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Esterification of α -pinene using TCA/Zeolite Y catalyst

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Abstract Indonesian turpentine oil contains α -pinene (70-90%), β -pinene (5-10%), and 3-carene (4-10%). This study aims to determine the effect of temperature, time, and mass of the catalyst on the α -pinene esterification. The esterification was carried out at 25, 40 and 50°C for 1, 2, 3, and 4 hours with variations in the catalyst mass of 100, 300 and 500 mg. This reaction was carried out in a three neck round bottom flask equipped with a heater, thermometer and magnetic stirrer. The ester produced in the α -pinene transformation through the esterification is carvyl acetate. The optimum results were obtained at temperature of 40°C and the addition of catalyst of 500 mg with α -pinene conversion of 67.81% and selectivity of carvyl acetate at 81.92% for 1 h.

1. Introduction

Pine tree is widespread throughout Indonesia's forests. Indonesian pine tree consist mainly of the species of *Pinus merkusii*, which contain around 82% α -pinene and 12% carene with various other components such as camphene, β -pinene and limonene. One of the efforts to develop the derivative of α -pinene was the transformation through the α -pinene esterification. The esterification is reversible and generally runs very slowly so that it requires a catalyst to speed up the reaction. The addition of catalysts can increase the selectivity of a reaction. Alpha pinene as the main compound of pine resin can be used as a raw material to produce several compounds using an acid catalyst. The production of some of these compounds can be performed by hydration, isomerization, and esterification [1-5]. Esterification with acid catalysts can be carried out using organic acids such as acetic acid [6], and natural zeolite [7]. Without catalyst, esterification can also be carried out using one molecule of carboxylic acid and reagent excessively [8].

The reaction of α -pinene with acetic acid is able to produce two types of products, esterification products and rearrangement products. The esterification products include bornyl acetate, phenyl acetate, and α -terpenyl acetate, while repetitive products include camphene, limonene, and terpineol [7-8]. The use of heterogeneous catalysts can be an alternative in the chemical industry, because of the ease in the process of separating catalysts from products, more environmentally friendly, reusable, and the price is generally lower than homogeneous catalysts [1-8].

Heterogeneous catalyst often used in esterification are zeolite A, zeolite X, zeolite Y, zeolite β , ZMS-5, MCM-41, Amberlyst UP15, and modernit [9-13]. Gainsford et al., (2001) has converted α -pinene to terpenyl acetate with the zeolite H-beta catalyst, the optimum results obtained at room temperature with a reaction time of 24 hours [9]. Liu et al., (2008) carried out the α -pinene esterification to α -terpenyl



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acetate with the highest α -terpenyl acetate selectivity of 27,8% using an acidic liquid ionic catalyst $[\text{HSO}_3-(\text{CH}_2)_3-\text{NEt}_3]\text{H}_2\text{PO}_4$ [12]. Synthesized terpenyl acetate using odesyl amine ethoxylate ionic liquid as a catalyst, optimum conditions were achieved in the ratio of n (α -pinene): n (ionic liquid): n (acetic acid) = 5: 0.3: 20; where n (α -pinene) = 0,05 mol; carried out at a temperature of 30°C with a reaction time of 10 hours to obtain yield of terpenyl acetate of 35.70% [13].

Zeolite Y is a type of zeolite with a large pore mouth size with a mean pore radius of around 0.75 nm. This relatively large pore mouth can be passed by molecules of long and large chain hydrocarbons such as α -pinene which are estimated to have a molecular size of 0.62 x 0.59 x 0.53 nm [14]. Properties of zeolites that is important as a heterogeneous catalyst is its acidity as a catalyst active site, which is the acidic site Bronsted and Lewis [15]. The addition of acidity from zeolite can be performed by developing active component salts such as Trichloroacetic Acid (TCA). This research aims to study the effect of temperature, reaction time, and mass of the esterification of α -pinene using a TCA/zeolite Y catalyst.

2. Method

The apparatus of this research are Gas Chromatography (GC) Agilent 6820, Gas Chromatography-Mass Spectrometry (GC-MS) Shimadzu QP-5000, and Fourier Transform Infrared (FT-IR) Shimadzu Instrument Spectrum One 8400 S. While the materials used are turpentine oil (Perum Perhutani Unit 1 Central Java), acetic anhydride (Panreac; Mr = 102,09; 99%, dichloromethane (Merck; Mr = 84,93 g/mol; 99%), distilled water, NH_4 -Zeolite Y (Riogen, Si / Al = 2,55; 98%), TCA (Merck; Mr = 163,38 g/mol; 99%), Na_2SO_4 anhydrous (Merck; Mr = 142,04 g / mol; 96%), saturated NaHCO_3 , NH_3 (Merck; 25%), and N_2 gas.

The α -pinene esterification was carried out by mixing 1 g of α -pinene obtained from turpentine oil, 12.5 mL acetic anhydride; 5 mL aquadest; and 10 mL dichloromethane. The α -pinene esterification was carried out at 25, 40, and 50°C temperature variations with the addition of 500 mg TCA/zeolite Y catalyst after the temperature was reached. During the reaction, 1 mL sample was taken after 1, 2, 3, and 4 hours at temperature variations to obtain the optimum temperature. The reaction mixture was then separated from the catalyst with a centrifuge for 10 minutes at a stirring speed of 350 rpm. The α -pinene esterification was also carried out on the TCA/zeolite Y 100, 300, 500 mg catalyst mass variation at the optimum temperature in order to obtain the optimum catalyst mass addition. The results were analyzed using FT-IR, GC, and GC-MS.

3. Result and Discussion

TCA for H-zeolite Y was prepared using the impregnation method. The impregnation is a method of attaching a material to a material that has a large pore and surface area in the solvent. The IR spectra of the TCA/zeolite Y catalyst revealed U stretching OH absorption at wave number 3468 cm^{-1} , OH buckling vibrations at 1637 cm^{-1} , O-Si-O/O-Al-O asymmetric stretch vibration at 1049 cm^{-1} , single carbon oxygen CO bond appear at 1099 cm^{-1} , stretching vibration O-Si-O symmetry/O-Al-O at 795 cm^{-1} , double ring at 579 cm^{-1} and vibration buckling Si-O/Al-O at 465 cm^{-1} (Figure 1).

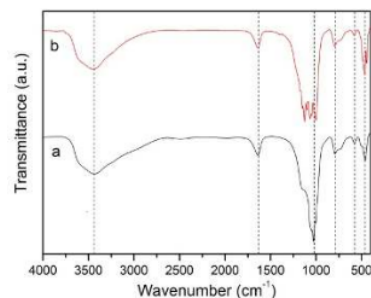


Figure 1. IR spectra of (a) H-zeolite Y; and (b) TCA/zeolite Y

The transformation of α -pinene from turpentine oil through the α -pinene esterification has been carried out in this study using acidic TCA/zeolite Y catalysts. Variations made in the α -pinene esterification were variation of time (1, 2, 3 and 4 hours), temperature (25, 40 and 50 °C) and mass of catalyst (100, 300, and 500 mg). Then the reaction product was analyzed using GC and IR. The transformation of α -pinene through the α -pinene esterification is presented in Figure 2.

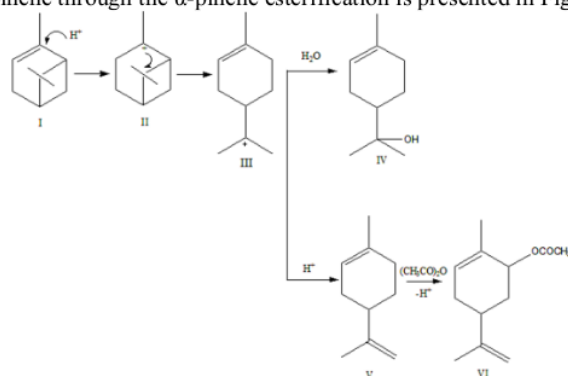


Figure 2. Schematic of α -pinene esterification: (I) α -pinene; (II) pinanyl; (III) p-menthenyl cation; (IV) α -terpineol; (V) limonene; and (VI) carvyl acetate

Transformation of α -pinene through esterification occurs in two stages of the reaction to produce α -terpineol and carvyl acetate. The transformation of α -pinene through the esterification was carried out at 25, 40, and 50°C for 1 h. The esterification results with a α -pinene mole ratio with acetic anhydride of 1:30 and the addition of 500 mg of catalyst. The effect of temperature on the conversion of α -pinene and selectivity of carvyl acetate produced is presented in Figure 3. The conversion of α -pinene and selectivity of carvyl acetate was fluctuated. In this study, selectivity of carvyl acetate with temperature variations of 25, 40, and 50°C obtained optimum results at temperatures of 40°C with a selectivity of 85.01%. The increase in temperature resulted in a very active movement of the reactants so that there are hindrance between the active side of the reactant molecule and the active site of the catalyst. In addition, the decrease in conversion results can be caused by decreased catalyst performance due to the closure of the surface of the catalyst by reactant molecules that are not ducted [14].

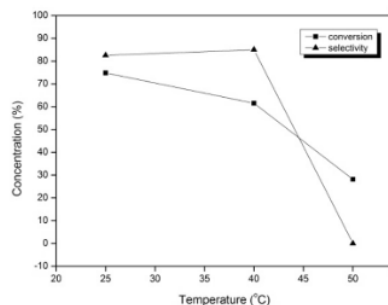


Figure 3. Effect of temperature on α -pinene conversion and carvyl acetate selectivity

The optimum temperature of α -pinene esterification was at 40°C. Furthermore, the α -pinene esterification was carried out with variations of time of 1, 2, 3, and 4 hours at 40°C and 500 mg of catalyst. The effect of reaction time on α -pinene conversion and the selectivity of carvyl acetate is presented in Figure 4. the α -pinene conversion occurs with increasing reaction time. The selectivity of carvyl acetate with variations in reaction time of 1, 2, 3, and 4 hours resulted optimum results at the reaction time of 1 h with α -pinene conversion of 61.55% and selectivity of 85.01%.

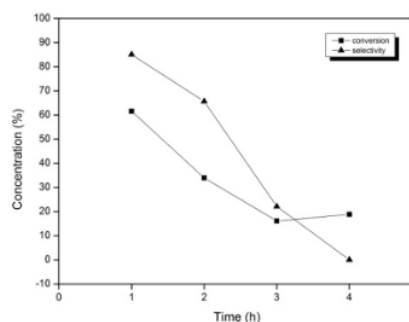


Figure 4. Effect of reaction time on α -pinene conversion and carvyl acetate selectivity

The results obtained should be increased conversions with increasing time [15]. This is because the α -pinene continues to react with the reactants to produce products over an increasing amount of time. While increased selectivity indicates that the desired product is increasing and the selectivity is decreasing due to the desired product has reached its maximum point or undergoes further chemical reactions so that it turns into another product [16]. Incompatibility of the results obtained due to the hydrolysis of esters. Esterification is a reversible reaction that produces a by-product in the form of water. The presence of water will cause the reaction to shift to the left side so that the methyl ester will be hydrolyzed. In addition, if the equilibrium of the reaction has been reached then increasing the reaction time will not be beneficial because it does not increase the results.

The α -pinene esterification was carried out with a catalyst mass variation of 100, 300, and 500 mg using an optimum temperature of 40°C with a reaction time of 1 hour. The effect of catalyst mass variation to α -pinene conversion and carvyl acetate selectivity is presented in Figure 5.

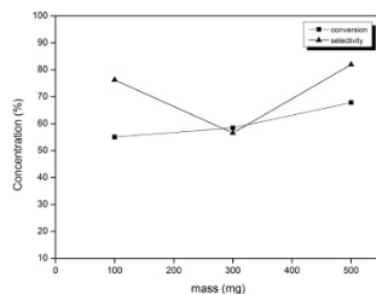


Figure 5. Effect of catalyst mass variation on α -pinene conversion and carvyl acetate selectivity

The α -pinene conversion increases with increasing mass of the catalyst. While the selectivity of carvyl acetate products fluctuated. In this study, the optimum addition of catalyst mass was the addition

of 500 mg with α -pinene conversion of 67.81% and selectivity of 81.92%. Increasing amount of catalyst mass causes the increasing number of active sides, which will give the opportunity for more product formation or higher conversions. The more catalysts used, the more surface area of the catalyst so that the acidic sites on the catalyst are utilized during the reaction and more products will be produced [17].

4. Conclusion

The esterification reaction using the TCA / Zeolite Y catalyst produced carvyl acetate with 81.92% selectivity at 40°C, 1 hour reaction time and 500 mg catalyst mass with α -pinene conversion of 67.81%.

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