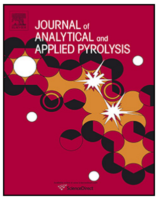
Journal of Analytical and Applied Pyrolysis xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



Catalytic cracking of binary hydrocarbons of *n*-dodecane and *iso*-dodecane under supercritical conditions

Ya Wang[§], Xiaochao Xian[§], Xu Hou, Xiangwen Zhang, Li Wang, Guozhu Liu*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:
Available online xxx

Keywords:
Binary mixture
n-Dodecane
Supercritical cracking
HZSM-5

ABSTRACT

The mutual effect between different kinds of hydrocarbons would influence supercritical catalytic cracking behavior of jet fuel, and thus may affect the chemical heat sink. Highly branched *iso*-dodecane (mainly 2,2,4,6,6-pentamethylheptane, PMH) and *n*-dodecane were chosen as model hydrocarbons. The cracking of the binary system with different *iso*/*n*-dodecane ratios was conducted over HZSM-5 zeolite under supercritical conditions (673 K, 4.0 MPa). The results show that the cracking of *n*-dodecane in binary mixture is first inhibited but then accelerated with the increase of concentration of PMH, while the cracking of PMH was hardly effected. Limited by the inertness of PMH, total conversion of binary mixture is obviously lower than pure *n*-dodecane.

1. Introduction

Jet fuel is served as the primary coolant to solve thermal management problem in the supersonic and hypersonic flight of the future. Heat sink offered by jet fuel includes physical sensible heat and absorbed heat by various endothermic reactions, such as thermal cracking, catalytic cracking, dehydrogenation, etc. Among those endothermic reactions, catalytic cracking has been taken as one of the most promising processes for the potential applications due to its numerous advantages, such as higher reaction rates, better product selectivity, as well as the ideal combustion performances of products [1–8].

In the heat exchanger for cooling technology of advanced aircrafts, the fuel has to work under high pressure and temperature (>3.0 MPa, >673 K), i.e., supercritical conditions. Previously, catalytic cracking of mono-component hydrocarbons were well studied under supercritical conditions. Sicard et al. [9] compared catalytic and thermal cracking of *n*-dodecane under supercritical conditions, and found significant difference in the decomposition rate and product distribution. Süer et al. [10] and Dardas et al. [11] investigated the real-time catalytic cracking and kinetics of *n*-heptane over a commercial Y-type zeolite under supercritical and subcritical conditions using in situ CIR-FTIR, and observed that the catalytic activity could be kept at a relatively high level due to the extraction of carbon deposits and corresponding precursors by the supercritical hydrocarbons themselves. To further describe their extraction effect on the catalytic cracking, Xian et al. [12] developed a Langmuir–Hinshelwood kinetics model with a modified decay function which satisfactorily predicted the experimental results of catalytic cracking of supercritical *n*-dodecane over HZSM-5 zeolites. They also defined an index of CRSE to directly describe the effect of supercritical fluid on the catalytic activity. Recently, Luo and Gorte [13] investigated the catalytic cracking of *n*-hexane in the pressure range of 0.03–137 bar, and observed significant changes in the activation energy caused by pressures. However, hydrocarbon fuel used in the aircrafts is usually multi-component, including linear and branched alkanes, cycloalkanes, and small amount of alkenes and aromatics. Unfortunately, catalytic cracking of hydrocarbon mixture under supercritical conditions was few reported.

It was well recorded that catalytic cracking of one hydrocarbon would be strongly influenced by another one. Namba et al. [14] observed that some hydrocarbons, such as 2,2-dimethylbutane, cyclohexane, toluene, inhibited the catalytic cracking of *n*-octane over HZSM-5 zeolite, attributing to the difference in the diffusivity and concentration of these hydrocarbons. Lu et al. [15] investigated the catalytic cracking of *n*-octane and *n*-hexadecane, as well as their mixture, over different zeolites, and found that *n*-hexadecane in mixture had much lower conversion than pure *n*-hexadecane while the catalytic cracking of *n*-octane in mixture was enhanced slightly over ferrierite and Si-ZRP-5 zeolite. But they did not observe those differences mentioned above on other different catalysts, for

---

* Corresponding author. Tel.: +86 22 27892340; fax: +86 22 27892340.
E-mail address: gliu@tju.edu.cn (G. Liu).
[§] Both authors contributed equally.

http://dx.doi.org/10.1016/j.jaap.2014.11.015
0165-2370/

instance, ZRP-5 zeolite. The interaction between different hydrocarbon components during catalytic cracking would be enhanced under supercritical conditions. Therefore, a further study on catalytic cracking of hydrocarbon mixtures consisting of different hydrocarbon types under supercritical conditions is still needed, which would be very helpful to strengthen the understanding on the catalytic cracking of supercritical hydrocarbons.

The objective of this work is to investigate supercritical catalytic cracking of the binary system of *n*-dodecane and *iso*-dodecane (mainly 2,2,4,6,6-pentamethylheptane, PMH) over HZSM-5 zeolite. Different *iso*/*n*-dodecane ratios are used to study the interaction between *n*-alkane and *iso*-alkane under supercritical conditions. This work would provide some new insights into the catalytic cracking of supercritical hydrocarbons.

2. Experimental

2.1. Materials

n-Dodecane with the purity of 99% was obtained from Sinopharm Chemical Reagent Co., Ltd. Its critical temperature and pressure were 658 K and 1.81 MPa separately. Highly branched *iso*-dodecane was actually multi-component, and its chemical composition identified by gas chromatograph was listed in Table 1. Its critical temperature and pressure estimated by group contribution method were about 630 K and 1.99 MPa separately. Extruded HZSM-5 zeolite with Si/Al ratio of 50 was obtained from Nankai University Catalyst Co., Ltd. Fresh catalyst was used after some mechanical preprocessing.

2.2. Experimental procedure

Experiments were carried out in a 316 stainless steel tube reactor, 400 mm long and 10 mm inner diameter. The catalyst bed was located in the constant temperature zone, which was set at the middle of the tube, and about 30 mm long. Both ends of the catalyst bed were filled with inert ceramic chip. Before each experiment, 1.5 g catalyst was first placed in the catalyst bed, and then pretreated about 1 h in nitrogen atmosphere under 673 K. The feed was pumped into the tube at a flow rate of 4.00 mL/min under room temperature using a high pressure liquid chromatography pump. The reaction system pressure was maintained at 4.0 MPa by a back pressure valve. After temperature and pressure being stable, liquid products of different TOS were collected at 10 min interval and analyzed qualitatively by gas chromatograph–mass spectrometer and quantitatively by gas chromatograph. Meanwhile, the content of hydrogen in gas products was measured by on-line gas chromatograph, and corresponding off-line gas sample was collected by special gas bags. At the end of each run, the reaction system was cooled and swept under nitrogen atmosphere.

To verify the influence of thermal decomposition, blank experiments without catalyst were also conducted under the same conditions. We found that the thermal cracking conversion of individual *n*-dodecane and PMH was very low (<1.6%) and ignorable.

Table 1
The chemical composition of high branched *iso*-dodecane.

Component	Content (wt%)
2,2,4,6,6-Pentamethylheptane	83.36
2,2-Dimethyldecane	0.54
2,2,4,4-Tetramethyloctane	6.72
2,6,10-Trimethyldodecane	3.02
2,5-Dimethylundecane	2.34
3,3,4-Trimethyldecane	1.00
Others	3.02

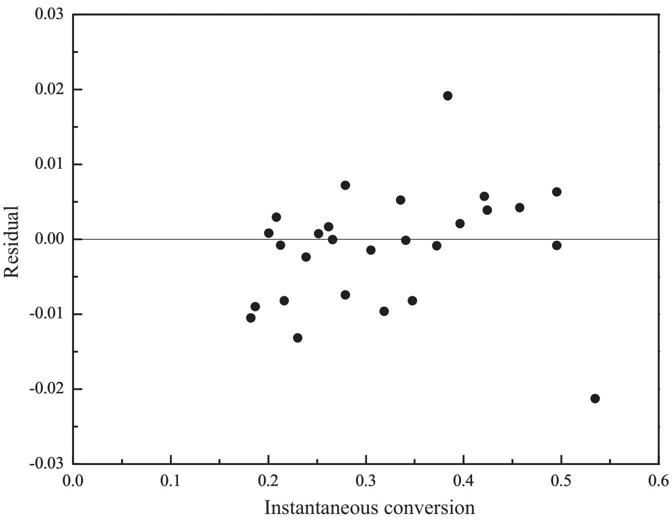


Fig. 1. Residual versus experimental value of instantaneous conversion of pure *n*-dodecane during supercritical catalytic cracking. Experimental conditions: 673 K, 4.0 MPa, pure *n*-dodecane 1.00–4.00 mL/min, 1.5 g HZSM-5.

2.3. Kinetic model

In this work, the kinetic model, describing the catalytic cracking of *n*-dodecane under supercritical conditions, is derived from S–C model suggested by Xian et al. [12], in which the supercritical extraction to coke precursor on catalysts is taken into consideration. The main expressions include reaction rate equation (Eq. (1)) and catalyst decay function (Eq. (2)) as follows.

$$\frac{dX}{d\tau} = \frac{A(1 - X/1 + \varepsilon X)}{1 + B(1 - X/1 + \varepsilon X)}\theta \tag{1}$$

$$-\frac{d\theta}{dt} = k_{md}\theta^{m} - k_{in}F^{n} \tag{2}$$

where X is the instantaneous conversion, τ is the residence time, ε is the volume expansion coefficient, A and B are apparent reaction rate constant and adsorption equilibrium constant respectively, θ is the catalyst active site fraction, t represents TOS, k_{md} is the deactivation rate constant and m is the reaction order, k_{in} is the activity regeneration constant and n is the reaction order, and F is the feed flow rate.

The nonlinear least-squares method is used to optimize the objective function *Obj* (Eq. (3)) and estimate the model parameters.

$$Obj = \sum_{i}^{n} (\bar{X}_{ei} - \bar{X}_{ci})^2 \tag{3}$$

where n is the number of experimental points, $\bar{X}_{ei}$ and $\bar{X}_{ci}$ are the experimental and calculated value of instantaneous conversion respectively. The residual value, as indicated in Fig. 1, shows a narrow distribution with good symmetry, indicating that the model is reasonable. Combined with the high correlation coefficient, it can be deduced that the model is reliable and available for supporting and complementing the experiment results.

3. Results and discussion

The instantaneous conversion of *n*-dodecane in binary mixture, which is defined as the mass-change rate of single *n*-dodecane in binary mixture before and after catalytic cracking, is displayed in Fig. 2 as a function of TOS. The conversion of *n*-dodecane in mixture with 25% PMH is comparable to that of pure *n*-dodecane. With increasing content of PMH, the conversion of *n*-dodecane

Please cite this article in press as: Y. Wang, et al., Catalytic cracking of binary hydrocarbons of *n*-dodecane and *iso*-dodecane under supercritical conditions, J. Anal. Appl. Pyrol. (2014), http://dx.doi.org/10.1016/j.jaap.2014.11.015