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Simulation of heavy-oil thermal cracking process on the basis of carbon number-based component approach

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Abstract

Simulation of heavy oil thermal cracking process is very important but few researches have been published now. In this paper, a simulation framework based on the carbon number-based approach(CNCA) has been established. A systematic division rule is put forward for dividing cracked products into 59 carbon number components. Then the cracking reaction network has been structured and the corresponding reaction rate equations have been obtained. The reaction rate constants were fitted with the experimental data. A plug fluid model is used to model the cracking reactor and the simulation procedure for heavy-oil thermal-cracking process has been developed. The calculated results are compared with the plant data.

Keywords: heavy oil, thermal cracking, reactor, simulation, carbon number-based component

1. Introduction

There is about 50~70% heavy component in crude oil, so heavy-oil has been the world's largest petroleum resources for supplying energy and raw material. Cracking heavy oil would convert heavy and low value oils into lighter and high value fuels, such as gasoline and light olefins. The typical technologies are fluid catalytic cracking (FCC) and thermal cracking. The presence of metals and asphaltenic molecules in the heavy oil has been a serious obstacle to the use of catalytic processes, which might lead to the de-activation of catalyst (Kajiyama, et al., 1989; Maciel Filho and Sugaya, 2001). Hence the thermal cracking technology is still dominant at present. However, although the economical and industrial importance of thermal cracking has been obvious, the simulation of process is rather empirical (Sugungun et al., 1998) and few in the open literature(Maciel Filho and Sugaya, 2001). The main reason is that the cracking mechanism is complicated from both hydrodynamic and chemical points of view because heavy oil and cracking products are the mixture of thousands upon thousands compounds, which has not been realized till now based on the compositional analysis, and also, the cracking reaction network and the corresponding kinetics parameters are difficult to be determined. The general approach to deal with this complicated system is lump model that divides the heavy-oil and the products much more roughly (Narendra

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et al., 1993; Bianco A. Del et al., 1993). Since 1960', lump-model has been developed rapidly from 3-lump to 16-lump model, in which the "Pseudo boiling range" approach is used to divide the mixture, and lumping kinetic models were used to predict the composition of cracking product, such as gas, gasoline, gasoil1, gasoil2 and coke. The limitations of lump-model approach are: 1) can not express the thermodynamic properties and structure of each "pseudo composition" with the classical thermodynamic model; 2) can not predict the properties of oil products, such as PONA, octane number(ON), cetane number(CN) and so on; 3) The TBP curve of certain heavy oil feedstock must be offered according to the experimental measure. In this work, we propose a new and systematic approach which is called carbon number-based component approach(CNCA) to divide thermal cracking products, corresponding thermodynamic models and reaction networks are established for cracking reaction. The simulation procedure of thermal cracking of heavy oil process is developed. The research result will give a further understanding of the cracking process and explain the complicated mechanism of the conversion of the feedstock partly.

2. Carbon number-based approach

2.1 Approach description

Since 1980's, lump model has been regards as an effective method to research heavy oil(such as vacuum residues, VRs) and the cracking products. Takatsuka et al.(1989) proposed four-fraction model to describe the residual oil, and the cracked product was divided into four lumps. Zhou et al. divided the vacuum residues into six fractions, i.e., saturates, light and heavy aromatics, light and heavy resins and asphltenes. The cracked product was divided into gas, gasoline, gas oil1, gas oil2 and coke. So 11-lump model had been used to set up the thermodynamic model and reaction rate equation for thermal cracking VR (Zhou et al., 1999a, 1999b). At present, much finer division approach has been proposed and used. However, in fact, the principle of division is still based on the boiling point and distillation range of mixture without considering the structures and properties of real molecules.

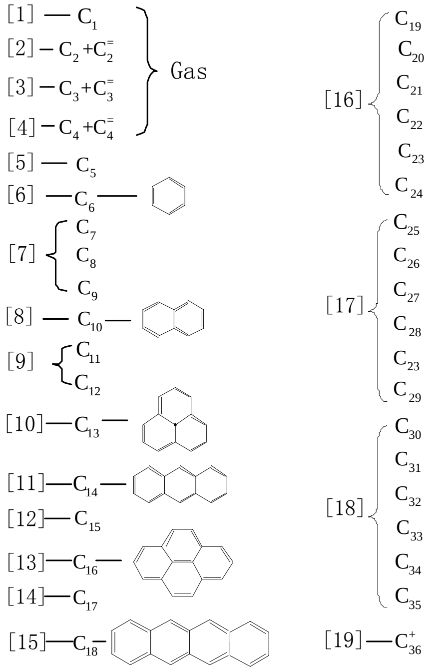

Figure 1. The division result with carbon-number based approach

In order to express the cracking products much strictly, we proposed CNCA according to molecular structure and properties of compounds in the cracked products, as well as the fact that the mixture of cracking products consists of a series compounds with continues molecular weight. The rules of division are: 1) The cracked products are divided into 19 carbon groups based on the carbon number and the molecular structure, such as number of phenyl rings and their positions, which is shown in Figure 1; 2) Each carbon group is then further divided into four components, paraffin, olefin, naphthene and aromatics when carbon number is greater than 5. Considering the coke, the total number of carbon components is 64.

CNCA can avoid the limitation of lumping model which only consider the interactions between the lumps rather than the interaction between molecular components in the mixture. Although interactions between real molecular also would not been expressed perfectly with CNCA, it is offer an available and effective approach to deal with such complicated system, which is close to express the real compounds.

2.2 Thermodynamic properties

Basic thermodynamic property and phase equilibrium model are very important for the process simulation. The concentration profile and thermodynamic properties of feedstock expressed with four-fraction model are derived from the experiment (Que and Liang, 1992). The basic thermodynamic properties of carbon component, such as molecular, boiling point, critical properties and density are calculated based on the general mixing rules considering the concrete compounds included in this carbon component. The saturated pressure of carbon component is calculated with generalized Antoine equation. Vapour-liquid phase equilibrium relationships are predicted with Grayson-Streed model(Grayson and Streed, 1963). PONA, ON and CN values for each carbon component will be determined based on the concrete compounds with special mixing rules.

3 Rates of thermal cracking reactions

In this work, it is assumed that all cracking reactions are parallel, which means the reactions between products do not occur, and also the reversible reactions will not be considered. A pseudo-first-order rate should give a better approximation to this thermal cracking process. Then the reaction sub-networks of saturate, aromatics, colloid and asphaltene can be set up based on the assumption above. Figure 2 shows the reaction network scheme of saturate cracking. In this network, cracking saturate will produce 59 carbon components. Similarly, the reaction sub-networks of aromatics, colloid and asphaltene will be established too. Except for aromatics, colloid and asphaltene, saturate does not crack to produce coke. The rate equations of cracking reaction for saturate is given by:

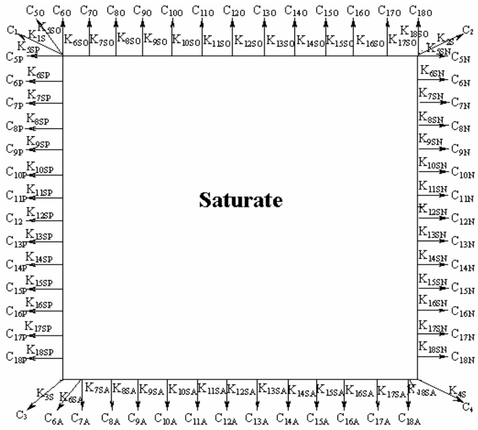

Figure 2 Reaction network of

$$\frac{dX_{C_i}}{dt} = a_{iS} K_{iS} X_S, \qquad i = 1,2,3,4$$

$$\frac{dX_{C_{iP}}}{dt} = a_{iSP}K_{iSP}X_S, \qquad i = 5,6,\ldots\ldots,19$$

$$\frac{dX_{C_{iO}}}{dt} = a_{iSO}K_{iSO}X_S, \qquad i = 5,6,\ldots\ldots,19$$

$$\frac{dX_{C_{iN}}}{dt} = a_{iSN}K_{iSN}X_S, \qquad i = 5,6,\ldots\ldots,19$$

$$\frac{dX_{C_{iA}}}{dt} = a_{iSA}K_{iSA}X_S, \qquad i = 6,7,8,\ldots,\ldots 19$$

$$-\frac{dX_S}{dt} = (\sum_{i=1}^{4}K_{iS} + \sum_{i=5}^{19}K_{iSP} + \sum_{i=5}^{19}K_{iSO} + \sum_{i=5}^{19}K_{iSN} + \sum_{i=6}^{19}K_{iSA})X_S$$

Where a, b is stoichiometry of reactions； X is concentration of carbon component； K is reaction rate constant; t is time; i refers to carbon component. The subscripts S, P, O, N and A express saturate, paraffin, olefin, naphthene and aromatics, respectively. Arrhenius-type relationship is used to express the rate constant of reaction, and the frequency factor and activation energie are fitted with experimental data and verified with industrial data. The comparison of experimental data and simulation result with regressive parameters is shown in Figure 3, which indicate good agreement.

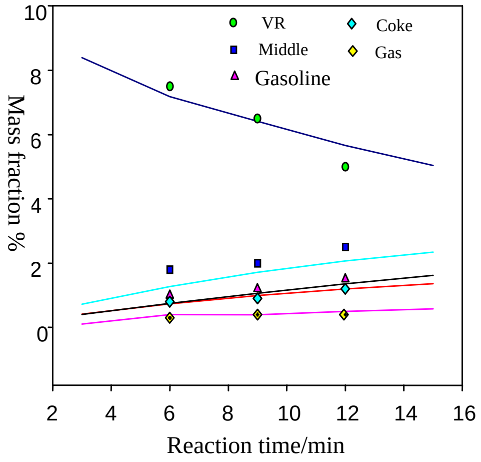

Figure 3 Comparison of exp. (Zhou, 1999a) and cal. result for VRs, line: cal. value; Point: exp. value

4 Simulation of cracking reactor and cracking process

Thermal cracking processes are becoming an important technology for managing the recently increasing demand for light oil. Various types of processes have thus appeared: Delay Coker, Eureka, Fluid Coker and Flexcoker. They are operated in rather different modes and the products are very process specific in order to reach the targets, such as higher yield of light cracked oil, increasing total liquid yield, reduction of utility cost and reduction of construction cost. Reaching these targets partially relays on the reliable simulation model. However, corresponding simulation research is few till now in the open literature (Takatsuka et al., 1988). In this work, we select delay cracker process as the research objective, and the simulations of units and flowsheet are developed with the thermodynamic model and kinetics model based on the carbon number-based approach.

Soaking reactor can be considered as tube reactor, in which the heavy oil cracking reaction is carried out. The feedstock enters into the reactor and the heavy oil is pyrolysed to be the mixture of cracked oil and then is flushed out of the reactor, the coke is discharged from the bottom. In this work, plug fluid model is used to model the cracking reactor. Equilibrium-stage model is used to simulate the fractionator to separate the cracked mixture to obtain the cracked products, such as gasoline, gasoil1 et al. Because the industrial cracking process is very complicated, we simply the industrial flowsheet to be the model flowsheet considering the main units and main streams that is shown in figure 4. This simplification would not affect significantly our understanding and analysis of the total process. The compositions of heavy oil(Vacuum residuum) from experiment(wt%): Asphaltene: 4.8%, Aromatics: 20.84%, Resin: 47.52%, Saturates: 26.84%(Que and Liang,1992).

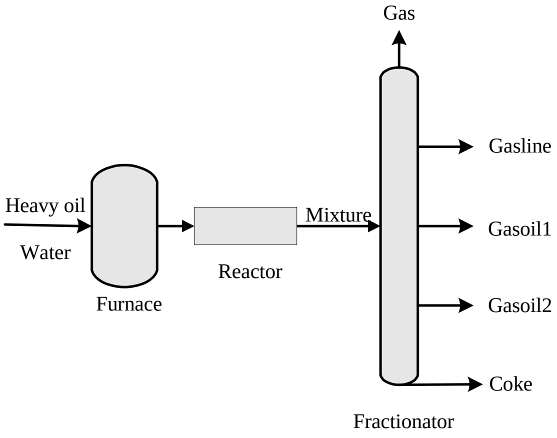

Figure 4 Simplified flowsheet of delay cracking process

5 Results and Discussion

We carry out this procedure in the ProII software. Figure 5 shows the effect of output temperature of furnace on the yields of products. The output furnace temperature is an important index of cracking process that will affect the cracking reaction depth, and then affect the yield and properties of products. From the figure we can know that with the increasing of temperature, yields of gas and coke are increased, and the yield of gasoline will be decreased gradually. The research result will offer an instruction to control the yields and properties of different products.

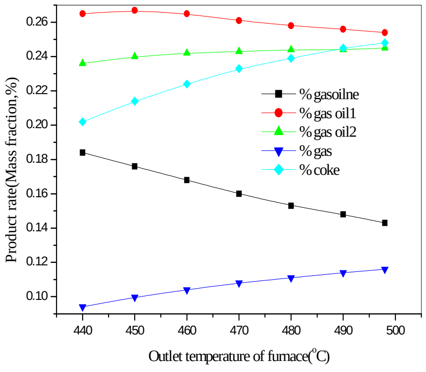

Figure 5 Effect of output temp. of furnace on the yields of products

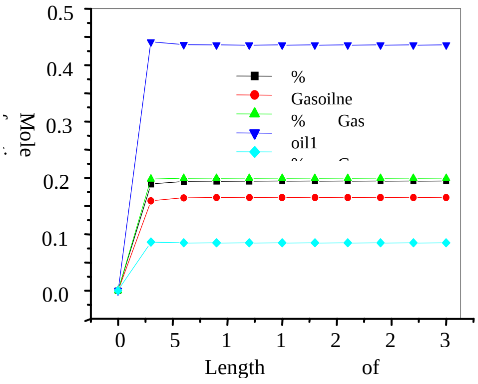

Figure 6 Profile of product concentrations along the reactor

Figure 6 shows the profile of product concentration along the reactor. In the early stage of reaction, the reaction rate of thermal cracking is fast, but slows later. The reason is that in the early stage, there exist many molecules with long alkyl chains or with a structure represented by bibenzyl type bonding. So the reaction rate and the yield of cracked oil are high. In the subsequent stage, polycondensation of residue and gas production, such as from dehydrogenation, is dominant and little cracked oil is produced. The previous work had also proved this result (Takatsuka et al., 1989).

Table 1 shows the simulation results of products properties. The general ON value of thermal gasoline is 40~60, the CN value of thermal cracked diesel oil is 50~60, which indicates the good agreement with the simulation result. Also, from the simulation framework we can calculate the PONA values of cracked products.

Table 1 Properties simulation result of cracked products

Item	Value	
	Gasoline	Diesel oil
Octane Number	48.90	—
Cetane Number	—	50.06
P (Wt Paraffinic Content)	26.03	29.09
O (Wt Olefin Content)	38.31	37.11
N (Wt Naphthenic Content)	15.19	12.23
A (Wt Aromatic Content)	20.47	21.57

CNCA brings a new thought to deal with the heavy oil cracking process with complex component system and corresponding inarticulate thermodynamics and reaction kinetics, although the theory and methodology proposed in this paper is not much perfect. However, the thermodynamic model and reaction model can be improved by understanding the real components profiles in feedstock and cracked products and mechanism of reaction with more advance compositional analysis method and experimental research, then the parameters both in the thermodynamic model and reaction kinetic will be fitted accurately.

References

Bianco A., D. N. Panariti, M. Anelli, P. L. Beltrame and P. Carniti, 1993, Thermal cracking of petroleum residues 1. Kinetic analysis of the reaction. Fuel, 72:75-80.

Grayson, H. G. and C.W. Streed, 1963, Vapor-liquid equilibria for high temperature, high Pressure hdrocarbon-hydrocarbon systems, 6th World Congress, Frankfurt am Main, June 19-26.

Maciel Filho, R and M. F. Sugaya, 2001, A Computer Aided Tool for Heavy Oil Thermal Cracking Process Simulation. Computers and Chemical Engineering, 25: 683-692.

Narendra C. D., J. D. Gregory and U. Pinky, 1993, A four-lump kinetic model for the craking/coking of recycled heavy oil. Fuel, Vol. 72: 1331-1334.

Que G.H and W.J. Liang, 1992, Thermal conversion of Shengli residue and its constituents. Fuel, 71: 1483-1482.

Sugungun M.M., L.M. Kolesnikov, V.M. Vinogradov and S.I. Kolesnikov, 1998, Kinetic modeling of FCC process. Catalysis Today, 43: 315-325.

Takatsuka T., R. Kajiyama, H. Hashimoto, I. Matsuo and S. Miwa, 1988, A Practical Model of Thermal Cracking of Residual Oil. Journal of Chemical Engineering of Japan, 22(3): 304-310.

Zhou X., S. Chen, Y. Zhang, K. Chang and C. Li, 1999a, Thermal kinetics of fractions of vacuum residues. Shiyouxuebao, 15(1): 8-16(in Chinese).

Zhou X., S. Chen, B. Ma, C. Li and K. Chang. 1999b, Kinetic model for thermal conversion of vacuum residue. Shiyouxuebao, 15(2): 73-78(in Chinese).