

Continuous Production of α -Terpineol from α -Pinene Isolated from Indonesian Crude Turpentine

Arief Budiman¹, Tya Indah Arifta², Diana³ & Sutijan¹

¹ Chemical Engineering Department, Faculty of Engineering, Gadjah Mada University, Yogyakarta, Indonesia

² Biomedical Engineering Department, Graduate School, Gadjah Mada University, Yogyakarta, Indonesia

³ Chemical Engineering Department, Faculty of Industrial Technology, Islamic University of Indonesia, Yogyakarta, Indonesia

Correspondence: Arief Budiman, Chemical Engineering Department, Faculty of Engineering, Gadjah Mada University, Jalan Grafika 2, Yogyakarta, 55281, Indonesia. Tel: 62-274-902-170. E-mail: abudiman@ugm.ac.id

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Abstract

Pine trees in Indonesia are largely of the pine *mercusii* species which typically give turpentine that contains about 82% α -pinene, 12% carene and is balanced with numerous other components such as camphene, β -pinene and limonene. When treated with water in the presence of an acetic acid catalyst, α -pinene is hydrated to become a complex mixture of monoterpenes, alcohol and hydrocarbons, although α -terpineol predominates. This α -terpineol is a valuable compound which is widely used as a fragrant substance in the cosmetic industry as an anti fungal agent in the pharmaceutical industry, a disinfectant, an odorant in the cleaning industry and as a mineral flotation agent in the mining industry. A conventional configuration for this hydration process involves two steps, chemical reaction of α -pinene in a reactor followed by a separation step in a distillation column. In this experiment, we combined both chemical reactions and separation by distillation in a reactive distillation column to reduce the production and operating cost. Steady state condition, feed plate position, pressure and volumetric ratio of α -pinene and CAA solution were investigated to study the effect of using this method. A certain ratio of 87% weight of α -pinene and 5.3 M Chloroacetic Acid (CAA) solution as a catalyst were inputted to the reactive distillation column. The result shows that the highest purity of α -terpineol is 38.89 % weight.

Keywords: α -pinene hydration, α -terpineol, reactive distillation

1. Introduction

Turpentine is an essential oil obtained from pine trees. It is one of the most important substances with many applications, being widely used as a solvent in chemical industries, resins and as an ingredient in paints (Zinkel & Russel, 1989). Indonesia, especially Java Island, is extremely rich in pine forests. A substantial portion of these forest's resources is regularly tapped in to produce oleo pine rosin which is later processed in factories located close to the tapping in and collection centers across the island of Java to produce gum rosin and turpentine. Processed in four plants, Indonesia's annual turpentine production is approximately 50 000 000 kg (<http://www.perhutani.go.id>).

It is well known that turpentine cannot be used directly to make any derivatives since it contains several components, depending on the species of pine trees. Pine trees in Indonesia consist largely of the pine *mercusii* species, which typically give turpentine that contains about 82% α -pinene, 12% carene and is balanced with numerous other components such as camphene, β -pinene and limonene. Highly purified α -pinene can be obtained by vacuum-fractional distillation of turpentine that has to reach 97% purity (Budiman, 2009).

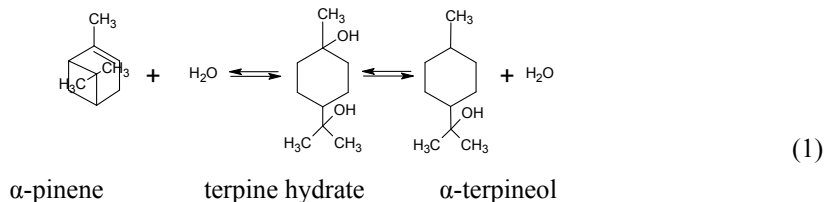
When treated with water in the presence of an acetic acid catalyst, α -pinene is hydrated to become a complex mixture of monoterpenes, alcohol and hydrocarbons, although α -terpineol predominates. This α -terpineol is a valuable compound which is widely used as a fragrant substance in the cosmetic industry as an anti fungal agent in the pharmaceutical industry (Pitarokili, Couladis, Panayoutaru, & Tzakou, 2002), a disinfectant (Yang, H.Y. Choi, W.S. Choi, Clark, & Ahn, 2004), an odorant in the cleaning industry (Arctander, 2000) and as a mineral flotation agent in the mining industry (Fuerstenau & Pradip, 1982). Park et al. (2012) reported that antimicrobial

effect of linalool and α -terpineol against periodontopathic and cariogenic bacteria, their concentration should be kept below 0.4 mg/ml if they are to be used as components of toothpaste or gargling solution.

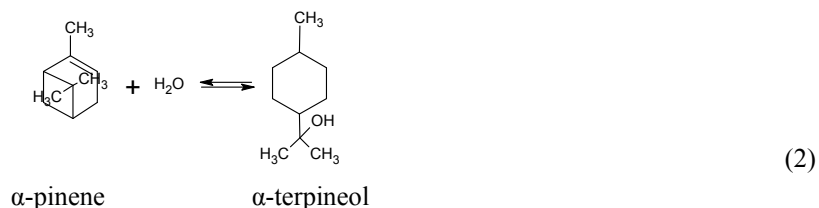
The hydration of α -pinene yielding α -terpineol by utilizing homogeneous catalyzed acid has been studied since the 1930s, when Charlton and Day (1937) studied the hydration of α -pinene using sulfuric acid at low temperatures. Several years later, in 1963 Valkanas and Iconomou reported improvement of selectivity when aqueous acetone was added to the acid catalyst.

Pakdel, Sarron, and Roy (2001) studied the hydration reaction of crude sulfate turpentine which contains 52% α -pinene and used sulfuric acid as a catalyst in the presence of acetone. They reported that the main hydration product, α -terpineol, was obtained at a yield of 77% of the initial α -pinene in the crude turpentine oil by reacting with 15% aqueous sulfuric acid and an excess of acetone. They also studied effects of good homogeneity of the initial mixture by the use of an emulsifier, but the results were not as good as expected because the yields were lower than those obtained without the emulsifier. In 2005, Roman-Aguirre, Torre-Saenz, Robau-Sanchez, and Elguezabal studied the role of chloroacetic, oxalic and acetic acid catalysts to hydrate α -pinene to terpineol using water as the hydroxyl group donor. They found chloroacetic acid to be a good catalyst for the production of α -terpineol from α -pinene due to its strong acidity, high solubility and affinity with aqueous and organic phases during reaction. The highest conversion was 99% with a selectivity of 70%.

A common method of α -terpineol synthesis consists of hydration of α -pinene with an aqueous mineral to give *cis*-terpine hydrate, followed by partial dehydration into α -terpineol (Surburg & Panten, 2006).



In the previous paper (Utami, Budiman, Sutijan, Roto, & Sediawan, 2010), we simplified the mechanism of α -terpineol synthesis as



Solid catalysts are, however, more desirable as they produce less waste and give high catalytic performance (Van der Wall, Van Bekum, & Vital, 1996; Lopez et al, 1998). Some small industrial plants already exist, but the concept for larger scale industrial application has not yet been found as it still needs optimization. To overcome this situation, homogenous acid is still an interesting option for the industrial application of the hydration of α -pinene with chloroacetic-acid being the main candidate for the acid catalyst of this hydration reaction due to its absence of chlorinated compounds and easy separation and purification from the reaction media compared to other homogeneous acid catalysts (Utami, Budiman, Sutijan, Roto, & Sediawan, 2011).

So far, terpineol production has been achieved through hydration in a batch reactor to produce terpene hydrate followed by de-hydration in a distillation column to produce perfumery α -terpineol. However, batch reactor for chemical production is simple, but it is only effective for the small production capacity of 500 – 10 000 tons product/year. For the capacity over 30 000 ton product/year, it will be more economical if the preparation conducted via a continuous process. Some works have been done which relate mainly to continuous-flow processes for chemical synthesis, such as the esterification processes of methyl or ethyl-acetate (Venkataraman, Chan, & Boston, 1990), MTBE (Huang, Wang, & Ding, 2008), propylene oxide (Bezzo, Bertuccio, Forlin, & Boarolo, 1999), bio-additive triacetin (Mufrodi, Rochmadi, Sutijan, & Budiman, 2014), biodiesel (Kusumaningtyas, Purwono, Rochmadi, & Budiman, 2014), etc. Reviews of the research, design, operation, scale-up and commercial application of this interesting area have been done by Harmsen (2007). In 2013, Chen and Huang has been designed reactive distillation using external recycle and simulation the reactive distillation using Aspen Plus has been investigated by Liu, Yang, Lu, and Yi (2013). Authors have also studied synthesis of α -terpineol from α -pinene and simulated in a continuous configuration (Tya, Sutijan, & Budiman, 2010).

In this article, we integrate the chemical reaction in the reactor and the physical separation in the distillation

column into one unit. This combined unit operation is called reactive distillation. This configuration presents numerous advantages, such as improving conversion and selectivity, a reduction of the catalyst requirement, and the avoidance of zeotrope. Since the reactor and distillation column are combined in the same vessel, the most important benefits are evident in the reduction in capital investment, plant operating costs and energy demands which are due to its heat integration (Doherty & Buzad, 1992). Besides that, we can reduce the catalyst requirement because condensate of catalyst is returned to the reactive distillation column by reflux system, reaction will be more effective and high conversion can be reached.

2. Materials and Methods

2.1 Material

Raw materials used in this study are α -pinene isolated by low-pressure distillation from crude turpentine derived from pine woods of PT Perhutani, Indonesia, and chloroacetic acid of Merck as a catalyst. Composition of crude and isolated products of turpentine is shown in Table 1.

Table 1. Composition of solution of turpentine and α -pinene

Components	turpentine	α -pinene
α -pinene	73.30	87.05
Camphene	2.09	1.64
β -pinene	5.19	2.88
Carene	13.71	3.42
Limonene	1.80	0.22

2.2 Equipment and Procedures

The experiments were performed in a continuous reactive distillation column with a capacity of 15 L/day, as shown in Figure 1. This column consists of a packed column with a diameter of 5 cm and a height of 100 cm, a condenser on the top and a re-boiler at the bottom. A pre-mixer for α -pinene and chloroacetic acid was installed before entering the column. Raschig rings were used as packing inside the column with a diameter of 0.5 cm and a length of 1 cm.

The experimental procedure to carry out the production of α -terpineol consists of a 1-h period for the startup of the electrical resistance and attainment of the programmed temperature conditions, where the reboiler, i.e., 500 ml of a three-neck flask, has been filled with 250 ml of α -pinene and 5.3 M chloroacetic acid as a catalyst at a particular volume ratio. After this period, α -pinene with a rate of 6 ml/min and catalyst were fed into a pre-mixer for unity and mixing stability. After the vacuum pump had reached 84.65 inHg, the recycle stream was allowed to flow. The reactive distillation column was operated at the total reflux, so the top product was returned to the column. Thereafter, 2-h of feedstock was passed through the column, the distillate was dripped and the bottom liquid was allowed to flow and a sample was analyzed every 30 minutes by means of Gas Chromatography. After verifying the stability of the product specification, the column operation was stopped. Total time of operation for each experiment was approximately 5 h, resulting in one experiment per day.

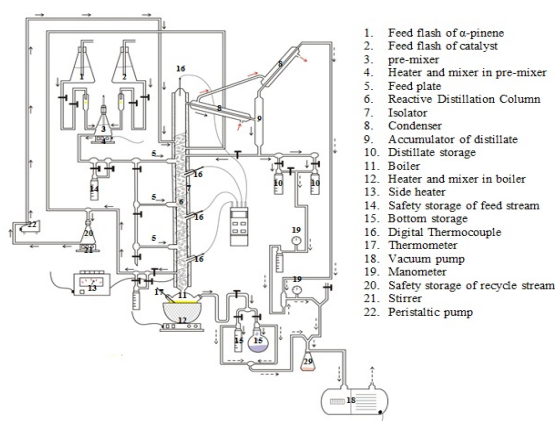


Figure 1. Series of research experiment

2.3 Analysis

Sample analysis was carried out using GC (Gas Chromatography) with the specifications attached to column HP-5 (Cross-linked 5% Phenyl methyl siloxane), length of column 30 mm, inside diameter (of column) 0.32 mm and a 0.50 μm thick film layer.

3. Results and Discussions

3.1 Steady State Condition and Feed Plate Optimum

Steady state condition in a process needs to be found with the intention of knowing when a process can be expressed as steady or how long it takes from start up until the steady condition is reached, $t = 0$ minutes was calculated when the reactive distillation column was operating normally, signaled by the stabilization of the feed stream. The recycle stream was already running and had begun to form distillate, simultaneously outputting current on the bottom flow. Observation time of the steady state condition can be done by taking samples of products from the bottom every 30 minutes starting from $t = 0$ up to $t = 150$ minutes to determine the purity of α -terpineol. This is indicated by the changes of purity of the α -terpineol which is either fairly constant or small. Table 2 shows the relationship of time and the yield of α -terpineol on a variety of feed plates.

Table 2. Purity α -terpineol and α -pinene on the bottom of products for various times with position of the feed plate

t, minutes	purity of α -terpineol, % mass			purity of α -pinene, % mass		
	Feed plate upper	Feed plate Middle	Feed plate lower	Feed plate upper	Feed plate middle	Feed plate Lower
0	28.1532	27.2503	25.9700	27.6452	29.536	30.3237
30	29.6706	29.1209	28.1104	15.9271	16.6143	18.1532
60	31.5660	30.7153	29.0149	10.1511	13.3626	14.9139
90	35.8608	34.4001	31.4670	7.9313	11.5384	13.0879
120	38.8899	36.1651	35.1214	5.6636	10.6584	11.1629
150	31.2134	30.7153	29.0149	5.1199	9.3246	9.7937

Note. t=time.

From Table 2, it can be seen that the purity of α -pinene is progressively reduced. This suggests that even though the purity of the product obtained, α -terpineol, had been maximized, the α -pinene still continued to reduce and react or be isomerized into other pinene products. It means that by the increasing time, conversion of α -pinene was increased but selectivity of α -terpineol was decreased.

The feed plate is an important parameter in a reactive distillation column because the position of the feed plate affects the effectiveness of the reaction in the reactive distillation column. In this study, three-positions of feed plate, upper, middle, and lower, were used in the reactive distillation column. Figure 2 shows the relationship of yields of α -terpineol at various times and with feed plate variations.

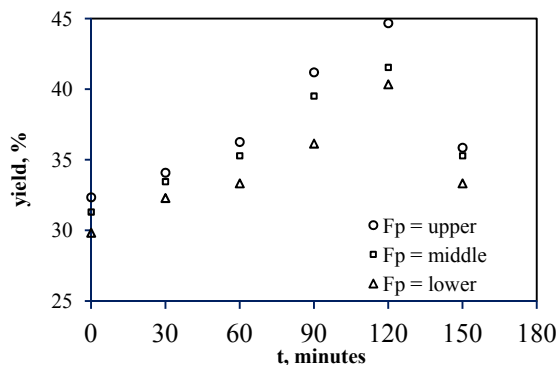


Figure 2. Relationship of time and yield of α -terpineol on a variety of feed plates

From Table 2 and Figure 2, it can be shown that as the position of the feed plate nears the bottom α -terpineol yields become lower. This is because the position of the feed plate relative to the bottom can provide a shorter reaction zone, which in turn means that contact between the reactants becomes shorter. Therefore, in subsequent studies the feed plate was located at the top in the reactive distillation column in order to achieve the countercurrent flow in the reactive section of the column, the high-boiling reactant is usually fed into the column above the reaction solution, and the low-boiling reactant is fed below the reactive section of the column, and 2 hours was expressed as the time of steady state.

3.2 Pressure

Vacuum pressure was also selected in this study. It was intended to decrease the boiling point of the components involved in the reaction, especially α -pinene as the reactant is easily converted to other isomers at high temperatures, in addition to which, α -terpineol is a product with a high boiling point. Therefore, varying the operating conditions of vacuum pressure was expected to decrease heat consumed in the reactive distillation column and avoid damage to the existing materials. Figure 3 shows the yield α -terpineol at various pressures.

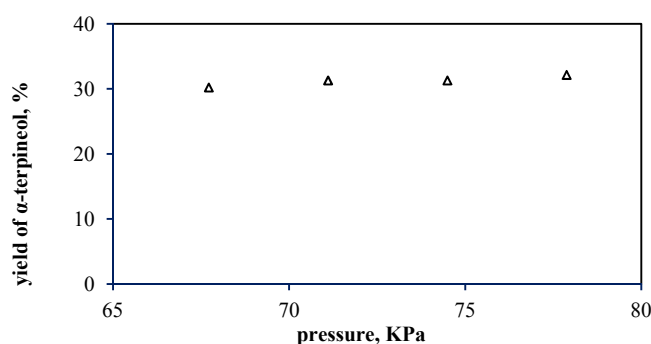


Figure 3. Yield of α -terpineol at various pressures

When the pressure was lowered, the operating temperature also dropped. Hydration of α -pinene is an endothermic reaction that requires heat. Increasing the pressure will increase the temperature and the reaction equilibrium will shift to the right, or to the product, so that the yield obtained with increased pressure becomes higher. In this study a small ΔP was used, so that the changes in yield can be said to be small or relatively constant. It is also due to the hydration reaction occurring in the liquid which involves two phases that are not mutually soluble, so that the pressure of the system is described as equation below:

$$P_T = P_1^0 + P_2^0 + P_U \quad (3)$$

P_T = total pressure of a system

P_1^0 = saturated vapor pressure of liquid 1

P_2^0 = saturated vapor pressure of liquid 2

P_U = air pressure

3.3 Ratio of Volumetric Flow

An increase in the ratio of catalyst solution to solution of α -pinene accelerates the hydration and increases the amount of water in the reactant. In fact, the conversion of α -pinene increases with an increase in the ratio of catalyst solution to α -pinene solution, but the selectivity of α -terpineol decreased. This is due to isomerization of α -pinene which produces limonene and γ -terpinene as byproducts. In other words, we want to find either the optimum composition or the most effective ratio between the solution of chloroacetic-acid catalyst and the solution of α -pinene which will provide both purity of α -terpineol and maximum yield.

Table 3. Relationships of volume ratio of chloroacetic acid and the α -pinene with the purity of waste and byproducts

catalysts/ α -pinene (v/v)	α -pinene, % mass	α -terpineol, % mass	γ -terpinene, %mass	limonene, % mass
0.5	23.3471	31.0711	17.5129	9.0072
1.0	18.5691	28.7963	19.0981	10.3452
1.5	15.2693	25.8881	22.7313	11.6308
2.0	15.5299	25.0344	22.2714	12.8938
2.5	14.7025	21.1875	24.6934	13.7635

Table 3. shows relationships of volume ratio of chloroacetic acid and the α -pinene with the purity of waste and byproducts. It shows that the more chloroacetic-acid solution is present, the more conversion of α -pinene will be increased, but the selectivity of α -pinene to α -terpineol decreases. This can be proven by the data shown in Figure 4.

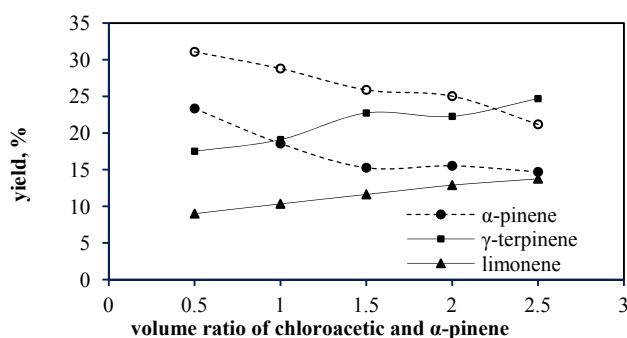


Figure 4. Relationships of volume ratio of chloroacetic acid solution and the solution of α -pinene to yield α -terpineol

A percentage of limonene 0.22% mass is shown in the feed solution while the product shows that the limonene percentage has significantly increased as well as a newly discovered product, namely γ -terpinene. From these results it can be concluded that the reaction between α -pinene hydration with water using the catalyst chloroacetic acid will be followed by isomerization of α -pinene into γ -terpinene and limonene. The more presence of acid catalyst, the more limonene and γ -terpinene will be produced as described in Figure 5.

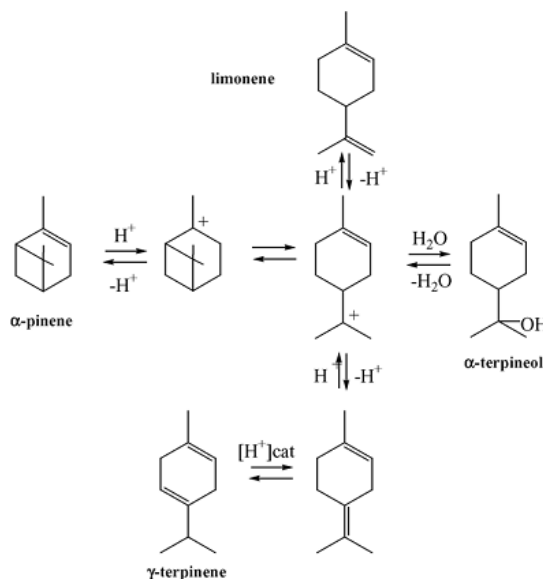


Figure 5. Synthesis of byproduct of α -pinene

4. Conclusions

The time needed for the operation to achieve the steady state is 2 hours. A higher position of the feed plate produces a higher yield of α -terpineol. Pressure changes do not affect the α -terpineol yield significantly. The higher the composition of catalyst and α -pinene, the lower the yield of α -terpineol. The reaction of the hydration of α -pinene into α -terpineol is followed by isomerization of α -pinene to become limonene and γ -terpinene.

The reactive distillation column in this experiment is more appropriately called a reaction column because the separation process was not done by setting the total reflux. From the 2 steps of α -terpineol forming from α -pinene, the controlling reaction is the hydration of α -pinene to become terpine hydrate not the reaction of dehydration of terpine hydrate to be α -terpineol.

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