

## Improvement of Isopropyl Propionate Esterification Reaction using a Vapor Permeation Membrane Reactor

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### ABSTRACT

In this study, a vapor permeation-integrated heterogeneous catalytic esterification reaction was investigated to improve the ester conversion of propionic acid and isopropanol. The reaction was carried out using Amberlyst 15 (Rohm & Haas) as a catalyst with different weight fractions of 3%, 4%, 10%, and 12% wt. relative to propionic acid. A hydrophilic PERVAP®2201 membrane (Sulzer) was used to remove water vapor from the glass reactor. Different molar ratios (1:1, 1.5:1, and 3:1) of alcohol to acid were used in the feed mixture. Applying the coupled membrane system, using 12wt.% of catalyst, increased the acid conversion from 39% (when no membrane was employed) to nearly 90% for three hours after the beginning of the process.

**Keywords:** Reaction, Isopropyl Propionate, PERVAP®2201, heterogeneous catalyst

### 1. Introduction

Recently, the combination of the pervaporation process and chemical reaction with traditional processes is a fascinating subject and has become known as pervaporation membrane reactors. The ability of pervaporation membranes to separate organic components with close boiling points and mixtures that form azeotrope and the inherent advantages over reactive distillation and other combined separation methods have attracted special attention [1,2]. The majority of such reactors consist of membranes of dense polymers that are useful for selectively transferring one or more of the reaction products by pervaporation. Most of these reactors use hydrophilic membranes such as polyethyramide, polyamide, polyvinyl alcohol, and zeolite membranes. In this type of combined process, the pervaporation unit increases the conversion percentage of the reactor. The use of membrane reactors removes water continuously from the reaction medium and disturbs the chemical equilibrium. For example, Shameli and Ameri, for the methyl acetate reaction using nanocomposite membranes, nearly a complete

conversion rate has been reported [3]. The esterification of alcohol with monocarboxylic acids has been extensively studied by researchers [3-7]. The production of esters plays the main role in the production of flavors and fragrances, solvents, plasticizers, pesticides and herbicides, medicinal and surface-active agents. Isopropyl propionate has a fruity type odor and a fruity type flavor, which uses as a flavor and fragrance agent. Based on the extensive application of esters in the industry [8], it is supposed that the number of commercial esters exceeds 500, with over 100 manufacturers [9]. The investigation on the esterification reaction includes homogeneous and heterogeneous catalysts. In this process, homogeneous catalysts such as hydrochloric acid and sulfuric acid are used because of advantages such as low cost and high reaction speed. However, these types of catalysts are very poisonous and corrosive, and it is very problematic to eliminate them from the reaction medium [10]. The use of catalysts also changes the color of the product. In this process, in addition to sulfuric acid, alternative acid catalysts such as para toluene sulfonic acid and ion exchange resins are used [11]. Meanwhile, sulfonic acids have good catalytic activity, and in general, their use reduces the occurrence of adverse reactions to sulfuric acid. The use of mineral catalysts in the industry

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has disadvantages. For this reason, the use of ion exchange resins has received much attention. Application of these catalysts, such as Amberlyst 15, has several advantages; recovery of the catalyst is simply obtained by filtration [12]; continuous operation in columns is probable; the purity of the products is superior compared with a homogeneous catalyst; waste or disposal problems are deleted; isolation of reaction intermediates is possible [13]. Among the methods of breaking the equilibrium in the esterification reaction, membrane separation processes are relatively new methods. The construction of new membranes has made it possible to perform separations that were previously technically difficult or even impossible. In this regard, the reaction distillation process can be used to solve the equilibrium problem in the esterification reaction. However, the application of this method requires the use of a distillation column unit to separate the products, which requires a lot of energy. In addition, the use of this method is not recommended when chemicals or temperature-sensitive biocatalysts are present in the mixture. To solve these problems, pervaporation membrane reactors have been used. In recent years, pervaporation alone has been used as a practical and useful method for dehydration, disposal, or recovery of organic matter from the aqueous solution. In the meantime, many researchers have studied the combined process of pervaporation and esterification reactions. Kasaeni et al. succeeded in improving the esterification reaction of isobutyl acetate along with the pervaporation membrane unit using the PERVAP 2201 commercial membrane [14]. Ethyl acetate production was investigated in a continuous membrane reactor using two zeolite membranes, Mordenite and Type A. In this study, a pervaporation filled with catalytic resins called Amberlyst 15 was used to facilitate the reaction [15]. Figueroa et al. investigated the esterification reaction of acetic acid and ethanol in a pervaporation membrane reactor using the Amberlyst 15 and Amberlyst 35 catalysts. They achieved conversion rates above 60% [16]. The combined process of esterification of lactic acid and ethanol in the presence of a catalyst was studied experimentally and numerically by Wasavar et al. In this study, the effect of temperature, membrane surface to reactor volume ratio, and feed molar ratio on the combined process was investigated using the pervaporation process [17]. Uragami and Nishikawa used laboratory-made composite membranes of polystyrene sulfonic acid and polyvinyl alcohol to improve the progression of several esterification reactions, including ethanol, methanol, propanol, and acetic acid [18]. Diaz et al. investigated the effect of a reactive system containing water, ethanol, ethyl lactate,

and lactic acid using a pervaporation process with PERVAP™ 3100, PERVAP™ 2216, and PERVAP™ membranes. The membrane showed high affinity for the acid. The acid permeation showed a vital role in the water/alcohol and water/ester selectivity [19]. Ameri et al. examined the esterification process of isopropyl alcohol and propionic acid with the use of para toluene sulfonic acid catalyst and along with the vapor permeation membrane process using two different membrane types, NaA and PERVAP®2201 [6]. The aim of this work was the study of the esterification reaction of propionic acid with isopropanol catalyzed by Amberlyst 15 integrated with a vapor permeation unit. Experiments were carried out in a semi-batch reactor coupled with an external vapor permeation unit using the commercial polymeric membrane PERVAP® 2201 in order to shift the equilibrium by removal of water from the reaction mixture. The vapor permeation technique could avoid the direct contact between the acidic feed phase and the membrane and subsequently aid to make membrane stability. In addition, the effects of catalyst loading and alcohol/ acid molar ratio of the feed on acid conversion and water permeation flux were investigated.

## 2. Experimental

### Chemicals

Isopropyl alcohol with 99.8% and propionic acid with 99 % purity were prepared from Merck. The alcohol-to-acid molar ratios in the feed mixtures was 1:1, 1.5:1, and 3:1, respectively. The esterification reactions were catalyzed with Amberlyst 15 (Rohm & Haas). The Amberlyst 15 has an active proton site as a Lewis acid that binds with the propionic acid, weakens the carbonyl bond, and makes lower energy activation. The protonation of the carbonyl group directs to the carbocation, and after the nucleophilic attack of the isopropyl molecule, ester was finally formed [20-21]. The properties of Amberlyst 15 are presented in **Table 1**.

**Table 1.** The properties of Amberlyst 15 (Rohm and Haas Company, U.S.A.)

Ionic form as shipped	Hydrogen	
Concentration of active sites	> 1.7 eq/L	>4.7 eq/kg
Moisture holding capacity	52 to 57% (H+ form)	
Shipping weight	770 g/L (48 lbs/ft <sup>3</sup> )	
Harmonic mean size	0.600 to 0.850 mm	
Surface area	53 m <sup>2</sup> /g	
Average pore diameter	300 Å	
Total pore volume	0.40 ml/g	

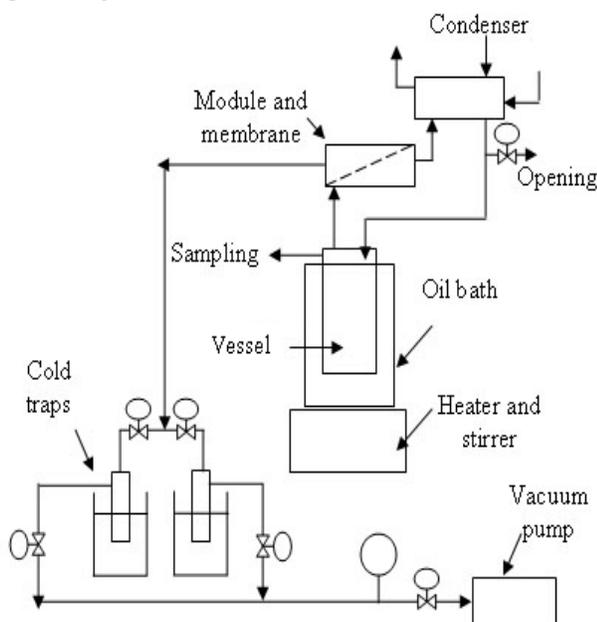
### Experimental Setup

The experiments were conducted by using the polymeric membrane PERVAP® 2201 (Sulzer) in a Teflon module. The membrane had a surface area of 5x12.5 cm<sup>2</sup>.

The experimental setup is presented in **Fig. 1**. A temperature regulator was controlled the temperature of the reactor. The esterification reaction and vaporization happened instantaneously in a batch reactor, and the vapor was conducted into the membrane module. A vacuum pump (Mod. MD1, Vacuubrand, GMBH, Germany) was utilized to maintain the vacuum on the permeate side at 2mbar. The vapor phase exited from the membrane module was condensed in a vessel and then fed to the reactor.

An Amino HPX-87H HPLC column (Jasco, Germany) was used to analyze the permeate samples. A RI detector functioned at 40°C, and a UV detector operated at a wavelength of 210 nm was used for the detection of alcohol and acid in the samples, respectively. The temperature of the oven was maintained at 60°C, and the eluent was 0.005M sulfuric acid.

A packed GC column (P-4410, Philips) was utilized to analyze the reaction mixture samples. The initial temperature was maintained at 80°C for 3 minutes and was formerly increased to 150°C. The detector (FID) and the injector temperatures were 250°C and 150°C, respectively.



**Fig. 1.** Vapor permeation setup.

### 3. Results and Discussion

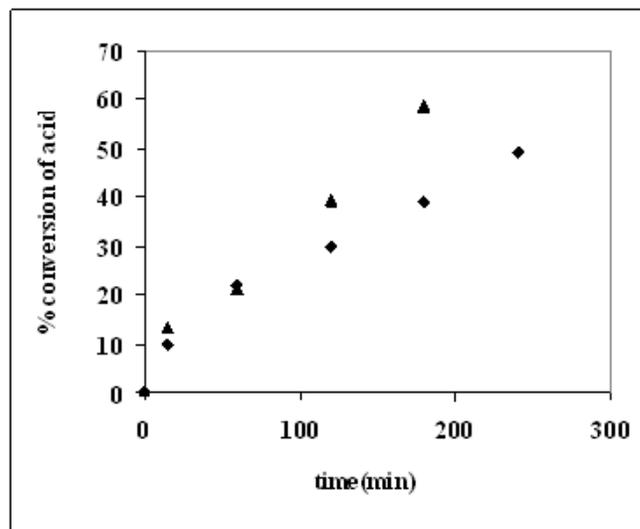
#### Effect of the membrane

The tests were done with 1.5: 1 molar ratio of alcohol/ acid. The loading of Amberlyst 15 was adjusted to 10 wt.% (with respect to acid). **Fig. 2** shows that the acid conversion of the reversible esterification reaction was low and equaled to 49% (at 240 min) in the test without a polymeric membrane. But, integrating the membrane separation process with the esterification reaction could improve the acid conversion by removing water from the reactor. In this manner, the conversion of acid was increased to 59% for the 180 min.

In general, **Fig. 2** shows that combining the reaction process with the separation process increases the rate of reaction progress. In this composite process, the membrane removes the by-product of water from the reactant phase, based on Loshatolie's law, breaking the reversible reaction equilibrium and ultimately increasing the conversion percentage. Similar results have been obtained by other scientists [3-4, 6-7].

#### Catalyst loading effect on the hybrid process

**Fig. 3** shows the percentage conversion of acid to time with an alcohol/acid molar ratio of 1.5: 1 and the use of Amberlist 15 catalysts with values of 3, 10, and 12 wt.% using a polymer membrane. According to these curves, it can be concluded that with increasing the amount of catalyst, the percentage of acid conversion at different times of the process were improved. As a result of the study of these three diagrams, at the end of 3 hours in experiments using 3, 10, and 12 wt.% of catalyst, the



**Fig. 2.** Acid conversion versus time, alcohol/ acid molar ratio: 1.5:1, 10 wt.% of Amberlyst 15 (respect to acid), with the membrane (▲) and without membrane(◆).

conversion percentage was equal to 49.8, 58.6, and 87%, respectively. The results show that the difference between the values of the conversion percentage at each time for two experiments with the highest and lowest catalysts was increased. In **Fig. 3**, due to the low conversion percentage in the initial times of the process, the difference between the conversion percentage values in the two experiments with the lowest and highest amount of catalyst used was low. With the passage of time, the difference between conversion percentage values in the two processes with catalyst consumption at 12 and 3 wt.% were increased due to the effect of the vapor permeation membrane that removed the water from the reactor and broke the equilibrium. In this regard, Torabi and Ameri, for an integrated pervaporation/ reaction process, reported that the final conversion achieved by using 5 and 15 wt.% of Amberlist 15 was 64% and 94%, respectively [4].

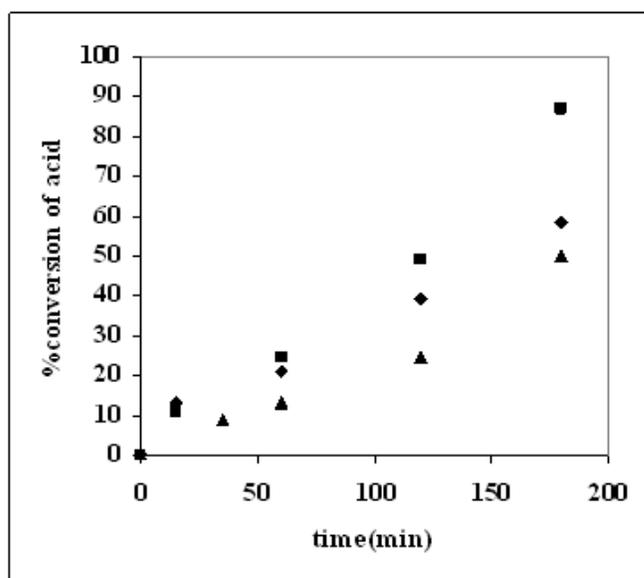
#### Effect of catalyst loading on the separation process

**Fig. 4** displays the water permeation rates with time in a molar ratio of alcohol to acid equal to 1.5: 1 and the use of catalyst with values of 3, 10, and 12 wt.%. **Fig. 4** shows that with the enhancement of the amount of catalyst, the water flux penetrating from the membrane was also increased. For example, in the first hour of the process, for experiments with catalyst consumption of 3, 10, and 12 wt.%, water fluxes were reported 48, 77, and 89 g/m<sup>2</sup>, respectively. Also, for the experiment with the highest amount of catalyst, it is observed that the slope of flux variations with time between the second and third hour was increased compared to the first hour. This result is not unexpected considering the growth rate of conversion percentage from 49.3% to 87% in the period between the second and third hours of the process. It is noteworthy that in coupled processes in which heterogeneous catalysts were used, due to the low reaction rate relative to the separation process, the polymeric membrane had the ability to completely extract water from the reaction mixture.

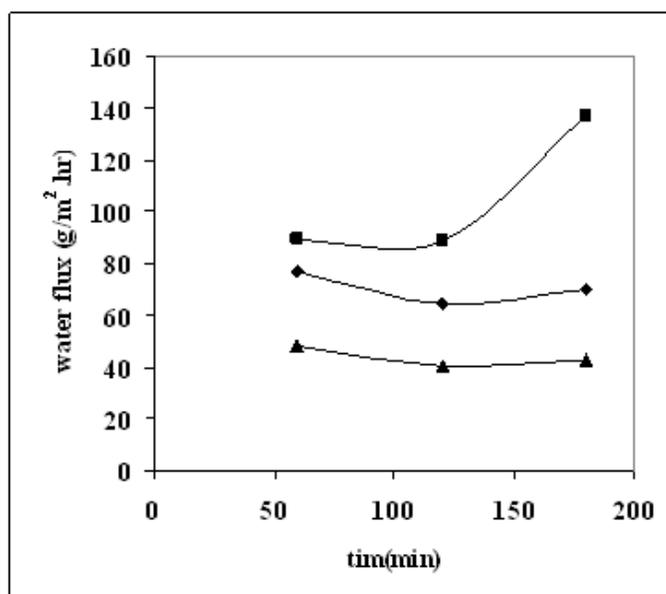
#### Influence of alcohol / acid molar ratio

**Fig. 5** shows the acid conversion versus time for the different molar ratios of 1:1 to 3:1, with catalyst loading of 12 wt.%. As seen in Fig. 5, at the minimum and the maximum of the molar ratios, the final acid conversion were found to be 41% (after 2 hours) and 72% (after 4 hours), respectively. But, the final acid conversion improved to 87% after 3 hours from the beginning of the reaction, when the alcohol/acid molar ratio was 1.5:1. Comparison between acid conversions shows that the enhancement of the alcohol acid molar ratio from 1:1 to 1.5 had the significant positive effect on the progressing of the esterification reaction. In this regard, Salahchini

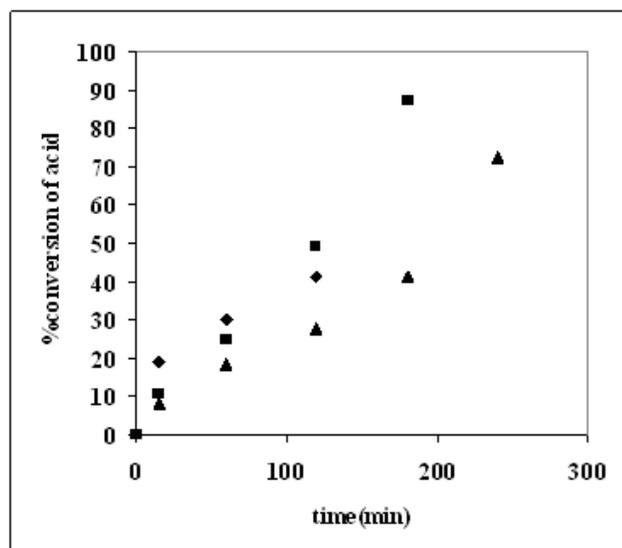
and Ameri and Torabi and Ameri studied methanol acetate esterification reaction with nanocomposite membranes and showed that the acid conversion increased with the enhancement of the alcohol / acid molar ratio [4,5]. **Fig. 5** also shows that further enhancement in the molar ratio of alcohol and acid from 1.5:1 to 3:1 led to a decrease in the conversion of the limiting reactant. Moreover, acid conversion was decreased when the alcohol/ acid molar ratio enlarged from 1.5:1 to 3:1.



**Fig. 3.** Acid conversion versus time with different catalyst loading of 3 (▲), 10 (◆), and 12 (■), alcohol/acid molar ratio:1.5:1.



**Fig. 4.** Water permeation flux versus time with different catalyst loading of 3 (▲), 10 (◆), and 12 (■), alcohol/acid molar ratio:1.5:1.



**Fig. 5.** acid conversion versus time with different molar ratios :1:1 (♦), 1.5:1 (■) and 3:1 (▲) catalyst loading of 12 wt.%

The reason for observing this trend can be attributed to the temperature at which the esterification happens. Since the temperature of the reaction mixture during the process is equal to the boiling point of this mixture (see **Table 2**), increasing the alcohol/ acid ratio will decrease the boiling point of the mixture and finally reduce the acid conversion. Therefore, in the early stages of the reaction, a reduction in the amount of alcohol/ acid molar ratio increases the acid conversion.

After one hour, the trend of acid conversion percentage changes with time, so that the highest conversion percentage belongs to the mixture with an alcohol/acid ratio of 1.5: 1, equal to 90%. In the experiment with a minimum alcohol/acid molar ratio, the slope of the changes in the percentage of acid conversion versus time, in the second hour was significantly reduced, and the conversion percentage for this test at this time is close to 42% of equilibrium conversion. The conversion percentage in the test with the maximum alcohol/ acid ratio approaches 76% after 3 hours.

From the general study of **Fig. 5**, it can be concluded that the temperature factor has a conclusive role in the reaction rate. In this group of experiments, after 1 hour, the amount of alcohol in the reaction mixture decreases due to consumption as a raw material in the reaction on the one hand and also by leaving the reaction mixture and passing through the membrane. Reducing the quantity of alcohol in the mixture is associated with growing the boiling point, which is a flavor to the reaction rate and has a negative effect on the separation process by reducing the evaporation rate and reducing the flow rate of the steam that is, the feed of the separation process. In other words, reducing the

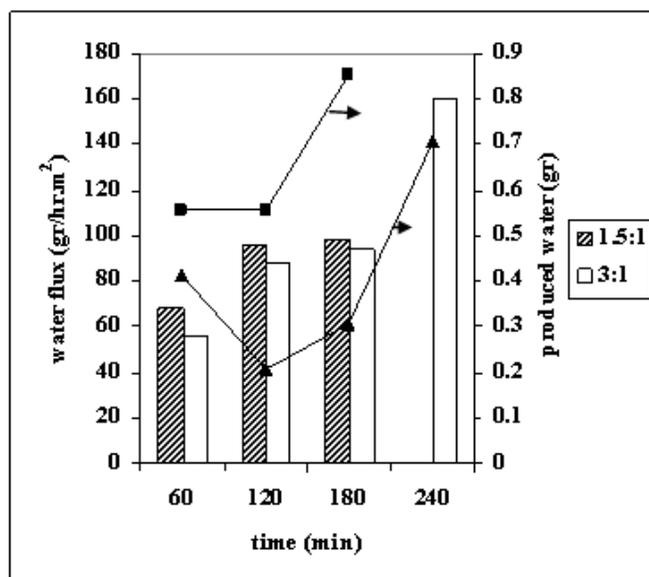
intensity of the separation process has a negative effect on the development of the equilibrium reaction. In general, it can be concluded that reducing the amount of alcohol to acid has a direct positive effect and an indirect negative effect on the reaction. This result could be observed in the previous investigations [22-25]. Moreover, while the isopropanol concentration was increasing in the feed, more alcohol was vaporized and led to an increase the amount of alcohol in the vapor phase passing the membrane, which unflavored to the membrane separation process. Increasing the alcohol concentration in the vapor phase generated more sites faced with the isopropanol molecules on the membrane site. As a result, the contact between water molecules and the membrane surface was decreased, and therefore water permeation through the membrane was reduced. In addition, decreasing water partial pressure in the vapor led to consequently reduce driving force for the separation process. As a result, based on Loshatolie's law, the acid conversion was low in the test with an alcohol/acid molar ratio of 3:1. As shown in **Fig. 6**, for the test with alcohol / acid molar ratios of 1.5:1 and 3:1, the result for the water flux and the produced water from the reaction confirmed this result. **Table 3** presents the removed water from the reactor in the final time interval, too.

From observing **Fig. 6**, it can be found that the quantities of water produced from the reaction and water flux have higher values for the experiment with a molar ratio of 1.5:1 during the process time, as mentioned before. Also, according to the data given in this figure, the amount of the produced water in the final time interval was high for the two aforementioned processes.

This was due to the enhancement of the boiling point temperature of the reactant combination at this duration of time. Moreover, due to the endothermic nature of the reaction, the rising temperature of the reactant mixture led to more acid conversion and therefore caused to a sharp enhancement for the quantity of produced water, and consequently, more water flux was obtained. This result can be seen in similar researches [26, 27].

**Table 2.** Boiling point temperature of feed mixtures at different initial water content.

molar ratio of the reactants	Boiling point(°C)
1/1	92
1.5/1	86
3/1	81



**Fig. 6.** Water permeation flux and produced water versus time with different molar ratios of 1.5:1 and 3:1, using 12 wt.% of catalyst.

**Table 3.** Amount of removed water (gr) from the reactor.

molar ratios	removed water (gr)			
Time (min)	60	120	180	240
1.5:1	0.4226	0.5988	0.6145	---
3:1	0.3476	0.5476	0.6176	0.9991

#### 4. Conclusions

In this work, using the vapor permeation process instead of the pervaporation reduced the probability of vulnerability of membrane sensitive to acidic environments, and as a result, the polymeric membrane was consequently stable due to the indirect contact of acidic liquid feed.

Results showed that increasing the catalyst concentration increased the reaction rate and caused to enhance the acid conversion from 49% to 87% after passing 3 hours of processing time. The vapor permeation performance of the VPMR system was evaluated by means of flux. It was found that high fluxes could be obtained from VPMR, while reaction conversion was reported by high values during the reaction time. In this case, the alcohol-to-acid molar ratio was equal to 1.5:1, and the same effect was achieved for all molar ratios evaluated in this work. Results also showed that the alcohol/acid ratio had a significant effect on the acid conversion during the process. Enhancement of the alcohol/acid molar ratio

from 1:1 to 1.5:1 (with catalyst loading of 12 wt.%) caused to improve the acid conversion. However, increasing of alcohol/ acid molar ratio from 1.5:1 to 3:1 led to reduce acid conversion from 87% to 41%.

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