carrageenan further diminishes [21]. The preparation of composite membranes by combining materials with differing characteristics aims to enhance pervaporation performance [8]. Carrageenan, as a hydrophilic polymer,

serves as a selective layer in the ethanol-water dehydration process. Hydrophilic membranes are designed to exploit interactions such as dipole-dipole, hydrogen bonding, and ion-dipole interactions between water and membrane materials [12]. The high hydrophilicity of carrageenan effectively enhances water permeation from ethanol mixtures.

Chitosan-based membranes exhibit excellent mechanical strength due to the presence of negatively charged hydroxyl groups and positively charged amine groups, enabling strong ionic bonding [20], [22]. As reported by Ismillayli et al. (2021), the tensile strength of chitosan (4.81 MPa) is significantly higher than that of carrageenan (0.2 MPa) [23]. Furthermore, Ali & Gherissi (2017) highlighted that incorporating chitosan into composite membranes improves their mechanical strength, making them more robust for the pervaporation process [21].

3.1.2 Morphology of membranes

The morphology of the membrane was analyzed using scanning electron microscopy (SEM), which provides images of the surface and cross-section of the composite membrane through electron microscopy. SEM is a valuable tool for examining the homogeneity of the composite, identifying voids, evaluating the dispersion of nanoparticles within a continuous matrix, detecting aggregates, and assessing the possible orientation of nanoparticles [24].

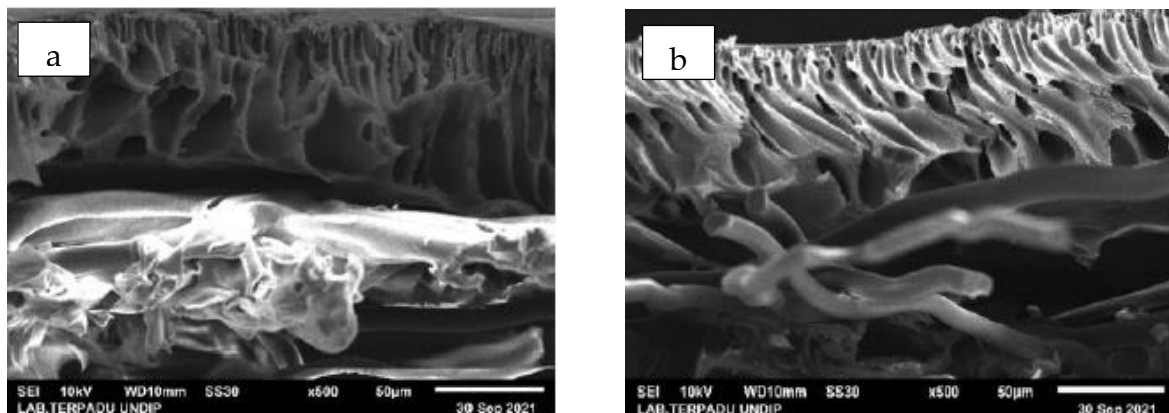


Fig. 2 SEM images of membrane cross-section: a) before crosslinking and b) after crosslinking

Figure 2 presents cross-sectional images of the carrageenan-chitosan composite membrane. Figure 2(a) shows the membrane before immersion in the glutaraldehyde crosslinking agent, while Figure 2(b) depicts the membrane after immersion. As observed in Figure 2, the membrane prior to glutaraldehyde treatment does not exhibit bonding between the PES, chitosan, and carrageenan layers. In contrast, after crosslinking, tighter bonds are evident between the PES and the chitosan-carrageenan layers.

According to Davydova et al. (2020), the combination of carrageenan and chitosan biopolymers forms a complex polyelectrolyte bond [25]. Glutaraldehyde, as a crosslinking agent, stabilizes the chitosan membrane by reacting its aldehyde groups with the amine groups in chitosan, creating covalent bonds that connect chitosan polymers [26]. Additionally, crosslinking with glutaraldehyde involves reactions between the hydroxyl groups of carrageenan and the aldehyde groups of glutaraldehyde.

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3.2 Performance of pervaporation

3.2.1 The effect of carrageenan: chitosan ratio on the selectivity.

The effect of the carrageenan-to-chitosan ratio on selectivity in the pervaporation process for ethanol dehydration is presented in Figure 3. The addition of chitosan to the composite membrane enhances selectivity, with the highest selectivity observed at a carrageenan-to-chitosan ratio of 50:50. However, further increases in chitosan content lead to a decline in selectivity. According to Ismillayli et al. (2021), the strongest interaction between the protonated amine groups of chitosan and the sulfate groups of carrageenan occurs at a chitosan-to-carrageenan ratio of 1:1 [23]. These findings align with those reported by Kononova et al. (2018) [27].

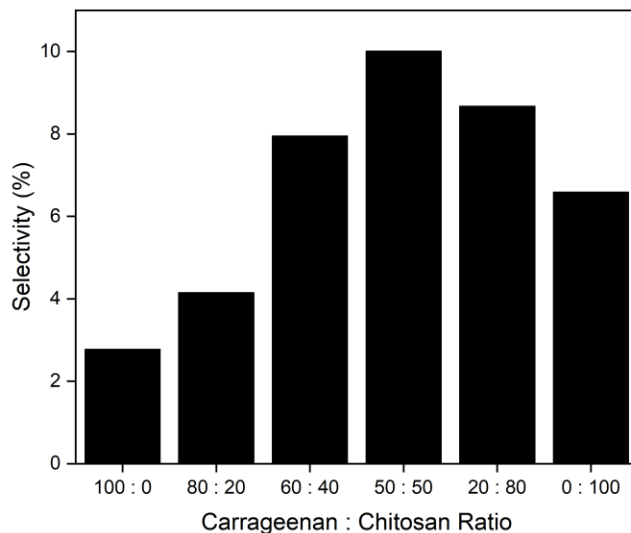


Fig. 3. Effect carrageenan: chitosan ratio on selectivity

The selectivity and separation rate of the membrane are influenced by both the membrane's characteristics and the design of the pervaporation process [20]. According to Luis (2018), a higher swelling degree enhances the membrane's ability to bind water, facilitating its separation into the permeate phase [12]. In composite membrane materials, carrageenan contributes high hydrophilicity, which increases the swelling degree for water. However, carrageenan's low mechanical strength makes it prone to brittleness. As a result, not only water but also ethanol can pass through to the permeate phase, leading to a decrease in selectivity.

3.2.2 The effect of the glutaraldehyde concentration as a crosslinking agent on selectivity

The performance of a pervaporation membrane is commonly evaluated based on its selectivity. One approach to improving selectivity is by immersing the membrane in a crosslinking agent solution [4]. In this study, glutaraldehyde was employed as the crosslinking agent. Figure 4 illustrates that the selectivity value increases as the glutaraldehyde concentration rises from 0% to 1%, achieving its highest value at 1%. Beyond this concentration, the selectivity value declines steadily, reaching its lowest point at a glutaraldehyde concentration of 2.5%. The membrane without crosslinking (0% glutaraldehyde) exhibits the lowest selectivity, highlighting the importance of crosslinking in enhancing membrane performance.

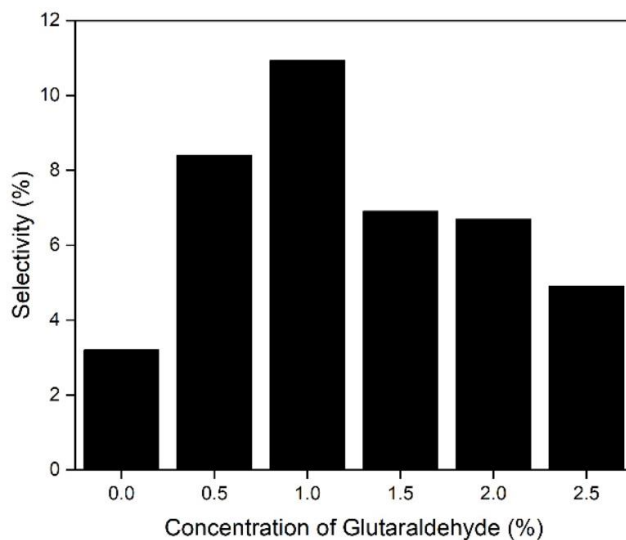


Fig. 4 Effect concentration of glutaraldehyde on selectivity

According to Kildeeva et al. (2009), crosslinking between the aldehyde groups in glutaraldehyde and the free amino groups in chitosan occurs through covalent bonding [28]. Additionally, the hydroxyl groups in carrageenan also interact with the aldehyde groups in glutaraldehyde. As a result, increasing the concentration of glutaraldehyde enhances the membrane's mechanical strength. Membranes prepared without crosslinking exhibit weaker inter-polymer bonds compared to crosslinked membranes, making them more fragile during the pervaporation process. The larger free volume in uncrosslinked membranes allows ethanol to permeate, leading to the lowest selectivity value in membranes with 0% glutaraldehyde. However, selectivity decreases when the glutaraldehyde concentration is increased beyond the optimal level. Excessive glutaraldehyde addition reduces matrix strength and increases the brittleness of the composite film, as reported by Arianita et al. (2019) [29].

3.2.3 Effect of immersing time glutaraldehyde solution on selectivity

The duration of immersion in the crosslinking solution significantly influences the membrane's characteristics and its pervaporation selectivity [30]. In this study, carrageenan-chitosan composite membranes with a 50:50 ratio were immersed in a 1% glutaraldehyde solution for varying durations to evaluate their performance.

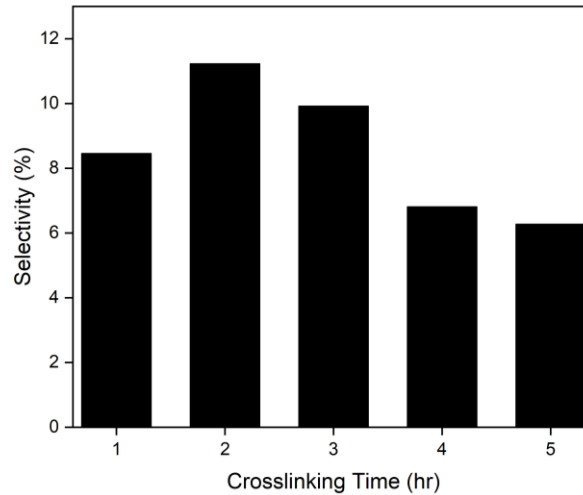


Fig. 5 Effect crosslinking time on selectivity

Figure 5 shows that the selectivity value increases with immersion times from 1 to 2 hours but decreases with longer immersion durations. According to Ghazali et al. (1997), longer crosslinking times increase the crosslinking density, resulting in a more compact and rigid membrane structure [31]. At higher degrees of crosslinking, the membrane becomes denser with reduced chain mobility, which decreases the diffusivity of permeating molecules.

4. CONCLUSION

The highest swelling degree in water was observed in the membrane film made entirely of carrageenan (100%). Adding chitosan to the composite membrane reduced the swelling degree in water, while it increased the swelling degree in a 95% ethanol solution. Incorporating chitosan into the composite membrane film enhances selectivity. However, when the chitosan concentration exceeds that of carrageenan, the pervaporation selectivity decreases. Immersing the composite membrane in a glutaraldehyde solution with an optimal concentration and duration further improves pervaporation selectivity. The morphology of the crosslinked composite membrane shows more intricate interpolymer bonds compared to non-crosslinked membranes, contributing to improved performance.

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