



High-efficiency pervaporative separation of fuel bioadditive methylal from methanol by poly(vinyl alcohol)/poly(vinylpyrrolidone) blend membrane

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Abstract

Methylal is a fuel bioadditive. The purification of methylal has been conducted by the pervaporation process. The purification of methylal from the reaction mixture is required to use the methylal as a fuel additive for diesel or biodiesel. In this study, poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP) polymers were used and the blend membrane was prepared by using these polymers. The prepared PVA/PVP blend membranes have been utilized for the separation of methylal/methanol binary mixtures and methylal/methanol/water ternary mixtures in a pervaporation process. Membranes were characterized by Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), contact angle measurements and X-ray Diffraction Analysis (XRD). Pervaporation tests were performed at different feed concentrations, operation temperatures and PVP loading ratios. The best separation performance was obtained at 10 wt. % of PVP loaded membrane. Optimum process conditions were determined as 30 °C of operation temperature and 5 wt. % of feed methanol concentration. Under these conditions, methanol flux and methanol selectivity values were 0.21 kg/m² h and 98.01, respectively. Approximately, 99% of purity methylal has been achieved in the retentate stream by removing the methanol. The innovation of this study is to develop an alternative method, which is of high purity and low energy consumption according to the literature, for the purification of methylal biofuels.

Keywords Fuel bioadditive · Membrane · Methanol · Methylal · Pervaporation · Separation

List of symbols

α	Selectivity
F_a, F_b	Mass fraction of a and b components in the feed
J	Flux (kg/m ² h)
m	Permeate weight (g)
P_a, P_b	Mass fraction of a and b components in the permeate
S	Effective membrane area (m ²)
t	Time (h)
MeOH	Methanol
PVA	Poly(vinyl alcohol)
PVP	Poly(vinylpyrrolidone)
w_s	Weights of swollen membranes (g)
w_d	Weights of dried membranes (g)

Introduction

Methylal, also called dimethoxymethane, is a non-toxic, biodegradable fuel bioadditive material. It is 100% miscible with diesel and biodiesel fuel. Methylal is an oxygenate that comprises 42% oxygen by mass. It has a high hydrogen-to-carbon ratio, a low cetane number and autoignition temperature. The addition of methylal to fuel significantly improves the combustion features and decreases emission levels. Methylal has 55% of the energy density of diesel fuel (Dong et al. 2018; Lu et al. 2007). In addition, because of its good toxicological profile and biodegradability, methylal is used as a green solvent in many industrial applications such as the cosmetic industry, paint and varnish production, pharmaceuticals, polymers, resins, and adhesives. And also, methylal has extraordinary solvent power, amphiphilic character, very low viscosity and high evaporation rate. The diversity of usage areas significantly increases its global demand (Carretier et al. 2003; Xia et al. 2012).

Methylal is generally synthesized by the catalytic reaction of formaldehyde or paraformaldehyde with methanol.

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After the production process, methylal is obtained as a mixture containing different amounts of methanol and water (Dong et al. 2018; Wanget al. 2012). The obtainment of methylal as pure is rather important for its usage as a solvent and fuel additive. Therefore, a purification process is required for the achievement of pure methylal from the mixture. At atmospheric pressure, methylal and methanol form an azeotrope mixture with 94.06 wt. % methylal (Dong et al. 2018). Therefore, conventional distillation methods are not appropriate for the separation of these binary and ternary mixtures. Pervaporation, reactive distillation and extractive distillation processes have been used in the literature to separate the methylal/methanol mixtures (Carretier et al. 2003; Dong et al. 2018; Wang et al. 2012; Xia et al. 2012).

There is only one study in the literature about the dehydration of methylal mixtures by pervaporation. That study was conducted by Carretier et al. (2003). Carretier et al. studied the pervaporative separation by using some commercial membranes such as Sulzer1060, 2256, 2200, SS304. The best separation performance was obtained with a zeolite based SS304 membrane. The used polymeric membranes displayed low flux values and the active layers of the membranes were destroyed with time. Therefore, usage for a long time and reuse are not possible for these membranes. Besides, the use of commercial membranes is not economical (Carretier et al. 2003).

Other studies about methylal/methanol separation in the literature are related to the distillation process and simulation applications. Wang et al. (2012) investigated the separation of methylal/methanol mixtures using the Aspen Plus simulation programme. Extractive distillation was used for the separation. The requirement of additional chemicals (entrainers) and the harmful structure of used chemicals are the major disadvantages of the extractive distillation process. Dimethylformamide is usually chosen as an entrainer in extractive distillation applications. Dimethylformamide is absorbed through the skin and causes skin problems. It has a strong toxic effect. The addition of the entrainer results in an increment in the relative volatility of the light (methylal) and heavy key (methanol) components, because the entrainer shows different affinities to the key components and facilitates the separation (Wang et al. 2012). Zhang et al. (2011) examined the synthesis and purification of methylal in catalytic distillation. The methylal purity was obtained as 92.1% (Zhang et al. 2011). Distillation processes are high cost, high energy consuming processes. Besides, the use of additional harmful chemicals (entrainers) causes waste products (Huang et al. 2006).

In this study, the pervaporation process is preferred for the separation of methylal/methanol mixtures and membranes are synthesized in the laboratory. Pervaporation is an alternative process to conventional separation processes.

Pervaporation is a process in which a component in a mixture diffuses selectively along a membrane. The differences in the chemical activity of components create a driving force for transport. In this process, one of the components in the feed mixture sorbs and then dissolves on the upper surface of the membrane according to its affinity with the membrane. This solute component is selectively transported through a dense membrane. While this component forms a permeate stream, the other insoluble component is called the retentate stream. Since the pressure applied at the downside of the membrane is lower than the vapor pressure of the feed mixture at atmospheric pressure, the phase change occurs and the permeate stream is in the vapor phase. The vapor stream is condensed in the cold traps. This transport mechanism of the solute is called the solution-diffusion model (Hajilary et al. 2019; Karimi et al. 2021; Huang 1991; Linet al. 2013; Baker 2000; Vane 2009).

Pervaporation has some features such as low energy consumption, low cost, prevention of additional chemical usage, environmentally friendly, high separation efficiency (Haaz et al. 2020; Ebneyamini et al. 2018; Farhadi et al. 2017; Unlu and Hilmioğlu 2016). The purification percentage and energy consumption of the different separation techniques used for ethanol purification are given in Table 1.

As seen in Table 1, the purification percentage of the pervaporation process is high, the energy requirement for the separation process is quite low compared to other processes. The pervaporation process uses this small amount of energy to convert the liquid phase in the feed to the vapor phase. Besides these advantages, the flux value of pervaporation is lower than other separation processes. Therefore, pervaporation application is limited. However, new types of membranes can be synthesized to overcome this problem.

Mass transfer of pervaporation is based on the interaction between the feed components and the membrane. The structure of membrane materials and the chemical nature of the feed mixture are key factors for the determination of membrane performance (Basile et al. 2015; Thorat et al. 2017). These factors should be considered in the selection of polymeric materials for separation. These are high chemical and mechanical stability and sorption and diffusion capacity. The preparation of a membrane with the desired properties

Table 1 Energy consumption in processes used to purify ethanol (Huang vd. 2006)

Process	Purification (%)	Energy requirement (kJ/kg EtOH)
Distillation	8.0–99.5	10,376
Azeotropic distillation	95.0–99.5	3305
Pervaporation	95.0–99.5	423

is very important to obtain good separation performance (Das et al. 2007).

In this study, Poly(vinyl alcohol) (PVA) and Poly(vinylpyrrolidone) (PVP) were chosen as the membrane matrix. Due to its good film-forming ability and low cost, PVA is one of the most widely used hydrophilic polymers in the pervaporation process. It shows high chemical and mechanical resistance (Wang et al. 2017). PVP is chosen as the additive material to blend with PVA. PVP is a good hydrophilic membrane material that can easily blend with other polymeric materials. The addition of PVP aims to hinder the crystallization of PVA with the hydrogen bonds between the PVA and PVP, and the permeability of the membrane is increased. Furthermore, the affinity between PVP and methanol is much stronger than that between PVP and methylal. It is expected that the separation performance of pure PVA membrane will be increased by incorporating PVP (Zhu et al. 2013). While the polarity of PVA is in the range of 12.40–13.60, the polarity of PVP is approximately 11. Considering the polarity values of water, methanol and methylal, respectively, these values are 16, 12.3, and 1.8, respectively. The polarity values reveal that the PVA-based membrane will show affinity for water and methanol, but will not act selectively against methylal (Barton 1992; Hansen 2000).

No study is available in the literature on the membranes synthesized in the laboratory and used in the separation of methylal/methanol mixture by pervaporation. There is no result of an investigation into the selectivity value of pervaporation. All the results in the literature are related to flux and mass fraction values. Membranes were characterized by FTIR, SEM, TGA and contact angle. The optimum operation conditions for the pervaporation process were investigated. According to the author's knowledge, this is the first study on pervaporative separation using membranes synthesized in a laboratory for the separation of methylal/methanol mixture.

Experimental

Materials

Both poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP) were purchased from Sigma Aldrich. PVA has an average molecular weight of 89,000–98,000 with a degree of hydrolysis of 99%. The molecular weight of the used PVP was 125,000. The following chemicals were utilized for membrane crosslinking treatment. Hydrochloric acid, acetone and glutaraldehyde were purchased from Sigma Aldrich. The separation mixture components, methylal and methanol were supplied by Sigma Aldrich.

Preparation of blend membrane

The desired amount of PVA (wt. %) solution was prepared by dissolving PVA in water at 90 °C. The desired amount of PVP (wt. %) in water was prepared and mixed at room temperature vigorously. The blend of PVA/PVP membrane was synthesized to assemble both the solutions at different blend ratios (10, 20, 30, 40, 50 wt. %). The solutions were then cast on a clean glass petri dish. For 36 h, the membrane was dried at room temperature with a relative humidity level of 30–35%. The synthesized blend membranes were crosslinked by immersing them in an acetone solution consisting of 2 ml of glutaraldehyde and 2 ml of HCl for a period of 4 h in room conditions to improve the chemical and mechanical stability as well as separation features. Membrane thickness was measured by using a micrometer as 35–40 μm .

Blend membrane characterization

FTIR

The chemical bond interactions of PVA and PVA/PVP blend membranes have been specified by utilizing Fourier transform infrared spectroscopy. FTIR spectra were detected in the Thermo Nicolet 5700 spectrometer, with 4 scans at 4 cm^{-1} resolution. The analyses were performed in the range between 400 and 4000 cm^{-1} .

TGA

The thermal stabilities of PVA membranes and PVA/PVP blend membranes were acquired using a Mettler Toledo thermal analyzer. The membrane sample was tested over temperatures ranging from 25 to 600 °C at a heating rate of 10 °C/min under nitrogen flow.

SEM

The surface and cross section SEM images of the PVA membrane and PVA/PVP blend membranes were achieved by using a Carl Zeiss/Gemini 300 Scanning electron microscope (SEM). Before analysis, membrane samples were prepared by breaking in liquid nitrogen and coated with gold via sputtering.

Contact angle

The hydrophilic features of membranes were specified by contact angle analysis. Contact angle analysis was carried out with an Attension, KVS Instrument. Measurements

were performed with methanol. Contact angle values were taken from different regions of the test piece and the mean values were calculated.

XRD

The XRD patterns of the membrane samples were characterized by a Bruker AXS/Discovery D8 Xray diffractometer using Cu Ka radiation. The angle of diffraction was varied from 5° to 40° using a step size of 0.02°.

Swelling tests

The sorption degrees of different ratios of PVP loaded membranes were determined with swelling tests. The broken membrane samples were weighted. Membranes were immersed in methanol solvent and then were taken away from the solvents periodically, dried well with filter paper and weighted again. The measurements were continued until the membranes reached a constant mass. The sorption degrees of the membranes were calculated by using Eq. (1);

$$\text{Sorption degree (\%)} = \frac{w_s - w_d}{w_d} * 100 \quad (1)$$

w_d and w_s indicate the dry membrane weight and swollen membrane weight (g), respectively (Lee et al. 2020).

Pervaporation experiments

The binary (methylal/methanol) and ternary (methylal/methanol/water) mixtures were separated by using a pervaporation system which was shown in Fig. 1.

A membrane cell was placed in an oven and temperature control was provided with this oven. The feed side of the membrane cell was filled with feed mixtures and kept at atmospheric pressure. The volume of the feed mixture was 50 ml. The reflux condenser has been used on feed side of the membrane cell. The aim of the used reflux condenser is to prevent the loss of solvent by evaporation. The permeate side of the membrane cell was maintained at a vacuum pressure (5 mbar). The phase change occurred at this pressure difference. Therefore, the permeate stream was obtained in the vapor phase and condensed in cold traps and obtained in the liquid phase. The collected sample in trap weighted and flux value was calculated by using Eq. 2.

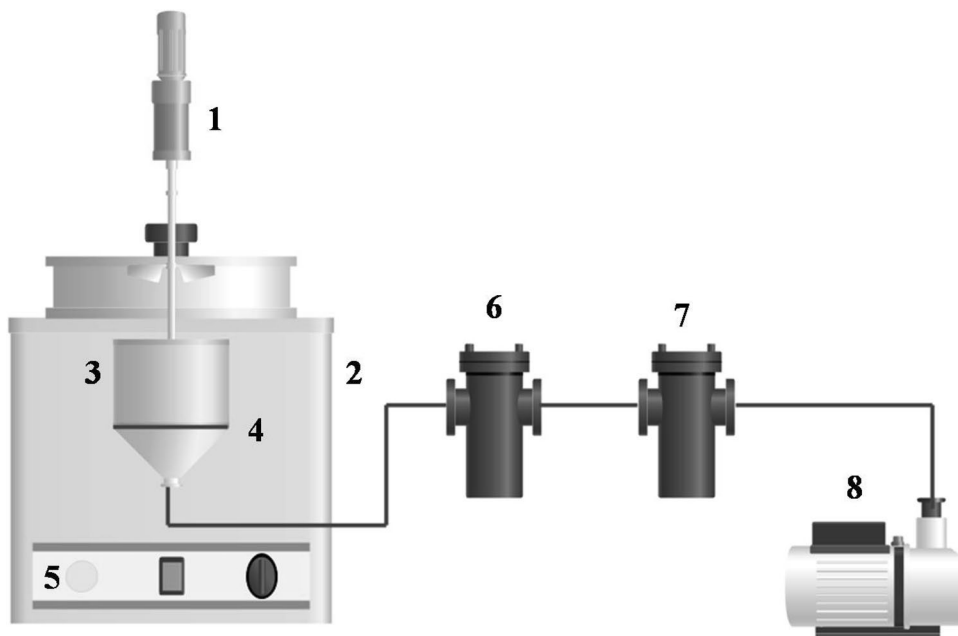
$$J = \frac{w}{S.t} \quad (2)$$

In this equation, J is the flux ($\text{kg/m}^2 \text{ s}$), w is the mass of the permeate stream, S is the membrane area and t is the permeation time. In this study, the effective membrane surface area was 9.62 cm^2 , experiments were performed for 6 h.

The determination of concentrations of components was conducted by gas chromatography and the determined values were used to compute selectivity.

The selectivity of the membrane is specified by using Eq. (3):

Fig. 1 Schema of pervaporation: (1) mechanical mixer, (2) oven, (3) membrane cell, (4) membrane, (5) temperature controller, (6, 7) cold traps, (8) vacuum pump



$$\alpha = \frac{P_a/P_b}{F_a/F_b} \quad (3)$$

where α is the selectivity, F and P present the mass percentages of the target component in the feed side and permeate side, respectively (Zhai et al. 2020).

Results and discussion

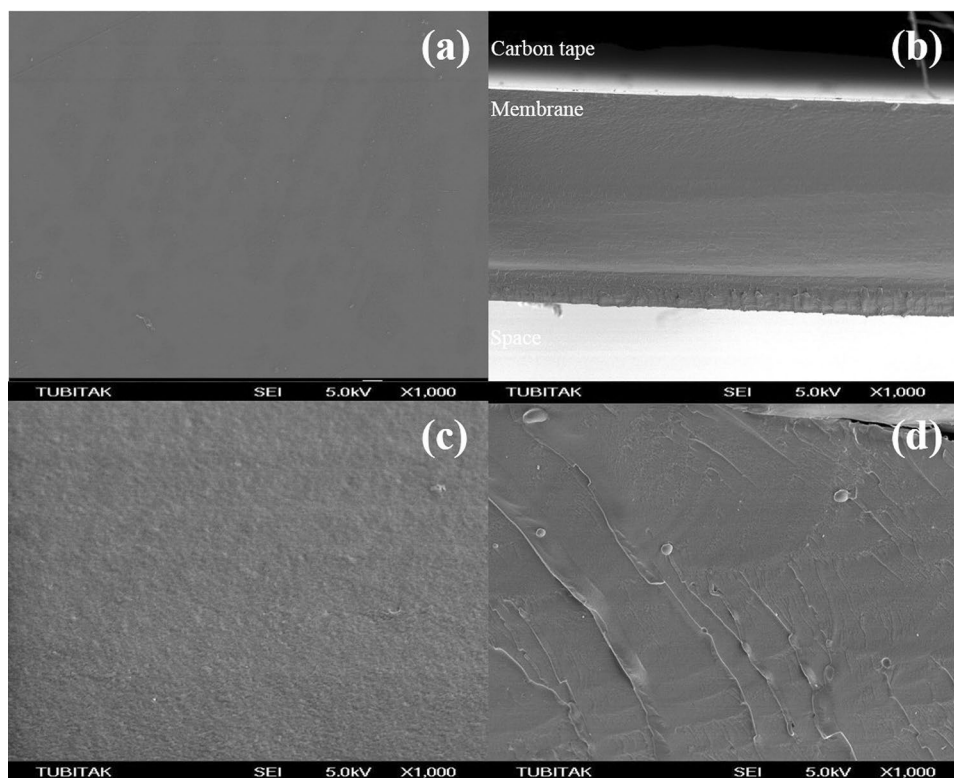
Membrane characterization

SEM

The surface and cross section SEM images of the pristine PVA and PVA/PVP blend membranes are displayed in Fig. 2.

Figure 2a displays the homogeneous surface of the pristine PVA membrane. There is no defect on the membrane surface. The cross section image of the PVA membrane was also shown that the pristine membrane occurs only one polymer. The PVA/PVP blend membrane displays a uniform surface. This is related to the good compatibility between the polymers in the membrane (Fig. 2c). Figure 2d indicates that the miscibility and compatibility between PVA and PVP were rather good. There are no signs of phase separation in the blend membranes.

Fig. 2 SEM images of the **a** pristine PVA membrane surface **b** pristine PVA membrane cross-section **c** PVA/PVP blend membrane surface **d** PVA/PVP blend membrane cross-section



FTIR

Figure 3 shows the FTIR spectrum of PVA and some of the prepared PVA/PVP blend membranes.

Figure 3a shows the characteristic bands in the pristine PVA membrane. The peaks at 3278, 2924, 1710, and 1085 cm^{-1} indicate the presence of $-\text{OH}$, $\text{C}-\text{H}$, $\text{C}=\text{O}$, and $\text{C}-\text{O}$ bonds, respectively. Figure 3b depicts the spectrum of the 10% PVP loaded blend membrane. The peaks of $\text{C}=\text{O}$, $\text{C}-\text{N}$ bonds in the PVP membrane are located at 1659 cm^{-1} and 1358 cm^{-1} , respectively. The characteristic peaks of 30 wt. % PVP and 50 wt. % PVP loaded blend membranes have been shown in Fig. 3c and d, respectively. The peak around 1200 cm^{-1} is related to the formation of ether bonds by blending PVA with PVP to form their polymer blends. A sharp peak at 1652 cm^{-1} is the free $\text{C}=\text{O}$ group. An increase in the intensity of the $\text{C}=\text{O}$ peak compared to the PVA membrane confirms the presence of the $\text{C}=\text{O}$ group of PVP and the $\text{C}=\text{O}$ groups of glutaraldehyde. Also, this peak (1652 cm^{-1}) indicates the formation of hydrogen bonds between the $\text{C}=\text{O}$ bond of the PVP membrane and the $\text{O}-\text{H}$ of the PVA membrane. The peak around 1040 and 1060 cm^{-1} is related to the formation of acetal groups between the $-\text{OH}$ and $-\text{CHO}$ groups. The intensity of this peak increases with the amount of PVP in the membrane. The other peaks at 3370 and 2900–2800 cm^{-1} correspond to $-\text{OH}$ and $\text{C}-\text{H}$ groups in the PVA/PVP blend membrane (Zhu et al. 2013).

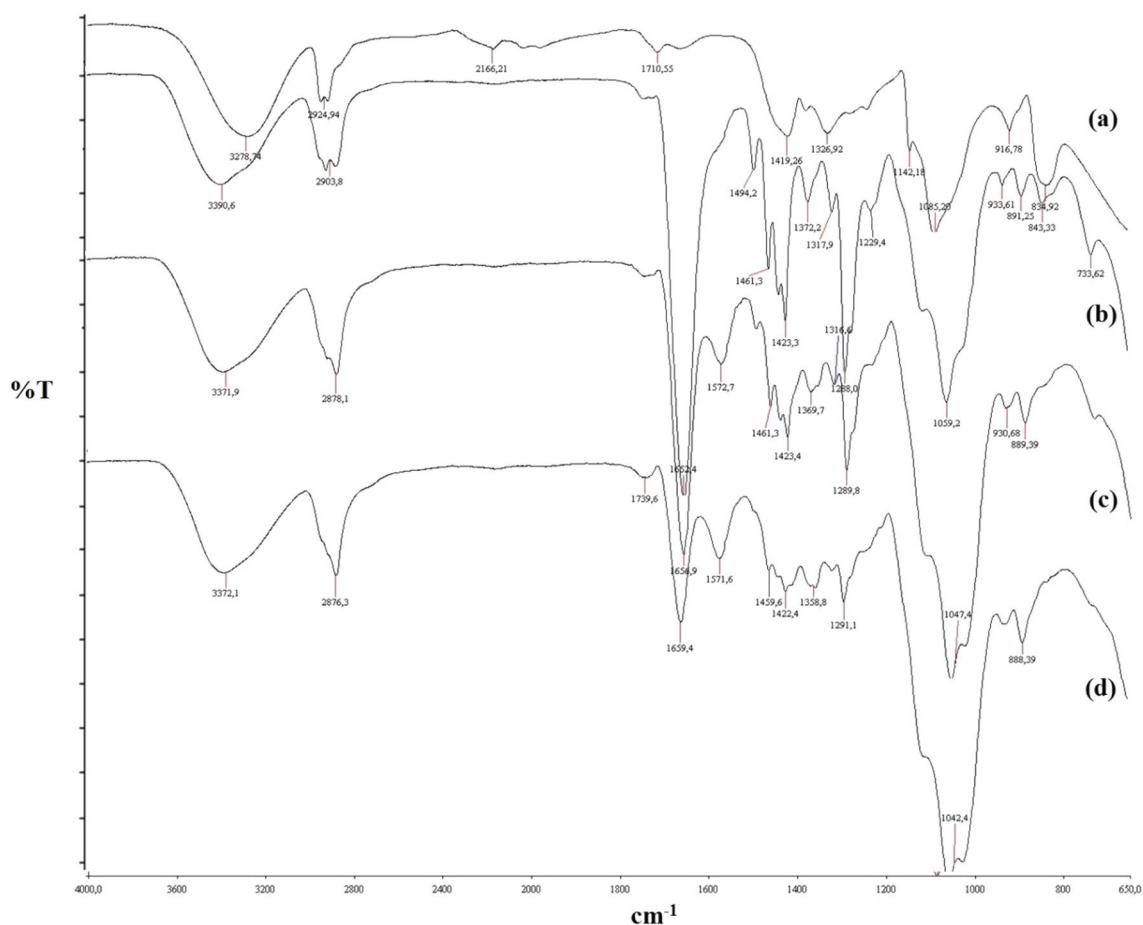


Fig. 3 FTIR spectra of **a** pristine PVA membrane, **b** 10 wt. % PVP loaded blend membrane **c** 30 wt. % PVP loaded blend membrane **d** 50 wt. % PVP loaded blend membrane

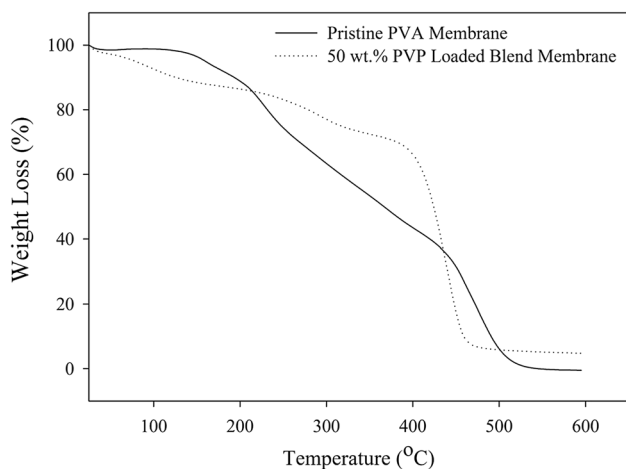


Fig. 4 TGA data of membranes **a** Pristine PVAmembrane **b** 50 wt. % PVP loaded blend membrane

TGA

The thermal degradation of the membranes with temperature is shown in Fig. 4.

TGA curves are provided for a pristine PVA membrane and a 50% PVP loaded blend membrane. Pristine PVP membrane has not been synthesized due to the fragile structure of the PVP polymer. All the membranes show a weight loss of approximately 15% between 100 and 200 °C due to the vaporization of small molecules like water in the membrane structure. The pristine PVA membrane has two weight loss regions. The first weight loss between 250 and 400 °C is attributed to the thermal decomposition of the main polymeric chains. The structural degradation of PVA membranes is observed around 450 °C. The PVA–PVP blend membranes show the extent of weight loss between 250 and 400 °C. This degradation is related to the pristine PVA (around 250 °C) and PVP (around 400 °C) degradation temperatures. The thermal stability of the PVA–PVP blend membranes is higher than that of the pristine PVA and PVP membranes (Devi et al. 2006).

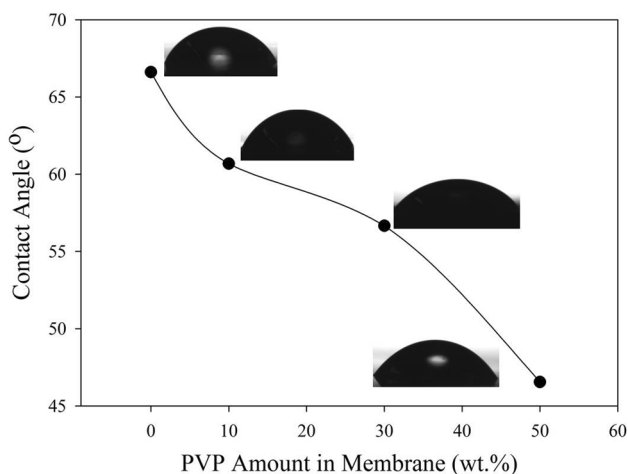


Fig. 5 The contact angle values of membranes

Contact angle

The separation success of a blend membrane is regarded with the hydrophilic features of the membrane. As shown in Fig. 5, the pristine PVA membrane has a high contact angle value. An increase in PVP concentration in the membrane resulted in a decrement in contact angle value. It means that the PVP addition makes the membrane more hydrophilic because there are unreacted CO groups in the blend membrane (see FTIR Figure). These unreacted CO groups are linked by hydrogen bonding with methanol, and these bonds facilitate the diffusion of methanol through the membrane (Zereshki et al. 2010a, b).

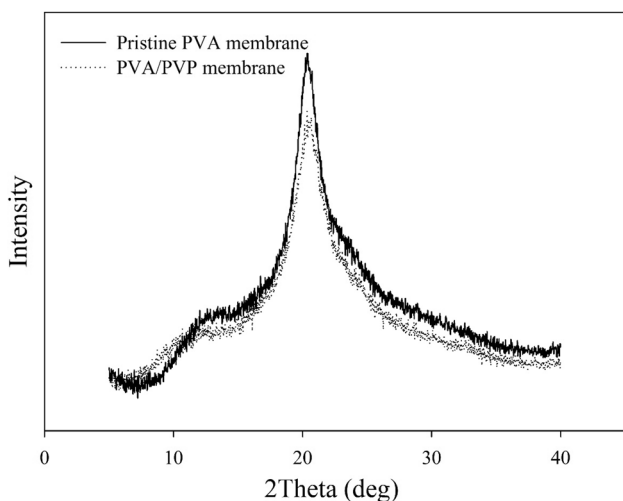


Fig. 6 XRD of pristine PVA membrane and 10 wt. % PVP loaded PVA–PVP blend membrane

XRD

Figure 6 depicts XRD patterns of pristine PVA membranes and PVA–PVP blend membranes loaded with 10% PVP.

It was seen clearly that the peak intensity of the typical diffraction peak of the blend membrane decreases at $2\theta = 20^\circ$. This decrement shows that the crystallinity was decreased with PVP addition. This means PVP is less crystalline than PVA. The addition of PVP increases the amorphous regions. These amorphous regions facilitate the transport of molecules through the membrane. It is expected that the permeation flux of PVA–PVP blend membranes will be increased according to the PVA membrane (Zhu et al. 2013).

Swelling results

Sorption degree is a significant method that determines the sorption ability and solvent affinity of membranes. This method gives information about the separation success of the membrane. The hydrophilic structures in the membrane provide the methanol sorption for methylal/methanol separation.

The sorption degree increased with the addition of PVP to the membrane (wt. %) as shown in Fig. 7. The addition of PVP enhances the interaction of methanol with the membrane and shows the rather high selective property towards the methanol during separation. More methanol absorption at high PVP ratios results in higher sorption degrees. The increment of PVP concentration made the membrane more hydrophilic, so the blend membrane showed a higher affinity towards methanol than the pristine PVA membrane and the sorption degree of methanol was enhanced (Zereshki et al. 2011).

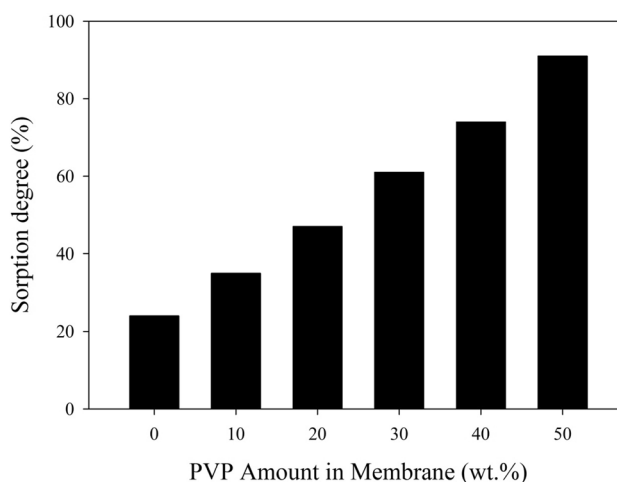
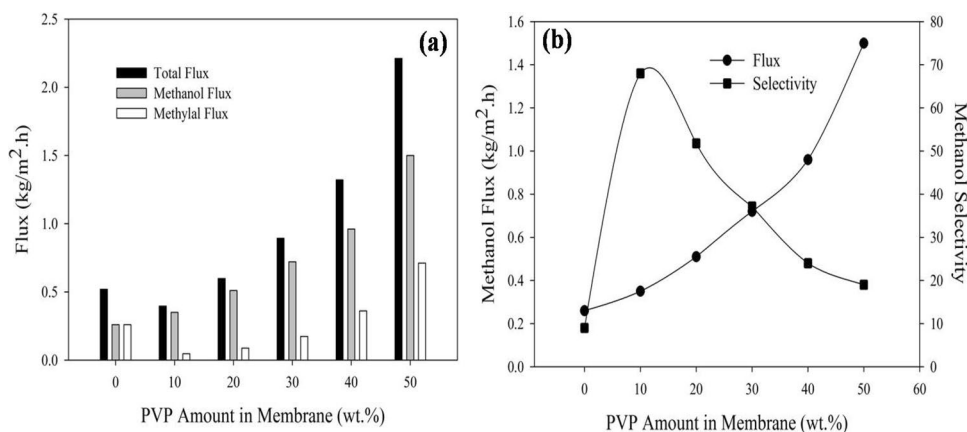


Fig. 7 The sorption degree of membranes

Fig. 8 Effect of PVP amount in membrane **a** total, methanol, methylal flux **b** methanol flux and methanol selectivity



Pervaporation results

Effect of PVP amount in membrane

Figure 8 presents the influence of the PVP amount in PVA/PVP blend membranes on the pervaporation of methylal/methanol mixtures. The feed concentration of methanol was 10 wt. % and the operation temperature was 40 °C. Due to the hydrophilic character of PVP, the blend membrane showed more affinity for methanol than the pristine PVA membrane. As the PVP amount was increased, the hydrophilicity of the blend membrane increased and the variation in flux and selectivity was observed.

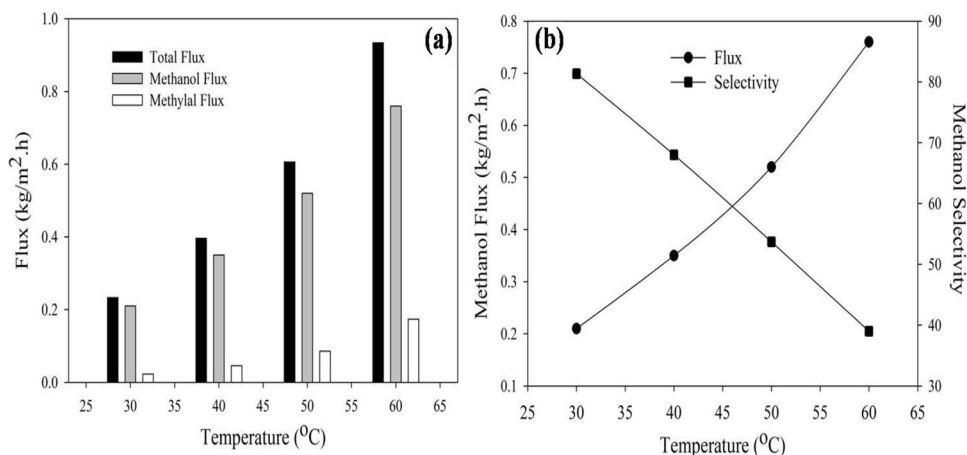
Due to the close solubility parameter, PVP exhibits a high affinity for methanol. Due to the high methanol affinity of PVP, as the PVP concentration in the membrane increases, methanol uptake of the membrane rises. This result was confirmed by swelling test results. The transport of methanol through the membrane increased with PVP. Therefore, permeation flux steadily increased with the PVP concentration in the membrane. As the methanol flux increased, diffusion paths of the membrane enlarged and the other component methylal also diffused easily along the membrane. The high

PVP ratio in membranes also affects the crystallinity of the membrane structure. The amorphous zone in the membrane increases with the PVP ratio. Polymeric membrane chains acquire flexibility (Zhu et al. 2013). As a result, the methanol and methylal fluxes and total flux increased. The methanol and methylal fluxes and consequently total flux increased (Fig. 8a). Selectivity values display the opposite trend to flux values. The methanol selectivity decreased with PVP addition. The expanding membrane channels of PVP allow the transport of methylal molecules together with methanol molecules (Zhu et al. 2013; Wu et al. 2008; Han et al. 2013; Zereshki et al. 2010a, b). The highest selectivity value was obtained as 68.01 in a 10 wt. % PVP loaded blend membrane. (Fig. 8b).

Effect of operation temperature

Operation temperature is a critical parameter in the pervaporation process and influences the separation performance significantly. The change of flux and selectivity are present in Fig. 9. In these experiments, a 10 wt. % PVP loaded blend membrane was utilized and the feed methanol concentration was 10 wt. %.

Fig. 9 Effect of temperature **a** total, methanol, methylal flux **b** methanol flux and methanol selectivity



The influence of operation temperature was tested in a temperature range of 30–60 °C. The flexibility and mobility of polymer chains increases with temperature. The diffusion channels expand, and free volume increases in the polymer matrix. This high degree of flexibility and mobility facilitates component diffusion. Thus, the diffusion rates of the molecules have increased (Zhang et al. 2009; Castro-Muñoz et al. 2019; Zhou et al. 2014). The more methylal molecules that have the opportunity to diffuse across the membrane, the lower the methanol selectivity value (Fig. 9a and b).

An increase in temperature also results in high vapor pressure on the feed side, and the vapor pressure on the permeate side was not affected by this change. This pressure difference creates the driving force for the mass transfer of the components. The driving force increases with the increment of temperature (Magalad et al. 2010). As a consequence, the transport of components increases, and this is also concluded to increase flux. The other component together with the target selective component diffused along the membrane by high flux and the separation selectivity dropped.

Effect of feed concentration

The pervaporation performance of the PVA/PVP blend membrane was examined in different feed methanol concentrations. Figure 10 shows that the feed composition has a substantial effect on flux and selectivity. The effect of feed methanol concentration on pervaporation was examined in ranges from 5 to 20 wt. % in the mixture at 30 °C. 10 wt. % PVP loaded blend membrane was used in these tests.

As the methanol concentration increases in the feed mixture, the swelling degree of the membrane increases. Diffusion channels of the membrane expand, methanol and methylal molecules penetrate the membrane easily. Methanol's size is smaller than that of methylal. The membrane, which has a high swelling degree, also allows the transport of a little amount of methylal. Therefore, methanol can be diffused more than methylal along the membrane (Wang et al. 2007; Qin et al. 2014; Aliabadi et al. 2012). As the number of

molecules carried increases, the flux increases. In permeate streams, methylal is found with methanol together, so selectivity decreases. A high methanol concentration in the feed mixture causes more methanol sorption in the membrane. Due to the structure of the membrane, the membrane has a highly preferential interaction with methanol. Therefore, the flux value of methylal is rather lower than the methanol flux. The total flux value is very close to the methanol flux. This result is related to the methanol-selective nature of the membrane (Fig. 10a).

Separation of the ternary mixture

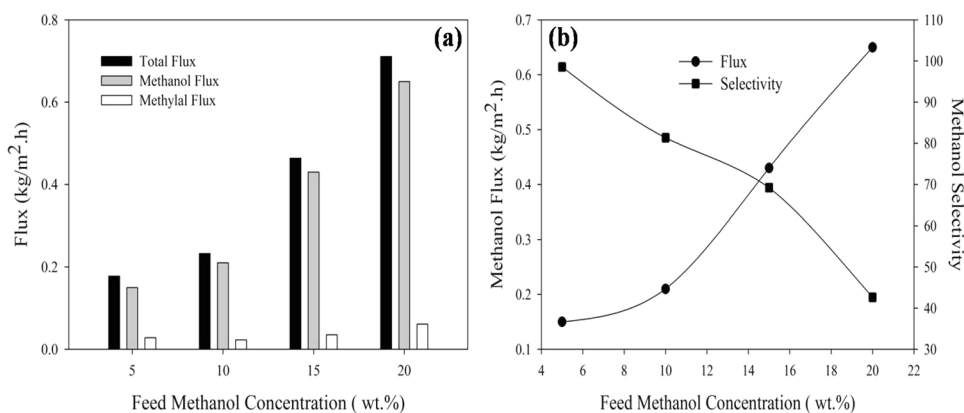
The PVA/PVP blend membrane was evaluated for the separation of ternary methylal–methanol–water mixtures. The studied concentration of components in the ternary mixtures and the obtained results are given in Table 2. The operation temperature was 30 °C and the PVP loading ratio was 10 wt. %.

An increase in the feed methanol concentration increases the flux and decreases the selectivity of water. The high methanol concentration resulted in the high diffusion of methanol along the membrane. This situation can be explained by the affinity of the membrane (Unlu 2020). Under these conditions, total flux increases, methanol and water selectivity decrease. The diffusion rate of water

Table 2 The separation results of the ternary mixture

Feed water concentration (wt. %)	Feed methanol concentration (wt. %)	Flux (kg/m ² h)	Water selectivity	Methanol selectivity
2	4	0.341	20	48.72
5	10	0.719	15	8.52
5	15	0.967	9	6.92
4	2	0.543	72	12.25
10	5	0.864	65	1.65
15	5	1.245	48	1.21

Fig. 10 Effect of feed methanol concentration **a** total, methanol, methylal flux **b** methanol flux and methanol selectivity



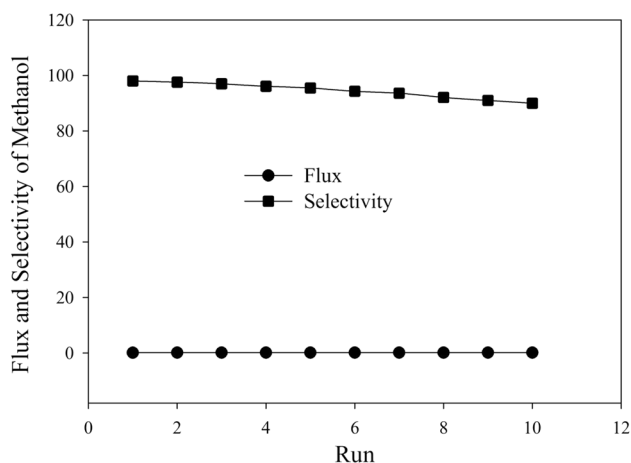


Fig. 11 Blend membrane stability and reusability

decreases at high methanol concentrations. As a result, the water concentration in the permeate stream decreases and accordingly, the selectivity of water decreases. In other words, as the methanol concentration decreased with water, the water sorption and diffusion along the membrane surface increased, and the swelling degree of the membrane increased due to the hydrophilic structure of the membrane. Consequently, the swollen membrane facilitates the permeation of water and methanol components. However, the number of water molecules in the permeate stream was higher than the methanol molecules. Even though there is an increase in water concentration on the permeate side, the selectivity of the water decreases with the transport of methanol. As a result, the attainment of a high water selectivity value is possible with less methanol concentration in the feed mixture.

Reusability of PVA/PVP blend membrane

The reusability tests of the PVA/PVP blend membrane were conducted at 30 °C, 5 wt. % of the feed methanol mixture. An optimum blend ratio (10 wt. % PVP loaded ratio) was used in reusability experiments. Figure 11 shows the separation performance for ten cycles.

In each reusability experiment, the membrane was taken out from the membrane cell and washed with distilled water and put on dry, and then reused. The flux and selectivity values versus runs are presented in Fig. 11. After ten runs, the PVA/PVP blend membrane has good chemical and mechanical stability. The obtained results show that differences in the flux and selectivity values were acceptable after 10 runs. The methanol flux value increased from 0.15 to 0.175 kg/m² h from the 1st run to the 10th run. The methanol selectivity decreased from 98.01 to 90.

Conclusion

In this research, methylal, which is used as a green solvent and fuel additive, was purified by using a PVA/PVP blend membrane. Binary and ternary methylal mixtures were separated successfully. The synthesized blend membranes were characterized by different analysis methods. In FTIR, the characteristic peaks of membranes and bond changes were determined. The thermal stabilities of membranes were analyzed by TGA. SEM revealed the surface and cross section structures of membranes. The effect of PVP addition on the hydrophilicity of the blend membrane was tested by the contact angle. As a result of the characterization tests, the PVA/PVP blend membrane showed high hydrophilicity. The results of swelling and pervaporation tests also supported the characterization results. In pervaporation tests, the effects of PVP amount, operation temperature, and feed concentration on separation performance were investigated under moderate experimental conditions, high separation efficiency was obtained in the pervaporation process. The acquired results are consistent with the high affinity of the membrane for water and methanol. When the pervaporative separation was performed in feed conditions of 5% methanol, an operation temperature of 30 °C, and a 10% wt. % PVP loaded blend membrane, the highest separation performance was achieved at 0.21 kg/m² h of flux and 98.01 of selectivity. Approximately, 99% purity of methylal has been reached in the retentate stream by removing the methanol. Moreover, the ternary mixture was separated by a 10 wt. % PVP loaded blend membrane. The water and methanol selectivity values were acquired as 72 and 12.25, respectively, while the methanol and water amounts in the feed mixture were 4 wt. % and 2wt. %, respectively. Experimental studies show that pervaporation is an alternative process for the separation of methylal. The prepared PVA/PVP blend membrane displayed high separation efficiency for the separation of the methylal/methanol mixture.

Declarations

Conflict of interest The author declares no conflict of interest.

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