

Esterification of α -Pinene from Turpentine Oil Using Natural Zeolite Catalyst

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Abstract. Turpentine is one of the oils obtained from pine trees with >80% α -pinene composition. Turpentine oil has a high selling value by making α -pinene derivative through an esterification reaction. The esterification reaction was carried out with time variation and reaction temperature using natural zeolite. Characterization of the catalyst using X-Ray Diffraction, IR spectroscopy and Scanning Electron Microscopy. The esterification reaction product was analyzed by IR spectroscopy, and Gas Chromatography - Mass Spectroscopy. The main product of α -pinene esterification reaction was α -terpinyl acetate (21.40%), and the selectivity of 28.87 %, produced at 40 °C for 3 hours.

1. Introduction

Most of the pine trees in Indonesia is the kind of Pinus which produces turpentine with a composition of 82% α -pinene and other components. Attempts to get oil terpentin added value is through a distillation process that produces components of turpentine oil. One effort that turpentine oil has a high sales value is by conducting an esterification reaction α -pinene to produce α -terpinyl acetate which is used widely in the perfume industry, especially on the soap. However, the presence of the wild-bit terpenil acetate and the need is less economical so as to get it done by isolating it from the plant [1-3]. Natural zeolites are zeolites are widely available on the volcano and mined directly from nature that cost far less than the zeolite synthesis. The main content of natural zeolite mineral mordenite, the ratio Si / Al is high so it has high thermal stability [4].

Esterification reaction between α -terpineol and acetic anhydride with a yield of 5.57% and a purity of 67.50% at room temperature. Gainsford et al [1] carry out the conversion of α -pinene into α -terpinyl acetate with H-beta zeolite at room temperature in 24 hours resulted in a 29% yield. Liu et al [2] conducted an esterification reaction α -pinene into α -terpinyl acetate selectivity α -terpinyl highest acetate 27.8% using acidic ionic liquid catalyst is $[\text{HSO}_3-(\text{CH}_2)_3-\text{Net}_3] \text{H}_2\text{PO}_4$. Li et al [3] conducted a synthesis terpenil acetate using an ionic liquid as a catalyst octadecyl amine ethoxylates, optimum condition is achieved at a ratio of n (α -pinene): n (ionic liquids): 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 terpenil acetate yield of 35.70%.

This work to study to change the oil component of turpentine in the form of a compound α -pinene to terpenil acetate by the esterification reaction using natural zeolite catalyst.

2. Method

The tools used in the study is a fractional distillation under reduced pressure, IR spectrophotometer, X-ray diffraction, Scanning Electron Microscopy (SEM), and Gas Chromatography-Mass Spectrometer. The material used is turpentine oil, distilled water, natural zeolite, ammonia, pyridine, Na_2SO_4 , acetic anhydride, filter paper, dichloromethane, saturated sodium bicarbonate.



Esterification of α -pinene,

α -Pinene 0.5g were mixed in 10 mL of acetic anhydride, 10 mL H_2O , 10 mL of dichloromethane and then stirred using a mechanical stirrer for 3 hours at a temperature of 40 °C with 0.5 g of activated natural zeolite in a closed flask equipped with a thermometer. The reaction products were tested with the GC, FTIR, GC-MS.

3. Result and Discussion

3.1. Characterization of natural zeolite

Natural zeolites are shaped chunks of crushed then pulverized and sieved with a 100 mesh sieve in order to be the same size and the natural zeolite surface area becomes larger. Activation of natural zeolite with acid and salt treatment aims to improve the performance of natural zeolite. Natural zeolites are already activated with HF 1% and then soaking with 6M HCl solution aimed dealuminated natural zeolite can improve the ratio of Si/Al.

The results of the analysis of activated natural zeolite with XRD in Figure 1 shows that there are three highest peaks in the H/ZA is at $2\theta = 27,21^\circ$; $21,34^\circ$ and $25,09^\circ$. The specific peaks is the peak of morderitie at $2\theta = 20,9^\circ$; $25,63^\circ$; 26° ; $26,25^\circ$; $27,67^\circ$. While the typical peak for morderit located on the highest peak at $2\theta = 25,631^\circ$ and $27,651^\circ$ (JCPDS No. 700232). Suitability pattern difraktogram H/ZA with morderit can be concluded that the samples H/ZA has type structure mordernit

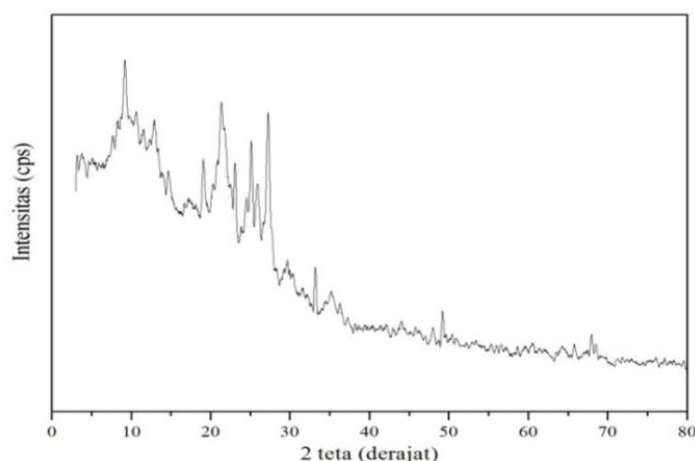


Figure 1. Diffractograms of catalyst H/ZA

Determination of the number of catalyst acid sites H/ZA with ammonia of 0.81 mol / g, whereas with pyridine of 0.79 mol/g. The total number of acid sites with ammonia on the H/ZA catalyst is higher than the number of acid sites with pyridine. This is because ammonia is a stronger base than pyridine. In addition, the size of the ammonia molecule is relatively smaller than the pyridine adsorbed onto the surface in the pores, while the pyridine is only adsorbed on the outer surface (pore mouth).

The results of the scanning using SEM in Figure 2, obtained a morphological picture of H/ZA at 5000x magnification showed that the size of the distribution reached 20 micrometers scale. at 10,000x magnification shows that the distribution size reaches 10 micrometers scale. The molecular size of H/ZA is uneven and irregularly shaped.

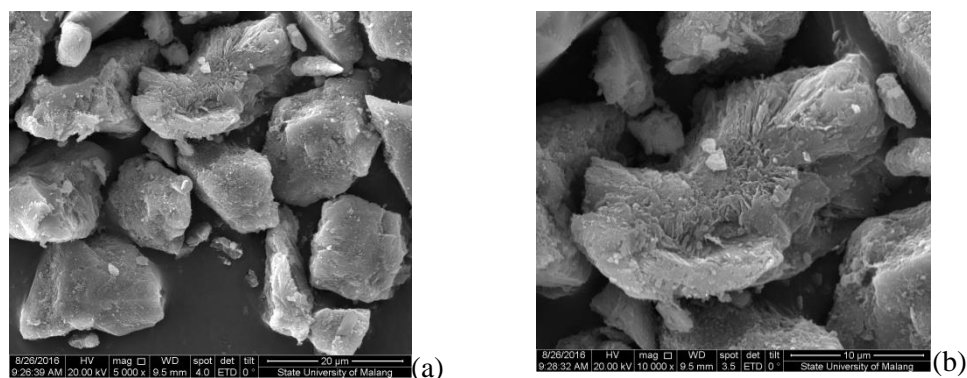


Figure 2. The morphology of H/ZA (a) magnification 5.000x (b) magnification 10.000x

3.2. The Esterification from turpentin oil

The main component of turpentin oil are the monoterpene compounds. The monoterpenes are essential ingredients in fine chemical industry and flavor and perfume industry. The most important constituents of monoterpenes are α - and β -pinene (Figure 3).

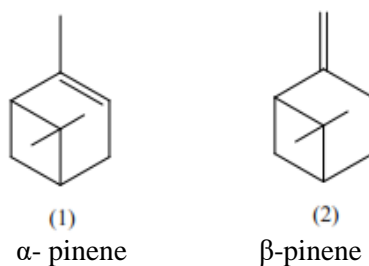


Figure 3. (1) α - and (2) β -pinene

The turpentine oil are mobile liquids, usually non-coloured or slightly colored. The boiling point of the turpentine oil between 155-156°C, the specific gravity (20°C) varies between 0.854-0868 g/mL and the refractive index (20°C) between 1.4656. The oils are not soluble in water, but soluble in ethers, dichloromethane and in other oils. Highly pure α - and (2) β -pinene can be obtained by fractional distillation of turpentine oil. The main component of turpentine oil are α -pinene. Indonesia turpentine oil contains about 57-86% α - pinene, 8-12% β -pinene and other groups monoterpenes with a number of minor (Figure 4). The main products obtained from turpentine oil are camphene, limonene, terpinene, terpinolene, α -terpineol, and terpinyl acetate, etc. [5].

The results of the identification of physical compound α -pinene which is a liquid, colored clear and distinctive smell like turpentine. Based on the analysis using FTIR, α -pinene, group C = C at wave number 1650 cm^{-1} showed that α -pinene including alkenes [6-7]. From gas chromatographic yield of α -pinene turpentine oil isolated by 98.10%. The content of turpentine oil is the largest in the compound α -pinene about 82%.

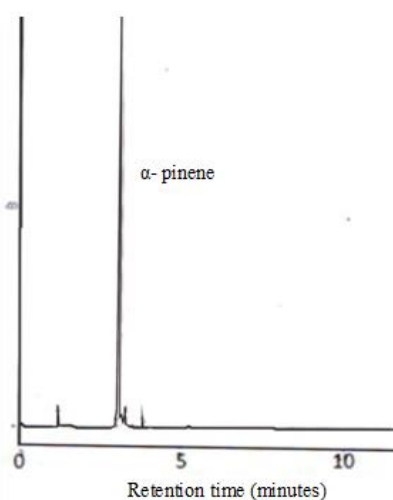


Figure 4. Chromatogram of turpentine oil

Alpha pinene esterification reaction takes place in situ in a reaction that occurs through hydration reactions prior to the addition of distilled water to form α -terpineol then α -terpineol formed will undergo an esterification reaction with acetic anhydride to form α -terpinyl acetate. In this case allow for other products in the esterification reaction α -pinene as fencyl acetate, bornil acetate, fencyl alcohol, α -terpineol and borneol.

The α -pinene esterification reaction with variation of reaction time of 2, 3 and 4 hours yields terpinyl acetate with yields of 16.04, 21.40, and 28.77% with the conversion of 51.57, 74.13 and 94.68%.

Table 1. Results of α -pinene esterification reaction time variations

Time (h)	C (%)	Yield (%)						Selectivity α -terpinyl acetate
		Fencyl alcohol	Borneol	α -terpineol	Fencyl acetate	Bornil acetate	α -terpinyl acetate	
2	51.57	1.06	1.44	26.45	2.42		16.04	31,10
3	74.13	1.67	0.44	43.31	3.76	1.02	21.40	28,87
4	94.68	3.16	1.49	55.32	3.62		28.77	30,38

Reaction conditions: 0.5 g of pinene, 10 mL of acetic anhydride, 5 mL H₂O, 10 mL dichloromethane, T = 40 °C

The α -pinene esterification with temperature variations of 30, 40 and 60 °C with reaction time of 3 hours and the ratio of pinene acetic anhydride compound (1:15) yielded α -terpinyl acetate with 0.18, 21.40, and 14.72% with the conversion of 4.99, 74.13 and 52.44.

The effect of reaction temperature on α -pinene esterification is shown in Table 2. When the temperature was low, the yield of α -terpinyl acetate was low. As the temperature was increased, the yield of α -terpinyl acetate increased accordingly. When the temperature was high, the yield of α -terpinyl acetate tended to decreased. The results showed the yield of α -terpinyl acetat first increased and then decreased with increasing temperature [3].

Table 2. The effect of reaction temperature on α -pinene esterification reaction

Temp (°C)	C (%)	Yield (%)						Selectivity α -terpinyl acetate
		Fencyl alcohol	Borneol	α -terpineol	Fencyl acetate	Bornil acetate	α -terpinyl acetate	
30	4,99	0,15	0,14	0,74	0,33	0,94	0,18	3,68
40	74,13	1,67	0,44	43,31	3,76	1,02	21,40	28,87
60	52,44	0,35	23,62	1,21	1,65	1,65	14,72	28,08

Reaction conditions: 0.5 g of pinene, 10 mL of acetic anhydride, 5 mL H₂O, 10 mL dichloromethane, t = 3 hours

The results of the analysis of esterification of α -pinene using FTIR in Figure 5 that the aliphatic CH absorptions at wave number 2923 cm^{-1} , group C = C at wave number 1617 cm^{-1} , group C = O at wave numbers between $1735\text{--}1750\text{ cm}^{-1}$ and the peak of the C-O group at wave numbers between 1050 to 1300 cm^{-1} can be concluded that the compounds produced an ester compound. α -pinene that no group C-O and C = O indicates that the compounds produce ester esterification of alkenes.

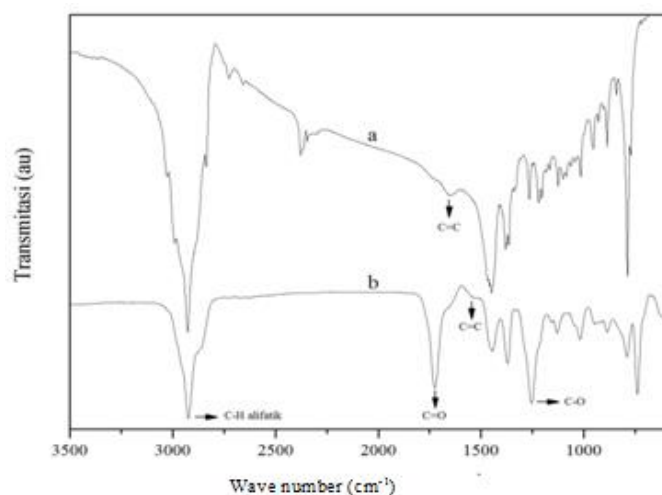


Figure 5. The IR spectrum (a) compound α -pinene (b) the results of esterification results of α -pinene esterification reaction time of 3 hours, a temperature of $40\text{ }^{\circ}\text{C}$.

The α -pinene compound has a fairly stretchy structure and the presence of a double-bonded reactive ring within the α -pinene structure makes it easy to participate in cycle-opening reactions and molecular rearrangement reactions. The esterification reaction mechanism of the α -pinene compound is shown in Figure 6.

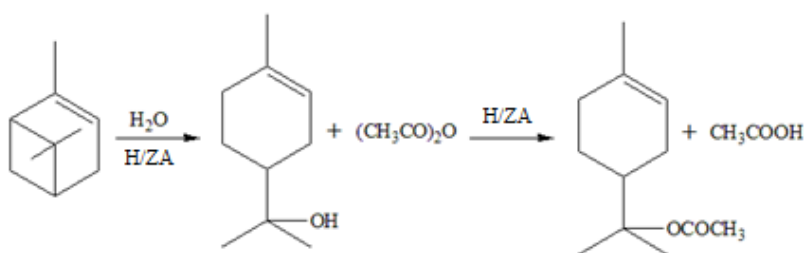


Figure 6. The esterification reaction mechanism of the α -pinene compound

4. Conclusion

The α -pinene esterification reactor using natural zeolite catalyst at $40\text{ }^{\circ}\text{C}$ for 3 hours with a reactant mole ratio between α -pinene and acetic anhydride (1:15) yielded α -terpenyl acetate of 21.40% and selectivity 28.87 %

5. Acknowledgement

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6. References

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