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Kinetic Study on the Hydrocracking Reaction of Vacuum Residue Using a Lumping Model

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Abstract: Based on the experimental hydrocracking of vacuum residue, a kinetic study using a lumping model was carried out to gain insight into the characteristics of catalytic reactions. The lumped species were the saturates, aromatics, resins, and asphaltenes (SARA) constituents in the residue (798 K^+) fraction and gas, naphtha, kerosene, gas oil, vacuum gas oil, and coke in the products. The pyrite reaction favoring hydrocracking to lighter products was more temperature-dependent than that using a mixture of pyrite and active carbon. The kinetic study showed that the addition of active carbon to pyrite limited the transformation of resins to asphaltenes.

Keywords: hydrocracking, kinetic study, lumping model, vacuum residue

INTRODUCTION

With the depletion of crude oil, heavier crude oils are presently been produced, and further resource depletion is anticipated. Simultaneously, the demand for lighter products is increasing, while the demand for heavy fuel oil is decreasing. In addition, the need to upgrade heavy oil is increasing, reflecting the recent hike in crude oil prices.

In refineries, petroleum residue is converted into lighter fractions using processes such as coking, hydrocracking, and residue fluid catalytic cracking to maximize the gain of high-value fuels. The product distribution differs depending on the process used, operating conditions, and more essentially, the characteristics of the crude. It is important to be able to predict how the feedstock is converted into distillable fractions and to obtain the desired products in maximum yield.

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We have proposed the use of an active carbon catalyst for hydrocracking heavy oils (Terai et al., 1998, 1999). This is especially suitable for extra heavy oils containing such heavy hydrocarbons and impurities as asphaltene, sulfur, nitrogen, and heavy metals (nickel and vanadium). In a hydrocracking experiment using vacuum residue, active carbon was observed to effectively convert heavy fractions into distillable fractions, while preventing asphaltenes from poly-condensing to form coke. Here, we conducted a kinetic study using a lumping model based on the saturates, aromatics, resins, and asphaltenes (SARA) constituents in residue (798 K^+) and gas and distillates of cracked volatile products. The predictions of the kinetic model and experimental data were compared using two different catalysts, and the effectiveness of active carbon is discussed.

EXPERIMENTAL

Hydrocracking Test

Hydrocracking tests of vacuum residue (VR) were carried out in a 1-L semi-batch magnetically stirred autoclave. Hydrogen was introduced at a constant flow rate during the reaction to maintain a constant hydrogen partial pressure. The excess hydrogen and gaseous products were collected in a bag for analysis. The reaction was conducted at a hydrogen pressure of 10 MPa, reaction temperatures of 688 and 718 K, and a reaction time of 60 to 240 min.

After the experiments, the gaseous products were analyzed using gas chromatography and hydrogen sulfide was determined using a detecting tube. The amounts of naphtha (IBP-444 K), kerosene (444–505 K), gas oil (505–616 K), vacuum gas oil (VGO: 616–798 K), and residue (798 K^+) in the liquid product were determined using a gas chromatography distillation method after separating the catalyst and coke by filtering the liquid product. The

Table 1. The properties of vacuum residue

Gravity API	5.3
Total sulfur, wt%	4.02
Nitrogen, wt%	0.53
CCR, wt%	22.4
Asphaltenes (nC7Insols.), wt%	6.9
Metal Ni/V, wppm	53/180
C/H, wt%	84.8/10.2
SARA, wt% (ASTM D 4124-84)	
Saturates	8.3
Aromatics	35.6
Resins	45.4
Asphaltenes	10.7

Table 2. The catalysts used

Pyrite	10 wt% as Fe on vacuum residue
Mix-cat	(3 wt% as Fe + 5 wt% AC) on vacuum residue

Pyrite: Purity of FeS_2 99.9 wt%; size $<149\ \mu$m.

Active carbon: BET surface area 832 m^2/g; pore volume 0.98 cm^3/g; size $<74\ \mu$m.

amount of coke was determined as the toluene-insoluble residue on the filter using Soxhlet extraction. The hydrocracking conversion was defined as follows:

$$\text{Conversion (\%)} = ((100 - \text{weight \% of } 798\ \text{K}^{+} \text{ in products})/ (\text{weight \% of } 798\ \text{K}^{+} \text{ in feed vacuum residue})) \times 100.$$

The residue fraction obtained after hydrocracking was divided into the SARA fractions using a method based on ASTM D4124-84 to determine the composition change of the VR fraction under various reaction conditions.

The properties of the VR used as feedstock are shown in Table 1. Pyrite and a mixture of pyrite and active carbon (mix-cat) were used as catalysts in this study (Table 2).

Kinetic Model

Many kinetic studies and lumping models of thermal cracking (Hayashitani et al., 1978; Moritomi et al., 1982; Schucker, 1982; Phillips et al., 1985; Yoshiki and Phillips, 1985; Banerjee et al., 1986; Antonio and Donald, 1988a, 1988b; Takatsuka et al., 1989), noncatalytic hydrocracking (Schucker and Kewshan, 1980; Koseoglu and Phillips, 1987, 1988), and catalytic hydrocracking (Trejo and Ancheyta, 2005; Sanchez et al., 2005) have been reported. The feedstock and product are lumped into pseudo-components based on distillation fractions or similar chemical or physical properties. Different authors define the lumped components in different ways, such as gas, distillable oils, light oils, heavy oils, asphaltenes, and coke; gas, maltenes, asphaltenes, and coke; saturates, aromatics, resin, asphaltenes, coke, and volatiles; and heptane soluble, heptane insoluble/toluene soluble, toluene insoluble/quinoline soluble, and quinoline insoluble. Recently, Ancheyta et al. (2005) reviewed the scientific literature on the kinetic modeling of heavy petroleum fraction hydrocracking based on the lumping technique, continuous mixtures, structure-oriented lumping, and single-event mode.

Antonio and Donald (1988a) reported the thermal cracking of the separated SARA fractions of Athabasca bitumen and then developed a model for intact Athabasca bitumen. In their model study, Antonio and Donald (1988b) introduced the extent of reaction effect (ERE) proposed by Lin et al. (1984) in the form of $W = ae^{-bT}$ to incorporate the effect of the decrease in the high initial rate constants of the components as the reaction progressed. Here, we assume that the decrease in the reactivity of the VR fraction is reflected by the concentration change of the SARA fractions of VR as the hydrocracking reaction progress.

In this experiment, the products of hydrocracking were the volatiles gas, naphtha, gas oil, and vacuum gas oil and coke as the poly-condensed product of asphaltenes. With hydrocracking conversion, the profile of the product distribution showed a consistent increase in gas, naphtha, kerosene, and gas oil with the increase in conversion and a decrease in vacuum gas oil after the maximum yield peak, as shown in Figure 1. Despite the decreasing reactivity of the VR fraction, the fraction lighter than vacuum gas oil increased at the expense of the yield of vacuum gas oil. More vacuum gas oil appeared to be cracked into lighter components as the reaction progressed.

Based on these experimental observations, in the reaction model, we lumped gas, naphtha, kerosene, and gas oil as Lo; the other components were vacuum gas oil (VGO), coke (Coke), saturates (Satu), aromatics (Aroma), resins (Resin), and asphaltenes (Asp).

The reaction model and paths are shown in Figure 2. The hydrocracking reactions were assumed to be pseudo first order with respect to the concentra-

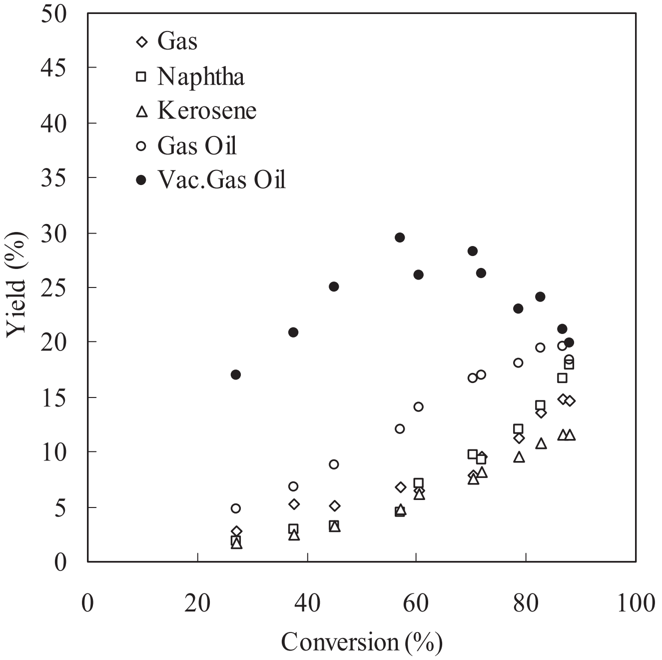

Figure 1. Conversion vs. yield.

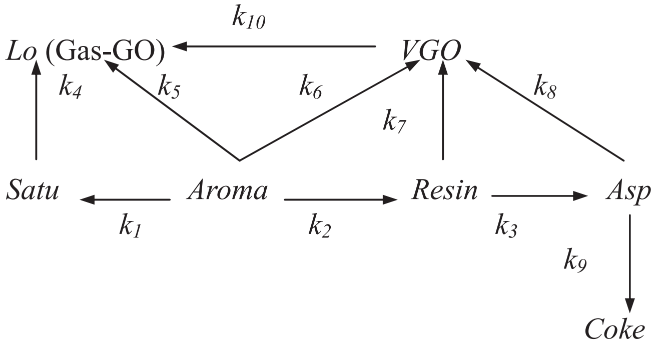

Figure 2. The reaction model.

tion of each lump. The following differential equations describing this model were used to calculate the reaction rate constants:

Satu: $dx_1/dt = k_1x_2 - k_4x_1$

Aroma: $dx_2/dt = -(k_1 + k_2 + k_5 + k_6)x_2$

Resin: $dx_3/dt = -(k_3 + k_7)x_3 + k_2x_2$

Asp: $dx_4/dt = -(k_8 + k_9)x_4 + k_3x_3$

Lo: $dx_5/dt = k_4x_1 + k_5x_2 + k_{10}x_6$

VGO: $dx_6/dt = -k_{10}x_6 + k_6x_2 + k_7x_3 + k_8x_4$

Coke: $dx_7/dt = k_9x_4$

The applicability of the model was judged using the closest fit of the component concentrations with the experimental data against reaction time and the temperature dependence of reaction-rate constants for the Arrhenius expression. The activation energy, E_a, and frequency factor, A_0, for each reaction path were then obtained.

RESULTS AND DISCUSSION

Kinetic Model

As examples, the model predictions and experimental data with the two different catalysts at reaction temperatures of 688 and 708 K are compared in Figures 3 and 4, respectively. The agreement between model prediction (no suffix) and experimental data (suffix .ex) was very good.

The rate constants and kinetic parameters are shown in Table 3.

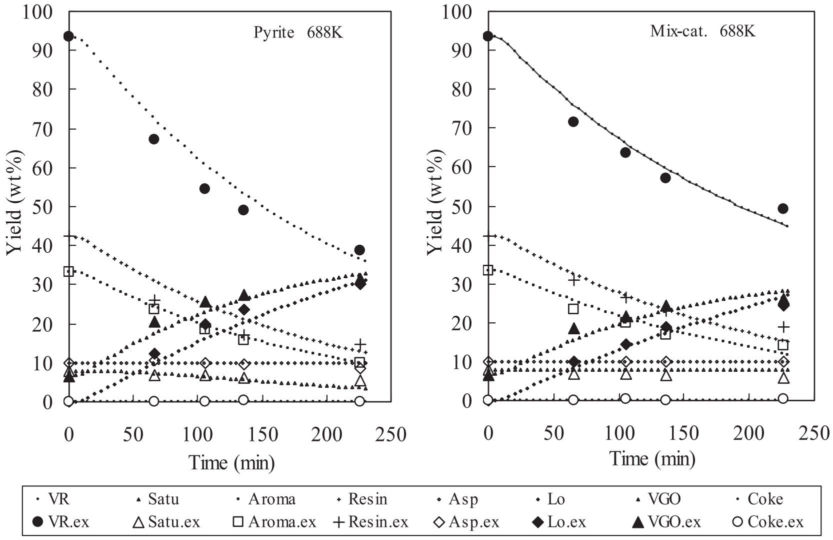

Figure 3. Comparison of the model predictions and experimental data at 688 K.

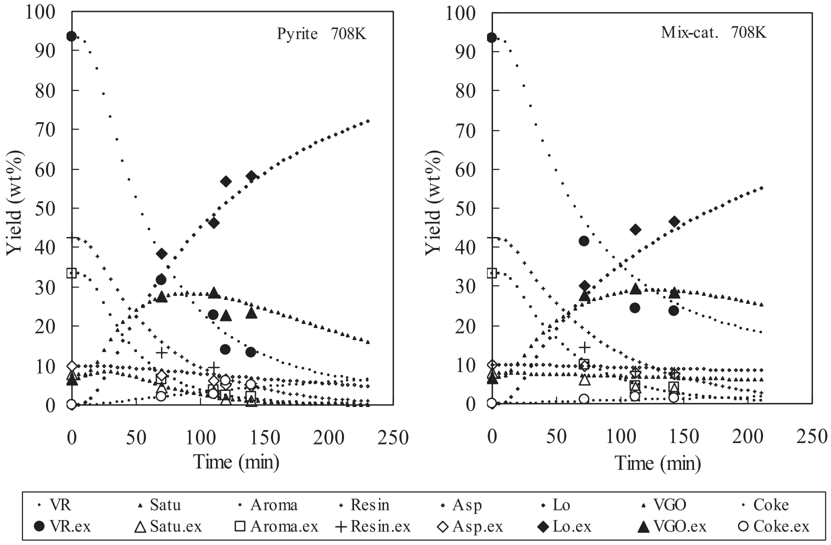

Figure 4. Comparison of the model predictions and experimental data at 708 K.

Table 3. Kinetic parameters

Temp., K	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	k_9	k_{10}
Rate constants for pyrite ($\times 10^{-3}$ h^{-1})										
688	4.76	0.0135	0.00354	18.2	0.796	0.0244	5.42	0.00484	0.0356	0.709
708	16.6	0.0141	0.634	46.5	5.67	3.45	16.6	0.130	4.23	7.11
718	30.3	0.0146	7.62	72.7	14.5	3.71	28.3	0.632	41.8	21.5
E_a $kJmol^{-1}$	253	10	1,050	189	397	1,002	226	667	967	467
Ln A_0 h^{-1}	43.09	−5.31	175.25	33.21	66.48	168.85	38.43	108.47	163.00	78.46
Rate constants for mix-cat ($\times 10^{-3}$ h^{-1})										
688	0.00884	0.0149	0.0122	0.0141	4.68	0.0140	4.65	0.0124	0.0157	1.29
708	0.0118	0.0154	0.0137	1.27	19.5	0.0149	13.6	0.0129	0.912	4.28
718	0.0125	0.0157	0.0145	10.9	38.7	0.0154	22.8	0.0131	6.39	7.61
E_a $kJmol^{-1}$	47	7	24	910	289	13	217	7	822	243
Ln A_0 h^{-1}	0.78	−5.80	−3.05	152.10	49.33	−4.82	36.77	−5.93	136.81	40.01

Characteristics of the Catalytic Reaction

The magnitudes of the rate constants for each reaction path for the catalysts pyrite and mix-cat are visualized using the height of the bar chart in Figure 5. Most of the reaction rates for pyrite were more temperature-dependent than those for mix-cat, except k_2 (Aroma to Resin), which was not the main reaction path for either catalyst. For pyrite, the hydrocracking reactions to lighter products k_1 (Aroma to Satu) and k_4 (Satu to Lo) were observed to progress at any reaction temperature. Reaction k_3 (Resin to Asp) accelerated

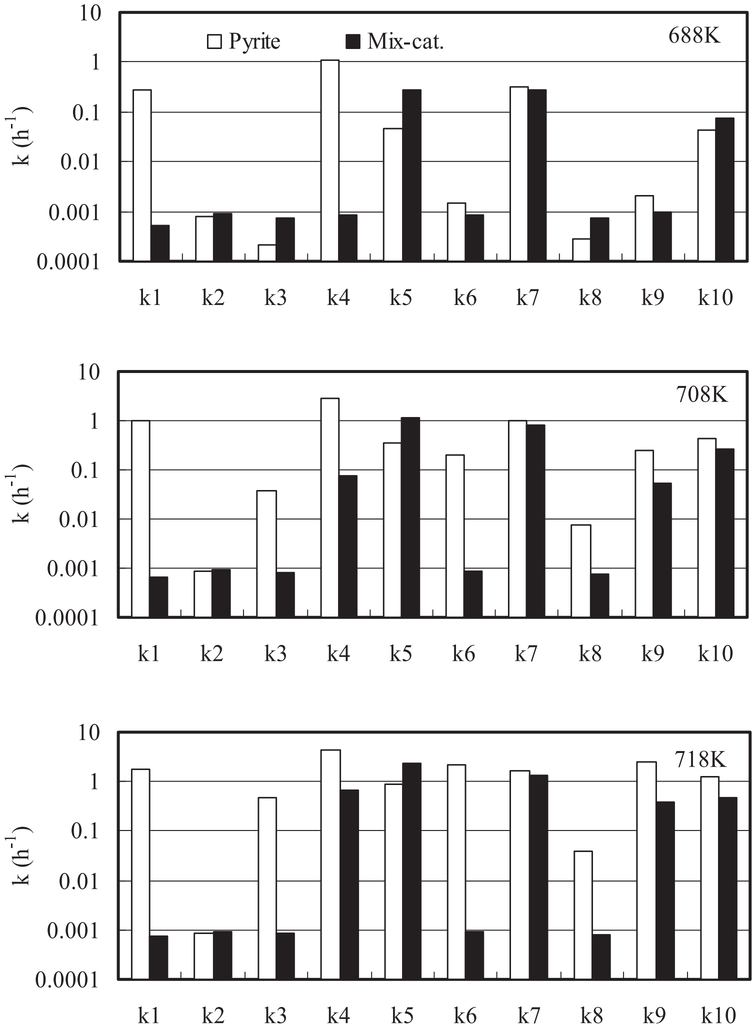

Figure 5. The reaction rate constants.

as the temperature increased for pyrite, while this reaction path was restricted with mix-cat. The addition of active carbon to the hydrocracking reaction appeared to prevent the formation of new asphaltenes. Reaction rate k_9 (Asp to Coke) increased with temperature for both pyrite and mix-cat, which reflects the tendency of coke to form via the polycondensation of higher molecule species like asphaltenes at higher reaction temperatures. For both pyrite and mix-cat, reaction rate k_{10} (VGO to Lo) was high at all reaction temperatures. This might reflect the decrease in the yield of vacuum gas oil after it peaks as the reaction proceeds, as shown in Figure 1. Overall, the characteristics of the catalytic reactions seen in the kinetic model conformed to the observed reaction phenomena well.

The kinetic model study suggested that the use of pyrite alone as the catalyst tends to promote both hydrocracking reactions, producing relatively lighter products and the polycondensation reaction producing asphaltenes and then coke. In contrast, the mixture of pyrite and active carbon promotes the reactions retaining the middle fractions in the products and restricts the polycondensation reaction of heavy components, such as the path (Resin to Asp).

CONCLUSIONS

Our kinetic study was based on a lumping model using the SARA constituents in the residue (798 K^+) fraction and gas, naphtha, kerosene, gas oil, vacuum gas oil, and coke as products. The agreement between the model predictions and experimental data was very good.

Most of the reaction rates with pyrite as the catalyst were more temperature-dependent than for the mixture of pyrite and active carbon. With pyrite, the hydrocracking reactions that give lighter products, such as aromatics to saturates and saturates to gas, naphtha, kerosene, and gas oil, progressed at any reaction temperature. The condensation reaction (resins to asphaltenes) was accelerated at higher temperatures with pyrite, while this reaction path was restricted by the mixture of pyrite and active carbon. The formation of new asphaltenes in the hydrocracking reaction seemed to be prevented by the addition of active carbon.

The high reaction rate of vacuum gas oil to lighter products was observed for both pyrite and the mixture of pyrite and active carbon at any reaction temperature, which likely reflected the decrease in the yield of vacuum gas oil after it reaches a maximum as the reaction proceeds. The characteristics of the catalytic reaction in the kinetic model conformed to the observed reaction phenomena well.

The results suggested that the use of active carbon results in the reactions retaining the middle fractions in the products, while restricting the polycondensation of heavy components from resins to asphaltenes. This kinetic study verified the effectiveness of active carbon in the hydrocracking reaction.

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