Isomerization of Raw Turpentine Using Various Combination of Strong and Weak Acid Catalyst for Eucalyptol Production

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Abstract. There has been large interest to isomerize raw turpentine to produce a number of derivative products that has higher economic value. This process is often conducted using homogenous acid catalysts. Catalyst screening is often challenging to target a certain derivative product, such as cineole. The aim of present work is investigate various combination of strong and weak acid catalyst to obtain cineole.

Strong acids used in this research were PTSA, hydrochloric acid, sulfuric acid. In addition, the weak acids were oxalic acid dihydrate, citric acid, and formic acid. Commercial turpentine was mixed with strong and weak acid with 4:1:6 ratio respectively, heated up to 85°C for 6 hours for each combination of strong and weak acid.

The result from GC-MS analysis shows that combination of hydrochloric acid and formic acid gave the highest eucalyptol yield around 9.67% along with other valuable product such as camphene, limonene, and α-terpinolene.

1. Introduction

Turpentine is a compound with molecular formula of C₁₀H₁₆ which is produced from the hydrodistillation process of pine sap as a top product, and this product has distinctive odor that is widely used in fragrance, pharmaceutical, and food industries [1]. Turpentine can be used raw as an organic solvent in paints or coatings. However, with further processing, turpentine can produce numerous compounds with wider application with higher values in market [2]. The main components contained in turpentine compound are α- and β- pinene. In this process, α-pinene compound can be isomerized into various derivative product using an acid catalyst to produce cyclic and bicyclic derivative compounds. One of the promising product is eucalyptol or 1,8-cineole which is a valuable derivative compound that has the most expensive market price. This oil shows antibacterial, antiseptic, antioxidant, anti-inflammatory, and anticancer activities as at its wide application on perfumery, cosmetics, aromatherapy, phytotherapy, food beverages, and pharmaceutical industries [3].

Cineole produced from α-pinene isomerization has 2 isomers, namely 1,8-cineole (eucalyptol) and also 1,4-cineole and can be isomerized from turpentine using a combination of strong and weak acid catalyst to increase the selectivity of α-pinene to cineole compounds [4]. Previous work by Putra et al.[5] reported that the use of this acid catalyst can reduce the activation energy so that even low temperatures can facilitate the reaction. The acid catalyst in this reaction provides H⁺ ions that attack the double bonds in the α-pinene ring and produce pinanyl cation. This carbocation component is a key intermediate and
a precursor for the next two reaction steps. The first is the ring expansion step which gives rise to bicyclic
and tricyclic products such as camphene and tricyclene. The second path yields monocyclic products
such as limonene and cineole [6]. The reaction mechanism is as illustrated in Figure 1.

![Isomerization mechanism of α-pinene into its derivatives from several studies][2,7].

Several studies showed that the isomerization of turpentine using catalyst combination of PTSA and
oxalic acid was able to produce 21.7% wt of cineole [8]. Other study conducted by Lana et. al. showed
that the isomerization of a-terpineol with H₃PW₁₂O₄₀ gave 50-90% conversion of a-terpineol with
selectivity of 25% for 1,8-cineole and 23-27% for 1,4-cineole [9]. The use of temperature of 85°C was
chosen into this research because this condition is the optimization result based on previous research
[5]. The purpose of turpentine isomerization to cineole is to change the composition of a-pinene into
eucalyptol. In general, eucalyptol has been obtained as byproduct from the hydration process of α-pinene
into terpineol. Meanwhile, this process is considered very difficult and costly because it still requires
further distillation to get the pure eucalyptol. Therefore it is necessary to have an optimal synthesis
pathway in the production of cineole, one of which is the isomerization process of turpentine to cineol
using various acid catalysts. The objective of present work is to conduct acid catalyst screening to obtain
high 1,8-cineole yield using combination of strong and weak acids. The strong acids used in this work
are PTSA, HCl and H₂SO₄. In addition, a number of weak acids such as citric, formic and oxalic acid
have been used.

2. Material and Methods

2.1. Material
The material used was commercial raw turpentine which contained 73.21% α-pinene along with other isomer compound such as α-terpinolene (1.156%), Camphene (1.243%), o-cymene (1.676%), and limonene (1.597%). The acid used in this research were sulphuric acid, oxalic acid, PTSA, as strong acid component, and formic acid, oxalic acid, and citric acid as the weak acid component. All materials (commercial grades) were obtained from Coal, Gas and Petroleum Technology Laboratory, Chemical Engineering Department, Universitas Gadjah Mada.

2.2. Methods

2.2.1. Sample Preparation. 6.4 mL of turpentine oil was taken from turpentine flask and 0.01 mol HCl solution was prepared by dissolving 3.1 mL of 37% HCl in 100 mL of aquadest. Subsequently, 25 mL of the HCl solution was used in the reactor. For the weak acid, 0.06 mol formic acid was taken directly from the 98-100% formic acid as much as 2.3 mL and later was placed into a three neck flask. The experiment was repeated with 0.01 mol of sulfuric acid, 0.01 mol of PTSA acid and 0.06 mol of oxalic acid and citric acid with different combinations.

2.2.2. Batch Reactor Experiment. A mixture of strong acid, weak acid, turpentine, and a magnetic stirrer were placed into the three-neck flask reactor. The three neck flask equipped with condenser was submerged in an oil heater using clamps. The reaction initiated by adjusting the hotplate stirrer magnetic controller and temperature control to mix and heat the mixture until the temperature reading in the alcohol thermometer shows 85°C. This process was maintained for 6 hours duration. The samples that contained the oil layer which was located on the top was taken using a pipette and put into a vial bottle for storage.

2.2.3. Sample Analysis. The process of analyzing each product from using the combination of acids was carried out using Shimadzu GC-MS QP-2010 with Rtx-5MS capillary column at Laboratory of Analysis and Instrumentation, Chemical Engineering Department, Faculty of Engineering, Universitas Gadjah Mada. For data processing, the α-pinene and eucalyptol normalization area (N_{α-pine} & N_{eucalyptol}) were evaluated by using total normalization method from α-pinene and eucalyptol peak to give fair comparison result between initial and after reaction[10]. The eucalyptol yield (Y_{eucalyptol}) were also evaluated to give precise number of eucalyptol produced by isomerization reaction. Below are the equations used.

\[
N_{α-pine} = \frac{A_{α-pine} \times 100\%}{A_{α-pine} + A_{eucalyptol}}
\]

\[
N_{eucalyptol} = \frac{A_{eucalyptol} \times 100\%}{A_{α-pine} + A_{eucalyptol}}
\]

\[
Y_{Eucalyptol} = \frac{A_{Eucalyptol \ product} - A_{Eucalyptol \ initial}}{A_{α-pine \ initial}} \times 100\%
\]

3. Result and Discussion

As advantageous essentials oil, eucalyptol can shows various beneficial biological activities such as antimicrobial agent against many pathogens and exhibit antioxidant properties as well as good odor in fragrance industries. Eucalyptol which is a monoterpenoid compound derivative α-pinene from turpentine was isomerized to produce eucalyptol using various acid catalyst combination and analyzed using GC-MS to identify the component present in 9 sample combination. Based on GC-MS results, the
isomerization reaction produces many peaks which indicated the presence of numerous components in the final reaction product as shown in the chromatogram of Figure 2.

As seen in Figure 2, it is shown that there are several peaks. It also indicated that the resulting product cannot solely lead to the formation of eucalyptol. From Table 1, it can also be seen that in addition to the desired main product in the form of eucalyptol there are also new by-products in the form of other essential compounds that were not previously found in turpentine such as α-terpinolene, γ-terpinene, and 1,4-cineole or existing ones such as camphene, cymene, and limonene. These compounds are the side products of this isomerization reaction but fortunately can have higher price than pine oil. Small amount of it can be further challenge in the products purification.

This reaction product distribution is due to the poor selectivity of the acid combination to direct the conversion of α-pinene into the desired main product. This product distribution does not apply only to the combination of hydrochloric acid and formic acid but applies to all acid combinations used in this study.

Table 1. Major Product Distribution of Turpentine Isomerization Using Various Acid Combination.

| Acid Combination | A   | B   | C   | D   | E   | F   | G   | H   |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| HCl + Citric     | 80.706 | 1.708 | 3.519 | 2.137 | 2.221 | 1.357 | 0.637 | 0.656 |
| HCl + Oxalic     | 13.926 | 1.726 | 3.778 | 2.958 | 10.774 | 4.467 | 2.518 | 2.985 |
| HCl + Formic     | 34.167 | 2.013 | -   | -   | 19.74 | 6.668 | 5.542 | 4.542 |
| H2SO4 + Citric   | 73.842 | 1.381 | 1.986 | 1.381 | 1.388 | 0.815 | 0.992 | 0.558 |
| H2SO4 + Oxalic   | 55.27 | 1.824 | 3.153 | -   | 8.432 | 4.916 | 3.639 | 4.273 |
| H2SO4 + Formic   | 76.171 | 1.381 | 2.122 | 1.441 | 3.07 | 0.962 | 1.77 | 0.992 |
| PTSA + Citric    | 18.212 | 1.467 | 2.848 | 1.892 | 1.905 | 1.036 | 0.47 | 0.413 |
| PTSA + Oxalic    | 14.143 | 1.425 | 3.151 | 2.005 | 2.832 | 0.975 | 0.975 | 1.005 |
| PTSA + Formic    | 65.622 | 1.74 | 3.032 | 3.163 | - | - | 2.479 | 3.163 |
| Raw Turpentine   | 73.21 | 1.243 | 1.676 | 1.597 | - | - | - | - |

Note: A = α-pinene, B = Camphene, C = O-Cymene, D = Limonene, E = α-terpinolene, F = γ-terpinene, G = 1,4-Cineole, H = Eucalyptol (1,8-Cineole)

The application of a combination of hydrochloric acid and formic acid catalyst for the turpentine isomerization reaction gives quite good product results consistently where the entire composition of the components consisting of the main product and by-products has the highest percentage compared to the use of other catalyst combination. Each combination of strong and weak acids has different interaction
where there is no single type of strong acid catalyst or weak acid catalyst that consistently provides high eucalyptol yield. For PTSA and HCl, good result of eucalyptol composition achieved, if combined with formic acid (HCOOH) in the isomerization reaction, while for sulfuric acid interacts well with oxalic acid. In this study, citric acid gave the smallest yield in all of its combinations with strong acids. All of the catalysts used is also classified as not selective for the formation of cineole. The low selectivity of these acid combinations in isomerizing α-pinene is probably due to the ratio of the amount of the strong acid catalyst with the turpentine used [4]. This unbalanced ratio could reduce the ability of the weak acid catalyst in the reaction to produce the desired compound, but leads to uncontrolled reactions that occurred for all types of catalyst combinations used.

Table 2. The α-pinene and Eucalyptol Area on GC-MS Chromatogram.

| Acid Combination  | α-pinene Area | Eucalyptol Area |
|-------------------|---------------|-----------------|
| HCl + Citric       | 10,240,145,790.90 | 83,213,544.00   |
| HCl + Oxalic       | 1,975,730,624.00    | 423,468,896.00  |
| HCl + Formic       | 5,633,158,144.00    | 748,833,856.00  |
| H₂SO₄ + Citric     | 8,228,521,936.00    | 57,640,040.00   |
| H₂SO₄ + Oxalic     | 8,269,096,039.80    | 639,247,616.00  |
| H₂SO₄ + Formic     | 8,298,675,584.00    | 108,055,664.00  |
| PTSA + Citric      | 2,172,861,408.00    | 49,278,836.00   |
| PTSA + Oxalic      | 1,717,492,000.00    | 122,083,128.00  |
| PTSA + Formic      | 8,430,150,144.00    | 406,333,280.00  |
| Raw Turpentine     | 7,742,696,512.00    | 0               |

The analysis of GC-MS result can also be conducted from the change of α-pinene area as displayed in Table 2. As seen, there are several acids that have increased chromatogram area. The addition of the chromatogram area is possible because this isomerization reaction not only undergoes a one-way reaction, but also undergoes a reversible reaction. Hence, probably some derivative compounds previously present in the turpentine feed were isomerized to α-pinene, since most of α-pinene derivatives formed by alpha terpinyl cation intermediates so it needed further study to identify whether the derivative compound present in raw turpentine could be isomerized into α-pinene by this isomerization process (Figure 3).

Figure 3. Reversible Reaction of Turpentine Isomerization [11].

By using the chromatogram area data in Table 2, we can determine the normalized of α-pinene and eucalyptol area. In addition, we can also estimate the eucalyptol production yield. An illustration of α-pinene conversion and eucalyptol yield calculation from the chromatogram area based on the HCl + Citric in Table 2 is as follows.
\[ N_{\text{pinene}} = \frac{10,240,145,790.90}{10,240,145,790.90 + 83,213,544.00} \times 100\% = 99.19\% \]

\[ N_{\text{eucalyptol}} = \frac{83,213,544.00}{10,240,145,790.90 + 83,213,544.00} \times 100\% = 0.81\% \]

\[ Y_{\text{Eucalyptol}} = \frac{83,213,544.00 - 0}{7,742,696,512.00} \times 100\% = 1.07\% \]

The calculations were carried out for other acid combinations to obtain the normalized area of \( \alpha \)-pinene and eucalyptol area as presented in Table 3. Further, the eucalyptol yield is presented in Figure 4.

**Table 3. The Calculation of Normalized Area of \( \alpha \)-pinene & Eucalyptol.**

| Acid Combination  | \( \alpha \)-pinene Area Normalization (%) | Eucalyptol Area Normalization (%) |
|-------------------|----------------------------------------|----------------------------------|
| HCl + Citric      | 99.19                                  | 0.81                             |
| HCl + Oxalic      | 82.35                                  | 17.65                            |
| HCl + Formic      | 88.27                                  | 11.73                            |
| H\textsubscript{2}SO\textsubscript{4} + Citric | 99.30                                  | 0.70                             |
| H\textsubscript{2}SO\textsubscript{4} + Oxalic | 92.82                                  | 7.18                             |
| H\textsubscript{2}SO\textsubscript{4} + Formic | 98.71                                  | 1.29                             |
| PTSA + Citric     | 97.78                                  | 2.22                             |
| PTSA + Oxalic     | 93.36                                  | 6.64                             |
| PTSA + Formic     | 95.40                                  | 4.60                             |
| Raw turpentine    | 100                                    | 0                               |

**Figure 4.** Result of Calculation based on Chromatogram Area.
Based on Table 3, it is known that the use of HCl with oxalic acid and formic acid are the only combination which are able to achieve an α-pinene composition below 90% after normalization value. These results indicate that HCl is effective to be used as a catalyst to produce 1,8-cineole with high yield compared to other strong acids when combined with provided weak acid. To obtain more accurate information in determining the optimal catalyst type, normalization comparisons are not used but using the highest eucalyptol yield calculation in Figure 4. From the calculation, it was obtained that the highest yields produced from the combination of HCl and HCOOH. This type of acid combination gives the best yield due to HCOOH is a weak organic acid with good solubility in both polar and non-polar compound [4]. In addition, as inorganic acid, it is good if we could pair the strong acid such as hydrochloric acid as shown in Figure 4 which gives the highest eucalyptol yield.

4. Conclusion
The present work has conducted acid catalyst screening for turpentine isomerization using combination of strong and weak acid catalysts. Our results showed that all combinations of strong and weak acid catalysts could produce eucalyptol compounds with various selectivity. It was also found that there are many side products other than eucalyptol. The combination of hydrochloric acid with oxalic acid or formic acid catalyst in this study has shown a promising result as it provides good results of lesser α-pinene composition to eucalyptol composition compared to the other acid combinations. The highest eucalyptol product was obtained at 9.67% with the combination of hydrochloric acid and formic acid. This research was carried out a reaction with types of catalyst that are still not selective in the isomerization of α-pinene to produce cineole, so further research is needed to increase the selectivity of α-pinene into eucalyptol.

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