

Esterification of Indonesian Turpentine with Acetic Acid over Ion-Exchange Resin

Diana^{1,2}, Sutijan², Rochmadi² and Arief Budiman²⁺

¹ Chemical Engineering Department, Islamic University of Indonesia, Jl. Kaliurang KM 14.5 Yogyakarta, Indonesia

² Chemical Engineering Department, Gadjah Mada University, Jl. Grafika 2 Yogyakarta 55281, Indonesia

Abstract. Pine trees in Indonesia are largely of pine mercusii species which typically give turpentine that contains about 79% α -pinene, 12% carene and balanced with other numerous components such as camphene, β -pinene and limonene. In this work, heterogeneously-catalyzed liquid phase reaction of turpentine with acetic acid was studied. The catalytic experiments were carried out over Amberlyst 36 wet and Dowex 50x4 catalysts. Reactions at atmospheric condition and various temperatures were investigated. The effects of α -pinene concentration in turpentine were taken into account. The reaction produced two series of products, esterification products (acetates) and rearrangement products (isomers). The objective of this work was to study the feasibility of using crude of Indonesian turpentine in batch esterification of α -pinene to produce bornyl acetate. It was found that purification of turpentine up to 88% α -pinene does not give significant difference to its original. Experiment shows that original turpentine reached 100% conversion of α -pinene and 26% selectivity of bornyl acetate after 6 hours of reaction at 90°C.

Keywords: Turpentine, esterification, bornyl acetate, ion-exchange resin catalyst

1. Introduction

α -Pinene (C₁₀H₁₆) is the main constituent of turpentine oil. It is naturally occurring monoterpenes used as substrates for the production of monoterpenoid flavours and fragrances. Acid catalyzed hydration and esterification of terpenes are among the important synthetic routes to valuable terpenic alcohols and esters which find many applications in perfumery and pharmaceutical industry [1]. Bornyl acetate and α -terpinyl acetate are important fine chemicals that can be synthesized by direct esterification of α -pinene with acetic acid. This reaction can produce two series of products, esterification products and rearrangement products. The rearrangement products are isomers of α -pinene, such as camphene, limonene, and terpinolene [2].

Strong mineral acid such as H₂SO₄ is frequently used for esterification of terpenes. However, in addition to difficulties in separation, the disposal of this catalyst poses a serious environmental problem. Therefore, solid acid catalysts have been considered to solve this problem. The reaction of α -pinene and acetic acid has been earlier investigated by several research groups by using various solid catalysts, namely zeolite beta [3], SBA-15 with sulfonic acid [4], heteropoly acids [5] and Amberlyst 70 [6]. The use of acidic ionic liquid as a heterogenous catalyst also has been reported [2].

In this work, we studied esterification of turpentine with glacial acetic acid using cation exchange resin (Amberlyst 36 wet and Dowex 50x4) as catalyst. In general, ion-exchange resins are often employed in various esterification, dehydration, alkylation, and hydrolysis.

2. Objectives

⁺ Corresponding author. Tel.: +628164262111.
E-mail address: abudiman@chemeng.ugm.ac.id.

The effect of turpentine purity, catalyst and temperature in esterification of α -pinene were studied in this paper. It is aimed to select the best raw material and catalyst, as well as reaction condition to produce bornyl acetate.

3. Materials and Methods

3.1. Materials

Turpentine was obtained as a gift from Perhutani Pine Chemical Industry (Indonesia). It was vacuum distilled to get higher purity of α -pinene. GC analysis confirmed that the concentration of α -pinene in the original turpentine and distilled turpentine were 79% and 88% respectively. Glacial acetic acid (Merck) and the catalysts (Amberlyst 36 wet and Dowex 50Wx4) were purchased and used without further treatment.

3.2. Apparatus and General Reaction Procedure

The experiments were conducted using three necked glass reactor equipped with condenser and thermocouple. The reactor was immersed in a thermostatic oil bath in order to maintain the reaction temperature. In batch reactor, the same volume (50 mL) of turpentine and glacial acetic acid were heated up to the required temperature. Once it was reached, 5 g of catalyst was loaded. The mixture was magnetic stirred and the reaction time was started to be counted. Aliquots were taken and analyzed in GC.

3.3. Product 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 Pacard 5890 Series II) equipped with flame ionization detector/FID and a HP-5 capillary column. Helium was used as the carrier gas in the GC (flow 25 mL/min) with the following temperature programming: the detector and injection port temperature of 250 °C, column temperature ranging from 70 to 280 °C with the holding time of 5 min at the initial temperature and the heating ramp of 5 °C/min.

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; 30 m; 0.25 mm ID was used as the column and the carrier gas was helium. 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. Pressure: 13.7 kPa; Total flow: 60.0 mL/min; Column flow: 0.5 mL/min.

The concentrations of reactants and products were directly shown by the system of GC chemstation according to the area of each chromatograph peak. The α -pinene conversion, product selectivities and yields were calculated as follows:

$$X (\%) = \frac{(\text{GC peak area of } \alpha\text{-pinene})_{\text{initial}} - (\text{GC peak area of } \alpha\text{-pinene})_{\text{final}}}{(\text{GC peak area of } \alpha\text{-pinene})_{\text{initial}}} \times 100 \quad (1)$$

$$S_i (\%) = \frac{\text{GC peak area of product } i}{(\text{GC peak area of } \alpha\text{-pinene})_{\text{initial}} - (\text{GC peak area of } \alpha\text{-pinene})_{\text{final}}} \times 100 \quad (2)$$

4. Results and Discussion

4.1. Effect of Turpentine Purity

The effect of turpentine purity was examined at 75 °C with Amberlyst 36 wet as catalyst, and the results are presented in Fig. 1 and 2. Distribution of esterification products (acetates) and rearrangement products (isomers) during the process are described in Fig. 1. Camphene, limonene, terpinenes, and terpinolene are the isomers from the rearrangement reaction. Bornyl acetate is the main esterification product. GC analysis also identified small amount of fenchyl acetate and terpinyl acetate.

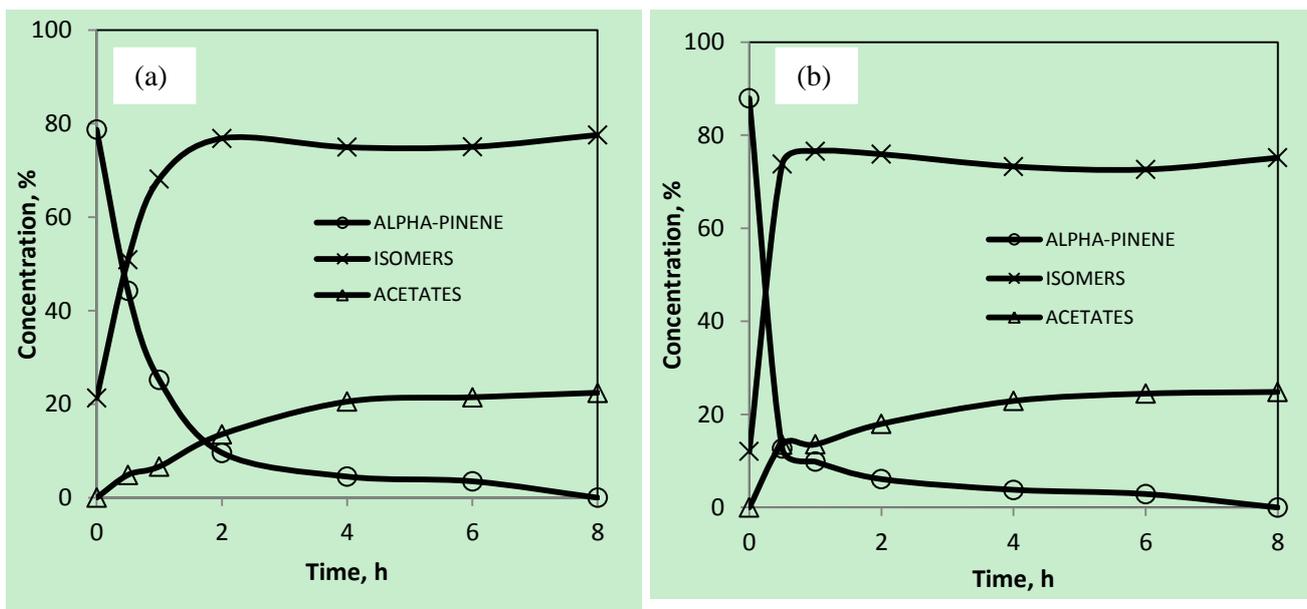


Fig. 1: The concentration evolution over time. (a) original turpentine (b) distilled turpentine (catalyst: Amberlyst 36 wet, temperature: 75°C)

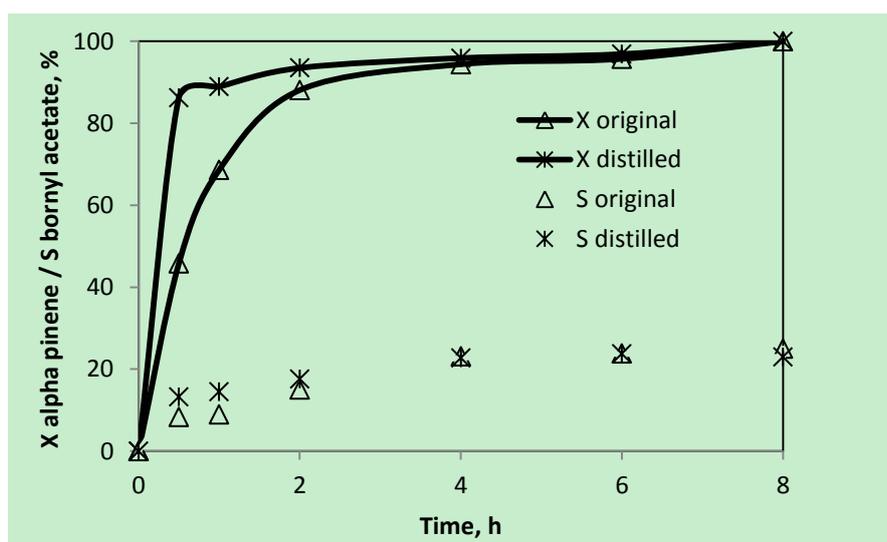


Fig. 2: Effect of turpentine purity on the conversion of α -pinene and selectivity of bornyl acetate (catalyst: Amberlyst 36 wet, temperature: 75°C)

From Fig. 2. it can be observed that both original turpentine (79% α -pinene) and distilled turpentine (88% α -pinene) perform significantly different only in the first 2 hours. In the beginning, concentration of α -pinene in distilled turpentine is higher than the one in original turpentine thus it leads to enhance the reaction rate. But after 4 hours of reaction, the conversion of α -pinene and the selectivity of bornyl acetate are similar and tend to be constant. Both turpentine could reach 100% of conversion after 8 hours of the process.

The selectivity of bornyl acetate is increasing during the process. The highest selectivity that can be achieved by original turpentine is 25%. Previous researcher studied acetoxylation of α -pinene with cation exchanged zeolite beta for 24 hours, resulted in 14% of bornyl acetate selectivity [3]. When SBA-15 with sulfonic acid group was applied as catalyst, it only attain 7% after 30 hours of reaction [4]. Meanwhile, esterification of α -pinene using acidic ionic liquids for 10 hours can reach 42.1% of bornyl acetate [2]. At 100°C and high pressure (20 bar) condition, the selectivity can get 40.6% after 10 hours of reaction using Amberlyst 70 wet [6].

4.2. Effect of Catalyst Type

A comparison was drawn between two type of cation exchange resins, under the same experimental condition. The physical properties of both catalysts are shown in Table 1. It is found that the average particle size of Amberlyst 36 wet is larger than that of Dowex 50 Wx4 but their surface area are similar. Moreover, the acid sites of Dowex Wx4 is nearly half of Amberlyst 36 wet's acid site. This could be inferred that the conversion of turpentine as well as bornyl acetate selectivity catalyzed by Amberlyst 36 wet would be higher than those catalyzed by Dowex 50 Wx4, as is shown in Fig. 3.

Table 1: Physical Properties of the Cation Exchange Resins

Properties	Amberlyst 36 wet	Dowex 50 Wx4
Physical form	Beads	Beads
Ionic form as shipped	Hydrogen	Hydrogen
Concentration of acid sites	2.07 eq./L	1.2 eq./L
Particle size (mm)	0.700 – 0.950	0.149 – 0.297
Surface area (m ² /g)	33	30
Average pore diameter (nm)	24	n/a
Max operating temperature (°C)	150	n/a

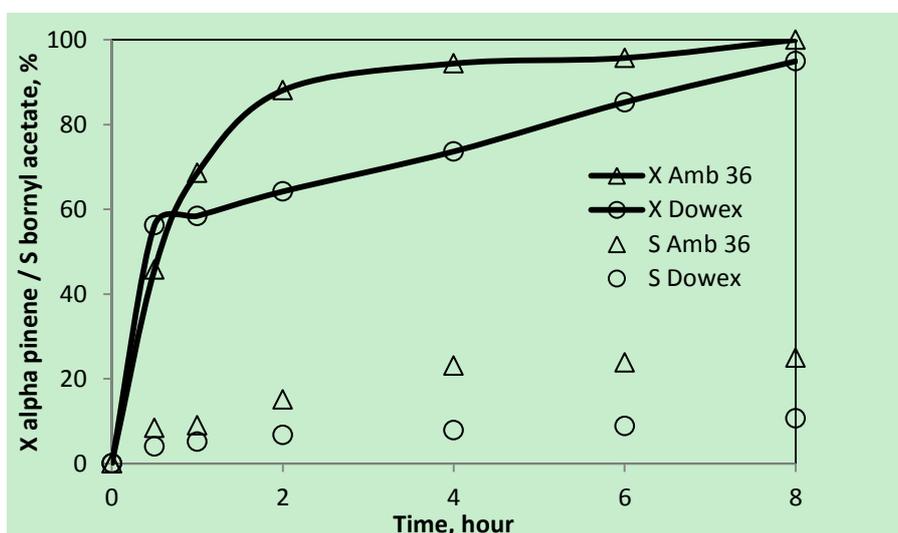


Fig. 3: Effect of catalyst on the conversion of α -pinene and selectivity of bornyl acetate (original turpentine, temperature: 75°C)

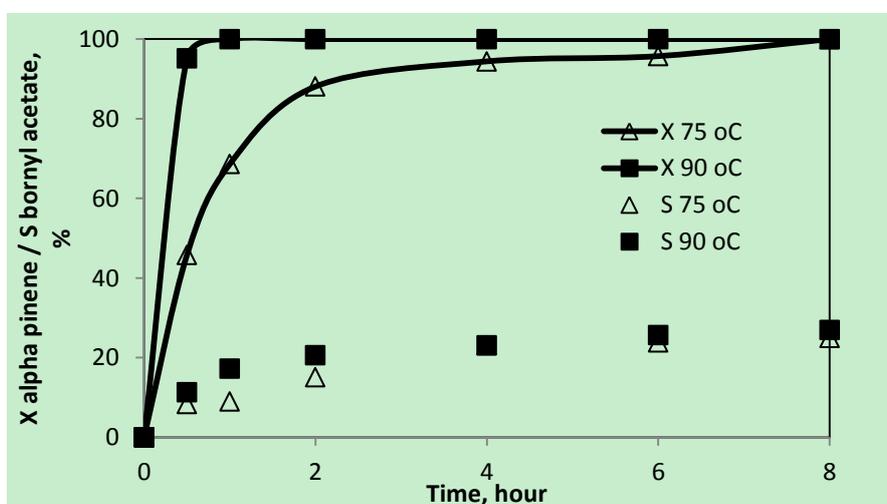


Fig. 4: Effect of temperature on the conversion of α -pinene and selectivity of bornyl acetate (original turpentine, catalyst: Amberlyst 36 wet)

4.3. Effect of Temperature

The effect of temperature on the conversion of turpentine and the selectivity of bornyl acetate was investigated. The catalytic experiments using original turpentine were carried out at temperatures of 75°C and 90°C. Fig. 4 shows the influence of temperature on the esterification of α -pinene in turpentine. It was observed that the conversion of α -pinene and the selectivity of bornyl acetate increase with the temperature.

At temperature of 90°C, complete conversion is reached only after 1 hour of experiment, but the selectivity of bornyl acetate still increases hereafter. This indicates that α -pinene converted to bornyl acetate via intermediate compound.

5. Conclusion

Turpentine (79% α -pinene) can be esterified with glacial acetic acid using cation exchange resin as catalyst to produce bornyl acetate. Purification of turpentine up to 88% α -pinene does not give significant difference to its original. Equivolume of original turpentine and glacial acetic acid, added with 5% Amberlyst 36 wet as catalyst reached 100% conversion of α -pinene and 26% selectivity of bornyl acetate after 6 hours of reaction at 90°C. The potential of using raw turpentine is interesting. Vacuum distillation that is applied to purify turpentine is an energy consumed process. It will be a great advantage if this step can be neglected.

6. Acknowledgements

The authors would like to acknowledge the Directorate General of Higher Education, Ministry of National Education, Indonesia, for financial support of this work through research grant of Hibah Disertasi 2013-2014, Islamic University of Indonesia and the scholarship of doctorate program (BPPDN) at Gadjah Mada University.

7. References

- [1] W. E. Erman, Chemistry of monoterpenes, an encyclopedic handbook. Marcel Dekker, New York.
- [2] Shiwei Liu, Congxia Xie, Shitao Yu, Fusheng Liu, and Kaihui Ji. Esterification of α -pinene and acetic acid using acidic ionic liquids as catalyst. *Catalysis Communications*. 2008. 9:1634–1638.
- [3] M. K. Yadav, M. V. Patil and R. V. Jasra. Acetoxylation and hydration of limonene and α -pinene using cation-exchanged zeolite beta. *Journal of Molecular Catalysis A: Chemical*. 2009. 297: 101–109.
- [4] J. Machado, J. E., Castanheiro, J. Matos, A. M., Ramos, J. Vital, and I. M. Fonseca. SBA-15 with sulfonic acid groups as a green catalyst for the acetoxylation of α -pinene. *Microporous and Mesoporous Materials*, 2012. 163:237-242.
- [5] P. A Robles-Dutenhefner, K. A. da Silva, M. R. H. Siddiqui, I. V. Kozhevnikov, and E. V., Gusevskaya. Hydration and acetoxylation of monoterpenes catalyzed by heteropoly acid. *Journal of Molecular Catalysis A: Chemical*. 2001. 175: 31–42.
- [6] M. Golets, S. Ajaikumar, D. Blomberg, H. Grundberg, J. Warna, T. Salmi, and J. P., Mikola. Liquid phase acetoxylation of α -pinene over Amberlyst-70 ion-exchange resin. *Applied Catalysis A: General*. 2012, 435-436:43–50.