A four kinetic model for delayed coking process of Qingdao vacuum residues

Na Li¹, Yonggang Wang¹, Dan Zhao¹

¹ Department of Environment Engineering and Chemistry, Luoyang Institute of Science and Technology, Luoyang, 471023, PR China

The corresponding author’s e-mail: ln450001@126.com

Abstract: Batch coking reaction experiments of Qingdao vacuum residues were carried out in the temperature range of 420–480 °C and at reaction times in the range of 5–90 min. A four lump kinetic model was developed for delayed coking process of Qingdao vacuum residues. The feedstock and products were considered as a unique and three separated lumps, respectively, in the model. The product lumps were included gas (C₁~C₄), distillate (C₅+~500 °C) and coke (toluene insoluble and 500+ °C). Reactions were assumed in first order and based on Arrhenius reaction rates. The kinetic model was developed to predict unconverted feed values and product yields. The results showed a very good agreement between the experimental yield and predicted yield of different pseudocuts was obtained.

1. Introduction

Delayed coking was a conventional vacuum residue conversion process. The vacuum residue is completely converted into coking gas, liquid fuels products and petroleum coke. This process had lower investment cost and simple process scheme, which was suitable for processing inferior vacuum residues[1]. The coking process of heavy hydrocarbons was consisted of cracking reactions, condensation reactions. The selectivity of reaction products is related to the chemical properties of the raw feedstocks and operating conditions, such as reaction time, reaction temperature and pressure. Xiao et al[2] studied thermal conversion of heavy petroleum hydrocarbon by a laboratory scale reactor. It was assumed that all the coking reactions were first-order ones. There are no secondary reactions occurred for the intermediates. A twelve lumped reaction model for product distribution in thermal conversion of heavy stock was developed. The model was fit well to the experimental data at low thermal conversion. Zhou et al[3] investigated the effect of operating parameters and technologies on reaction behaviors in three industrial delayed coking units. The results illustrated that the temperature of the liquid streams and yields for gasoline and diesel in the coke drum were all stable after a few hours. The thermal cracking of vacuum residue had also been investigated by many researchers[4~8]. Above investigations would be helpful for theoretical analysis and simulation and optimization of the coke drum. The multi-lumps kinetic models with simple reaction networks are more useful in industries. In this research, a four lumps kinetic model for coking reaction of Qingdao vacuum residue was developed based on experimental results that were obtained in a batch reactor. The effects of reaction temperature and reaction time on reactions of Qingdao vacuum residue in delayed coking were investigated, with the purpose to provide necessary information for the optimum operating parameter to maximize the yield of liquid products in an industrial delayed coking unit.
2. Experiment method and feed

Vacuum residues were collected from the delayed coking unit in Qingdao refinery of SINOPEC. Table 1 summarizes the main physic-chemical properties of VR.

Table 1 Properties of Qingdao vacuum residue

| Item                        | VR          | Item                        | VR          |
|-----------------------------|-------------|-----------------------------|-------------|
| Density (20 °C), kg·m⁻³     | 999.9       | SARA, wt%                   | 21.63       |
| Viscosity (100 °C), mm²·s⁻¹ | 1329        | Saturates                   | 42.53       |
| CCR, wt%                    | 17.80       | Aromatics                   | 50.02       |
| Pour points, °C             | > 50        | Resins                      | 5.82        |
| Carbon, wt%                 | 86.45       | n-C₆ Asphaltenes             | 30.02       |
| Hydrogen, wt%               | 11.29       | Fe                          | 58.1        |
| Sulfur, μg·g⁻¹              | 9830        | Ni                          | 50.6        |
| Nitrogen, μg·g⁻¹            | 8980        | V                           | 46.1        |
| H/C Ratio                   | 1.56        | Ca                          | 25.1        |
| Average molecular weight, g·mol⁻¹ | 902 | Na                          | 18.7        |

The tests performed in a 30 mL stainless batch reactor. A schematic diagram of experimental apparatus was illustrated in Fig.1.

Figure 1 Schematic diagram of thermal cracking experimental equipment for Qingdao vacuum residue

1-gas product collector, 2-liquid product collector, 3-condenser, 4-molten tin bath, 5-reactor, 6-transducer, 7-control box, 8-signal line, 9-control system

In thermal cracking experiments of VR, about 10 g of the sample was loaded into the reactor. The reactor was purged with nitrogen by five times to maintain an inert environment. The reactor was preheated up to 360 °C. This preheating could reduce the time which reached the specified temperature. As soon as the feedstock reached the preheating temperature, the reactor was immediately immersed into the molten tin bath. The raw feedstocks rapidly reached the target temperature. The reaction time was calculated from the moment when the reaction temperature approached the target temperature. After a certain reaction time, the reactor was removed from the molten tin bath and cooled below 300 °C to terminate any further reaction. The gaseous products and distillate were collected and quantified separately. After the reactor is quenched to the ambient temperature, the mass in the reactor was extracted by toluene and coke. The amounts of distillate products, coke, and unconverted vacuum residues were measured. Figure 2 shows the complete reaction scheme and analysis of the reaction products. The toluene insoluble material was separated by the literature research method[9]. The gas and distillates were quantitatively analyzed by using different gas chromatograph. The Qingdao vacuum residue were thermally cracked at four temperatures (420 °C, 440 °C, 460 °C, 480 °C) and at reaction times(5, 10, 15, 20, 30, 60 and 90 min).
3. Reaction kinetic
A four lumps kinetic model of Qingdao vacuum residue was considered in Figure 3. In this model, Qingdao vacuum residue was divided into a unit lump and thermal reactions products were divided in three lumps, that include gas, distillate and coke. The different reaction pathways possible from the proposed kinetic scheme i.e., formation of gas, distillates, coke and conversion of vacuum residue have been modeled with first order kinetics.

Based on reaction pathways of Figure 3, the following first order rate equations can be given by the following set of differential equations:

$$\frac{d\omega_R}{dt} = -(k_1 + k_2 + k_3) \omega_R$$

$$\frac{d\omega_G}{dt} = k_4 \omega_R + k_3 \omega_D$$

$$\frac{d\omega_D}{dt} = k_2 \omega_R - (k_4 + k_5) \omega_D$$

$$\frac{d\omega_C}{dt} = k_5 \omega_R + k_3 \omega_D$$
Where $\omega_i$ is the mass fraction of lump $i$. At initial time ($t=0$ min), the amount of VR (initial weight percent of feed) is equal to 95 wt% and product yields are equal to 5%. As the equations are homogeneous and differential, they can be solved with above mentioned initial conditions.

The estimation of the rate constants was obtained by non-linear regression, which involves minimization of the sum of square of error (SSE) objective function given as follows:

$$SSE = \sum_{i=1}^{m} \sum_{j=1}^{n} \left( y_{\text{exp}_j} - y_{\text{pred}_j} \right)^2$$

The values of kinetic rates were measured by programming in MATLAB software. The calculated results was listed in the Table 2.

Table 2 Reaction rate constant of thermal conversion reactions for Qingdao vacuum residue

| Temperature, °C | $k_1$     | $k_2$     | $k_3$     | $k_4$     | $k_5$     |
|-----------------|-----------|-----------|-----------|-----------|-----------|
| 420             | $1.5136E-03$ | $1.6024E-02$ | $0.0000E+00$ | $1.5112E-03$ | $3.8104E-03$ |
| 440             | $4.4937E-03$ | $2.7085E-02$ | $2.3947E-03$ | $0.0000E+00$ | $3.7386E-03$ |
| 460             | $7.8383E-03$ | $4.9733E-02$ | $9.5403E-03$ | $1.5268E-04$ | $2.5907E-03$ |
| 480             | $1.3399E-02$ | $7.8152E-02$ | $2.3491E-02$ | $2.4474E-04$ | $1.2454E-03$ |

Figure 4 shows the comparison between the experimental and predicted values for gas, liquids, coke and Qingdao vacuum residue, respectively in the proposed kinetic scheme. A four lump, three rate parameter model has been proposed to explain the mechanism of cracking and coking reactions. A very good agreement between the experimental yield and predicted yield of different products was obtained.

Figure 4 Comparison between model prediction and experimental values of VR at different temperature
4. Conclusions
In this work, a four lump kinetic model was developed for delayed coking of Qingdao VR. The experiments achieved in a batch reactor at different temperatures and reactions times. All kinetic rates assumed first order and based on Arrhenius reaction rate. The kinetic rate functions were developed to predict unconverted feed values and product yields. The results showed a very good agreement between the experimental yield and predicted yield of different products was obtained.

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