e-ISSN: 2582-5208
International Research Journal of Modernization in Engineering Technology and Science
(Peer-Reviewed, Open Access, Fully Refereed International Journal)
Volume:04/Issue:05/May-2022 Impact Factor- 6.752 www.irjmets.com

MODELLING FLUID CATALYTIC CRACKING REACTOR FOR CRACKING OF GAS OIL

Desire Alexander Jack[*1], **Dr. Eruni Uku Philip**[*2], **Prof. Ujile Awajiogak**[*3]

[*1]B.Tech, Chemical Engineering, Rivers State University, Portharcourt, Rivers State, Nigeria.

[*2]Phd, Chemical Engineering, Rivers State University, Portharcourt, Rivers State, Nigeria.

[*3]Professor Of Chemical Engineering, Rivers State University, Portharcourt, Rivers State, Nigeria.

ABSTRACT

In the present work, a mathematical model for the Riser Reactor of Fluid Catalytic Cracking unit has been presented. The riser is considered as a one dimensional plug flow reactor incorporating the six lump model for kinetics of cracking reactions. The mass and energy conservation equations have been properly applied to predict the outputs. Outputs, representing feedstock charge, Diesel fraction, Gasoline fraction, LPG fraction, Light Gas and Coke, are employed to approach the kinetic of reactions. The fourth order Runge-Kutta's method is used to integrate the coupled, non-linear ordinary differential equations of the riser. The model has been validated using the plant data of a commercial FCC unit (NPHRC),with a reactor dimension of (Height=22.9m , Diameter =2.9m) which predicted Gasoline(model=0.469, plant=0.459), Diesel (model=0.217, plant=0.18), LPG (model=0.145, plant =0.17), Dry Gas(model=0.043, plant=0.054), Coke(model=0.051, plant=0.052). A parametric sensitivity analysis was also carried out and from observation, Catalyst Circulation Rate has strong influence on Gas-Oil conversion as well as Feed Preheat Temperature, Feed-Rate, Catalyst Temperature in the yield of Gasoline, Diesel, LPG, etc as elaborately discussed in the Results . However, at a constant feed rate of 67.8kg/s, this simulation model predicted an optimum Gasoline yield of 0.47 (at 3% deviation from plant data) at a feed temperature of 592kelvin and a Catalyst to Oil Ratio of 5.48 and a maximum Diesel yield of 0.2470 at a Catalyst to Oil Ratio of 3.0 for enhanced productivity of the FCC Unit

Keywords: Riser, Reactor, Cracking, Simulation, Model.

I. INTRODUCTION

Fluidization is the operation by which solid particles are transformed into a fluid like state through continuous contact in a gas or liquid.

Cracking is the breaking down of heavy hydrocarbon molecules into products of lighter molecular weight. This process can either be thermal or catalytic. Catalytic cracking involves the catalytic breaking down of heavy molecular weight hydrocarbons in the presence of a catalyst and high temperature. It can be either be carried out in a continuous, slowly descending layer of spherical catalysts or in a fluidized bed of a powdered or micro-spherical catalyst.

Fluid catalytic cracking (FCC) is one of the most important processes used in transforming heavy hydrocarbons to Gasoline and other valuable products with a higher octane value in petroleum refineries. It is majorly used in converting crude oil hydrocarbon fractions with high molecular weight into more valuable products like Gasoline, olefinic gases, and other products.

Fluid catalytic cracking is a technology in existence, more than 70 years . It was designed to continuously crack heavy divisions of petroleum fractions, having replaced other cyclic processes used previously. FCC is mainly used to crack vacuum Gas-Oil and other heavy fractions of petroleum. The main product that is desired from the FCC is Gasoline, which can constitute about 60% of the Gasoline pool in a refinery. Figure 1.0 shows where and how the FCCU is connected to the remaining processes of a refinery.

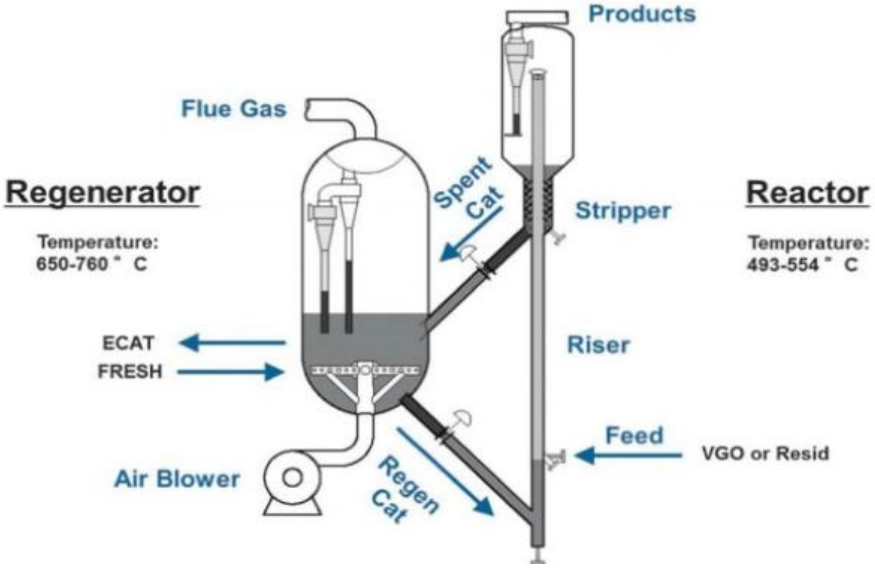

Figure 1: A Schematic Diagram Of a Fluid Catalytic Cracking Unit by Hans[1]

In previous years, cracking of petroleum hydrocarbons was usually carried out via thermal cracking, but of recent years, it has been almost completely replaced by catalytic cracking due to its increased production of Gasoline with a higher octane rating. It also produces gases as bye product e.g olefins, which has more economic value, than those produced by thermal cracking.

The feedstock to FCC unit is usually that portion of the crude oil(e.g Heavy Gas-Oil or vacuum Gas-Oil) with a boiling temperature of 330C or higher at normal atmospheric pressure and an average molecular weight ranging from about 210 to 620 or higher. This portion of crude oil is often referred to as heavy Gas-Oil or vacuum Gas-Oil (HVGO). In the fluid catalytic cracking process, the feedstock is heated to a high temperature, moderate pressure, and brought into intimate contact with a hot, powdered catalyst which facilitates the cracking process. The catalyst breaks the long-chain of the high-boiling hydrocarbon liquids into shorter molecules, which are eventually received as a vapour.

In the present energetic framework, upgrading heavy petroleum fractions have become of more increasing importance since the world demand of energy is on the continuous increase .Hence Conversion of Vacuum Gas Oils into more valuable transportation fuels by fluid catalytic cracking or hydro cracking pose a major issue for the refining industry. Vacuum Gas Oils (VGOs) are high boiling point petroleum fractions(350-550C) that contain large quantities of sulfur and nitrogen compounds. Since these hetero-atomic compounds are poisonous to the process catalysts, Vacuum Gas Oils have to be reformed by a hydro treating stage before any further transformation processing. Among these chemical families, particular attention has to be paid to basic and non-basic nitrogen compounds(respectively acridine and carbazole-derivates) which are known to pose or exhibit inhibitory or refractory behavior to most hydrotreating reactions depending on their basic or non-basic nature.

A modern FCC unit is made up of different sections such as a riser reactor, a stripper, a disengager, a regenerator, a main fractionator, catalyst transport lines (spent catalyst standpipe and regenerated catalyst standpipe) and several other auxiliary units such as: cyclones, air blower, expander, wet gas compressor, feed pre-heater, air heater, catalyst cooler, etc.

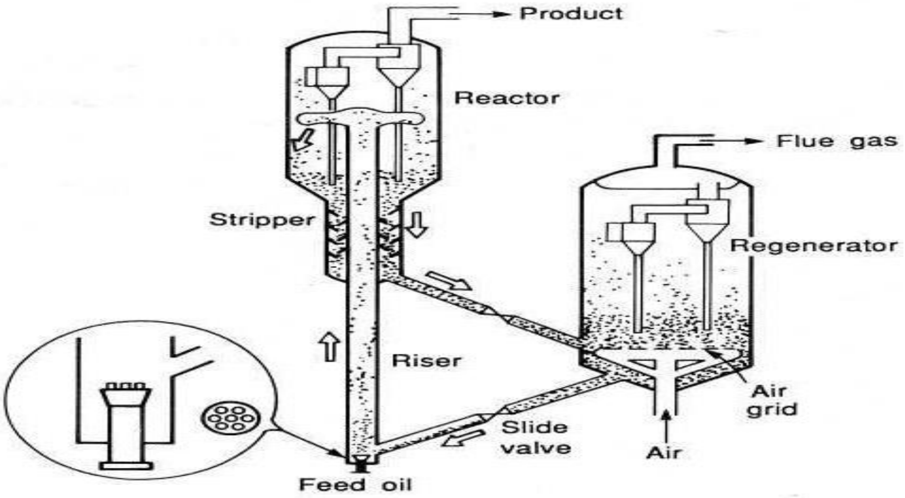

Figure 2: A Schematic Diagram Of FCCU Plant by Kunni [2]

The heteroatomic compounds in fluid catalytic cracking are poisonous to the process catalysts, Vacuum Gas Oils have to be reformed by a hydrotreating stage before any further transformation processing. Among these chemical families, particular attention has to be paid to basic and non-basic nitrogen compounds (respectively acridine and carbazole-derivates) which are known to pose or exhibit inhibitory or refractory behavior to most hydro-treating reactions depending on their basic or non-basic nature.

II. PROCESS DESCRIPTION

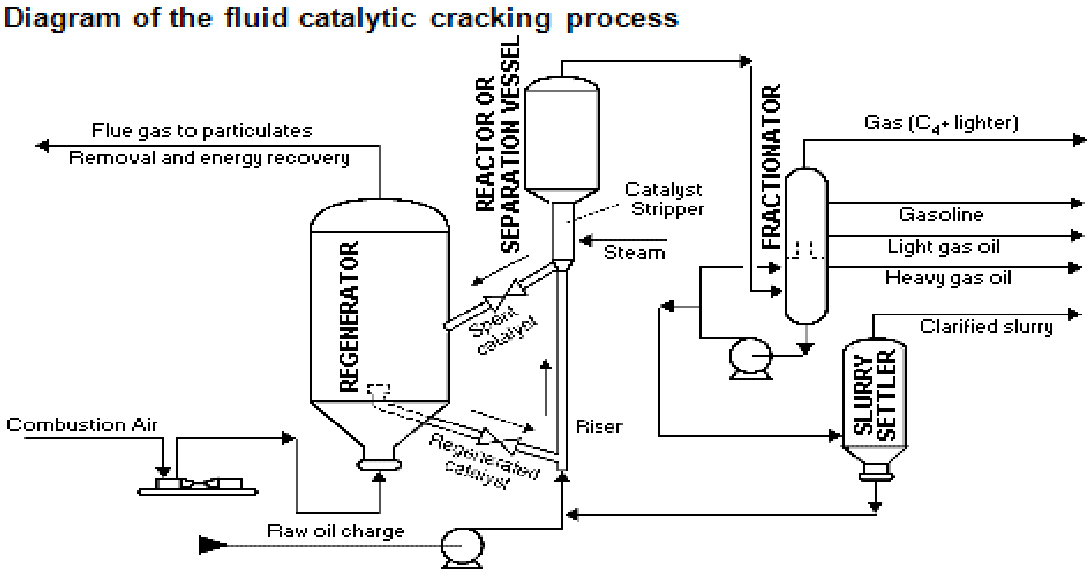

Figure 3: Schematic Diagram Of a Fluid Catalytic Cracking Unit by Yadav[3].

A Fluid Catalytic Cracking Unit (FCCU) obtains it's feed which are residues from different parts of a refinery (atmospheric and vacuum distillation units). It's main purpose is the cracking of heavy molecules of the residues. This process is endothermic in nature, and it takes place in a vertical tube reactor with ascending flow (riser).

The FCC process starts with the injection of the feed, especially VGO, into the riser. It is injected with special nozzles to create some droplets. The feed can also be blended with an inert gas to aid in the atomisation process. After being injected The feedstock charge gets in intimate contact with a catalyst at a high temperature (500 to 700C) and it is cracked to give valuable products, such as Gasoline and LPG. After that, the products are separated from the catalyst to halt its further cracking and to prevent loss of performance of the process. The reactions also produce, light gasoil, fuel gas and Coke that is eventually deposited on the surface of the catalyst. The Coke deposition reduces the reaction rate and hence the conversion of the reactant. In order to recover its activity and purity, the catalyst is sent to a regenerator. Air is blown in the regenerator which eventually forms a non-homogeneous fluidized bed with the catalyst. The Coke on the catalyst surface is thus burnt in this bed. The burning of the Coke has two essential functions: a-) the regeneration of the catalyst, restoring its catalytic activity and, b-) the increase of the catalyst temperature to provide energy to the cracking when it returns to the riser.

The main catalyst used in FCC reaction is the Zeolite catalyst. It enables the conversion process to take place. This catalyst sometimes break into fine particles due to the pneumatic transportation required, which eventually leads to losses of the catalysts through various system network, most especially at the gas and catalysts separation points and the cyclones. Of recent, there are over 360 fluidized catalytic cracking (FCC) units in different refineries around the world, producing almost 400 million gallons of Gasoline daily. This catalytic cracking process is regarded as one of the most important developments of Chemical Engineering of the last century (NACS, 2002). Because of its flexibility in it's operation, the FCC process is quite popular, as it can be optimised to meet the demands of the local or foreign market. The process converts residual fractions having low commercial value into Gasoline and GLP hereby enhancing profit. The cracking process takes place in the presence of catalyst pellets (e.g silica or alumina), which are heated at high temperatures. As the catalytic cracking reaction progresses, there is a gradual deposition of Coke on the catalyst surface, hence negatively altering it's activity. Because of the importance of FCC unit in refining, a formulation of realistic mathematical models that can describe the dynamic behaviour of FCC unit equipments in steady state condition is very important. Accurate models can be used as a powerful tool in studying the influence of process variables on the output of the system.

III. MODELING AND ANALYSIS

3.1 Overview

This section aims at developing a mathematical model of a Riser in an industrial fluid catalytic cracking unit. It considers the chemical reactions in the Riser, some of it's hydrodynamics, and also uses a six lump model to approach the reaction kinetics while stating the assumptions made during model development. This mathematical model is developed via the application of conservation principle of mass and energy on a differential section of the riser.

3.2 Methodology

In this section, the contextual logical scheme utilized in this research which involves the collection of data, it's utilization in line with the earlier aforementioned objectives was briefly discussed as given below:

3.2.1 Collection of Data

Data on the feed and products in this work were sourced for and documented. These sources include various textbooks, Chemical Engineering handbooks, journals, operating manuals and internet sites. Data collected from PHRC include mass flow rates for feed and products.

3.2.2Data Utilization

Some of the data obtained were used to carry out the necessary mass and energy balance necessary to model or characterize the system.

3.2.3 Method of Analysis

The method used in this work involves modelling the catalytic cracking process and determining the effect of the variables on the fluid catalytic cracking riser performance via application of the conservation principle on mass and energy and also incorporating the pressure drop equation and the hydrodynamic model which estimates the Froude's number and the particle terminal velocity in the riser via the Archimedes and Reynolds number relationship based on the intermediate regime. The measure used in quantifying the products is in weight fractions.

3.3 Kinetic Model

A six lump Kinetic model was used to approach the reaction kinetics. The six lump is actually a modification of the model given by Du [4], and was given by Raj [5].

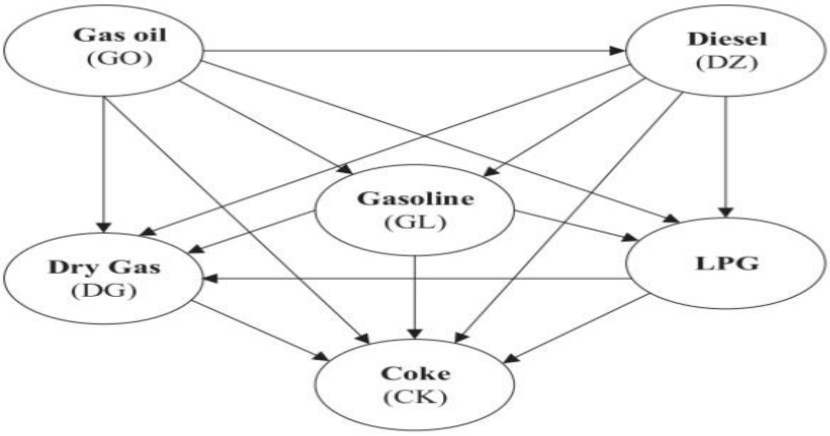

Figure 4: Six Lump Catalytic Cracking Model by Raj [5]

Reaction rate of the individual component has earlier been given in equation 2.10,in the previous chapter as:

$r_{i,j}=\Sigma K_{ij}*y_i^n*\eta*h$,

Where

h=Catalyst deactivation constant,

$r_{i,j}$ = Rate constants for the respective lumps

η = Effectiveness factor:

n=2 for Gas-Oil,

n=1 for other components

3.4 Riser Model:

Figure. 5 Shows an hypothetical representation of an industrial riser in most FCC Units. In this research, the reactants, products and catalyst are assumed to be in plug flow and the riser is modelled as a plug flow reactor.

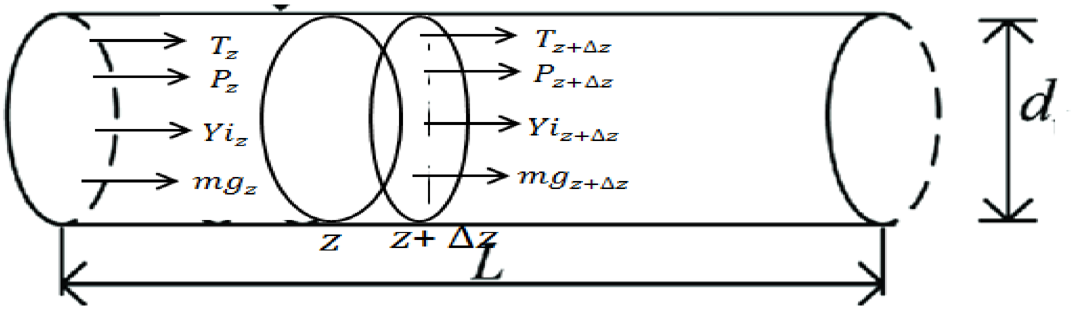

Figure 5: A Differential Section of a Riser

Where T, P, y_i , dz , is the reactor temperature, pressure, mass fraction of component "i", riser differential length.

3.4.1. Model Assumptions

The following assumptions were made while developing the riser model:

- One dimensional plug flow without axial mixing prevails in the riser
- Steady state operation
- The riser wall is well thermally insulated so heat loss is negligible .
- The pressure drop through the riser length is due to the static head of the catalyst
- Vaporization occurs instantaneously in entrance of the riser.
- Two distinct phases (i) solid phase (catalyst and Coke), and (ii) gas phase (vapors of feed and product hydrocarbon, and steam) describe each volume element.
- Each volume element, solid and gas phases are assumed to be well mixed so that the two phases have the same temperature.
- The gas-solid flow along the riser height is fully developed.

The rate of reaction (r_i) can be gotten from the six lump scheme earlier given in Figure 4

$$-r_1 = (K_{12} + K_{13} + K_{14} + K_{15} + K_{16})y_1^2\eta h \quad (1)$$

$$-r_2 = ((K_{23} + K_{24} + K_{25} + K_{26})y_2 - K_{12}y_1^2)\eta h \quad (2)$$

$$-r_3 = ((K_{24} + K_{35} + K_{36})y_3 - K_{13}y_1^2 - K_{23}y_2)\eta h \quad (3)$$

$$-r_4 = \left((K_{45} + K_{46})y_4 - (K_{14}y_1^2 + K_{24}y_2 + K_{34}y_3)\right)\eta h \quad . \quad (4)$$

$$-r_5 = (K_{15}y_1^2 + K_{25}y_2 + K_{35}y_3 + K_{45}y_4 - K_{45}y_5)\eta h \quad (5)$$

$$-r_6 = (K_{16}y_1^2 + K_{26}y_2 + K_{36}y_3 + K_{46}y_4 + K_{56}y_5)\eta h \quad (6)$$

Where K_{ij} are the rate constants for the respective lumps

h=Catalyst deactivation constant,

η = Effectiveness factor:

$$\eta = {}^{1}/_{u} * \left({}^{1}/_{tanh(3u)} - {}^{1}/_{3u}\right) \quad (7)$$

Where, u= Thiele-modulus

$$u = {}^{R}/_{3} = ({}^{K_j}/_{D_e})^{0.5} \quad (8)$$

Equation (8) is for first order reaction

While for n_{th} order reactions

$$u = ({}^{(n+1)}/_{2})^{0.5} * {}^{R}/_{3} * \left(\frac{K_j * y_j^{(n-1)}}{D_e}\right)^{0.5} \quad (9)$$

Where K_j is the reaction rate constant for the individual lumps,

D_e = Effective diffusivity (m/s²).

$h = Exp(-K_d * t_c)$xp(-K_d*t_c) (10)

Where K_d is the catalyst deactivation coefficient which is expressed as

$$K_d = k_{do}exp({}^{-E}/_{RT}) \quad (11)$$

Catalyst bulk density, ρ_b is given by

$$\rho_b = \rho_c(1 - E_g) \quad (12)$$

Where E_g=Gas fraction.

Solid volume fraction:

$$E_s = m_s/(\rho_s * V_s * A_r) \quad (13)$$

Gas fraction (E_g):

$$E_g = m_g/\left(\rho_g * V_g * A_r\right) \quad (14)$$

3.4.3 Model Equations For The Various Lumps

By combining the respective rate laws given in Equation(1-6) ,we obtain:

For Vacuum Gas-Oil Lump:

$$ {}^{dy_1}/_{dz} = \rho_g A_r {}^{E_g}/_{m_{fg}} (K_{12} + K_{13} + K_{14} + K_{15} + K_{16})y_1^2\eta h \quad (15)$$

For Diesel Lump:

$$ {}^{dy_2}/_{dz} = -\rho_g A_r {}^{E_g}/_{m_{fg}} ((K_{23} + K_{24} + K_{25} + K_{26})y_2 - K_{12}y_1^2)\eta h \quad (16)$$

For Gasoline Lump:

$$ {}^{dy_3}/_{dz} = -\rho_g A_r {}^{E_g}/_{m_{fg}} ((K_{24} + K_{35} + K_{36})y_3 - K_{13}y_1^2 - K_{23}y_2)\eta h \quad (17)$$

For LPG Lump:

$$ {}^{dy_4}/_{dz} = -\rho_g A_r {}^{E_g}/_{m_{fg}} \left((K_{45} + K_{46})y_4 - (K_{14}y_1^2 + K_{24}y_2 + K_{34}y_3)\right)\eta h \quad (18)$$

For Dry Gas (C_1-C_2) Lump:

$$ {}^{dy_5}/_{dz} = \rho_g A_r {}^{E_g}/_{m_{fg}} (K_{15}y_1^2 + K_{25}y_2 + K_{35}y_3 + K_{45}y_4 - K_{45}y_5)\eta h \qquad (19)$$

For Coke Lump:

$$ {}^{dy_6}/_{dz} = \rho_g A_r {}^{E_g}/_{m_{fg}} (K_{16}y_1^2 + K_{26}y_2 + K_{36}y_3 + K_{46}y_4 + K_{56}y_5)\eta h \qquad (20)$$

3.4.4 Effective Diffusivity of Gas-Oil and its Products

$$D_e = D_k a {}^{\sigma_c}/_{\tau} \qquad (21)$$

Where D_e=Effective diffusivity of the gas

σ_c=Constriction factor.

D_k=Knudsen diffusivity.

τ =Tortuosity

The Knudsen diffusivity, D_k, can be estimated thus

$$D_k = {}^{d_{pore}}/_3 (8R_g {}^{T_g}/_{(\pi MW_i)}))^{0.5} \qquad (22)$$

d_{pore}= Particle pore diameter

MW_i=Average molecular weight of the oil-gas. .

R_g=Universal gas constant

3.5 Catalyst Residence Time:

The Catalyst Residence Time can be expressed as:

$$ {}^{dt_c}/_{dz} = {}^1/_{U_p} \qquad (23)$$

$$t_c = \int_0^H {}^1/_{(U_p)} dz \qquad (24)$$

Where,

U_p = Solid Particle Velocity;

t_c = Catalyst Residence Time

3.6 Gas Phase Residence Time:

Similar to the Catalyst Residence Time for the riser's differential section , the Gas Phase Residence Time can be expressed as

$$ {}^{dt_g}/_{dz} = {}^1/_{U_g} \qquad (25)$$

$$t_g = \int_0^H {}^1/_{(U_g)} dz \qquad (26)$$

3.7 Hydrodynamic Model of the FCCU Riser Reactor:

The hydrodynamics presented herein tries to describe or mimic the real situation in a FCCU-riser reactor.. The correlation of Patience [6], for slip factor evaluation was used in this work, whereby the numerical value of the slip factor , defined as the ratio of the gas interstitial velocity, U_g, to the average particle velocity, Up .

$$\Psi = {}^{U_g}/_{U_p} \qquad (27)$$

Where,

U_g=Vapour phase velocity,

U_p =Average particle velocity,

Slip factor can also be written as

$$\Psi = 1 + {}^{5.6}/_{Fr} + 0.47Fr_t^{0.41} \qquad (28)$$

Fr =Froude's number

Fr_t=Froude's number at terminal velocity

$$Fr = U_0(gd)^{-0.5} \tag{29}$$

$$Fr_t = U_t(gd)^{-0.5} \tag{30}$$

The Superficial Gas Velocity (U_o) can be expressed as

$$U_o = {}^{m_g}\!/_{A\rho_g} \tag{31}$$

Vapour Phase Velocity (U_g):

$$U_g = \frac{U_o}{E_g} = {}^{m_g}\!\Big/_{(A\rho_g E_g)} \tag{32}$$

The Average Particle Velocity (U_p) is given below:

$$Up = {}^{(m_{catalyst}\Psi + \rho_c m_g\ /\rho_g)}\Big/_{(\ \rho_c A\Psi)} \tag{33}$$

While E_g gives,

$$\mathrm{E}_g = \left({}^{\rho_c m_g}\Big/_{(\rho_g m_{catalyst}\Psi + \rho_c m_g)} \right) \tag{34}$$

Where $\rho_g = \frac{PMw_g}{RT}$ (35)

$U_g = {}^{m_g}\Big/_{(A\rho_g E_g)}$ earlier given in Equation(32) can be fully expressed as

$$U_g = \frac{\left(m_{catalyst}\Psi + \rho_c\left(mf_g(1-y_6)+m_{steam}\right)*\frac{RT}{PMw_g}\right)}{A\rho_c} \tag{36}$$

Where, Mw_g (Vapor Phase Average Molecular Weight)

$$Mw_g = \frac{(1-y_6+\frac{m_{ds}+m_{ls}}{mf_g})}{(\frac{y_1}{Mw_1}+\frac{y_2}{Mw_2}+\frac{y_3}{Mw_3}+\frac{y_4}{Mw_4}+\frac{y_5}{Mw_5}+\frac{m_{ds}+m_{ls}}{0.018mf_g})} \tag{37}$$

3.7.1 Particle Terminal Velocity:

There are different correlations that exist in literature for calculating the particle terminal velocity, Ut. In general sense, the terminal velocity is usually estimated for three zones: Stokes, intermediate, and Newton zones. These zones are classified according to Archimedes number, Ar_n , which defines the limit or boundaries amongst the zones. The Stokes regime is valid for $Ar_n < 32.9$, intermediate regime holds for $32.9 < Ar_n < 106.5$, and the Newton regime is defined for $Ar_n > 106.5$. In this study, the following correlation for intermediate regime was used in calculating Reynolds number based on particle terminal velocity.

$$Ar_n = \frac{\rho_g(\rho_c-\rho_g)gd_p^3}{\mu_g^3} \tag{38}$$

Where Ar_n=Archimedes number.

$$Re_t = \frac{Ar_n}{(18+(2.3348-1.7439sph)*{Ar_n}^{0.5})} \tag{39}$$

Re_t = Reynold's number at the terminal velocity

But $U_t = Re_t\mu_g/(d_p * \rho_g)$ (40)

, Substituting "Re_t" in Equation 39 into 40, we have

$$U_t = \frac{Ar_n*\mu_g}{(18+(2.3348-1.7439sph)*{Ar_n}^{0.5})*(d_p*\rho_g)} \tag{41}$$

Substituting the value of Ar_n earlier given in equation (38) ,

$$U_t = \frac{(\rho_g(\rho_c-\rho_g)gd_p^3)}{\left(18+(2.3348-1.7439sph)*(\frac{\rho_g(\rho_c-\rho_g)gd_p^3}{\mu_g^3}\ )^{0.5}\right)*(d_p*\rho_g)*{\mu_g}^2} \tag{42}$$

Putting the value of U_t in the above expression, we obtain a new expression for Fr_t we have,

$$Fr_t = \frac{(\rho_g(\rho_c-\rho_g)gd_p^3)*(gd)^{-0.5}}{\left(18+(2.3348-1.7439sph)*(\frac{\rho_g(\rho_c-\rho_g)gd_p^3}{\mu_g^3})^{0.5}\right)*(d_p*\rho_g)*\mu_g{}^2} \qquad (43)$$

3.8 Pressure Gradient Along the Riser:

$$\frac{dP}{dz}=\rho_{cat}g(1-E_g) \qquad (44)$$

It can also be put in the form

$$\frac{dP}{dz}=\rho_{cat}g\ ({\rho_g m_{catalyst}\Psi}/{(\rho_g \mathrm{m}_{catalyst}\Psi+\rho_c m_g)}) \qquad (45)$$

3.9 Energy Balance:

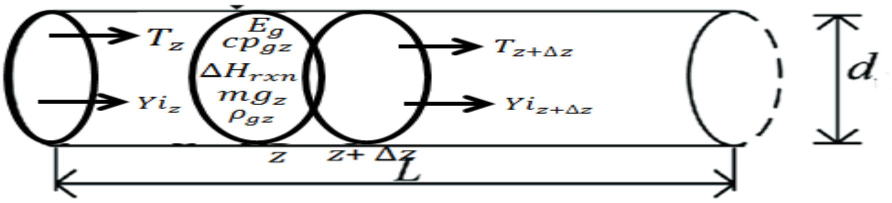

Figure 6: Flow of Energy Along the Riser

The model equation for the energy balance is given below:

$$dT/_{dz} = -\frac{1}{(M_{cat}*Cp_{cat}+M_{coke}*Cp_{coke}+M_g*Cp_g+M_{steam}*Cp_{steam})} * AE_g\rho_g h((K_{12}\Delta H_{12}+K_{13}\Delta H_{13}+K_{14}\Delta H_{14}+K_{15}\Delta H_{15}+K_{16}\Delta H_{16})y_1^2+(K_{23}\Delta H_{23}+K_{24}\Delta H_{24}+K_{25}\Delta H_{25}+K_{26}\Delta H_{26})y_2+(K_{34}\Delta H_{34}+K_{35}\Delta H_{35}+K_{36}\Delta H_{36})y_3+(K_{45}\Delta H_{45}+K_{46}\Delta H_{46})y_4+(K_{56}\Delta H_{56})y_5) \qquad (46)$$

3.9.1 Estimating the Mixing Temperature Between the VGO and Steam

$$T_{mix} = (M_{vgo}\left[Cp_{vgo}^l(T_{vgo}-T_{vap})+Cp_{vap}T_{vap}-\Delta H_{vap}\right]+M_{steam}Cp_{steam}T_{steam})/(M_{vgo}Cp_{vgo}^l+M_{steam}Cp_{steam}) \qquad (47)$$

3.9.2 Estimating the Inlet Temperature (T_{inlet})

Specific Heat Capacity of Steam

$$\frac{8.314}{0.018}*(3.470+0.001450*T+12100*T^{-2}) \qquad (48)$$

Mean Cp of Steam:

$$\frac{1}{T-T_{steam}}\int_{T_{steam}}^{T}\frac{8.314}{0.018}(3.470+0.001450T+12100T^{-2})\,dT \qquad (49)$$

$$=\frac{8.314}{0.018}(3.470+0.001450(T+T_{steam})/2+12100(T_{steam}T)^{-1}). \qquad (50)$$

Heat lost by catalyst =Heat gained by steam +Heat gained by VGO.

$$M_{cat}Cp_{cat}(T_{cat}^0-\mathrm{T})=(M_{steam}Cp_{steam}^{avg}(T-T_{steam})+M_{vgo}Cp_{vgo}^l(T_{vgo}^{vap}-T_{vgo}^l)+M_{vgo}\Delta H_{vap}+M_{vgo}Cp_{vgo}^v(T-T_{vgo}^{vap})).. \qquad (51)$$

Where,

Cp_{steam}^{avg}=Average specific heat capacity of steam from T_{steam} to the equilibrium temperature (T) earlier given in equation (50)

ΔH_{vap}=Heat of vaporization (J/Kg) ,

T_{steam} =Temperature of steam inlet (K),

T_{vgo}^{vap}=VGO Vaporization Temperature (K)

T_{vgo}^l=VGO Liquid Temperature (K)

The energy balance Equation can be solved analytically or put in the form below, and solved numerically to estimate T=T_{inlet}.

$$T = 1/(M_{cat} * Cp_{cat} + M_{steam} * Cp_{steam}^{avg} + M_{vgo} * Cp_{vgo}^{v}) * (M_{cat} * Cp_{cat} * T_{cat}^{0} + M_{steam} * Cp_{steam}^{avg} * T_{steam} - M_{vgo} * Cp_{vgo}^{l} * (T_{vgo}^{vap} - T_{vgo}^{l}) - M_{vgo} * \Delta H_{vap} + M_{vgo} * Cp_{vgo}^{v} * T_{vgo}^{vap}) \quad (52)$$

Specific heat capacity of Coke by smith [7]

$$Cp_{coke} = \frac{8.314}{0.0144} * (1.771 + 7.71T * 10^{-4} - 8.67T^{-2} * 10^{4}) \quad (53)$$

IV. RESULTS AND DISCUSSION

4.1 Overview:

The model equations previously developed, gave a set of 10 ordinary differential equations which were solved using the fourth order Runge - Kutta's method using suitable Pythonic codes.

Since the Gas-Oil is cracked to give the various products, the mass fraction of gas-oil at the inlet of the Riser is taken to be unity. while the other feed components are assumed to be zero. The above mentioned boundary conditions is stated mathematically as:

Z=0:y1=1,y2=0,y3=0,y4=0,y5=0,y6=0. Where y1 represents Gas-Oil, y2,y3------y6 represents Diesel, Gasoline, etc.

4.2 Operating parameters

The operating parameters were gotten from the plant data from the FCC unit of the New PortHarcourt Refinery , Nigeria.

Table 1 shows the physical properties of the feed and products, while Table 2 shows the physical properties of the catalyst, the specific heat capacity of the feed, etc. Table 3 shows the feed composition

while Table 4 shows the reactor dimensions

Table 1. Properties of feed and products of FCC (NPHRC [8])

Component	API Gravity	Composition, (wt%)	Flowrate (Kg/s)
Gas-oil feed	21.2	100	67.8
Fuel gas	-	5.4	3.66
C3 LPG	-	6.3	4.27
C4 LPG	-	10.7	4.27
Gasoline	60	45.9	31.12
Light cycle oil	14	17.8	12.07
Bottoms	0.5	8.8	5.97
Coke	-	5.1	3.46

Table 2. Physical properties of reacting species and catalyst (Oboho [9])

Parameter	Value
Vapor density, kg/m3	9.52
Liquid density, kg/m3	924.8
Specific heat of gas, kJ/kg K	3.3
Specific heat of liquid, kJ/kg K	2.67
Heat of vaporization, kJ/kg	156
Bulk density of catalyst, kg/m3	975
Particle size of catalyst, m	75×10^(-6)
Specific heat capacity of catalyst, kJ/kg K	1.12
Mass flow rate of catalyst from the riser to the regenerator,kg/hr	1729750

Table 3. Feedstock composition (NPHRC [8])

Hydrocarbon	**% Mass**
Paraffins	35.4
Naphthenes	16.1
Aromatics	48.5

Table 4. Dimensions of some components of FCC unit from NPHRC [8]

Parameter	Value (m)
Reactor height	22.9
Reactor diameter	2.9
Disengager height	24.49
Cyclone height	14.24
Cyclones diameter	1.5

Table 5. Estimated kinetic parameters by Raj Patel [5]

Reaction	Frequency factor k_{ij}(1/s)	Activation energy(kj/kmol)	Heat of reaction (kj/kg)
Gas-oil->Diesel (k12)	7957.29	53,927.7	190.709
Gas-oil->Gasoline (k13)	14,433.4	57,186.6	128.45
Gas-oil->LPG (k14)	2337.1	51,308.6	209.192
Gas-oil->Dry gas (k15)	449.917	48,620.4	44.543
Gas-oil->Coke (k16)	40.253	32,433.6	458.345
Diesel->Gasoline (k23)	197.933	48,114.5	513.568
Diesel->LPG (k24)	3.506	67,792.9	90.894
Diesel->Dry gas (k25)	3.395	64,266.6	204.381
Diesel->Coke (k26)	75.282	61,159.4	305.925
Gasoline - >LPG (k34)	2.189	56,194.4	225.082
Gasoline - >Dry gas (k35)	1.658	63,319.1	19.667
Gasoline - >Coke (k36)	2.031	61,785.1	117.212
LPG - >Dry gas (k45)	3.411	55,513.0	17.618
LPG - >Coke(k46)	0.601	52,548.2	11.839
Dry gas - >Coke (k56)	2.196	53,046.0	52.863

Table 6. Molecular weights of Feed and Products (H. X Weng [10])

SPECIES	MOLECULAR WEIGHT (Kg/mol)
VGO	0.386
Diesel	0.1786
Gasoline	0.1178
LPG	0.0467
DRY GAS	0.0188

Table 7. Comparison between model predictions and plant data from FCC reactor(NPHRC)

SPECIES	Plant data(wt%)	Model predictions(wt%)	|Deviation|
VGO	0.088	0.0745	0.0135
Diesel	0.179	0.217	0.038
Gasoline	0.459	0.469	0.010
LPG	0.17	0.145	0.025
DRY GAS	0.054	0.043	0.011
Coke	0.052	0.051	0.001

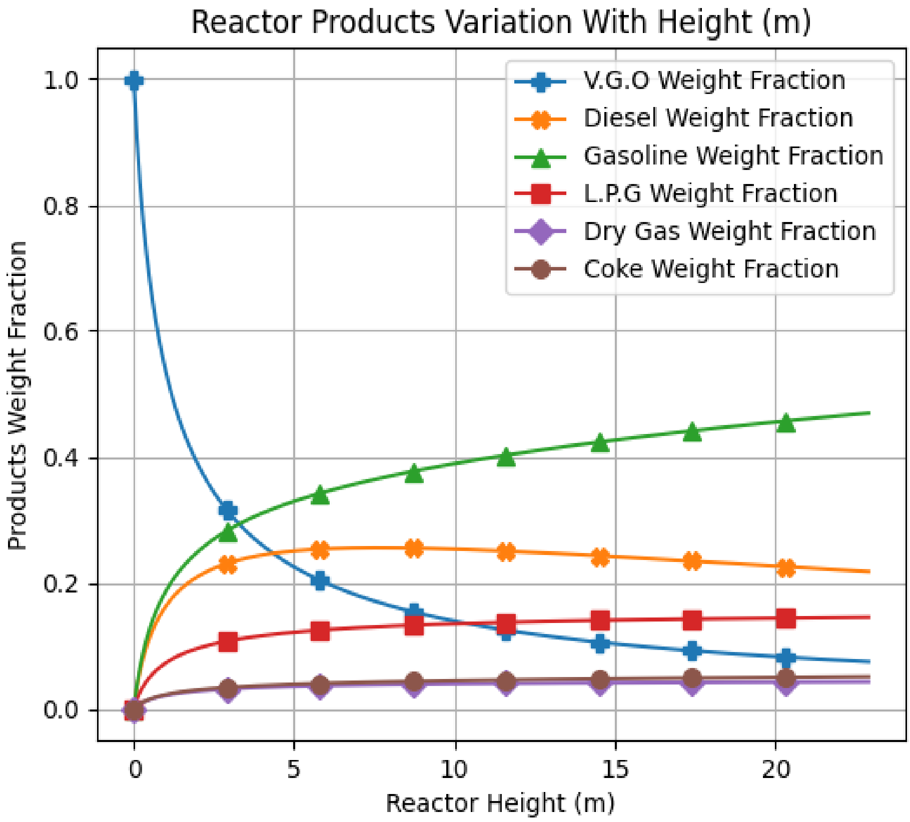

Figure 7: Products Variation with the Riser Length

Figure 7 shows the variation of mass fraction of Gas-Oil and the various products of the catalytic cracking process with the height of the riser-reactor, indicating that the mass fraction of Gas-Oil decreases as the height of the riser-reactor increases, while the mass fractions of Gasoline , LPG, Fuel Gas, and Coke , increase as the riser-height increases. Diesel increases at first due to its rapid formation and then decreases as it is been cracked while it flows through the reactor.

As Gas-Oil enters the riser-reactor in contact with the catalyst , it is cracked into the various products as it is conveyed up the reactor .

As the height of the Riser increases, the cracking of Gas-Oil and the contact time of Gas-Oil and catalyst increase as well, hence, the mass fraction of Gas-Oil decreases from an initial value of unity (=1) at the inlet of the riser-reactor to a minimum value at the outlet of the reactor, while the mass fraction of individual product increases from an initial value of zero from the inlet of the riser-reactor to a maximum value at the outlet of the reactor.

From the diagram above ,there is a sharp decrease in the concentration gradient of Gas-Oil near the inlet of the Riser, with a corresponding increase in the product concentration , which indicates that majority of the cracking reactions occur near the base of the Riser.

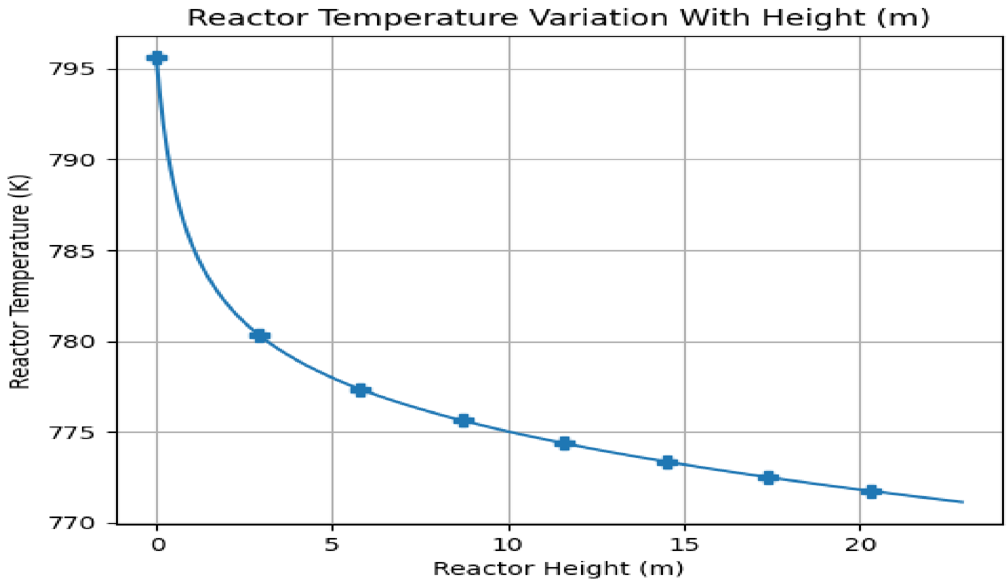

Figure 8: Variation of Riser Temperature with Reactor Length

Figure 8 shows the temperature progression along the riser-reactor, where the temperature inside the reactor(796K) drops very quickly in the first few metres near the Riser bottom zone, hence indicating that most of the reactions occur in this zone. Since the endothermic cracking reactions take place along the riser-reactor, the temperature and the catalyst activity decreases with the height of the reactor, which as well causes a decline in both the reaction rate(dependent on the temperature and catalyst activity) and the heat absorbed by the cracking reactions.

Even though the temperature varies along the Riser height, the temperature at any point along the riser-reactor does not change with time which means that the riser-reactor operates at steady-state.

In most F.C.C units, Reactor temperature is the prime control of the reactor severity. Increasing the reactor temperature set point will signal the regenerated catalyst valve to increase the hot catalyst flow as necessary to achieve the desired riser outlet temperature. The increased catalyst circulation rate results in increased conversion.

Higher cracking temperature also increase gasoline octane and LPG olefinicity -with their potential for alkylation feed- , cracked gasoline from high temperature operation are particularly useful blending components for leadfree gasoline

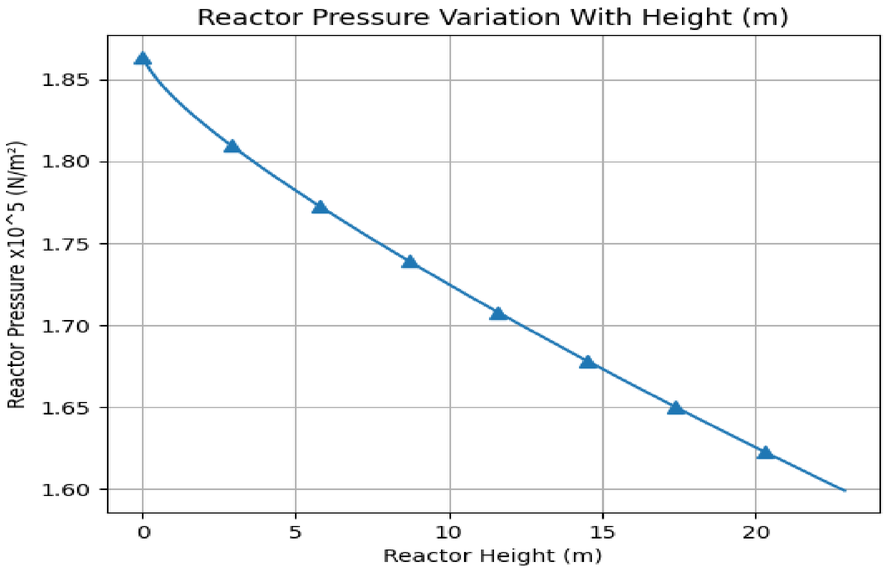

Figure 9: Pressure Drop along the Riser

The pressure profile diagram shows a quasi-linear drop in the pressure profile along the riser. In the model given, it was assumed that the pressure drop is due to static head of catalyst.

Reactor pressure varies slightly with changes in feed rate and loading of the main column. The operator usually has some element of control, and must ensure that pressure be kept within narrow limits around the design value to avoid problems with riser and cyclone velocities

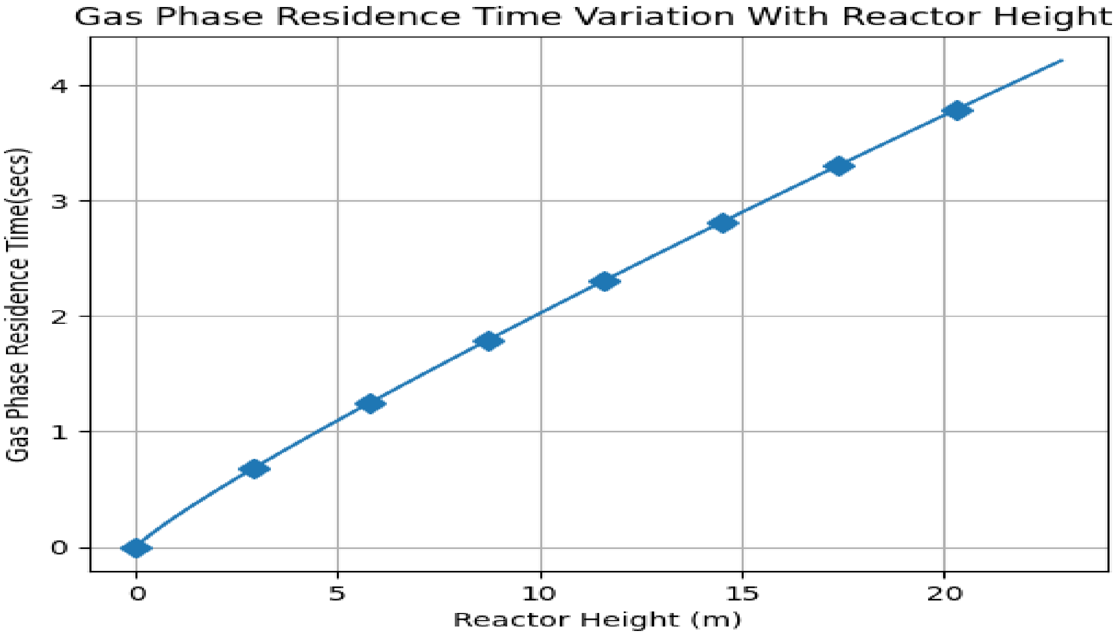

Figure 10: Gas Phase Residence Time against Riser Height:

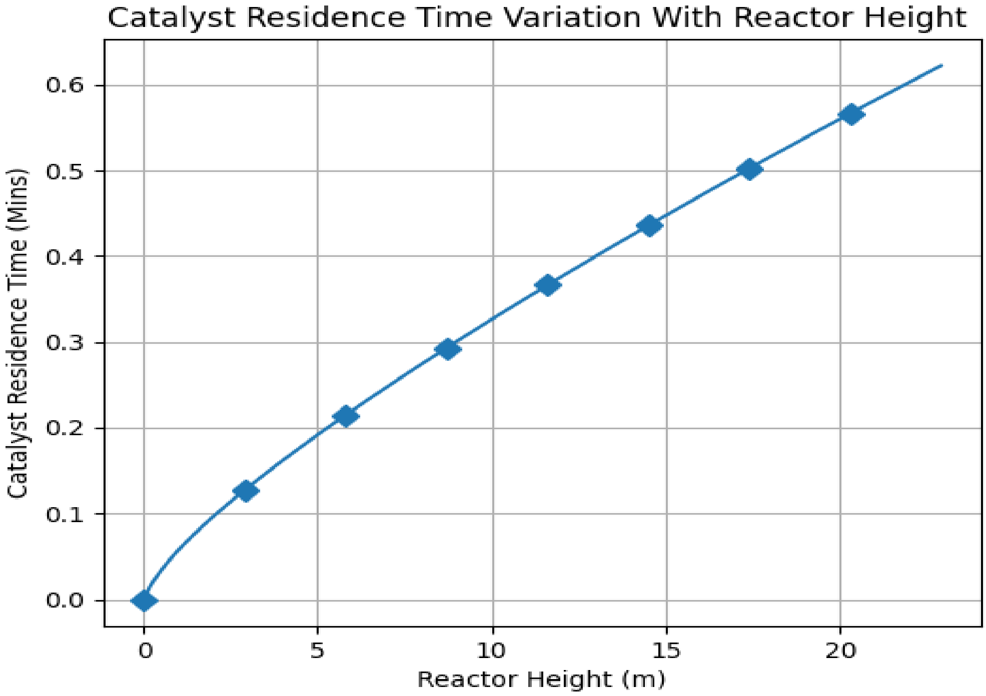

Figure 11: Catalyst Residence Time Vs Riser Height.

One distinguishing feature of most riser reactors is catalyst-oil slip, which is the difference in upward velocity between the vapor and solid phases in the reactor. Both catalyst and oil travel vertically upward, but the oil moves faster owing to the less influence of gravity on its speed , flowing through the spaces between the slower catalyst particles.

The ratio of catalyst and oil residence time is called the slip factor. It is important to note that slip occurs because gravity acts to a greater extent on the solids than on the vapor, retarding the catalyst flow to a larger degree. If the flow were not opposed to gravity, this effect would be minimal. In commercial risers having diameters of several feet, slip is one of various flow irregularities which occur.

Figure (10&11) show the residence time for the gas phase and the catalyst also. The gas phase has a smaller residence time than the catalyst owing to it's lighter weight as shown in the diagram.

4.3 Parametric Sensitivity Analysis :

In optimizing a plant performance, choosing the optimum operating conditions becomes a necessity. Hence a sensitivity analysis is carried out to investigate the sensitivity of the process output with respect to the decision variables.

In these analysis, the variables studied are:

- Catalyst to Oil Ratio
- Feed Rate
- Feed Temperature
- Catalyst Temperature

4.4.1 Effect of Catalyst to Oil Ratio On FCC Riser Performance at Constant Feed Rate And Feed Temperature

4.4.1.1 Effect On Products Yield :

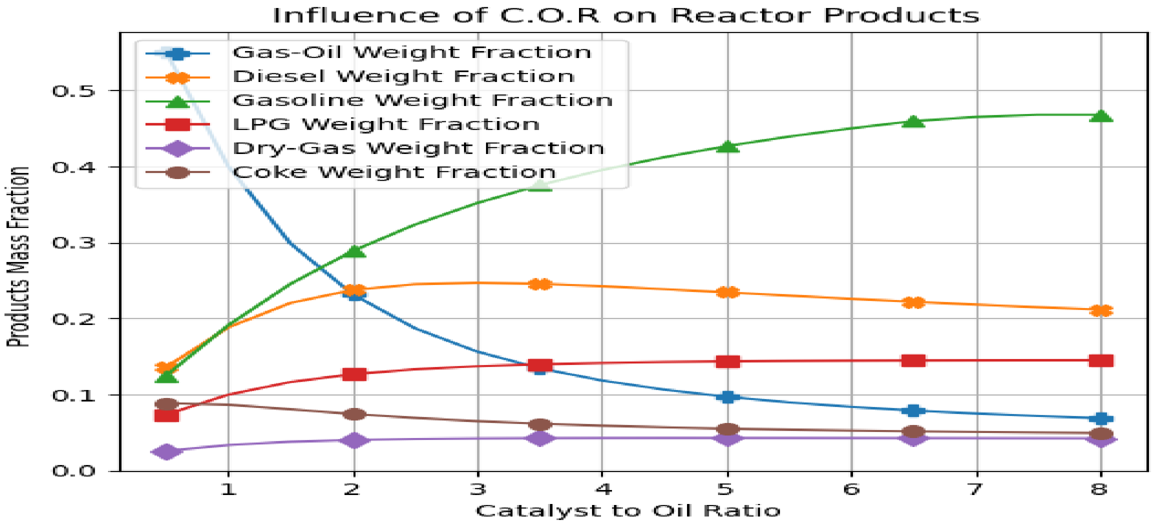

Figure 12a: Catalyst to Oil Ratio (COR) versus products yield at Constant Feed-Rate(67.8kg/s)

From figure 12a, At a feed rate of 67.8kg/s and a reactor inlet temperature of approximately 708kelvin, Diesel had the highest yield at a Catalyst to Oil Ratio (COR) of 3.0 approximately, which gave (0.2470) of Diesel.

LPG is favored as the catalyst circulation rate is increased, as evidenced in figure 12a due to the increase in the catalyst active sites for secondary cracking of the higher molecular weight products. As long as the feed, Diesel and Gasoline are formed in large concentrations, increasing the C.O.R would increase their secondary cracking, yielding more LPG and Dry Gas.

At a constant feed rate of 67.8kg/s,and feed temperature of 505kelvin, Gasoline yield increases with increasing Catalyst to Oil ratio at low Catalyst to Oil Ratios. However, the rate of increase in Gasoline yield decreases at higher values of Catalyst to Oil Ratio. This is due to the fact that at substantially high catalyst concentration, secondary cracking reactions of components in the Gasoline range increases, which eventually causes a decrease in the Gasoline yield at higher Catalyst to Oil Ratio. Consequently, increasing the Catalyst to Oil Ratio leads to increase in catalyst in the unit, which means more active sites available for reaction, hence increase in rate of both primary and secondary cracking. Diesel yield increases with Catalyst to Oil Ratio as long as the Ratio is below the optimum value for maximum Diesel yield. However, when this optimum ratio for Diesel yield is exceeded, Diesel output declines while Gasoline yield increases.

In general terms, the optimum C.O.R for maximum Diesel yield is lesser than the optimum ratio for maximum Gasoline yield partially due to the combined effect of a lesser severity of Feed Oil cracking at low catalyst to oil ratios and also, a lesser rate of Diesel cracking which majorly favors Diesel, while Gasoline requires more circulation to crack both the Gas-Oil and any Diesel formed.

Maximum Diesel forming close to the base of the Riser is not usually desirable If our goal is to maximize Diesel yield at the outlet, since most of it would get cracked as it flows through the Riser Instead, it would be preferable to step down the catalyst circulation rate, so the peak value of Diesel forms close to the riser outlet.

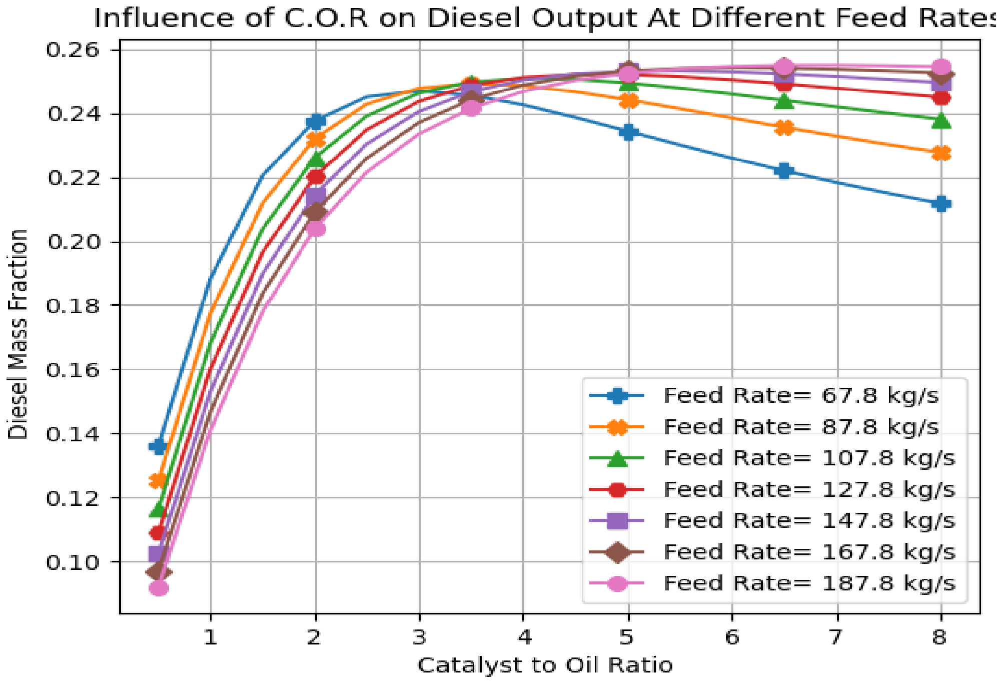

Figure 12b: Effect of C. O. R on Diesel Output at Different Feed Rates

Figure 12b shows that for every feed rate, there is an optimum catalyst circulation rate(Optimum C.O.R) and vice versa for maximum Diesel yield. It could easily be observed that at a feed rate of 67.8kg/s, the catalyst to oil ratio for maximum Diesel yield is quite different from the catalyst to oil ratio for maximum Diesel yield at a feed rate of 87.8kg/s. This is partly due to the fact that as the feed rate increases, there is a reduction in the contact/residence time, and for maximum production of Diesel, an increase in catalyst circulation is needed to compensate for the increase in feed rate and the reduced residence time, to maximally extract the Diesel component before the feed exits the reactor. Thus at a larger feed rate, a larger catalyst circulation rate is needed for optimum Diesel yield.

4.4.1.2 Effect On Reactor Inlet & Outlet Temperature(k) :

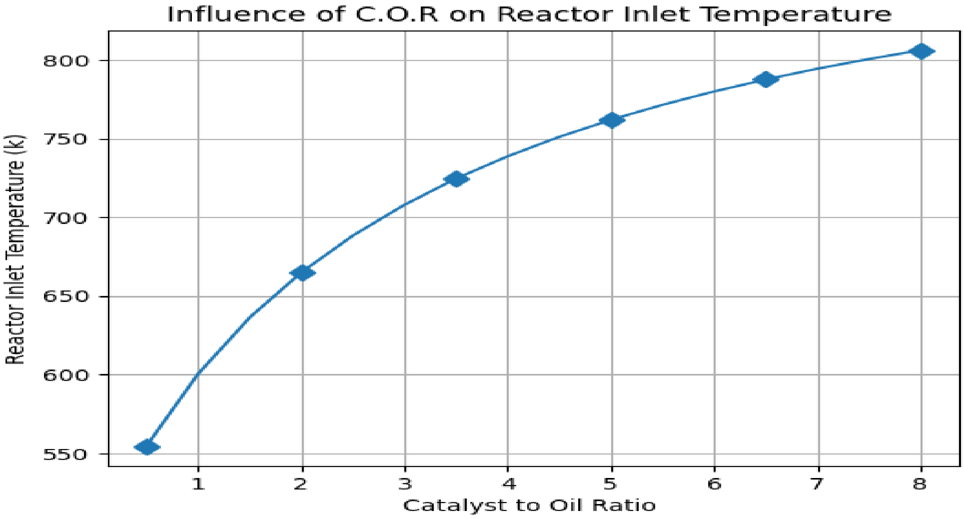

Figure 13: Catalyst to Oil Ratio (COR) versus Reactor Inlet Temperature

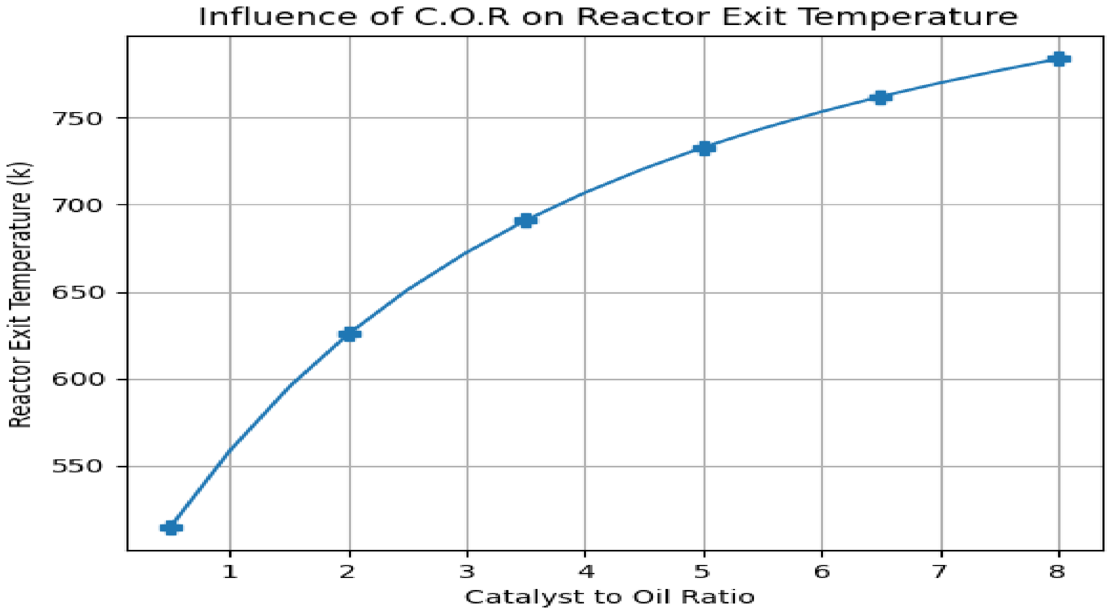

Figure 14: Effect of Catalyst to Oil Ratio On Reactor Outlet Temperature

As the Catalyst to Oil Ratio is increased, there is an increase the inlet and exit temperature as shown in figure 13 and 14 due to increase in enthalpy of the hot stream inlet . As the temperature increases, there is an increase in the rate of cracking.

4.4.2 Effect of Feed Rate On FCC Riser Performance at Constant Catalyst Circulation Rate & Feed Temperature

4.4.2.1. Effect On Products Yield :

The Feed Rate was varied as shown in figure 15, while the catalyst circulation rate was kept constant at 480.486kg/s and the corresponding effect on the output was studied as given below.

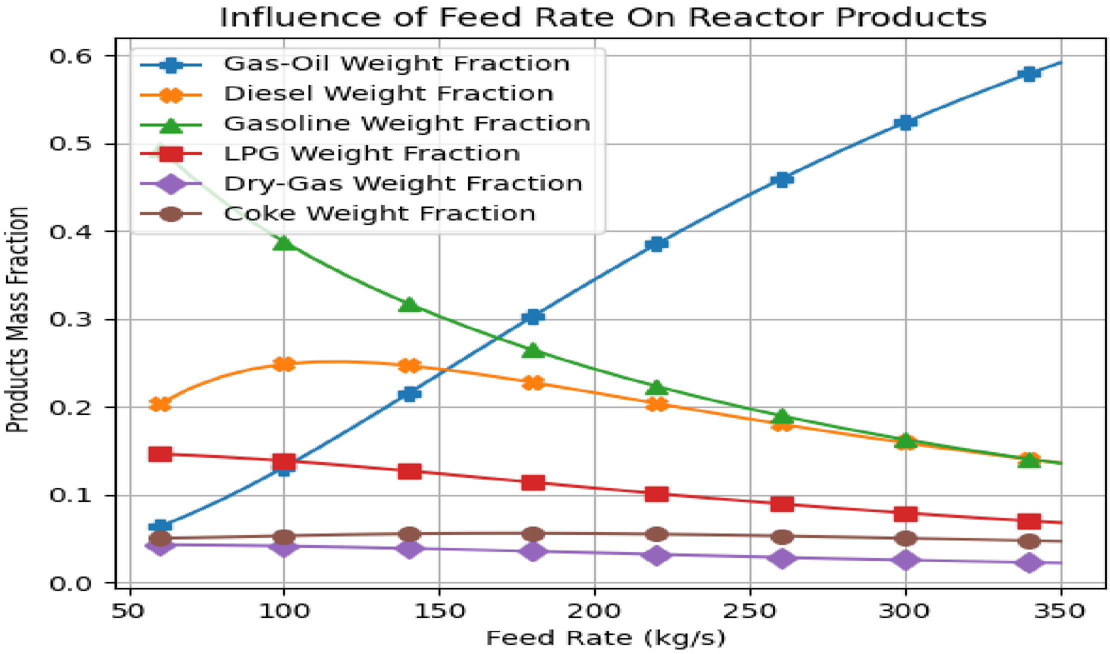

Figure 15: Effect of Feed Rate On Products Yield

It can be observed in figure 15, that as the feed flow rate increases at constant catalyst flow rate, the reactor inlet temperature as well as the Catalyst to Oil Ratio reduces, which to an extent reduces the cracking of Gas-Oil and Diesel to give Gasoline. Increasing the feed rate increases the Diesel yield as long as the C.O.R is above the optimum Catalyst To Oil Ratio for maximum Diesel yield, after which the yield decreases upon further increment in the feed rate. This can be explained on the basis of an insufficient quantity of catalyst to crack the feed as it is increased beyond that which the catalyst can handle and also a reduction in the residence/contact time between the feed and the catalyst as the feed rate is increased . As the flow rate is increased, the residence time of the feed in the riser decreases. This causes lesser amount of Gas-oil cracking to occur which negatively affects Gasoline, LPG, Dry Gas yield . If the flow rate is decreased , the residence time increases and increased cracking takes place. If the flow rate is low enough, it may cause secondary reactions to occur, which will cause a decrease in the Diesel yield as the compounds in this range are further cracked. As the feed rate increases at constant catalyst circulation rate, Gasoline yield reduces since the temperature and the residence time reduces, hence minimizing the cracking of Gas-oil and the secondary cracking of Diesel. The total conversion decreases with increase in the flow rate partly due to insufficient quantity of catalyst to crack the feed and also a reduced residence time which cause lesser cracking.

In figure 15 , for a fixed catalyst flowrate of 480.486kg/s, a feed flow rate of 116 kg/s gave the highest Diesel yield of 0.2514 at a reactor inlet temperature of 742.54 kelvin(The inlet temperature was obtained by tracing the feed rate of 116 kg/s in figure 16),which corresponds to a Catalyst to Oil Ratio of (480.486/116=4.15). So a feed rate of 116 kg/s requires a Catalyst to Oil Ratio of 4.15 for maximum Diesel yield.

4.4.2.2 Effect On Reactor Inlet & Outlet Temperature :

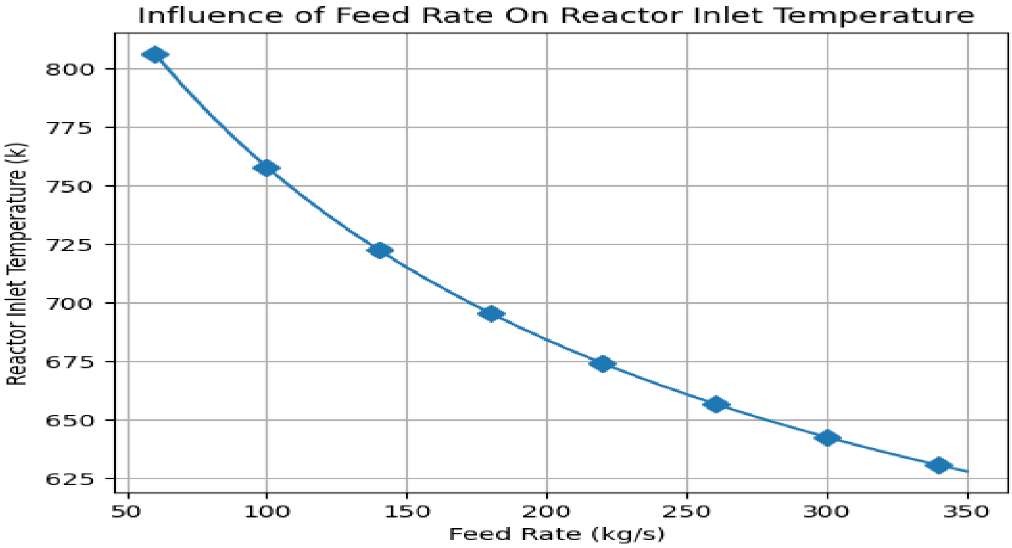

Figure 16: Reactor Inlet Temperature vs Feed flowrate(kg/s)

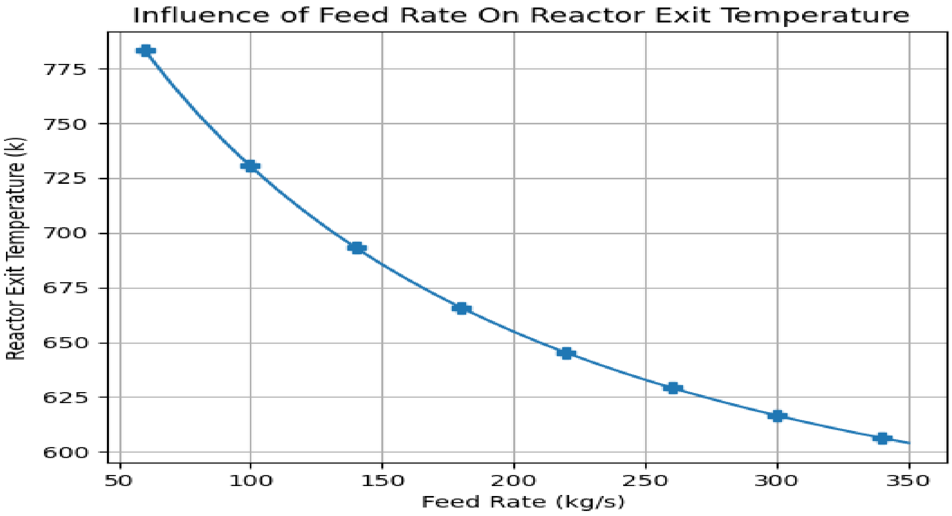

Figure 17: Effect of Feed Rate(kg/s) on Reactor Exit Temperature

Figure 17 shows that Reactor Exit Temperature decreases with increase in the feed rate. As the feed rate keeps increasing, The effect of the feed rate becomes more pronounced as compared to Catalyst to Oil Ratio , there is net decrease in the Reactor Exit Temperature , which is to be expected since the Regenerator Temperature is fixed . To keep the Regenerator Temperature constant, air flow rate must be increased since the sensible heat brought in the regenerator by the catalyst is less at lower Reactor Exit Temperature.

4.4.3 Effect of Feed Temperature at a Constant Feed Rate and Varying Catalyst Circulation Rate

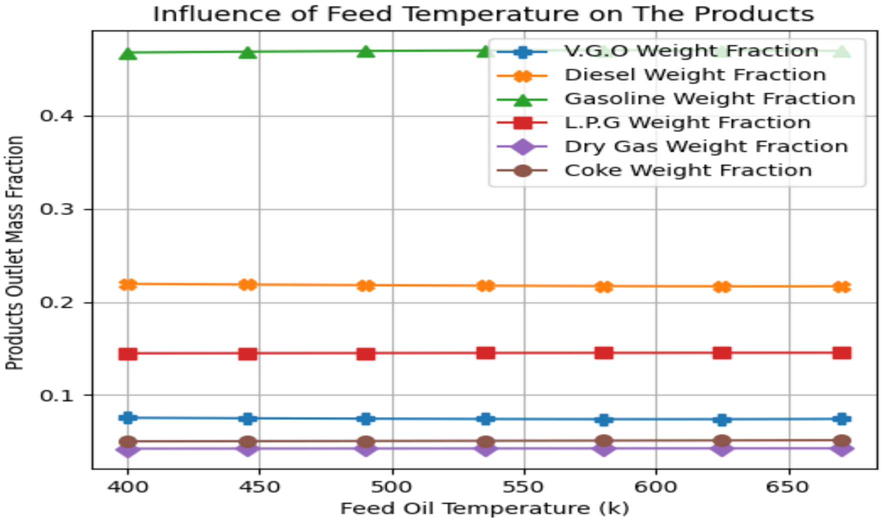

Figure 18: Effect of Feed Temperature On The Products Yield

As the feed temperature is increased while the feed rate is held constant (67.8kg/s) , the difference in temperature between the feed and the riser reactor decreases, which means a lesser energy is required for its cracking. This in turn reduces the quantity of catalyst to be circulated through the standpipe, thus, having a lesser catalyst to oil ratio.

In Figure 18 given above, as the feed temperature is increased, the catalyst circulation rate reduces gradually with a slight increase in Gasoline yield and decrease in Diesel yield. But as the feed temperature is continually increased, the Gasoline yield becomes its peak at 0.470 while Diesel was 0.2118 with coke(0.051) at a Catalyst to Oil Ratio of 5.484 and a feed temperature of 592 kelvin. Further increase in its temperature resulted in a decrease in Gasoline yield and a slight increase in Diesel yield due to a low catalyst to oil ratio which implies a less interfacial contact area for cracking of Gas-Oil and Diesel to yield Gasoline.

4.4.4 Effect of Catalyst Temperature on Products Yield at Constant Feed/Catalyst Circulation Rate

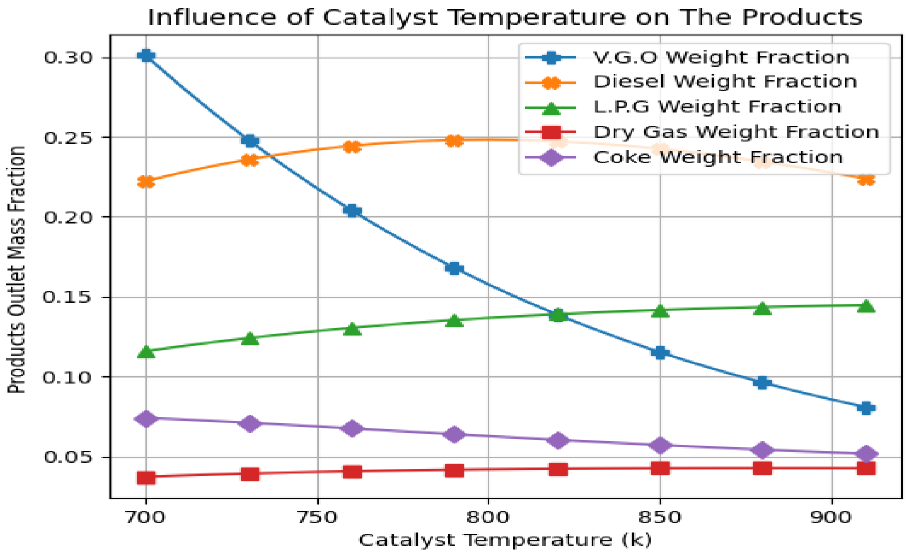

Figure 19: Effect of Catalyst Temperature On The Products

In figure 19, Increasing the catalyst temperature while keeping other variables constant increases the cracking severity of Gas-Oil which inturn increases the Output. Increasing the catalyst temperature increases Diesel yield to a maximum (0.2482) with a coke content of 0.063 at a catalyst temperature of 799 kelvin and a reactor temperature of 707.4 kelvin, after which it decreases upon further increment in the catalyst temperature due to increased cracking of the Diesel fraction yielding other fractions.

V. CONCLUSION

This research work presents the mathematical model for predicting the outputs as well as the properties along the riser height in a fluid catalytic cracking process. It independently predicts Gas-oil, Diesel, Gasoline, LPG, Dry Gas, Coke and takes into account, the secondary cracking of LPG and Dry Gas to also yield Coke which is usually ignored by other researchers. From observation, for a feed rate of 67.8kg/s, a feed preheat temperature of 592 k at a C. O. R of 5.48 was predicted to give optimal Gasoline yield, while Diesel can be optimized by :

- Reducing the Catalyst Circulation Ratio to 2.9~3 at a Reactor Temperature of 708kelvin
- Reducing the Catalyst Temperature to 799 kelvin at a C. O. R of 7 and a reactor temperature of 707.4 kelvin while keeping other variables constant for enhanced productivity of the FCC Unit.

ACKNOWLEDGEMENTS

The authors can acknowledge professor, friend or family member who help in research work in this section.

VI. REFERENCES

[1] Hans, I.-S. and C.-B. Chung (2001); "Dynamic Modeling and Simulation of a Fluidized Catalytic Cracking Process. Part I: Process Modeling," Chem. Eng. Sci., 56, 1951–1971

[2] Kunii, D. and Levenspiel, O. (1991) Fluidization Engineering. 2nd Edition, Butterworth-Heinemann, Boston

[3] Yadav, P.K. & Garg, R.K. (2017). Modeling and Simulation of Fluidized Cracking Riser Reactor Using Pseudo Reaction Kinetics: A Review, International Journal of Engineering and Technology (IJET) 9(3): 1667 – 1681.

[4] Du, Y.P., Yang, Q., Zhao, H. & Yang, C.H.(2014). "An integrated methodology for the modeling of Fluid Catalytic Cracking (FCC) riser reactor". Applied Petrochemical Research; 4:423–33.

[5] Yakubu, M.J., Raj, P., Mustapha, A. & Iqbal, M. (2019)."Parameter Estimation of a Six-Lump Kinetic Model of an Industrial Fluid Catalytic Cracking Unit". Elsevier Ltd.

[6] Patience ,G.S., Chaouki, J. & Kennedy, G.(1991). Circulating Fluidized Bed Technology III, Pergamon, Oxford.

[7] Sinnot, R. & Towler, G. (2013). Chemical engineering design, vol. 6,5th edn. Oxford : Butterworth-Heinemann (An imprint of Elsevier).

[8] E. O. Oboho, J. G. Akpa, Modelling of a Fluid Catalytic (FCC) Riser Reactor: The Four-Lump Model, Journal of Modeling, Design and Management of Engineering Systems, 2002, 1, 1, 39–52

[9] Weng, H. X., Ren, J. & Liu, F.Y. (1993)."Study on Composition and Structure of Heavy Oil.", Petroleum processing, 24(9) : 56–61.

[10] Weekman, V.W.J.(1968). A model of catalytic cracking conversion in fixed, moving, and fluid-bed reactors. l&EC Process Des Develop ;7:90–5.

[11] Mariaca, D. & Maya, R.Y.(2003)."Fluid catalytic cracking operation complexities and their initiating factors".

[12] Leuenberger, E.L., Moorehead, E.L. & Newell, D.F. (1988). Effects of Feedstock Type on FCC Overcracking : Proceedings of the NPRA Annual Meeting, San Antonio TX, March 20-22, A.M:88-51.

[13] Maya,Y.R., Salazar, S.D., Mariaca, D.E., Rodríguez, S.S. & García, M.L. M.(2006):Fluidized-bed catalytic cracking units emulation in pilot plant, Revista Mexicana de Ingeniería Química, vol. 5, núm. 2, pp. 97-103

[14] Ai, H. & Rohani, S. (1997). Dynamic modeling and simulation of a riser-type fluid catalytic cracking unit. Chem. Eng. Tech., 20: 118-130.

[15] Okeke, E.O. (1997). Catalyst application in Nigeria: prospects for local sourcing, Conference Proceedings of the Nigerian Society Of Chemical Engineers Kaduna/Zaria 1997.