Modeling of Non-isothermal Fluid Catalytic Cracking Riser Reactor

Raj kumar Gupta, *Member, IAENG* , Vineet Kumar, and V.K. Srivastava

***Abstract*—A non-isothermal model for the fluid catalytic cracking riser reactor is presented. The heat of cracking is estimated by taking the difference in the heats of combustion of products and reactants. Fifty pseudo-components (lumps) are considered in the cracking scheme used in the model. This kinetic scheme is discussed in detail elsewhere. Heat capacities of product and reactant pseudo-components as a function of local temperature are estimated using Lee-Kesler's correlations. Heat of vaporization of the gas oil (feed) is estimated using Reid's correlation. The effect of local temperature on the kinetic constants is also incorporated for the prediction of more realistic temperature profile along the riser height. Thousands of cracking reactions are considered to be occurring in parallel in the riser reactor, for handling these reactions, the riser is divided into a number of small volume elements placed over each other in series. The rates of cracking reactions in a volume element are evaluated based on the concentrations of the pseudo-components at the inlet of that volume element. This model also incorporates two phase flow (cluster phase and gas phase) and catalyst deactivation.**

The proposed model is capable of predicting the products' yields, velocities of cluster phase and gas phase, riser temperature, and heat of cracking all along the riser height.

***Index Terms*—Fluid catalytic cracking (FCC), heat of cracking, modeling and simulation, riser kinetics.**

I. INTRODUCTION

Fluid catalytic cracking (FCC) unit converts high molecular weight petroleum fractions (heavy gas oil) to low molecular weight fractions, such as gasoline and hence plays a major role in the profitability of a refinery. In spite of large variations in the design of FCC units, all of them consists of two basic units, a reactor in which the hot catalyst is brought in contact with the feed (gas oil), and a regenerator in which the coke deposited on the catalyst during the cracking reactions is burned off for regenerating the catalyst. Modeling of the riser reactor is of prime importance as the cracking reactions take place in the riser. Mathematical modeling of riser behavior is quite complex due to the presence of thousands of unknown components in the feed, unknown cracking kinetics, complex hydrodynamics, and interaction between the riser reactor and regenerator. There are many important models of the riser reactor developed by various authors in recent past [1]-[9]. A detailed literature review of riser modeling is presented in [10].

In the above mentioned models one or the other important aspect of the riser behavior is ignored. Some of these models assumed constant temperature throughout the riser reactor for the evaluation of kinetic constants [3] and [5], while some other considered the adiabatic riser with constant average heat of cracking reactions throughout the riser [2] and [9]. The heat of cracking varies along the riser height having larger values in the bottom part of the riser reactor owing to cracking of the heavier fresh feed in the bottom half [11], taking constant value for the heat of cracking affects the temperature profile and yield profile all along the riser height. Overall, the reactions taking place in the riser are endothermic and the temperature of the reaction mixture decreases progressively. Assuming constant temperature throughout the riser height ignores the temperature dependence of the rate constants which in turn affects the predictions of the products' yields profiles. Also, the regenerator operation is affected by the temperature drop across the riser.

Several authors, [4], [6] and [8] neglected the volumetric expansion due to cracking which leads to the prediction of incorrect residence time in the riser and hence the products' yield profiles are affected. In [8] authors have used a three lump kinetic scheme in their model which is not capable of predicting the coke yield separately and hence can not be integrated with a regenerator model. In [1] and [7] authors have predicted the axial catalyst holdup by fitting the plant data using correlation relating slip factor to the riser height. Such data may vary considerably from plant to plant and may lead to incorrect prediction of the rates of various cracking reactions occurring in the riser. Very recently, a non isothermal model for the FCC riser is developed [11]. The authors incorporated this model into CATCRACK [5] which assumes plug flow in the riser and considers a ten lump cracking kinetics.

In the present work a non isothermal model of the FCC riser is developed which incorporates two phase flow (variation in the axial velocity of gas phase and cluster phase due to molar expansion), catalyst deactivation, a new pseudo-components based cracking kinetics model, effect of temperature on the kinetic constants, and variable heat of cracking reactions all along the riser height. Coke (one of the products of cracking reactions) is also considered for the calculation of the heat of reaction.

Manuscript received March 21, 2007.

Raj kumar Gupta is with Department of Chemical Engineering , Thapar University, Patiala-147 004, India (Phone: +91-175-2393452, Fax: +91-175-2364498, Email: rkgupta@tiet.ac.in).

Vineet Kumar is with Department of Chemical Engineering, Thapar University, Patiala-147 004, India (Email: vikumar@tiet.ac.in).

V.K. Srivastava was with Department of Chemical Engineering, Indian Institute of Technology, Delhi-110 016, India (Email: vks@chemical.iitd.ernet.in).

II. METHODOLOGY

The following commonly used assumptions are made for the development of this model:

- At the riser inlet, hydrocarbon feed comes in contact with the hot catalyst coming from the regenerator and instantly vaporizes. The vapor thus formed move upwards in thermal equilibrium with the catalyst [1], [6], [11], and [12].
- There is no loss of heat from the riser and the temperature of the reaction mixture (hydrocarbon vapors and catalyst) falls only because of the endothermic cracking reactions [6], [8], [13] and [14].
- Gas phase velocity variation on account of gas phase temperature and molar expansion is considered. Ideal gas law is assumed to hold [14].
- Catalyst holdup is estimated by local force balance assuming two phase flow (cluster phase and gas) in the riser [14].
- Heat and mass transfer resistances are neglected [1], [6], [7] and [13].

The detailed kinetic scheme used in this work is presented in our earlier works [15] and [16], and is briefly discussed below. This scheme is based on the pseudo-components (hypothetical pure components) cracking. It is assumed that one mole of a pseudo-component on cracking gives one mole each of two other pseudo-components and some amount of coke may also form (depending on the stoichiometry of the reaction). The cracking reaction for an i^{th} pseudo-component may be written as:

$$PC_i \xrightarrow{k_{i,m,n}} PC_m + PC_n + \alpha_{i,m,n} \tag{1}$$

where i, m, and n are pseudocomponents' numbers, $\alpha_{i,m,n}$ is the amount of coke formed (kg) when one kmole of i^{th} pseudocomponent cracks to produce one kmole each of m^{th} and n^{th} pseudocomponents. The value of $\alpha_{i,m,n}$ can be calculated by taking difference in molar masses of reactant and product pseudo-components as follows:

$$\alpha_{i,m,n} = MW_i - (MW_m + MW_n) \tag{2}$$

A reaction is considered unfeasible when $\alpha_{i,m,n}$ becomes negative (i.e, the sum of molecular weights of product pseudo-components can not be more than the molecular weight of reactant pseudo-component). A schematic diagram of reaction mechanism is given in Fig. 1. A new, semi empirical, approach is also proposed to estimate the cracking reactions' rate constants for this cracking mechanism. This methodology makes the kinetic model more versatile. Six tunable parameters have been introduced to adjust more than ten thousand reaction rate constants of the above mentioned reaction scheme. The final form of the function used to estimate the kinetic constants of equation (1) is

$$k_{i,m,n} = \left\{\left[k_0 MW_i^{\mu}\right] e^{-\tau_1 (MW_m - MW_n)^2}\right\} e^{-\frac{E_0 MW_i^{\nu}}{RT}} \left[\frac{e^{-\alpha_{i,m,n}/\tau_2} - e^{-MW_i}}{1 - e^{-MW_i}}\right] \tag{3}$$

In equation (3), parameters to be estimated by using experimental data are k_0, μ, E_0, ν, τ_1, and τ_2. The term within the curly bracket is frequency factor in the Arrhenius type rate constant equation. This parameter depends on the molecular weights of reactant and product pseudo-components. Parameters μ and τ_1 correlate frequency factor in terms of molecular weight of the cracking pseudo-component. E_0 and ν are used to determine activation energy for the cracking of i^{th} pseudo-component, and τ_2 is an indicator of coking tendency and its value will depend on the nature of the feed.

Fifty pseudo-components are considered in this kinetic scheme. The pseudo-components are generated using the integral method proposed in [17] and [18]. Two phase flow, for considering the effect of molar expansion, incorporated in the present model is based on the hydrodynamic model as in [14], and catalyst deactivation is based on the model as in [19].

In fluid catalytic cracking process thousands of cracking reactions of unknown hydrocarbons occur in parallel, therefore the calculation of heat of reactions is quite difficult. A reasonable estimate of the heat of reaction may be made by taking the difference in the heat of combustion of products pseudo-components and reactant pseudo-component for all the feasible reactions. Heat of combustion of a pseudo-component i, $Hcomb_i$ (BTU/lb), is estimated by the following equations as a function of its API gravity:

$$Hcomb_i = 57.6\,API_i + 17700 \qquad \text{for } 25 < API_i \tag{4}$$

$$Hcomb_i = -0.1727\,API_i^2 + 24.875\,API_i + 839.7\ln(API_i) + 15923.175 \qquad \text{for } 25 \le API_i \le 50 \tag{5}$$

$$Hcomb_i = 24\,API_i + 18820 \qquad \text{for } API_i > 50 \tag{6}$$

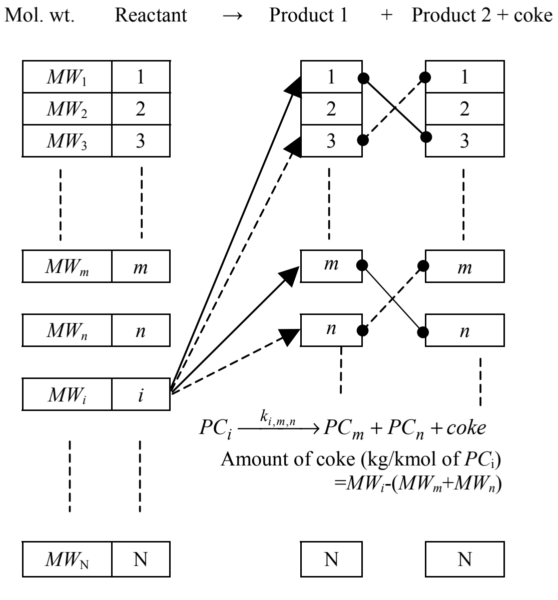

Fig.1: Schematic diagram of reaction mechanism

The above equations are obtained by curve fitting of graphical data reported in [20]. Curve fitting was done in such a way that there is no discontinuity in the heats of combustion values predicted by these three equations. Thus for the cracking of i^{th} pseudo-component, giving m^{th} and n^{th} pseudo-components heat of reaction (kJ/kmole) becomes:

$$\begin{aligned}(\Delta H_r)_{i,m,n} &= \alpha_{i,m,n} \cdot H_{coke} + (MW_m Hcomb_m \\ &+ MW_n Hcomb_n - MW_i Hcomb_i) \times 2.326\end{aligned} \tag{7}$$

In the above equation heat of combustion is converted from BTU/lb to kJ/kg, and H_{coke} is the heat of combustion of coke (kJ/kg). The heat of reaction for each feasible reaction can be calculated using equation (7) and summed up to find the overall heat of reactions occurring in each volume element.

There are approximately ten thousand feasible reactions as per the reaction scheme. For handling such a large number of reactions, the riser reactor is conceptualized as having a number of volume elements of circular cross-section placed one over the other. The kinetic constants in a volume element are evaluated at the local temperature at the inlet of that volume element. The various properties of both the phases (gas phase- containing product and reactant hydrocarbons and steam; cluster phase- containing catalyst particles moving in clusters and coke deposited on these clusters) are assumed to be invariant in a volume element. These properties are then estimated again at the local conditions at the exit of the each volume element.

The inlet conditions at the bottom of the riser reactor are known. Instant vaporization of the feed is assumed at the inlet of the riser reactor. The specific heats of liquid feed and the hydrocarbon vapor are calculated using the Lee-Kesler's correlations [21]. The heat of vaporization of the gas oil (feed) is estimated using the correlation developed in [22]. The hot regenerated catalyst provides the sensible heat and heat of vaporization of the feed oil. It is also assumed that the gas comes in thermal equilibrium with the catalyst at the inlet of the riser. The temperature of the inlet stream (gas phase and catalyst) is calculated from the enthalpy balance. This temperature serves as inlet temperature at the first volume element. The following calculations were done in a j^{th} volume element of the riser reactor for the solution of the model:

- The properties from the outlet of the $j\text{-}1^{th}$ element serve as inlet conditions for the j^{th} element. Based on the cracking kinetics the pseudo-components composition at the outlet of the volume element j is calculated.
- Using the material balance equations the change in moles of each component over the j^{th} volume element is calculated.
- Using equation (7) heat of reaction can be calculated for all the feasible reactions. The temperature drop over the j^{th} volume element is calculated as:

$$\Delta T_j = \frac{\left(\sum_i \sum_m \sum_n r_{i,m,n} \cdot \Delta Hr_{i,m,n}\right)_{for\ all\ feasible\ reactions}}{\left(McatCp_{cat} + Mcoke_{j-1} Cp_{coke} + MstCp_{st} + \sum_{i=1}^{N} P_{i,j-1} MW_i Cp_i\right)} \tag{8}$$

- The temperature at the outlet of the j^{th} volume element is calculated: $T_j = T_{j-1} - \Delta T_j$.
- The values of gas phase velocity, solid phase velocity, and superficial gas velocity are calculated at the exit of the j^{th} volume element using the riser hydrodynamics.
- The values of Cp_i s are evaluated at the exit temperature of the j^{th} volume element.
- The procedure is repeated till we reach at the exit of the riser reactor.

III. Results And Discussion

The physical dimension of the riser reactor and the process conditions (plant data) used for the simulation are given in Table I. The various other data used for the riser simulation are listed in Table II. Boiling point characteristics (simulated distillation, SD) and other data of feed reported in [23] is used for generating the pseudo-components. The values of the parameters of equations (3) used in this work are: $\tau_1 = 0.01$; $k_0 = 0.009$; $\mu = 0.0$; $E_0 = 1540$; $\nu = 0.43$; $\tau_2 = 17.0$.

The yields of various products (gas, gasoline, and coke) are plotted all along the riser height in Fig. 2. Gasoline yield reaches near its maximum value in the first 10 m of the riser height. Beyond this height the net change in the gasoline yield is very less. The change in gas yield with respect to riser height is less sharp and is almost constant beyond first few meters of riser height. Overall conversion (sum of the three yields) also keeps on increasing with the riser height.

Table I: Plant Data used for the simulation of riser reactor [6]

Riser height	33 m
Riser diameter	0.8 m
Riser pressure	2.9 atm
Catalyst Temperature	960 K
Feed rate	20 kg/s
Feed temperature	496 K
C/O ratio	7.2

Table II: Parameters used for the simulation of riser reactor

Parameter	Value	Source
Heat of combustion of coke	-32950 kJ/kg	[24]
Molecular weight of coke	12 kg/kmol	[4]
Initial volume fraction of clusters	0.5	[14]
Specific heat of catalyst	1.15 kJ/kg K	[6]
Specific heat of steam	2.15 kJ/kg K	[25]
Mass flow rate of steam	1.33 kg/s	[25]
Feed temperature	494 K	[6]
Latent heat of feed vaporization	96 kJ/kg	[14]
Catalyst Particle density	1200 kg/m^3	[14]
Catalyst particle diameter	75 μm	[14]
Specific gravity of feed	0.9292 g/cm^3	[23]
Cluster diameter	6 mm	[12]

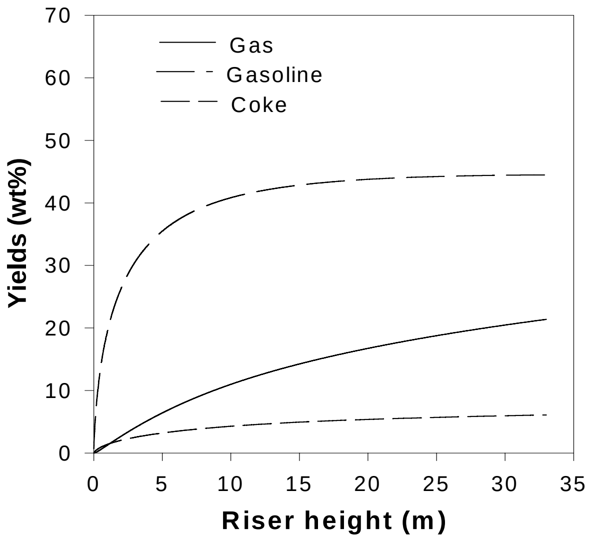

Fig. 2: Product yields profiles along the riser height

The riser temperature profiles for various feed oil temperatures are shown in Fig. 3. For 496 K feed temperature, the riser temperature drops from 873 K to 783 K in the first 10 m height of the riser. The temperature at the outlet of the riser is 749 K. The temperature decline is sharp in the first 10 m of the riser height because most of the cracking reactions take place in this region of the riser. Temperature of reaction mixture and catalyst activity decreases along the riser height, and thus causes a decline in the reaction rate (dependent on activity and temperature) hence the temperature gradient falls appreciably with the increasing riser height. The other curves (for 596 K and 696 K feed temperature) also follow the same trend.

Figure 4 shows an initial decline in the gas velocity which can be attributed to the combined effect of initial sharp rate of decrease in the mass of the hydrocarbons (hydrocarbons converting to coke) and the sharp rate of increase in the available area for gas flow. After this initial adjustment up to first 1 m of riser height, the predicted slip factor is 3 which gradually decreases along the riser height and finally reaches at 1.8.

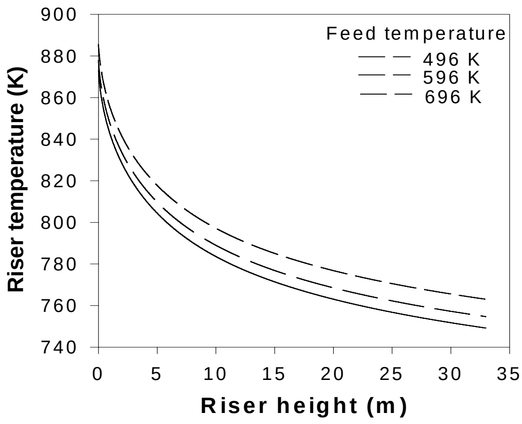

Fig. 3: Temperature profiles along the riser height for different feed oil temperatures

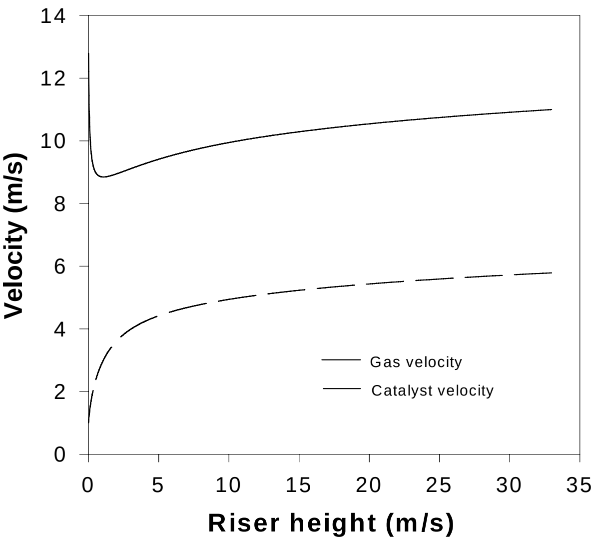

Fig. 4: Gas phase and solid phase velocity as a function of riser height

Heat of cracking varies from the bottom of the riser to the top of the riser as shown in Fig. 5. The variation in the heat of cracking from about 1100 kJ/kg at the bottom, to about 860 kJ/kg at the top of the riser is predicted. In reference [23] authors have reported 800-1070 kJ/kg values for the heat of cracking. The values of heat of cracking obtained in this work (860-1100 kJ/kg) matches very closely with the values obtained in [23]. As the heat of cracking largely depends on the type of feed, this observation is very relevant as we have used the SD data of the feed used by the same authors.

IV. CONCLUSION

A non isothermal model for the FCC cracking riser reactor is developed. This model is based on a new pseudo-components' based cracking scheme. The model incorporates the effect of local temperature on the kinetic constants and also takes into account the effect of volumetric expansion and temperature drop on the gas phase velocity. The heats of combustion of

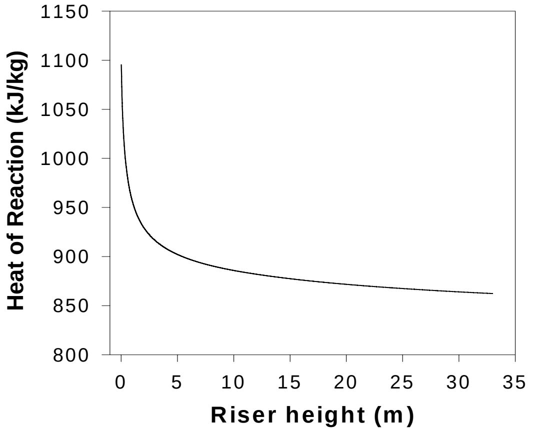

Fig.5: Variation of heat of reaction along the riser height

pseudo-components and heat of combustion of coke is used to estimate the heat of cracking. The heat of cracking predicted by the model varies from 1100 kJ/kg at the bottom of the riser to 860 kJ/kg at the top of the riser. This variation shows that assuming constant heat of reaction along the riser height will lead to erroneous products' yield profiles. This error may further magnify in case of cracking of heavier feeds.

NOMENCLATURE

Cp_{cat}	Specific heat of catalyst (kJ/kg)
Cp_{coke}	Specific heat of coke (kJ/kg·K)
Cp_i	Specific heat of i^{th} pseudo-component (kJ/kg·K)
Cp_{st}	Specific heat of steam (kJ/kg·K)
$(\Delta H_r)_{i,m,n}$	Heat of reaction for the cracking of i^{th} pseudo-component to produce m^{th} and n^{th} pseudo-components (kJ/kmol)
ΔE_i	Activation energy term in $k_{\max,i}$ expression (kJ/kmol)
$Hcomb_i$	Heat of combustion of i^{th} pseudocomponent (Btu/lb)
H_{coke}	Heat of combustion of coke (kJ/kg)
$k_{i,m,n}$	Rate constant for the cracking of i^{th} pseudo-component to produce m^{th} and n^{th} pseudo-components [m^3/(kgCat.s)]
$k_{max,i}$	Maximum value of rate constant for the cracking of i^{th} pseudo-component [m^3/(kgCat.s)]
$k_{0,i}$	Frequency factor in the $k_{max,i}$ expression [m^3/(kgCat.s)]
$Mcat$	Mass flow rate of catalyst (kg/s)
$Mcoke_j$	Mass flow rate of coke at the outlet of j^{th} volume element (kg/s)
Mst	Mass flow rate of steam (kg/s)
MW_i	Molecular weight of i^{th} pseudo-component (kg/kmol)
MW_m	Molecular weight of m^{th} pseudo-component (kg/kmol)
MW_n	Molecular weight of n^{th} pseudo-component (kg/kmol)
N	Number of pseudo-components considered in the reaction scheme
$P_{i,j}$	Molar flow rate of i^{th} pseudo-component, PC_i, through j^{th} volume element (kmol/s)
PC_i	Pseudo-component i
PC_m	Pseudo-component m
PC_n	Pseudo-component n
$r_{i,m,n}$	Rate of reaction of i^{th} pseudo-component giving m^{th}, and n^{th} pseudo-components (kmol/s)
R	Gas constant [kJ/(kmol K)]
T	Temperature (K)
T_j	Temperature of reaction mixture leaving j^{th} volume element (K)

SUBSCRIPTS

i, m, n	i^{th}, m^{th}, and n^{th} component
j	j^{th} volume element in the riser starting from the bottom

GREEK LETTERS

$\alpha_{i,m,n}$	Mass of coke formed when one kmole of pseudocomponent PC_i cracks to give one kmole each of PC_m and PC_n, (kg coke/kmol PC_i)

REFERENCES

[1] M. P. Martin, P. T. Derouin, M. Forissier, G. Wild, and J. R. Bernard, "Catalytic cracking in riser reactors. Core-annulus and elbow effects," *Chemical Engineering Science*, vol. 47, 1992, pp. 2319-2324.

[2] S. S. E. H. Elnashiae, and S. S. Elshishini, "Digital simulation of industrial fluid catalytic cracking units-IV: Dynamic behaviour," *Chemical Engineering Science*, vol. 48, 1993, pp. 567-583.

[3] R. C. McFarlane, R. C. Reineman, J. F. Bartee, and C. Georgakis, "Dynamic simulator for a model IV fluid catalytic cracking unit," *Computers and Chemical Engineering*, vol. 17, 1993, pp. 275-300.

[4] A. Arbel, Z. Huang, I. H. Rinard, R. Shinnar, and A. V. Sapre, "Dynamics and control of fluidized catalytic crackers. Modeling of the current generation FCC's," *Industrial and Engineering Chemistry Research*, vol. 34, 1995, pp. 1228-1243.

[5] S. Kumar, A. Chadha, R. Gupta, and R. Sharma, "CATCRACK: A process simulator for an integrated FCC-regenerator system," *Industrial and Engineering Chemistry Research*, vol. 34, 1995, pp. 3737-3748.

[6] H. Ali, S. Rohani, and J. P. Corriou, Modeling and control of a riser-type fluid catalytic cracking (FCC) unit, *Transactions of the Institution of Chemical Engineers*, vol. 75, 1997, pp. 401-412.

[7] C. Derouin, D. Nevicato, M. Forissier, G. Wild, and J. R. Bernard, "Application of a single-event kinetic model in the simulation of an industrial riser reactor for the catalytic cracking of vacuum gas oil," *Industrial and Engineering Chemistry Research*, vol. 36, 1997, pp. 4504-4515.

[8] K. N. Theologos, A. I. Lygeros, and N. C. Markatos, "Feedstock atomization effects on FCC riser reactors selectivity," *Chemical Engineering Science*, vol. 54, 1999, pp. 5617-5625.

[9] J. M. Arandes, M. J. Azkoiti, J. Bilabo, and H. I. de Lasa, "Modeling fcc units under steady and unsteady state conditions," *Canadian Journal of Chemical Engineering*, vol. 78, 2000, pp. 111-123.

[10] R. Gupta, V. Kumar, and V. K. Srivastava, "Modeling and simulation of fluid catalytic cracking unit," *Reviews in Chemical Engineering*, vol. 21(2), 2005, pp. 95-131.

[11] V. K. Pareek, A. A. Adesina, A. Srivastava, and R. Sharma, "Modeling of a non-isothermal FCC riser," *Chemical Engineering Journal*, vol. 92, 2003, pp. 101-109.

[12] M. Flinger, P. H. Schipper, A. V. Sapre, and F. J. Krambeck, "Two phase cluster model in riser reactors: Impact of radial density distribution on yields," *Chemical Engineering Science*, vol. 49, 1994, pp. 5813-5818.

[13] J. Corella, and E. Frances, "Analysis of the riser reactor of a fluid catalytic cracking unit. Model based on kinetics of cracking and deactivation from laboratory tests," In fluid catalytic cracking-II: Concepts in catalyst design (edited by M.L. Occelli), *ACS Symposium Series*, Americal Chemical Society, Washington, Vol. 452, 1991, pp. 165-182.

[14] A. Gupta, and D. Subba Rao, "Model for the performance of a fluid catalytic cracking (FCC) riser reactor: Effect of feed atomization," *Chemical Engineering Science*, vol. 56, 2001, pp. 4489-4503.

[15] R. K. Gupta. Modeling and simulation of fluid catalytic cracking unit. Ph.D. Thesis, Thapar University, Patiala.

[16] R. K. Gupta, V. Kumar, and V. K. Srivastava, "A new generic approach for the modeling of fluid catalytic cracking (FCC) riser reactor," *Chemical Engineering Science*, vol. 62, 2007, pp. 4510-4528. doi:10.1016/j.ces.2007.05.009

[17] J. Miquel, and F. Castells, "Easy characterization of petroleum fractions," *Hydrocarbon Processing*, vol. 72, 1993, pp. 101-105.

[18] J. Miquel, and F. Castells, "Easy characterization of petroleum fractions," *Hydrocarbon Processing*, vol. *73*(1), 1994, pp. 99-103.

[19] I. Pitault, M. Forissier, and J. R. Bernard, "Kinetic model on a molecular description for catalytic cracking of vacuum gas oil," *Canadian Journal of Chemical Engineering*, vol. 73, 1995, pp. 498-503.

[20] J. B. Maxwell, *Data book on hydrocarbons*. New York: Robert E. Krieger Publishing Co., Inc., 1968.

[21] M. G. Kesler, and B. I. Lee, "Improve prediction of enthalpy of fractions," *Hydrocarbon Processing*, vol. 55(3), 1976, pp. 153-158.

[22] R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The properties of gases and liquids*. New York: McGraw-Hill, 1977.

[23] A. Pekediz, D. Kraemer, A. Blasetti, & H. de Lasa, "Heats of catalytic cracking. Determination in a riser simulator reactor," *Industrial and Engineering Chemistry Research*, vol. 36, 1997, pp. 4516-4522.

[24] G. T. Austin, *Shreve's chemical process industries*. Singapore: McGraw-Hill, 1984.

[25] A. Blasetti, & H. de Lasa, "FCC riser unit operated in the heat-transfer mode: Kinetic modeling," *Industrial and Engineering Chemistry Research*, vol. 36, 1997, pp. 3223-3229.