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STUDY OF RISER REACTOR DESIGN USING SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS (ODE)

*R. Mahfud**

Health, Safety and Environmental Department, International College of Engineering and Management. Muscat, Oman
**Corresponding author*

ABSTRACT Mathematical modelling of chemical reactors are commonly used in the petroleum refinery industry and petrochemical industries to model the performance of any production unit by formulating the governing microscopic model equations. The purpose of this work is to answer the question of whether simultaneous ODEs are capable to use for designing the fluidized bed reactors. To answer this question, this work adopts microscopic approach for the design of riser reactor of fluid catalytic cracking unit (FCC) that are used for high gasoline production. The model equations were represented by a system of simultaneous ordinary differential equations and were used to teach the application of theoretical concepts learned in a differential equations course. Several assumptions were made for developing the equations that derived by using shell mass balance. The ordinary differential equations are simultaneously solved using MATLAB code based on ode45 solver. The predicted results are the reactant conversion and the products yield from the riser reactor of the FCC. The results showed good agreement with actual plant data.

Notation

$\emptyset$	Catalyst activity
ε_g	Hydrocarbon gases void fraction
ρ_g	Density of gas phase
A	Notation for vacuum gas oil
B	Notation for gasoline
C	Notation for coke
D	Notation for gas
A_C	Crossectional area of the riser reactor
ΔV	Volume of the reactor shell
Δz	Thickness of the reactor shell
r_j	The rate of consumption of reactant *j* per unit catalyst volume (*j* = A, B, C, D)
k_{ij}	Reaction rate constants between species i and j, where $i \neq j$ (K_{AB}, K_{AC}, K_{AD}, K_{BC} and K_{BD})
F_j	Hydrocarbon gases mass flow rate of j specie in the riser (*j* = A, B, C or D)
y_i	Weight percent of hydrocarbons in the riser (*i* = A,B,C, or D)

1. Introduction

The mathematical modelling of chemical reactions contributes to the design of more efficient chemical reactors. Reactor designs for elementary chemical reactions were successfully implemented by carrying out material balance and reaction kinetic expressions. Although the chemical reactors represented the most dangerous operational units in the chemical industry, the performance of these reactors can be managed during the production phase by using mathematical models (Gupta and Subba, 2003a, 2001b; Lee *et al*., 1989; Reza, 2000). The fluid catalytic cracking unit, FCC, helps to increase the gasoline production of the refining process by increasing the conversion of the heavy petroleum fractions into lower molecular-weight products. Many improvements have been made in FCC operation; these include feed preparation, catalyst development, equipment design, and operating strategies (Ali *et al*., 1997; Vogt and Weckhuysen, 2015). The chemical reaction initiated and completed in a short-contact-time inside a vertical reactor that is called a riser (Mahfud, 2016; Reza, 2000). Inside this riser, the catalyst is pneumatically conveyed from the bottom to the top by steam and hydrocarbon vapours, this leads to efficient mixing of catalyst and hydrocarbons and as a result of that the catalytic cracking reactions will be enhanced. However, the hot catalyst vaporizes the feed and catalyses the cracking reactions to produce components including liquefied petroleum gases, gasoline, coke, and light gas oil (Ali *et al*., 1997; Gupta et al, 2010). Since the cracking reaction is endothermic, burning coke can generate the required energy. The regenerator in the FCC unit used to burn the coke deposited on the catalyst to reactivate the catalyst and to supply the heat required for cracking reaction in the riser (Gupta *et al*., 2010). The accurate prediction of the amount of coke deposited on the catalyst helps to estimate the endothermic heat needed in the riser.

For modelling of cracking kinetics, 3-lump model proposed and lumped reactant and all products into three major groups; feed, coke plus C1-C4 hydrocarbons, and gasoline (Gupta and Subba, 2003). A more complicated and detailed 10- lump model proposed to lump the reaction feed into paraffins, napthenes, and aromatic groups, and two product groups of C1-C4 plus coke and gasoline (Gupta *et al*., 2010). The accurate prediction of coke formation helps to estimate the endothermic heat needed in the reactor. However, the models developed so far have no advantage for estimating the amount of coke, whereas the 4-lump model is developed to estimate the accurate amount of deposited coke (Ali e *et al*., 1997).

The microscopic shell balance approach has been used in literature to drive partial differential equations or simultaneous differential equations that can describe the products yields and the reactants conversions in tubular reactors as a function of residence time, position, temperature, pressure, velocity, catalyst feed ratio, gas void fraction, type of catalyst, inlet feed droplet size, reactor height, inlet catalyst temperature, mean boiling point of inlet feed, reactor radius, etc. (Ali *et al*., 1997; Fogler, 1999; Lee, 1989; Reza, 2000; Vogt and Weckhucysen, 2015). This study employed the microscopic approach for the riser reactor modelling. The approach combines the kinetic models, by considering the

reactions occurring at a microscopic scale, and the mass flow rate of the components through the reactor system.

2. Microscopic approach

The FCC riser reactor, Figure 1, is used in the production of gasoline form the cracking of heavier petroleum fractions where the catalyst pellets deactivated very rapidly by coking. In the FCC riser reactor, the catalyst and the reactant feed enter together from the bottom point and the gas velocity also increases continuously along the riser height because of decrease in vapor density due to formation of lower molecular weight products on cracking of vacuum gas oil (VGO). The catalyst particles are carried through at the same velocity as the gas velocity (Ali *et al*., 1997; Gupta *et al*., 2010). A microscopic approach was used to write a mass balance across the control volume as depicted in Figure 1 (Mahfud, 2016). A mass balance on the component j (j = A, B, C and D) over the riser reactor volume $\Delta V=A_C\Delta z$ is done based on the following assumptions: steady state process, one-dimensional flow process, isothermal process, isobaric process, and ideal-gas behaviour. The species mass balance over the control volume includes gas phase only.

Differential balance equations were performed on an infinitesimally small control volume. These equations enable us to determine how mole fractions of the components vary with the height of the riser reactor.

$$F_j|_z - F_j|_{z+\Delta z} + r_j A_C \Delta z = 0 \tag{1}$$

Dividing by Δz and taking the limit as $\Delta z \rightarrow 0$ we obtain

$$\frac{dF_j}{dz} = r_j A_C \tag{2}$$

Equation 2 is the design equation of the reactor. The four-lump kinetic model, Figure 2, is based on the following assumptions: Gas oil cracking reaction is second order, gasoline cracking reaction is first order, gas flow in the reactor is an ideal plug flow, and gas does not produce coke. The rate of consumption of reactant j per unit catalyst volume was expressed as (Ali *et al*., 1997):

$$-r_j = k_j\left(\frac{C_j}{C_{jo}}\right)^n C_j \emptyset \tag{3}$$

where C_j is the concentration of component j, C_jo is the initial concentration of pure component j, n=1 for vacuum gas oil (VGO), and n=0 for gasoline cracking, ∅ catalyst activity.

Combining Equations 2 and 3 gives the following ordinary differential equations:

Vacuum gas oil, VGO (A): $$\frac{dy_A}{dz} + K_m[k_{AB} + k_{AC} + k_{AD}]y_A^2 = 0 \quad (4)$$

Gasoline (B): $$\frac{dy_B}{dz} + K_m[(k_{BC} + k_{BD})y_B - k_{AB}y_A^2] = 0 \quad (5)$$

Coke (D): $$\frac{dy_D}{dz} - K_m[k_{BD}y_B + k_{AD}y_A^2] = 0 \quad (6)$$

Gas (C): $$\frac{dy_C}{dz} - K_m[k_{BC}y_B + k_{AC}y_A^2] = 0 \quad (7)$$

where $K_m = \frac{\emptyset\, A_C \varepsilon_g L \rho_g}{F_g}$.

Figure 1 Schematic of FCC Unit (left), the riser reactor control volume (right)

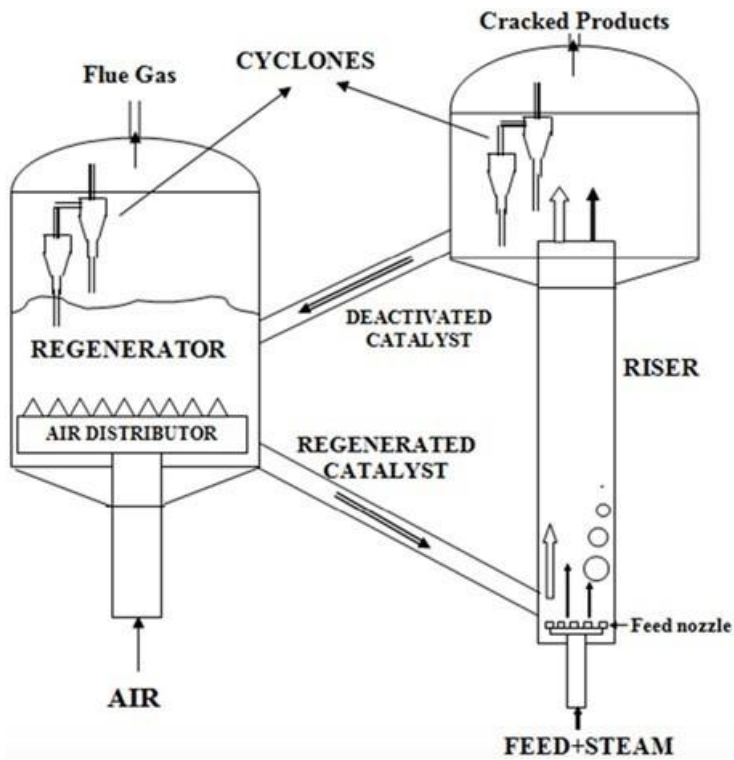
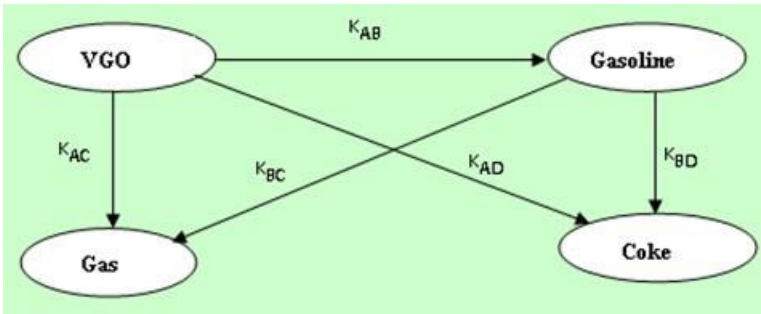


Figure 2 The reaction scheme of four lump kinetic model (Ali *et al*., 1997)



With the boundary conditions, at z=0: $y_A(0)=1$, $y_i(0)=0$; i = B, C and D where: y_i; weight percent of hydrocarbons in the riser (i = A, B, C and D), k_{ij}; reaction rate constants between species i and j, where $i \neq j$, $m_r^3/(m_{cat}^3.s)$, AC; cross-sectional area of the riser (m^2), Fg ; hydrocarbon gases mass flow rate in the riser, $kg.sec^{-1}$, ε_g; hydrocarbon gases void fraction in the riser, $\Phi = 0.2$ (Gupta and Subba, 2003); catalyst activity, ρ_g; density of gas phase in the riser, $kg.m^{-3}$, L; riser height, m.

Each of the first order ordinary differential equations is accompanied by one initial condition. These first order ordinary differential equations are simultaneous in nature but can be solved by the numerical methods such as Runge-Kutta methods for differential-algebraic equations. The four-lump kinetic model was developed based on a number of assumptions, which may not be applicable to all systems. The validity of the model should be checked against experimental data prior to the laborious computations.

3. Results and discussions

Experimental catalytic cracking data were utilized at three temperatures 482, 549, and 616 °C (Ali *et al*., 1997; Gupta *et al*., 2010). The dependence of the rate constant K_{ij} of chemical reactions on the temperature T and activation energy E_a are given by Arrhenius equation (Gupta *et al*., 2010):

$$K = K_o e^{-E_a/RT} \tag{8}$$

K_o represents the frequency factor (second), and R represents the gas constant.

Table 1 shows the values of the reaction rate constant at different temperatures that are calculated from the following equation:

$$K_{ij}(T) = K_{ij}(756) \times EXP\left[\frac{E_a}{R}\left(\frac{1}{756} - \frac{1}{T}\right)\right] \tag{9}$$

Table 1 Kinetic constants

Kinetic constant	Value $m_r^3/(m_{cat}^3.s)$ at 756, 822 and 889 K		
	756 K	822 K (Eq. 9)	889 K (Eq. 9)
K_{AB}	68.3	163.61	347.82
K_{AC}	17.15	53.85	144.63
K_{AD}	2.32	5.3	10.82
K_{BC}	0.20	0.39	0.70
K_{BD}	0.55	2.41	8.63

The specific heat capacity of each lump in the reactor was not considered as function of temperature, which was not introduced into the model equations. The model equations were only adopted to investigate the influence of the riser temperature on the rate of reaction as a consequence of increasing the reaction rate constant that described by Arrhenius equation. However, the rate of reaction (Equation 3) could probably be doubled or tripled as a result of increase in the reactor temperature, inside the riser, especially at the catalyst surface, where the reaction rates are controlled by reaction kinetics which affects the conversion or yields of products.

More details can be found in the included tables. In this result, the kinetic constants reported by Gupta and Subba (2003) were used. For the riser, 0.8 m is the inside diameter, 33 m is the riser height, 20 kg/s is the feed flow rate, 4.5 kg/m^3 is the gas phase density. The kinetic constants, the molecular weights of the components, the activation energy for cracking reaction, and the industrial riser data are summarized in Tables 2–5, respectively. The reaction rate constants at different temperatures are calculated by using Equation 9 and listed in Table 1, were used in all the calculations. It should be noted that production data for VGO conversion and for product yields were predicted by Ali *et al*. (1997) with a predictive four lumps kinetic model, where lumps represented VGO, gasoline, gas and coke.

Table 2 Kinetic constants (Gupta and Subba, 2003)

Kinetic constant	Value $\frac{m_{reactant}^3}{m_{catalyst}^3.s}$ at 756 K
K_{AB}	68.30
K_{AC}	17.15
K_{AD}	2.32
K_{BC}	0.20
K_{BD}	0.55

Table 3 The component molecular weight (Gupta and Subba, 2003)

J	1	2	3	4
Component	VGO	Gasoline	Gas	Coke
Mol. Wt.	382	120	45	-

Table 4 Activation energy for cracking reaction (Gupta and Subba, 2003)

Cracking reaction	Activation energy E_j, K_{cal}/K_{mol}
VGO ⟶ gasoline	16328
VGO ⟶ gasoline	21388
VGO ⟶ gasoline	15449
Gasoline ⟶ gas	12612
Gasoline ⟶ coke	27621

Table 5 Industrial FCC unit data (Gupta and Subba, 2003)

Variable	Value
Riser inside diameter	0.8 m
Riser height	33 m
Feed flow rate	20 kg/s
Density of gas phase	4.5 kg/m^3

Equations 4 to 7 are initial value ordinary differential equations (ODEs) and solved using MATLAB ODE45 solvers (see Figure 3). Figure 4 illustrates the effect of temperature on the yields (wt %) of Gas, Gasoline, Coke and conversion of vacuum gas oil (wt %). The mean average boiling point of the vacuum gas oil is equal 690 K (Ali *et al*., 1997), and the cracking reactions are endothermic reactions for that reasons the reactor temperature were selected to be higher than 690 K. Figure 5 compares the predicted data and the actual plant data. Obviously, the derived models indicate reasonable predictions for the outlet data from the riser reactor. The continuous cracking of VGO and Gasoline leads to increase the Gas and Coke, to avoid increasing the yield of the unwanted products such as Gas and Coke the contact time has to be short (less than 0.5 seconds) (Gupta *et al*., 2010).

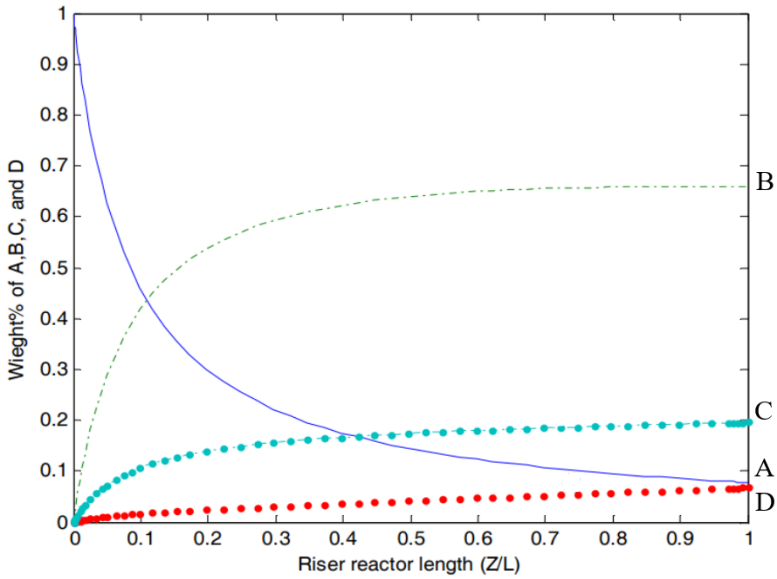
Increasing reactor temperature leads to increase both liquefied petroleum gas yield and coke yield, and to decrease the gasoline yield. Table 1 gives the products yields of the FCC unit at three different operating temperatures 756 K, 822 K and 889 K. 756 K gives the highest gasoline yield, and higher than this riser temperature leads in over-cracking of the feed gas oil and resulting in more light hydrocarbons (Gas) and more deposited coke on the catalyst surface.

Figure 3 MATLAB ODE45 code

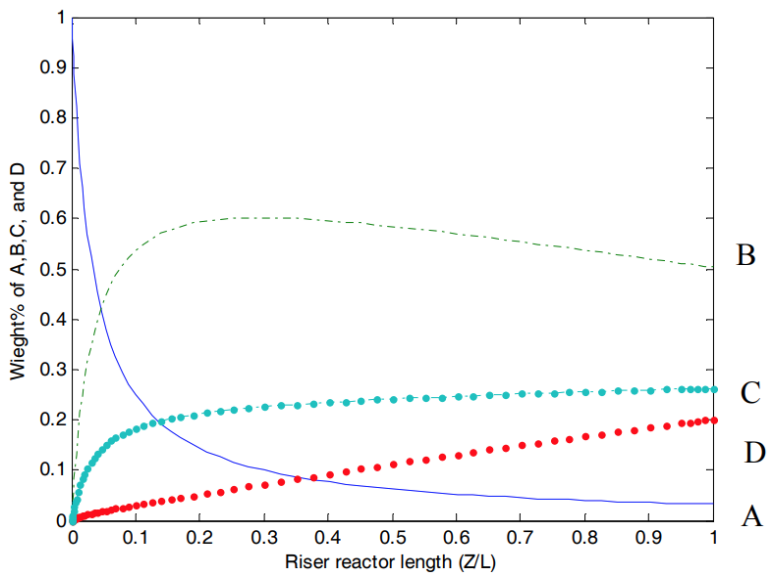
```
[z,y] = ode45(@rigid,[0 1],[1 0 0 0])
plot(z,y(:,1),'-',z,y(:,2),'-.',z,y(:,3),'.',z,y(:,4),'-
..')
%title('Hydrocarbons fractions in the riser reactor at
temperature = 756 K')
xlabel('Riser reactor length (Z/L)')
ylabel('Wieght% of A,B,C, and D')


function dy = rigid(z,y)
%   File rigid.m
%   This subroutine will solve four simultaneous ordinary
%   differential equations of 1st order using ode45 Runge-
Kutta solution
%   method.
%
%   To run this file you will need to specify the boundary
conditions:
%   yA(0)= 1.
%   yB(0)=0.
%   yc(0)=0.
%   yD(0)=0.
%
%   The code will return the vector y.
%
T=756    % temperature K
Ea1=16328; Ea2=21388; Ea3=15449; Ea4=12612; Ea5=27621 %
activation energy
km=.2*.2*.5*30*4.5/20     % void fraction=20%, catalyst
deactivity=20%
kAB=68.3*exp(16328/1.985*(1/756-1/T))
kAC=17.15*exp(21388/1.985*(1/756-1/T))
kAD=2.32*exp(15449/1.985*(1/756-1/T))
kBC=0.2*exp(12612/1.985*(1/756-1/T))
kBD=0.55*exp(27621/1.985*(1/756-1/T))
dy = zeros (4,1);                          % a column vector
dy(1) = -km*(kAB+kAC+kAD)*y(1)^2           % VGO differential
equation
dy(2) = -km*((kBC+kBD)*y(2)-kAB*y(1)^2)    % Gasoline
differential equation
dy(3) = km*(kBD*y(2)+kAD*y(1)^2)           % Gas differential
equation
dy(4) = km*(kBC*y(2)+kAC*y(1)^2)           % Coke
differential equation
```

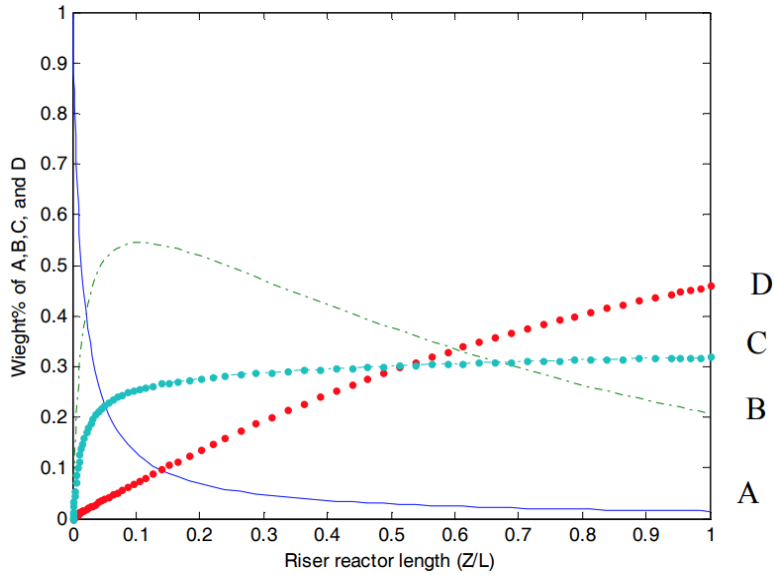
Figure 4 Hydrocarbons weight fraction along the riser reactor height, where; A: VGO, B: Gasoline, C: Gas, D: Coke.



(a) Reactor operating temperature: 756 K

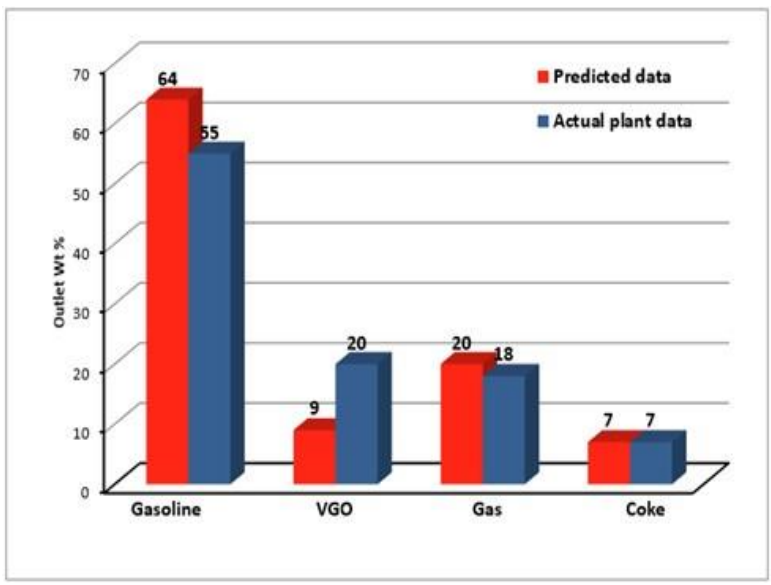


(b) Reactor operating temperature: 822 K



(c) Reactor operating temperature: 889 K

Figure 5 Comparison between predicted data and actual plant data (Gupta and Scubba, 2003)



4. Conclusion

There are a number of chemical kinetic models available in the literature and used to improve and predict the FCC process. Detailed production data such as compositional distributions along a riser is necessary to estimate the appropriate length for maximum gasoline yield. However, using a simplified four-lump kinetic model is quite useful if the validity of the model is verified with comparing to actual plant data. A shell balance was used to derive simultaneous ordinary differential equations (ODEs) that employed to determine the products yield from the riser. The best gasoline yield was being obtained (64%) for conditions specified above. Operating temperature was varied and its effect on the gasoline yield, coke yield and total conversion for a riser FCC unit was studied. The cracking product distribution is measured at three different temperatures 756 K, 822 K, and 889 K. Results of simulation showed good agreement with actual plant data. These ODEs are perfect in predicting the amount of precipitated coke at the catalyst surface. The obtained results of the products yield from the riser show that the four lump kinetic model of Ali *et al*. (1997) is predictive as it is coupled with the predicted simultaneous ODEs, that is, the reaction rate constants are independent of the feed type.

5. References

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