



## SIMPLE KINETICS MODEL FOR ESTERIFICATION OF INDONESIAN CRUDE TURPENTINE OVER AMBERLYST 15

Diana<sup>1,2</sup>, Sutijan<sup>2</sup>, Rochmadi<sup>2</sup> and Arief Budiman<sup>2,3</sup>

<sup>1</sup>Chemical Engineering Department, Islamic University of Indonesia, Jalan Kaliurang Yogyakarta, Indonesia

<sup>2</sup>Chemical Engineering Department, Gadjah Mada University, Jalan Grafika, Bulaksumur, Yogyakarta, Indonesia

<sup>3</sup>Center for Energy Studies, Gadjah Mada University, Sekip K1A, Yogyakarta, Indonesia

EMail: [diana@uii.ac.id](mailto:diana@uii.ac.id)

### ABSTRACT

A study of crude turpentine esterification was carried out using strong acidic cation exchange resin Amberlyst 15 as catalyst. During the esterification process, the isomerization of  $\alpha$ -pinene also took place under the catalytic condition. To obtain the optimal reaction conditions in a stirred-tank reactor, the effect of different parameters such as mixing speed, ratio of reactants, temperature and the reusability of catalyst on the conversion of  $\alpha$ -pinene and the selectivity of bornyl acetate were investigated. Kinetics of the reaction was also performed in the temperature range of 50 – 100 °C. To explain the reaction rate equation and to determine the reaction rate constants and reaction activation energy, reaction products were grouped as acetates and isomers and a pseudo homogeneous - first order reaction model was used. The proposed kinetic model shows a good agreement with the experimental data.

**Keywords:** turpentine, esterification, bornyl acetate, kinetics.

### INTRODUCTION

Pine trees in Indonesia are largely of pine mercurii species which typically give turpentine that contains about 75-85%  $\alpha$ -pinene, 10-12% carene and balanced with other components such as camphene,  $\beta$ -pinene and limonene.  $\alpha$ -Pinene (C<sub>10</sub>H<sub>16</sub>) is naturally occurring monoterpenes used as substrates for the production of monoterpenoid flavours and fragrances [1].

One of the most important synthetic routes to valuable terpenic alcohols and esters is acid catalyzed hydration of terpenes. Hydration of  $\alpha$ -pinene will produce  $\alpha$ -terpineol, an important compound in perfume and pharmaceutical industry. The use of reactive distillation significantly enhanced the reaction [1 – 3].

Bornyl acetate and  $\alpha$ -terpenyl acetate are also important fine chemicals that have been widely used in the field of organic synthesis, medicine, and cosmetic. Traditionally they are prepared in two stage process. Direct reaction of  $\alpha$ -pinene with acetic acid can produce two series of products, esterification products and rearrangement products. The rearrangement products are isomers of  $\alpha$ -pinene, such as camphene, limonene, terpinene and terpinolene. Bornyl acetate, fenchyl acetate and  $\alpha$ -terpinyl acetate are the esterification products [4].

Strong mineral acid such as H<sub>2</sub>SO<sub>4</sub> is frequently used for esterification of terpenes. However, the disposal of this homogenous catalyst not only poses a serious environmental problem but also facing difficulties in separation. To solve this problem, the use of heterogeneous acid catalysts has been considered. Several research groups have been investigated the reaction of  $\alpha$ -pinene and acetic acid using heterogeneous catalysts. Liu *et al.* [4] employed acidic ionic liquid as a heterogeneous catalyst. The use of various solid catalysts, namely zeolite beta [5], SBA-15 with sulfonic acid [6], heteropoly acids [7] and Amberlyst 70 [8] also has been reported.

In general, ion-exchange resins are often employed in various processes such as esterification, dehydration, alkylation, and hydrolysis. Amberlyst 15 wet is a strongly acidic macroporous ion-exchange resin catalyst applicable in various terpene transformations. Our study found that Amberlyst 15 showed better performance among ion-exchange resin tested [9].

Direct use of crude Indonesian turpentine is promising as it contains high concentration of  $\alpha$ -pinene. Vacuum distillation that is applied to purify turpentine is an energy consumed process. It will be a great advantage if this step could be neglected. In this work, we studied the feasibility of using of crude Indonesian turpentine in batch esterification of  $\alpha$ -pinene over Amberlyst 15. The reaction conditions were explored for aiming an efficient conversion of  $\alpha$ -pinene to a mixture of valuable products, particularly bornyl acetate.

In kinetic study, the reactions were simplified into two parallel reactions i.e: isomers and acetates. Kinetics of the reaction was modeled with the first-order pseudo – homogeneous model, and the reaction rate constants and reaction activation energy were figured out. So the result could be used as a reference for the industrial application of turpentine esterification.

### EXPERIMENTAL

#### Materials

Turpentine (85%  $\alpha$ -Pinene) was obtained as a gift from Perhutani Pine Chemical Industry (Indonesia). Glacial acetic acid (Merck) and Amberlyst 15 wet (Rohm and Haas) were purchased and used without further treatment.

#### Procedure and apparatus

The experiments were conducted in a three necked flat bottomed flask equipped with magnetic stirrer,



condenser and thermocouple. The reactor was immersed in an oil bath in order to maintain the required reaction temperature. Turpentine and glacial acetic acid were proportionately added to the batch reactor. The mixture was magnetic stirred and heated up to the required temperature. Once it was reached, catalyst was loaded and the reaction time was started to be counted. Aliquots were withdrawn at set times and analyzed in GC. Selected samples were analyzed in GC-MS as well.

### Analysis

The progress of the reaction was monitored by withdrawing samples at different time intervals during the reaction. Analysis of the reaction products was performed by Gas Chromatography (GC) (Hewlett Packard 5890 Series II) equipped with flame ionization detector/FID and a HP-5 capillary column. Nitrogen was used as the carrier gas in the GC with the detector and injection port temperature of 250 °C, column temperature ranging from 70 to 280 °C. Holding time of 5 min at the initial temperature and the heating ramp of 5 °C/min was applied.

GC-MS analysis (gas chromatography coupled to mass spectrometry) was utilized in the detailed product analysis and identification. For the GC-MS analysis, QP2010S Shimadzu was used. AGILENT DB-5 was used as the column and the carrier gas was nitrogen. The temperature of the column was adjusted to 70 °C for 5 min and then increased to 280 °C by 5 °C/min. The injection and detection temperatures were set to be 290 and 300 °C.

The concentrations of reactants and products were directly shown by the system of GC according to the area of each chromatograph peak. The  $\alpha$ -pinene conversion (X) and selectivity of bornyl acetate (Si) were calculated using Equations. (1) and (2).

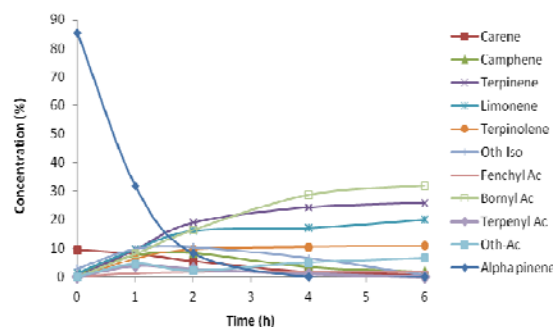
$$X = \frac{(96 \text{ area of } \alpha\text{-pinene})_0 - (96 \text{ area of } \alpha\text{-pinene})_t}{(96 \text{ area of } \alpha\text{-pinene})_0} \times 100 \quad (1)$$

$$Si = \frac{96 \text{ area of bornyl acetate}}{(96 \text{ area of } \alpha\text{-pinene})_0 - (96 \text{ area of } \alpha\text{-pinene})_t} \times 100 \quad (2)$$

### RESULTS AND DISCUSSIONS

The experiments were conducted using crude turpentine reacted with glacial acetic acid. GC analysis shows that the composition of turpentine is 85%  $\alpha$ -pinene, 1.3% camphene, 11.2% carene, and the rest is limonene. Distribution of the reaction product performed at a temperature of 65 °C, atmospheric pressure is shown in Figure-1.

The concentration of  $\alpha$ -pinene decreased over time as it is converted into several products. The main product of the reaction are fenchyl acetate, bornyl acetate, and terpinyl acetate also camphene, limonene, terpinene, and terpinolene. Other minor products are grouped as 'other acetates' and 'other isomers'.



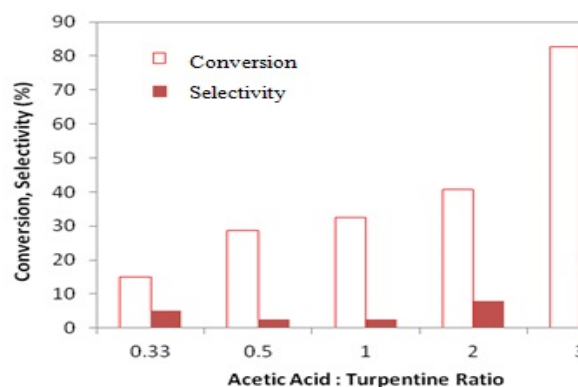
**Figure-1.** The concentration evolvement over time (Amberlyst 15 wet as catalyst; cat loading: 0.04 g/L; ratio of turpentine:acetic acid: 3:1)

### Effect of initial ratio of reactants

The esterification reaction requires one mole of acetic acid per mole of  $\alpha$ -pinene. Excessive use of one reactant will enhance the amount of product formed. In addition, the ratio of reactants also affects the selectivity of the product.

To study the influence of initial ratio of reactants, experiments were conducted over 0.02 g/mL Amberlyst 15 wet at 60 °C. Volume ratio of acetic acid with turpentine varied at a value of 3; 2; 1; 0.5 and 0.33. This ratio is equivalent to a molar ratio of 9.69; 6.45; 3.22; 1.61 and 1.07. Alpha pinene conversions and selectivities bornyl acetate obtained are shown in Figure 2.

The graph from Figure 2 shows that the volume ratio of acetic acid: turpentine (R) = 1 : 3 conversion of  $\alpha$ -pinene is 14.95%. The greater the ratio, the higher the conversion and the highest conversion (82.77%) achieved at R = 3. In addition, generally the increase of reactants ratio also led to increase in selectivity of bornyl acetate. Ratio changes from 0.5 to 3 raise bornyl acetate selectivity from 2.54% to 19.36%.



**Figure-2.** Effect of initial reactant ratio on conversion of  $\alpha$ -pinene and selectivity of bornyl acetate.

Conversion of  $\alpha$ -pinene and selectivity of bornyl acetate increases with the increase of the ratio. Excessive amount one of the reactants will encourage the formation

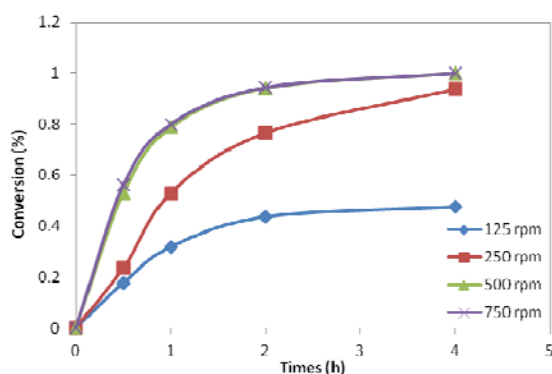


of more products, so the conversion becomes higher. This is in accordance with the principle of Le Chatelier. From the kinetic theory point of view, higher concentration of the reactants will increase the reaction rate so high conversion would be achieved in a shorter time. In addition, the presence of excessive acetic acid will increase the likelihood of collisions between molecules of acetic acid with  $\alpha$  - pinene, lead the selectivity to increase.

### Effect of mixing speed

Figure-3 shows the effect of mixing speed on the conversion of  $\alpha$  - pinene in turpentine. Experiments conducted at four different speeds.

The conversion of  $\alpha$  - pinene is affected by the stirring speed if speed less than 500 rpm is applied. In contrast, at a speed of 500 rpm and 750 rpm obtained a similar conversion. This meant that the conversion of  $\alpha$  - pinene was independent of the mixing speed. This shows the influence of external diffusion at a speed of 500 rpm or above can be neglected.



**Figure-3.** Effect of mixing speed on conversion of  $\alpha$  - pinene.

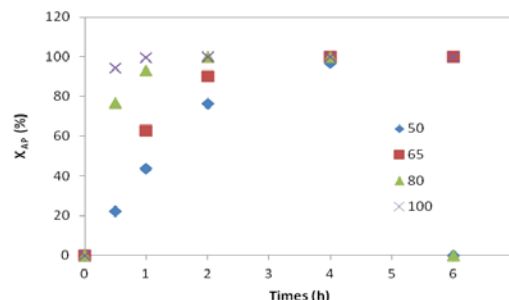
### Effect of temperature

To study the effect of temperature on the esterification reaction between turpentine and acetic acid, experiments using Amberlyst 15 (0.04 g/mL), with the ratio of reactants 3 and stirring speed of 500 rpm are conducted. The temperature ranging from 50 to 100 °C was investigated. Temperature is limited to 100 °C as Amberlyst 15 withstand up to 120 °C only.

Figure-4 shows that after 6 hours of reactions,  $\alpha$  - pinene conversion reached 100% at all temperatures tested. After 1 hour of reaction, the conversion of  $\alpha$  - pinene increased from 43.5% to 100% when the reaction temperature is raised from 50 °C to 100 °C. This suggests that the rise in temperature have a significant influence on the rate of the reaction between  $\alpha$  - pinene and acetic acid.

From the kinetics point of view, higher temperatures will increase the reaction rate constants. Molecules will only react if it has enough energy. When the temperature is raised, the molecular energy levels will get extra energy. This causes the molecule to become

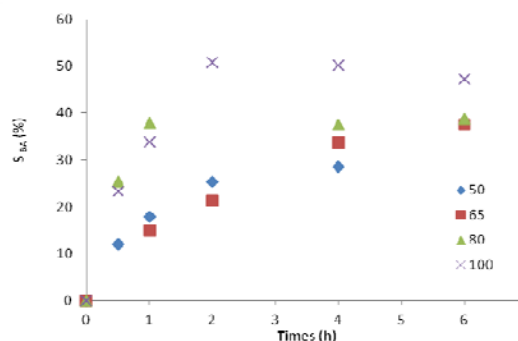
more active and more often collide and eventually increase the reaction speed.



**Figure-4.** Effect of temperature on conversion of  $\alpha$  - pinene.

Selectivity of bornyl acetate at various temperatures is shown in Figure-5. The temperature rise not only raises the conversion of  $\alpha$  - pinene but also improve the selectivity of bornyl acetate. After 4 hours of reaction, bornyl acetate selectivity increased from 28% at 50 °C to 50% at 100 °C. At temperatures of 50 and 65 °C, the increase is still going on up to 6 hours of reaction time. Meanwhile, at a temperature of 80 °C and 100 °C, the maximum selectivity achieved in 2 hours of reaction time.

When turpentine reacts with acetic acid, there is competition between esterification and isomerization. The rise of temperature not only increases the rate of esterification reaction, but also to the isomerization reaction. At higher temperatures,  $\alpha$  - pinene converted faster into both products. This cause bornyl acetate selectivity tends to be constant after 2 hours of reaction.



**Figure-5.** Effect of temperature on selectivity of bornyl acetate.

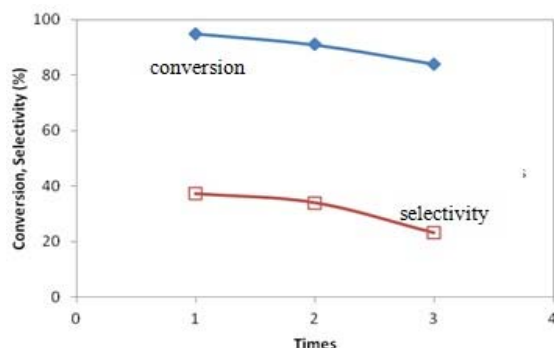
From Figures-4 and 5, it is observed that when the entire  $\alpha$  - pinene has been converted there is still the addition of bornyl acetate. This indicates a consecutive reaction in the formation mechanism of bornyl acetate. This compound does not directly form of  $\alpha$  - pinene but through an intermediate product.

### Reusability of catalyst

The advantage of the solid catalyst is that it can be easily separated and reused. The ability to be used



repeatedly is an indicator of the performance of the solid catalyst. The reusability of Amberlyst 15 wet was tested for repeated reactions at the same reaction conditions and the result is shown in Figure-6. Before being used in the subsequent reaction, the catalyst was washed using ethanol and dried. In this study, the catalyst Amberlyst 15 wet reused up to 3 times. The reaction is run at a temperature of 90 °C, for 6 hours with the ratio reactant of 1.

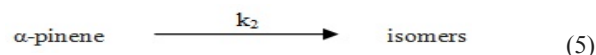
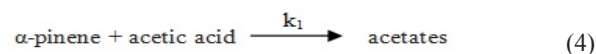


**Figure-6.** Result of catalyst repeated use.

Figure-6 shows that the conversion of  $\alpha$ -pinene and selectivity of bornyl acetate decreased after reusing the catalyst. The conversion decreased from 94.95% (1<sup>st</sup> use) to 91.02% (2<sup>nd</sup> use) and 83.97% (3<sup>rd</sup> use), while the selectivity decreased from 37.20% (1<sup>st</sup> use) to 34.03% (2<sup>nd</sup> use) and 23.29% (3<sup>rd</sup> use). This is possible because of the active group is separated from the catalyst surface so that the site acidity is reduced.

### Simple kinetic model

The reaction between  $\alpha$  - pinene with acetic acid compounds will produce isomerization products, i.e. camphene, limonene, terpinene, terpinolene, and esterification products, i.e. fenchyl acetate, bornyl acetate, and terpinyl acetate. These products can be classified into two groups: acetates and isomers. This simplification neglects the consecutive reaction and only forms 2 parallel reactions. So, the reaction can be written as follows:



For the purposes of reaction kinetics studies, experiments were conducted with the catalyst Amberlyst 15 wet (0.04 g / mL), with the ratio of reactants 3. In this study, a speed of 500 rpm was used to ensure that there is no influence of external diffusion in the reaction, as described in previous section. With no limits on particle diffusion then the reaction rate can be expressed by the model of pseudo homogeneous. In addition, acetic acid is added excessively, so it can be assumed that the esterification reaction follows the first order.

Our literature review showed that the models and assumptions of pseudo homogeneous – irreversible – 1<sup>st</sup> order reaction, suitable to describe the kinetics of  $\alpha$ -pinene isomerization [10] and hydration of  $\alpha$ -pinene [11] using a solid catalyst. Analogue with those reactions, the rate of esterification reaction can be expressed by a simple pseudo homogeneous (PH) model in the absence of any external diffusional limitation.

According to the power law, the total reaction can be expressed as:

$$\frac{dC_{AP}}{dt} = -KC_{AP} \quad (6)$$

The kinetics of the reactions can be expressed by the following differential equation:

$$r_1 = \frac{dC_1}{dt} = -k_1 C_{AP} C_{AA} \quad (7)$$

$$r_2 = \frac{dC_2}{dt} = -k_2 C_{AP} \quad (8)$$

where  $C_1$  and  $C_2$  are the molar concentration of acetates and isomers, respectively.

Since the molar concentration of acetic acid was much higher than that stoichiometric requirement for esterification of  $\alpha$ -pinene, the concentration of acetic acid can be considered as constant. So Equation. (7) can be written as:

$$\frac{dC_1}{dt} = -k'_1 C_{AP} \quad (9)$$

with  $k' = k_1 C_{AA}$  at  $t = 0$  the value of  $C_{AP} = C_{AP0}$  so Equation. (6) can be solved as

$$C_{AP} = C_{AP0} e^{-Kt} \quad (10)$$

Substitution of Equation. (10) to Equations. (7) and (8) will give

$$C_1 = \frac{k_1 C_{AP0}}{K} (1 - e^{-Kt}) \quad (11)$$

$$C_2 = \frac{k_2 C_{AP0}}{K} (1 - e^{-Kt}) \quad (12)$$

Equations (4) and (5) are parallel reactions, so it can be obtained a correlation:  $K = k'_1 + k_2$ . The value of the total reaction rate constants ( $K$ ) in Equation. (6) is determined from experimental data, which was a slope of the plot chart formed between  $\ln(C_{AP} / C_{AP0})$  with  $t$ . While reaction rate constants of acetates ( $k_1$ ) and isomers ( $k_2$ ) were calculated by Equations. (7) - (9). The values of the reaction rate constants at various temperatures shown in Table-1 below.

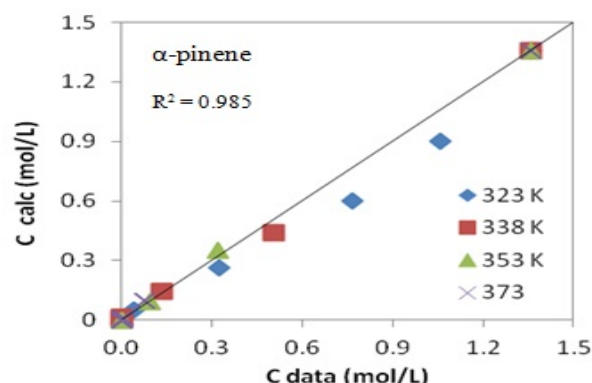
**Table-1.** The values of reaction rate constant at different temperatures.

T (K)	K (h <sup>-1</sup> )	k' <sub>1</sub> (h <sup>-1</sup> )	k <sub>1</sub> (Lmol <sup>-1</sup> h <sup>-1</sup> )	k <sub>2</sub> (h <sup>-1</sup> )
323	0.8177	0.6032	0.2145	0.0164
338	1.1264	0.8034	0.3230	0.0246
353	2.7024	1.6730	1.0294	0.0785
373	5.2621	2.7047	2.5574	0.1950

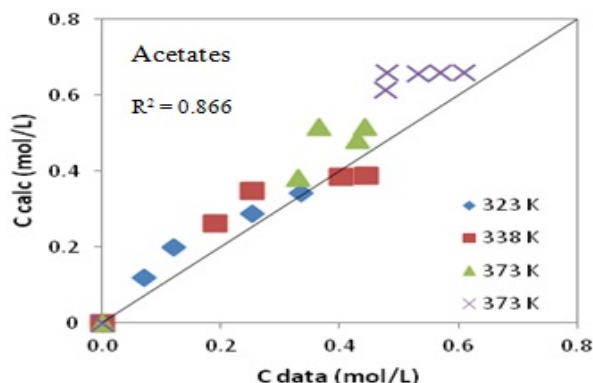




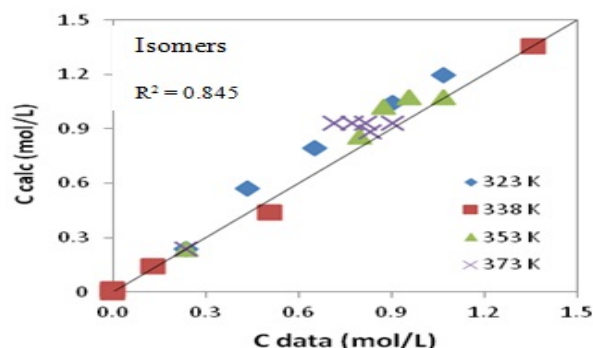
A pseudo homogeneous – 1<sup>st</sup> order model was used to describe the kinetics of the esterification of turpentine with acetic acid. Comparison between the experimental and calculated data was drawn and presented in Figure-7 - 9. From the figure can be seen that the data calculation is quite close to the experimental data for temperatures below 80 °C.



**Figure-7.** Comparison between the measured and the calculated concentration of  $\alpha$ -pinene at different temperatures.



**Figure-8.** Comparison between the measured and the calculated concentration of acetates at different temperatures.



**Figure-9.** Comparison between the measured and the calculated concentration of isomers at different temperatures.

The rate constant of total reaction (K) and the sub-reactions ( $k_1$  and  $k_2$ ) can be described with Arrhenius law:

$$K = A_{\text{total}} e^{-\frac{E_{\text{total}}}{RT}} \quad (13)$$

$$k_1 = A_1 e^{-\frac{E_1}{RT}} \quad (14)$$

From Equations. (13 – 14), plotting  $\ln K$  or  $\ln k$  versus  $1/T$ , a straight line can be drawn. And from its slope the value of activation energy can be obtained. The equation of the reaction rate constants can be written as:

$$K = 1.94 \times 10^6 \exp\left(-\frac{52052}{RT}\right) \quad (15)$$

$$k_1 = 4.34 \times 10^6 \exp\left(-\frac{31654}{RT}\right) \quad (16)$$

$$k_2 = 7.37 \times 10^4 \exp\left(-\frac{31654}{RT}\right) \quad (17)$$

The value of the activation energy in the equation above point out that the reactions proceed quite slowly. In addition, the value of activation energy of esterification (52052 kJ/kmol) is greater than the isomerization reaction (31654 kJ/kmol). This indicates that the temperature rise will be affecting the speed of esterification reaction than the isomerization reaction.

## CONCLUSIONS

The esterification of crude turpentine with acetic acid over Amberlyst 15 wet as catalyst in batch reactor system has been studied. Meanwhile, the isomerization reaction also took place. The optimum condition was observed at 2 hours of reaction time, ratio of acetic acid/turpentine of 3, catalyst concentration of 0.04 g/mL, stirring rate of 500 rpm, and at reaction temperature of 100 °C. At the optimum condition, the conversion of  $\alpha$ -pinene reached 100% with 50% selectivity of bornyl acetate.

Reaction products were grouped into acetates and isomers. The kinetic study was performed using the pseudo homogeneous first-order model. It is found that the reaction rate is slow in the temperature range 50 – 100 °C. Activation energy of the esterification and isomerization reaction was determined to be 52052 kJ/kmol and 31654 kJ/kmol, respectively.

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