Fractionation of Turpentine

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Abstract. Turpentine (pine oil) is a liquid phase of the Pinus mercusii gum that consists of α-pinene, β-pinene, δ-carene, limonene, and others. These components, if separated, have a higher added value compared to selling crude pine oil. Separation process by distillation is the common method to fractionate all of the components. However, distillation at atmospheric pressure has a potential to decompose some turpentine components. This study aims to obtain the optimum operating conditions that produce compounds of turpentine. The experimental method used consisted of three stages. The first stage is the analysis of components from the main raw material, turpentine. The second step is the turpentine fractionation with the process of party vacuum distillation. The third step is the analysis of the distillate results using Gas Chromatography with FID. The experiment was carried out by varying the operating pressure of the vacuum distillation process which is at 0.2 atm; 0.45 atm and 1 atm. The experimental results show that thermal degradation did not occur at pressures of 0.45 atm and 0.2 atm. The experimental results are in accordance with the simulation results with a column efficiency of 45%. Better results can be obtained by adding stages to 25 stages from 10 stages used and can achieve composition results up to analyst grade (> 99.9%). Distillation of 0.2 atm pressure is the best operating condition judging from the profit generated and its energy consumption.

1. Introduction
Turpentine which is a liquid phase of the Pinus mercusii gum product that consists of various cyclic monoterpene hydrocarbon compounds, such as α-pinene, β-pinene, δ-carene and limonene, with general molecular formula of C_{10}H_{16} [1]. Depending on the type of trees, different composition of species could be found but pinenes showed to be the largest fraction of turpentine (about 80-90% of the total component) [2]. Indonesian turpentine consists mainly of α-pinene 65-85%-wt, β-pinene 1-3%-wt, δ-carene 10-18%-wt, and δ-limonene 1-3%-wt [3].

The above fractionated products of turpentine usually have higher selling value compared to crude turpentine or mixed pine oil. Table 1 shows the comparison of the value added of turpentine derivative products and the world demand for these products [4].

| No. | Chemicals | Price (USD/ton) | Value added | Demand (ton/year) |
|-----|-----------|----------------|-------------|-------------------|
| 1.  | Turpentine | 3.400          | -           | -                 |
| 2.  | α-pinene  | 4.930          | 45%         | 300.000           |
| 3.  | β-pinene  | 5.916          | 74%         | 300.000           |
| 4.  | Limonene  | 6.630          | 95%         | 45.000            |
The quality of the separation of the components of turpentine can be reviewed by comparing the concentrations of the compounds of turpentine before, during and after distillation. This research will study the effect of operating pressure factors on boiling point and the quality of the separation of turpentine compounds, so that it can be known what operating conditions must be pursued to get good separation quality.

2. Experimental Setup
In this study, the experiment was carried out in three stages. The first stage was the initial analysis of raw materials (crude turpentine). The raw material used is turpentine from Perhutani Pine Chemical Industry (PPCI), Pemalang, Indonesia. First, the raw material was analyzed using Gas Chromatography (GC) to determine the composition of species in the feed. The second step was the fractionation process of turpentine with the vacuum distillation process at different operating pressures. The last part was the analysis of distillate obtained from the results of vacuum distillation using GC.

Feed and distillation products were analyzed using Gas Chromatography (GC-2010 Plus type with a Rtx-5 column specifying a length of 30 meters, a diameter of 0.25 mm) with helium as a carrier gas. The analysis was carried out at a Flame Ionized Detector temperature of 240°C, column temperature of 70-190°C with an initial temperature of 70°C for 6 minutes and the temperature rose to 170°C with a rise in temperature at 5°C/minute.

Distillation process was carried out under vacuum with a pressure range of 0.2 to 1 atm. A vacuum condition was required to reduce the operating temperatures that can make the constituent components of turpentine thermally degraded. Vacuum distillation operation was started by charging 5 L of raw turpentine into a 10 L distillation flask. Once the distillation apparatus is ready, the pressure was adjusted according to the experiment variations and feed turpentine was heated by adjusting the heater at certain temperature. Sampling procedure of distillate was carried out after distillate volume was reaching 1500, 3000, and 4000 mL, respectively. Distillation sample was put into vials then analyzed the content using GC.

3. Result and Discussion
This section presents experimental results and interpretations of the results obtained. The influence to be reviewed is the effect of pressure. The performance parameters reviewed in the effect given are the purity of the components of the terpene oil and whether or not a new product is formed due to thermal

| 5. | α-terpineol | 8.160 | 141% | 330.000 |
|---|---|---|---|---|
| 6. | Cineol | 12.478 | 267% | 1.100 |

Figure 1. Schematic diagram of vacuum distillation unit.
degradation caused by too high distillation temperatures and the economic analysis of the experiments that have been carried out.

3.1. Turpentine Oxidation at Atmospheric Distillation Condition

Turpentine distillation at atmospheric pressure was reviewed to determine the effect of atmospheric pressure and to compare the purity of its components with turpentine distillation under vacuum pressure. The operating condition of the column with atmospheric pressure produces boiling point of turpentine on the first drop of 152°C. This is quite close to the literature which says that turpentine has a boiling point in the range 154-170°C [4].

![Figure 2. Feed color (left) and degraded product (right).](image)

The boiling point of turpentine which is boiled at atmospheric pressure has a high enough temperature, which is 152°C. These operating conditions support the thermal decomposition of turpentine into compounds such as isoprene, benzene, toluene, xylene, naphthalene, phenanthrene, anthracene, and methylanthracene [3]. Limonone which is a constituent of converted turpentine by 30-50% produces isoprene, while α-pinene and β-pinene are converted by 10% each producing isoprene when boiled under atmospheric pressure [3]. Isoprene which is a compound from thermal degradation of turpentine is an undesirable product in the turpentine fractionation process. The formation of isoprene compounds is characterized by changing turpentine from colorless to turbid yellow, which is the color of isoprene compounds. The change in color of turpentine feed after distillation with the atmospheric pressure operating conditions is shown in Figure 2.

| Sample Condition                   | Component | Concentration (%-mol) |
|-----------------------------------|-----------|-----------------------|
| Original Feed                     | α-pinene  | 79.1                  |
|                                   | β-pinene  | 2.5                   |
|                                   | δ-carene  | 11.6                  |
|                                   | Limonene  | 0.01                  |
| Oxidized Feed (after distillation at atmospheric condition) | α-pinene  | 70.3                  |
|                                   | β-pinene  | 0.2                   |
|                                   | δ-carene  | 24.6                  |
|                                   | Limonene  | 0.05                  |
The color change from turpentine feed to a turbid yellow color indicates the process of thermal decomposition of the compounds of turpentine with the formation of isoprene compounds which reduces the number of compounds making up of turpentine such as α-pinene and β-pinene. The oxidation process of turpentine compounds was also supported by the results of the gas chromatography analysis of the two samples which detected the addition of 5 compounds, from 29 peaks to 34 peaks. In addition, it can be concluded that after turpentine undergoes a process of distillation at atmospheric pressure, the concentrations of turpentine compounds such as α-pinene and β-pinene experience a significant decrease when compared to the initial feed condition with the feed condition after distillation at atmospheric pressure. The α-pinene compound decreased by 8.9%, while the β-pinene compound decreased by 2.3%. Concentrations of α-pinene, β-pinene, δ-carene, and limonene from the results of gas chromatography analysis in the initial feed and the feed after distillation at atmospheric pressure are presented in Table 2.

Decreased concentrations of compounds containing turpentine such as α-pinene and β-pinene indicate these compounds have largely been oxidized to other compounds such as isoprene and other compounds. While the limonene compound was not reviewed because the distillation process carried out had not yet reached the time when the limonene had begun to be fractionated.

3.2. Influence of Pressure to the Distillation Product and Operation

The sampling time of the distillation experiment were done when the distillate volume reached 1500 mL, 3000 mL and 4000 mL in each variation of the experiment. The chromatographic results were quantified using peak area ratios after comparison with standard. The results of the experimental data were compared with the simulation results and shown in Figure 3 and 4.

![Figure 3](image1.png)

**Figure 3.** Purity comparison of α-pinene, β-pinene, δ-carene and limonene with respect to pressure: (a) 0.2 atm; (b) 0.45 atm and (c) 1 atm

The results obtained are in accordance with the simulation results with the efficiency of each stage that is not ideal that is equal to 0.45-0.6. Drickamer and Bradford predicted distillation of compounds with viscosity such as turpentine will have an efficiency of 45.5% so that the number of effective stages decreases according to that efficiency. The purity of α-pinene obtained is similar to the simulation results.
but slightly higher at the end of the experiment. This is because there were variations in the composition of $\alpha$-pinene at the beginning of the experiment. The $\delta$-carene component trend also has a similar profile.

![Figure 4](image_url)

**Figure 4.** Simulations of the composition of turpentine compounds to the distillate volume under different pressures: (a) 0.2 atm; (b) 0.45 atm and (c) 1 atm

The $\beta$-pinene and limonene compounds obtained showed an upward trend, according to the simulation. However, the concentration varies between experiments and does not show a trend, this can be caused by turpentine feed that is used has a number of variations in composition.

Experimental results have shown the suitability of the results with simulations with an efficiency of 0.45, if the efficiency of each stage can be changed to an ideal or the number of stages is changed to 25 stages still with no reflux, better results can be obtained with higher purity. Based on the simulation results, a decrease in pressure from atmospheric pressure to 0.45 atm and 0.2 atm pressure will increase $\alpha$-pinene recovery by 19.54% and 27.97%, respectively.

3.3. Economic Analysis

The economic aspect is seen from the increase in profits from the addition of the amount of distillate if the distillation can be carried out ideally and changes in operating costs due to the procurement of vacuum conditions. The $\alpha$-pinene product obtained is assumed to be sold entirely at market prices.

**Table 3.** Energy consumption comparison

| Energy Consumption | Vacuum pump (kJ) | Heater (kJ) | Total (kJ) |
|--------------------|------------------|-------------|------------|
| 0.2 atm            | 6876             | 12374       | 20428      |
| 0.45 atm           | 5157             | 12008       | 17545      |
The use of energy in distillation is divided into three, for reboilers, condensers and vacuum pumps. The use of vacuum reduces energy consumption in the reboiler and condenser, but there is an increase in energy in the vacuum pump. Based on the calculation results, the energy used by the heater and condenser is almost the same. Following is the energy consumption in each trial with a duration of 5 hours which is presented in Table 3.

Table 4. Cost comparison

| Pressure | Additional profit (USD) | Additional cost (USD) | Net profit (USD) |
|---------|------------------------|----------------------|-----------------|
| 0.2 atm | 3.55                   | 0.35                 | 3.2             |
| 0.45 atm| 2.51                   | 0.27                 | 2.24            |
| 1 atm   | -                      | -                    | -               |

Energy consumption for vacuum pressure distillation was higher than atmospheric pressure by 98% and 130% at pressures of 0.45 atm and 0.2 atm, respectively. The calculation is based on an α-pinene price of 4.93 USD/kg and an electricity price of 0.11 USD/kWh. Comparison among experimental runs were presented in Table 3. The calculation shows that the best results are obtained at an operation pressure of 0.2 atm.

4. Conclusion
The conclusions obtained from the study entitled Turpentine Fractionation with Vacuum Distillation carried out are:
1. Turpentine distillation is carried out at a pressure of 0.45 atm or lower to avoid thermal degradation that can occur.
2. Distillation experimental results in accordance with simulations with column efficiency of 45%.
3. Turpentine distillation operating conditions are best obtained at conditions of 0.2 atm; 0.45 atm and 1 atm respectively.

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