Modeling Fluid and Heat Transport in a New Type Thermal Isomerization Fluidized Bed Reactor

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Abstract. In the current work, with a new concept of resident ratio which impacts the reaction time, a fluid flow and heat transfer model were employed for simulating pressure drop, temperature profile and fluid flow properties of new type thermal isomerization reactor. The thermal isomerization experiment of β-pinene was performed using the reactor. Momentum equation, energy equation and kinetic equations were used to describe the fluid flow and heat transfer. The experimental results were in good agreement with theoretical simulation which indicated that the temperature difference between boundary and initial can be decreased by using steel balls and this modified fluidized bed can improve the yield and selectivity of the products effectively.

1. Introduction
Myrcene is widely used in the commercial production of various terpenic alcohols, chemical aromas, it can also be used as the starting point of vitamins A and E. Myrcene can be produced from β-pinene, which is obtained through the distillation of turpentine. The yield of myrcene from β-pinene could be increased if the reaction conditions were optimized. Varieties type reactors have been used in relatively researches. He Jindong et al. compared gas-phase and liquid-phase thermal isomerization reaction of α-pinene, and obtained the difference of their selectivity and best temperature. Regularly, pipe type reactors were utilized for monoterpenes isomerization. Goldblatt et al. used a reactor of 20mm diameter, 1m long, and nitrogen as carrier gas at 403°C for β-pinene rearrangement to produce myrcene. A steel pipe of 1.4mm diameter, 30cm long was employed by Savich et al. for myrcene production at 580-750°C, whose resident time is about 0.01 to 0.1 second. Tanaka et al. employed a quartz tube of 20mm diameter, 300 mm long to rearranged gaseous pinene at 400-500°C. Zhang Zhongfu used the stainless steel tube coiled into three Φ1m circles which can effectively improve the fluid turbulence and increase the chance of molecular collision. But in these reactors, the inputted heat mainly transferred nearby the pipe wall through fluid convection and finite heat radiation what resulted in the total heat transfer coefficient is low, so the wall temperature was much higher than the interior which caused the tendency that carbon deposition appeared in the pipe wall, so it was necessary to use a slender pipe to ensure a high flow rate and avoid local overheating. In production, it showed that the coke cleaning cycle of this type reactor was short, along with side reactions.

We proposed a sump type fluidized bed reactor which combined the advantages of packed bed and fluidized bed which consisted of large steel balls and copper powder. The steel balls make the channel narrow and variable what resulted in the turbulence. The copper powder could distributed more uniform in the axial direction, its disordered collision make the reactor had the self-cleaning function. In addition, this reactor could be made as the common reactor for conveniently arrangement,
maintenance and reducing investment, it also has the potential for the use of flue gas heating and reducing operating costs. Based on the experimental data and mechanism of the reactor, the present work mainly focused on the modelling of the fluid flow and heat transfer for the pressure drop and the temperature profile in an isomerization fluidized bed reactor.

2. System Descriptions

2.1 Experimental Device

The diagrammatic sketch of reactor was shown in Figure 1, the feedstock was preheated and transported to the bottom of the reactor, rapidly isomerized in 400–550 °C. Then the target product was obtained after cooling by the condenser pipe, the whole system was carried out under auxiliary gas assisted streaming and different pressures. The reactor is made of stainless steel pipe with the specification of Φ45×3.5 and 600mm long, which filled with particles of Φ16mm and Φ150μm copper powder and automatically controlled by the resistant furnace.

![Figure 1. Diagrammatic sketch of reactor for thermal isomerization.](image1)

2.2 Reactor Model and Mechanical Properties of Cold State Fluid

In Figure 2, when the fluid flowed across, the original flow region was distributed into each direction and converged again before the next ball, by repeating these units, the reaction time was prolonged and the temperature was well-distributed. Li Jian et al. simulated the effect of sphere size on flow properties by CFD, and turned out that larger sphere could minimize the boundary effect. In order to study the mechanical properties of cold fluid, the influence from the steel balls to fluid resistance and flow length were considered.

![Figure 2. The fluid flow state in the reactor.](image2)
In the cold state experiment, by adding copper powder, we observed some obviously resident areas performing behind the steel balls. In this study, the fluid unit in each channel was divided into three zones which is shown in Figure 2:

Steady distribution zone A: The fluid is hindered by the downstream particles and thanks to the expansion of the flow channel, the main flow direction of the 3 dimensions began to diffuse, it can be simply expressed as the flow past body in the 2 dimensions;

Hedging mixture zone B: The fluid generates a periodic trailing vortex in this zone. Fluids from different directions come together and mix totally. In this zoom, some particles will stay at the vortex, so we put forward a new accept-resident ratio;

Steady reduced zone C: The blended fluid goes through the minimum channel with increasing speed and decreasing flow pressure, meanwhile under the limitation from particles, the fluid has a definite flow direction and the turbulence has been suppressed sharply. The volume of resident area is related to the particle scale, following the experience formula, the relationship between void content and resident content is proposed by Dai Gance et al.:

\[ \varepsilon_b = 1.6(\varepsilon - 0.2)(1 - \varepsilon) \]  \hspace{1cm} (1)

Where \( \varepsilon \) is the void content of the entire bed and \( \varepsilon_b \) is resident content. The resident area is assumed to be a symmetrical triangle whose base is an arc in two dimensions which illustrated in Figure 2. This area can be calculated by following equation:

\[ \frac{R_b}{2} - \left( \frac{1}{6} \pi R^2 - \frac{\sqrt{3}}{4} R^2 \right) = A_b = A_{\varepsilon_b} \]  \hspace{1cm} (2)

2.3 Kinetic model
As shown in Figure 3, during the isomerization of \( \beta \)-pinene (CAS: 127-91-3), side reactions lead to the formation of not only myrcene (CAS: 123-35-3), but also little limonene (CAS: 5138-86-3) and psi-limonene. Kolicheski et al. compared two situations for the absence and presence of myrcene decomposition reactions, suggested that the second model is better. However, the decomposition model appears not to be sufficient, since predicted yields are greater than experimental yields.

![Figure 3. The molecular rearrangements during the isomerization of \( \beta \)-pinene.](image)

Depending on Arrhenius equation, the apparent rate constant \( k_i \) can be calculated by following equation:

\[ k_i = \frac{1}{T} \ln \frac{[A_{i,h}]}{[A_i]} (i = 1,2,3) \]  \hspace{1cm} (3)

Based on the theory of parallel reaction, the rate of \( \beta \)-pinene reduction is equal to the sum of product formation rate:

\[ k_1 = k_2 + k_3 + k_4 \]  \hspace{1cm} (4)

3. Numerical Analysis

3.1 Fluid Dynamics
In order to implement the flow models, tube-to-particle diameter ratios and drag from reactor wall were disposed like packed bed: Churchill et al. described the wall drag by taking the surface area of the tube into account in the definition of the hydraulic diameter. Winterberg et al. handled the radial porosity variation and wall drag in packed tubes. As the pressure drop consisted of pipe flow drop and
resident drop owing to the resident effect and the resident drop, Cheng Yi et al. has concluded the pressure drop by using Ergun equation:

$$\Delta P = 150 \frac{\mu u}{d_p^2} \times \left( \frac{1}{\varepsilon} \right)^2 + \frac{7}{4} \times \frac{\rho u^2}{d_p^2} \times \frac{1}{\varepsilon^2} L_{eff} + (1 - \sigma)(1 - \varepsilon) L_{eff} \rho$$

(5)

Where $d_p$ is particle diameter, $u$ is flow rate, $\mu$ is viscosity and $\sigma$ is resident ratio.

3.2 Heat Transfer

Quantities of works have been carried out on heat transfer. The approach using effective thermal conductivity of the packed bed is most acceptable. Slavin et al. used the measurable parameter, surface roughness of the particle to avoid the use of any adjustable parameters in the determination of effective thermal conductivity for uniform metallic spheroids filled with ideal gas with no compression of particles. Sharma et al. considered the effective thermal conductivity model for radiation transport by modifying shape factor using the extinction coefficient and also developed the heat transfer model using single control volume applied to the reactor. Guangzhan Xu et al. have reported that the temperature is much higher in the gap and dorsal to the ball, and the heat transfer coefficient increases with the decrease of the porosity.

The effective thermal conductive can be regarded as the sum of thermal conductivity and thermal emissivity:

$$\lambda_{eff} = \lambda_{bed}^k + \lambda_{bed}^l$$

(6)

Where $\lambda_{bed}^k$ is radiation thermal conductivity, $\lambda_{bed}^l$ is contact thermal conductivity. Kandula et al. had proposed Cell Model while investigating the effective thermal conductivity of particle bed; Breitbach et al. improved equation (7) for thermal radiation. Depending on the investigation of different rules of particle volume of the heat flow by Prasad et al., the contact thermal conductive could be obtained by equation (8).

| Table 1. The equations of radiation thermal conductivity and contact thermal conductivity |
|-------------------------------------------------------------------------------|
| $\lambda_{bed}^k = \left\{ 1 - (1 - \varepsilon)^{1/2} \varepsilon + \frac{(1 - \varepsilon)^{1/2}}{\varepsilon - 1} \cdot \frac{8 + 2 \varepsilon + 1}{\varepsilon + 2} \cdot \frac{1 - \frac{1}{(1 - \varepsilon_{br})^2}}{1 - \frac{1}{(1 - \varepsilon_{br})^2}} \right\} 4 \sigma T^3 d$ |
| radiation thermal conductivity, $\varepsilon_r = 0.7$ |
| Where B = 1.25 $\left( \frac{1 - \varepsilon}{\varepsilon} \right) ^{10}$ |
| $\Lambda = \frac{\lambda_s}{4 \sigma T^3 d}$ |
| directly heat radiation |
| $\frac{\Lambda_{bed}^l}{\Lambda} = \left[ \frac{3(1 - \varepsilon_p^2)}{4R_s} \right] ^{3/2} \cdot \frac{1}{0.5315 \left( \frac{N_A}{N_L} \right)}$ |
| contact thermal conductivity |
| Where $f = \rho \frac{S_p}{N_A}$, $N_A = \frac{1}{4R s}$, $N_L = \frac{1}{2r}$ and $\mu_p = 0.25$ |

4. Results and Discussion

4.1 Resident Ratio

Resident ratio is a novel parameter in present study, there is the recirculation region at the downstream of each sphere, it provides a stagnant space for fluid, which results in the increase of reaction time. Although the resident area is constant, the resident ratio varies with fluid density which is influenced by flow rate. The influence from flow rate to resident ratio is shown Figure4, with the increasing of the flow rate and fluid mass, the resident ratio is decreasing apparently. The resident ratio can be regressed from the experimental data as:

$$\sigma = -0.51 lnu - 0.4 \frac{m}{V} + 2.145$$

(9)
4.2 Fluid Flow Validation of Cold State Fluid

The experimental pressure drop with cooper powder was compared with calculation data in Figure 5. As expected, the pressure drop increased with the increase of flow rate. Meanwhile, by increasing fluid mass, marked pressure drop embodied that higher flow mass much more fit the model.

4.3 Temperature and Reaction Simulation

Figure 6 shows the CFD results of temperature distribution and concentration of β-pinene and myrcene in blank pipe and filled pipe that outlet temperature were 850K and 765K, respectively. In the blank pipe, temperature is higher near the wall, β-pinene has higher concentration at bottom and central region, myrcene is less wherever in the wall or central region, percent conversion of the reaction is low. The situation improves obviously in the filled pipe, the temperature can distribute uniform in radial direction and reach the highest temperature quickly, β-pinene still concentrates at bottom but sharp falling to a low level, meanwhile myrcene reaches a high level as expected. This enhancement proves that this new type reactor can prolong the reaction time so that β-pinene can almost entirely convert to myrcene at a lower temperature.
Figure 6. Simulation results of β-pinene, myrcene and temperature distribution

Table 2 Experimental results of productions through rearrangement of β-pinene

| Temperature /°C | β-pinene content /% | β-pinene selectivity /% | myrcene content /% | myrcene selectivity /% | psi-limonene content /% | psi-limonene selectivity /% | limonene content /% | limonene selectivity /% |
|-----------------|----------------------|------------------------|-------------------|------------------------|-------------------------|---------------------------|-------------------|------------------------|
| 720             | 54.7                 | 43.4                   | 36.4              | 86.6                   | 1.6                     | 3.8                       | 4.1               | 9.8                    |
| 730             | 36.1                 | 62.7                   | 53.0              | 87.3                   | 2.4                     | 3.9                       | 5.8               | 9.6                    |
| 740             | 21.2                 | 78.1                   | 65.2              | 86.2                   | 3.0                     | 4.0                       | 7.0               | 9.3                    |
| 750             | 8.3                  | 91.4                   | 75.5              | 85.4                   | 3.6                     | 4.1                       | 8.0               | 9.1                    |
| 760             | 2.5                  | 97.5                   | 78.8              | 83.6                   | 4.0                     | 4.2                       | 8.5               | 9.0                    |
| 770             | 0.8                  | 99.2                   | 77.8              | 81.1                   | 4.2                     | 4.4                       | 8.7               | 9.1                    |

5. Conclusion
Fluid flow and heat transfer model for new type fluidized bed thermal isomerization reactor was presented for simulating the concentration, temperature profile and fluid flow properties. Depending on the present theory of particle bed fluidity mechanics, a flow physical model was proposed, and resident ratio was firstly put forward the pressure drop correlation in reactor. The selectivity and yield of monoterpenes was influenced by temperature and resident time. Typical fluidized bed reactor could not control the resident time effectively, which could bring byproducts. The filling of particles gave uniformity channels on section area and better distribution. The new type thermal isomerization fluid bed reactor combines the advantages of the fluid bed and fixed bed reactor. The experiments proved that the flow rate of 15m³/h at 760K for myrcene was the best conditions.

6. Acknowledgements
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7. References
[1] He Jindong, Gong Y, Zhao W. A comparative study on the gas-phase and liquid-phase thermal isomerization reaction of α-pinene, Journal of Physical Organic Chemistry, 2013
[2] Peng YuXing, Liu JL, Cun LF, Dai HS, Vapor phase thermal isomerization of α- and β-pinene*, Journal of the American Chemical Society, 1941
[3] Tanaka, J., Katagiri, T., Ozawa, K., The thermal isomerization of pinane and its products, Bulletin of the Chemical Society of Japan, 1971
[4] Zhang Zhongfu, *On the production process of beta pinene pyrolysis of myrcene*, Chemical engineering and equipment, 2013

[5] Li Jian, Song XM, Lu JC, *CFD simulation study of the influence of the sphere bed scale on the pore flow characteristics*. Nuclear power engineering, 2013

[6] Dai Gance (2008). Momentum transfer. In: Transfer phenomenon introduction, vol 3. Chemical Industry Press.

[7] Kolicheski, M. B., Cocco, L. C., Mitchell, D. A., Kaminski, M,*Synthesis of myrcene hpyrolysis of β-pinene: analysis of decomposition reactions*, Journal of Analytical and Applied Pyrolysis, 2007

[8] Churchill, S. W,*Viscous flows*, 1988

[9] Winterberg, M., E. Tsotsas,*Impact of tube-to-particle-diameter ratio on pressure drop in packed beds*, Aiche Journal, 2000

[10] Cheng Y, Liu LJ, Li R,*Fluid characteristics and cold state experiment validation of novel sump type fluidized bed*, Chemistry and industry of forest products, 2015

[11] Xu GZ, Sun ZN, Meng XK,*Numerical simulation of fluid flow and heat transfer in pebble bed reactor*, Nuclear Power Engineering, 2013

[12] Kandula, M,*On the effective thermal conductivity of porous packed beds with uniform spherical particles*, Journal of Porous Media, 2011

[13] Breitbach, G., Barthels, H,*Radiant heat transfer in the htr core after failure of the afterheat removal systems*, Trans. Am. Nucl. Soc.1978