A New Lumped Kinetic Model of an Industrial Hydrocracking Process

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Hydrocracking is a catalytic cracking process for the conversion of heavy oil fractions, such as vacuum gas oil (VGO), into valuable products with lower boiling point, such as diesel, kerosene and gasoline. Due to the flexibility of the process, high yields and good quality of liquid products, hydrocracking has become an important unit in modern refinery. However, the study of kinetic modelling towards hydrocracking reactor (HCR) is limited due to its complicated reaction mechanism. In this study, the reactor model is established based on a new six-lump model considering the velocity change along the reactor, different thermal effects and kinetic differences between hydrotreater (HT) and hydrocracker (HC). Compared with the previously reported lumped kinetic models, the fine-tuned model (calibrated by differential evolution algorithm) can predict products yields more accurately, in particular outlet temperature of each beds and the detailed yields and temperature distribution along with the reactor beds. The proposed lump based kinetic model can be applied to the optimization and control of industrial hydrocracking process.

1. Introduction

Hydrocracking is a catalytic cracking process for the conversion of heavy oil fractions, such as vacuum gas oil (VGO) into valuable products with lower boiling point, such as diesel, kerosene and gasoline (Mao et al., 2015). There is increasing need for sophisticated refining technology with the increasing demand of middle distillates and stringent quality requirements (Becker et al., 2016). Although hydrocracking is more costly for upgrading oil fractions than the traditional method, such as catalytic cracking, it offers refiners more flexibility through improving product quality and the possibility of processing heavier feedstocks (Browning et al., 2016). Moreover, hydrocracking can produce a broad range of products by processing a wide range of feedstocks of different characteristics (Bhutani et al., 2006). Hydrocracking process now plays an increasingly important role in modern refineries (Jia and Zhang, 2011).

Due to the huge number of hydrocarbons involved in hydrocracking, it is difficult to build a detailed kinetic model considering each compound and all the possible reactions (Ancheyta et al., 2005). Lumping technique is the most used method nowadays to describe hydrocracking process due to its simplicity. Sadighi et al. (2010) reported a 4-lump kinetic model including hydrogen consumption for hydrocracking of vacuum gas oil in a pilot scale reactor. This approach considers VGO and unconverted oil as one lump, and the others are distillate, naphtha and gas. The average absolute deviation (AAD) of prediction is 5.92 % and about 8.59 % for hydrogen consumption for hydrocracking. Then Sadighi (2016) proposed a two-dimensional hydrocracking model with the same 4 lumps which the AAD of predict yields is 5.85 %. Sánchez et al. (2005) proposed a 5-lump hydrocracking model: unconverted residue (538 °C+), vacuum gas oil (VGO; 343-538 °C), distillates (204-343 °C), naphtha (IBP-204 °C), and gases. This model could achieve an average absolute error of less than 5 %. Martínez and Ancheyta (2012) adopted the same lump method to model hydrocracking process of heavy oil in a continuous stirred tank reactor (CSTR) involving short term catalyst deactivation. In order to test various operating parameters on maximizing the aviation turbine kerosene (ATK) yields, Elkilani and Fahim (2014) proposed a 6-lump (vacuum gas oil, heavy aviation turbine kerosene, light aviation turbine kerosene, heavy naphtha, light naphtha and gas) model to describe the kinetics of VGO hydrocracking. However, the hydrocracking reactions were considered to be isothermal in this model. Li et al. (2008) also developed a

6-lump model for one practical residue hydrocracking reactor. This model, including 6 lumps (crude oil, diesel oil, aviation kerosene, heavy naphtha, light naphtha and gas), took both mass balance and kinetics equations into consideration. However, Li's model considered that activity energy and reaction heat were the same in hydrotreater (HT) and hydrocracker (HC), which is inconsistent with practical hydrocracking process.

The present work employs the same lump method defined by Li et al. (2008). We modify the mass-balance error in Li's model. Based on our knowledge, this new model considers the velocity change along the reactor, different thermal effects and kinetic model between HT and HC for the first time. By applying these new improvements, the present model can predict products yields more accurately, in particular outlet temperature of each beds and the detailed yields and temperature distribution along with the reactor beds. The effect of the form of objective function to the results of parameter calibration is also discussed, and a reasonable form is suggested.

This paper is organized as follows. In section 2, the HCR model is established and properties are calculated. Section 3 reports the methods of model calibration and validation, and the results are presented and discussed. Finally, section 4 gives the conclusion of this study.

2. Mathematical model description

2.1 Kinetic model

In this work, the lump method is determined by the number of feeds and products. In the studied hydrocracking process, there are one feed (FE) and six products: bottoms (BO), diesel (DI), kerosene (KE), heavy naphtha (HN), light naphtha (LN) and light ends (LE). Since that: (1) the properties of feed and bottoms are similar, (2) bottoms can be thought of as unconverted feed, the present work considers feed and bottoms as one lump. Based on this, a 6-lump model is adopted for modelling the industrial HCR process. We take the following assumptions into consideration: (1) Each lump could translate into a lighter lump. (2) All the reactions are first-order and irreversible. (3) Polymerization and diffusion of the reactants are neglected. (4) The flow state of all reactants is plug flow and the reactors are adiabatic. (5) The velocity is changed along with the two reactors. (6) The pressure in HT and HC is fixed, namely the pressure change is neglected.

Based on these consumptions, the kinetic model of HCR can be developed. The present work employs the same 6-lump model defined by Li et al. (2008), but some modifications have been made to their model. In order to ensure the integrity of the reaction system and intelligibility, we list all the kinetic equations below. Eq(1) is the reaction rate equation.

$$R_j = K_j C_j \tag{1}$$

Here, R_j is the reaction rate vector of the jth reactor bed. K_j denotes the reaction rate constants matrix, which is presented in Eq(2). C_j is the mole density of the 6 lumps presented in Eq(6).

$$K_j = \begin{bmatrix} \sum_{i=1}^{5} k_{i,j} & 0 & 0 & 0 & 0 & 0 \\ -a_{1,2}k_{1,j} & \sum_{i=6}^{9} k_{i,j} & 0 & 0 & 0 & 0 \\ -a_{1,3}k_{1,j} & -a_{2,3}k_{1,j} & \sum_{i=10}^{12} k_{i,j} & 0 & 0 & 0 \\ -a_{1,4}k_{1,j} & -a_{2,4}k_{1,j} & -a_{3,4}k_{1,j} & \sum_{i=13}^{14} k_{i,j} & 0 & 0 \\ -a_{1,5}k_{1,j} & -a_{2,5}k_{1,j} & -a_{3,5}k_{1,j} & -a_{4,5}k_{1,j} & \sum_{i=15}^{15} k_{i,j} & 0 \\ -a_{1,6}k_{1,j} & -a_{2,6}k_{1,j} & -a_{3,6}k_{1,j} & -a_{4,6}k_{1,j} & -a_{5,6}k_{1,j} & 0 \end{bmatrix} \tag{2}$$

Where $a_{l,m}$ is reaction coefficient calculated by Eq(3). $k_{i,j}$ is the first-order rate constant for the cracking of the ith reaction in the jth bed and is obtained from Eq(4).

$$a_{l,m} = \frac{Mn_l}{Mn_m} \tag{3}$$

$$k_{i,j} = k_{i0} \exp\left(-E_{i,j}/RT_j\right) \tag{4}$$

In Eq(3), Mn_l denotes the relative molecular mass of the lth lump ($l = 1, \cdots, 6$ represent the lump of feed/bottoms, diesel, kerosene, heavy naphtha, light naphtha and light ends). In Eq(4), k_{i0} is pre-exponential factor, $E_{i,j}$ is the activation energy of the ith reaction in the jth bed, R is the gas constant and T_j denotes temperature.

In this work, we assume that $E_{i,j}$ is the same when one lump cracks into any lighter lumps in the jth bed. For example, feed cracks into diesel, kerosene with the same activation energy. In the first reactor, namely HT, because the main reactions are the hydrotreating of feed, the cracking activity is lower compared with the second reactor (HC), which also means a lower conversion rate of feed in HT. In order to reflect the different cracking activity, the present work creatively employs a proportion factor - *Eplus*, see Eq(5) - to modify the activation energy for different reactor models.

$$E_{i,j1} = Eplus * E_{i,j2} \tag{5}$$

Where $E_{i,j1}$ and $E_{i,j2}$ denote the activation energy in HT and HC.

$$\boldsymbol{C}_j = \begin{bmatrix} C_{1,j} & C_{2,j} & C_{3,j} & C_{4,j} & C_{5,j} & C_{6,j} \end{bmatrix}^T \tag{6}$$

Where $C_{l,j}$ represents the mole density.

2.2 Reactor model

Plug flow reactors have been adopted to model the industrial hydrocracking process. Because there are seven beds in the hydrocracking process (3 hydrotreating beds and 4 hydrocracking beds), seven cascade plug flow reactors are used to present hydrotreating beds and hydrocracking beds.
The material balance equation in each bed is given in Eq(7).

$$u\frac{dC_{l,j}}{dl_j} + C_{l,j}\frac{du}{dl_j} = -\boldsymbol{R}_j(l) \tag{7}$$

Here, u is the axial velocity of all the reactants and l_j is the length of the jth reactor bed. Note that u is changing with heavy lumps (e.g. feed) cracking into relatively lighter lumps (e.g. light ends), so the second term on the left-hand side in Eq(7) is not equal to zero. However, the measurement of u in hydrocracking process is difficult and unnecessary in practice. In the present work, the derivative term of u versus l_j (defined as velocity factor, *VF*) is assumed to be constant across each bed, which is determined by Aspen HYSYS (AspenTech, 2017) in section 3.
The heat balance equation in each bed is given in Eq(8).

$$\frac{dT_j}{dl_j} = \Omega_j \frac{(-\Delta H_j)\sum_{l=1}^{6}\boldsymbol{R}_j(l)}{G_{in}\overline{Cp} + G_{RH,j}Cp_{RH}} \tag{8}$$

Here, Ω_j is the cross sectional area of reactor bed, G_{in} is the total mass flow rate of reactants except recycle hydrogen (RH) and $G_{RH,j}$ is the mass flow rate of RH. Note that the ΔH_j (reaction heat) varies in different beds due to the various type of reactions, which is further define by Eq(9). Cp_{RH} and $\overline{Cp}$ (calculated by Eq(10)) are the mass heat capacity of RH and the mixture of 6 lumps.

$$\Delta H_j = HF_j * \Delta H \tag{9}$$

Here, ΔH is reaction heat constant, and HF_j is the heat factor.

$$\overline{Cp} = \frac{\sum_{l=1}^{6}G_l Cp_l}{\sum_{l=1}^{6}G_l} \tag{10}$$

Here, G_l and Cp_l denote the mass flow rate and the mass heat capacity of the lth lump.

2.3 Property calculation

In the present work, molecular weight and mass heat capacity of the 6 lumps are needed to model the hydrocracking process. Because the work about properties calculation is not the main issue of the present work, Aspen HYSYS is adopted to calculate these properties. The present work assumes that the effects of temperature and pressure to mass heat capacity are neglected. Table 1 shows the results of properties calculation at classical temperature and pressure of industrial hydrocracking process, which are used in the present model. It is worth noting that the temperature of RH (mainly composed of hydrogen) usually changes little around 63 °C in hydrocracking process, so the properties of RH is calculated at 63 °C. Note that the mass heat capacity becomes larger with the molecular weight decreasing, which is consistent with the practice.

Table 1: The results of calculated molecular weight and mass heat capacity

		FE	DI	KE	HN	LN	LE	RH
Temperature	°C	370	370	370	370	370	370	63
Pressure	MPa	14.5	14.5	14.5	14.5	14.5	14.5	14.5
Molecular Weight	g*mol^{-1}	350.39	220.32	152.97	102.06	71.58	23.15	3.50
Mass Heat Capacity	kJ*kg^{-1}*°C^{-1}	3.05	3.18	3.19	3.41	3.50	3.58	8.89

3. Model calibration and validation

The 6-lump model total contains 29 parameters to be determined. We divide these parameters into 2 classes, manual-calibration parameters (1 velocity factor VF and 7 heat factors HF_j) and automatic-calibration parameters (15 pre-exponential factors k_{i0}, 5 activation energy $E_{i,l2}$ and 1 proportion factor $Eplus$). VF is determined by Aspen HYSYS in this study. HF_j is determined by trial and error to achieve reasonable temperature rises of each reactor bed. Both VF and HF_j keep unchanged once determined. The minimization of the objective function expressed in Eq(11) is adopted to find the best set of the other 21 parameters. This process is optimized by standard differential evolution algorithm (Das and Suganthan, 2011).

$$objective\ function = \sum_{data\ set=1}^{n} \sqrt{\left(\sum_{j=1}^{7} w_j^2 * \left(T_j^{model} - T_j^{plant} \right)^2 + \sum_{l=1}^{6} w_l^2 * \left(Y_l^{model} - Y_l^{plant} \right)^2 \right) \bigg/ 13}$$ (11)

In the objective function, the absolute error is considered instead of relative errors. This can be interpreted through calculating the relative error, by assume

$$w_{l1} = w_{l2}, \left(Y_{l1}^{model} - Y_{l1}^{plant} \right) = \left(Y_{l2}^{model} - Y_{l2}^{plant} \right), Y_{l1}^{plant} < Y_{l2}^{plant}, \forall l1, l2 \in \left(1, \cdots, 6 \right).$$

This will result

$$\left(w_{l1} * \left(Y_{l1}^{model} - Y_{l1}^{plant} \right) \bigg/ Y_{l1}^{plant} \right)^2 > \left(w_{l2} * \left(Y_{l2}^{model} - Y_{l2}^{plant} \right) \bigg/ Y_{l2}^{plant} \right)^2.$$

This indicates that the error of less valuable product (with small yield in hydrocracking process usually, e.g. light ends) takes more in the objective function, which will result a small simulation error for less valuable product but a big simulation error for more valuable product (with big yield in hydrocracking process usually, e.g. kerosene and naphtha).

3.1 Calibration of process model

Three data sets are used to calibrate the presented model. Figure 1 gives the graphic results of one data set. It is worth noting that the increase of slope in Figure 1(a) means the increase of reaction rate, which is consistent with fact. In the first 3 hydrotreating beds (Horizontal axis ranges from 0 to 24 m, loaded with hydrotreating catalyst), the hydrotreating catalyst has lower cracking activity as compared to the cracking section, which leads to a small slope. Conversely, in the subsequent 3 hydrocracking beds (Horizontal axis ranges from 24 to 36 m, loaded with hydrocracking catalyst), the slope becomes larger. Moreover, the slope in the last bed becomes smaller with the consumption of reactants. In Figure 1(b), the first reactor bed (R1B1, Reactor 1 Bed 1) has the highest temperature rise because the hydrotreating is a highly exothermic reaction. In the subsequent 2 hydrotreating beds, the temperature rise become smaller due to the gradual accomplishment of hydrotreating. The temperature rise become larger again in hydrocracking beds with the increase of reaction rate.
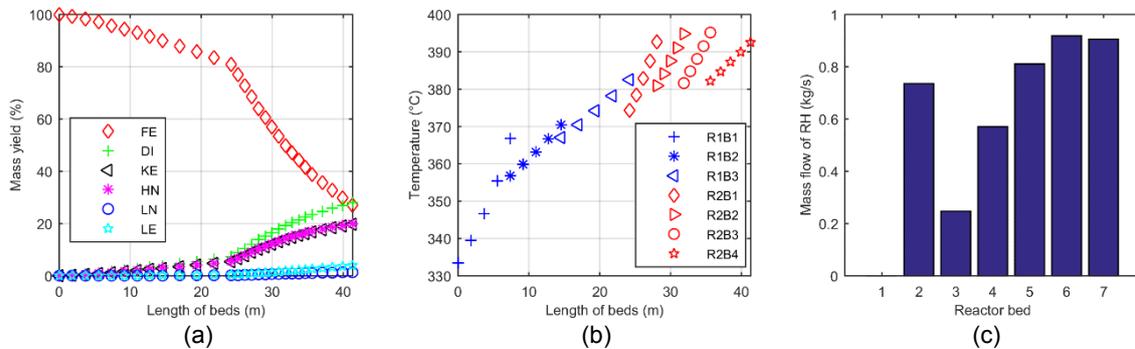

Figure 1: Calibration results ((a): detailed mass distribution of 6 lumps along reactor beds. (b): detailed temperature distribution of reactor bed. (c): consumption of recycle hydrogen of each reactor bed)

3.2 Validation of process model

Nine sets of plant data are used to validate the fine-tuned model. Table 2 illustrates the validation results (AAR, average absolute error; ARE, average relative error). The ARE of light naphtha is the highest, the only one higher than 6 %, due to the lowest yield (only 1.5 %). It is worth noting that the AAE of predicted product yields is only 0.5 % and ARE (except light naphtha) is only 2.9 %. The detailed comparison of mass yields between model and industry is illustrated in Figure 2. Predicted outlet temperature is illustrated in Figure 3, from which it can be concluded that this model can predict outlet temperature very well for all reactor beds. To conclude, our proposed lumped model shows excellent accuracy on predicting the yield and temperature rise for hydrocracking process, which enable us to apply this model in optimization and control in the future work.
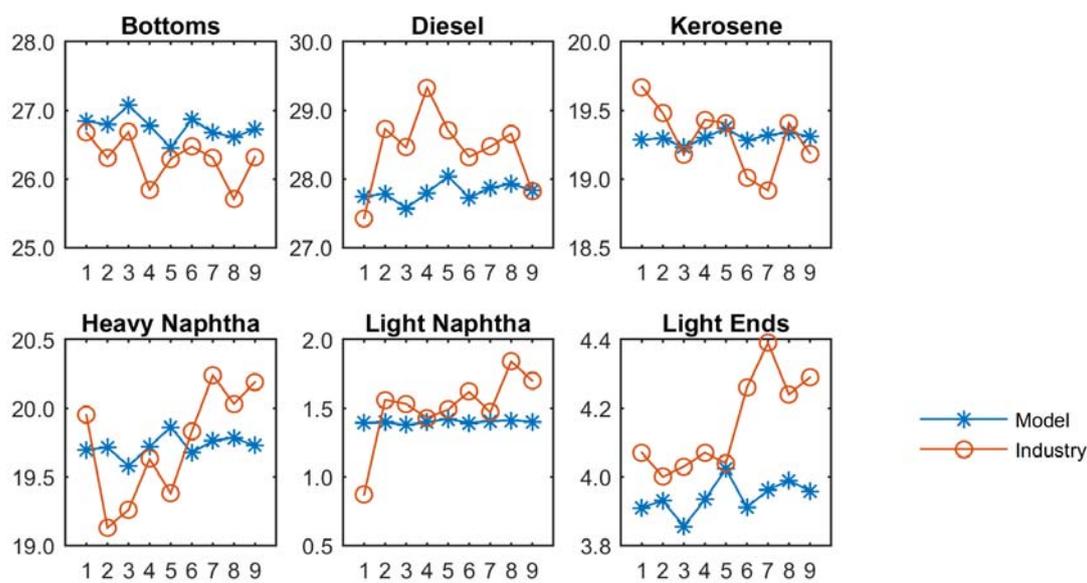

Figure 2: Predicted mass yields tendency for the validation data sets, horizontal axis: data set, vertical axis: mass yield (%)
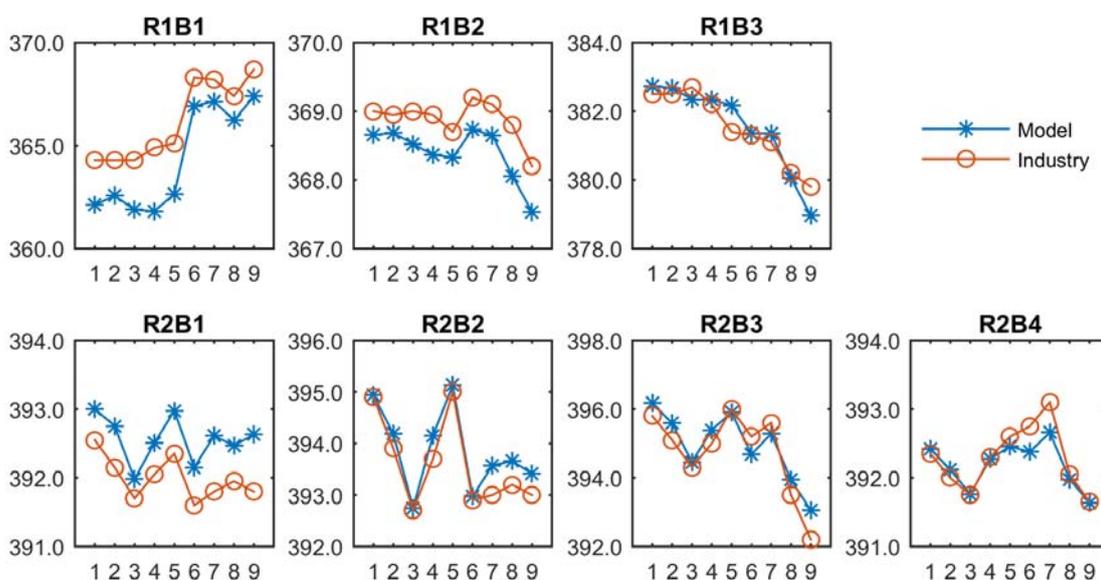

Figure 3: Predicted outlet temperature tendency of each reactor bed for the validation data sets, horizontal axis: data set, vertical axis: outlet temperature (°C)

Table 2: Validation accuracy

		AAE (°C)	ARE (%)			AAE (%)	ARE (%)
Temperature	R1B1	1.9	0.51	Yields	BO	0.9	3.57
	R1B2	1.0	0.26		DI	0.7	2.44
	R1B3	0.3	0.09		KE	0.4	1.88
	R2B1	1.1	0.29		HN	0.3	1.73
	R2B2	0.3	0.07		LN	0.2	16.34
	R2B3	0.4	0.10		LE	0.2	5.04
	R2B4	0.3	0.07				
	Average	0.8	0.20		Average	0.5	5.17

4. Conclusions

By introducing of proportion factor (*Eplus*), heat factor (*HF$_j$*) and velocity factor (*VF*), the proposed new 6-lump model can give detailed yields and temperature distribution along with the reactor beds. Compared with the previously reported lumped kinetic models, the proposed model can predict products yields more accurately, with AAE of only 0.5 % and ARE (except light naphtha) of only 2.9 %. In particular, this model can predict outlet temperature very well for almost every reactor beds, with AAE of 0.8 °C. The effect of the form of objective function to the results of parameter calibration has also been discussed, based on which the form of absolute error is suggested.

Acknowledgments

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