

ENHANCING THE ESTERIFICATION CONVERSION USING PERVAPORATION

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Abstract

Coupling of a pervaporation membrane unit with an esterification reactor has been undertaken with a view to improve the overall efficiency of the esterification process through removal of one of the products. The esterification reaction of acetic acid with methanol in the presence of two alternative heterogeneous catalysts Nafion resin (NR) and silica sulfuric acid (SSA) is investigated on the laboratory scale. The system consists of a batch reactor externally coupled with pervaporation (PV) module containing a Nafion membrane. The effect of different parameters on the esterification / pervaporation system is explored. The studied parameters include reactants molar ratio, temperature, and catalyst weight percent. The results show that the water diffusion through the PV membrane helps to break the thermodynamic equilibrium barrier of reversible esterification reaction and improve the reaction conversion. The maximum conversion reached 96.76 % after 60 min at 60 °C, 3% silica sulfuric acid as catalyst, with a reactant to acid molar ratio of 8:1, and a membrane surface area to reactor volume of 1.3 cm⁻¹.

Keywords: Membrane separation technology, Pervaporation reactor, Esterification, Heterogeneous catalysis.

1. Introduction

Esterification is a reversible reaction, which has low conversion. A mineral acid catalyst (e.g., sulfuric or hydrochloric acid) is usually used to enhance the reaction rate [1-6]. The amount of the unreacted mineral acid is separated by neutralization after reaction completion [2, 7, 11]. Although, the liquid acid is an effective cheap

Abbreviations

MR	Molar Ratio
NR	Nafion resin
PV	Pervaporation
PVMR	pervaporation membrane reactor
S/V	surface area of membrane to the volume mixture
SEM	Scanning electronic microscopy
SSA	silica sulfuric acid

Heterogeneous solid catalysts such as ion exchange resins in esterification reactions have been used instead of mineral acid in order to simplify their separation. These new solid catalysts have the advantages of being non-polluting and non-corrosive [3, 4, 12]. In any case, conversion can be increased by adding an excess of one of the reactants or removing one of the products. Reactive distillation is an alternative of product separation, but it is associated with high energy consumption. [13-19].

Pervaporation (PV) is considered a low energy consuming technology providing for a high separation efficiency of azeotropic mixtures, hydrocarbon mixtures, and isomers. Integration of pervaporation and reaction in a pervaporation membrane reactor (PVMR) will therefore offer an opportunity for inexpensive separation besides increasing the conversion of the reaction. In a pervaporation process, the selected compound from the liquid mixture is adsorbed and diffuses through the pervaporation membrane; it is then desorbed in a vapor phase. Pervaporation is a pressure driven process; the driving force is the differential partial pressure between the two sides of the membrane [5-21].

Pervaporation membrane reactors (PVMR) have received more attention in recent years. The majority of PV reactors use dense membranes that successfully select one or more component to be removed from a mixture. Coupling of pervaporation with esterification in PVMR is an ideal candidate used to enhance esterification and overcome the disadvantages of other alternatives. Esterification-pervaporation coupled reactors are also anticipated to provide time saving, low energy consumption, clean operation and minimum waste [6-21].

Esterification process has been enhanced by pervaporation, which is used to catalyse the reaction through removing one of the products. Qinglin et al. [22] studied the esterification of acetic acid with n-butanol, in perfectly stirred reactor catalysed by $Zr(SO_4)_4 \cdot 4H_2O$, pervaporation-aided esterification was conducted and the major operating parameters on the coupling process were studied. It was conducted from the experiments that water content is increased earlier during the reaction and then decreased after it reached to the maximum amplitude due to water removal through pervaporation membrane. Sevinc et al. [23] tested the homogeneous (sulphuric acid) and heterogeneous (Dowex 50W-X8) catalysts in pervaporation-esterification in a batch pervaporation membrane reactor (PVMR). The effects of catalyst loading, catalyst type, reaction time, membrane thickness, temperature and initial molar ratio of reactants were investigated.

In the present work, esterification reaction of methanol and acetic acid was used as an example to study the effect of coupling of a PV membrane separation with esterification on the performance of the process. Two solid catalysts were used,

Nafion resin and nanosilica sulfuric acid, which is safe, easy to handle, environmentally friendly, are used as a catalyst. Nafion membrane was used in pervaporation step.

2. Experimental Work

2.1. Materials

Experiments carried out with and without PV were accompanied using acetic acid (Sigma-Aldrich, 99.8 %) and methanol of analytical grade; they are purchased from Sigma-Aldrich Chemical Company. Concentrated sulfuric acid (SDFCL Co. 98%), Nafion resin (NR-50, Sigma-Aldrich), and prepared silica sulfuric acid were used as a catalyst.

2.2. Methodology

Pervaporation of water proceeded by applying vacuum on the permeate side. The membrane used is Nafion NRE-115-30 sheet having a thickness of 2 mm purchased from Fuel cell earth, LLC Company. After the end of each run the membrane was rinsed in the de-ionized water and then dried with soft tissues for reuse.

The nanosilicasulfuric acid catalyst was prepared by adding concentrated H_2SO_4 (3 ml) to a slurry containing 10 g of silica gel (AlGomhoria Co., 98%) and 50 ml of dry diethyl ether (Sigma-Aldrich, 98 %) while shaking for 5 min. The solvent was evaporated under low pressure to obtain dry $H_2SO_4 \cdot SiO_2$ catalyst; then heated to $120^\circ C$ for 3 hrs [8]. To reuse the catalyst, it is percolated and washed with distilled water, dried at $120^\circ C$ for 2 hr, and then reused without further treatment.

2.2.1. Membrane morphology

Scanning electronic microscopy (SEM) was used to characterize the membrane morphology and surface topography. The dried samples were gold sputtering covered in order to provide for electrical conductivity. Pictures were taken on a JEOL 5410 scanning electron microscope (SEM) operating at 10 kV [24].

2.2.2. Fourier transforms infrared (FTIR)

FTIR analysis at 16 scans per min at resolution of 4 cm^{-1} was carried out on the prepared silica sulfuric acid. The prepared catalyst was dissolved in dimethyl formamide (DMF) and stored in sample vials. Polytetrafluoroethylene infrared (IR) cards were used to form transparent films. The IR data were collected [25].

2.2.3. Esterification and PVP process

Two different experimental techniques were carried out; batch experiments for the conventional esterification process and the batch reaction coupled with pervaporation. Figure 1 presents the experimental set-up used for the conventional batch esterification process. A hot plate of variable temperature, glassware, and sampling vials were purchased from the local market.

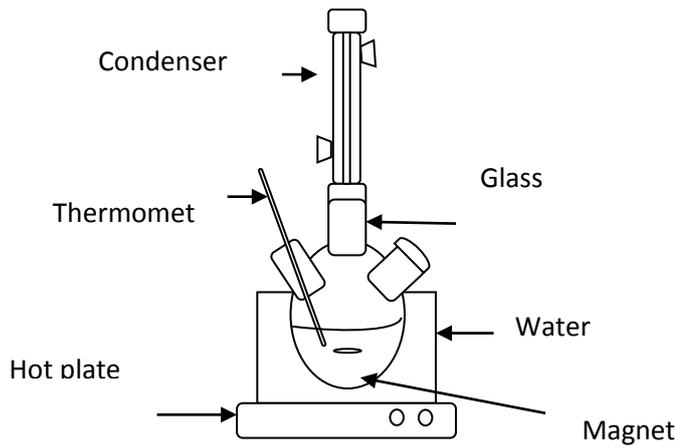


Fig. 1. Set-up of batch esterification reactor.

Figure 2 illustrates the batch reactor set up coupled with the pervaporation system. The pervaporation system consists of a pervaporation cell containing the Nafion flat sheet membrane and it is equipped with a peristaltic pump (YT600-1JKZ35, longer pump co, China), operating at a flow rate of 14.9 ml/s. All plastic tubing used in the set up was purchased from the local market. A vacuum pump, -0.8 bar (DOA-P504-BIU, GAST, INC, China) and a permeate condenser (designed and manufactured at the workshop of the National Research Centre, Egypt) were connected to a circulating water bath and the downstream side of the cell. Membrane cell has an effective membrane area of 145.19 cm²; it was purchased from Sartorius Company, USA.

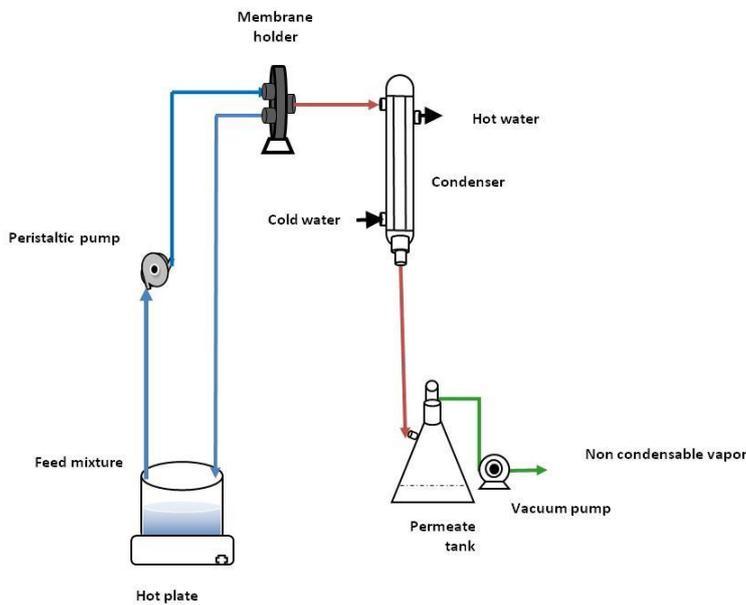


Fig. 2. Schematic diagram of the pervaporation experimental setup.

Analysis of the reaction mixture was done by withdrawing two samples every 30 minutes from the reactor and the trap flask to determine the unreacted acetic acid and permeate water respectively. The samples were titrated with 0.1 N KOH. The number of moles of residual acid was used to obtain the number of moles of reacted acid.

3. Results and Discussion

3.1. Membrane morphology

Scanning electron micrographs, SEM were used to verify surface topography and morphology of the hydrophilic Nafion membrane. The SEM is shown in Fig. 3 with the magnification of 2000x shows a clear dense membrane since the pores of the membrane do not appear.

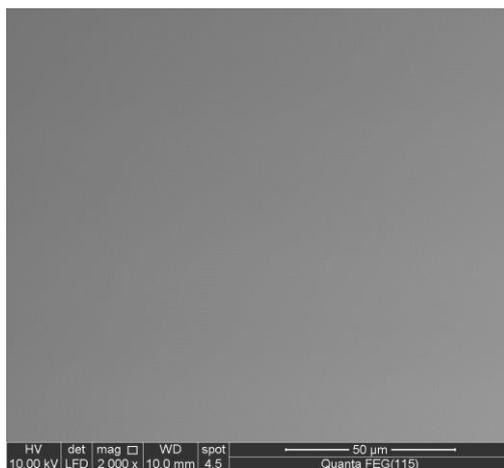


Fig. 3. Scanning electron micrograph of Nafion dense membrane.

3.2. Fourier transforms infrared (FTIR) analysis

The silica sulfuric acid catalyst FTIR spectrum is depicted in Fig. 4. The peak at 465.7 cm^{-1} is attributed to the Si – O rocking vibrations. The peaks at 797.4 and 1083.8 cm^{-1} are assigned to the symmetric and asymmetric vibrations of (Si – O– Si) of silica sulfuric acid. Sulfonic acid functional group appears on FTIR with different absorption extents of the S=O different stretching mode which lie in the $1010\text{--}1080\text{ cm}^{-1}$ range, and of the vibration band of S – O appearing at about 585.3 cm^{-1} . The FTIR diagram shows the imbrications of asymmetric and symmetric expanding bands of SO_2 with Si-O-Si expanding bands in the silica sulfuric acid. The figure also shows a wide OH stretching absorption around 2928.38 and 3750.87 cm^{-1} [9].

3.3. Comparison between homogeneous and heterogeneous acid catalysts

Comparative batch esterification experiments were performed at a methanol to acetic acid molar ratio of 8:1 and at a 60°C . The used catalysts were sulfuric acid

as homogeneous liquid catalyst and silica sulfuric acid and nafion resin as heterogeneous solid catalysts having an acid capacity 4 meq H⁺/gm catalyst. Figure 5 illustrates the effect of different acid catalysts on the reaction conversion. SSA catalyst enabled a conversion of 91.5% after 60 min.

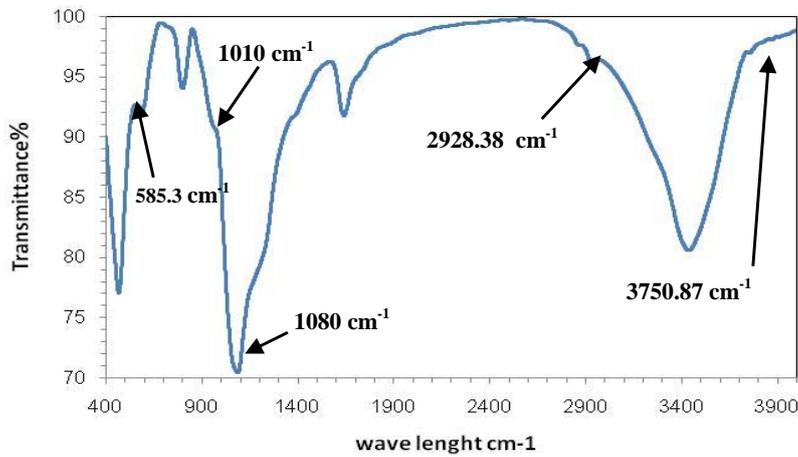


Fig. 4. FTIR spectrum for silica sulfuric acid catalyst.

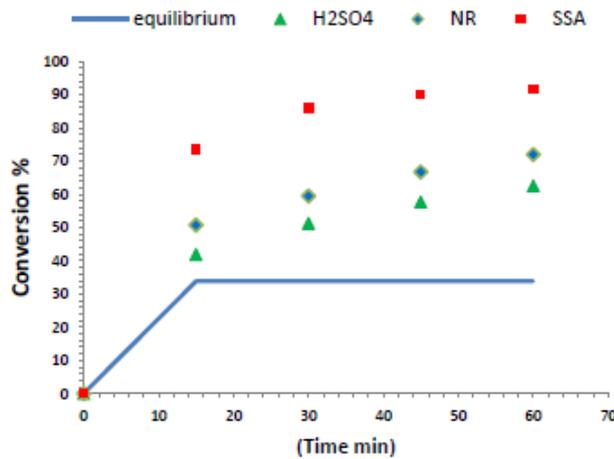


Fig. 5. Effect of different acid catalysts on conversion.

3.4. Esterification using heterogeneous catalysts

Batch experiments were carried out using the above solid catalysts with different weight percentages under different conditions of temperature and methanol to acetic acid molar ratio.

3.4.1. Effect of temperature

The effect of temperature on conversion was studied at different temperatures (30, 40, 50, and 60°C) at a methanol to acetic acid molar ratio of 8:1 and a weight

percent of 3% for each of the Nafion resin and the SSA catalysts. A conversion of 76.96 % was reached after 1 hour at 60°C for the NR catalyst as shown in Fig. 6. The results indicate that increasing the reaction temperature increases reaction conversion [9]. The effect of temperature on the esterification reaction was studied under the same conditions but with SSA catalyst. A maximum conversion of 91.5 % was reached after 1 hour at 60°C and at a methanol to acetic acid molar ratio of 8:1 as shown in Fig. 7.

3.4.2. Effect of catalyst weight percent (wt. %)

The effect of the solid catalyst Nafion Resin (NR) weight percent was studied (1%, 2%, and 3% by weight) under fixed operating conditions of methanol to acetic acid molar ratio of 8:1 and 60°C. Figure 8 depicts the obtained results; where the conversion reached 76.96% at 3% by weight NR after 1 hour. Experiments using SSA were carried out under the same conditions. Figure 9 shows the effect of change in SSA weight percent on the conversion of the reaction. The conversion reached 91.5% at 3% by weight SSA after 1 hour. It is seen that SSA catalyst shows a higher catalytic activity.

3.4.3. Effect of molar ratios (MR)

The effect of molar ratio on conversion was studied at methanol to acetic acid molar ratios of 2:1, 4:1, 6:1 and 8:1. The batch esterification reaction was conducted at 60°C with 3% by weight Nafion resin; NR. Figure 10 illustrates the effect of molar ratio on the reaction conversion using NR catalyst. Increasing the molar ratio of reactants resulted in increasing the reaction conversion. At a MR 2:1 the conversion reached only 52.35%, while for a MR of 8:1 the conversion reached 76.9% after 60 min. The effect of different molar ratios was also studied at 3% by weight SSA. Figure 11 illustrates that conversion increases with increasing the molar ratio. At MR 2:1 the conversion reached 74.5 %, while at MR 8:1 the conversion reached 91.5% both after 60 min.

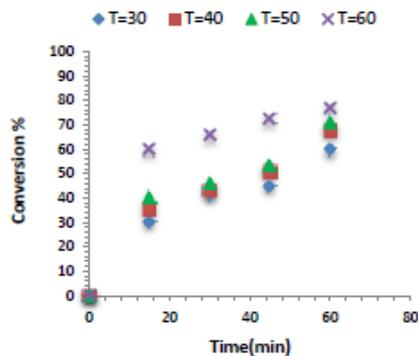


Fig. 6. Effect of temperature on esterification reaction conversion catalysed by NR at MR=8:1, wt. %=3%.

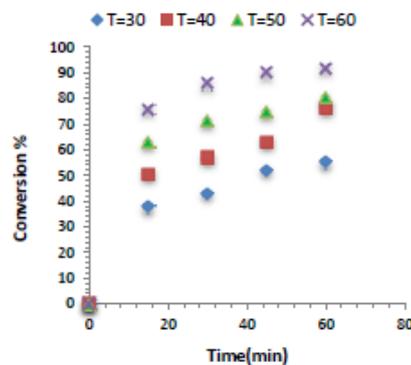


Fig. 7. Effect of temperature on esterification reaction conversion catalysed by SSA at MR=8:1, wt. %=3%.

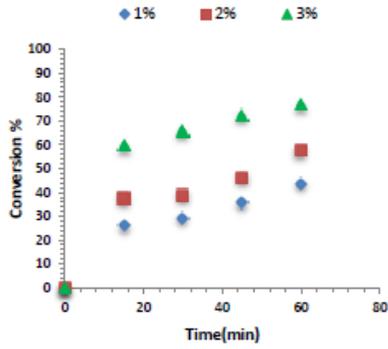


Fig. 8. Effect of change in NR weight percent on conversion at 60°C, and MR=8:1.

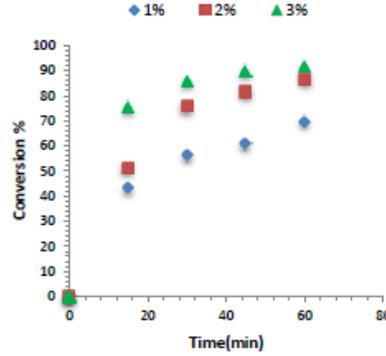


Fig. 9. Effect of change in SSA weight percent on conversion at 60°C, and MR=8:1.

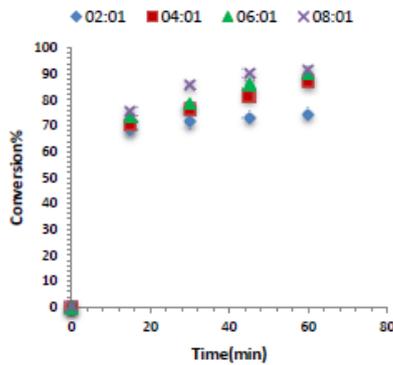


Fig. 10. Effect of change in molar ratios on conversion at 60°C, NR wt%=3%.

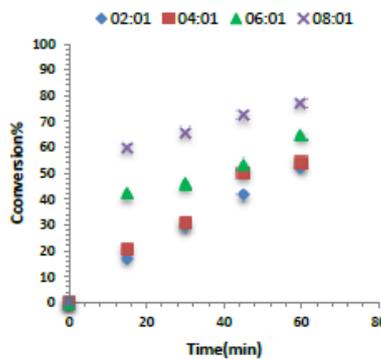


Fig. 11. Effect of change in molar ratios on conversion at 60°C, SSA wt%=3%.

4. Esterification Enhanced by Pervaporation

4.1. Effect on equilibrium conversion

The results of PV experiments are compared with the results of esterification without PV using SSA catalyst in Fig. 12. The reaction was carried out at 60°C with reactants molar ratio of 8:1 and catalyst weight percent of 3%. The reaction with PV gave a conversion of 91.5% after 15 min while the conversion was 75.6% after 15 min without PV. This demonstrates the enhancement of reaction conversion with PV due to water adsorption through PV membrane. Figure 13 illustrates the effect of PV membrane on the water adsorption.

4.2. Effect of temperature

Figures 14(a), (b), (c) and (d) depict the effect of different reaction temperatures on conversion percentage and water content in the reactor. The temperature was varied from 30 to 60°C at a fixed percent of SSA catalyst weight of 3%, reactants

ratio (MR=8:1 methanol to acetic acid respectively) and surface area of membrane to the volume mixture ($S/V=1.3\text{ cm}^{-1}$). The conversion increased with increasing temperature to reach 96.67% at 60°C after 60 min. The water production increased with increasing temperature at the beginning of the reaction, it then decreased gradually due to water adsorption through the PV hydrophilic membrane [10]. This phenomenon is shown in Fig. 15.

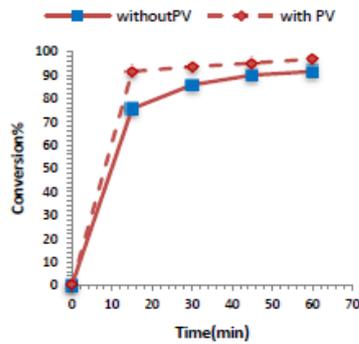


Fig. 12. Comparison of experimental results for esterification reaction with and without PV at $T = 60^\circ\text{C}$, $\text{MR}=8:1$, $\text{wt}\%=3\%$, $S/V=1.3\text{cm}^{-1}$.

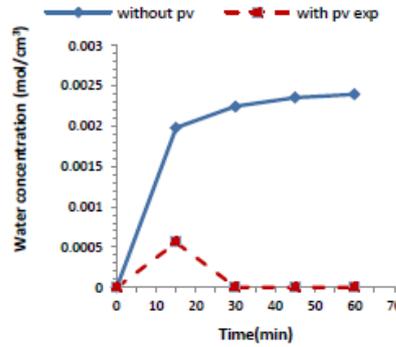


Fig. 13. Comparison of experimental results for water concentration for esterification reaction with and without PV at $T = 60^\circ\text{C}$, $\text{MR}=8:1$, $\text{wt}\%=3\%$, $S/V=1.3\text{cm}^{-1}$.

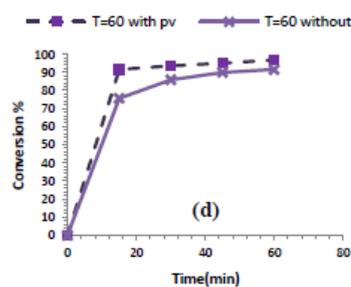
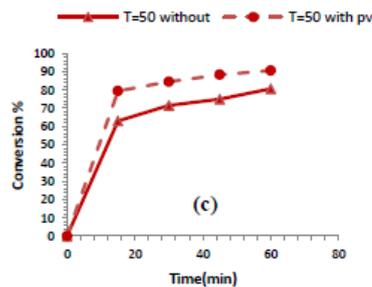
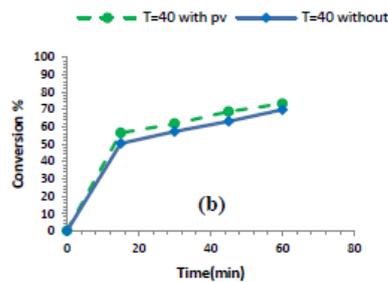
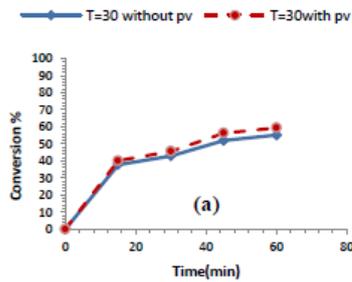


Fig. 14. Experimental results of esterification reaction conversion with and without PV catalysed by SSA ($\text{wt}\%=3$) for initial molar ratios (8:1) and S/V (1.3cm^{-1}) at [a) $T=30^\circ\text{C}$, b) $T=40^\circ\text{C}$, c) $T=50^\circ\text{C}$ and d) $T=60^\circ\text{C}$].

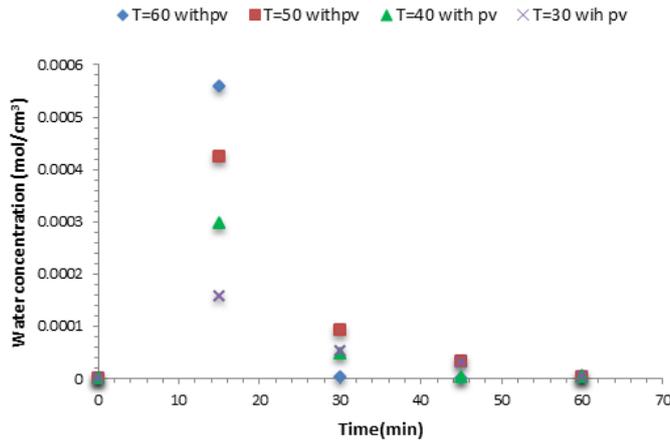


Fig. 15. Experimental results for the effect of temperature on produced water concentration with PV catalysed by SSA (wt%=3) at initial molar ratios (8:1) and S/V (1.3 cm^{-1}).

4.3. Effect of catalyst weight percent

The esterification reaction coupled with PV using different weight percentages of SSA (1, 2, and 3%) were studied at 60°C for a methyl alcohol to acetic acid ratio 8:1, and surface area of membrane to reaction volume ratio (S/V) of 1.3 cm^{-1} . The results indicated that the highest conversion reached 96.76% after 60 min using 3% SSA, while at 1% SSA the reaction conversion was 94.67%. Figures 16(a), (b), and (c) show the effect of SSA weight percent from 1% to 3% on the reaction conversion. It is seen that using excess SSA catalyst weight percent increases the conversion due to high catalyst activation surface area. Increased conversion is an indication of water removal from the reaction medium and hence as conversion increases the amount of remaining water in the reactor decreases. The obtained results agreement with what investigated in previous works [10, 22]. Water is decreased due to its adsorption through the PV membrane. Figure 17 illustrates the effect of SSA% on water content in the reactor. The highest concentration of water was $6.244\text{E}-06 \text{ mol/cm}^3$ after 30 min at 1% and the lowest water concentration was $4.11\text{E}-06 \text{ mol/cm}^3$ after 30 min at 3%.

4.4. Effect of molar ratios

The effect of methanol to acetic acid molar ratio on reaction conversion was investigated at 60°C , 3% of SSA and using S/V of 1.3cm^{-1} . The highest conversion was 96.76% at a methanol to acetic acid molar ratio 8:1 after 60 min. Figures 18(a), (b), (c) and (d) illustrate the effect of change in different molar ratios between 2:1 up to 8:1 on conversion with PV using SSA. Increasing the molar ratio to 8:1 leads to an increase in the reaction rate, that is fairly matched with published [10, 23]. The reaction conversion reached 91.5% after 15 min at MR 8:1, while the reaction conversion reached 76% after 15 min at MR 2:1. The effect of molar ratio on water concentration is illustrated in Fig. 19, it is seen that the concentration of water decreased in the reactor at high molar ratio.

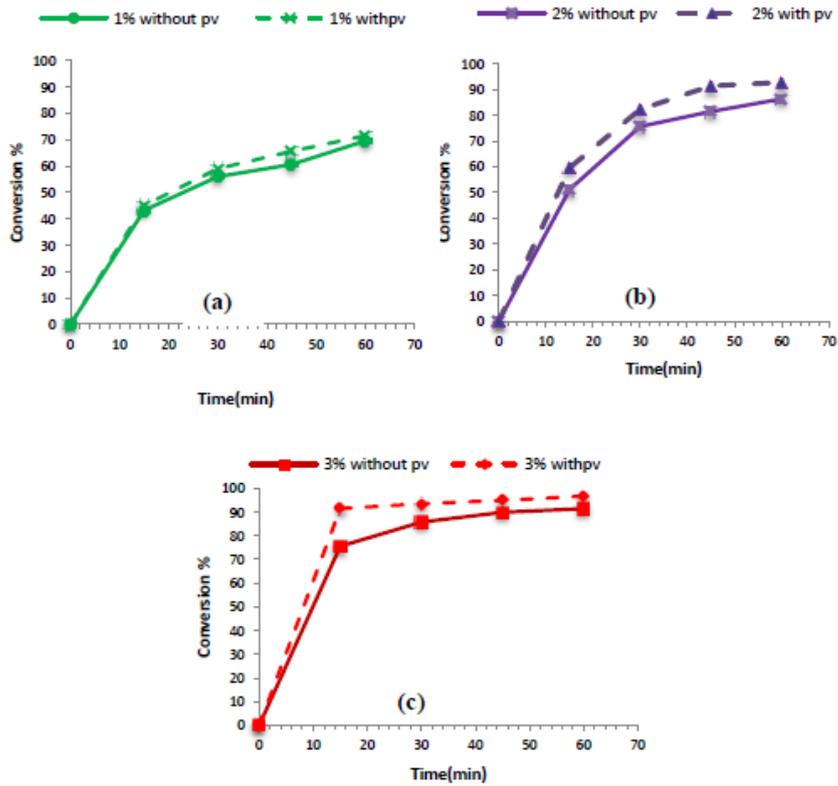


Fig. 16. Experimental results of the esterification reaction conversion with and without PV with MR=8:1 for temperature (60 °C) and S/V (1.3cm⁻¹) at [a- 1%, b-2% andc-3% of SSA].

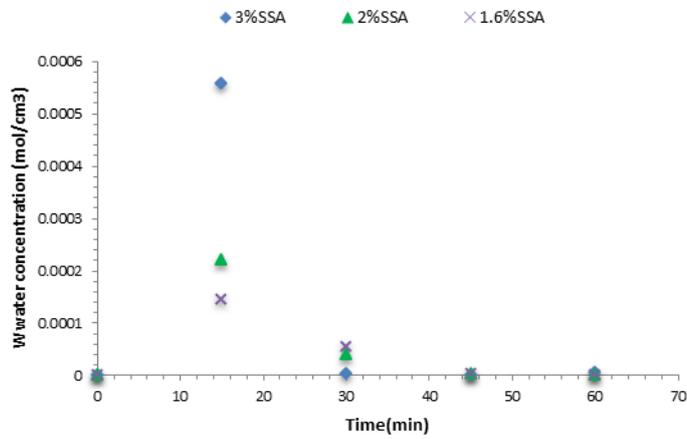


Fig. 17. Experimental results for produced water concentration with PV with MR=8:1 for temperature (60 °C) and S/V (1.3 cm⁻¹).

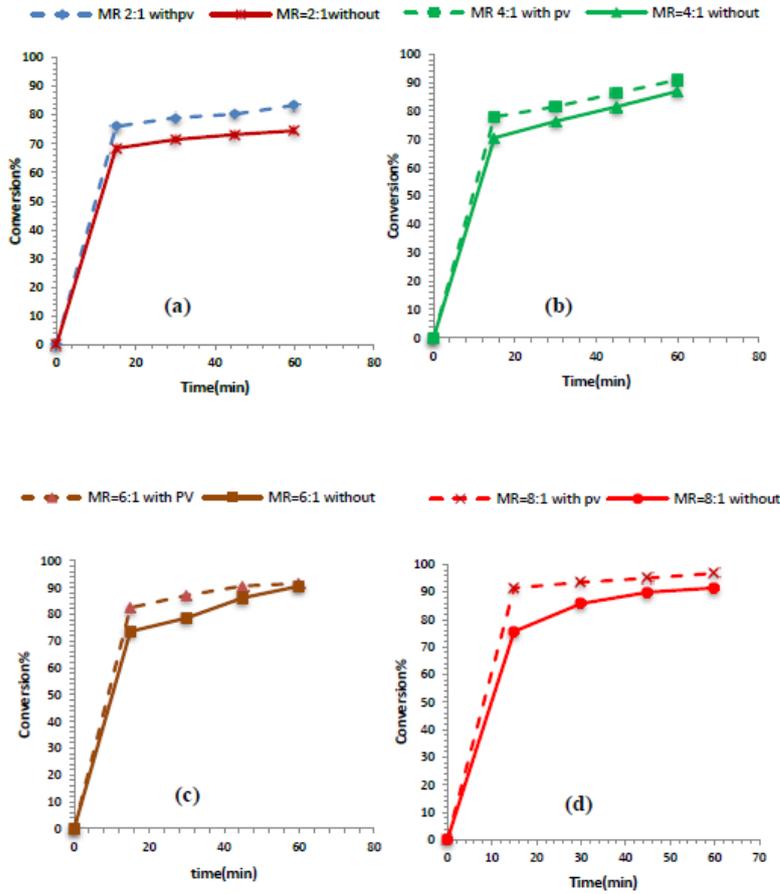


Fig. 18. Experimental results of conversion with and without PV catalysed by SSA (wt%=3) for temperature (60 °C) and S/V (1.3cm⁻¹) at [a-MR =2:1, b- MR =4:1, c-MR =6:1, d- MR =8:1].

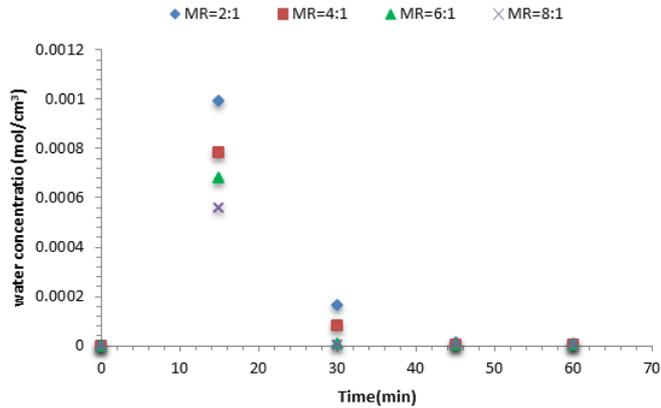


Fig. 19. Experimental results for produced water concentration with PV catalysed by SSA (wt%=3) for temperature (60 °C) and S/V (1.3 cm⁻¹).

5. Conclusion

Esterification enhanced by pervaporation revealed very encouraging results. Compared to the conventional esterification the same conversion is obtained in minutes rather than in hours. Water adsorption by the pervaporation membrane can help shift the equilibrium conversion by breaking the thermodynamic equilibrium barrier. The conventional esterification method with heterogeneous catalyst (silica sulfuric acid) provided the best results at a ratio of methanol to acetic acid of 8:1, weight of catalyst 3% at 60 °C. The influence of the pervaporation process was analyzed by studying the effects of different parameters such as temperature, SSA weight percentage, and reactant ratio on conversion of acetic acid and water extraction. Some concluding observations from the investigation are given below.

- The conversion increased with increasing temperature.
- The increase of molar ratio increases the conversion, and the maximum conversion was 96.76% at a molar ratio of 8:1 methanol to acetic acid after 60 min.
- As the catalyst weight percentage increased the conversion increased from 71.6% to 96.76% on increasing SSA wt% from 1 % to 3% after 1 h.

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