

## Kinetics Modeling for Synthesis of Terpeneol from Turpentine

Herti Utami<sup>\*1</sup>, Arief Budiman<sup>1</sup>, Sutijan<sup>1</sup>, Roto<sup>2</sup>, Wahyudi Budi Sediawan<sup>1</sup>

<sup>1</sup>Chemical Engineering Department, Gadjah Mada University, Jl. Grafika No.2 Yogyakarta, Indonesia

<sup>2</sup>Chemistry Department, Gadjah Mada University, Yogyakarta, Indonesia

Email address: hertie19@hotmail.com

**ABSTRACT:** Turpentine is one of the essential oils obtained from pine tree and is a very important substance in many applications such as solvent in pharmaceutical industries and in processing of oils, resins and varnishes. Substantial part of pine tree of the forest is regularly tapped and processed to produce gum, rosin, and turpentine. Most of pines in Indonesia are pine mercusii species, which typically produce turpentine that contains of about 82% alpha pinene, 12% delta carene and balanced with other numerous components such as camphene, beta-pinene and limonene. In order to obtain more valuable products, the alpha pinene in the turpentine can be hydrated in dilute mineral acid solutions to produce terpeneol, which can be used as perfume, repellent of insect, antifungal and disinfectant. In this work, a kinetics model for synthesis of terpeneol from turpentine was developed to quantitatively describe effects of hydration process of alpha pinene in aqueous acid solution. The results of this study show that kinetics modeling of the hydration of alpha pinene using both chloro acetic acid and oxalic acid as catalyst could be approached with the heterogeneous model. The constants of the reaction rate for the first method were  $k_1 = 13,2476$  and  $k_1' = 8,6836 \times 10^{-03} \text{ ml.mol}^{-1}.\text{min}^{-1}$  for chloro acetic acid, and  $k_2 = 17,0005$  and  $k_2' = 7,3042 \times 10^{-02} \text{ ml.mol}^{-1}.\text{min}^{-1}$  for oxalic acid. The sum of squares of error of the first and the last catalysts were 0,3273 % and 0,1627%, respectively. The constants of the reaction rate for the second method were  $k_1 = 0,03130$  and  $k_1' = 0,01239 \text{ ml.mol}^{-1}.\text{min}^{-1}$  for chloro acetic acid, and  $k_2 = 0,0267$  and  $k_2' = 0,04198 \text{ ml.mol}^{-1}.\text{min}^{-1}$  for oxalic acid. The sum of squares of error of the first and the last catalysts were 0,3596 % and 0,02653%, respectively.

**Keywords:** turpentine, terpeneol, hydration, kinetics

### INTRODUCTION

Turpentine is distilled from oleo resin obtained from various species of pinus. It is colorless and transparent oily liquid with a strong specific odor and a pungent bitter taste. It is insoluble in water but soluble in alcohol, ether, chloroform and carbon disulphite (Pandhe, T.K., et al, 1994). The composition of different turpentines depends on the species of pine from which they are extracted. Most of pines in Indonesia are pine mercusii species, which typically produce turpentine that contains of about 82% alpha pinene, 12% delta carene and balanced with other numerous components such as camphene, beta-pinene and limonene. In order to obtain more valuable products, the alpha pinene in the turpentine can be hydrated in dilute mineral acid solutions to produce terpeneol, which can be used as perfume, repellent of insect, antifungal and disinfectant.

Alpha pinene is the main constituent of turpentine oil. The acid-catalyzed hydration and isomerization of alpha-pinene yields a complex mixture of monoterpenes, alcohols, and hydrocarbons. The main products are alpha-terpeneol, limonene, and terpinolene. Minor amounts of camphene, alpha and gamma-terpinene, alpha and beta-fenchol, isoborneol, borneol, gamma-terpeneol, and 1,8-terpene are

also formed (Monteiro, J.L.F., 2004). Alpha-terpeneol is one of the most important monocyclic monoterpene alcohols and one of the top 30 commonly used flavor compounds. It is produced on an industrial scale by hydration of alpha-pinene or turpentine oil to the cis-terpin hydrate with aqueous mineral acids, followed by its partial dehydration to alpha-terpeneol (Bauer, K., 1985). This process presents some difficulties such as the production of complex mixtures and the disposal of mineral acids.

Hydration and isomerization of alpha-pinene producing alcohols and terpene hydrocarbon had been studied since 1947. In 1947, Mosher studied the product distribution of acid-catalyzed alpha-pinene hydration products. The author brought to the fore the treatment of alpha-pinene with 1-chloro-4-naphthalene sulfonic acid which led to the formation of beta-pinene, limonene, terpinolene, and alpha-terpinene. The

hydration/isomerization of alpha-pinene at 329 K catalyzed by zeolite H-beta (Van der Waal, J.C., 1996) is fast and leads mainly to monocyclic terpenes and alcohols with alpha-terpeneol as the main product (up to 48%). The selectivity toward the commercially interesting bicyclic products (such as borneol and camphene) is about 26%, which is significantly better than that observed when  $\text{H}_2\text{SO}_4$  is used as catalyst. The reaction rate increases with increasing Si/Al ratio, which is possibly due to the increase of hydrophobicity of the zeolite; the selectivities are, however, not significantly affected (Van der Waal, J.C., 1996)

Pakdel et al (2001) used sulphate acid as catalyst to synthesize terpeneol from turpentine, in the presence of excess acetone as solubility promoter. They reported 67% of selectivity to terpeneol although the conversion was not reported. Aguirre et. al (2005) used hydrochloride acid, acetate acid, chloro acetic acid and oxalic acid as catalyst for the hydration of alpha-pinene. Chloro acetic acid was found as good catalyst for the production of terpeneol from pinene. The highest selectivity was 95.5% with the conversion of 10%, whereas the higher conversion was 99% with selectivity of 69% after 4 h of reaction at 70°C.

The reaction is schematically shown in figure 1:

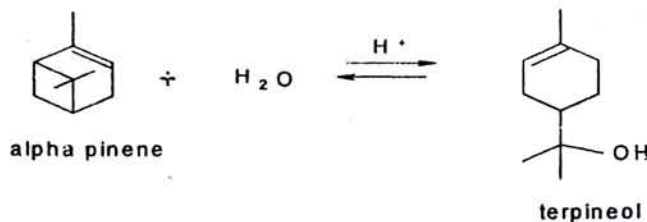


Figure 1. The reaction of alpha-pinene

### MATERIALS AND METHODS

A simulation taking into account a heterogeneous model kinetics is performed utilizing MATLAB 7. Experimental data were obtained from the paper of Aguirre, et. al.(2005) in which hydration with several kinds of catalyst (hydrochloride acid, acetate acid, chloro acetic acid and oxalic acid) had been

done. The temperature of hydration was 70°C and 6,4 mol/L catalyst concentration was applied. The reaction time studied was in the range of 25 to 240 minutes. The conversion was in the range 0,27 to 0,62 for chloro acetic acid, and in the range 0,19 to 0,27 for oxalic acid. This paper reports the kinetics modeling of hydration using chloro acetic acid and oxalic acid as catalyst.

**RESULTS AND DISCUSSION**

A heterogeneous kinetics model for synthesis of terpeneol from turpentine was developed to quantitatively describe effects of hydration process of alpha pinene in aqueous acid solution. Turpentine is assumed to be insoluble in water. The following assumption were applied :

1. The reaction take place in the oil phase.
2. The liquid film thickness is very small.
3. The reaction in liquid film is negligible and the oil does not diffuse into the water phase.

**Kinetics Model**

Mass balance water (B) in the water phase

$$\frac{dm}{dt} = k_c M_B A_c (C_{Bm}^* - C_{Bm}) \tag{1}$$

Mass balance water (B) in the oil phase :

$$\frac{dC_{Bm}}{dt} = \frac{dm}{dt} \frac{1}{M_B} \frac{1}{V_m} + k_1 C_{Am} C_{Bm} - k_1' C_{Tm} \tag{2}$$

Mass balance alpha-pinene (A) in the oil phase :

$$\frac{dC_{Am}}{dt} = k_1 C_{Am} C_{Bm} - k_1' C_{Tm} \tag{3}$$

$$\frac{dC_{Bm}}{dt} = \frac{dm}{dt} \frac{1}{M_B} \frac{1}{V_m} + \frac{dC_{Am}}{dt} \tag{4}$$

Boundary condition :

$$t = 0 ; m = m_0 ; C_{Bm} = 0 ; C_{Am} = C_{Amo}$$

Adjustable parameter :  $(k_c A_c), C_{Bm}^*, k_1$  and  $k_1'$

The kinetics model is then solved using Runge Kutta method (MATLAB 7). Evaluation of the parameters were conducted in the two methods. The first method was determining the values of  $(k_c A_c), C_{Bm}^*, k_1$  and  $k_1'$  by curve fitting method, where the sum of squares of errors (SSE) was minimized. The generated profiles are depicted in fig. 2 to 5. Fig. 2 and 4 show that the alpha pinene concentration decreases with the increase of reaction time. The conversion increases with the increase of reaction time (Fig.3 and 5). The constants of the reaction rate were found to be  $k_1 = 13,2476$  and  $k_1' = 8,8836 \times 10^{-03} \text{ ml.mol}^{-1}.\text{min}^{-1}$  for chloro acetic acid, and  $k_1 = 17,0005$  and  $k_1' = 7,3042 \times 10^{-02} \text{ ml.mol}^{-1}.\text{min}^{-1}$  for oxalic acid. The sum of squares of error of the first and the last catalysts were 0,3273 % and 0,1627%. Fig. 2 to 5 show that the kinetics model proposed can quantitatively describe the hydration of alpha-pinene using chloro acetic acid and oxalic acid as catalyst.

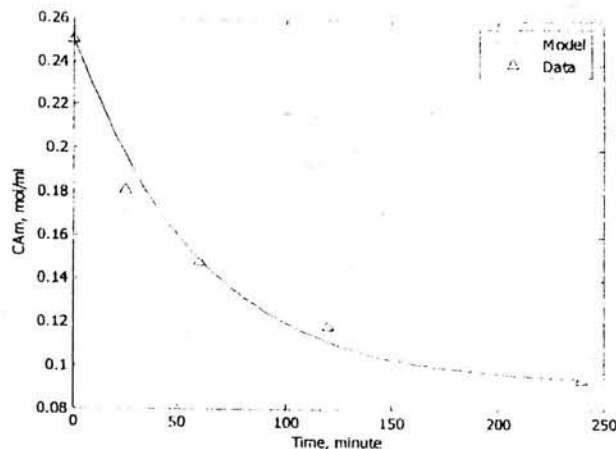


Figure 2. Concentration Profile for Chloro Acetic Acid Catalyst

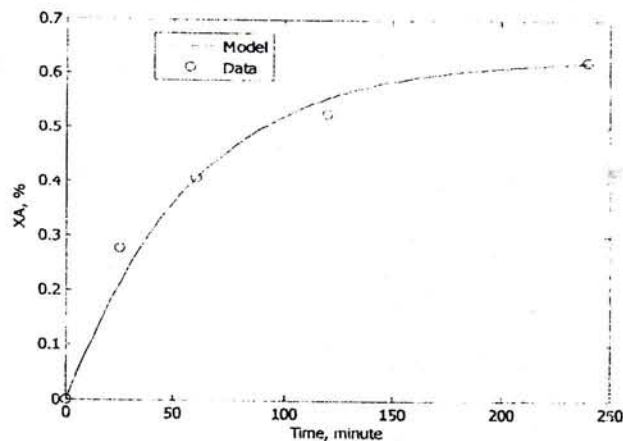


Figure 3. Conversion Profile for Chloro Acetic Acid Catalyst

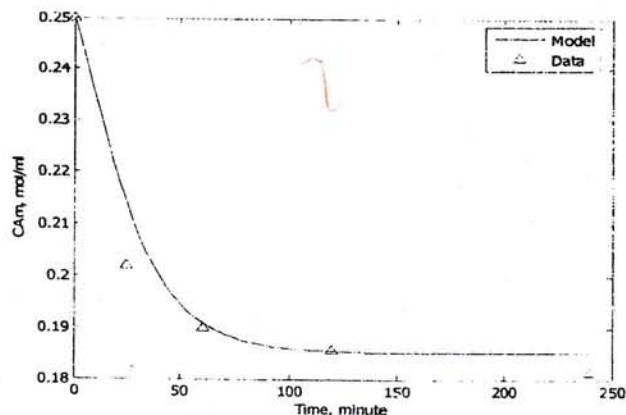


Figure 4. Concentration Profile for Oxalic Acid Catalyst

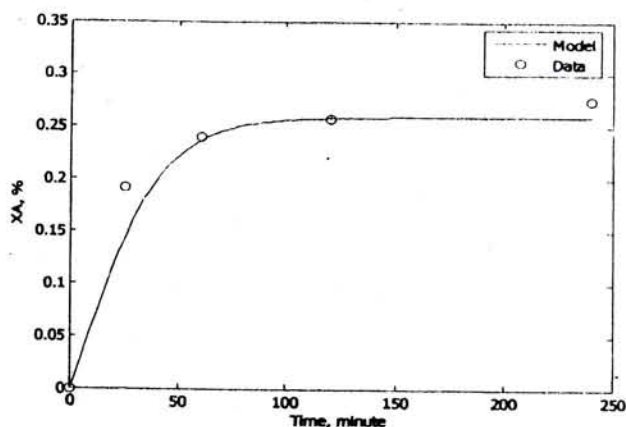


Figure 5. Conversion Profile for Oxalic Acid Catalyst

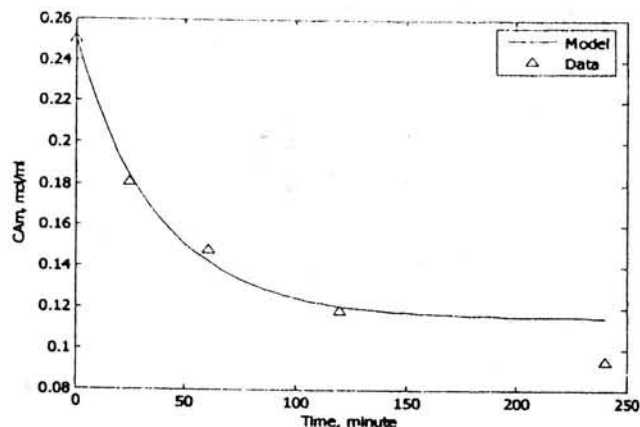


Figure 6. Concentration Profile for Chloro Acetic Acid Catalyst

In the second method, the values of  $C_{Bm}^*$  and  $K$  were approximated from the available data (Aguirre, et al.,2005) at equilibrium condition, approximately 240 minutes ( $x_A^* = 0,54$ ) for chloro acetic acid and 60 minutes ( $x_A^* = 0,25$ ) for oxalic acid, respectively. The stoichiometric equation implies :

$$C_{Am}^* = C_{Amo}(1 - x_A^*) \quad (5)$$

$$C_{Tm}^* = C_{Amo}x_A^* \quad (6)$$

$$C_{Bm}^* = C_{Bmo} - C_{Amo}x_A^* \quad (7)$$

where,

$$\frac{k_1'}{k_1} = K = \frac{C_{Tm}^*}{C_{Am}^*C_{Bm}^*} \quad (8)$$

Based on the approximated values of  $x_A^*$  from the approximated data, the values of  $C_{Bm}^*$  and  $K$  can be calculated by equations (5), (6), (7) and (8). It turned out that for chloro acetic acid,  $C_{Bm}^* = 0,465$  mol/mL and  $K = 2,525$ , while for oxalic acid,  $C_{Bm}^* = 0,5364$  mol/mL and  $K = 0,636$ . Since  $C_{Bm}^*$  and  $K$  have been calculated, the adjustable parameter variables are then  $(k_{Ac})$  and  $k_1$ . The values of parameter  $(k_{Ac})$ , and  $k_1$  were determined by the same method, where the sum of squares of errors (SSE) was minimized. Fig. 6 shows that the alpha pinene concentration decreases with the increase of reaction time for chloro acetic acid catalyst. The similar trend also occurs on the fig. 8 for oxalic acid catalyst. The constants of the reaction rate were  $k_1 = 0,03130$  and  $k_1' = 0,01239$  ml.mol<sup>-1</sup>.min<sup>-1</sup> for chloro acetic acid, and  $k_1 = 0,0267$  and  $k_1' = 0,04198$  ml.mol<sup>-1</sup>.min<sup>-1</sup> for oxalic acid, whereas, the sum of squares of error of the first and the last catalysts were 0,3596 % and 0,02653%, respectively. Figures 6 to 9 show the similar results in which the kinetics model proposed can quantitatively describe the hydration of alpha-pinene using chloro acetic acid and oxalic acid as catalyst. The parameters evaluation in the second method was simpler than in the first method. It is suggested the values obtained by the second method were more accurate since less adjustable parameters applied and the values of  $C_{Bm}^*$  and  $K$  were directly evaluated from the experimental data.

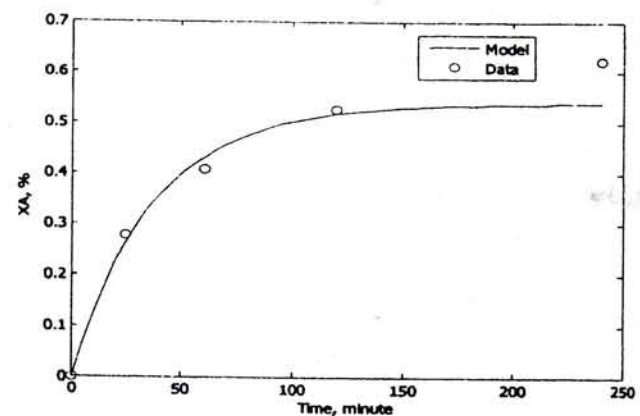


Figure 7. Conversion Profile for Chloro Acetic Acid Catalyst

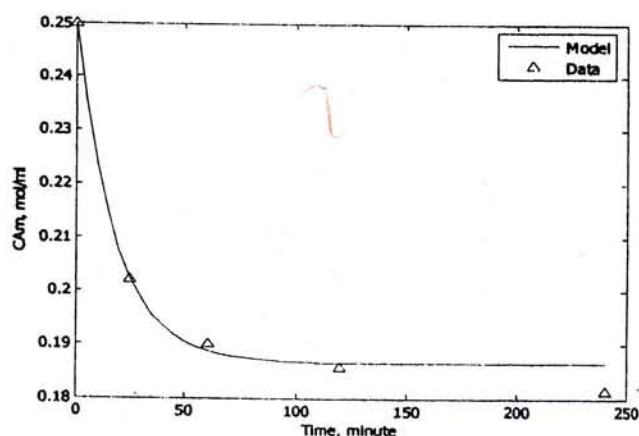


Figure 8. Concentration Profile for Oxalic Acid Catalyst

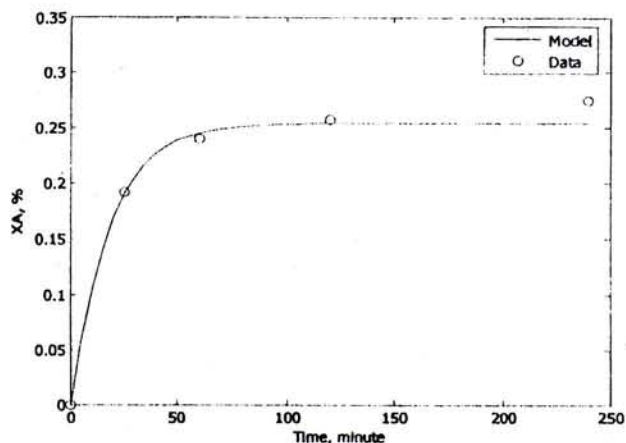


Figure 9. Conversion Profile for Oxalic Acid Catalyst

### CONCLUSIONS

The results of this study show that kinetics modeling of the hydration of alpha pinene using both chloro acetic acid and oxalic acid as catalyst could be approached with the heterogeneous model. Evaluation of parameters for the heterogeneous model were conducted in the two methods. The constants of the reaction rate for the first method were  $k_1 = 13,2476$  and  $k_1' = 8,8836 \times 10^{-03} \text{ ml.mol}^{-1}.\text{min}^{-1}$  for chloro acetic acid, and  $k_1 = 17,0005$  and  $k_1' = 7,3042 \times 10^{-02} \text{ ml.mol}^{-1}.\text{min}^{-1}$  for oxalic acid. On the other hand, the sum of squares of error of the first and the last catalysts were 0,3273 % and 0,1627%. The constants of the reaction rate for the second method were  $k_1 = 0,03130$  and  $k_1' = 0,01239 \text{ ml.mol}^{-1}.\text{min}^{-1}$  for chloro acetic acid, and  $k_1 = 0,0267$  and  $k_1' = 0,04198 \text{ ml.mol}^{-1}.\text{min}^{-1}$  for oxalic acid. While, the sum of squares of error of the first and the last catalysts were 0,3596 % and 0,02653%, respectively. The parameter evaluation in the second method was simpler than in the first method. It is suggested the values obtained by the second method were more accurate since less adjustable parameters applied and the values of  $C_{Bm}^*$  and  $K$  were directly evaluated from the experimental data.

### NOTATION

- $A_c$  = Mass transfer area = total area interface,  $\text{cm}^2$   
 $C_{Am}$  = Concentration alpha-pinene in oil phase,  $\text{mol/mL}$   
 $C_{Bm}$  = Water concentration in oil phase,  $\text{mol/mL}$   
 $C_{Amo}$  = Initial of concentration alpha-pinene in oil phase,  $\text{mol/mL}$   
 $C_{Bmo}$  = Initial of water concentration in oil phase,  $\text{mol/mL}$   
 $C_{Tm}$  = Terpeneol concentration in oil phase,  $\text{mol/mL}$   
 $C_{Um}^*$  = Water concentration in equilibrium,  $\text{mol/mL}$   
 $C_{Am}^*$  = Alpha-pinene concentration in equilibrium,  $\text{mol/mL}$   
 $C_{Tm}^*$  = Terpeneol concentration in equilibrium,  $\text{mol/mL}$   
 $k_c$  = Mass transfer coefficient  
 $k_1$  = Constant kinetic reaction,  $\text{ml.mol}^{-1}.\text{min}^{-1}$   
 $k_1'$  = Constant kinetic reaction,  $\text{ml.mol}^{-1}.\text{min}^{-1}$   
 $K$  = Constant equilibrium reaction  
 $m$  = Water mass in water phase,  $\text{gr/mL}$   
 $m_0$  = Initial of water mass,  $\text{gr/mL}$   
 $M_B$  = Molecular weight water,  $\text{gr/gmol}$   
 $t$  = Time reaction, minute  
 $V_m$  = Total volume of oil,  $\text{mL}$   
 $X_A$  = Conversion  
 $X_A^*$  = Conversion at equilibrium

### REFERENCES

- Aguirre, M.R, et al, (2005), Synthesis of Terpeneol from  $\alpha$ -pinene by Homogeneous Acid Catalysis, *Catalysis Today* 107-108, p. 310-314.  
 Bauer, K., Garbe, D., and Surburg, H., (1985), Common Fragrance and Flavor Materials, Preparation, Properties and Uses, VCH, Weinheim  
 Monteiro, J.L.F, and Veloso, C.O., (2004), Catalytic Conversion of Terpenes Into Fine Chemicals, *Topics in Catalysis*, Vol. 27, Nos. 1-4  
 Mosher, W.A., 1947, The Acid-catalyzed isomerization of  $\alpha$ -pinene, *J. Am. Chem. Soc.*, 69, 2139-2141.  
 Pandhe, T.K., Pani, S., Hiran, S., Rao, V.V.B., Shah, H., Vishwanathan, K.A., (1994), Turpentine poisoning : A Case Report, *Forensic Science International*, 65, 47-49  
 Pakdel, H., Sarron, S., Roy, C., (2001),  $\alpha$ -Terpeneol from Hydration of Crude Sulfate Turpentine Oil, *J. Agric. Food Chem.*, v. 49, 4337-4341  
 Van der Waal, J.C., Van Bekkum, H., Vital, J.M., (1996), The Hydration and Isomerization of  $\alpha$ -Pinene Over Zeolit Beta. A New Coupling Reaction between  $\alpha$ -Pinene and Ketones, *Journal of Molecular Catalysis*, 185-188