# Kinetics Modeling of Hydration α-Pinene to α-Terpineol Using Solid Catalyst

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## Abstract

α-Pinene is the main component of the most turpentine oils. The hydration of α-pinene with acid catalysts leads to a complex mixture of monoterpenes. By controlling the reaction variables it is possible to make the reaction highly selective towards the desired products, namely α-terpineol. The data on synthesis of α-terpineol from α-pinene in the presence of different catalysts have been studied. The hydration of α-pinene can also be accomplished with catalyst of zeolite H-beta.

In this paper, a kinetics model was developed to quantitatively describe hydration of α-pinene for α-terpineol synthesis using solid catalyst. The model is assumed that the zeolite catalyst is porous and sphere shaped particle. It is found that the kinetics model is in agreement with the experimental data.

**Keyword:** α-Pinene, α-Terpineol, Hydration, Kinetics, Solid catalyst

## Introduction

Turpentine is a mixture of cyclic monoterpene hydrocarbons, such as α-pinene, champene, β-pinene and 3-carene in which α-pinene the predominant constituent [2]. α-Pinene and β-pinene are important compounds for fine chemical synthesis and important intermediates in pharmaceutical industry and perfumery [4]. 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 [5]. α-Terpineol ($C_{10}H_{18}O$) is the most important of the monocyclic monoterpene alcohols. Terpineol can be used as perfume, repellent of insect, antifungal and disinfectant [1].

The synthesis of alcohols from α-pinene in the presence of different catalyst has been well studied. Vital et al. (2001) investigated the hydration of α-pinene over the catalyst of polydimethylsiloxane (PDMS) membranes loaded with USY zeolite. The main reaction product is α-terpineol, while being simultaneously formed are a number of minor products, mainly terpenic hydrocarbon [8].

The hydration/isomerization of α-pinene at 56$^{o}$C catalyzed by zeolite H-beta is fast and leads mainly to monocyclic terpenes and alcohols with α-terpineol 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 $H_2SO_4$ 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 [7].

Avila et al. (2010) reported the use of solid acid catalyst. The catalyst was prepared by impregnating trichloroacetic acid (TCA) on different supports such as silica, titania and zirconia ($TCA/SiO_2$, $TCA/TiO_2$, and $TCA/ZrO_2.nH_2O$, respectively) [3]. Arias et al. (2000) reported the hydration of turpentine oil using dealuminated faujasite as catalyst. The main product was the monocyclic alcohol, α-terpineol (44%) while the non alcoholic isomerization co-product was only 24% [2].

## Material and Methods

A simulation taking into account a heterogeneous model kinetics is performed. Experimental data were obtained from the paper of Van der Waal, et. al (1996) in which hydration with zeolite H-beta (Si/Al = 10)

catalyst had been done. The reaction temperature was 56°C.

## Results and Discussion

### Kinetics Model

A heterogeneous kinetics model for synthesis of α-terpineol from α-pinene was developed to quantitatively describe effects of hydration.

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

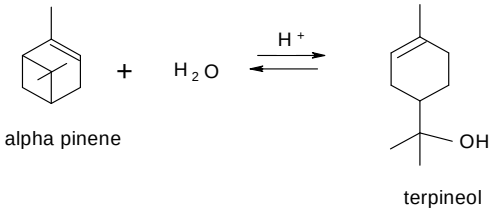


Fig.1. The reaction of α-pinene

The mechanism of reaction proceed in the following steps.

1. α-Pinene molecule diffuses from bulk liquid to the surface of solid catalyst
2. Water molecule diffuses from bulk liquid to the surface of solid catalyst
3. Diffusion of α-pinene molecule inside porous particle through pore solid catalyst
4. Diffusion of water molecule inside porous particle through pore solid catalyst
5. α-Pinene molecule is adsorbed onto the surface of pore solid catalyst
6. Water molecule is adsorbed onto the surface of pore solid catalyst
7. The reaction takes place on the surface of solid catalyst pore
8. α-Terpineol products are desorbed from the pore surface
9. Diffusion of α-terpineol products to the particle surface through the pore
10. α-Terpineol molecule diffuses from the surface of solid catalyst to the bulk of liquid

The kinetic model is developed based on the following assumptions:

1. Isothermal and isobaric reaction conditions
2. The zeolite catalyst is porous and sphere shaped particle
3. The steps of 3,7 and 9 control the overall process.

The reaction rate can be written as (1).

$$-r_A = k_1(C_A C_B - \frac{1}{K} C_T) \quad (1)$$

where $K = \frac{k_1}{k_2}$.

Mass balance of α-pinene in the spherical particle can be written as (2).

$$\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}\frac{\partial C_A}{\partial r} - \frac{k_1}{D_e}(C_A C_B - \frac{C_T}{K}) = \frac{1}{D_e}\frac{\partial C_A}{\partial t} \quad (2)$$

If the water concentration in the particle equals to the one in the bulk of liquid, and $\frac{k_1}{D_e} = \beta$, equation (2) becomes :

$$\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}\frac{\partial C_A}{\partial r} - \beta C_{Bf} C_A + \beta \frac{C_T}{K} = \frac{1}{D_{e1}}\frac{\partial C_A}{\partial t} \quad (3)$$

The mass of catalyst can be written as (4).

$$m_C = N_c \rho_c V \quad (4)$$

where $N_c$ = the number of particles, $\rho_C$ = the density of particle and V = volume of catalyst. The particle is assumed to be sphere shaped particle. The number of catalyst can be calculated as :

$$N_c = \frac{3m_c}{4\pi\rho_c R^3} \quad (5)$$

The number of α-pinene moles reacted per unit time is defined as $m_A$. In the element volume, it can be written as (6).

$$dm_A = k_1(C_A C_{Bf} - \frac{1}{K} C_T)\, 4\pi r^2 dr \quad (6)$$

which on integration becomes :

$$m_A = k_1 N_c \int_0^R (C_A\ C_{Bf} - \frac{1}{K} C_T)\, 4\pi r^2 dr \quad (7)$$

where $m_A = -V_f \frac{dC_{Af}}{dt}$, the equation (7) can be written in the following equation.

$$-V_f \frac{dC_{Af}}{dt} = k_1 N_c 4\pi \int_0^R (C_A\ C_{Bf} - \frac{1}{K} C_T) r^2\, dr \quad (8)$$

Mass balance of α-terpineol in porous and sphere particle can be written as (9).

$$\frac{\partial^2 C_T}{\partial r^2} + \frac{2}{r}\frac{\partial C_T}{\partial r} + \beta C_A C_{Bf} - \beta \frac{C_T}{K} = \frac{1}{D_{e2}}\frac{\partial C_T}{\partial t} \quad (9)$$

The relationship between $D_{e1}$ and $D_{e2}$ was approached by [6] :

$$\frac{D_{e2}}{D_{e1}} \approx \left(\frac{M_1}{M_2}\right)^{0.5} \quad (10)$$

Where $M_1$ = molecular weight of α-pinene (136.24 g/mole) and $M_2$ = molecular weight of α-terpineol (154.25 g/mole). The equation (9) becomes :

$$\frac{\partial^2 C_T}{\partial r^2} + \frac{2}{r}\frac{\partial C_T}{\partial r} + \beta C_A C_{Bf} - \beta \frac{C_T}{K} = \frac{1}{0.94 D_{e1}}\frac{\partial C_T}{\partial t} \quad (11)$$

The boundary conditions are :

t = 0, 0 < r < R, $C_A = 0$, $C_T = 0$; t > 0, r = 0, $\frac{\partial C_A}{\partial r} = 0$, $\frac{dC_T}{dr} = 0$; t > 0, r = R, $C_{A\,|\,R,t} = C_{Af\,|\,t}$, $C_{T\,|\,R,t} = C_{Tf\,|\,t}$

The values of parameter : $D_{e1}$, $k_1$ and K were determined by curve fitting method, where the

sum of squares of errors (SSE) was minimized. The SSE was defined as equation (10).

$$SSE = \sum\left(C_{Afcalc} - C_{Afdata}\right)^2 \qquad (10)$$

The model is simulated with the set of parameters of zeolite density, $\rho_C$= 2.4 g/cm$^3$, radius of particle zeolite = 0.2 cm, the mol ratio of water to α-pinene = 2.

Fig. 2 shows the concentration profile in the bulk of liquid. From Fig.2, the α-pinene and water concentration decrease with the increase of reaction time. The concentration of α-terpineol has a tendency to increase by the increase of the reaction time, because the longer reaction time leads to the more collisions of molecules and gives the higher conversion.

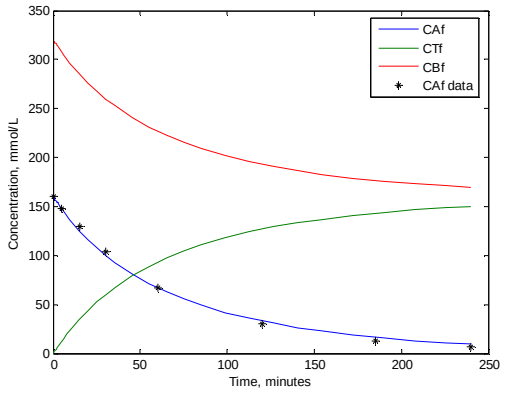


Fig. 2: Concentration profile in the bulk of liquid

Fig.3 and Fig.4 show the concentration of α-pinene and α-terpineol profile in the solid catalyst. It can be seen that α-pinene concentration increases with the increase of radius of particle. Conversely, the α-terpineol concentration decreases with the increase of radius of particle.

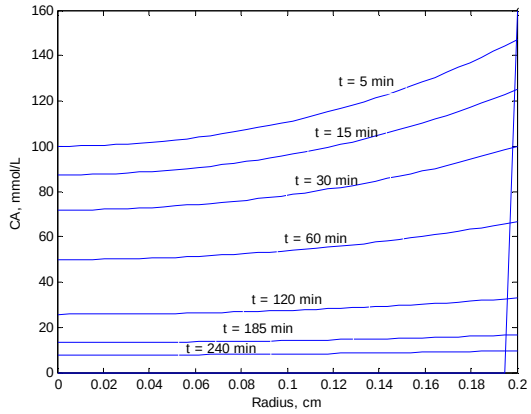


Fig. 3: Concentration of α-pinene profile at various time and radius of solid catalyst

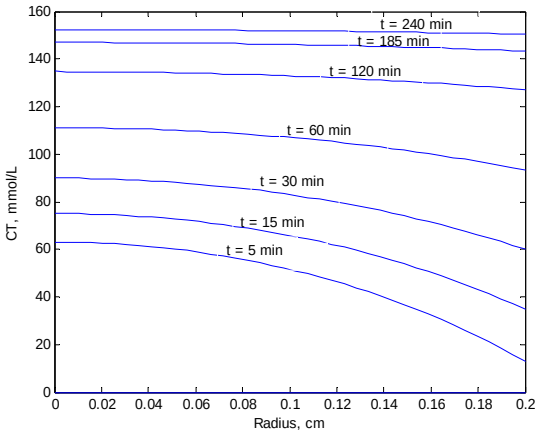


Fig. 4: Concentration of α-terpineol profile at various of time and radius of solid catalyst

The parameters obtained were, $D_{e1}$ = 0.0505 cm$^2$/min, $D_{e2}$ = 0.0475 cm$^2$/min, $k_1$ = 0.0103 L.mmol$^{-1}$.min$^{-1}$ and K =17.6386. The simulation showed good agreement with the experimental results by Van der Waal [7].

## Conclusion

The results of this study show that the kinetics of the hydration of α-pinene using solid catalyst (zeolite H-beta) could be modeled with a heterogeneous model. The values of the parameters in the model were obtained by curve fitting method.

## Notification

$C_A$ = α-Pinene concentration in catalyst, mmol/L
$C_B$ = Water concentration in catalyst, mmol/L
$C_T$ = α-Terpineol concentration in catalyst, mmol/L
$C_{Af}$ = α-Pinene concentration in bulk of liquid, mmol/L
$C_{Bf}$ = Water concentration in bulk of liquid, mmol/L
$C_{Tf}$ = α-Terpineol concentration in bulk of liquid, mmol/L
$D_{e1}$ = effective diffusivity of α-pinene, cm$^2$/min
$D_{e2}$ = effective diffusivity of α-terpineol, cm$^2$/min
$k_1$ = Constant of kinetic reaction, L.mmol$^{-1}$.min$^{-1}$
$k_2$ = Constant of kinetic reaction, L.mmol$^{-1}$.min$^{-1}$
K = Constant of equilibrium reaction
$m_A$ = The number of α-pinene moles reacted per unit time, mmol/min
$N_c$ = The number of particles
R = Radius of catalyst, cm
t = Reaction time, min

$V_f$ = Volume of liquid, L
$\rho_C$ = The density of particle, g/cm$^3$

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