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ABSTRACT

Under normal Fluid Catalytic Cracking (FCC) conditions, coke is the most important factor that affects catalyst activity. A pseudo homogeneous two - dimensional (2D) model of an industrial 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 riser residence time while under-predicting the reaction time. Mass transfer resistance was incorporated in the reactor model to enhance the accuracy of the results. Finite difference was used to discretise the model equation. This investigation has advanced research into the modeling of FCC riser by predicting catalyst coke content as a function of reaction temperature. The yields of LCO, gasoline, gas and coke that were predicted by the model for industrial risers were 15.54wt%, 49.70wt%, 18.01wt% and 4.90wt% respectively. A feed stock (VGO) conversion of 79.28% was predicted by the model. An optimal operating temperature range of 786K<T<788K was predicted for the riser.

Key words: 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 [2]. 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 and heavy feed stocks (molecular weight > 250) from other refinery operations into high octane gasoline, light fuel oils and gases [2].

FCC unit comprises mainly of the riser, the regenerator and the main fractionators. However, the reactor section of FCC units has been the most active area of research in the industry and academia alike as evidenced by the works of previous researchers [1-9]. Most of the reported works were based on assumptions that either over-simplified the obtained models [1-4, 6 and 8-9] or unduly over-complicated it [5 and 7]. For example, Weekman and Nace [1], did not account for coke formation in their model. Hence, the model of the authors could not predict the coking of FCC catalyst. Fernandes *et al.* [2], 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 over-simplified their models thereby undermining the utility of the predictions.

A 4-lump, 1D model was used by Ahari et al. [3]. The authors were able to capture the temperature drop along the riser and they predicted a gasoline yield of 45%. The major setback of their model was also the assumption of negligible gas phase dispersion. A 5lump reaction scheme was used by Alsabei [4]. The author also based his investigation on negligible dispersion which contradicts the basic principles of heterogeneous catalysis, especially, for porous catalysts such as the molecular sieve type commonly used as FCC catalysts. You and Zhu [6], used a 1D, 4lump model to predict the products yield of FCCU riser, the average gas density, solid and gas phase velocity profiles all as a function of the riser height. The authors predicted a gasoline yield of 45%. non-incorporation However, of mass transfer resistance in their model over-simplified the model. A

4-lump, 1D scheme was also used by Heydari *et al.* [8], to model an industrial riser. The yield of gasoline along the riser under varying conditions of temperature and catalyst-to-oil ratio was predicted by the authors.

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. Even though some of these cited works were able to predict quite reasonable gasoline yield value (45 - 48%), the models are very limited in utility due to their wholesome empirical nature. They offer little understanding of the process, hence restricting scale up to within the process parameters range investigated.

Models of higher dimensionality have also been used by other authors [5, 7 and 9]. Souza et al. [9], used a 2D hydrodynamic, 6-lump model to simulate an industrial riser. The model predicted a gasoline yield of 48%. The authors also neglected mass transfer resistance in their model. Gupta [5], and Lopes et al. [7], used 3D models in their investigations. Gupta [5], used a mechanistic approach involving 50 lumps (pseudo species) to model an industrial FCCU. Lopes et al. [7], 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. However, 3D models are very complex and unwieldy. They also have high costs of computation. In all the models aforementioned, the authors did not simulate the catalyst coke content thereby leaving room for more work to be done in that respect.

This work sought to improve on the existing reports by incorporating a semi-empirical approach via integration of mass transfer resistance scheme, thereby accounting for the lower experimental gasoline yield and longer reaction time when compared to the over-simplified models. This work also explains in real engineering terms the empirical results earlier models reported as functions of vessel geometry. This is to involve a model more amenable to extrapolation. A two-dimensional (2D) quasi-steady state model of an industrial riser is here presented. In this work, a five-lump reaction scheme was used to model the FCC reactions. This investigation has also advanced the works of 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.

2. MATERIALS AND METHODS

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.
- 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 [5].
- 4. There is no heat loss from the riser, and the temperature of the reaction mixture (hydrocarbon vapors and catalyst) falls only because of the endothermicity of the cracking reactions [5].
- 5. The riser dynamic is fast enough to justify a quasisteady state model.

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



Figure 1: Five-lump model [10]

In Figure 1, k_j is the rate constant of reaction j 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:

$$r_{j} = \frac{ac_{i}}{\left(\frac{1}{k_{g}} + \left(\frac{1}{\eta k_{j}}\right)\right)} \quad j = 1, \dots, 8$$

$$\tag{1}$$

In Equation (1), r_j is the rate of reaction of the jth reaction in kg species (kg catalyst)⁻¹s⁻¹, *a* represents

catalyst exponential activity decay given by Equation (2), c_i = species concentration (weight fraction), k_a = mass transfer coefficient of reactant in m/s, $\eta =$ particle effectiveness factor which is given by Equation (3), k_i = reaction rate constant in s⁻¹.

 $a = exp(-k_d c_{coke})$ (2)Where k_d is the catalyst decay constant and has a value of 8.2 [10].

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

 φ is the Thiele modulus.

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

 D_e = effective diffusivity in m/s². Equation (1) is the model rate equation which incorporates mass transfer resistance terms, k_q and η . Equation (1) reverts to the classical first order rate equation when $\frac{1}{k_q} = 0, \eta = 1$. (Previous researchers [10] used the classical first order rate equation: $r_i = k_i c_i$). 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 solid catalysis and it is a function of Thiele modulus. Equation (4) holds for spherical particles. Thiele modulus, φ is the ratio of intrinsic reaction rate to diffusion rate and as such Equation (4) provides a vardstick for determining the rate-determining step in heterogeneous reactions involving solid catalysts.

The basic parameters to be determined in Equations (1)-(4) are D_e and k_g . D_e was estimated from empirical correlations in literature [11], while k_a was estimated from Sherwood number for gases [12].

2.2 Riser reactor model equations

Figure 2 depicts the 2D riser reactor, while the control volume used in deriving the model equations from conservation laws is shown in Figure 3 [11].

2.2.1 Continuity equation

The component continuity equation for the model is as given in Equation (5):

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

Where the superficial velocity, u is given by Equation (6).

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

q is the volumetric flow rate of the gas through interparticle bed voidage, $m^3(fluid)s^{-1}$, D_z and D_r effective diffusivities are in $m^{3}(fluid)m^{-1}(vessel)s^{-1}, (-r_{i})$ is in kg species $kg^{-1}(catalyst) s^{-1}$, A_c is the crosssectional area of the riser in m², c_i is concentration of species, i in weight fraction, ρ_B is the density of the bed in kg/m^3 , r and z are the radial and axial distances respectively in m.



Figure 2: Control volume in riser reactor



Figure 3: Control volume

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) [3]:

$$\psi = \frac{u_0}{\varepsilon v_p} = 1 + \frac{5.6}{Fr} + 0.47 F r_t^{0.47} \tag{7}$$

In (7), Fr is the Froude number and Fr_t is the Froude number at terminal velocity, ψ is the catalyst slip factor, ε is the average voidage of the reactor and v_p is the average particle velocity in the riser in m/s.

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

Here, *g* is the acceleration due to gravity (m^2/s) , D is the diameter of the riser in m. The average particle velocity in the riser, v_p is given by Equation (9).

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

 G_s is the catalyst mass flux in kg/m².s, ρ_s is density of solid in kg/m³. 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.

$$\varepsilon = 1 - \frac{G_s \psi}{u_0 \rho_s + G_s \psi} \tag{10}$$

2.2.3 Energy balance

Equation (11) is the model energy balance.

$$k_{z}\frac{\partial^{2}T}{\partial z^{2}} + k_{r}\left(\frac{\partial^{2}T}{\partial r^{2}} + \frac{1}{r}\frac{\partial T}{\partial r}\right) - G_{s}c_{p}\frac{\partial T}{\partial z} + \rho_{B}\sum_{i=1}^{8}(-r_{i})(-\Delta H_{Ri}) = 0 \quad (11)$$

In (11), k_z and k_r are the effective thermal conductivities in W/m.K, c_p is specific heat capacity in J/kg-K, ΔH_{Ri} is enthalpy of cracking of species i in J/kg. The coupling between the riser and the regenerator is expressed in the model by Equation (12).

$$F_{cat}c_{pcat}(T_0 - T_{cat}) + F_f c_{pfl}(T_{vap} - T_f) + F_f c_{nfn}(T_0 - T_{van}) + F_f \Delta H_{van} = 0 (1)$$

 $+ F_f c_{pfv}(T_0 - T_{vap}) + F_f \Delta H_{vap} = 0$ (12) F_{cat} is catalyst flow rate in kg/s, F_f is feed flow rate in kg/s, c_{pcat} is the specific heat capacity of the catalyst in kJ/kg-K, c_{pfl} is the specific heat capacity of liquid feed in J/kg-K, c_{pfv} is the specific heat capacity of vapor feed in J/kg-K, T_0 is inlet temperature of riser in K, T_{cat} is inlet temperature of catalyst in K, T_f is feed inlet temperature in K, T_{vap} is feed vaporization temperature in K and ΔH_{vap} is enthalpy of vaporization of the feed in /kg. The governing equations, Equations (5) and (11) were expressed in a general, normalized form as follows:

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

Here, $\sigma = {c_i/c_0} \text{ or } T/T_0$, $r^* = r/R$, $z^* = z/H$. The coefficients in Equation (13) are given by the following expressions:

$$\begin{aligned} \alpha_{1} &= \alpha_{2} = 1 , \ \beta_{1} = \frac{R^{2} D_{z}}{H^{2} D_{r}}, \ \beta_{2} = \frac{R^{2} k_{z}}{H^{2} k_{r}}, \ \gamma_{1} = \frac{-UR^{2}}{HD_{r}}, \ \gamma_{2} = \frac{-G c_{p} R^{2}}{Hk_{r}}, \\ \lambda_{1} &= \frac{R^{2} \rho_{B}}{D_{r} c_{0}}, \ \lambda_{2} = \frac{R^{2} \rho_{B}}{k_{r} T_{0}} \end{aligned}$$
(14)

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

Boundary conditions:

Finite difference numerical scheme was used to discretize the governing equation; Equation (13) that was developed for the model. A code was written in MATLAB to solve the model equations. Data obtained from open literature [2] and from Kaduna Refinery and Petrochemicals Company (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.

2.3 Model data

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

Table 1: Kinetic const	nts for five-lun	np model
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Reaction number	Kinetic constant, 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	
a [1 a]		

Source [10]

Table 2: Entha	lpies of	cracking
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S/N	Cracking reaction	Enthalpy, 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

Source [3]

MODELLING AND SIMULATION OF COKING IN THE RISER OF AN INDUSTRIAL FCC UNIT,

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

Source [3]

|--|

Property	Value	Source
Specific gravity	0.89-0.93	[5]
Viscosity	1.4x10 ⁻⁵ N.s/m ²	[3]
Vaporization temperature	698K	[3]
Enthalpy of vaporization	190kJ/kg	[3]

Table 5: Model parameters (Source: KRPC Plant data)

IaDIE	5. Mouel parameters (50		Flain uala)
S/N	Parameter	Value	Source
1	Reactor inlet temperature, T ₀ (K)	791	KRPC Plant data
2	Feed inlet temperature, T _f (K)	613	KRPC Plant data
3	Catalyst inlet temperature, T _{cat} (K)	927	KRPC Plant data
4	Specific heat capacity (liquid feed), cpfl (J/kg-K)	2.67e3	[3]
5	Specific heat capacity (vapor feed), cpvf (J/kg-K)	3.30e3	[3]
6	Specific heat capacity (catalyst), cpcat (I/kg-K)	1.09e3	[3]
7	Feed vaporization temperature, T _{vap} (K)	698	KRPC Plant data
8	vaporization, delHvap	190e3	[3]
9	Density (solid catalyst), ρ_s (kg/m ³)	1250	KRPC Plant data
10	Catalyst velocity, <i>U_c</i> (m/s)	5	[5]
11	Gas superficial velocity, U (m/s)	18	KRPC Plant data
12	Slip factor, psi	2	KRPC Plant data
13	Feed flow rate, F _f (kg/s)	35.5	KRPC Plant data
14	Riser diameter, D _R (m)	1.146	KRPC Plant data
15	Riser height, H (m)	25	KRPC Plant data

	S/N	Parameter	Value	Source
	16	Pore diameter, P ₄ (m)	2.00e-9	KRPC
	10		21000	Plant data
	17	Particle diameter, D_p	60e-6	KRPC Diant data
		(III) Gas average density		Flaint uata
18	ρ_a (kg/m ³)	0.92	Plant data	
	10	Gas average viscosity	1 40 5	[0]
19	μ_g (Pa.s ⁻¹)	1.40e-5	[3]	
	20	Riser pressure, P	2 94	KRPC
	20	(atm)	2.74	Plant data
	21	Particle tortuosity, τ_n	7	[11]

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 literature and plant (KRPC) data (Table 5). Figure 4 shows that the products of FCC reactions are formed within the first 2m of the reactor (the reaction zone). This is because feed vaporization occurs in the reaction zone followed by cracking which occurs instantaneously as the vapor feed contacts the hot catalyst entering the riser from the regenerator. Also, in Figure 4, it can be seen that after reaching the peak value, the yield of each of the products remains constant throughout the remaining length of the riser. This is because the residence time for industrial risers is set at 2s so that the gaseous products are separated from the catalyst soon enough to avoid over-cracking of gasoline [5].

Figure 5 presents the predicted conversion of VGO as a function of reactor height. A conversion of 79.28% was predicted by the model. In Figure 5, VGO conversion is observed to occur within the first 2m of the reactor which corresponds to the reaction zone of the reactor. The reaction zone is also the zone within which the products are formed as depicted in Figure 4. The other zones of the reactor are the middle and upper zones. The middle zone is the region of gasoline over-cracking for maximum gas production when gas becomes the key product.

The validation of model results with KRPC and literature data is as shown in Table 5. The deviation of the model predictions from KRPC plant data were computed and presented in the last column of Table 5. The industrial riser model here presented compare favorably well with KRPC plant data and literature results because the maximum deviation of the predictions is 3.54%. This value is less than the error limit of 5%.

0.9



Table 5: Validation of model results with plant data

Species	Conv./Yield, wt% (KRPC plant data)	Conv./Yield, wt% [2]	Conv./Yield, wt% (Model)	% Dev. from Plant data
VGO	80.00	78.00	79.28	0.90
LCO	15.15	10.00	15.54	2.57
Gasoline	50.00	48.00	49.70	0.60
Gas	17.88	18.00	18.01	0.73
Coke	5.08	5.00	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. In Figure 6, it can be seen that the reactor temperature increases monotonously as the catalyst-to-oil ratio (COR) increases. This is because the enthalpy of the incoming catalyst from the regenerator determines the temperature at the inlet and the outlet of the riser.

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 temperature operating 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). Plant operation at reduced coking rate will reduce the cost of catalyst regeneration which in turn increases plant profitability.
- iii. High operating temperature regime (T>788K): In this temperature zone, the two curves tend to 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).

Figure 7 depicts the variation of COR and the yield of gasoline with reactor temperature. The average yield of gasoline within the proposed optimum temperature range (786K<T<788K) is 47.33%; this value falls within the range of gasoline yield predicted in

literature [2 and 10] and obtainable from KRPC (45%-50%).

4. CONCLUSIONS

At the end of this investigation, the yields of LCO, gasoline, gas and coke predicted by the model for industrial risers are 15.54wt%, 49.70wt%, 18.01wt% and 4.90wt% respectively. A VGO conversion of 79.28% was predicted by the model. It can be inferred from the results of this investigation that an operating temperature range of 786K<T<788K and a catalyst to oil ratio (COR) range of 4.60-4.71 are optimal for FCC. Amongst the operational objectives of FCC unit are plant operation at reduced coking rate (coke is expensive to burn off the catalyst) and that gas production should not be in excess for gas is less valuable and yet expensive to compress. FCC riser operation within the optimal temperature range ensures that these economic objectives are achieved by minimizing the coking of the catalyst while ensuring that the desired product (gasoline) is not over-cracked to gas. The results of this investigation also showed that feed stock conversion and product formation occur within the first 2m of the reactor.

NOMENCLATURE

а	Catalyst activity
C;	Species concentration (weight fraction)
C_n	Specific heat capacity (I/kg-K)
d AD	Collision diameter (m)
D_{AB}	Molecular diffusivity (m/s^2)
D_{AB}	Effective diffusivity (m/s^2)
D_{ν}	Knudsen diffusivity (m/s^2)
D_n	Particle diameter (m)
D^{*}	Overall diffusivity (m/s^2)
F_i	Flow rate of species i (kg/s)
Ğ	Catalyst mass flux $(kg/m^2.s)$
ΔH_{Ri}	Enthalpy of cracking of species <i>i</i> (kJ/kg)
ΔH _{vap}	Enthalpy of vaporization (kJ/kg)
Р	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 _d	Catalyst decay constant
k _r , k _z	Effective thermal conductivity (W/m.K)
k_{g}	Mass transfer coefficient (m/s)
t	Time (s)
Х	Conversion
Mi	Molecular weight species <i>i</i> (kg/kmol)
m	Node number in the horizontal direction
Т	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

Number of divisions in radial direction
Number of divisions in axial direction
Reactor volume (m ³)
Stoichiometric coefficient
Average particle velocity (m/s)
Reactor height (m)
Superficial velocity (m/s)
Volumetric flow rate (m ³ /s)
Cross-sectional area (m ²)
Froude number
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:

 N_r

 N_z

 $V\\ v_{ij}\\ v_p$

Η

u

q

Ac Fr

 Δz

KRPC

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