Kinetic studies of turpentine isomerization using hydrochloric acid and acetic acid as catalysts

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Abstract. Turpentine is a non-wood forest product derived from pine trees. Turpentine oil can be produced from the distillation of pine tree sap (family Pinaceae). The main component of turpentine is \(\alpha\)-pinene, and turpentine isomerization may produce various derivative products. The objective of the present study was to investigate the isomerization products of turpentine oil with two acid catalysts: hydrochloric and acetic acid. Here, the influence of acid concentration was investigated by using various concentrations of hydrochloric and acetic acid concentrations between 0.4 to 1 M. Further, the combination of acetic acid and hydrochloric acid as catalyst was also investigated by varying the molar ratio of HCl:Acetic=1 : 0.5 and 1:1. The experiments were carried out in a batch reactor equipped with heater, condenser, and stirrer. The reaction temperatures were maintained at 150\(^\circ\)C and reaction time of 6 h. The resulting products from turpentine isomerization were analyzed using GC-MS. The results showed that the largest isomerization product obtained with HCl and combination of HCl:H.Acetic was trans sabinene hydrate. Additional products that could be detected varied among \(\alpha\)-terpinolene, \(\alpha\)-terpineol, \(\alpha\)-terpinene, \(\gamma\)-terpinene and \(\delta\)-carene. The experimental data showed that \(\alpha\)-pinene conversion as high as 62, 63 and 57\% were obtained by using HCl concentrations of 0.4, 0.7 and 1 M, respectively. In addition, the use of HCl:H.Acetic=1 :0.5 and 1:1 gave final conversion of 63 and 61\%. The modeling results showed the kinetic model for pinene conversion for both catalysts was

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\frac{dX}{dt} = 0.5222 \cdot (1 - X)^{2.5219} C_{\text{HCl}} - 0.2233 \cdot (1 - X)^{4.5300} C_{\text{HAc}}
\]

1. Introduction

Indonesia is one of the key players in turpentine production in the world by producing more than 13000 tons of turpentine in 2017 [1]. Turpentine is made from pine tree sap which is commonly collected by the local farmers in Java Island. Pine sap processing via distillation may produce turpentine (as top product) and gum rosin (as bottom products). Both turpentine and gum rosin have economic values. Turpentine can be used as raw material for various applications such as paints, solvents, pharmaceuticals and rosin [2,3]. Currently, those products are exported mainly to China and India. In addition to the export market, the demand for gum rosin and turpentine in Indonesia also steadily increased.

The main compound in turpentine is \(\alpha\)-pinene which can be converted to various derived products through the isomerization process with acid catalysts [4,5]. Production of various chemicals from...
turpentine is attractive as it may offer flexibility to cope with the volatile price of turpentine and its derivative products in the market. The price of turpentine derivative products varied greatly from 2000 USD/ton up to 15000 USD/ton.

Production of cineole from turpentine has been reported by Ardiyanto et al. [6] and showed that combination of PTSA and oxalic acid gave cineole yield as high as 21.7 wt.%. Production of α-terpineol from turpentine has also been largely investigated in the present literature. Production of terpineol by hydration of turpentine using low price acid catalyst has been reported by Prakoso et al. [7]. They found that the use of mixed phosphoric acid and acetic acid as catalyst gave terpineol yield as high as 53.5 wt.%. Continuous production of terpineol with reactive distillation has also been investigated in [8].

Kinetic study of turpentine isomerization is useful to predict performance of various catalysts. Utami et al. [9] studied the kinetic of turpentine conversion to terpineol over chloroacetic acid catalyst using a heterogeneous model. In addition, Diana et al [10] reported a kinetic model for acetoxylation of turpentine using a pseudo-homogenous approach. A kinetic model for dual acid catalysts could play an important role to accelerate the screening for combination of acid catalysts.

The objective of present work is to investigate the influence of single catalyst HCl and combination of HCl and Acetic Acid (H.Acetic) as catalysts for isomerization of turpentine. In addition, this study also aimed to investigate product distribution using both acid catalysts. Subsequently, a kinetic model was developed for both systems. The model is expected to serve as a tool to evaluate pinene conversion with the use of mixed HCl and H.Acetic as catalysts.

2. Experimental Method

2.1. Sample preparation
All materials were obtained from Laboratorium Metodika Perancangan dan Pengendalian Proses, Department of Chemical Engineering, Institut Teknologi Bandung which includes: HCl solution, Acetic Acid solution and aquadest. Initially, HCl solutions with concentration of 1 M were prepared in the lab. In addition, the HCl solution was diluted with aquadest to obtain 0.4 and 0.7 M as varied parameters in the present study. In addition, the acetic acid solution of 1 M and 0.5 M were also prepared in the lab. Crude turpentine was received from Perhutani Pine Chemical Industry (PPCI) Pemalang. For the first part of the experiments, we have used a single catalyst of HCl solution to study the turpentine isomerization. In the second part, both HCl and Acetic Acid solutions were used to investigate the influence of dual catalysts to isomerize the turpentine.

2.2. Batch reactor experiment
The experiments of turpentine isomerization were conducted in a three-neck flask reactor equipped with condenser, stirrer, and thermometer. In the first part of the experiment with a single catalyst, 40 ml of HCl solutions with varied concentrations (0.4, 0.7 and 1 M) were added to the reactor. Next, 10 ml of turpentine was also added. The reactor was then heated to 150°C with the total duration of 6 h. The stirrer speed was maintained at 250 rpm or scale 6. The mixed solution forms two phases namely oil phase in the top layer as well as the water phase in the bottom phase. Similarly, for experiment with dual catalyst, 40 ml of acetic acid and 40 ml of HCl solution were added to the reactor. For this part, 20 ml of turpentine was added to form mixed solution of turpentine and acid catalysts. The sample was collected with small pipette from the reactor after 3 h (for dual catalysts system) and 6 h of experiments. When the experiments were finished, both phases were separated. The resulting oil products of isomerization was then weighed to measure the yield of isomerization products. There are 3 measurements of GC-MS using HCl concentrations of 0.4, 0.7 and 1 M after 6 h of experiment. Additionally, there are 4 measurements at 3 h and 6 h using combination of HCl: H Acetic=1 M: 0.5 M and 1 M: 1 M.
2.3. Sample analyses
The samples that have been collected in vials were analyzed using Gas Chromatography-Mass Spectrometer (Shimadzu GCMS-QP-2010 with Rtx-5MS capillary column). The α-pinene conversion ($X_{\text{pinene}}$) was evaluated from the following equation:

$$X_{\text{pinene}} = \frac{A_{\text{pinene, product}} - A_{\text{pinene, feed}}}{A_{\text{pinene, feed}}} \times 100\%$$  \hspace{1cm} (1)

$A_{\text{pinene}}$ is the chromatographic peak area of α-pinene in the initial and final states of each experiment.

3. Modeling Method
A mathematical model was developed from mole balance of a batch reactor. For a single homogenous catalyst, the lumped kinetic model, as well as the reaction rate which was based on the mol of catalyst, could be presented as follows:

$$V_{\text{tot}} \frac{dC_A}{dt} = -r_A \cdot N_{\text{HCl}}$$ \hspace{1cm} (2)

$$V_{\text{tot}} \frac{dC_A}{dt} = -k_1 \cdot C_{A0}^{n1} \cdot (1 - X)^{n1} \cdot N_{\text{HCl}}$$ \hspace{1cm} (3)

$$V_{\text{tot}} \frac{dX}{dt} = k_1 \cdot C_{A0}^{n1} \cdot (1 - X)^{n1} \cdot C_{\text{HCl}} \cdot V_{\text{tot}}$$ \hspace{1cm} (4)

$$\frac{dX}{dt} = k_1' \cdot (1 - X)^{n1} \cdot C_{\text{HCl}}$$ \hspace{1cm} (5)

Similarly, when we use dual catalysts, the kinetic model was:

$$\frac{dX}{dt} = k_1' \cdot (1 - X)^{n1} \cdot C_{\text{HCl}} + k_2' \cdot (1 - X)^{n2} \cdot C_{\text{HAc}}$$ \hspace{1cm} (6)

As a result, there are 4 parameters to estimate namely $k_1'$, $k_2'$, $n1$ and $n2$ from 7 experimental data of pinene conversion. For parameter estimation, the simulation was conducted in Matlab by using both ode and lsqnonlin solvers.

4. Results and Discussion
Turpentine isomerization was investigated by using HCl and combination of HCl and acetic acid as catalysts. Here, we focused on analysis of product distribution based on GC-MS analyses. A kinetic model was developed to reveal the influence of each catalyst.

4.1. Product distribution based on GC analysis
Figure 1 shows the example of chromatogram from turpentine isomerization by using HCl solution concentrations of 0.4, 0.7 and 1 M as catalysts. As seen here, there are several products that can be detected with various retention times. Several notable peaks that can be detected were 3.7, a range of peaks between 4-4.5 and a peak at 5.2. It could also be observed that there are minor products that could be detected above 5.2 showing the absence of important products.
Figure 1. Chromatogram of turpentine isomerization products from GC-MS using various HCl concentration as a catalyst

4.2. Quantitative analysis of product distribution based on GC-MS analysis

Analysis of product distribution was conducted using Mass Spectrometer. The analysis here shows percentage area of 11 largest peaks. Figure 2a shows the chromatogram of crude turpentine. As depicted in Figure 2a, the dominance peak is, as expected, α-pinene. It is interesting to note that the crude turpentine also already contained δ-carene. Other minor products that can be detected were β-pinene and δ-limonene.

By using HCl solution of 0.4 M as the catalyst, the three major products include trans sabinene hydrate, α-terpinolene, and α-terpineol (Figure 2b). By using 0.7 and 1 M of HCl solutions (Figure 2c-d), it is interesting to note that trans sabinene hydrate remains as the largest compound. However, the second and third largest compound varied among α-terpinene, α-terpinolene and γ-terpinene.
Figure 2. GC-MS chromatogram of (a) crude turpentine and product distribution of isomerization by using (b) 0.4 M of HCl, (c) 0.7 M of HCl and (d) 1 M of HCl solutions.

The product distribution from the use of dual catalysts system is presented in figure 3. The product distribution appears to be similar to trans sabinene hydrate as the largest product. The next important products varied among α-terpinene, α-terpinolene and δ-carene. For a single catalyst with HCl solutions, the pinene conversions were 62, 63 and 57% by using HCl 0.4 M, 0.7 M and 1 M, respectively. It is worth noting that the highest HCl concentration of 1 M gave a lower conversion of pinene conversion. With dual catalysts of HCl and H.Acetic, the conversion of pinene increased with the increase of reaction time. By using HCl:H.Acetic=1:0.5 M, it gave conversion of 55% and 63% for 3 h and 6 h, respectively. Similarly, by using HCl:H.Acetic=1:1 M, it gave conversion of 55 and 61% for 3h and 6h, respectively. Hence, it could be inferred that the increase of pinene conversion as a result of H.Acetic addition is relatively small, an increase from 57% by using only HCl 1M to 61 and 63% with addition of H.Acetic.

Figure 3. Product distribution analysis of turpentine isomerization using HCl and CH$_3$COOH as catalysts with molar ratio of (a) HCl:CH$_3$COOH=1M:0.5M and (b) HCl:CH$_3$COOH=1M:1M

4.3. Modeling results
Figure 4 shows the modeling results for both single and dual catalysts system. As illustrated in figure 4a, the model could capture relatively well for HCl concentration of 0.7 M. On the other hand, larger
offset was obtained for 0.4 and 1 M. This is due to the increase of HCl concentration from experimental data of 0.7 to 1 M which gave lower conversion. The kinetic parameters of $k_1'$ and $n_1$ are 0.5222 and 2.5210 which was obtained with HCl as the catalyst.

Figure 4. Modeling result for single catalyst of (a) HCl solutions and (b) dual catalysts of HCl:H.Acetic

Figure 4b shows the modeling results for dual catalysts system. Here, we have two points at 3 h and 6 h. The model could generally capture the data well for 3 h and 6 h. The kinetic model proposed here was developed to accommodate the influence of both acids. In addition to $k_1'$ and $n_1$, we could also estimate the values of $k_2'$ and $n_2$ as -0.2233 and 4.5300, respectively. The influence of acetic acid appears to be negative as the model predicted too high conversion for HCl 1 M as 68.4%, higher than that of 57.07% of experimental data (Figure 4a). Hence, the model tried to compensate the calculation by putting negative coefficient of $k_2'$. The negative value that we obtained here should only be used as an indicator to evaluate the influence of dual catalysts system and can be used as a tool for extensive screening of any combination of acid catalysts. From this work, the final kinetic equation for dual catalyst system of HCl and H.Acetic is:

$$\frac{dX}{dt} = 0.5222 \cdot (1 - X)^{2.5210} C_{HCl} - 0.2233 \cdot (1 - X)^{4.5300} C_{HAc} \quad (7)$$

Figure 5. Modeling result for quantification of reaction rate by using dual catalysts using equation (2)

Quantification of reaction rate by using equation (2) is presented in Figure 5. As indicated by equation (7), addition of H.Acetic tends to lower the reaction rate and thus found to be disadvantageous. It is also possible that other kinetic models such as the heterogeneous kinetic model as in [9] or pseudo homogenous model [10] could probably improve the present model.
In addition, the present work also indicated that HCl as well as combination of HCl:H.Acetic did not selectively produce a specific product. Instead, it produced a rather large variety of 11 possible products. Hence, further work is needed to improve the selectivity of turpentine isomerization to a specific product which may improve the economic value of turpentine.

5. Conclusions

Turpentine isomerization has been investigated by using two acid catalysts: hydrochloric and acetic acid. Here, the influence of acid concentration was investigated by using various concentrations of hydrochloric and acetic acid concentrations between 0.4 to 1 M. The results showed that the largest isomerization product obtained with HCl and combination of HCl:H. Acetic was trans sabinene hydrate. Additional products that could be detected varied among α-terpinolene, α-terpineol, α-terpinene, γ-terpinene and δ-carene.

The experimental data of α-pinene conversion showed that the pinene conversions were 62, 63 and 57% by using 0.4, 0.7 and 1 M of HCl solutions. In addition, the use of HCl:H. Acetic=1 M :0.5 M gave the final conversion of 63%. Similarly, by using HCl:H. Acetic=1 M:1 M gave the final conversion of 61%. Hence, it is apparent that the increase of acetic acid concentration lowered the pinene conversion.

The modeling results showed the kinetic model for pinene conversion using both catalysts was:

$$\frac{dx}{dt} = 0.5222 \cdot (1 - X)^{2.5210}C_{HCl} - 0.2233 \cdot (1 - X)^{4.5300}C_{HAc}$$

This model is useful to predict pinene conversion by using various concentrations of HCl and acetic acid as catalysts.

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