Preparation of fatty acid methyl ester through temperature gradient driven pervaporation process

Baisali Sarkar[a], S. Sridhar[b], K. Saravanan[a], Vijay Kale[a,*]

[a] Lipid Science and Technology Division, Indian Institute of Chemical Technology, Hyderabad, Andhra Pradesh 500607, India
[b] Membrane Separations Group, Indian Institute of Chemical Technology, Hyderabad 500607, India

ARTICLE INFO

ABSTRACT

Fatty acid esters are useful functional molecules in pharmaceutical, cosmetic and lubricant industries. The conversion of esters may be enhanced by continuous removal of the water produced during the esterification process which is a reversible reaction. Non-porous hydrophilic pervaporation membranes have the ability to remove water using milder conditions compared to conventional technologies. The potential of pervaporation driven by temperature gradient has been investigated in this study for esterification of oleic acid, a long chain (C_{18}) fatty acid, with methanol. Composite polyvinyl alcohol (PVA) membrane was cast on polyether sulfone (PES) ultraporous substrate in view of its feasibility for scale-up in the form of plate and frame modules. Characterization of the membrane was carried out by measuring the thickness of membrane layers, scanning electron microscopy (SEM) studies, thermogravimetric analysis (TGA) and tensile strength testing before and after esterification experiments. The swelling studies of the composite membrane were also carried out in binary mixtures of methanol and water. The water removing efficiency of the membrane was evaluated in terms of flux and separation factor when methanol was spiked with 1–3 wt% water. Separation of water from methanol is a bigger challenge compared to dehydration of higher alcohols due to the polar nature of both molecules. The performance of the same membrane was evaluated as percentage conversion of ester during reaction between oleic acid and methanol, catalyzed by sulfuric acid. Research thrust was to minimize the amount of the corrosive sulfuric acid without compromising on conversion. The reaction conditions such as reactant ratio and temperature were varied and optimized in order to get maximum conversion of ester. Using PVA composite membrane, 99.9% conversion of methyl ester having acid value 0.2 could be obtained using 0.3 wt% sulfuric acid at 65 °C. As per international specification for biodiesel, the acid value of the ester should be below 0.5. Pervaporation aided esterification, driven by temperature gradient eliminated the necessity of using an inert sweep gas or vacuum on the downstream side. The % ester conversion was found to be better than the result in the absence of pervaporation. Results observed with the indigenous membrane were comparable to performance exhibited by commercial membrane.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Long chain fatty acid methyl esters such as methyl oleate are widely used in biodiesel and biolubricant industry, food and pharmaceutical formulations, plasticizers, emollients in cosmetics, and as a precursor for manufacture of oleyl alcohol which is an important ingredient in liquid detergents, pharmaceuticals and antifoaming agents [1–3]. Esterification of fatty acids with alcohols in the presence of sulfuric acid catalyst is a conventional way to synthesize fatty acid esters due to low cost and availability of H_2SO_4, which brings about high conversion. 90% conversion of fatty acid ester was reported at high temperature (130 °C) during esterifica-

tion of palm fatty acids (containing 41% oleic acid) with ethanol and methanol using 0.1 wt% H_2SO_4 [4]. The same conversion was achieved with >2% H_2SO_4 at lower temperature (55 °C) [5]. 94% conversion of methyl ester was reported by Chongkhong et al. [6] using 1.8 wt% H_2SO_4 at 75 °C. Cardoso et al. [7] carried out esterification of oleic acid in the presence of $SnCl_2·H_2O$ catalyst where they had shown excess addition of alcohol for 90% conversion of fatty acid in 12 h whereas 94–95% conversion was obtained in 8 h with 3.5 wt% H_2SO_4. Literatures stated above showed that 90–95% conversion of fatty acid esters could be obtained when the reaction is carried out either with moderately high concentration of H_2SO_4 catalyst or at relatively high temperature. Sulfuric acid is corrosive in nature and forms several by-products [8], therefore, research thrust should be on its minimal use with maximum possible conversion. Esterification is a reversible reaction which produces water along with the ester whose conversion can be maximized by con-

tinuous elimination of the produced water [9]. Several attempts like azeotropic distillation and dehydration using molecular sieves have been adopted to remove water from esterification reaction mixture [10–12]. Lucena et al. [13] had shown that esterification of oleic acid with methanol at 100 °C with 1 wt% H_2SO_4 increased the conversion of fatty ester from 88% to 97% when the reactor system was attached with an adsorption column. Powdered silica gel was used as water adsorbent during the esterification of oleic acid with fusel oil fraction where the conversion was 97.3% [14].

Hydrophilic pervaporation (PV) membranes have the ability to selectively remove the produced water from the reactor. Pervaporation assisted esterification of carboxylic acids with different alcohols is widely reported. Esterification of acetic acid with methanol [15], 1-propanol [16], 2-propanol [17], isopropanol [18], has been performed using commercial PVA composite membrane. PVA based commercial dehydration membrane, GFT-1005, was applied by Benedict et al. [19] for the solid catalyzed esterification of lactic acid and ethanol. The same GFT membrane was applied for the enzymatic esterification of oleic acid with i-amyl alcohol [20]. PVA/ceramic composite pervaporation membrane was prepared by Liu et al. [21] in the laboratory and applied during the esterification of acetic acid with n-butanol in the presence of $Zr(SO_4)_2$ catalyst. Cellulose acetate PV membrane was applied for the enzymatic esterification of the long chain (C_{18}) oleic acid with butanol [22], whereas polyimide asymmetric PV membrane was used for the esterification of oleic acid with ethanol in the presence of p-toluenesulfonic acid at 98 °C under elevated pressure [23]. Esterification of oleic acid, with fusel oil (a mixture of alcohols) in the presence of enzyme catalyst was found 92% complete only after 12 h whereas 99.8% conversion was obtained in the same time in the presence of pervaporation [24]. More than 99% conversion of oleic acid to ethyl oleate was reported in 6 h by PV aided esterification where the authors have used asymmetric polyetherimide (PEI) membrane cast in the laboratory which exhibited high flux but low selectivity for water/ethanol binary system [25]. Pervaporation facilitated esterification reactions reported in the literature are associated with membranes which are either free standing PVA films or commercially available PVA membranes supported on porous substrates other than PES. Preparation of composite PVA membrane on polyethersulfone (PES) substrate has the prospect of scale-up into plate and frame modules for commercial application. According to Guo et al. [26] hydrophobic PES support layer will increase the swelling resistance whereas highly hydrophilic PVA surface layer will increase the permeability and selectivity. Moreover, the adverse effects of H_2SO_4 used as catalyst in esterification reaction could be overcome by using very low quantity of H_2SO_4 when coupled with pervaporation. Reports on the application of temperature gradient as driving force for PV facilitated esterification are not available in literature and thus forms the focus of this study.

With this background, our present investigation aims to fabricate flat sheet composite PVA membrane on PES substrate followed by its characterization for thermal stability by thermogravimetric analysis (TGA) and determination of tensile strength in feed solution containing sulfuric acid. Surface and cross-sectional morphologies of the prepared membrane before and after reaction were carried out by scanning electron microscopy (SEM). The water stability of the indigenous membrane was examined by swelling studies in methanol–water binary system. The membrane performance was evaluated by estimation of water flux and separation factor with binary mixtures of methanol and water. Separation of water from methanol through pervaporation membrane is a bigger challenge compared to dehydration of higher alcohols. The performance of the prepared membrane was also determined for the esterification of oleic acid with methanol where sulfuric acid was used as catalyst. Conversion of ester was optimized by changing

the reactant ratios, catalyst concentration and temperature in a test cell attached with the indigenously prepared flat sheet membrane. The result was compared to the esterification reaction carried out at optimized conditions in a round bottom flask under constant stirring condition without PV membrane. The performance of the indigenously synthesized membrane was compared with a commercial membrane based on PVA–poly(acrylonitrile) composite.

2. Materials and methods

2.1. Reagents

Polyvinylalcohol (PVA) (M_W 50,000, T_g 220 °C and density 1.37 g/cm^3) was purchased from Loba Chemie, Mumbai, India. Nonwoven fabric was supplied by BBA Nonwovens, Walpole, Veratec, USA, whereas polyethersulfone (PES) of M_W 18,600 for preparing the substrate was supplied by Solvay Advanced Polymers, Ohio, USA. DMF, propionic acid and glutaraldehyde of LR grade purity were procured from Ranbaxy, Mumbai, India. De-ionized water was generated using a reverse osmosis unit in our laboratory. Oleic acid (LR grade; 65% purity; acid value 195), methanol (LR grade; 99% purity and 0.25% water content), sulfuric acid (AR grade) and Karl Fischer reagent (pyridine free) were purchased from s. d Fine Chem. Ltd., Mumbai, India.

2.2. Description of PV test cell

The permeation test cell was made of thick glass and heated with an electrical heating coil wound around the cell. PV membrane with an effective surface area of 20 cm^2 was placed on a stainless steel support plate. The PV membranes used in our experiments are, PVA composite membrane cast in our laboratory and commercial membrane supplied by CM-Celfa, Switzerland. Permeate side was connected to a trap having connection to a vacuum pump. The trap was kept in dry ice/acetone mixture for condensation of permeate at −70 °C.

2.3. Analytical methods

The permeate sample collected in the trap was analyzed for water content by Karl Fischer titration.

During reaction, the collected sample was washed repeatedly with hot water until the pH of the water became neutral. Acetone was added to the sample containing moisture. Acetone, methanol and water were removed from the sample under vacuum in a rotavapor unit. The sample was then thoroughly dried under high vacuum and the concentration of unreacted oleic acid was determined by titrating against standardized KOH solution. The measure of fatty acid concentration remaining in the product is indicated by acid value which is calculated as:

$$\text{acid value} = (V_s - V_b) \times 56.1 \times \frac{N}{W} \tag{1}$$

where

V_s and V_b = mL of KOH consumed by sample and blank,
N = normality of KOH and
W = dry sample weight.

3. Experimental

3.1. Preparation of PVA composite membrane

Nonwoven fabric was tightly affixed onto a clean glass plate of A4 size. 15% (w/v) PES dope in dimethylformamide (DMF) was

prepared with continuous stirring along with addition of 3% propionic acid. The bubble free solution was cast onto the fabric to the desired thickness and gelled in ice cold water bath for 10 min to obtain PES substrate of 50,000 molecular weight cut off (MWCO). 5% (w/v) PVA in de-ionized (DI) water was heated with continuous stirring at 90 °C for 3–4 h to get a clear solution which was allowed to cool down to room temperature. A crosslinker, 2% glutaraldehyde, was added to the PVA solution and then cast on the PES substrate using doctor's blade. Solvent was evaporated at room temperature followed by heating in an oven at 110 °C for 5–10 min.

3.2. Membrane characterization

3.2.1. Thermogravimetric analysis (TGA)

Thermal stability and decomposition characteristics of indigenous and commercial membranes were examined by Seiko 220TG/DTA analyzer from 40 to 400 °C temperature range at a rate of heating 10 °C/min with N_2 flushing.

3.2.2. Mechanical properties

The mechanical properties of membrane samples were evaluated by Universal Testing Machine (UTM), Shimadzu make, model AGS-10kNG, Japan. The operating load was 5 kN. The membrane samples with 1 mm width were placed between the grips of the testing machine with grip length 5 cm. The tensile strength was calculated by Eq. (2)

$$\text{tensile strength} = \frac{\text{max load}}{\text{cross-sectional area}} (\text{N/mm}^2) \tag{2}$$

The tensile test of wet membrane samples with same dimension were performed after soaking them in a solution containing oleic acid/methanol in 1:27 mole ratio and 0.3 wt% H_2SO_4 for 48 h.

3.2.3. Thickness of membrane layers

The thickness of the three membrane layers was measured using Mitutoyo ABS Digimatic Calipers supplied by Trade Combine, Mumbai, India.

3.2.4. Scanning electron microscopy (SEM)

The membrane samples were dried thoroughly. Their surface and cross-sectional morphologies were studied by SEM using Hitachi S2150 microscope. The surface view of PVA composite membrane was studied again after esterification reaction.

3.2.5. Swelling studies

In order to obtain the water stability data of the composite membrane, the swelling studies were performed on pre-weighed dry membrane in methanol–water binary mixture containing 0–5 wt% water. The experiment was carried out in pure water as well. After 48 h soaking, the membrane samples were taken out and wiped immediately to record the final weight. The degree of swelling was calculated according to the formula (3):

$$\% \text{ swelling} = \frac{W_f - W_i}{W_i} \times 100 \tag{3}$$

where W_i and W_f are initial and final weights of the membrane samples respectively.

3.3. Pervaporation experiments with methanol/water binary mixture

Pervaporation experiments were performed on methanol mixed with water at 1, 2.2 and 3 wt% concentrations. 0.3 wt% H_2SO_4 was added to the binary mixture and experiments were conducted at reflux temperature where the vapor pressure difference across the membrane was found sufficient for permeation of water. Therefore,

vacuum was not applied on the permeate side in all the experiments. These experiments have shown that temperature gradient can be successfully used to enable mass transfer in pervaporation in the absence of vacuum or inert gas which are generally used to aid the concentration gradient. Permeate collected in the trap after 3 h was analyzed for water content. Water separation efficiency of the membrane was calculated on the basis of total flux and separation factor (α) according to the following formulae (4) and (5).

$$J = \frac{Q}{A \cdot t} \tag{4}$$

$$\alpha = \frac{Y_W/Y_M}{X_W/Y_M} \tag{5}$$

where Q is permeate collected at time t and A is the effective membrane surface area. X and Y indicate the weight fractions in the feed and permeate respectively. W and M stand for water and methanol. Total flux multiplied by weight fraction of water in permeate gives the value of water flux.

3.4. Pervaporation aided esterification of oleic acid with methanol

The esterification reaction of oleic acid with methanol in the presence of H_2SO_4 catalyst was carried out in the pervaporation test cell with 73 mL feed volume under reflux temperature and in the absence of vacuum. Ratio of membrane surface area to feed volume was kept at 27.3 m^{-1}. H_2SO_4 catalyst concentration was varied from 0.1 to 0.5 wt% of oleic acid and molar ratio of oleic acid/methanol was maintained between 1:9 and 1:27. Effect of temperature was also studied in the range 35–65 °C. The retentate samples were collected intermittently and washed with water to remove sulfuric acid and analyzed for acid value using the procedure mentioned in 2.3. Optimization of reactant ratios, catalyst concentration and temperature was done on the basis of acid value and % conversion of ester calculated according to Eq. (6).

$$\% \text{ ester conversion} = \frac{A_i - A_f}{A_i} \times 100 \tag{6}$$

where A_i and A_f are initial and final acid values of the collected samples respectively.

The quantity of by-products formed during the reaction of oleic acid and methanol due to the presence of H_2SO_4 was negligible as demonstrated by the product purity. The same was also confirmed by material balance calculations.

The results of esterification reaction using PVA composite membrane at optimized conditions were compared to those of esterification done without pervaporation. This reaction was carried out in a round bottom flask under constant stirring condition attached with an air condenser. A comparison was also made with performance exhibited by another composite pervaporation membrane supplied by CM-Celfa, Switzerland.

4. Results and discussions

4.1. Membrane characterization studies

4.1.1. Thermogravimetric analysis (TGA)

Thermal degradation behavior of PVA composite membrane was compared to the PVA free film as well as to commercial composite membrane and thermograms are displayed in Fig. 1. It was observed that, the indigenously developed PVA composite membrane is thermally stable up to almost 360 °C whereas the commercial membrane started decomposing slowly after 300 °C. The indigenously prepared composite membrane shows improved thermal stability possibly due to the difference in nature of substrates used and degree of cross-linking. The PVA composite membrane prepared in our laboratory can therefore be safely used for high
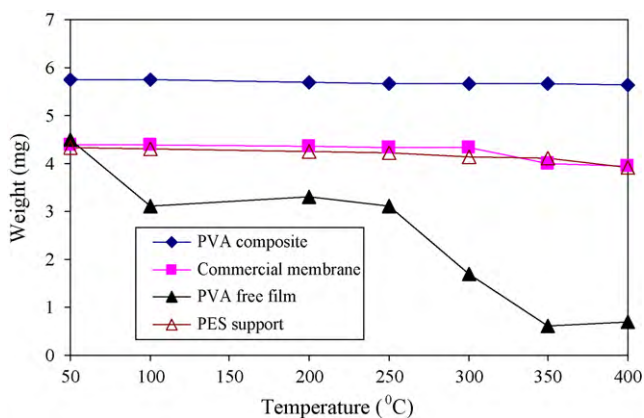
Fig. 1. TGA curves of indigenous PVA composite membrane, commercial membrane, PES support and PVA free film.

temperature applications. In our previous work [27] and as well as in Fig. 1, it was observed that PVA free film started exhibiting decomposition at 250 °C which may be due to the loss of water through decomposition of –OH groups. In case of indigenous PVA composite, where PVA constitutes 17% of the composite, the –OH bonds are crosslinked with the support layer and therefore need extra energy for breakage of the linkage as compared to the free PVA film. Fig. 1 also shows that the presence of thermally robust PES substrate in the composite contribute to enhanced thermal stability compared to the free PVA film due to higher T_g and melting points of the support materials. The curve representing PES substrate underlines this fact. Loss of solvent is obvious only in case of free standing film between the temperature range of 50–100 °C.

4.1.2. Tensile strength

Data on the tensile strength and % elongation at break point of PVA composite membrane and commercial membrane in dry and soaked conditions are provided in Table 1.

The indigenous membrane exhibited lower tensile strength but better flexibility when compared to the commercial membrane. This observation could be attributed to different substrates used for casting the two membranes and varying extents of cross-linking of the selective PVA layer. The mechanical strength of both the membranes did not reduce in dilute acidic conditions containing 0.3% H_2SO_4 which indicates their chemical stability in acidic medium. After 48 h of soaking in a medium containing oleic acid and methanol in 1:27 molar ratio and 0.3% H_2SO_4, both the membranes exhibited enhanced tensile strength. The increase in mechanical strength may be attributed to the sorption and interaction of bigger molecular sized fatty acid molecules with hydrophilic polar groups present in the membrane. Under the soaking conditions both the membranes have displayed comparable tensile strength and % elongation values due to the plasticization effect of the oleic acid.

4.1.3. Thickness of membrane layers

The thickness of the three polymer layers from bottom to upper layer in the composite membrane is indicated in Table 2.

Table 1
Tensile strength and % elongation of PVA composite and commercial membrane in dry and soaked conditions.

Membrane type	Tensile strength (N/mm²)	% elongation
PVA composite (dry)	14.86	20.4
Commercial (dry)	34.75	11.2
PVA composite (soaked)	41.8	16.22
Commercial (soaked)	48.9	15.4

Table 2
Thickness of different layers in indigenous PVA composite membrane.

Membrane layers	Thickness (μm)
Non woven fabric	100
PES substrate	45
PVA dense layer	30

4.1.4. SEM studies

SEM images of the surface of PVA composite membrane before and post esterification are displayed in Fig. 2(a) and (c). It can be seen that the surface does not exhibit any defects in Fig. 2(c) which indicates the inert chemical nature of the polymer in the acidic reaction medium. Moreover the non-porous nature of the surface in both the images reveals that the membrane will allow only those chemical species which have interaction with the functional groups of the polymer and the mechanism of mass transfer would be sorption followed by diffusion and then desorption. The cross-sectional view of the composite PVA membrane is presented in Fig. 2(b) which shows the existence of a non-porous skin layer of PVA supported on a porous substrate made of PES. The bottom white portion of the image represents the nonwoven polyester fabric. It can be concluded that the top selective layer penetrates to some extent into the porous PES layer. Overall, the SEM analysis shows uniform surface morphology and there are no agglomerations or clusters found to exist.

4.1.5. Swelling studies

The degree of swelling of the indigenous composite membrane with wt% of water in methanol–water binary feed is depicted in Fig. 3. The degree of swelling of the membrane in pure methanol is 32.5% and it increases with increase in feed water concentration. The degree of swelling was found to be 44.6% in pure water. Therefore, it can be stated that the degree of swelling of the indigenous membrane is between 32% and 47% for the feed water concentration varying from 0% to 100%.

4.2. Pervaporation experiments with methanol/water binary mixture

Fig. 4 shows that the flux increases from 1.6 to 5.4 g/m² h with increasing feed water concentration from 1 to 3 wt%. With increasing feed water concentration, the hydrophilic PVA polymer undergoes greater swelling due to preferential affinity for water. This causes plasticization which enhances flux and reduces separation factor since more number of methanol molecules can penetrate the swollen membrane. Moreover, both water and methanol are polar molecules and since the latter is also more volatile, there exists competitive sorption and permeation which is reflected in the moderate separation factors that have been observed. The performance of the membrane for separation of methanol/water mixture was observed over a period of three months and found to be reproducible.

4.3. Pervaporation aided esterification of oleic acid with methanol

Esterification of oleic acid with methanol was carried out at reflux temperature (65 °C) by varying the molar ratio of oleic acid to methanol using 0.3 wt% H_2SO_4 catalyst. The results are shown in Fig. 5. It was observed that after 6 h of reaction between oleic acid and methanol at 1:9 molar ratio, the acid value came down to 2.7 from 195, i.e. 98.6% ester conversion was achieved. As the goal of the present study was 99.9% conversion of ester, methanol content was increased to 1:18 and then 1:27. Using 1:18 molar ratio of fatty acid to methanol, the acid value was found to be 1.2 after 6 h and at 1:27 molar ratio, the acid value
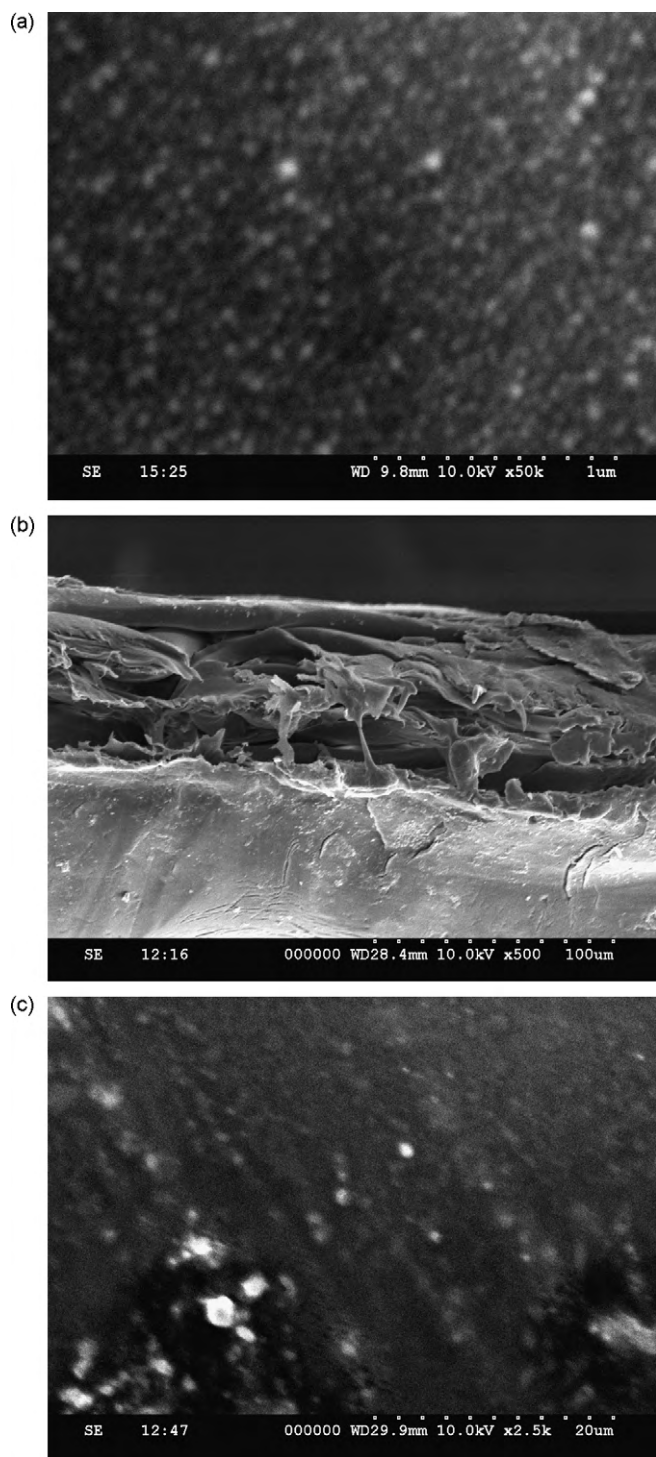
Fig. 2. SEM images of (a) surface morphology, (b) cross-sectional view of indigenous PVA composite membrane and (c) surface view of indigenous PVA composite membrane after esterification.

Fig. 3. Degree of swelling of indigenous PES/PVA composite membrane with wt% water in feed.

Fig. 4. Variation of water flux and separation factor with feed water content.

Fig. 5. Esterification of oleic acid with methanol at varying molar ratios (0.3 wt% H_2SO_4, $T = 65\,°C$).

Fig. 6. Esterification of oleic acid with methanol for varying catalyst concentrations (1:27 molar ratio, $T = 65\,°C$).

was 0.2 which corresponds to 99.9% conversion of ester after 6 h.

After optimizing the molar ratio of reactants at 1:27, experiments were conducted by varying H_2SO_4 concentration from 0.1 to 0.5 wt% as shown in Fig. 6. At 0.1% and 0.2% H_2SO_4 concentration, the conversion of methyl ester was found to be 97.8% and 99.5% respectively for 6 h of reaction duration. 99.9% ester conversion was achieved after 6 h using 0.3 wt% H_2SO_4 and within 5 h by using 0.5 wt% of the catalyst. As one of the targets of the present study
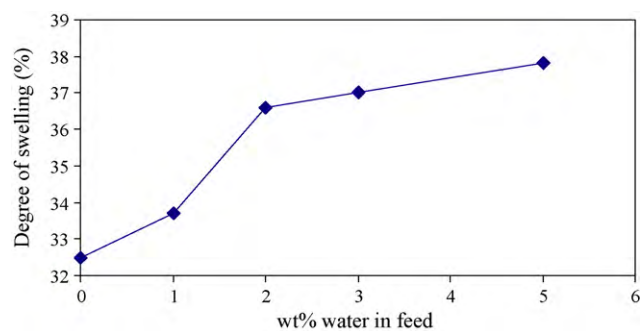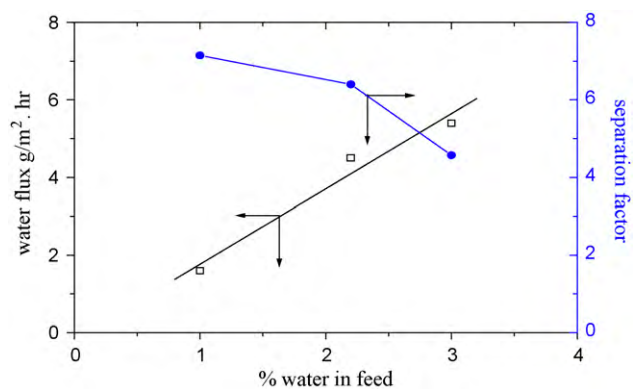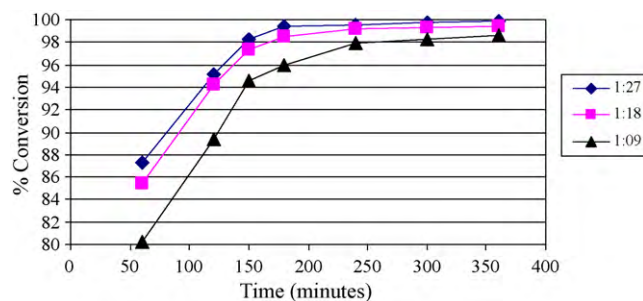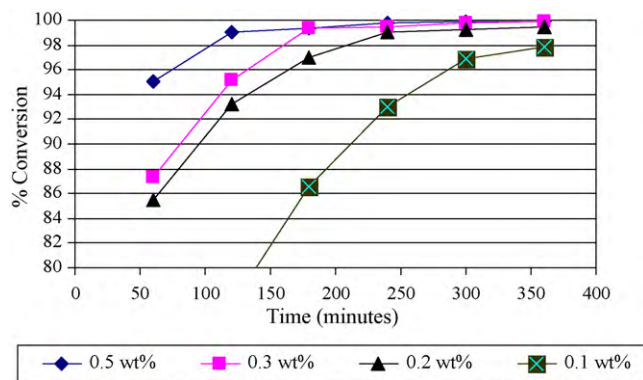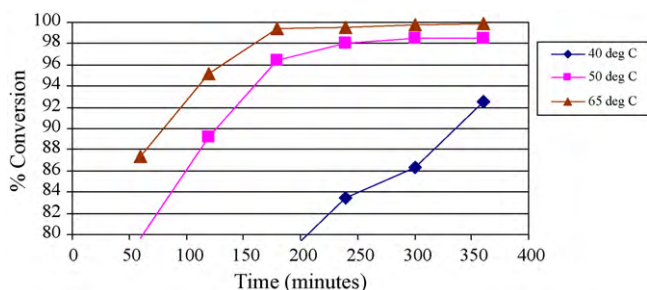
Fig. 7. Esterification of oleic acid with methanol at different temperatures (1:27 molar ratio, 0.3 wt% H_2SO_4).

was to minimize the concentration of H_2SO_4 for maximum conversion of ester, the H_2SO_4 concentration was optimized at 0.3 wt% of fatty acid for future experiments.

The effect of temperature on pervaporation aided esterification reaction at 1:27 molar ratio of oleic acid and methanol using 0.3 wt% H_2SO_4 is represented in Fig. 7. The major driving force in PV operation is the difference in vapor pressure across the membrane. The vapor pressure difference may be generated either by reducing vapor pressure at the permeate side by applying vacuum or by increasing vapor pressure on the feed side of the membrane. In our present study, vapor pressure of the feed was enhanced by raising the feed temperature. Therefore, temperature is a crucial factor which should be optimized to maximize membrane performance and minimize polymer degradation. Experiments were carried out at 40, 50 and 65 °C (the reflux temperature of methanol). It was observed that the ester conversion was 99.9% at reflux temperature (65 °C).

After optimization of the reaction parameters, the material balance of the esterification reaction was calculated as shown in Table 3.

The material balance for the esterification indicates that negligible amount of side products are formed during the reactions.

4.4. Comparison of performance with commercial membrane and esterification without PV

After optimizing the reaction conditions such as reactant ratio, catalyst concentration and temperature in order to achieve maximum conversion of ester using indigenous PVA composite membrane, the results were compared to (1) using commercial PV membrane and (2) in the absence of PV. The results are graphically represented in Fig. 8. It showed that the esterification reaction under constant stirring condition and without PV was initially rapid but as soon as more water was produced, the backward reaction started taking place simultaneously and conversion could not reach beyond 98.7% after 3–4 h. PV membrane has the potential of removing the water produced in the esterification reaction and steady rate of increase in the ester conversion was observed in PV aided esterification reaction. The results of esterification with PVA composite membrane were found to be comparable with commercial compos-
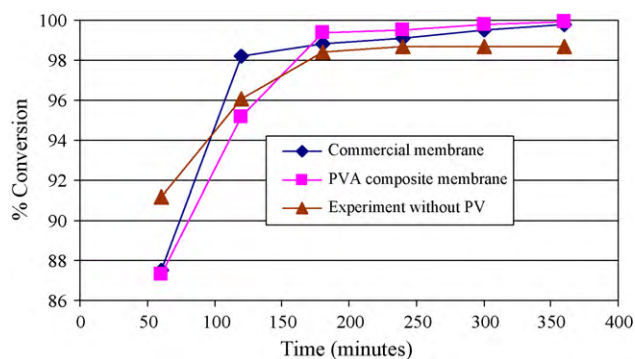

Fig. 8. Comparison of ester conversion using indigenous PVA membrane with commercial PV membrane and reaction without PV.

ite membrane. Since the experiments were performed in a test cell housing having an effective membrane surface area of only 20 cm², the optimum conversion was attained after 6 h. If the reaction is performed in a cross-flow PV system with greater membrane area, it would reduce the reaction time.

5. Conclusion

Nearly complete conversion of oleic acid to methyl oleate was achieved during PV aided esterification of oleic acid with methanol at 1:27 molar feed ratio of fatty acid to alcohol, using 0.3 wt% of H_2SO_4 catalyst and at reflux temperature (65 °C) of methanol. PVA composite membrane prepared in our laboratory has profound influence on the equilibrium limited reaction through elimination of water. The results are superior to the esterification reaction carried out in the absence of pervaporation. Thermal stability of both indigenous and commercial composite membranes appeared to be better than the free standing PVA film, thus rendering them suitable for high temperature reactions. Stability of cross-linking and permeation properties of the membrane was tested over a period of three months with methanol–water system and found to be sustainable. Stirring of reactants in the cell and vacuum on the permeate side may be eliminated if the reaction is carried out at reflux temperature.

According to EN14214, ASTM B6751-07, IS 15607-2005, the acid value of the methyl esters to be used as biodiesel should be lower than 0.5 which corresponds to a conversion of 99.7%. Esterification of oleic acid with methanol under constant stirring condition resulted in a maximum conversion of 98.7% which corresponds to an acid value of 2.5, whereas 99.9% conversion was achieved in pervaporation assisted system where the final acid value was 0.2. Therefore, pervaporation has appreciable influence in esterification reaction in order to achieve 99.9% conversion of ester.

The study clearly exhibited the enormous potential of temperature gradient pervaporation for esterification of long chain fatty acids. Scale-up of the PVA–PES composite flat sheet into plate and frame modules is feasible. However, further efforts are required to fabricate spiral wound modules after tackling problems related to sealing under high temperature conditions.

Acknowledgement

References

[1] www.amberlyst.com/fatty_acids.htm.

Table 3
Material balance of the esterification reaction (oleic acid to methanol 1:27 mole ratio; 0.3 wt% H_2SO_4; 65 °C temperature).

	Input (g)		Output (g)
Oleic acid	15	Methyl oleate	15.68
Methanol	45	Oleic acid	0.06
H_2SO_4 at 0.3 wt%	0.045	Methanol	43.3
		H_2SO_4	0.045
		Water	0.95
Total	60.045		60.045

[2] N. Dormo, K. Belafi-Bako, L. Bartha, U. Ehrenstein, L. Gubicza, Manufacture of an environment safe biolubricant from fusel oil by enzymatic esterification of solvent free system, Biochem. Eng. J. 21 (2004) 229–234.

[3] Y. Pouilloux, F. Autin, A. Piccirilli, C. Guimon, J. Barrault, Preparation of oleyl alcohol from the hydrogenation of methyl oleate in the presence of cobalt-tin catalysts, Appl. Catal. A: Gen. 169 (1998) 65–75.

[4] D.A.G. Aranda, R.T.P. Santos, N.C.O. Tapanes, A.L.D. Ramos, O.A.C. Antunes, Acid catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids, Catal. Lett. 122 (2008) 20–25.

[5] J.M. Marchetti, A.F. Errazu, Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides, Biomass Bioenergy 32 (9) (2008) 892–895.

[6] S. Chongkhong, C. Tongurai, P. Chatpattananondh, C. Bunyahan, Biodiesel production by esterification of palm fatty acid distillate, Biomass Bioenergy 31 (2007) 563–568.

[7] A.L. Cardoso, S.C.G. Neves, M.J. da Silva, Esterification of oleic acid for biodiesel production catalyzed by $SnCl_2$: a kinetic investigation, Energies 1 (2008) 79–92.

[8] J. Aracil, M. Vicente, M. Martinez, M. Poulina, Biocatalytic processes for the production of fatty acid esters, J. Biotechnol. 124 (2006) 213–223.

[9] H. Kita, K. Tanaka, K. Okamoto, M. Yamamoto, The esterification of oleic acid with ethanol accompanied by membrane separation, Chem. Lett. (1987) 2053–2056.

[10] J. Marszalek, W. Kaminski, Environmental impact of bioethanol production, Proc. ECOpole 2 (1) (2008) 65–70.

[11] W. Kaminski, J. Marszalek, Pervaporation for drying and dewatering, Dry. Technol. 24 (2006) 835–847.

[12] W. Kujawski, Application of pervaporation and vapor permeation in the environmental protection, Pol. J. Environ. Stud. 9 (2000) 13–26.

[13] I.L. Lucena, G.F. Silva, F.A.N. Fernandes, Biodiesel production by esterification of oleic acid with methanol using a water adsorption apparatus, Ind. Eng. Chem. Res. 47 (18) (2008) 6885–6889.

[14] A. Ozgulsun, F. Karaosmanoglu, M. Tuter, Esterification reaction of oleic acid with a fusel oil fraction for production of lubricating oil, JAOCS 77 (1) (2000) 105–109.

[15] S. Assabumrungrat, J. Phongpatthanapanich, P. Praserthdam, T. Tagawa, S. Goto, Theoretical study on the synthesis of methyl acetate from methanol and acetic acid in pervaporation membrane reactor: effect of continuous flow modes, Chem. Eng. J. 95 (2003) 57–65.

[16] M.O. David, R. Gref, T.Q. Nguyen, J. Neel, Pervaporation esterification coupling. Part I. Basic kinetic model, Trans. IChemE 69 (1991) 335–340.

[17] L. Domingues, F. Recasens, M.A. Larrayoz, Studies of a pervaporation reactor: kinetics and equilibrium shift in benzyl alcohol acetylation, Chem. Eng. Sci. 54 (1999) 1461–1465.

[18] M.T. Sanz, J. Gmehling, Esterification of acetic acid with isopropanol coupled with pervaporation. Part II. Study of a pervaporation reactor, Chem. Eng. J. 123 (2006) 9–14.

[19] D.J. Benedict, S.J. Parulaker, S.P. Tsai, Esterification of lactic acid and ethanol with/without pervaporation, Ind. Eng. Chem. Res. 42 (2003) 2282–2291.

[20] Z. Koszorz, N. Nemestothy, Z. Ziobrowski, K. Belafi-Bako, R. Krupiczka, Influence of pervaporation process parameters on enzymatic catalyst deactivation, Desalination 162 (2004) 307–313.

[21] Q. Liu, Z. Zhang, H. Chen, Study on the coupling of esterification with pervaporation, J. Membr. Sci. 182 (2001) 173–181.

[22] S.J. Kwon, K.M. Song, W.H. Hong, J.S. Rhee, Removal of water produced from lipase catalyzed esterification in organic solvent by pervaporation, Biotechnol. Bioeng. 46 (4) (2004) 393–395.

[23] K. Okamoto, M. Yamamoto, Y. Otoshi, T. Semoto, M. Yano, K. Tanaka, H. Kita, Pervaporation aided esterification of oleic acid, J. Chem. Eng. Jpn. 26 (5) (1993) 475–481.

[24] N. Dormo, K. Belafi-Bako, L. Bartha, U. Ehrenstein, L. Gubicza, Manufacture of an environmental safe biolubricant from fusel oil by enzymatic esterification in solvent free system, Biochem. Eng. J. 21 (2004) 229–234.

[25] H. Kita, S. Sasaki, K. Tanaka, K. Okamoto, M. Yamamoto, Esterification of carboxylic acid with ethanol accompanied by pervaporation, Chem. Lett. (1988) 2025–2028.

[26] R. Guo, X. Fang, H. Wu, Z. Jiang, Preparation and pervaporation performance of surface crosslinked PVA/PES composite membrane, J. Membr. Sci. 322 (2008) 32–38.

[27] D. Anjali Devi, B. Smitha, S. Sridhar, T.M. Aminabhavi, Dehydration of 1,4-dioxan through blend membranes of poly(vinyl alcohol) and chitosan by pervaporation, J. Membr. Sci. 280 (2006) 138–147.