

ESTERIFICATION OF INDONESIAN TURPENTINE USING ION-EXCHANGE RESIN AS SOLID ACID CATALYST

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Abstract

α -Pinene is the main constituent of turpentine oil which can be derived to several valuable products. This paper studied heterogeneously-catalyzed liquid phase esterification of turpentine (79% α -pinene) with acetic acid. The catalytic experiments were carried out over various ion-exchange resins as solid acid catalysts. Reactions under atmospheric pressure and a temperature range of 45 – 90 °C were observed. Effect of α -pinene concentration in turpentine were investigated. Bornyl acetate was obtained to be the major esterification product. Small amount of fenchyl acetate and terpinyl acetate were detected. The reaction not only produced esterification products but also rearrangement products. The rearrangement products were mainly camphene, limonene, terpinene and terpinolene. It was found that purification of turpentine up to 88% α -pinene does not give significant difference to its original. Experiment shows that esterification of crude Indonesian turpentine over Amberlyst UP15 reached 100% conversion of α -pinene and 28.9% selectivity of bornyl acetate after 8 hours of reaction at 90°C. With the same condition, selectivity of bornyl acetate can achieve 26.2% when Amberlyst 36 wet is applied.

Keywords: Turpentine, Esterification, Bornyl acetate, Ion-exchange resin, Solid acid catalyst.

1. Introduction

Indonesia is one of the largest turpentine producer in the world. Indonesian turpentine is the volatile oil distilled from pine resin, which is obtained by tapping

Nomenclatures

Ac	concentration of active sites, eq./L
As	surface area, m ² /g
Cw	water retention capacity, %
Davg	average pore diameter, nm
Dp	mean size, mm
T	reaction temperature, °C
Tmax	maximum operating temperature, °C
S _i	selectivity of bornyl acetate, %
X	conversion of α-pinene, %

trees of the genus *Pinus merkusii*. Traditionally, turpentine has been employed as a solvent or cleaning agent for paints and varnishes. Nowadays, most turpentine is used as a source of chemical isolates which are then converted into a wide range of products.

Pine trees in Indonesia are largely of pine *merkusii* species which typically give turpentine that contains about 80% α-pinene, 12% carene and balanced with other components such as camphene, β-pinene and limonene. α-Pinene (C₁₀H₁₆) is naturally occurring monoterpenes used as substrates for the production of monoterpenoid flavours and fragrances. Among the most important synthetic routes to valuable terpenic alcohols and esters are acid catalyzed hydration and esterification of terpenes [1]. The reaction products find many applications in perfumery and pharmaceutical industry [2].

Direct reaction of α-pinene with acetic acid 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. Bornyl acetate, fenchyl acetate and α-terpinyl acetate are the esterification products [3]. Furthermore, bornyl acetate then can be saponified to produce borneol, which has many applications in medicine.

Strong mineral acid such as H₂SO₄ 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 α-pinene and acetic acid using heterogeneous catalysts. Liu et al. [3] employed acidic ionic liquid as a heterogeneous catalyst. The use of various solid catalysts, namely zeolite beta [4], SBA-15 with sulfonic acid [5], heteropoly acids [6] and Amberlyst 70 [7] also has been reported.

Direct use of crude Indonesian turpentine is promising as it contains high concentration of α-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 α-pinene over ion-exchange resins. The reaction conditions were explored for aiming an efficient conversion of α-pinene to a mixture of valuable products, particularly bornyl acetate.

2. Experimental

2.1. Materials

Turpentine and α -pinene (98% purity) were obtained as a gift from Perhutani Pine Chemical Industry (Indonesia). To get variation of turpentine purity, turpentine was vacuum distilled several times. GC analysis confirmed that the concentration of α -pinene in the crude turpentine (ori) was 79% while in the distilled turpentines were 88% (dist 1) and 93% (dist 2) respectively. Glacial acetic acid (Merck) and the catalysts (Amberlyst 36 wet, Amberlyst 15 wet, Amberlyst UP 15, and Dowex 50Wx4) were purchased and used without further treatment.

2.2. Apparatus and procedures

Three necked glass flask equipped with condenser and thermocouple was used as the reactor to conduct the experiments. The reactor was immersed in a thermostatic oil bath in order to maintain the reaction temperature. Equivolume of turpentine (50 mL) and glacial acetic acid (50 mL) were heated up in the batch reactor 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. Selected samples were analyzed in GC-MS as well.

2.3. 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 Packard 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 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; 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 and selectivity of bornyl acetate were calculated using Eqs. (1) and (2).

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

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

3. Result and Discussion

3.1. Effect of catalyst type

A comparison was drawn between four types of cation exchange resins, under the same experimental condition. The physical properties of the catalysts are shown in Table 1.

Table 1. Physical Properties of The Cation Exchange Resins.

Properties	Amberlyst 36 wet	Amberlyst 15 wet	Amberlyst UP15	Dowex 50Wx4
Physical form	Beads	Beads	Beads	Beads
Colour	Grey	Opaque	Black	Yellow
Ionic form	Hydrogen	Hydrogen	Hydrogen	Hydrogen
Ac (eq./L)	2.07	1.82	1.72	1.2
D_p (mm)	0.70 – 0.95	0.60 – 0.85	0.65 – 0.75	0.15 – 0.30
A_s (m²/g)	33	52	n/a	30
D avg (nm)	24	30	30	n/a
T max (°C)	150	120	n/a	n/a
C_w (%)	55.5	54.4	55.6	68

Figure 1 describes that the Amberlyst series converted α -pinene completely within 2 hours, while Dowex took 8 hours. This may be due to Dowex's active site is the smallest among other catalysts. The active site of Amberlyst 36 is higher than the other Amberlysts, but the surface area of Amberlyst 15 dan UP 15 are larger. This causes the experiments using Amberlyst series have similar conversion.

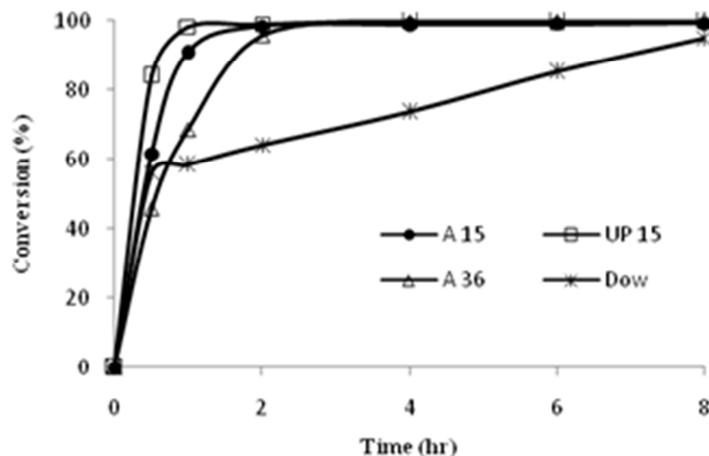


Fig. 1. Effect of catalyst type on conversion of α -Pinene.

The experiments were conducted with 0.05 g/mL catalyst at temperature of 75°C using original turpentine. Different type of catalyst gives different selectivity of product. From the tested catalysts, Amberlyst UP15 resulted in the highest selectivity of bornyl acetate (20.8%) and Dowex was the lowest (6%). Meanwhile, Amberlyst 15 and Amberlyst 36 produce similar bornyl acetate selectivity (Fig. 2).

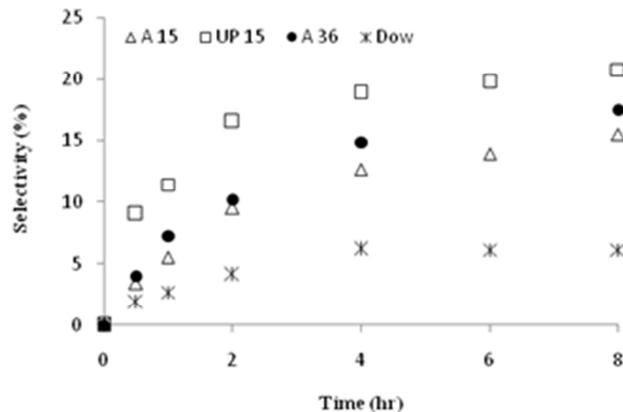


Fig. 2. Effect of catalyst type on selectivity of bornyl acetate.

3.2. Effect of temperature

The effect of temperature on conversion of α -pinene and selectivity of bornyl acetate was investigated. The catalytic experiments using original turpentine and 0.05 g/mL catalyst were carried out at different temperatures for 8 hours. The result is presented in Table 2.

Table 2. The Effect of Temperature on The Result of Esterification.

No.	Catalyst	T (°C)	X (%)	S _i (%)
1	Amberlyst 36 wet	45	56.9	2.8
2	Amberlyst 36 wet	60	98.5	8.4
3	Amberlyst 36 wet	75	100	17.5
4	Amberlyst 36 wet	90	100	26.2
5	Amberlyst UP15	60	99.2	10.1
6	Amberlyst UP15	75	100	20.8
7	Amberlyst UP15	90	100	28.9
8	Amberlyst 15 wet	75	99.6	15.5
9	Amberlyst 15 wet	90	100	25.8

It was observed that the rise of temperature up to 90°C not only increase conversion of α -pinene but also selectivity of bornyl acetate. At 90°C, reaction

over Amberlyst UP15 resulted the highest selectivity (28.9%), while Amberlyst 36 wet and Amberlyst 15 wet showed similar performance.

Figures 3 and 4 show the influence of temperature on the esterification of α -pinene in turpentine over Amberlyst 36 wet. Reaction for 8 hours at 45°C only resulted in 57% conversion of α -pinene as is shown in Fig. 3. At temperature of 90°C, complete conversion of α -pinene is reached only after 1 hour of process. Higher temperature will increase reaction rate constant, thus complete conversion will be reached more quickly.

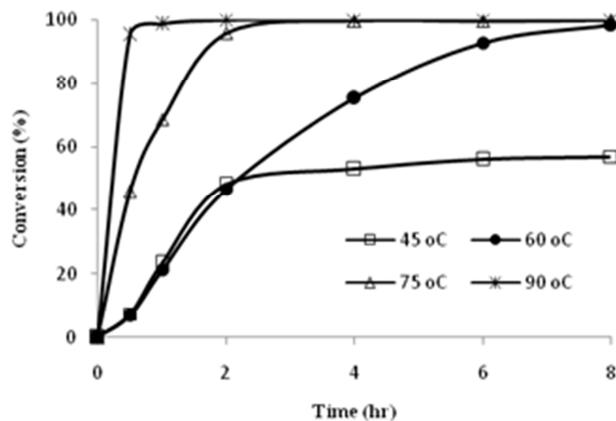


Fig. 3. Effect of temperature on conversion of α -Pinene.

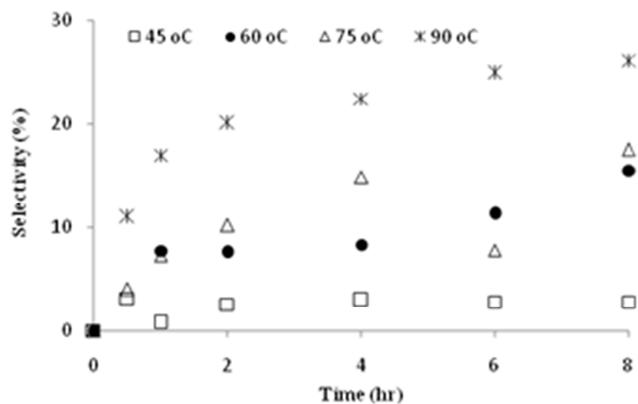


Fig. 4. Effect of temperature on selectivity of bornyl acetate.

After conversion of α -pinene reached 100%, the selectivity of bornyl acetate still increases hereafter. At 90 °C, selectivity of bornyl acetate increase from 17% at 1 hour to 26% at 8 hour of process. This indicates that α -pinene converted to bornyl acetate via intermediate compound.

Although Amberlyst UP15 showed better result, however it is not a commercial product and is not produced anymore. Therefore, Amberlyst 36 was chosen as the catalyst for the next experiments.

3.3. Effect of turpentine purity

The effect of turpentine purity was examined under atmospheric pressure at 75 °C with 0.05 g/mL Amberlyst 36 wet as catalyst, and the results are presented in Figs. 5 to 7. Distribution of esterification products (acetates) and rearrangement products (isomers) during the process are described in Fig. 5.

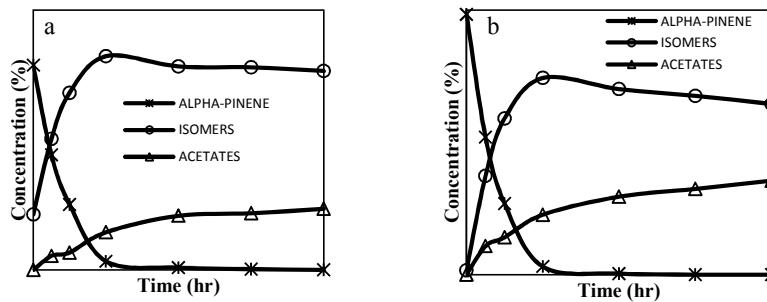


Fig. 5. The concentration evolvement over time.
(a) original turpentine (b) α -Pinene.

Camphene, limonene, terpinenes, and terpinolene are the isomers from the rearrangement reaction. Bornyl acetate is the main esterification product accompanied with fenchyl acetate and terpinal acetate. Reaction using higher purity turpentine resulted in higher amount of acetate products.

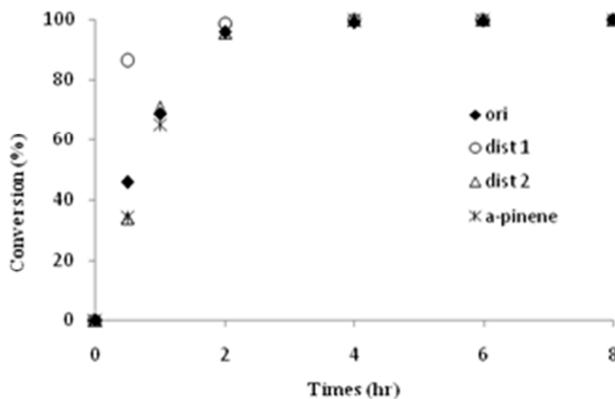


Fig. 6. Effect of turpentine purity on conversion of α -Pinene.

From the conversion point of view, the trend is similar among the turpentines (Fig. 6). It can be observed that there is no effect of turpentine purity on conversion of α -pinene. But, the influence of turpentine purity on the selectivity of bornyl acetate is obvious. Figure 7 shows that higher purity of turpentine increase the selectivity of bornyl acetate.

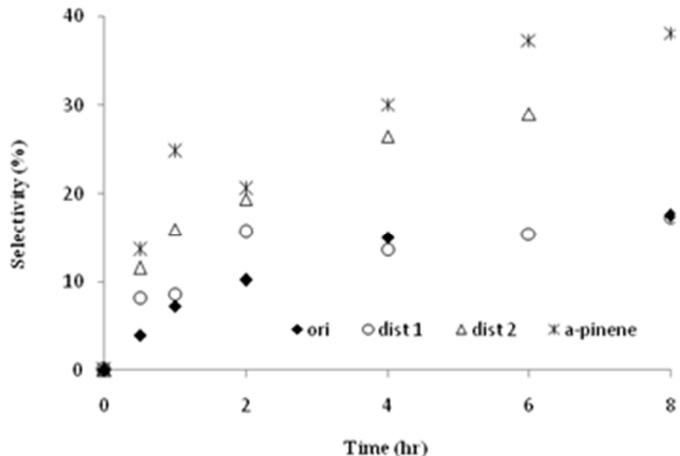


Fig. 7. Effect of turpentine purity on selectivity of bornyl acetate.

The selectivity of bornyl acetate is increasing during the process. The highest selectivity that can be achieved by original turpentine is 17.5%, while the use of α -pinene doubled the result (38%). Previous researcher studied acetoxylation of α -pinene with cation exchanged zeolite beta for 24 hours, resulted in 14% of bornyl acetate selectivity [4]. When SBA-15 with sulfonic acid group was applied as catalyst, it only attained 7% after 30 hours of reaction [4]. Meanwhile, esterification of α -pinene using acidic ionic liquids for 10 hours can reach up to 42.1% of bornyl acetate [3]. At high pressure and temperature (20 bar, 100°C), the selectivity of 40.6% is achieved after 10 hours of reaction using Amberlyst 70 wet [7].

4. Conclusions

An investigation has been made of the effect of catalyst type, temperature and turpentine purity on esterification of turpentine with acetic acid. Some concluding observation are given below:

- Purity of turpentine has no significant effect on conversion of α -pinene, however it affect the selectivity of bornyl acetate. The higher the purity, the higher the selectivity.
- In this experiments, catalyst of Amberlyst series perform better than Dowex. Amberlyst UP15 is the best catalyst tested, which can result in 28.9% selectivity of bornyl acetate.
- The rise of temperature not only increase conversion of α -pinene but also selectivity of bornyl acetate.

- Turpentine (79% α -pinene) can be esterified with glacial acetic acid using cation exchange resin as catalyst to produce bornyl acetate. 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 could be neglected.

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