

Heterogeneous Kinetics of Hydration of α -Pinene for α -Terpineol Production: Non-Ideal Approach

Herti Utami, Arief Budiman, Sutijan, Roto, Wahyudi Budi Sediawan

Abstract— α -pinene is the main component of most turpentine oils. In order to obtain more valuable products, α -pinene in the turpentine can be hydrated in dilute mineral acid solutions to produce α -terpineol, which can be used as perfume, repellent of insect, antifungal and disinfectant. This paper presents a study on heterogeneous kinetics model for synthesis of α -terpineol from α -pinene. In this work, the two kinetics models both the ideal and the non ideal solution assumption have been developed to quantitatively describe effects of hydration process of α -pinene in aqueous acid solution. The results of this study show that the kinetics model of the hydration of α -pinene can be approached by the heterogeneous model. A good agreement between the experimental data and the model has been observed.

Keywords— α -pinene, α -terpineol, hydration, kinetics

I. INTRODUCTION

TURPENTINE contains four major classes of components which are hydrocarbon, terpene alcohols, ethers, and sesquiterpenes [5]. α -Pinene ($C_{10}H_{16}$) is the main component of most turpentine oils. α -Pinene and β -pinene are the key compounds for the fine chemical synthesis and the important intermediates in pharmaceutical industry and perfumery [2]. The acid-catalyzed hydration and isomerization of α -pinene yields a complex mixture of monoterpenes, alcohols, and hydrocarbons. The main products are α -terpineol, limonene, and terpinolene. Minor amounts of camphene, α and γ -terpinene, α and β -fenchol, isoborneol, borneol, γ -terpineol, and 1,8-terpine are also formed [3]. α -Terpineol ($C_{10}H_{18}O$) is the most important compound of the monocyclic monoterpene alcohols. Terpineol can be used as perfume, repellent of insect, antifungal and disinfectant [1]. The hydration of terpene via acid catalysis is an important method for alcohol synthesis, and has several applications in the perfume and pharmaceutical industries. Aguirre et al. (2005) used hydrochloride acid, acetic acid, chloro acetic acid and oxalic acid as catalyst for the hydration of α -pinene. Chloro acetic

acid was found to be a good catalyst for the production of terpineol from pinene. After 4 h of reaction at 70°C, the highest selectivity was 95.5% with the conversion of 10%, whereas the higher conversion was 99% with selectivity of 69% [1]. Pakdel et al. (2001) used sulphuric acid as catalyst to synthesize terpineol from turpentine, in the presence of excess acetone as solubility promoter. They reported 67% of selectivity to terpineol although the conversion was not reported [4].

II. FUNDAMENTAL

A heterogeneous kinetics model for synthesis of α -terpineol from α -pinene was developed to quantitatively describe effects of hydration process of α -pinene in aqueous acid solution. α -Pinene is assumed to be completely insoluble in water. The following assumption were applied : the reaction takes place in the oil phase, the liquid film thickness is very small, so the reaction takes place in the bulk of the oil phase and the oil does not diffuse into the water phase.

Kinetics Model

The hydration reaction of α -pinene using acid catalyst is schematically shown in Figure 1:

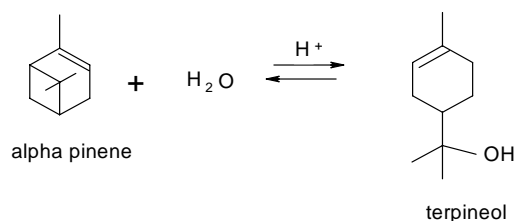
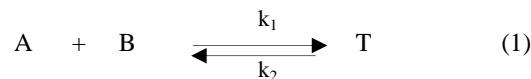


Figure 1. The reaction of α -pinene

The reaction in figure 1 can be written as (1)



where A = α -pinene, B = water, T = α -terpineol. The reaction rate can be written as (2) for the ideal solution assumption.

$$-r_1 = k_1 C_{Am} C_{Bm} - k_2 C_{Tm} \quad (2)$$

In the reaction modeling for a liquid system where the mixture is non ideal, correction must be made to the concentration. Usually, a phase model such as the UNIFAC and NRTL phase equilibrium models are used to predict this non ideality factor, the activity coefficient (γ). The rate equation is then written in terms of the activity of each component participating in the mixture (a_i). The reaction rate hence can be written as (3) for the non ideal solution.

$$-r_1 = \frac{k_1 C_{Tm}}{\gamma_{Am} \gamma_{Bm}} \left(a_{Am} a_{Bm} C_{Tm} - \frac{1}{K_y K} a_{Tm} \right) \quad (3)$$

Herti Utami is with the Lampung University, Bandar Lampung, Indonesia (corresponding author to provide phone : +62-0274-9232121; fax: +62-0274-902170; e-mail: hertie19@hotmail.com).

A. Budiman, is with the Gadjah Mada University, Yogyakarta, 55281, Indonesia. He is now with the Department of Chemical Engineering, Gadjah Mada University, Yogyakarta, Indonesia (e-mail: abudiman@ugm.ac.id)

Sutijan is with the Gadjah Mada University, Yogyakarta, 55281, Indonesia He is now with the Department of Chemical Engineering, Gadjah Mada University, Yogyakarta, Indonesia (e-mail: sutijan@chemeng.ugm.ac.id)

Roto is with the Gadjah Mada University, Yogyakarta, 55281, Indonesia. He is now with the Department of Chemistry, Gadjah Mada University, Yogyakarta, Indonesia (e-mail: roto05@ugm.ac.id)

W.B. Sediawan is with the Gadjah Mada University, Yogyakarta, 55281, Indonesia. He is now with the Department of Chemical Engineering, Gadjah Mada University, Yogyakarta, Indonesia (e-mail: wbsrby@indosat.net.id)

where $K = \frac{k_1}{k_2} = \frac{C_{Tm}}{C_{Am}C_{Bm}}$ and $K_Y = \frac{\gamma_{Tm}}{\gamma_{Am}\gamma_{Bm}}$ and $a_i = \gamma_i x_i$

For heterogeneous model, the mass balance of water (B) in the water phase can be written as (4)

$$\frac{dm}{dt} = k_c M_B A_c (C_{Bm}^* - C_{Bm}) \quad (4)$$

and the mass balance of water (B) in the oil phase can be written as (5)

$$\frac{dC_{Bm}}{dt} = \frac{dm}{dt} \frac{1}{M_B} \frac{1}{V_m} + (-r_1) \quad (5)$$

The mass balance of α -pinene (A) in the oil phase can be written as (6)

$$\frac{dC_{Am}}{dt} = r_1 \quad (6)$$

The mass balance of α -terpineol (T) in the oil phase can be written as (7), with the boundary condition : $t = 0 ; m = m_0 ; C_{Bm} = 0 ; C_{Am} = C_{Amo} ; C_{Tm} = 0$. The adjustable parameters encountered in the model are then $(k_c A_c)$, k_1 and k_d .

$$\frac{dC_{Tm}}{dt} = (-r_1) - k_d C_{Tm} \quad (7)$$

The kinetics model is then solved using Runge Kutta method. Evaluation of the parameters were conducted by curve fitting method. The chosen values were the ones which give the minimum values of the sum of squares of errors (SSE) for all runs, data. The SSE was defined as equation (8).

$$SSE = \sum (x_{calc} - x_{data})^2 \quad (8)$$

III. EXPERIMENT

Experiments were conducted using the batch reactor (three neck flask), condenser, thermometer, heating mantle, vials, pipettes and other glass wares. A 0.25 mol of α -pinene sample was poured into a three neck flask (pyrex 500 ml) equipped with condenser (pyrex), thermometer, stirrer and was warmed up to the desired temperature. In the other glasses, 0.6 mol of aquadest (the mol ratio aquadest to α -pinene was 2.4/1) and the chloro acetic acid catalyst (the catalyst concentration was 6 mol/L) were warmed up to the desired temperature. Once the desired temperature was reached, the aquadest and the catalyst was loaded into the flask. The mixture was stirred and the reaction time was started to be calculated. The temperature was kept constant during the process. A sample was taken at every 60 min time interval during the hydration and was kept in a small vial. The experiment was conducted with various temperatures at 60°C, 70°C, 80°C, and 90°C.

The samples were analyzed using a Gas Chromatograph (GC). The analysis was performed in a Hewlett-Packard model 5890 gas chromatograph. The separation was performed using HP-5 capillary column and Flame Ionization Detector with helium as a carrier gas. The GC oven temperature was set at initial temperature of 80°C, held for 5 minutes, increased at a rate of 5°C/min to 115°C and then increased to 280°C at a rate of 20°C/min. The injector and detector temperatures were set at 280°C respectively.

IV. RESULT AND DISCUSSION

The experiment provides data of temperature (T) and conversion of α -pinene (x_{data}) at various time (t) for each variable of temperatures. In the first model (ideal solution assumption), the values of C_{Bm}^* and K were approximated

from the experimental data. The stoichiometric equation implies :

$$C_{Am}^* = C_{Amo}(1 - x_A^*) \quad (9)$$

$$C_{Tm}^* = C_{Amo} x_A^* \quad (10)$$

$$C_{Bm}^* = C_{Bmo} - C_{Amo} x_A^* \quad (11)$$

where K can be written as (12)

$$K = \frac{k_1}{k_2} = \frac{C_{Tm}^*}{C_{Am}^* C_{Bm}^*} \quad (12)$$

Based on the approximated values of x_A^* from the experimental data, the values of C_{Bm}^* and K can be calculated by equations (9), (10), (11) and (12). The values of parameter : $(k_c A_c)$, k_1 and k_d were determined by curve fitting method, where the sum of squares of errors (SSE) was minimized. The generated profiles are depicted in Figure 2 and 3. Figure 2 shows that the conversion increases with the increase of reaction time. The α -pinene concentration decreases with the increase of reaction time (Figure 3). However the study revealed that the conversion decreased after 240 min (at the temperature of 80°C) and after 180 min (at the temperature of 90°C). The decrease of the conversion caused formation of by products. The constants of degradation rate were found to be $k_d = 0.0002 \text{ ml.mol}^{-1}.\text{min}^{-1}$ (at the temperature of 80°C) and $k_d = 0.0019 \text{ ml.mol}^{-1}.\text{min}^{-1}$ (at the temperature of 90°C).

The constants of the reaction rate, k_1 and k_2 are influenced by the temperature. The constants could be correlated by the Arrhenius's equation, and the equations can be written as (13) and (14). The relative errors in equation (13) and (14) are 2.540 % and 2.326%, respectively.

$$k_1 = 2.632 \cdot 10^{10} e^{\frac{-9897.03}{T}} \quad (13)$$

$$k_2 = 1.829 \cdot 10^8 e^{\frac{-8383.68}{T}} \quad (14)$$

Figure 2 and 3 show that the kinetics model proposed can quantitatively describe the hydration of α -pinene using chloro acetic acid as catalyst. The constants of equilibrium and mass transfer coefficient are listed in table I.

TABLE I
CONSTANTS OF EQUILIBRIUM AND MASS TRANSFER COEFFICIENT
(IDEAL SOLUTION)

Temperature (K)	K	$k_c A_c$ (1/minute)
333	1.4097	1.5379
343	1.8268	1.0115
353	2.3951	2.4185
363	1.9032	1.0459

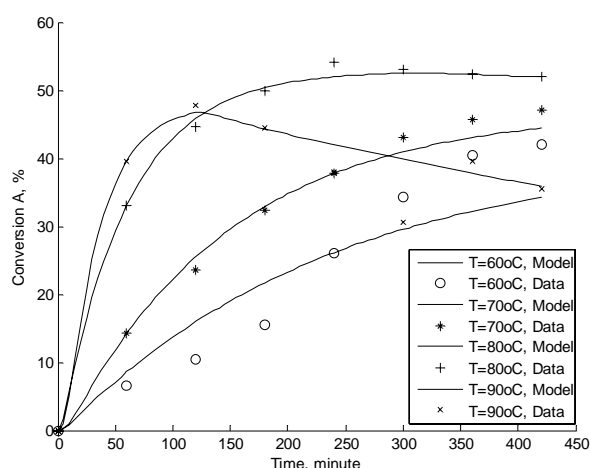


Figure 2. Conversion profile for the ideal solution assumption

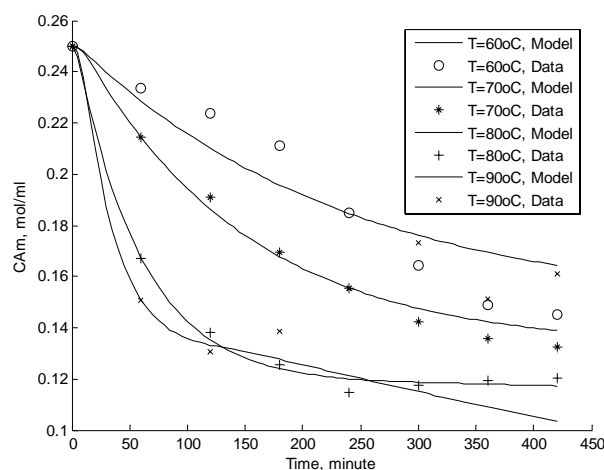


Figure 3. Concentration profile for the ideal solution assumption

For the non ideal solution approach, the activity coefficients were obtained based on the UNIFAC model. UNIFAC group contribution method is based on a principle that the prediction of the activity coefficient of a liquid mixture can be conducted by building each component from the individual components that the molecule is composed of and then using this to predict the activity coefficient based on the bulk mixture composition. The UNIFAC model is a correlation for determining the activity coefficient uses the contributions of the interactions between functional groups, such as $-OH$, $-CH_3$ etc., rather than the interaction between the molecules in the mixture. The UNIFAC model has a combinatorial contribution to the activity coefficients, essentially due to differences in size and shape of the molecules, and a residual contribution, essentially due to energetic interactions.

The values of parameter : $(k_c A_c)$, k_1 and k_d were determined by curve fitting method, where the sum of squares of errors (SSE) was minimized. For the UNIFAC model, the similar trend also occurs on Figure 4 and 5. Figure 4 shows that the conversion increases with the increase of reaction time. And the α -pinene concentration

decreases with the increase of reaction time (Figure 5). The conversion has a tendency to increase by the increase of the reaction temperature. For the UNIFAC model, the constants of degradation rate were found to be $k_d = 0.000108 \text{ ml}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ (at the temperature of 80°C) and $k_d = 0.000225 \text{ ml}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ (at the temperature of 90°C).

The constants of the reaction rate, k_1 and k_2 could be correlated by the Arrhenius's equation, and the equations can be written as (15) and (16). The relative errors in equation (15) and (16) are 5.547% and 4.734%, respectively.

$$k_1 = 5.283 \cdot 10^3 e^{\frac{-4989.19}{T}} \quad (15)$$

$$k_2 = 3.285 \cdot 10^2 e^{\frac{-4023.48}{T}} \quad (16)$$

The constants of equilibrium and mass transfer coefficient are listed in table II. In figure 4 and 5 show the similar results in which the kinetics model with non ideal approach (UNIFAC model) proposed can quantitatively describe the hydration of α -pinene using chloro acetic acid as catalyst.

TABLE II
CONSTANTS OF EQUILIBRIUM AND MASS TRANSFER COEFFICIENT
(NON IDEAL SOLUTION)

Temperature (K)	K	$k_c A_c$ (1/minute)
333	0.6730	0.4753
343	1.0464	0.1327
353	1.3691	2.2956
363	1.0428	2.3096

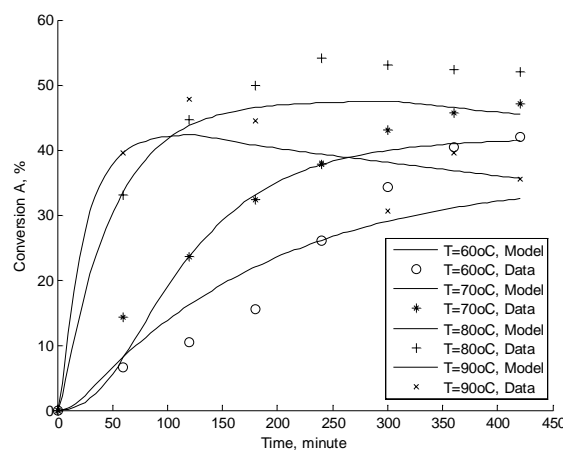


Figure 4. Conversion profile for the UNIFAC model

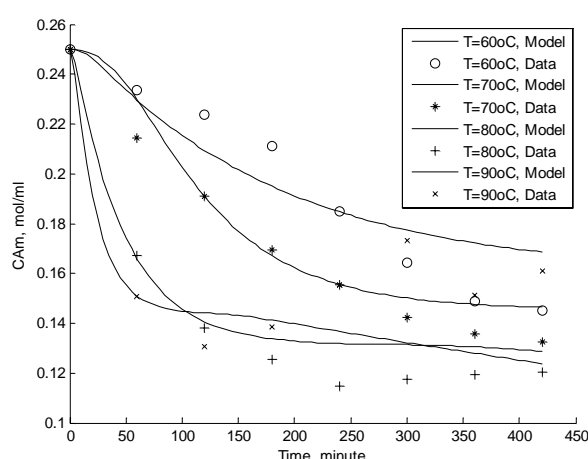


Figure 5. Concentration profile for the UNIFAC model

The proposed heterogeneous kinetics model for synthesis of α -terpineol from α -pinene could be approached with the ideal and non ideal solution assumption (UNIFAC model). The ideal solution approach model in Figure 2 and 3 fits the data better than the UNIFAC model in Figure 4 and 5. In the other words, the deviations found for the UNIFAC model are greater than the ideal equations model. The system consists of α -pinene (2,6,6-trimethylbicyclo (3.1.1) hept-2-ene), water, chloro acetic acid and α -terpineol that they are polar compounds. The slightly deviations of the UNIFAC model influenced by the group interaction parameter values for polar compounds. The system is thermodynamically deviating from ideal behavior due to several causes as the strong polarity of component, their association behavior, etc.

V. CONCLUSIONS

The results of this study show that kinetics modeling of the hydration of α -pinene using chloro acetic acid as catalyst could be modeled with a heterogeneous model. The different kinetics models both the ideal and the non ideal solution assumption (UNIFAC model) have been developed to quantitatively describe effects of hydration process of α -pinene in aqueous acid solution. Evaluation of parameters for the heterogeneous model were conducted. A good agreement between the experimental data and the model has been observed.

NOTIFICATION

A_C = Mass transfer area = total area *interface*, cm^2
 C_{Am} = α -pinene concentration in oil phase, mol/mL
 C_{Bm} = Water concentration in oil phase, mol/mL
 C_{Amo} = Initial concentration α -pinene in oil phase, mol/mL
 C_{Bmo} = Initial water concentration in oil phase, mol/mL
 C_{Tm} = α -Terpineol concentration in oil phase, mol/mL
 C_{Bm}^* = Water concentration in equilibrium, mol/mL
 C_{Am}^* = α -pinene concentration in equilibrium, mol/mL
 C_{Tm}^* = α -Terpineol concentration in equilibrium, mol/mL
 $k_c A_c$ = Mass transfer coefficient, 1/minute
 k_1 = Constant of kinetic reaction, $\text{ml}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$

k_2 = Constant of kinetic reaction, $\text{ml}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$
 K = Constant of equilibrium reaction
 m = Water mass in water phase, g/mL
 m_0 = Initial water mass, g/mL
 M_B = Molecular weight of water, g/gmol
 t = Reaction time, minute
 V_m = Total volume of oil, mL
 x_A = Conversion of α -pinene
 x_A^* = Conversion of α -pinene at equilibrium
 x_i = Conversion of i-component
 γ_{Am} = Activity coefficient of α -pinene in oil phase
 γ_{Bm} = Activity coefficient of water in oil phase
 γ_{Tm} = Activity coefficient of α -terpineol in oil phase
 γ_i = Activity coefficient of i-component

ACKNOWLEDGMENT

The authors acknowledge Directorate General of Higher Education of Indonesia (DIKTI) through Doctoral Grant no.LPPM-UGM/1166/2009 for funding of this research.

REFERENCES

- [1] Aguirre, M.R, De la Torre-Sa'enz,L., Flores, W.A., Robau-Sa'anchez, A., and Elgue'zabal, A., 2005, "Synthesis of Terpineol from α -Pinene by Homogeneous Acid Catalysis", *Catalysis Today*. 310-314, 107-108.
- [2] Deliy, I.V., and Simakova, I.L. 2008, "Kinetics and Thermodynamic of Liquid Phase Isomerization of α and β - Pinene Over Pd/C Catalyst", *React. Kinet. Catal. Lett.* 161-174, 95.
- [3] Fredenslund, A., Gmehling, J., and Rasmussen, P.,1977, "Vapor-Liquid Equilibria Using UNIFAC", Elsevier, Amsterdam.
- [4] Monteiro, J.L.F, and Veloso, C.O.,2004, " Catalytic Conversion of Terpenes Into Fine Chemicals", *Topics in Catalysis*. 1-4, 27.
- [5] Pakdel, H., Sarron, S., and Roy, C.,2001, " α - Terpineol from Hydration of Crude Sulfate Turpentine Oil ", *J. Agric. Food Chem.*4337-4341, 49.
- [6] Prausnitz, J.M., Lichtenthaler, R.N., Gomez de Azevedo, E., 1986, "Molecular Thermodynamics of Fluid-Phase Equilibria", 2nded., Prentice Hall, Inc., Englewood Cliffs, New Jersey.
- [7] Zinkel, D.F. and Russel, J., 1996, *Naval Stores: "Production, Chemistry and Utilisation"*, Pulp Chemicals Association, New York.