

Modeling of a Fluid Catalytic Cracking (FCC) Riser Reactor

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Abstract:

Fluid catalytic cracking (FCC) is used in petroleum refinery to convert the heavy gas oil into more valuable lighter hydrocarbon products such as gasoline. The conversion is done because of the catalytic cracking of the heavy gas oil on the catalyst surface. In this work, a simple four-lump kinetic model is proposed to describe the process, and the cracking product distribution is measured at three different temperatures. In addition, one-dimensional flow is assumed in the FCC riser reactor, and four

ordinary differential equations are derived using shell mass balance for the reactants and the products. Furthermore, 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 simulation done at three different temperatures 756 K, 822 K, and 889 K and the results showed good agreement with actual plant data.

Keywords: Fluid catalytic cracking (FCC) unit, four-lump kinetic model, shell mass balance, ode45 solver.

Introduction :

In modern petroleum refineries, figure (1), the fluid catalytic cracking (FCC) unit, figure (2), helps to maximize the profitability of the refining process by increasing the conversion of the heavy petroleum fractions into lower molecular-weight products, such as gasoline and light olefins. FCC technology has continued to evolve since its advent nearly half a century ago. During this time, many improvements have been made in FCC operation; these include feed preparation, catalyst development, equipment design, and operating strategies, [1].

The catalytic cracking reaction is initiated and completed in a short-contact-time vertical or upward reactor called the riser [1]. The catalyst is

pneumatically conveyed from the bottom to the top by steam and hydrocarbon vapors. Efficient mixing of catalyst and hydrocarbons enhances the catalytic cracking reactions. However, the hot catalyst vaporizes the feed and catalyzes the cracking reactions to produce components including liquefied petroleum gases, gasoline, coke, and light gas oil [2]. Since the cracking reaction is endothermic, the required heat is supplied via the regenerator in which the coke deposited on the catalyst is burnt to reactivate the catalyst. The residence time of the catalyst-hydrocarbon mixture in the riser is just for a few seconds and then the mixture is separated via cyclones [1, 2, 3].

For modeling of cracking kinetics, 3-lump model proposed and lumped reactant and all products into three major groups; feed, coke plus C_1 - C_4 hydrocarbons, and gasoline [4]. A more complicated and detailed 10-lump model proposed to lump the reaction feed into paraffins, naphthenes, and aromatic groups, and two product groups of C_1 - C_4 plus coke and gasoline [5]. In this 10-lump model very complicated mathematical equations were involved to predict the FCC process. 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 [6], whereas the 4-lump model is developed to estimate the amount of deposited coke [5, 6, 7].

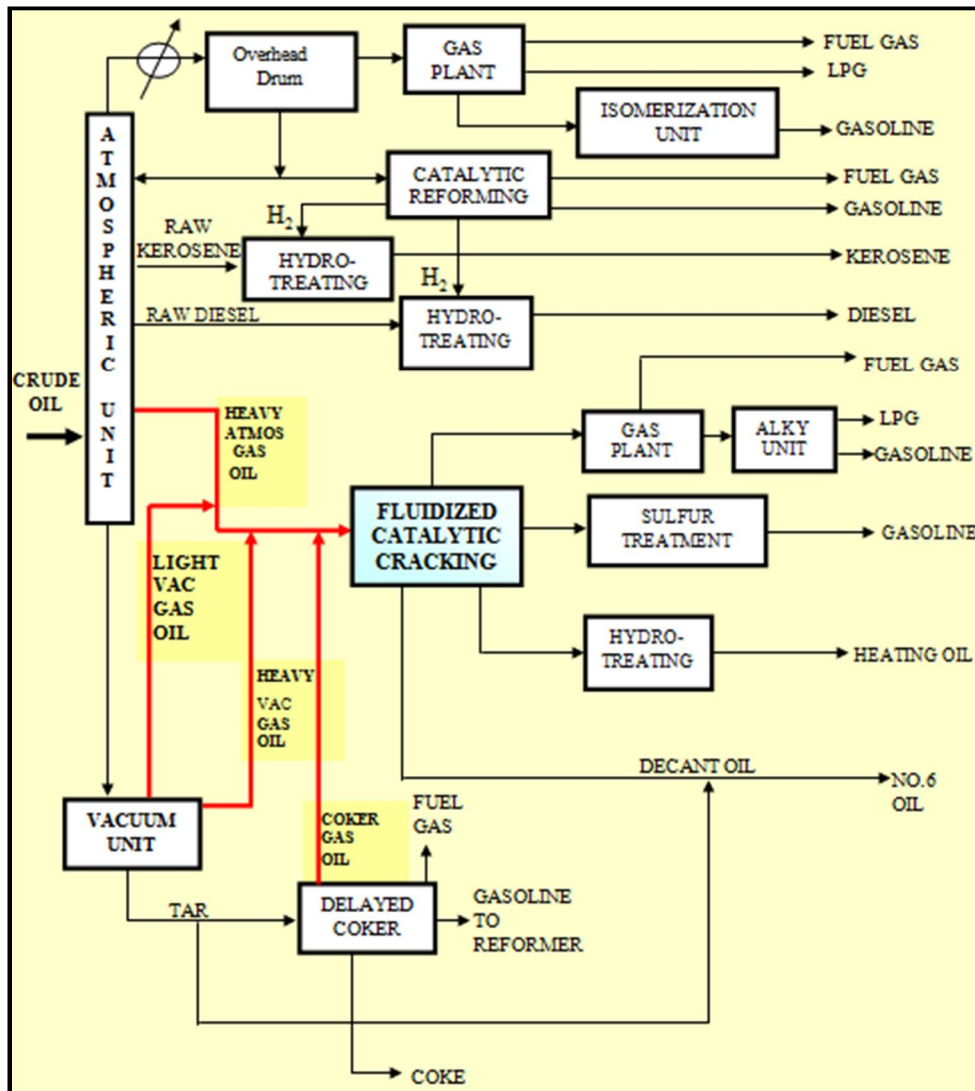


Figure (1): Flow diagram of modern petroleum refinery.

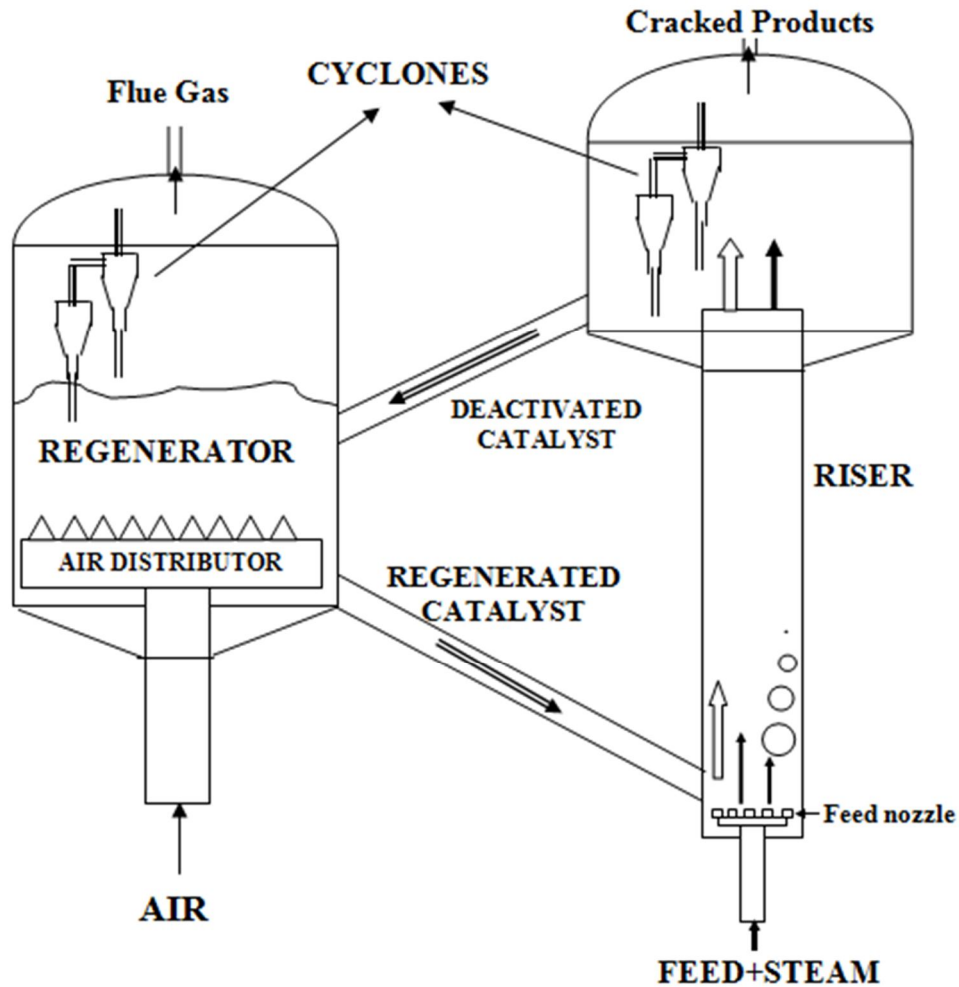


Figure (2): Schematic of FCC Unit

Modeling approach for FCC riser reactor:

The FCC riser reactor, figure (3), is used in the production of gasoline from the cracking of heavier petroleum fractions where the catalyst pellets deactivated very rapidly by coking.

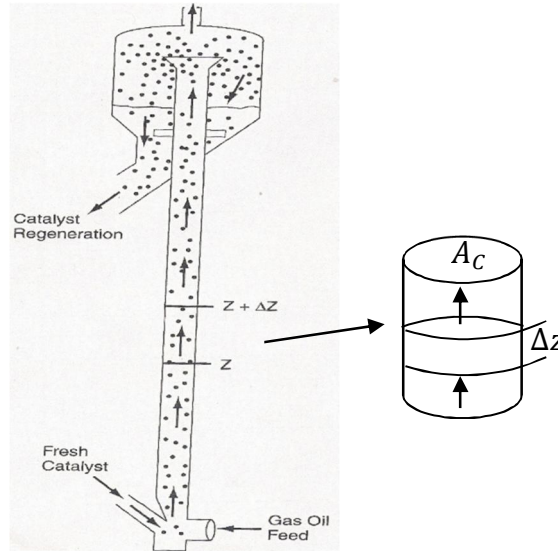


Figure (3): FCC riser reactor

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 [2, 3].

A mass balance on the component j over the riser reactor volume

$$\Delta V = A_C \Delta z$$

is done based on the following assumptions:

- Steady state process, no accumulation.
- One-dimensional flow process, axial flow.

- Isothermal process.
- Isobaric process.
- Ideal-gas behavior.

$$F_j|_z - F_j|_{z+\Delta z} + r_j A_c \Delta z = 0 \quad (1)$$

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

$$\frac{dF_j}{dz} = r_j A_c \quad (2)$$

The equation (2) is considered as the design equation of the reactor.

The four-lump kinetic model, figure (4), is based on the following assumptions:

1. Gas oil cracking reaction is second order.
2. Gasoline cracking reaction is first order.
3. Gas flow in the reactor is an ideal plug flow.
4. Gas does not produce coke.

The rate of consumption of reactant j per unit catalyst volume can be expressed as [2]

$$-r_j = k_j \left(\frac{C_j}{C_{j0}} \right)^n C_j \emptyset \quad (3)$$

Where C_j is the concentration of component j , C_{j0} is the initial concentration of pure component j , $n=1$ for vacuum gas oil (VGO), and $n=0$ for gasoline cracking, \emptyset catalyst activity.

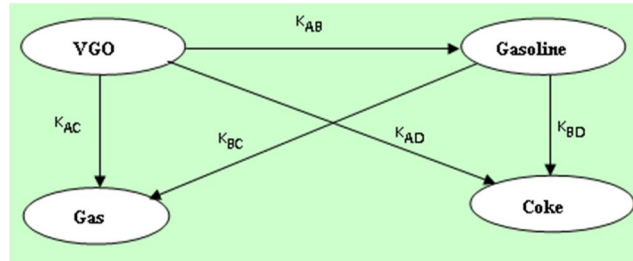


Figure (4): The reaction scheme of four lamp kinetic model

Combining equations (2) and (3) gives the following ordinary differential equations:

Vacuum gas oil, VGO (A):

$$\frac{dy_A}{dz} + Km[k_{AB} + k_{AC} + k_{AD}]y_A^2 = 0 \quad (4)$$

Gasoline (B):

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

Light hydrocarbon gases (D):

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

Coke (C):

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

$$Km = \frac{\Phi A_C \varepsilon_g L \rho_g}{F_g} \quad (8)$$

With the boundary conditions, at Z=0:

$$y_A(0) = 1$$

$$y_i(0) = 0; \quad i = B, C, \text{ and } D$$

Where ;

y_i weight percent of hydrocarbons in the riser ($i = A, B, C, \text{ and } D$)

k_{ij} reaction rate constants between species i and j , $m_r^3 / (m_{cat}^3 \cdot S)$

A_C area of the riser, m^2

F_g hydrocarbon gases mass flow rate in the riser, $kg \text{ sec}^{-1}$

ϵ_g hydrocarbon gases void fraction in the riser

Φ catalyst activity,

ρ_g density of gas phase in the riser, $kg \text{ m}^{-3}$

L riser length, 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.

Results and discussions:

The material balance equations were combined with reaction kinetics to obtain the weight fraction of each component coming out of the riser reactor. The model can predict the components weight fractions along the riser reactor height. Model validation is done as case study by using industrial data reported in the literature. Results of the simulator are being discussed in the following case study. Several assumptions are made to solve the derived model.

Case study:

In this case study, the experimental catalytic cracking data were utilized at three temperatures (482, 549, and 616 °C). The rate constants at each temperature were calculated, and the activation energies in the Arrhenius equation for each reaction in the four-lump model were predicted.

Industrial FCC plant data presented in Tables 1 to 5 were used in this case study [4, 5]. In this case five industrial data at the riser outlet gasoline yield, gas yield, unconverted hydrocarbon, and coke yield, and riser outlet temperature are available to obtain the rate constant parameters.

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, as shown below, [3]:

$$K = K_o e^{-E_a/RT} \quad (9)$$

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

The reaction rate constant at any temperature can be calculated from the following equation:

$$K_{ij}(T) = K_{ij}(756) \times EXP \left[\frac{E_a}{R} \left(\frac{1}{756} - \frac{1}{T} \right) \right] \quad (10)$$

The rate constants of the four-lump kinetic model at three temperatures (482, 549, and 616 °C) are tabulated in table (5), the calculations are done by using Equation (10).

Equations 4 to 7 are initial value ordinary differential equations (ODEs)

and solved using MATLAB ODE solvers. Initial value problems are typically solved with ODE45 for the nonstiff case. ODE45 is based on the Runge Kutta methods of order 4 and 5. The code is presented in the appendix, and the results are shown in the figures 5, 6, and 7.

Table (1) compares the predicted data and the actual plant data. Obviously the derived model indicates reasonable predictions for the outlet data from the riser reactor.

Figures (5) to (7) illustrate 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 [2], and

the cracking reactions are endothermic reactions for that reason the reactor temperature should be higher than 690 K.

The hydrocarbon gases void fraction in the riser is assumed constant along the riser highest and based on the literature the 0.2 value is chosen [4]. In addition, the reactor temperature is assumed to be constant, also the catalyst activity is assumed constant. When the process runs at 756 K it gives the highest gasoline yield. Increasing reactor temperature leads to increase both liquefied petroleum gas yield and coke yield, and to decrease the gasoline yield.

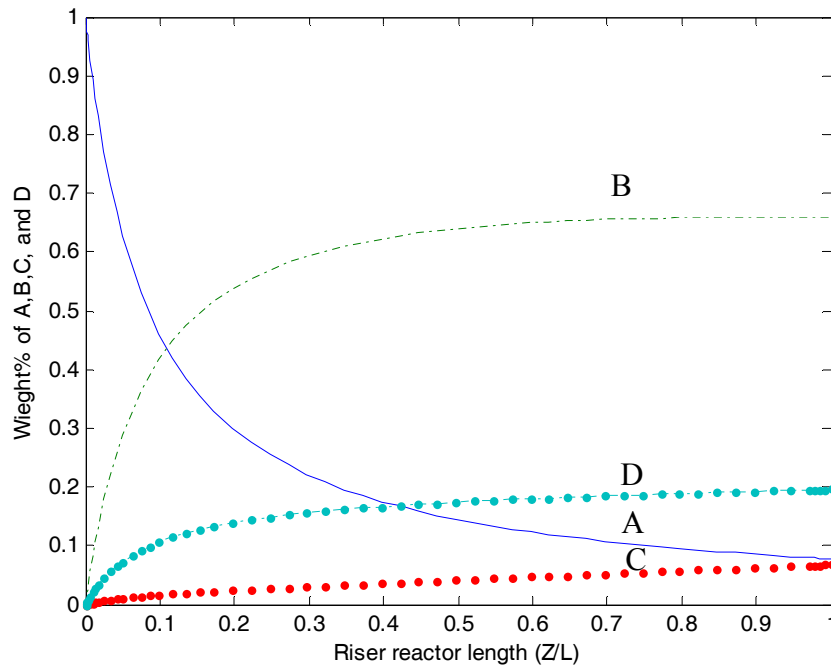


Figure (5): Hydrocarbons weight fraction along the riser reactor height at 756 K.
A: VGO, B: Gasoline, C: Gas, D: Coke

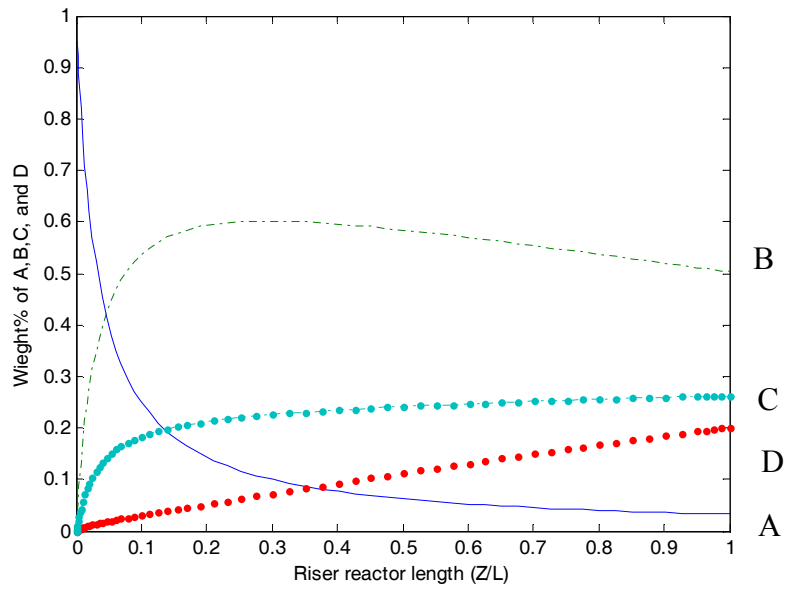


Figure (6): Hydrocarbons weight fraction along the riser reactor height at 822 K.
A: VGO, B: Gasoline, C: Gas, D: Coke

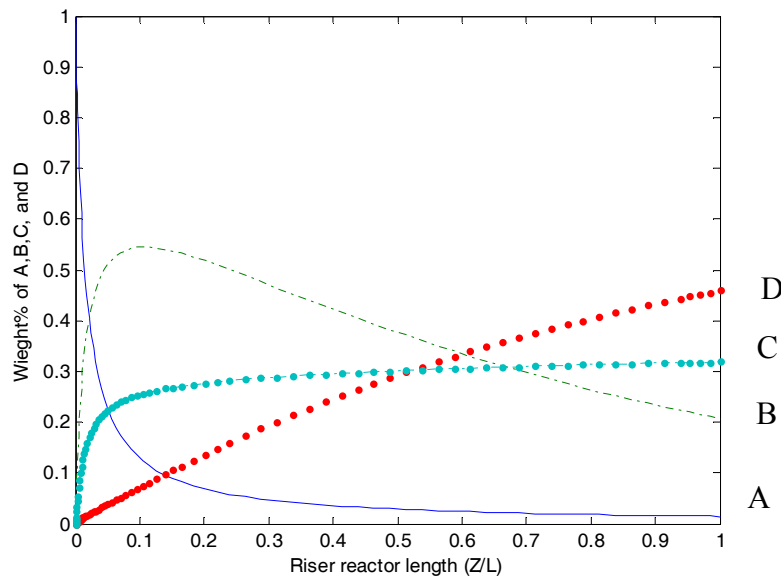


Figure (7): Hydrocarbons weight fraction along the riser reactor height at 889 K.
A: VGO, B: Gasoline, C: Gas, D: Coke

Table (1): Shows the comparison between predicted data and actual plant data.

Riser outlet data	Derived model	Plant data, [4]
Gasoline yield, wt%	64	55
VGO	9	20
Gas	20	18
Coke	7	7

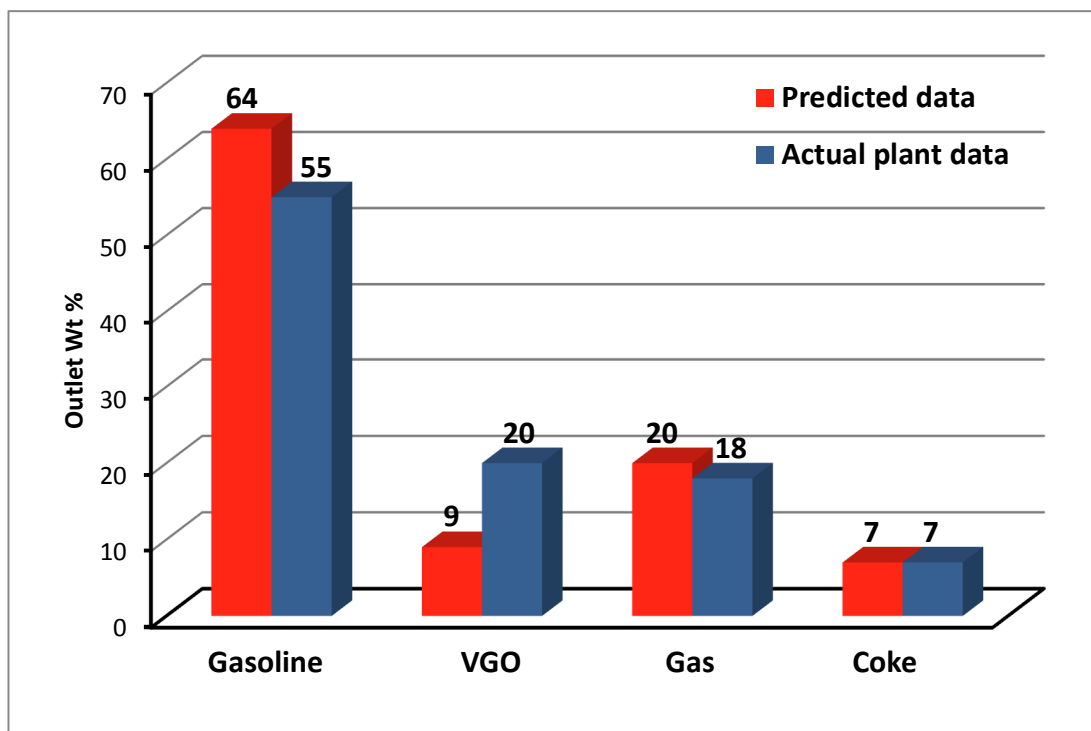


Figure (8): Shows the comparison between predicted data and actual plant data

Conclusion:

There are a number of chemical kinetic models available in the literature and used to improve and predict the FCC process. However, in most of the FCC riser simulation studies four lump kinetic schemes is used. This simplified four-lump kinetic model is quite useful if its validity can be verified.

An isothermal steady-state model for fluidized bed reactor is proposed, and a 4-lump kinetic model is applied. The cracking product distribution is measured at three different temperatures 756 K, 822 K, and 889 K. Kinetic constants are estimated by using Arrhenius equation. Results of simulation showed good agreement with actual plant data.

Appendix

A.1 FCC industrial data

Table (1): Kinetic constants [4, 6]:

Kinetic constant	Value $m_r^3/(m_{cat}^3 \cdot S)$ at 756 K
K_{AB}	68.30
K_{AC}	17.15
K_{AD}	2.32
K_{BC}	0.20
K_{BD}	0.55

Table (2): The components molecular weight, [4, 6]

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

Table (3): Activation energy for cracking reactions, [4, 6]

Cracking reaction	Activation energy E_j , Kcal/Kmol
VGO \longrightarrow gasoline	16328
VGO \longrightarrow gas	21388
VGO \longrightarrow coke	15449
Gasoline \longrightarrow gas	12612
Gasoline \longrightarrow coke	27621

Table (4): Industrial FCC unit data, [4, 6]

Variable	Value
Riser I.D.	0.8 m
Riser height	33 m
Feed inlet temp.	494 K
Feed flow rate	20 Kg/s
Riser pressure	2.9 atm

Table (5): Kinetic constants:

Kinetic constant	Value $m_r^3/(m_{cat}^3 \cdot S)$ at 756, 822 and 889 K		
	756 K	822 K (Eq. 10)	889 K(Eq. 10)
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

A.2 Matlab 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('Wiegth% 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
```

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