Prediction of the Optimal Reaction Temperature of the Riser of an Industrial Fluid Catalytic Cracking (FCC) Unit

Omotola F. Olanrewaju[1*]   Paul C. Okonkwo[2]   Benjamin O. Aderemi[2]

1.   National Agency for Science and Engineering Infrastructure (NASENI), Idu Industrial Area, Abuja, Nigeria.
2.   Faculty of Engineering, Department of Chemical Engineering, Ahmadu Bello University (ABU), Kaduna, Nigeria.

*E-mail of the corresponding author: sonictreasure@gmail.com

Abstract

A pseudo homogeneous two-dimensional (2D) model of an industrial Fluid Catalytic Cracking (FCC) riser is here presented. The FCC riser models of previous researchers were mostly based on the assumption of negligible mass transfer resistance and 1D plug flow. These assumptions undermine the accuracy of the models by over-predicting the optimum residence time of the riser. In this work the coke content of FCC catalyst was modeled as a function of the reactor temperature with the aim of predicting the operating conditions that will reduce coke on catalyst without undermining the yield of the key product (gasoline). Mass transfer resistance was incorporated in the reactor model to enhance the accuracy of the results. Catalyst deactivation was modeled based on the exponential decay function. The mass transfer coefficient and the catalyst effectiveness factor were estimated from empirical correlations obtained from literature. Data used for the simulation were sourced from an existing plant (KRPC) as well as from open literature. Finite difference numerical scheme was used to discretise the model governing equation. At the end of the investigation, three different operating temperature regimes were identified from the simulated results for the coking of FCC catalyst (low temperature, optimal temperature and high temperature regimes). An optimum operating temperature range of 786K-788K and an optimum catalyst-to-oil ratio (COR) range of 4.60-4.71 were predicted for the riser.

Keywords: FCC; Finite difference, Mass transfer resistance, Catalyst deactivation, Riser models.

1.   Introduction

Fluid Catalytic Cracking (FCC) is one of the most profitable processes in oil refineries. It is the major producer of gasoline in refineries and as such it is sometimes referred to as the heart of the refinery. FCC converts vacuum gas oils (VGO) and heavy feed stocks (molecular weight > 250) from other refinery operations into high octane gasoline, light fuel oils and gases (Fernandes *et al*. 2003).

FCC unit comprises mainly of the riser, the regenerator and the main fractionators. Among the major process variables of FCC (temperature, pressure and catalyst-to-oil ratio), the reactor temperature is the most sensitive variable that affects feed conversion, product yield and catalyst coking. The optimum reaction temperature in FCC is such that guarantees high yield of the desired product without quenching the reactions or causing over-cracking of the key product.

Fernandes *et al*. (2003), used a 6-lump, 1D model to simulate the riser of an industrial FCCU. Their model predicted a gasoline yield of 48%. The temperature, gas and solid phase velocity profiles were also predicted by the authors. However, the assumption of 1D plug flow and negligible mass transfer resistance by the authors oversimplified their models thereby undermining the accuracy of the predictions. Ahari *et al*. (2008) used a 4-lump, 1D model in their investigation. Their model predicted the temperature drop along the riser and they predicted a gasoline yield of 45%. The major limitation of their model was the assumption of negligible dispersion. The authors' work did not predict optimum parameters for the process. A 5-lump reaction scheme was used by Alsabei (2011). The author also based his investigation on negligible dispersion which contradicts the basic principles of heterogeneous catalysis especially for porous catalysts such as the FCC Zeolite catalyst. A 4-lump, 1D scheme was also used by Heydari *et al*. (2010) to model an industrial riser. Their model was also oversimplified and they did not predict optimum reaction temperature.

Models of higher dimensionality have also been used by other authors. Souza *et al*. (2007) used a 2D hydrodynamic, 6-lump model to simulate an industrial riser. They predicted a gasoline yield of 48%. Ahsan (2013) used a 2D, 4-lump riser model to predict gasoline yield and temperature profile of FCC. The author predicted a gasoline yield of 40%. Novia *et al*. (2006) used a 3D riser model to predict the hydrodynamic effect on the operation of the riser. They predicted the flow pattern of solid, the velocity vector of solid phases and the solid volume fraction. Gupta (2006) and Lopes *et al*. (2012) used 3D models in their investigations. Gupta (2006) used a mechanistic approach involving 50 lumps (pseudo species) to model an industrial FCCU. Lopes *et*

al. (2012) on the other hand, used a 4-lump reaction scheme to investigate the effects of various exit configurations of the riser on the hydrodynamics of the reactor as well as the yield of gasoline. They found that the T-shape exit configuration enhanced the yield of gasoline owing to enhanced solid (catalyst) reflux. In all the models aforementioned, the authors did not attempt to predict the optimal reaction temperature for FCCU riser.

A 2D quasi-steady state model of an industrial riser is here presented. 2D models approximate reality better because wall effects are accounted for unlike in 1D models. A 2D model requires less computational time and memory than is required for a 3D model. A five-lump reaction scheme was used to model the FCC reactions. The five-lump model that was used in this work accounted for coking unlike the over-simplified 3-lump reaction scheme. The five-lump model is also not as unwieldy to solve as the models that have larger number of lumps. This investigation has also advanced the works of the previous researchers in this field by simulating the catalyst coke content with a view to predicting the operating conditions that will minimize the coking of FCC catalyst thereby reducing the cost of regeneration of the coked catalyst. Finite difference numerical scheme was used to discretise the governing equations and a code was written in MATLAB to solve the equations. The model results were validated with data from an existing plant. Thereafter, the model was used to simulate coke on catalyst. The optimum reaction temperature was predicted from the simulation results.

2. Materials and Methodology

The FCCU reactor was modeled in this work using MATLAB (R2009a) on a Compaq HP CQ61 laptop.

The following assumptions were made in the development of the model:

1. Pseudo homogenous two-dimensional transport with axial and radial gradients. (In reality the riser is a 3D reactor. Simplifying the geometry to 1D is tantamount to predicting products yield just along the axis of the reactor. However turbulent the flow in the riser may be, a 1D model cannot adequately represent the entire geometry of the reactor because it does not account for wall effects).

2. The catalyst and gas are at thermal equilibrium

3. Hydrocarbon feed comes into contact with the hot catalyst coming from the regenerator and instantly vaporizes Gupta (2006).

4. There is no heat loss from the riser, the temperature of the reaction mixture falls only because of the endothermicity of the cracking reactions Gupta (2006). (The inner wall of the riser is known to be lined with refractory material.)

5. The riser dynamic is fast enough to justify a quasi-steady state model.

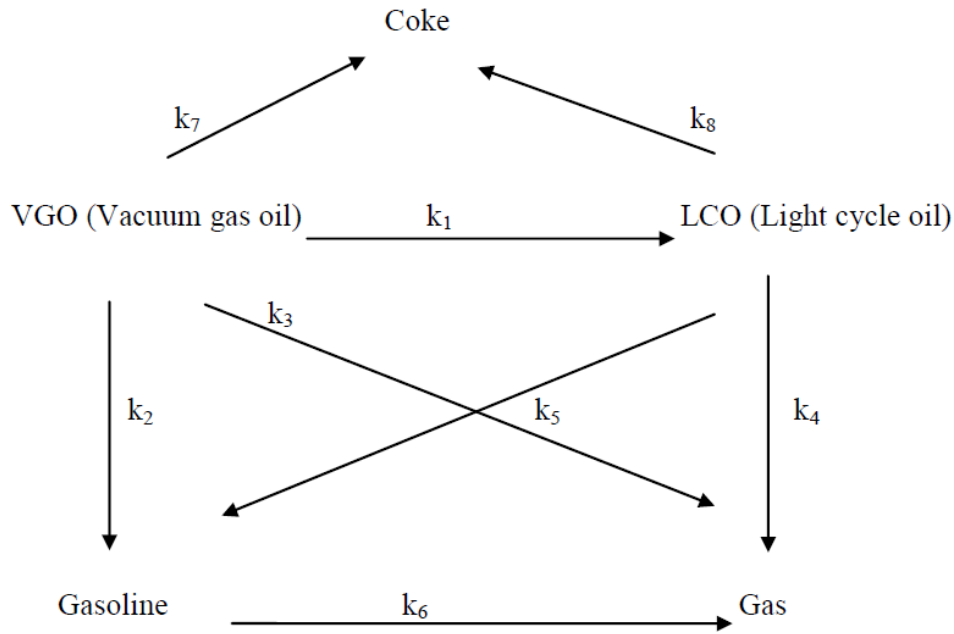Figure 1 depicts the five-lump reaction scheme that was used in this investigation.

Figure 1. Five-lump model (Den Hollander *et al.* 2003)

In Figure 1, k_j is the rate constant of the jth reaction in s^{-1} where j=1, 2, …, 8.

2.1 Model rate equation

In the five-lump model given in Figure 1, the eight reactions of the model are taken to follow first order kinetics as follows (mass transfer resistance taken into consideration):

$$r_j = \frac{ac_i}{\left(\frac{1}{k_g} + \left(\frac{1}{\eta k_j}\right)\right)} \quad j$$

$$= 1, … ,8 \tag{1}$$

$$a = exp(-k_d c_{coke}) \tag{2}$$

$k_d = 8.2$ (Den Hollander *et al.* 2003)

$$\eta = \frac{3}{\varphi}\left(\frac{1}{tanh\varphi} - \frac{1}{\varphi}\right) \tag{3}$$

$$\varphi = R\left(\frac{k_j}{D_e}\right)^{\frac{1}{2}} \tag{4}$$

c_i = species concentration (weight fraction), k_g = mass transfer coefficient of reactant in m/s, η = particle effectiveness factor, k_j =reaction rate constant in s^{-1}, φ = Thiele modulus and D_e = effective diffusivity in m/s^2. Equation (1) is the model rate equation which incorporates mass transfer resistance terms, k_g and η. Equation (1) reverts to the classical first order rate equation when $1/k_g = 0, \eta = 1$. The particle effectiveness factor, η expressed by Equation (3) is the ratio of the reaction rate when there is diffusion resistance to the rate when there is no diffusion resistance. It is a direct measure of the extent to which diffusion resistance reduces the rate of chemical reactions in heterogeneous catalysis and it is a function of Thiele modulus. Thiele modulus, φ is the ratio of intrinsic reaction rate to diffusion rate and as such Equation (4) provides a yardstick for determining the rate determining step in heterogeneous catalysis. Equation (4) holds for spherical particles assumed in this work.

The basic parameters to be determined in Equations (1) to (4) are D_e and k_g. D_e was estimated from empirical correlations in literature (Missen *et al.* 1999) while k_g was estimated from Sherwood number for gases (Geankoplis 2011).

2.2 Riser model equations

Figure 2 depicts the 2D riser while the control volume used in deriving the model equations from Conservation laws is shown in Figure 3 (Missen *et al.* 1999).
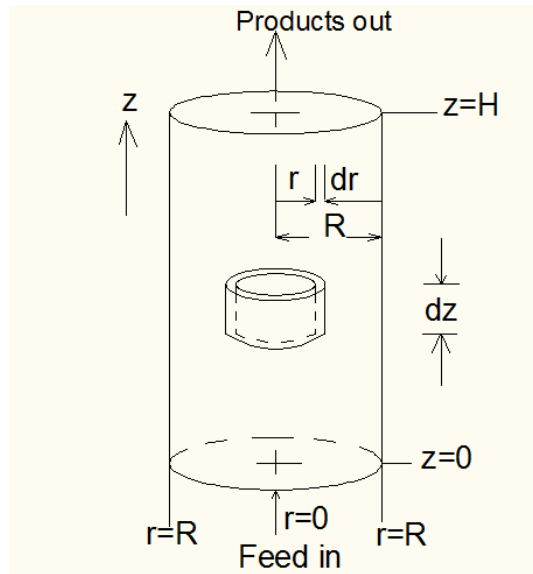

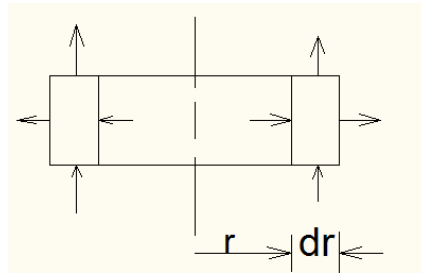Figure 2. 2D riser reactor (Missen *et al.* 1999)

Figure 3. Control volume (Missen *et al.* 1999)

2.2.1 Continuity equation

The component continuity equation for the model is as given below.

$$D_{zi} \frac{\partial^2 c_i}{\partial z^2} + D_{ri} \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) - \frac{\partial (u c_i)}{\partial z} - \rho_B (-r_i)$$
$$= 0 \qquad (5)$$

Where

$$u = \frac{q}{A_c}, m^3 (fluid) s^{-1} m^2 (vessel) \qquad (6)$$

q is the volumetric flow rate of the gas through interparticle bed voidage, $m^3 (fluid) s^{-1}$, D_z and D_r are effective diffusivities in $m^3 (fluid) m^{-1} (vessel) s^{-1}$, $(-r_i)$ is in $kg\ species\ kg^{-1} (catalyst)\ s^{-1}$.

2.2.2 Riser hydrodynamic model

The numerical value of the catalyst slip factor (the ratio of the gas interstitial velocity to the average particle velocity) can be predicted from Equation (7) (Ahari *et al.* 2008):

$$\psi = \frac{u_0}{\varepsilon v_p}$$

$$= 1 + \frac{5.6}{Fr} + 0.47 Fr_t^{0.47} \qquad (7)$$

Fr = Froude number and Fr_t = Froude number at terminal velocity.

$$F_r$$
$$= \frac{u_0}{(gD)^{0.5}} \qquad (8)$$

g = acceleration due to gravity (m^2/s).

The average particle velocity in the riser, v_p is given by Equation (9).

$$v_p$$
$$= \frac{G_s}{\rho_s(1 - \varepsilon)} \qquad (9)$$

G_s is the catalyst mass flux.

The expression for the average voidage in terms of the solid mass flux, superficial gas velocity, riser diameter and catalyst physical properties was derived from Equations (7) and (9). Equation (10) gives the average voidage of the reactor.

$$\varepsilon$$
$$= 1$$
$$- \frac{G_s \psi}{u_0 \rho_s + G_s \psi} \qquad (10)$$

2.2.3 Energy balance

The model energy balance, Equation (11) is given below.

$$k_z \frac{\partial^2 T}{\partial z^2} + k_r \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - G_s c_p \frac{\partial T}{\partial z} + \rho_B \sum_{i=1}^{8} (-r_i)(-\Delta H_{Ri}) = 0 \qquad (11)$$

Where

k_z and k_r are the effective thermal conductivities.

The coupling between the riser and the regenerator is expressed in the model by Equation (12).

$$F_{cat} c_{pcat}(T_0 - T_{cat}) + F_f c_{pfl}(T_{vap} - T_f) + F_f c_{pfv}(T_0 - T_{vap}) + F_f \Delta H_{vap}$$
$$= 0 \qquad (12)$$

The governing equations, Equations (5) and (11) were expressed in a general, normalized form as follows:

$$\alpha \left(\frac{\partial^2 \sigma}{\partial r^{*2}} + \frac{1}{r^*} \frac{\partial \sigma}{\partial r^*} \right) + \beta \frac{\partial^2 \sigma}{\partial z^{*2}} + \gamma \frac{\partial \sigma}{\partial z^*} + \lambda(-r_i)$$
$$= 0 \qquad (13)$$

$$\sigma = {c_i}/{c_0} \text{ or } {T}/{T_0}, \qquad r^* = {r}/{R}, \qquad z^* = {z}/{H}$$

The coefficients in Equation (13) are given by the following expressions:

$$\alpha_1 = \alpha_2$$
$$= 1$$

$$\beta_1 = \frac{R^2 D_z}{H^2 D_r},$$

$$\beta_2 = \frac{R^2 k_z}{H^2 k_r}$$

$$\gamma_1 = \frac{-UR^2}{HD_r},$$

$$\gamma_2 = \frac{-Gc_pR^2}{Hk_r}$$

$$\lambda_1 = \frac{R^2 \rho_B}{D_r c_0},$$

$$\lambda_2 = \frac{R^2 \rho_B}{k_r T_0} \tag{14}$$

Subscripts 1 and 2 in the coefficients in Equation (14) correspond to the continuity equation and energy balance respectively.

Boundary conditions:

Equation (15) gives the boundary conditions that were used to solve the riser model equation. The model variables were normalized. Hence, at the inlet of the reactor feed stock concentration as well as the reactor temperature is unity. The concentration of each of the products at the inlet (z^*=0) is equal to zero since no product is present in the feed stock at the inlet of the reactor.

@ $z^* = 0, 0 < r^* < 1$ (inlet): $\sigma_{vgo} = \sigma_T = 1, \sigma_{lco} = \sigma_{gasoline} = \sigma_{gas} = \sigma_{coke} = 0$

@ $z^* = 1, 0 < r^* < 1$ (outlet): $\frac{\partial \sigma}{\partial z^*} = 0$

@ $r^* = 0, 0 < z^* < 1$: $\frac{\partial \sigma}{\partial r^*} = 0$ (symmetry)

@
$r^* = 1, 0 < z^* < 1$: $\frac{\partial \sigma}{\partial r^*} = 0$ (15)

The governing equation, Equation (13) was solved to predict the yield of products. Finite difference numerical scheme was used to discretise Equation (13). A 20x20 grid was used to discretise the second-order governing equation; Equation (13). The discretised equation was expressed in terms of the six variables that were predicted in this work (concentrations of the five species and the riser temperature). A code was written in MATLAB to solve the six algebraic equations that resulted. Data obtained from open literature and from an existing plant (KRPC) were used to validate the model results. Thereafter, catalyst coke content was simulated to predict the coke content of the FCC catalyst for a selected reactor temperature range. The optimum temperature range for the fluid catalytic cracking of VGO was predicted from the results obtained.

2.3 Model data

The data used for the simulation are as given in Tables 1-5

Table 1. Kinetic constants for five-lump model (Den Hollander *et al*. 2003)

Reaction number	k (s^{-1})
1	1.90
2	7.50
3	1.50
4	0.00
5	1.00
6	0.30
7	0.21
8	0.50

Table 2. Enthalpies of cracking (Ahari *et al*. 2008)

S/N	Cracking reaction	ΔH(kJ/kg)
1	VGO to LCO	80
2	VGO to gasoline	195
3	VGO to gas	670
4	LCO to gas	-
5	LCO to gasoline	180
6	Gasoline to gas	530
7	VGO to coke	745
8	LCO to coke	600

Table 3. Molecular weights and heat capacities (Ahari *et al*. 2008)

S/N	Species	Molecular weight (kg/kmol)	Cp (kJ/kg.K)
1	VGO	333.0	2.67 (liquid), 3.30 (gas)
2	LCO	300.0	3.30
3	Gasoline	106.7	3.30
4	Gas	40.0	3.30
5	Coke	14.4	1.087

Table 4. Gas oil properties

Property	Value	Source
Specific gravity	0.89-0.93	Gupta (2006)
Viscosity	1.4x10^{-5}N.s/m^2	(Ahari *et al*. 2008)
Vaporization temperature	698K	(Ahari *et al*. 2008)
Enthalpy of vaporization	190kJ/kg	(Ahari *et al*. 2008)

Table 5. Model parameters (Source: Plant data)

S/N	Parameter	Value
1	Reactor inlet temperature, T_0 (K)	791
2	Feed inlet temperature, T_f (K)	613
3	Catalyst inlet temperature, T_{cat} (K)	927
4	Specific heat capacity (liquid feed), cpfl (J/kg-K)	2.67e3 (Ahari *et al.* 2008)
5	Specific heat capacity (vapour feed), cpvf (J/kg-K)	3.30e3 (Ahari *et al.* 2008)
6	Specific heat capacity (catalyst), cpcat (J/kg-K)	1.09e3 (Ahari *et al.* 2008)
7	Feed vaporization temperature, T_{vap} (K)	698
8	Enthalpy of vaporization, delHvap (J/kg)	190e3 (Ahari *et al.* 2008)
9	Density (solid catalyst), ρ_s (kg/m^3)	1250
10	Catalyst velocity, U_c (m/s)	5 (Gupta 2006)
11	Gas superficial velocity, U (m/s)	18
12	Slip factor, psi	2
13	Feed flow rate, F_f (kg/s)	35.5
14	Riser diameter, D_R (m)	1.146
15	Riser height, H (m)	25
16	Pore diameter, P_d (m)	2.00e-9
17	Particle diameter, D_p (m)	60e-6
18	Gas average density ρ_g (kg/m^3)	0.92
19	Gas average viscosity μ_g (Pa.s^{-1})	1.40e-5 (Ahari *et al.* 2008)
20	Riser pressure, P (atm)	2.94
21	Particle tortuosity, τ_p	7 (Missen *et al.* 1999)

3. Results and discussion

The results obtained at the end of the investigation were presented as shown in Figures 4, 5 and 6. The predicted yields of LCO, gasoline, gas and coke as depicted in Figure 4 are 15.54wt%, 49.70wt%, 18.01wt% and 4.90wt% respectively. These values compare favorably well with plant data (Table 5 referred) having percentage deviation value of <5% for all components.
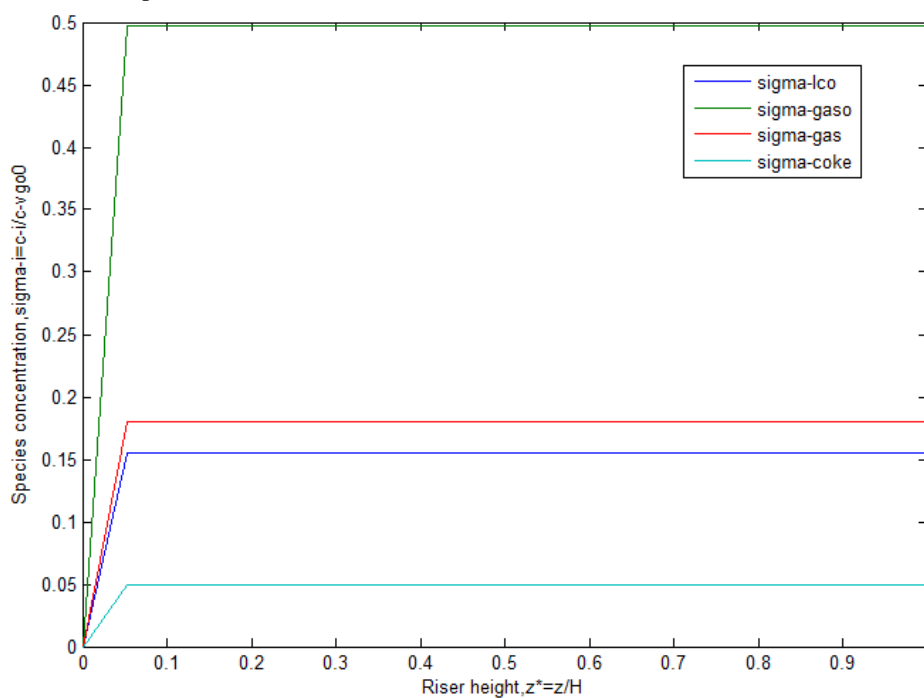

Figure 4. FCC products concentration (wt %) along riser height

Figure 5 presents the predicted conversion of VGO as a function of reactor height. A conversion of 79.28% was predicted by the model.
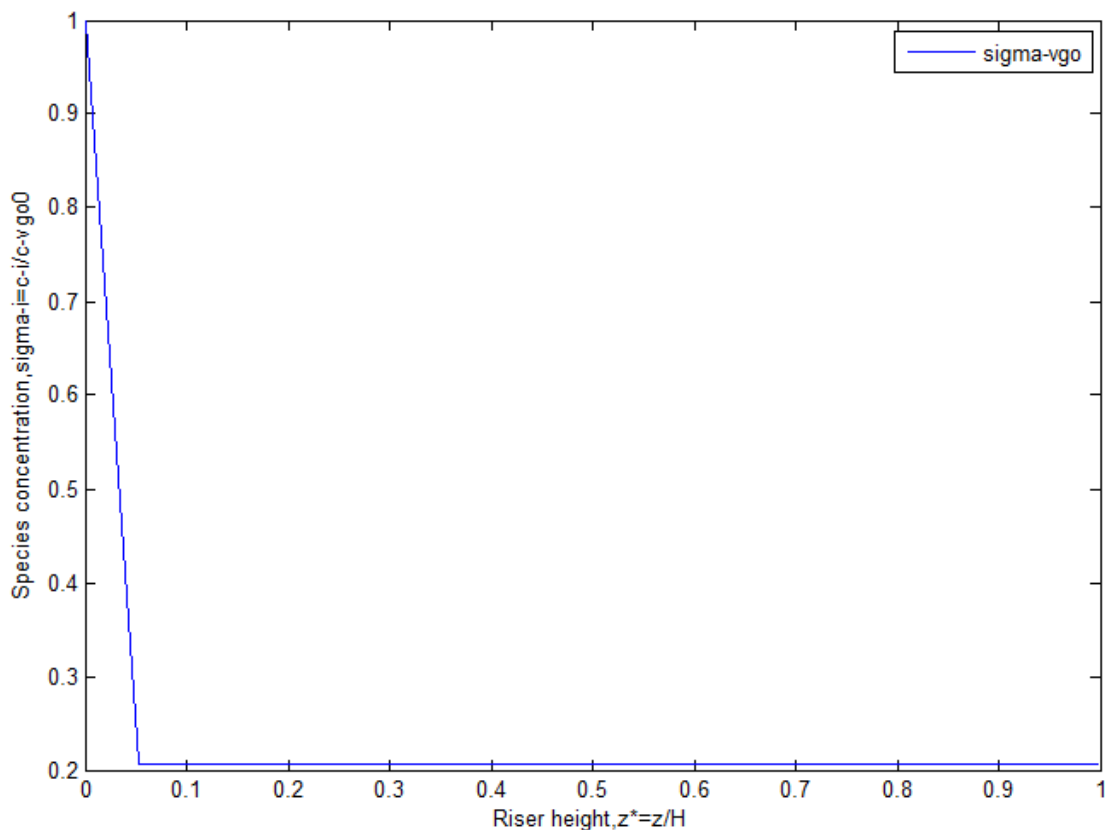

Figure 5. Feedstock (VGO) conversion along the height of the riser

Table 5. Validation of model results with plant data

Species	Conv./Yield, wt% (Plant)	Conv./Yield, wt% (Model)	% Deviation from Plant data
VGO	80.00	79.28	0.90
LCO	15.15	15.54	2.57
Gasoline	50.00	49.70	0.60
Gas	17.88	18.01	0.73
Coke	5.08	4.90	3.54

Coke on catalyst was simulated using the validated model. The result was presented as a plot of catalyst coke content as a function of reactor temperature as shown in Figure 6.
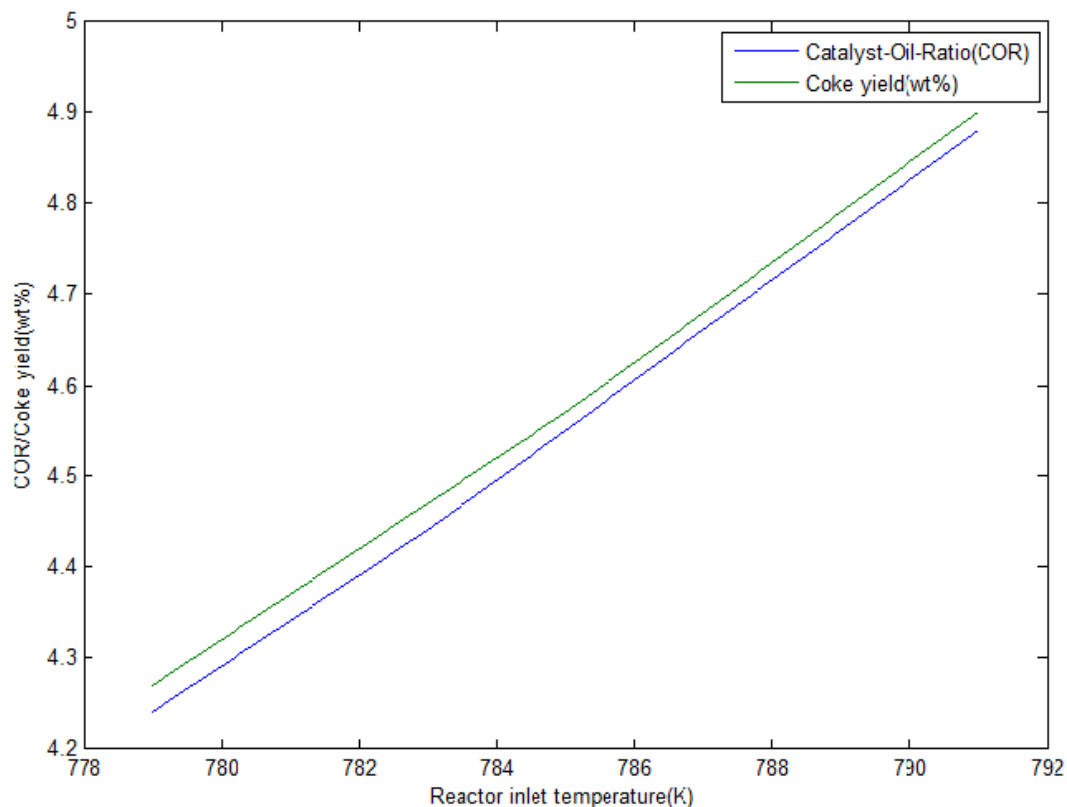
Figure 6. Model result for simulation of FCC catalyst coking

Three critical temperature regimes were identified from the plot in Figure 6. These are:

i. Low operating temperature regime (T<786K): If the riser is operated in this regime (lower region of the graph), the reactions will quench. Hence, operation in this regime is not advisable.

ii. Optimal operating temperature regime (786K<T<788K): In this temperature range, COR and catalyst coke content profiles taper towards each other as shown in Figure 6. This is the regime of optimal riser operation (without excessive coking).

iii. High operating temperature regime (T>788K): In this temperature zone, the two curves diverge from each other again symbolizing excessive coking of the catalyst. Unit operation in this temperature range is also not advisable because it leads to excessive coking and gas production at the expense of the most economical product (gasoline).

4. Conclusions

A 2D pseudo-homogeneous reactor model with a five-lump reaction scheme was used to model the reactions that occur in Fluid Catalytic Cracking (FCC) riser. Mass transfer resistance was incorporated in the model which resulted in the improvement of the accuracy of the model predictions from 89.46% to 98.33% (corresponding to 49.70 wt% gasoline from the present model). Hence, mass transfer resistance plays a significant role in FCC reactions and as such it should not be neglected in the modeling of FCCU riser.

The predicted yield of gasoline by the model here presented is 49.70% with VGO conversion of 79.28% and a coke yield of 4.90% (the degree of accuracy of the model predictions being 98.33%). The model results obtained in this work compare favorably well with plant design data (50% gasoline, 80% VGO conversion and 5% coke).

The coking of the FCC catalyst was also simulated for temperatures ranging from 779K to 791K. It can be inferred from the results of this investigation that an operating temperature range of 786K<T<788K is optimal for FCC. The predicted optimal temperature range corresponds to an optimal catalyst-to-oil ratio (COR) of 4.60-4.71. It is noted that operating an FCC riser within the optimum temperature range has the advantages of reduced catalyst coking rate and less gas production from gasoline over-cracking. Coke is a by-product of FCC; it is less valuable than the other products. It is also expensive to burn it off the catalyst in order to regenerate the catalyst. Gas, on the other hand, is less valuable than gasoline and it is also expensive to compress. Thus, operating the

riser within the optimal temperature range would increase plant profitability by minimizing the yield of coke and gas.

Nomenclature

a	Catalyst activity for non-coking reactions
c_i	Species concentration (weight fraction)
c_p	Specific heat capacity (J/kg-K)
d_{AB}	Collision diameter (m)
D_{AB}	Molecular diffusivity (m/s^2)
D_e	Effective diffusivity (m/s^2)
D_k	Knudsen diffusivity (m/s^2)
D_p	Particle diameter (m)
D^*	Overall diffusivity (m/s^2)
F_i	Flow rate of species i (kg/s)
G_s	Catalyst mass flux (kg/m^2.s)
ΔH_{Ri}	Enthalpy of cracking of species i (kJ/kg)
ΔH_{vap}	Enthalpy of vaporization (kJ/kg)
P	Pressure (atm)
r_e	Average pore radius (m)
r_i	Species reaction rate (kg species (kg catalyst)$^{-1}$s^{-1})
k	Reaction rate constant (s^{-1})
k_r, k_z	Effective thermal conductivity (W/m.K)
k_g	Mass transfer coefficient (m/s)
t	Time (s)
X	Conversion
M_i	Molecular weight species i (kg/kmol)
m	Node number in the horizontal direction
T	Temperature (K)
R	Radius (m)
Δr	Radial spatial interval (m)
n	Node number in the vertical direction
N_A	Molar flux (kmol/m^2.s)
N_{Re}	Particle Reynolds number
N_{sc}	Schmidt number
N_{sh}	Sherwood number
N_r	Number of divisions in radial direction
N_z	Number of divisions in axial direction
V	Reactor volume (m^3)
v_{ij}	Stoichiometric coefficient
v_p	Average particle velocity (m/s)
H	Reactor height (m)
u	Superficial velocity (m/s)
q	Volumetric flow rate (m^3/s)
A_c	Cross-sectional area (m^2)

F_r	Froude number
Δz	Axial spatial interval (m)

Greek letters:

α'	Decay function rate constant
α	Normalized parameter
β	Normalized parameter
γ	Normalized parameter
δ	Decay function constant
ε	Porosity
η	Particle effectiveness factor
η_0	Particle overall effectiveness factor
λ	Normalized parameter
μ	Viscosity (Pa.s^{-1})
π	Pi
φ	Thiele modulus
ψ	Slip factor
ρ	Density (kg/m^3)
σ	Normalized variable
τ	Tortuosity
Ω_D	Collision integral

Subscripts:

i	Species number
j	Reaction number

Abbreviations:

KRPC	Kaduna Refinery & Petrochemicals Company Ltd

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