

Thermal and Catalytic Hydrocracking of Iranian Paraffin: A Unique Lumped Kinetic Model

J. Zarkesh^{1,2}, M.M. Akbarnejad¹, A. Badakhshan^{2,3} and F. Khorasheh*

In this paper, thermal and catalytic hydrocracking of liquid paraffin hydrocarbons, from Tehran refinery, is studied using a pilot plant reactor. The experimental system consisted of a vertical tubular flow reactor where hydrogen and liquid products were fed from the top of the reactor and after passing through a bed of catalyst (or quartz beads in the case of thermal hydrocracking experiments), the liquid and gaseous products were separated and sampled for subsequent analyses. The reaction temperature was in the range of 410-430°C for catalytic hydrocracking and 440-470°C for thermal hydrocracking experiments. The space velocities for both sets of experiments varied between 0.5 to 1.5 volume of feed per volume of catalyst per hour (VVH). For the purpose of kinetic modeling, a unique lumping scheme was employed for both catalytic and thermal hydrocracking in which the lumps consisted of various boiling fractions. The predicted product distributions of the model are in good agreement with the experimental data. Extrapolation of the results indicates that the catalyst plays an important role in hydrocracking reactions even at low temperatures.

INTRODUCTION

As a consequence of the petroleum industry's trend towards processing heavier, less expensive crudes and with increasing profitability being derived from middle distillate production, emphasis is being placed upon the development of conversion schemes for residual feedstocks. Heavy feedstocks produced by Iran refineries mainly consist of waxy distillates, furfural extract, and most importantly, vacuum bottoms. Some of these residues are converted to more desirable products. In Iran, vacuum bottoms, which contribute to about 25% of Iranian crude oil, are only converted to bitumen and fuel oil and there is no process for converting them to middle distillates. Economic and environmental factors will dictate the upgrading of these heavy feeds in the near future.

There are many types of processes for residue upgrading, some of which are quite mild and only

involve a viscosity reduction to facilitate pumping operations. On the other hand, there are some very complicated processes which are often the most expensive process in a refinery. From one point of view, the residue upgrading processes can be classified as carbon removal and hydrogen addition processes and economic considerations may prompt one or a combination of upgrading methods. Catalytic or thermal hydrocracking for residue upgrading, which results in a high yield of liquid products, is one option for consideration. These are an attractive class of upgrading processes for heavy residue since under the high hydrogen pressure employed, cracking of the feed to lighter fractions is also accompanied by heteroatom removal.

For the purposes of reactor design, process optimization and catalyst selection, it is necessary to develop kinetic models which can accurately predict the product distributions under hydrocracking conditions. For hydrocarbon mixtures, the development of such kinetic models is a challenging task due to the presence of a great variety of structures. The problem is enhanced for heavier fractions as the number of various hydrocarbon and heteroatom structures increases with higher boiling point of the feed. On the one hand, the reaction of the individual compounds present in such mixtures can be considered. This would be very complicated due to the great variety of structures present in such mixtures which ultimately contribute

1. *Research Institute of Petroleum Industry, National Iranian Oil Company, NIOC-RIPI, I.R. Iran.*
 2. *Department of Chemical Engineering, Sharif University of Technology, Tehran, I.R. Iran.*
 3. *Department of Chemical Engineering, University of Calgary, Calgary, Canada.*
- *. *Corresponding Author, Department of Chemical Engineering, Sharif University of Technology, Tehran, I.R. Iran.*

to a very complex network of reactions. Compound by compound identification and quantification is at best very difficult, if not impossible. An alternative approach, on the other hand, is to consider the mixture in terms of selected lumps, which can be specified in terms of such properties as boiling ranges, molecular weight ranges, carbon numbers, solubility class fractions and other structural characteristics. Characterization of a complex hydrocarbon mixture in terms of Structural Group Analysis [1-3] or construction of random molecules [4] provides a means for kinetic modeling. Various lumping schemes have been applied for kinetic modeling of complex reactions of hydrocarbon mixtures [5-10] and, more recently, continuous lumping [11-14] and axial dispersion models [15] have also been proposed.

As a starting point in the development of a reliable and accurate kinetic model for hydrocracking of Iranian heavy feedstocks, catalytic and thermal hydrocracking of liquid hydrocarbon paraffins from Tehran refinery are evaluated using a pilot plant reactor. A unique kinetic model is developed through a lumping scheme based on boiling fractions to predict the feed conversion and product distributions for both thermal and catalytic hydrocracking reactions.

METHODS AND MATERIALS

The liquid paraffin feed (with boiling range of 260°C+) from the Ahvaz-Asmary crude was obtained from Tehran refinery. It was obtained from a stream that had been hydrotreated and the amounts of heteroatom compounds (sulfur, nitrogen and oxygen) and aromatics were below detectable limits. Table 1 shows the physical properties and the simulated distillation analysis of the feed. Commercial 96.5% pure hydrogen was used in the hydrocracking experiments. The impurity of the feed hydrogen was methane which is quite unreactive under the experimental conditions employed in this study.

The catalyst used in this study was a commercial Ni-Mo/ γ -alumina HDS catalyst. This type of catalyst is primarily intended for hydroprocessing of heavy petroleum fractions containing significant amounts of

Table 1. Physical properties of feed (kinematic viscosity at 40°C = 9.86 centistokes. Density at 15.6°C = 0.8255 g/cm³).

Simulated Distillation Results	
IBP	260.2°C
10 weight %	302.5°C
50 weight %	351.7°C
90 weight %	406.7°C
FBP	466.5°C

aromatic and heteroatom structures. The main role of such catalysts in hydroprocessing [16] is hydrogenation of aromatic structures and heteroatom removal and, therefore, is chosen as a candidate for catalytic hydroprocessing of residues from Iranian feedstocks. In this preliminary investigation, the above catalyst was used with a simpler and cleaner feed (in terms of the variety of structures that are present) containing, primarily, naphthenic and paraffinic structures. For processing of the feed used in this investigation, however, a more appropriate selection of catalyst would be Ni or Ni/Mo on Si/Al supports.

A schematic diagram of the experimental equipment is presented in Figure 1. The reactor was a continuous tubular (2 cm ID) flow reactor with a length of one meter. The reactor was filled with catalyst pellets for catalytic hydrocracking experiments and with quartz beads for thermal hydrocracking experiments. The liquid feed was injected by a diaphragm type metering pump. Compressed hydrogen was mixed with the liquid feed just before entering the top of the reactor. The volume ratio of hydrogen to liquid hydrocarbon feed at the reactor inlet was approximately 1000:1, to ensure an excess amount of hydrogen under reaction conditions. The reaction products were cooled by a simple water cooler which consisted of a double pipe heat exchanger. The gaseous products were separated from liquid products in a two stage (high and low pressure) separator for subsequent analyses. The reactor was heated by four electrical jackets. The reactor temperature and pressure were controlled through appropriate controllers and the feed rate was determined through continuous measurement of the mass of the feed container. The flow rate of gaseous products was measured by a gas flowmeter. The flow rate of the liquid products was determined through

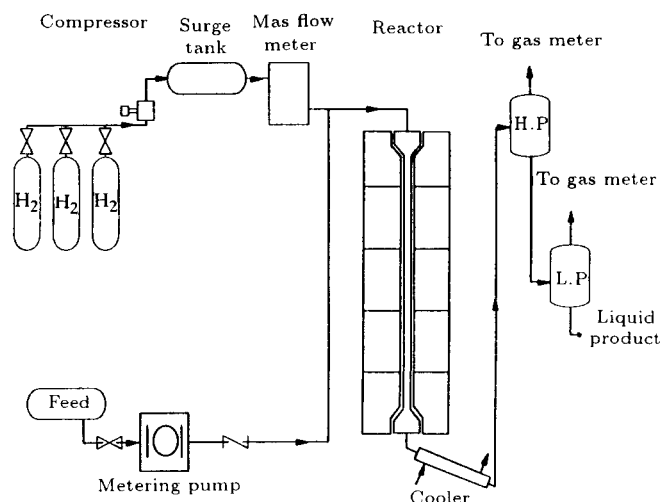


Figure 1. Schematic diagram of the experimental apparatus.

measuring the mass of the products accumulated in the product receiver.

The thermal and catalytic hydrocracking experiments were conducted under isothermal conditions in 440-470°C and 410-430°C ranges, respectively, with space velocities in the range of 0.5-1.5 VVH. The catalyst was pre-sulfided inside the reactor according to the following procedure. The reactor was pressurized to 120 bars by hydrogen and its temperature was raised to 180°C in about 4 hours. During this heat-up time, a flow of hydrogen passed through the reactor. A feed containing 2 weight percent dimethyl disulfide in hydrocracker gas oil was consequently fed into the reactor at a rate of 200 cm³/min. The reactor temperature was, then, increased to 260°C at a rate of 20°C/min and afterwards from 260°C to 310°C at a rate of 10°C/min. Once a stable operation was obtained at 310°C, pre-sulfiding was continued for 12 hours. The reactor pressure for both catalytic and thermal hydrocracking experiments was 120 bars.

RESULTS AND DISCUSSION

The liquid products were analyzed by simulated distillation and the gaseous products by gas chromatography. Under the relatively mild conditions employed in this study, feed conversions of about 5-40% were obtained. For the purpose of kinetic modeling, a lumping scheme was employed based on the boiling fractions defined as follows:

Gas, G	< IBP
Naphtha, N	IBP-141°C
Kerosene, K	141-260°C
Unreacted feed, F	260°C-FBP

The following definition was used for evaluation of the product yields:

$$X_i = \frac{\text{weight of lump } i}{\text{weight of feed}}$$

where X_i is the weight fraction of each lump. Experimental product yields for catalytic hydrocracking experiments at 410-430°C are presented in Figures 2 to 4, for different space velocities. Experimental product yields for thermal hydrocracking experiments at 440 and 470°C, for different space velocities, are presented in Figures 5 and 6, respectively. The lumps are considered as pseudo components and the reaction network can be constructed according to the conversion of one lump to others. In this study, different reaction networks are considered and the corresponding model parameters (stoichiometric coefficients and related Arrhenius parameters for the reaction rate constants) are obtained by an optimization procedure utilizing some of the experimental data while checking the accuracy of the model predictions with the remaining data. Among

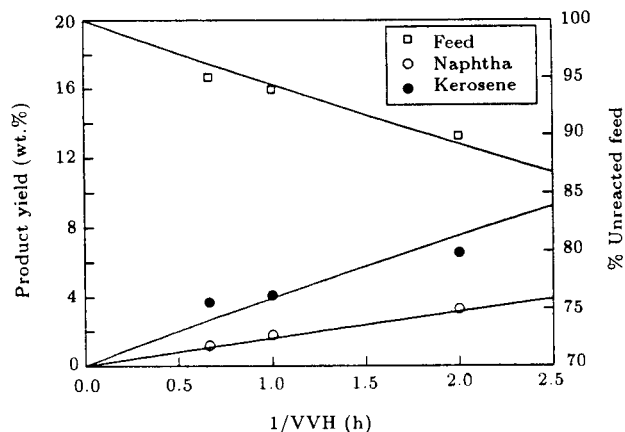


Figure 2. Experimental (symbols) and predicted (solid lines) product yields (wt. %) for catalytic hydrocracking at 410°C.

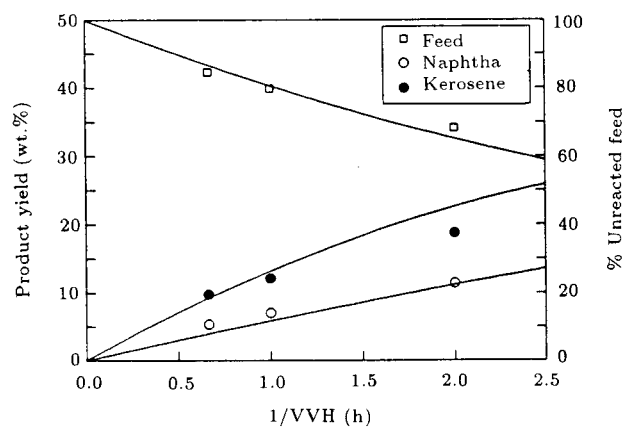


Figure 3. Experimental (symbols) and predicted (solid lines) product yields (wt. %) for catalytic hydrocracking at 430°C.

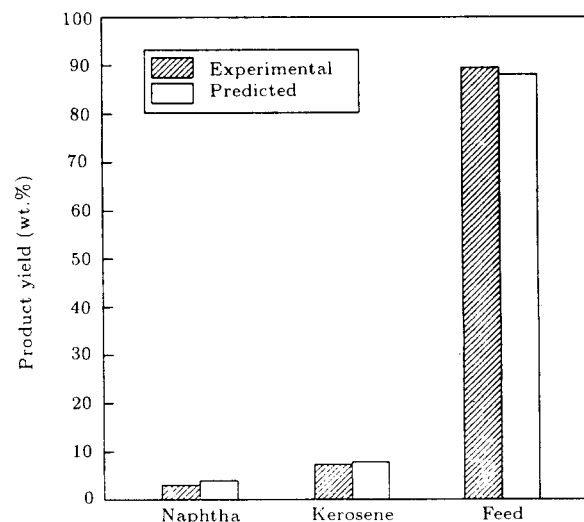


Figure 4. Predicted and experimental product yields (wt. %) for catalytic hydrocracking at 420°C and VVH=1.

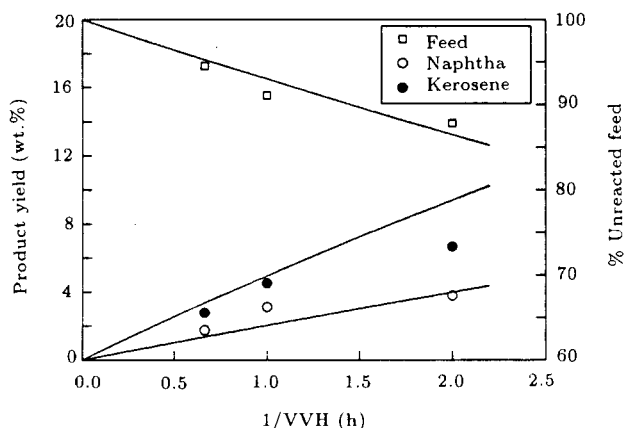


Figure 5. Experimental (symbols) and predicted (solid lines) product yields (wt. %) for thermal hydrocracking at 440°C.

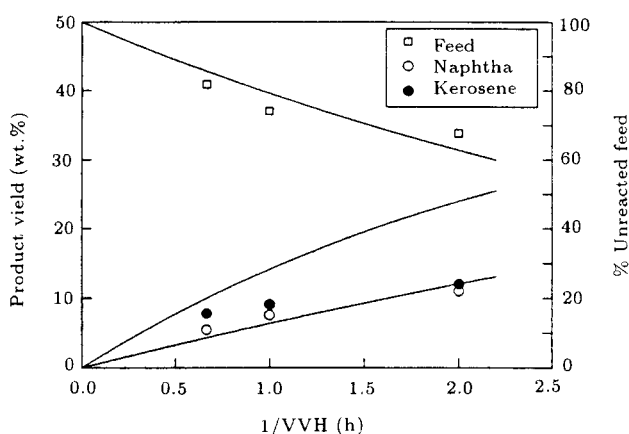
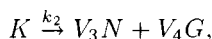
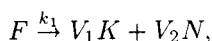


Figure 6. Experimental (symbols) and predicted (solid lines) product yields (wt. %) for thermal hydrocracking at 470°C.

the many kinetic models that were considered, the following was found to best fit the experimental results:



where V_i is the stoichiometric coefficient and k_j is the related rate constant that is obtained through the following procedure. The governing differential equations are:

$$-\frac{dX_F}{d\tau} = k_1 X_F, \quad (1)$$

$$\frac{dX_K}{d\tau} = V_1 k_1 X_F - k_2 X_K, \quad (2)$$

$$\frac{dX_N}{d\tau} = V_2 k_1 X_F + V_3 k_2 X_K, \quad (3)$$

$$\frac{dX_G}{d\tau} = V_4 k_2 X_K, \quad (4)$$

where τ is the residence time and the initial conditions are as follows:

$$X_{F0} = 100 \quad \text{and} \quad X_{K0} = X_{N0} = X_{G0} = 0.$$

Solutions of Equations 1 and 3 are utilized to estimate the model parameters that best fit the experimental data for the yield of naphtha fraction (N) and unreacted feed (F) using experimental data at 410 and 430°C for catalytic hydrocracking and 440 and 470°C for thermal hydrocracking experiments with three different space velocities. With the exception of thermal hydrocracking experiments at 470°C, the gas yields (Table 2) were quite low; less than 1 to 2 weight percent of the total products depending on the reaction severity. The gas product primarily consisted of unconsumed hydrogen and small amounts of light hydrocarbons produced from the cracking of the feed. Although gas samples were analyzed several times for hydrocarbon gases during the course of each experiment, the accuracy of the experimental gas yields were at best questionable and not used directly in parameter estimation. The model accuracy was tested by comparing the predicted yields of the kerosene fraction (using the optimized parameters) with experimental values. Predicted and experimental product yields that are presented in Figures 2 and 3 for catalytic experiments at 410 and 430°C, respectively, indicate that the accuracy of the model is quite satisfactory. A further test for the validity of the model is to compare the predicted product yields with experimental values for a catalytic hydrocracking experiment at 420°C (Figure 4) whose data are not used in the optimization procedure. Comparison of the predicted product yields with experimental values for thermal hydrocracking experiments at 440 and 470°C in Figures 5 and 6, respectively, indicates that the accuracy of the model for thermal hydrocracking is also reasonable under conditions of low feed conversion.

Examination of the model predictions versus experimental results indicates that the yields of various

Table 2. Experimental hydrocarbon gas yields in thermal and catalytic hydrocracking.

a) Catalytic Hydrocracking		
1/VVH (h)	Gas yields (wt. % of total products)	
	T = 410°C	T = 430°C
0.667	0.10	0.32
1.0	0.16	1.01
2.0	0.21	1.52
b) Thermal Hydrocracking		
1/VVH (h)	Gas yields (wt. % of total products)	
	T = 440°C	T = 470°C
0.667	0.98	5.12
1.0	1.31	9.39
2.0	1.75	9.30

fractions in the liquid products are accurately predicted for catalytic hydrocracking over the range of temperatures and residence times considered in this investigation. In the case of thermal hydrocracking, however, the error in predicted yields of the kerosene fraction becomes significant at high conversions in particular for the runs at 470°C. In the presence of the catalyst, the olefins that are produced from the cracking of the feed are rapidly hydrogenated and do not participate in secondary reactions. In the absence of such secondary reactions, only cracking reactions resulting in the formation of lighter components primarily occur and this process is adequately represented by the kinetic model. In the absence of the catalyst, however, the hydrogenation of olefins does not proceed to completion and secondary reactions involving the olefins become significant, especially under high conversion conditions where olefin concentration may become considerable. An important class of such secondary reactions under the thermal conditions employed in this study are radical addition reactions involving a variety of radicals and olefins that are produced as primary reaction products resulting in the formation of higher molecular weight compounds [17]. This process is not reflected in the kinetic model presented in this work and, thus, limits the model application to catalytic reactions (over the entire range of conversions) and thermal reactions at low feed conversions.

Another observation (Table 2) is that the model also significantly underpredicts the gas yields for thermal runs at 470°C. Catalytic experiments were conducted in 410-430°C range while thermal experiments were conducted at 440 and 470°C. The stoichiometric coefficients V_1 to V_4 , reported in Table 3, can accurately predict the product selectivities for catalytic runs and the thermal runs at 440°C. Under the high temperature

Table 3. Optimized parameters for the kinetic model.

1) Values of the Stoichiometric Coefficients		
$V_1 = 0.718$		
$V_2 = 0.282$		
$V_3 = 0.491$		
$V_4 = 0.508$		
2) Arrhenius Parameters		
$A =$ pre-exponential factor (h^{-1})		
$E =$ activation energy (kJ/mol)		
a) Catalytic Hydrocracking		
Rate Constant	A	E
k_1	5.676×10^{18}	261.4
k_2	2.806×10^{18}	262.0
b) Thermal Hydrocracking		
Rate Constant	A	E
k_1	2.113×10^{11}	170.1
k_2	2.821×10^{11}	170.7

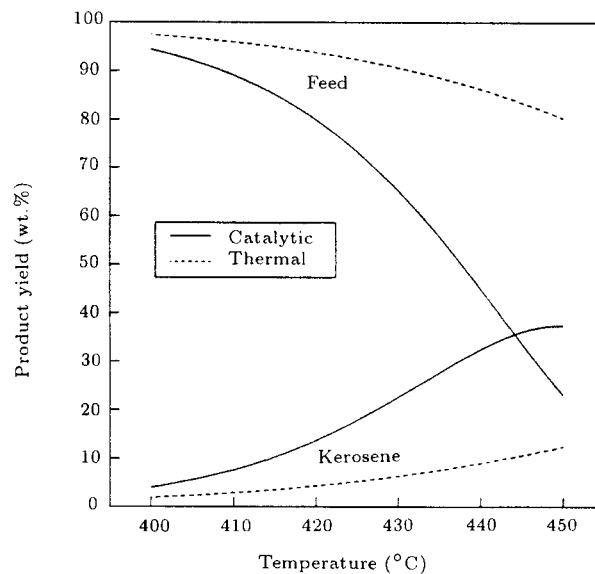


Figure 7. Model predictions for the yields (wt. %) of kerosene and unreacted feed as a function of temperature for $VVH = 0.5$.

conditions employed for thermal runs at 470°C, the products selectivity would shift towards lighter components and thus significant gas yields. Under such conditions, the optimized stoichiometric coefficients could be altered to account for the higher gas yields as well as lower kerosene yields.

The Arrhenius parameters for the rate constants were obtained using the rate constant estimates at the temperature ranges employed in this study. These are reported in Table 3. The results indicate that the apparent activation energy for catalytic reactions are higher than those for thermal reactions, demonstrating that in the presence of the catalyst, thermal cracking reactions (via free-radical mechanism) and catalytic cracking reactions (via carbocation ion mechanism) occur in parallel, thus, resulting in higher reaction rates and apparent activation energies in the presence of the catalyst.

The parameters reported in Table 3 were used to extrapolate model predictions over 400-450°C range for both catalytic and thermal hydrocracking reactions. The model predictions for the unreacted feed and the kerosene yields are presented in Figure 7 for VVH of 0.5 h^{-1} , which indicate that the presence of catalyst enhances the cracking reactions even at low temperatures. The results for other space velocities illustrate a similar trend.

CONCLUSIONS

Experimental data from thermal and catalytic hydrocracking of liquid paraffins were used to develop a simple kinetic model based on a lumping scheme involving boiling fractions. The model was capable

of predicting product yields with good accuracy in the range of 410-440°C for both thermal and catalytic reactions. At higher temperatures, the stoichiometric coefficients should be modified to account for product selectivities towards lighter components. In the case of thermal reactions, the accuracy of the model decreases with increasing feed conversion as secondary reactions involving olefins become significant. The presence of a catalyst has been found to enhance the cracking reactions even at low temperatures.

ACKNOWLEDGMENT

The authors wish to gratefully acknowledge the Catalyst and Crude Evaluation Departments of NIOC-RIPi for their valuable assistance with experiments and sample analyses.

REFERENCES

1. Khorasheh, F., Gray, M.R. and Dalla Lana, I.G. "Structural characterization of Alberta heavy gas oils", *Fuel*, **66**(4), pp 505-511 (1987).
2. Khorasheh, F., Gray, M.R. and Dalla Lana, I.G. "Structural changes in catalytic hydroprocessing of syncrude coker gas oil", *Can. J. Chem. Eng.*, **65**(1), pp 166-170 (1987).
3. Khorasheh, F., Gray, M.R., Dalla Lana, I.G. and Yeniova, H. "Correlation of reactivity with chemical structure: Thermal hydrogenation of gas oils", *Can. J. Chem. Eng.*, **67**(4), pp 628-634 (1989).
4. Khorasheh, F., Khaledi, R. and Gray, M.R. "Computer generation of representative molecules for heavy hydrocarbon mixtures", *Fuel*, **77**(4), pp 247-253 (1998).
5. Kuo, J.W. and Wei, J. "A lumping analysis in monomolecular reaction systems", *Ind. Eng. Chem. Fundam.*, **8**, pp 124-133 (1969).
6. Astarita, G. and Ocone, R. "Lumping non-linear kinetics", *AIChE J.*, **34**(8), pp 1299-1309 (1988).
7. Astarita, G. "Lumping non-linear kinetics: Apparent overall order of reaction", *AIChE J.*, **35**(4), pp 529-532 (1989).
8. Weekman, V.W. Jr. "Lumps, models and kinetics in practice", *Chem. Eng. Prog. Monogr. Ser.*, **75**(11), pp 3-29 (1979).
9. Stangeland, B.E. "Kinetic model for prediction of hydrocracker yields", *Ind. Eng. Chem. Process Des. Dev.*, **13**(1), pp 71-76 (1974).
10. Weekman, V.W. Jr. and Nace, D.M. "Kinetics of catalytic cracking and selectivity in fixed, moving and fluid bed reactors", *AIChE J.*, **16**(3), pp 397-404 (1970).
11. Chou, M.Y. and Ho, T.C. "Continuum theory of lumping non-linear reactions", *AIChE J.*, **34**(9), pp 1519-1527 (1988).
12. Chou, M.Y. and Ho, T.C. "Lumping coupled nonlinear reactions in continuous mixtures", *AIChE J.*, **35**(4), pp 533-538 (1989).
13. Astarita, G., Cicarelli, P. and Gallifuoco, A. "Continuous kinetic lumping of catalytic cracking processes", *AIChE J.*, **38**(7), pp 1038-1044 (1992).
14. Laxminarasimhan, C.S., Verma, R.P. and Ramachandran, P.A. "Continuous lumping model for simulation of hydrocracking", *AIChE J.*, **42**(9), pp 2645-2653 (1996).
15. Rajamani, K. and Sakena, A.K. "Use of an axial dispersion model for kinetic description of hydrocracking", *Chem. Eng. Sci.*, **44**(3), pp 703-712 (1989).
16. Gray, M.R., Khorasheh, F., Wanke, S.E., Achia, U., Krzywicki, A., Sanford, E.C., Sy, O.K.Y. and Ternan, M. "Role of catalyst in hydrocracking of residue from Alberta bitumens", *Energy & Fuels*, **6**(4), pp 478-485 (1992).
17. Khorasheh, F. and Gray, M.R. "High-pressure thermal cracking of n-hexadecane", *Ind. Eng. Chem. Res.*, **32**(9), pp 1853-1863 (1993).