Isomerization of Raw Turpentine for Cineole using Response Surface Methodology (RSM): Influence of Acid Ratios and Residence Time

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Abstract. Turpentine is a potential non-wood product from pine tree forest in Indonesia. Turpentine has a wide application in industry mainly as solvent. Isomerization of turpentine is an attractive route to obtain a higher value fine chemical such as cineole. Acid catalyst is often used for this purpose and screening of numerous combination of acid catalysts is often challenging. Therefore, an investigation of isomerization operating condition is important. The aim of present work is to investigate the influence of several acids ratios, and residence time. The raw turpentine was obtained from PT Perhutani Anugerah Kimia (PAK) Trenggalek, East Java. Here, we have investigated the influence of raw turpentine to acid catalyst ratios as well as residence time using central composite design (CCD) of 2² factorial design. In this work, the strong acid catalysts used is hydrochloric acid (HCl) and the weak acid catalysts is formic acid (HCOOH). The result from GC-MS analyses showed that isomerization of raw turpentine using combination of HCl and formic acid can produce cineole compound along with other valuable products such as camphene and limonene. Herein, we have reported the highest yield of cineole as high as 11.5% which is in close agreement with model prediction. It is expected that this work may provide a useful path for cineole production in a larger production scale.

1. Introduction
Turpentine oil in Indonesia are generally obtained from pine resin as a top product of the distillation process. This compound has greater potential because it can be processed into various derivative compounds that have higher economic value. One of potential product of turpentine isomerization is cineole or commercially known also as eucalyptol [1,2]. Cineole has a wide range of uses, especially in pharmaceutical industry. Cineole has been obtained as a byproduct from the hydration process of α-pinene to terpineol. In this case, the distillation process is still needed to obtain the cineole. This method is considered less economical and impractical because it still requires further separation method to obtain the pure cineole. Therefore, further research is needed to find suitable methods and formulations in order to obtain a more effective way of producing cineole from raw turpentine.

The composition of turpentine includes beta-pinene (1%-3%), 3-deltacarena (10%-18%), limonene (1%-3%), champhene (<1%), and α-pinene (65-85%) [3]. Alpha-pinene as the main component in turpentine is a key in processing this compound. Alpha-pinene can take part in isomerization reaction
with the help of acid catalyst to produce various isomerization products as shown in Figure 1. Isomerization of α-pinene can produce products in the form of monocyclic, bicyclic, etc. These bicyclic products such as camphene [4] and tricyclene. Meanwhile, monocyclic products are such as limonene [5] and terpineol [6].

![Figure 1. Isomerization reaction mechanism of α-pinene.](image)

In the present work, we have investigated the influence of turpentine-acid ratio and residence time using Central Composite Design (CCD) in conjunction with Response Surface Methodology (RSM) [7]. This type of method is useful collection of statistical and mathematical technique to develop and optimize a process which the response of this process is influenced by factors known as independent variables. For this study, the independent variables are residence time and the ratio of turpentine and acid catalyst. This method will provide mathematical as well as graphical modelling of current chemical process to correlate those two factors and the response which is yield of cineole produced from reaction. Furthermore, RSM can also provide the value of independent variables which can give the optimized value of cineole yield.

The use of low cost homogeneous catalyst in the form of a combination of strong and weak acids are commonly used for turpentine isomerization [3,8,9]. Homogeneous catalysts have advantages including not being easily poisoned by impurities and each molecule of the catalyst has an active function as a catalyst. Meanwhile, the disadvantages of this type of catalyst is the difficulty to separate from the mixture and easily decomposed at high temperatures. Here, we have investigated the influence of hydrochloric acid (HCl) and formic acid (HCOOH) for cineole production. This type of catalyst was selected based on our previous research where the turpentine isomerization was carried out at 85°C for 6 hours with variations in the type of catalyst from various combinations of strong and weak acids. It was obtained that the combination of HCl-HCOOH catalyst gave the highest cineole product, which is 9.67 % along with other valuable products such as limonene, camphene, etc.

This study aims to find the optimum setting of the various mixing ratio of the catalyst and residence time for cineole production using central composite design (CCD). We have focused on the use of HCl and HCOOH as a catalyst mixture to maximize cineole production.
2. Research Methodology

2.1 Material.
Raw turpentine in this research was obtained from PT. Perhutani Anugerah Kimia which is located in Trenggalek, East Java. The raw turpentine contains 85.68% α-pinene. The strong acid used was hydrochloric acid (HCl), meanwhile the weak acid used was formic acid (HCOOH). Water was also used as diluent for the acid solutions. The acids and the water were obtained from Coal, Gas and Petroleum Technology Lab at Department of Chemical Engineering, Universitas Gadjah Mada.

2.2 Methods

2.2.1 Design of Experiment. Minitab software was used to find the required variation of catalyst ratios and reaction time. The data collected from experiment was analyzed by Response Surface Methodology (RSM) design called Central Composite Design (CCD). In this software, a factorial design method with 2 factors and 2 levels of input were used. The first factor is weak catalyst ratio, which has minimum and maximum value input of 6 and 10 respectively. Meanwhile, the second factor is the residence time, which has minimum value input of 120 and maximum value of 300. The response analyzed in this study is the yield of the cineole. In order to simplify the calculations, the factors were coded to ±1 for the factorial points, ±1α for axial points, and 0 for the center points. The value of α depending on factors used as shown in equation (1) with n as the amount of factor analyzed. Hence the value of α is 1.414. From this method, it was found that 11 experiments with various ratios and residence time variations were needed as shown in Table 1 including 4 factorial and 4 axial points, as well as 3 replicates of center points to avoid error.

\[ \alpha = 2^{\frac{n}{4}} \] (1)

2.2.2 Sample Preparation. As much as 6.4 mL of raw turpentine was used to obtain 0.04 mol of raw turpentine. Hydrochloric acid (HCl) solution with the amount of 0.01 mol was prepared by diluting 3.9 mL of HCl 37% into 100 mL-volumetric flask and continued by taking 25 mL of this solution. Further, 0.08 mol of formic acid (HCOOH) was added to the mixture by taking 3.1 mL of HCOOH 98-100%.

![Figure 2.](image)  
**Figure 2.** Experimental set-up of turpentine isomerization.

2.2.3 Isomerization Reaction. Turpentine, weak acid, and strong acid with each required ratio and residence time were poured into a three-neck flask. Plugs, thermometers, condensers, stirrers, and heaters were installed. The reaction in the three-neck flask was run for the appropriate reaction time and
catalyst ratio with the temperature of 85°C. After a certain reaction time, the product was then cooled and poured into a beaker glass. The oil layer which is on the top layer of the mixture was then taken using a pipette. Approximately 10 mL of the product was taken and put into a vial bottle. From this experiment, we obtained 11 samples. The experimental set-up of this study is depicted in Figure 2.

2.2.4 Sample Analysis Using GC-MS. Furthermore, the sample resulting from the reaction was analyzed using the Shimadzu GC-MS QP-2010 with Rtx-5MS at Laboratory of Analysis and Instrumentation, Chemical Engineering Department, Universitas Gadjah Mada. From the analysis, the peak area parameter was used to evaluate the value of cineole yield. For each sample, cineole yield is defined as the percentage of the addition of cineole peak area divided by its initial peak area. Initial cineole peak area was found from the raw turpentine analysis.

\[
Yield_{\text{cineole}} = \frac{A_{\text{cineole, product}} - A_{\text{cineole, initial}}}{A_{\text{pinene, initial}}} \times 100
\]  

(2)

2.2.5 Sample Analysis Using Minitab Software. The response of cineole yield was then analyzed using Minitab software. Both ANOVA table and Response Surface Methodology (RSM) model were obtained from the software. In addition, we have made contour plot, surface plot, and response optimization to study the experiment results.

3. Result and Discussion

Based on the analysis using GC-MS, it was found that all samples with 11 variations in the catalysts ratio and residence time can produce cineole along with other compounds as shown in chromatogram for sample X1 by Figure 2.

![Figure 3. Chromatogram from GC-MS analysis of sample X1.](image)

Peak area of each compound is obtained from a chromatogram. Peak area of cineole in sample X1 and raw turpentine are 349,631,168.0 and 3,935,045.5 respectively. Meanwhile, the peak area of α-pinene in the raw turpentine is 10,473,374,880.0. Thus, the yield of the cineole for sample X1 can be calculated using equation (2) as follows.

\[
\text{Cineole yield}_{X1} = \frac{349,631,168.0 - 3,935,045.5}{10,473,374,880.0} \times 100\% = 3.3007\%
\]

Based on these data, it can be seen that the highest yield of cineole was obtained in sample X8 by using the turpentine, HCl, HCOOH ratio of 4 : 1 : 8 and the residence time of 337.279 minutes with the yield value of 11.5834 %. Meanwhile, the lowest amount of cineole was produced when the ratio of 4 : 1 : 10 was used for 120 minutes residence time in sample X4.
Table 1. Cineole yield of each sample.

| Sample | Coded Variable | Ratio\(^c\) | Residence Time (min) | Cineole Yield (%) |
|--------|----------------|-------------|----------------------|-------------------|
|        | \(x_1^a\) | \(x_2^b\)  |                      |                   |
| X1     | -1            | -1          | 4 : 1 : 6            | 120               | 3.3007            |
| X2     | 1             | -1          | 4 : 1 : 10           | 120               | 1.8407            |
| X3     | -1            | 1           | 4 : 1 : 6            | 300               | 7.8299            |
| X4     | 1             | 1           | 4 : 1 : 10           | 300               | 5.7786            |
| X5     | -1.414        | 0           | 4 : 1 : 5.1716       | 210               | 5.5979            |
| X6     | 1.414         | 0           | 4 : 1 : 10.8284      | 210               | 5.8384            |
| X7     | 0             | -1.414      | 4 : 1 : 8            | 82.72             | 3.9582            |
| X8     | 0             | 1.414       | 4 : 1 : 8            | 337.28            | 11.5834           |
| X9     | 0             | 0           | 4 : 1 : 8            | 210               | 5.9609            |
| X10    | 0             | 0           | 4 : 1 : 8            | 210               | 3.0975            |
| X11    | 0             | 0           | 4 : 1 : 8            | 210               | 5.2634            |

Note: \(^a\) \(x_1\) represents coded variable for factor 1 which is the amount of weak acid
\(^b\) \(x_2\) represents coded variable for factor 2 which is the residence time
\(^c\) Ratio represents mole ratio of turpentine, strong acid, and weak acid

Subsequently, the yield was analyzed using Analysis of Variance (ANOVA) in Minitab software. The result gained by this analysis is listed in the Table 2. It can be seen that residence time appears as the single factor which exhibits significant impact with p-value less than the value of \(\alpha=0.05\). Other factors such as weak acid catalyst ratio, interaction and quadratic terms were found to be insignificant. Perhaps, this is due to the small range of weak acid ratio that has been selected in this work.

Table 2. Analysis of Variance (ANOVA) by Minitab.

| Source                        | DF | Adj SS  | Adj MS  | F-Value | P-Value |
|-------------------------------|----|---------|---------|---------|---------|
| Model                        | 5  | 53,8174 | 10,7635 | 3.48    | 0.098   |
| Linear                       | 2  | 47,5805 | 23,7903 | 7.70    | 0.030   |
| Weak catalyst ratio          | 1  | 1,2572  | 1,2572  | 0.41    | 0.552   |
| Residence time               | 1  | 46,3234 | 46,3234 | 15.00   | 0.012   |
| Square                       | 2  | 6,1495  | 3,0748  | 1.00    | 0.433   |
| Weak catalyst ratio*Weak catalyst ratio | 1  | 0,0100  | 0,0100  | 0.00    | 0.957   |
| Residence time*Residence time | 1  | 5,4698  | 5,4698  | 1.77    | 0.241   |
| 2-Way Interaction            | 1  | 0.0874  | 0.0874  | 0.03    | 0.873   |
| Weak catalyst ratio*Residence time | 1  | 0.0874  | 0.0874  | 0.03    | 0.873   |
| Error                        | 5  | 15,4461 | 3,0892  |         |         |
| Lack-of-Fit                  | 3  | 10,9874 | 3,6625  | 1.64    | 0.400   |
| Pure Error                   | 2  | 4,4587  | 2,2293  |         |         |
| Total                        | 10 | 69,2635 | 3,0892  |         |         |

A second order model was proposed from the data to obtain:

\[
\text{Cineole yield} = Y = 4.0 + 0.14A - 0.0177B + 0.011A^2 + 0.000122B^2 - 0.00082AB \tag{2}
\]

with \(A\) = weak acid catalyst ratio  
\(B\) = residence time

Equation (2) represent cineole product that could be obtained from the isomerization reaction in terms of weak acid ratio (A) and residence time (B). The negative sign in the equation shows antagonistic effect while the positive sign indicates synergistic effect to cineole formation in the mixture. The benefit
of knowing this equation is that we could predict the cineole formed just by putting the weak acid ratio and residence time factor that we want to implement in our reaction system.

![Figure 4](image-url)  
**Figure 4.** Contour plot of yield vs catalyst ratio and residence time.

![Figure 5](image-url)  
**Figure 5.** Surface plot of yield vs catalyst ratio and residence time.

Next, the data can also be analyzed graphically as shown in **Figure 4** and **Figure 5**. From the graph, it is shown that the area with the red color give the highest yield of cineole with the value of up to 10%. This cineole yield was obtained by using less weak acid catalyst in the mixture and longer reaction time, so that the $\alpha$-pinene in raw turpentine could be optimally isomerized into cineole.

Furthermore, response optimization was also used in this analysis. From the Minitab, the maximum optimization result the yield of cineole of 10.9173 using the turpentine, HCl, HCOOH ratio of 4:1:5.1716 and the residence time of 337.2792 was obtained from the response optimizer.

![Figure 6](image-url)  
**Figure 6.** Response optimization.
Based on the graph, it is shown that the use of a lower amount of weak acid catalyst is favorable with respect to cineole yield. On the opposite, higher weak acid concentration in the mixture will reduce the cineole present in the product. Our previous work also indicated that the lower weak acid concentration gives higher α-pinene conversion which leads to higher amount of cineole [3].

From this analysis, it can also be seen that residence time has an effect on the yield value of the resulting cineol. The longer the reaction time, the higher the cineole yield. This phenomenon is also in agreement to a previous study by Prakoso et al. where the formation of terpineol from α-pinene isomerization also gave the same trend in the correlation between reaction time and terpineol yield [9]. Therefore, the longer reaction time let α-pinene forms more terpineol so that this compound reacts further to form cineole. A further study is needed to find the optimum reaction time to obtain maximum cineole yield. In addition, there is a need to further investigate this integrate the reaction and separation process in a continuous operating system.

4. Conclusion
A study of RSM has been presented to investigate the influence of weak acid and residence time to maximize cineole yield. All 11 combinations of catalyst ratio and residence time in the isomerization of turpentine oil can produce cineole with the highest yield obtained in the turpentine, HCl, HCOOH ratio of 4 : 1 : 8 and the residence time of 337.279 minutes with the yield value of 11.5834 %. The result of experiment is in close agreement with model prediction. From the ANOVA, the only factor which is significance to the production of cineole yield is residence time. The influence of weak acid catalyst here is insignificant that might be due to too small range of weak acid range that has been used in this work. This work provides better understanding and useful path on the screening of acid catalyst for cineole production from raw turpentine. A further study is however still needed to scale up this process in a continuous reactor.

References
[1] Putra I A, Azis M M, Soerawidjaja T H, and Indarto A. 2019 AIP Conference Proceedings 2085 020057
[2] Lena E J L, Rocha K A, Kozhevnikov I V, Gusevskaya E V. 2006 Journal of Molecular Catalysis A: Chemical. 259. 99-102.
[3] Azis M M, Qani’a F R, Pratiwi S I, Kristanto J, Purwono S, and Indarto A. 2020 IOP Conf. Ser. : Mater. Sci. Eng. 823 012042
[4] Findik S and Gunduz G. 1997 Journal of the American Oil Chemists’ Society 74(9) 1145-1151.
[5] Becerra J A and Villa A L. 2020 Chemical Engineering & Technology 43 (11) 2295-2306.
[6] Aguirre M R, Torre-Saenz I D, Flores W A, Robau-Sanchez A, Elguezabal A A. 2005 Catalysis Today 107-108 310-314
[7] Montgomery D C 2013 Design and analysis of experiments ed 8 (Arizona: Arizona State University) chapter 11 478-522
[8] Prakoso T, Hanley J, Soebianto M N, Soerawidjaja T H, and Indarto A 2018 Catalysis Letters 148 725-731.
[9] Prakoso T, Putra I A, Handojo L, Soerawidjaja T H, Winoto H P, and Indarto A 2020 Heliyon 6 e04984