Koc. J. Sci. Eng., 5(2): (2022) 205-211 https://doi.org/10.34088/kojose.1013196

Kocaeli University

Kocaeli Journal of Science and Engineering

http://dergipark.org.tr/kojose

Investigation Of Separability Of DMC/Methanol Azeotropic Mixtures By Chitosan Hybrid Membrane

Nazlı YENIHAN YUZER [1], Guler HASIRCI [2], Nilufer HILMIOGLU [3, *]

[1] *Department of Chemical Engineering, Kocaeli University, Kocaeli, 41001, Turkey,* ***ORCID:*** *0000-0001-5112-5450*
[2] *Department of Chemical Engineering, Kocaeli University, Kocaeli, 41001, Turkey,* ***ORCID:*** *0000-0001-7435-8118*
[3] *Department of Chemical Engineering, Kocaeli University, Kocaeli, 41001, Turkey,* ***ORCID:*** *0000-0002-2627-8890*

Article Info

Research paper

Received *: October 21, 2021*
Accepted *: December 31, 2021*

Keywords

Azeotropic Mixture,
Dimethyl Carbonate,
Hybrid Membrane,
Pervaporation

Abstract

Dimethyl carbonate (DMC) is a green solvent and an environmentally friendly fuel additive. It is produced by carbonylation of methanol The production cost of DMC is very high by conventional processes because DMC and methanol form azeotrope and cannot be separated by distillation. Its separation can be performed by pervaporation (PV) economically. Pervaporation (PV) is also an environmentally friendly membrane process in which liquid-liquid mixtures are separated under vacuum with high selectivity. Pervaporation selectivity is dependent on sorption selectivity and diffusion selectivity. Membrane used in the pervaporation process is a semi-permeable barrier and provides selective separation and transport. In PV development of an appropriate membrane material is important for obtaining pure substances. Hydrophilic membrane can separate methanol which is a polar component. Chitosan is a harmless, biodegradable, natural polymer and, despite having hydrophilic properties, cannot withstand aqueous conditions. Therefore, it should be modified by crosslinking. Tetraethoxysilan (TEOS) and tungstophosphoric acid (TPA) can be used as crosslinking agents and additive blending components in membrane production for increasing chemical and mechanical stability. In this study, sorption tests were carried out to determine the usability of chitosan-tetraethoxysilan (TEOS) and chitosan-Tungstophosphoric acid (TPA) hybrid membranes in separation of DMC-Methanol mixture with PV.

1. Introduction

Pervaporation (PV) draws attention as an effective process in separating azeotropic mixtures. It has been explained that PV provides up to 80% energy economy compared to distillation. Ethanol dehydration by PV using polymeric membranes is a commercial application. As a result of its strong interaction and affinity with water, hydrophilic membranes are used in the PV process is conducted in three stages: In the first stage, the components in the feed sorb on the upper surface of the membrane, in the second stage they diffuse through the membrane, in the third stage they are desorb into the lower surface of the membrane in vapor form. Since desorption is very fast, PV is controlled by the first two stages. The membrane; absorbs and passes the component of interest. PV performance depends on the surface properties of the membrane. Surface properties such as hydrophilicity and crystallinity can be made with a correct crosslinking. The suitability of the PV process can be determined by examining the sorption of the mixtures to be separated on the membrane.

Dimethyl carbonate (DMC) is a versatile compound compatible with the environment. It can be used instead of harmful compounds in the chemical industry. The properties of DMC such as high oxygen content, low toxicity, rapid biodegradation and low impact on air quality; allows it to be used as a fuel additive instead of other additives. Excessive methanol is used in the production of environmentally friendly DMC by carbonylation of methanol, instead of the current production technique that causes environmental pollution. In this method, the formation of methanol azeotrope with DMC causes purification problems. Various separation processes such as extractive distillation, pressure swing distillation, liquid-liquid extraction, adsorption, low temperature crystallization have been tried. PV usage is rare in the literature [1]. In recent years, separation of organic-

---

[*] Corresponding Author: niluferh@kocaeli.edu.tr

organic mixtures by PV has gained importance in the chemical and petrochemical industries. Due to the similarity of the physical and chemical structures of organic components, it is difficult to separate them by a conventional separation method such as distillation or other membrane processes. Hydrophobic polymers are used as membrane material to separate organic components. However, these materials do not show high selectivity for organic components. For the separation of DMC-Methanol mixture, hydrophilic materials are preferred, as methanol is polar. Since the interaction of these materials with methanol is stronger than DMC, they have more affinity to methanol. Therefore, methanol selectivity increases with a hydrophilic membrane. In addition, molecular size and polarity difference give higher selectivity. Biocompatibility, biodegradability and non-toxic properties of Chitosan, which is widely used, make it the brightest material of the future. Reactive amine groups together with hydroxyl groups give chitosan hydrophilic properties. These groups in the Chitosan membrane preferentially allow polar components such as water to sorb to membrane and diffuse from the membrane. Since Chitosan has good film forming properties, chemical resistance and high water selectivity, it is also used in the dehydration of many industrial solvents. However, its weakening physical and mechanical properties limit its use in practice because it swells too much in aqueous systems. One way to overcome these limitations is chemical crosslinking [2]. Commonly used crosslinking agents are glutaraldehyde and sulfuric acid. Tetraethoxysilane (TEOS) and Tungsto phosphoric acid (TPA) can be the new effective agents for the modification of chitosan. In addition, with the synergy created by the combination of the properties of two different materials, organic-inorganic hybrid membranes have extraordinary properties and the potential to be the new generation membrane material. When the studies in the literature are examined, it is seen that the sorption selectivity in DMC-methanol separation by pervaporation using chitosan/silicotungstic acid (STA) hybrid membrane is much greater than diffusion selectivity. In other words; separation mechanism is determined by sorption. It has been stated that with the addition of STA to the polymer, the amorphous region is more intense and the preferential methanol sorption increases [3].In another study in which 3-aminopropyltriethoxysilane (APTEOS) was added to chitosan, it was noted that the amorphous region was denser with increasing additive content and the preferential water sorption increased when used for ethanol-water separation by PV [4].

Chitosan is commonly used as blend membrane component in membrane preparation applications due to high hydrophilicity, good film forming character, excellent chemical resistant [3]. Since hydrophilic membranes swell too much in aqueous systems, their weakening physical / mechanical properties limit their use in practice. Therefore, crosslinking agents are used in preparing membranes. Tetraethoxysilane (TEOS) contains four $SiOC_2H_5$ groups and can be a crosslinking agent in membrane production [5]. Tungstophosphoric acid (TPA) which is a heteropolyacid can be used as a modification agent and blending component in membrane production [6]. High hydrophilicity of chitosan causes high swelling in the high polar component content and reduces its stability. Crosslinking with suitable agents is the most appropriate method to increase selective permeability and stability by suppressing this swelling. The crosslinking between the crosslinking agent and chitosan makes the amorphous region in CHM denser and tighter. Thus, the diffusion path of the components is narrowed and the passage of large molecules is prevented. In this study, in order to increase flux and selectivity together, new chitosan hybrid membranes (CHM) were prepared by cross-linking chitosan with TEOS AND TPA. CHM’s performances have been evaluated for its use in the separation of Dimethyl carbonate-methanol azeotropic mixture by PV. The effects of TEOS and TPA CONTENTS of CHM and methanol concentration in the feed mixture on sorption properties were investigated.

On the other hand, the importance of the subject can be explained as follows: Worldwide Fossil fuel consumption seriously and negatively our planet. Especially the air pollution caused by these fuels affects seriously and badly affects human health. Recently environmental issues have led countries to use energy sources that are alternative to fossil fuels. Biodiesel, which is an alternative to fossil fuels, is a renewable energy source and its production and consumption have increased in recent years. It is expected that worldwide biodiesel production will reach 23.57 billion liters by 2025 [7]. Biodiesel is obtained from renewable and sustainable sources by transesterification of vegetable oils or animal fats with methanol in the presence of acidic and basic catalysts. Glycerol is formed as a byproduct in a ratio of 1/10 (glycerol/biodiesel) by weight in biodiesel production [8]. In terms of sustainable and environmental economy, it is important to transform glycerol that is produced amounts as waste to other valuable chemicals. Glycerol is a versatile compound in the food, polymer and fuel industries [9]. It is an organic compound which is a low toxicity alcohol that consists of a three carbon chain with a hydroxyl group. Physically, it is a colorless, odorless, viscous, and sweet-tasting compound [10]. It can be transformed to other valuable chemicals by various reaction pathways. In addition, the conversion of glycerol into fuel additives has become an important research area. Glycerol carbonate production is one of these research areas. Glycerol carbonate (GC) (4-hydroxymethyl-1,3-dioxolan-2-one) is a five membered cyclic carbonate that synthesized from glycerol [11]. It has low toxicity, low flammability, good biodegradability and high boiling point [7]. Additionally, it has potential to be used as a fuel additive that improves the property of fuel. Glycerol carbonate is used in chemical, pharmaceutical, cosmetic, polymer; industries as a surfactant, solvent and plasticizer, and in electrolytes in li-ion batteries [12]. It can be produced by transesterification reaction of glycerol with dimethyl carbonate (DMC) or diethyl carbonate (DEC) in the presence of basic catalysts [13]. This method prevents unfavorable thermodynamic equilibrium, low reaction rate, toxic materials, high reaction temperature and difficult reaction conditions [14]. Pervaporation is a membrane process in which liquid-liquid mixtures are separated under vacuum with high selectivity [15]. Due to low temperatures and pressures, it is considered as one of the clean technologies that can effectively replace traditional separation processes [16].

Additionally, pervaporation is effective process for separating azeotropic mixtures that cannot be separated by classical distillation [4]. For this study, DMC and methanol form an azeotrope mixture at specific concentrations [3]. Membrane used in the pervaporation process is a semi-permeable barrier where selective separation and transport occurs. Since hydrophilic membranes have an affinity for water molecules, they can hold or pass some compounds that dissolve in water [17, 18]. As methanol is a polar compound, hydrophilic membranes are preferred for the separation of the DMC-Methanol mixture. Therefore, methanol selectivity increases with the use of hydrophilic membrane in DMC-Methanol mixtures [3]. Dong et al. carried out pervaporation removal of methanol from methanol/DMC azeotrope using organosilica membranes. These membranes ensured preferential sorption of methanol [19]. Wang et al. prepared SAPO34 zeolite membranes and they used them for Vapor separation of methanol-dimethyl carbonate mixture [20]. Chitosan that is produced from the deacetylation of chitin is a harmless, bio-soluble, natural polymer. Due to its biodegradability, biocompatibility, and no toxicity, it is one of the most common substances used for the separation of mixtures in the present and future [21].

2. Materials and Methods

2.1. Pervaporation

Transportation in membrane is explained by the dissolution diffusion mechanism in pervaporation process. Dissolution diffusion model has three stages [15]:

1. Sorption stage: Transport of the component throughout the liquid boundary layer to the membrane surface.
2. Diffusion stage: Transport of the component throughout the membrane.
3. Desorption stage: Desorption of the component in vapor form from the other side of the membrane.

In the pervaporation process, the separation ability of the membrane is expressed by permeation flux and selectivity. Permeation flux and selectivity are inversely proportional to each other. [22]. Flux is mass flow per unit time, per unit area. Membrane permeability and thickness affects permeation flux [23]. It is calculated as:

$$J=\frac{m}{A.t} \tag{1}$$

J; The total mass flux (kg / m^2.h), m ; The weight of the permeate, A; Effective area in membrane A (m^2), t ; time
Pervaporation selectivity is the passing ratio of the components in the mixture in contact with the membrane [24]. It is calculated as in Eq. 2:

$$\alpha_{pv} = \frac{y_a/y_b}{x_a/x_b} \tag{2}$$

y_a and y_b are permeate concentrations of a and b, x_a and x_b are feed concentrations of a and b.
Sorption selectivity according to the dissolution-diffusion model defines the selectivity of the sorption process and is shown in Eq. 3:

$$\alpha_{sorp} = \frac{(z_a/z_b)}{(x_a/x_b)} \tag{3}$$

z_a and z_b are component concentrations in the membrane, respectively and x_α and x_b are concentrations in the feed.

$$\alpha_{pv} = \alpha_{sorp} \times \alpha_{dif} \tag{4}$$

Pervaporation selectivity is equal to multiplication of sorption and diffusion selectivities. The relationship between them is shown in Eq. 4 [25].

In general, pervaporation selectivity is related to sorption selectivity. PV operation proceeds through sorption. Therefore sorption tests provide information about the separability mixtures by PV.

2.2. Chemicals

Tungstophosphoric acid (TPA) (powder form) Tetraethoxysilane (TEOS) (99.0%), Chitosan (CS) from Sigma Aldrich; Methanol (99.0%) and Acetic Acid (99.0%), HCl (99.0%), methanol, dimethyl carbonate (DMC) were purchased from Merck.

2.3. Membrane Preparation Method

TPA/CS and TEOS/CS hybrid membranes were prepared from solution by pouring-evaporation method. The powder chitosan, 1% by weight separately for both hybrid membranes, was dissolved in 1% acetic acid solution at 40 ° C for 24 hours until the solution became homogeneous. To the prepared homogeneous chitosan solutions, TPA was added in different proportions as 2, 4, 6, 8,10% and TEOS was added in different proportions as 1,3,5% to form a homogeneous mixture. They were mixed for a day. 0.5 M HCI was added to the TEOS loaded CS membrane for crosslinking. The homogeneous solutions obtained were poured into separate petri dishes and allowed to dry in a vacuum oven at 40 ± 1 ºC. TPA was used both as additive material and as crosslinking agent while TEOS was used only as additive material.

2.4. Sorption Test for Swelling Performance

The doped membrane films prepared as chitosan-teos and chitosan-tpa were weighed. The dry weights of the prepared doped membranes were weighed and prepared for use in sorption experiments (W_{dry}) and then immersed in solution in pure methanol and in different methanol concentration ranges for 24 hours at room temperature. At the end of 24 hours, the doped membrane pieces were removed from the solution mixtures and reweighed (W_{wet}). The formulation in Eq.5 is used to calculate the degree of swelling

$$Swelling\ Degree, (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} x100 \qquad (5)$$

3. Results and Discussion

The swelling degree values for DMC / methanol mixture in TPA-added chitosan membrane were given in Figure 1.

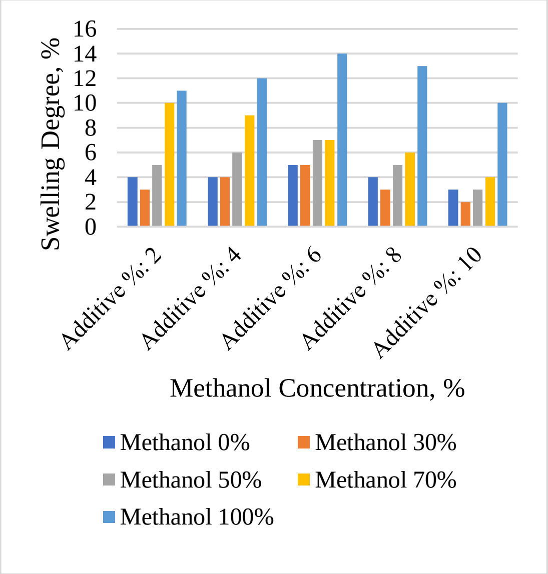

Figure 1. Swelling degree values for DMC/methanol mixture in TPA added chitosan membrane.

As shown in Figure 1 swelling increased by TPA addition until the TPA additive is 6%. After that value of swelling decreased with increased TPA addition. This may be because the additive material causes agglomeration in the polymer. All TPA doped membranes showed swelling in the pure DMC when the solution did not contain methanol. It indicates that these membranes will also pass DMC in the pervaporation application where DMC is sorbed.

The swelling degree values for DMC / methanol mixture in TEOS added chitosan membrane were given in Figure 2.

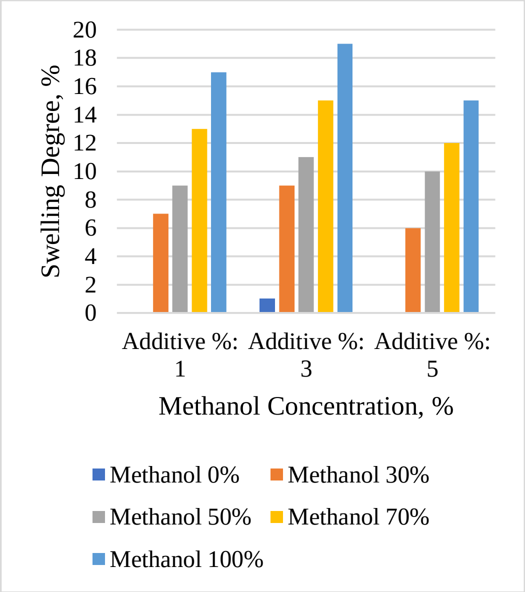

Figure 2. Swelling degree values for DMC/ methanol mixture in TEOS added chitosan membrane.

As seen in Figure 2, the swelling increased up to a TEOS of addition 3% and then decreased. Agglomeration may have caused the occurrence of this decrese. Only membranes with 3% TEOS added showed swelling in pure DMC. This indicates that the membrane will also pass DMC in the pervaporation application. The swelling degree value of the membrane with an added TEOS ratio of 1% is close to the one with the added TEOS ratio of 3%. The membrane with a TEOS ratio of 1% did not sorb. DMC. For this reason, it was understood in the study that the membrane loaded with TEOS at a ratio of 1% has optimum swelling degree and it can also be used in the pervaporation application. The relationship between methanol concentration and swelling degree for 6% TPA added membrane which shows the highest swelling degree among TPA doped membranes, was given in Figure 3.

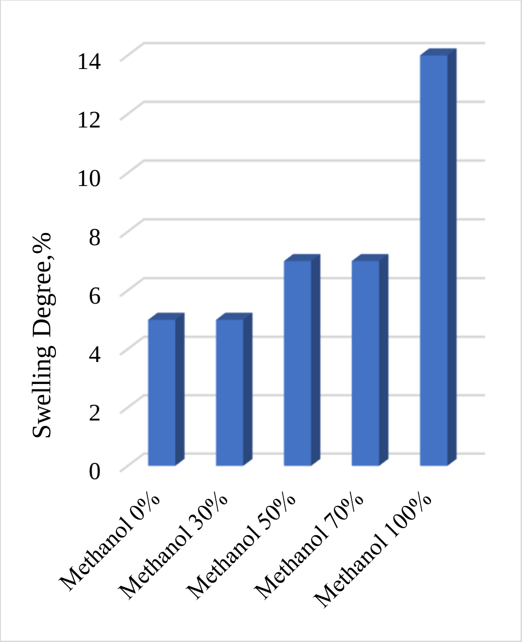

Figure 3. Methanol concentration and Swelling degree relationship for 6% TPA added membrane.

When looking at the relationship between the concentration of methanol and the degree of swelling in the 6% TPA added membrane, which has the highest sorption capacity for pure methanol, it was seen in Figure 3 that the swelling degree increased with the increase in methanol concentration and this membrane also retained DMC. The relationship between methanol concentration and the swelling degree in the chitosan membrane with a TEOS ratio of 1% was given in Figure 4.

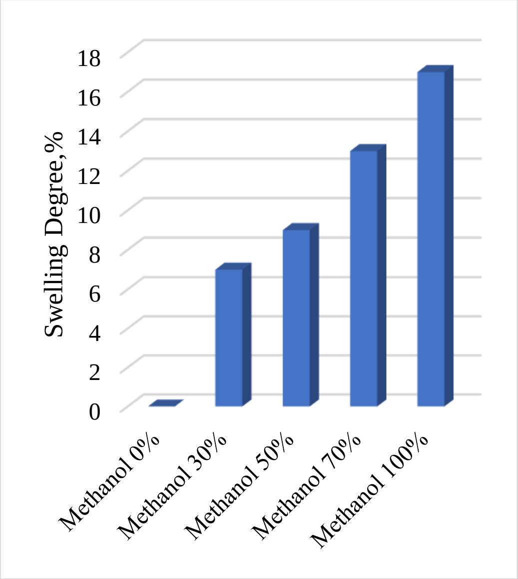

Figure 4. Methanol concentration and swelling degree relationship in chitosan membrane with 1% TEOS ratio.

As can be seen in Figure 4, it was observed that the degree of swelling of the chitosan membrane with 1% TEOS ratio increased as the methanol concentration increased. It was observed that this membrane did not hold DMC. The results of swelling degree values obtained from sorption tests in pure methanol for Pristine chitosan membrane and doped chitosan membranes that had high swelling values were given in Figure 5.

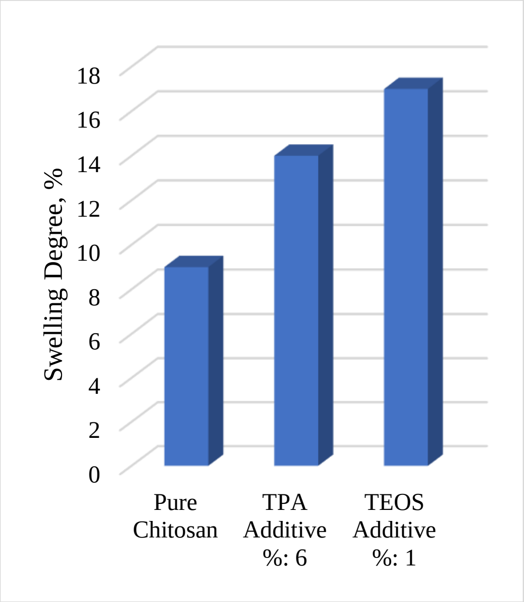

Figure 5. The swelling degrees of pure methanol for pristine chitosan and membranes with high swelling values.

When the values of swelling degree that show sorption results for pristine chitosan membrane and added membrane in pure methanol were analyzed it was decided that chitosan membrane with 1% TEOS ratio was the most suitable membrane. This outcome was deduced from Figure 5.

4. Conclusions

In this study, sorption tests were conducted to examine the usability of chitosan-tetraethoxysilan (TEOS) and chitosan-Tungsto phosphoric acid (TPA) hybrid membranes in separation of DMC-Methanol mixture by PV. CHM was formed by crosslinking between chitosan and additive. The effects of additive content and methanol concentration in the feed on the degree of swelling, a measure of sorption, were studied. As the content of the additive increased, the amorphous region in CHM increased and the hydrophilicity increased. Sorption was affected by the content of additives in CHM and the concentration of methanol in the feed. It was observed that the degree of swelling increased with the concentration of methanol in the feed. It has been observed that the degree of swelling increases up to a certain amount of additive and decreases after that point. This is because excess crosslinking restricts the movement of polymer chains and prevents excessive swelling. The performance of

CHM has increased compared to the pristine Chitosan membrane. It has been understood that the prepared composite hybrid membrane can be used in the separation of DMC-Methanol azeotropic mixtures.

The sorption tests of chitosan membrane and TPA and TEOS loaded chitosan membranes for DMC/methanol mixtures were made. TPA loaded chitosan membranes have ability of sorption for both methanol and DMC while TEOS loaded chitosan membranes have ability of sorption for methanol only. 1% TEOS loaded chitosan membrane has a potential for separation of DMC/methanol mixtures by pervaporation.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank to Kocaeli University Scientific Research Projects Unit for their support to the membrane R&D laboratory.

References

[1] Chen J., Liu Q., Fang J., Zhu A., Zhang Q., 2007b. Composite hybrid membrane of chitosan–silica in pervaporation separation of MeOH/DMC mixtures. Journal of Colloid and Interface Science, **316**, pp. 580-588.

[2] Won W., Feng X., Lawless D., 2003. Separation of dimethyl carbonate/methanol/water mixtures by pervaporation using crosslinked chitosan membranes. Separation and Purification Technology, **31**, pp.129-140.

[3] Chen J., Liu Q., Zhu A., Zhang Q., Fang J., 2008. Pervaporation separation of MeOH/DMC mixtures using STA/CS hybrid membranes. Journal of Membrane Science, **315**, pp. 74–81.

[4] Chen J., Liu Q., Zhang X., Zhang Q., 2007a. Pervaporation and characterization of chitosan membranes cross-linked by 3-aminopropyltriethoxysilane. Journal of Membrane Science, **292**, pp. 125–132.

[5] Tong B., Cheng C., Khan M., Wu Y., Xu T., 2017. Double cross-linking PVA-SiO2hybrid membranes for alkali recovery. Separation and Purification Technology, **174**, pp. 203-211.

[6] Ponce M. L., Prado L., Ruffmann B., Richau K., Mohr R., Nunes S. P., 2003. Reduction of methanol permeability inpolyetherketone–heteropolyacid membranes. Journal of Membrane Science, **217**, pp. 5-15.

[7] Chen W., Bhaskar T., Ong H., 2020. Biomass Processing for Biofuels, Bioenergy and Chemicals, Printed Edition of the Special Issue Published in Energies. MDPI, Basel, Switzerland.

[8] Trifoi A., Agachi Ş. P., Pap T., 2016. Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols. Renewable and Sustainable Energy Reviews, **62**, pp. 804-814.

[9] Nanda M., Yuan Z., Qin W., Ghaziaskar H. S., Poirier M. A., Xu C.C., 2014. Thermodynamic and kinetic studies of a catalytic process to convert glycerol into solketal as an oxygenated fuel additive. Fuel, **117**, pp. 470-477.

[10] Talebian-Kiakalaieh A., Amin N. A. S., Najaafi N., Tarighi S., 2018. A Review on the Catalytic Acetalization of Bio-renewable Glycerol to Fuel Additives. Frontiers in Chemistry, **6**, pp. 573.

[11] Christy S., Noschese A., Lomelí-Rodriguez M., Greeves N., Lopez-Sanchez J. A., 2018. Recent progress in the synthesis and applications of glycerol carbonate. Current Opinion in Green and Sustainable Chemistry, **14**, pp. 99-107.

[12] Teng W. K, Ngoh G. C., Yusoff R., Aroua M. K., 2014. A review on the performance of glycerol carbonate production via catalytic transesterification: Effects of influencing parameters. Energy Conversion and Management, **88**, pp. 484-497.

[13] Kumar P., With P., Srivastava V. C., Gläser R., Mishra I. M., 2015. Glycerol Carbonate Synthesis by Hierarchically Structured Catalysts: Catalytic Activity and Characterization. Industrial and Engineering Chemistry Research, **54**, pp. 12543-12552.

[14] Wang S., Hao P., Li S., Zhang A., Guan Y., Zhang L., 2017. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate catalyzed by calcined silicates. Applied Catalysis A, General, **542**, pp. 174-181.

[15] Jyoti G., Keshav A., Anandkumar J., 2015. Review on Pervaporation: Theory, Membrane Performance, and

Application to Intensification of Esterification Reaction. Journal of Engineering, **2015**, pp.1-24.

[16] Cannilla C., Bonura G., Costa F., Frusteri F., 2018. Biofuels production by esterification of oleic acid with ethanol using a membrane assisted reactor in vapour permeation configuration. Applied Catalysis A, General, **566**, pp. 121-129.

[17] Mulder M., 1996. Basic Principles of Membrane Technology, Second ed. Kluwer Academic Publishers, Dordrecht, Netherlands.

[18] Drioli E., Giorno L., 2016. Encyclopedia of Membranes, illustrated ed. Springer, Heidelberg. Berlin.

[19] Dong G., Nagasawa H., Yu L., Wang Q., Yamamoto K., Ohshita J., Kanezashi M., Tsuru T., 2020. Pervaporation removal of methanol from methanol/organic azeotropes using organosilica membranes: Experimental and modeling. Journal of Membrane Science, **610**, pp. 118284.

[20] Wang M., Li M., Chang N., Gao L., Wang M., Zhang Y., 2018. Vapor separation of methanol-dimethyl carbonate mixture on SAPO-34 zeolite membrane. Journal of Membrane Science, **565**, pp. 311-321.

[21] Ismail A. S., Darwish M. S. A., Ismail E. A., 2016. Synthesis and characterization of hydrophilic chitosan-polyvinyl acetate blends and their sorption performance in binary methanol–water mixture. Egyptian Journal of Petroleum, **26**, pp. 17-22.

[22] Huang R. Y. M., Yeom C. K., 1990. Pervaporation separation of Aqueous mixtures using crosslinked poly (vinyl alcohol) (PVA), II. Permeation of Ethanol-Water mixtures. Journal of membrane science, **51**, pp. 273-292.

[23] Feng X., and Huang R. Y. M., 2007. Liquid Separation By Membrane Pervaporation: A Review. Industrial & Engineering Chemistry Research, **36**, 1048-1066.

[24] Baker R. W., 2000. Membrane technology and application, second ed. John Wiley & Sons, West Sussex, England.

[25] Hilmioglu N., 1998. PhD Thesis, IPA/Su ve MTBE/Metanol Azeotropik Karışımlarının Pervaporasyon ile Ayrılması, İTU.