

Comparative Yield Patterns for FCC Unit Riser and Downer

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ABSTRACT

In the present work, a one dimensional heterogeneous two phase model of the adiabatic FCC reactor assuming a plug flow for both the solid and gaseous phases has been developed. The reaction kinetics of the cracking reactions are represented by four lump kinetic models. The hydrodynamics of the riser are considered, taking the slip factor into account. The model involves ordinary differential equations, which are solved in order to obtain the yield patterns and study the effect of process variables like input catalyst temperature, and catalyst oil ratio on the yield of gasoline. Additionally, a model is developed for the downer reactor using hydrodynamic modeling, mass and energy balances. The model developed is solved using Runge- Kutta IV order implemented in MATLAB® software V2016 and the differences in the axial profiles and gasoline yield as compared with the riser reactor are discussed.

Keywords: Fluidized Catalytic Cracking; Modeling; Simulation; Reactor; Riser; MATLAB®

INTRODUCTION

Fluid catalytic cracking (FCC) technology is one of the many processes of and the most important of all the units in a refinery because of its adaptability to changing feedstocks and product demands and because of the high margins that exist between the FCC feedstocks and converted FCC products [1]. Refineries use fluid catalytic cracking reactor to convert higher-molecular-weight hydrocarbons to lighter, more valuable products through contact with a powdered catalyst at appropriate conditions and to also correct the imbalance between the market demand for gasoline and the excess of heavy high boiling range products resulting from the distillation of crude oil [1, 2].

The FCC unit consists of a reaction section and a fractionating section. The reaction section includes two reactors, the riser reactor, where almost all the endothermic cracking reactions and coke deposition on the catalyst occur, and the regenerator reactor, where air is used to burn off the accumulated coke. The reactor can be of two types: riser and downer.

Modeling of riser reactor is very complex due to complex hydrodynamics, unknown multiple reactions coupled with mass transfer and heat transfer resistances. Also, the conditions keep changing all along the riser height due to cracking which causes molar expansion in the gas phase and influences the axial and radial catalyst density in the riser. Many authors [3-22], have developed mathematical models of FCC unit risers, which includes some dimensional mass, energy, and species balance; these models were based on the assumption of instantaneous and complete vaporization of the feed when contacted with the hot regenerated catalyst assuming modern high efficiency feed injection systems. These types of modeling are normally simple to formulate and to solve, while the very few attempts have been made to model the downer reactors. The main difference between the two kinds of reactors lies in the simple fact that in a riser reactor the feed and the catalyst particles are injected from the bottom of the reactor using dispersing steam, which is used to fluidize the catalyst particles while in a downer reactor the feed and catalyst particles enter from the top and flow in the direction of gravity. The difference in the flow of the gas and solid phases inside the riser and downer reactors results in a variation in the yield and axial profiles of the products. As the feed comes in

contact with the hot catalyst from the regenerator, it is vaporized and cracked into lighter products like gasoline, lighter gases and coke. The coke thus produced gets deposited on the catalyst surface leading to catalyst deactivation and the catalyst particles are sent to the regenerator where the coke is burnt off from the catalyst surface. This regenerated catalyst is re injected into the reactor.

The effective modeling and simulation of the fluid catalytic cracking, FCC operation broadly requires knowledge of material balance, reaction kinetics modeling, fluid dynamics modeling, and feed and catalyst effects.

Many empirical equations and catalyst deactivation model are available from the previous works of [22-26], which can be used to predict the deactivation of catalyst caused by coke deposition on the catalyst surface. The kinetic modeling is done by grouping the chemical species into lumps based on the boiling point range. The three lump kinetic model was first developed by Weekman *et al.* [24], and considered gasoil, gasoline and light gases and coke as the three lumps.

Since this model did not consider the coke as a separate lump a higher lump model was needed to predict the coke yield. Hence a four lump model was developed by Lee *et al.* [27], where gasoil, gasoline, light gases and coke were the four lumps considered. In literature kinetic models ranging from 3 to 19 lumps are available. The most widely used models are the 4 and 10 lump model. Many authors have considered same velocities for both the phases in the riser reactor. But it is advisable to consider a slip between the two phases. For this, a hydrodynamic model taking slip factor into account is used in the present paper as stated by Patience *et al.* [28].

FCC riser reactors have been widely used in the past for various industrial processes, but another type of circulating fluidized bed reactors i.e. the downer reactors have been used in the recent years. This present work seeks to wholly account for a comparatively yield pattern for both types of reactors. The development of downer reactor mainly comprises of mass and energy balance, kinetic model along with a hydrodynamic model for the two phases. The downer reactor provides a uniform contact time between the gas and solid phases.

In addition, the slip between the gas and catalyst particles, the

four-lump kinetic model necessary for the cracking mechanism and the exponential catalyst deactivation model to describe the decay of catalyst activity were considered in the derived model.

MATHEMATICAL MODELING

Since a number of complex phenomena occur simultaneously inside the FCC reactor a number of assumptions are made to simplify the model developed:

- ❖ One-dimensional transported ideal plug flow reactor
- ❖ Radial and axial dispersion inside the reactor are assumed to be negligible
- ❖ Constant heat capacities and viscosities are assumed for all components
- ❖ Negligible adsorption and dispersion effects are considered inside the catalyst particles
- ❖ The pressure changes that occur along the reactor length are assumed to be due to the static head of catalyst particles in the riser
- ❖ It is assumed that the coke on the catalyst does not affect the flow of the fluid inside the riser reactor
- ❖ The catalyst and gas temperature is assumed to be same in each section of the riser
- ❖ The catalyst and coke are assumed to have the same specific heat
- ❖ The dynamics of a reactor are assumed to be in quasi- steady state
- ❖ Instantaneous vaporization of feed

Mass and Energy Balance

The riser is divided into small cross sectional areas of infinitely small length. Each volume element of the riser is assumed to have two phases, a solid phase and a gaseous phase. Both the phases are assumed to be perfectly mixed with no heat and mass transfer resistances. For each section of the riser reactor mass balance for each individual chemical species, energy balance and hydrodynamic studies are carried out.

Taking the above mentioned assumptions into consideration following equations can be used to determine the mass balances in the FCC reactor:

$$F_z - F_{z+\Delta z} + (A * \Delta z) * \rho_{cat} * (1 - \varepsilon) * r_z = 0 \quad (1)$$

The above equation gives material balance for a component i between position z and $z + \Delta z$

$$\frac{dy_i}{dz} = \frac{A * (1 - \varepsilon) * \rho_{cat} * r_i}{F_g} \quad (2)$$

$$F_g = F_{go} + F_{ds} \quad (3)$$

Energy balance:

This equation is used to calculate the mixing temperature at the inlet of the riser:

@ $Z = 0$;

$$F_{cat} * Cp_{cat} * (T - T_{cat}) + F_{go} * Cp_{go}^l * (T_{vap} - T_{go}) + F_{go} * Cp_{go}^v * (T - T_{vap}) + F_{go} * \Delta H_{vap} + F_{ds} * Cp_{ds} * (T_{ds} - T) = 0 \quad (4)$$

Where T is the inlet temperature.

@ $Z = h$;

$$(F_g * Cp_g + F_{cat} * Cp_{cat}) * \frac{dT}{dz} = \sum_{i=1}^n r_i * \Delta H_i * A * (1 - \varepsilon) * \rho_{cat} \quad (5)$$

Pressure Balance

$$-\frac{dP}{dz} = \rho_{cat} * (1 - \varepsilon) * g \quad (6)$$

The density of the gaseous phase is calculated using the ideal gas law:

$$\rho_g = \frac{P * MW_g}{RT} \quad (7)$$

The average molecular weight of the gaseous phase is given by:

$$MW_g = \sum_{i=1}^4 y_i * MW_i \quad (8)$$

Kinetic Model

A four lump kinetic model is used in this paper to represent the kinetics of cracking reactions.

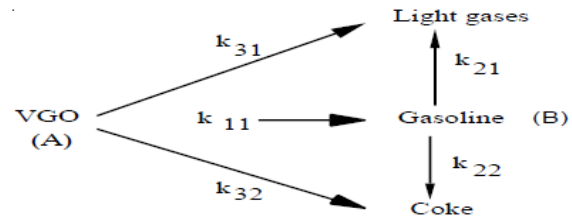


Figure 1. Representation of a four-lumped scheme

This scheme in Figure 1 considers the presence of four lumps namely: gasoil or the feed, gasoline, coke and light gases. The reaction orders for various cracking reactions which take place in the vapor phase are predicted.

- a) gas oil consumption rate: $-r_{go} = k_{11} \phi C_{go}^2$
- b) gasoline formation rate: $-r_g = k_{11} \phi C_{go}^2 - \phi (k_{21} + k_{22}) C_g$
- c) light gases formation rate: $r_{lg} = k_{31} \phi C_{go}^2 + k_{21} \phi C_g$
- d) coke formation rate: $r_c = k_{32} \phi C_{go}^2 + k_{22} \phi C_g$

The kinetic parameters for the cracking reactions such as the reaction rate constants (K_i) and the catalyst deactivation function Φ need to be estimated. All the kinetic parameters for the four-lump scheme cracking reactions is given in Table 1. Arrhenius equation is generally used to give the relation stating dependency of kinetic rate constants on temperature.

$$K'_i = K_{io} * \exp\left(-\frac{E_i}{RT}\right) \quad (9)$$

Where the values indicated by prime as predicted by Eq. 9 is the kinetic constant of the reaction, K_{io} the pre exponential kinetic constants for the respective lumps, and E_i are the activation energies of the different lumps. The following equations give the expressions for rate constants (K_i) and the stoichiometric coefficients (V_{ij}) of the various lumps.

$$K_i = K'_i * V_{ij} \quad (10)$$

$$V_{ij} = \frac{M_i}{M_j} \quad (11)$$

During the reaction, catalyst deactivation occurs due to deposition of coke on the catalyst surface. In the present work the activity factor - Φ which is a function of coke concentration of catalyst.

$$\phi = \frac{B+1}{B + \exp(A * C_{ci})} \quad (12)$$

The values for the parameters used in the above mentioned correlation for deactivation of catalyst; A and B as given in previous work is 4.29 and 10.4 respectively [23].

Hydrodynamic Model

For Riser Reactor:

To consider the slip factor arising due to difference in gas and solid flow, the correlation developed by Patience et al. is used in the present work. According to the correlation the gas interstitial velocity to average particle velocity ratio gives the value of slip factor and can be determined numerically. The empirical formula developed for the same is given as follows:

$$\Psi = \frac{U_o}{\varepsilon * U_p} = 1 + \frac{5.6}{Fr} + 0.47 Fr_t^{0.47} \quad (13)$$

Where

$$Fr = \frac{U_o}{\sqrt{g * D}} \text{ and } Fr_t = \frac{U_t}{\sqrt{g * D}} \quad (14)$$

The gas superficial velocity is given by

$$U_o = \frac{F_g}{A * \rho_g} \quad (15)$$

The average particle velocity, U_p in the riser used in Eq. 13 can be calculated using Eq. 16

$$U_p = \frac{G_s}{\rho_{cat} * (1 - \varepsilon)} \quad (16)$$

Combining and solving Equations 13 and 16 gives a new equation (Eq. 17) for calculating the average voidage in each section of the riser. It can be seen that average voidage is dependent upon solid mass flux, catalyst physical properties, superficial gas velocity and rise diameter which happen to be known quantities in FCC operation.

$$\varepsilon = 1 - \frac{G_s * \Psi}{U_o * \rho_{cat} + G_s * \Psi} \quad (17)$$

For downer reactor:

In order to study the hydrodynamics of the downer reactor, force balance is applied to a single particle of the gaseous phase stream. The equation developed is as follows:

$$\rho_p * V_p * \frac{\partial U_p}{\partial t} = \frac{1}{2} * \rho_g * \left| \frac{U_o - U_p}{\varepsilon} - U_p \right| * \left(\frac{U_o - U_p}{\varepsilon} - U_p \right) * A * C_D + (\rho_p - \rho_g) * V_p * g \quad (18)$$

In Equation (18) mentioned above, the inertial force is represented in terms of the drag force, gravitational force, and buoyancy force. The sign and value of slip velocity, which can be given as the difference between the average particle velocity and interstitial gas velocity determines the direction in which the drag force on the particles act. Hence a modulus sign is used in the above equation. The drag coefficient, C_D , is the only empirical parameter used in this model.

$$C_D = \frac{18.5}{Re_p^{0.6}}$$

$$Re_p^{0.6} = \frac{\rho_g \left(\frac{U_o}{\varepsilon} - U_p \right)}{\mu_g} * d_p \quad (19)$$

But from Equation (16), $G_s = \rho_{cat} * (1 - \varepsilon) * U_p$,

If the terminal velocity, U_t , of any particle is known then the d_p , particle diameter can be calculated in terms of equivalent diameter of a spherical particle. In the downer reactor when the solids flowing in the downward direction have achieved a steady state, i.e. the flow is fully developed then slip velocity is used to represent the terminal velocity for that particle. At a particular operating condition, the slip velocity can be determined as a function of gas superficial velocity, particle velocity and voidage given that the flow is completely developed.

$$U_s = \left(\frac{U_o}{\varepsilon} - U_p \right) \quad (20)$$

The slip velocity of a particle is equal to the terminal settling velocity of a particle falling through a fluid and is given by:

$$U_s = U_t = \sqrt{\frac{4d_p(\rho_p - \rho_g)g}{3 * \rho_g * C_D}} \quad (21)$$

In the above equation for a given gas superficial velocity, voidage and average particle velocity are not known. The additional correlations required are provided by the mass balance equations which help in determining the unknown parameters.

The model developed consists of a system of ordinary differential equations. The equations are not stiff in nature. Hence, MATLAB tool ODE 45 was used for solving the system of equations. A variable step Runge-Kutta Method was used by this tool in order to solve the system of ordinary differential equations numerically. The operating conditions in the four cases are used to validate the model while the operating conditions given in case I are used for analyzing the effects of various process variables on gasoline yield and to compare the riser and downer reactors.

The percentage deviation of calculated from plant data were estimated as follows:

$$\text{Percentage Deviation} = \left(\frac{\text{Plant Data} - \text{Calculated Data}}{\text{Plant Data}} \right) * 100\% \quad (22)$$

RESULTS AND DISCUSSION

The results obtained were compared with the results of the actual plant data, a good agreement between the plant data and the model prediction was observed.

A. Comparison of riser and downer reactors

The Figures 1 and 2 compare the yield of gasoline for a downer reactor and riser reactor respectively. As shown from the figures, the downer reactor gives a better conversion of the feedstock and higher yield for gasoline. It is observed that the yield in the first five meters of the riser reactor is more than the yield in the first five meters of the downer reactor. But along the length of the reactor the final yield of the downer reactor becomes greater than that of the riser reactor. This is because after first few meters the catalyst is deactivated and the extent of cracking reactions in the

riser reactor reduces while in the initial section of the downer the holdup of catalyst is less. Most of the conversion in the downer takes place throughout the length of the downer reactor, this occurs due to forward mixing the feedstock comes in contact with a fresh catalyst at any axial location thus resulting in a higher yield at a later stage.

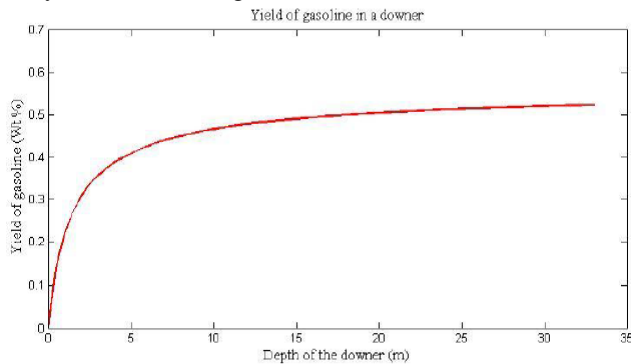


Figure 1: Yield of gasoline in a downer reactor at 960 °K

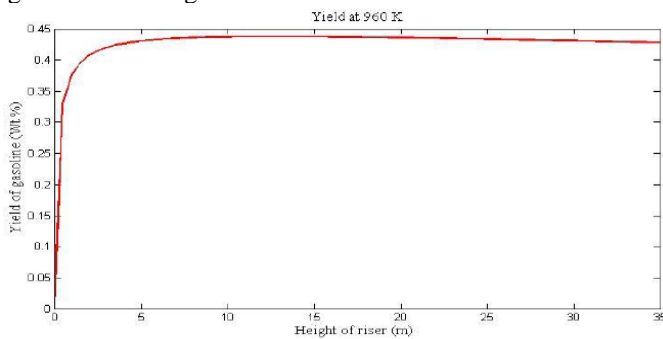


Figure 2: Yield of gasoline in a riser at 960 °K

Figures 3 and 4 compare the yields of coke in a riser and a downer reactor respectively. As expected the downer reactor gives a lower coke yield as compared to the riser reactor, thus indicating a reduced level of secondary cracking reactions. In a downer reactor the catalyst particles reach a terminal velocity after some time, which is higher than the gas phase velocity. Thus, as the gas phase flows down it comes in contact with the fresh catalyst thus reducing the secondary cracking reactions and hence the amount of coke. On the other hand, in a riser reactor the gas phase comes in contact with the deactivated catalyst after some time and a higher level of secondary reactions takes place.

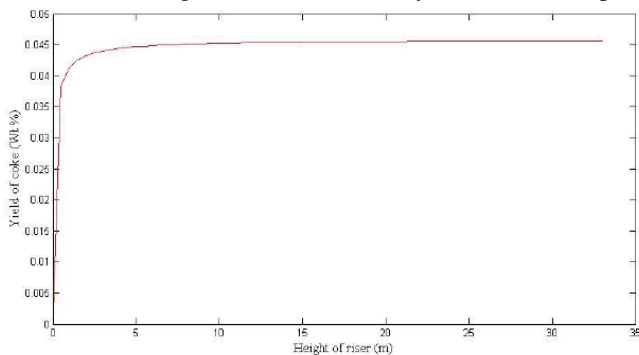


Figure 3: Yield of coke in riser reactor

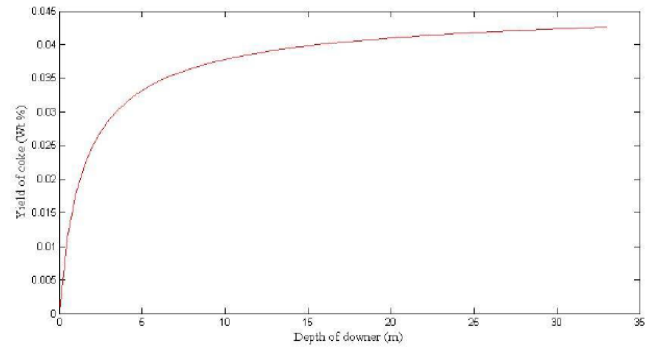


Figure 4: Yield of coke in downer reactor

Figure 5 gives the axial profiles of various chemical species present in the riser reactor. According to the figure the maximum conversion of gasoil occurs in the initial section of the riser reactor i.e. the first five meters of the reactor. This fact is in accordance with what most of the authors [3, 4, 13] have predicted till now. This can be reasoned based on the fact that:

- ❖ The concentration of regenerated catalyst at the bottom of the riser is very high. Also, since the catalyst in the bottom section of the riser is at a much higher temperature than in any other section of the riser. Hence, due to high catalyst activity the rate of reaction is high.
- ❖ Also the concentration of feedstock i.e. the gas oil vapor is maximum at the base of the riser as compared to any other section of the riser reactor where due to the reaction and molar expansion of gaseous phase the gas oil concentration decreases. Hence the rate of the reaction and therefore gas, oil conversion is highest at the bottom of the riser.

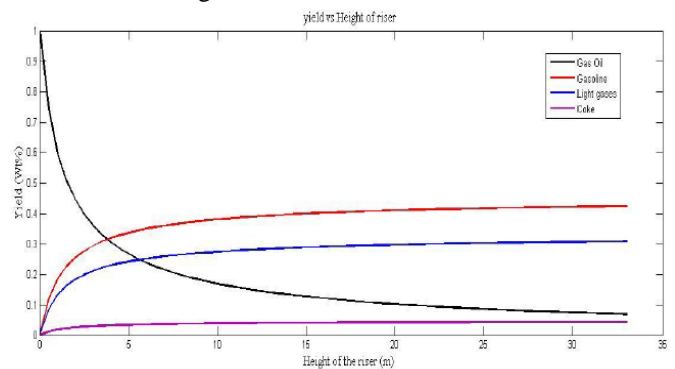


Figure 5: Yield patterns of Riser reactor

The following three figures give the temperature profile, the yield pattern of the species present and the pressure profile respectively. The temperature profile shown in figure 6 is decreasing in nature. This type of behavior can be reasoned by the endothermic nature of the reactions. Also, it is observed that a rapid decrease in riser temperature takes place in the first few meters of the riser length, thus accounting for the fact that most of the cracking reactions take place in the first few meters of the riser length.

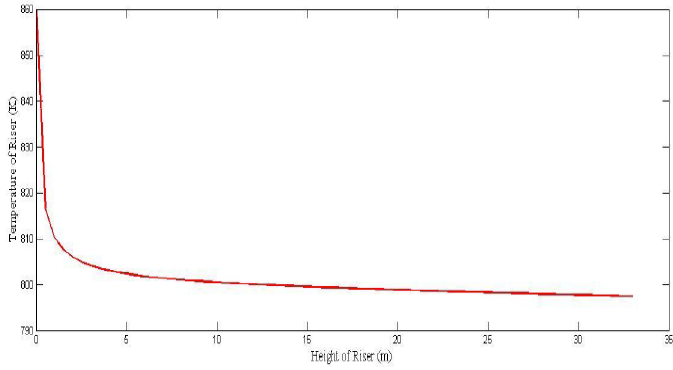


Figure 6: Temperature of riser v/s height of riser

B. Effect of Input catalyst temperature

Figure 7, 8 and 9 shows the axial profiles of gasoline at an input catalyst temperature of 960 °K, 860 °K and 760 °K respectively. As can be seen from the three figures the yield of gasoline decreases with decrease in catalyst temperatures. Also a higher rate of reaction is observed for a higher catalyst temperature.

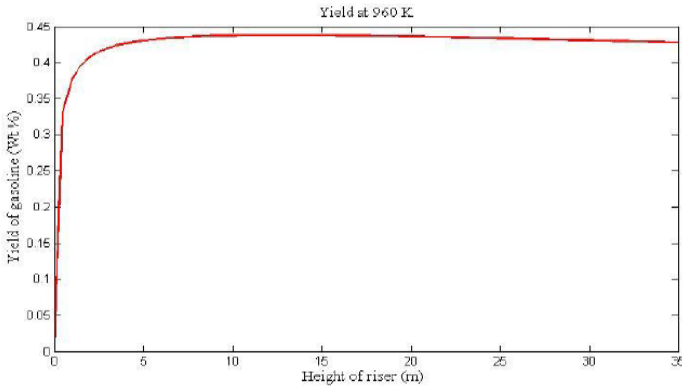


Figure 7: Gasoline yield at 960 °K

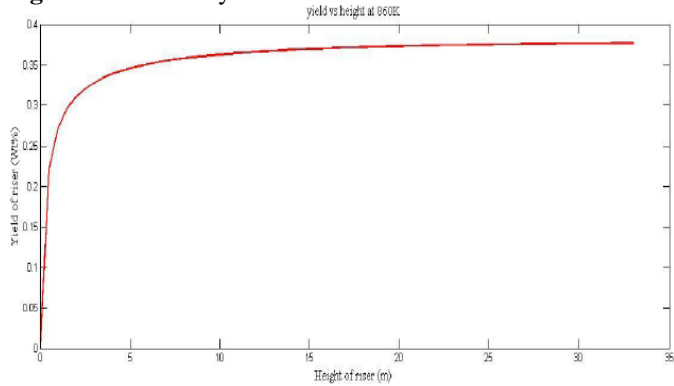


Figure 8: Gasoline yield at 860 °K

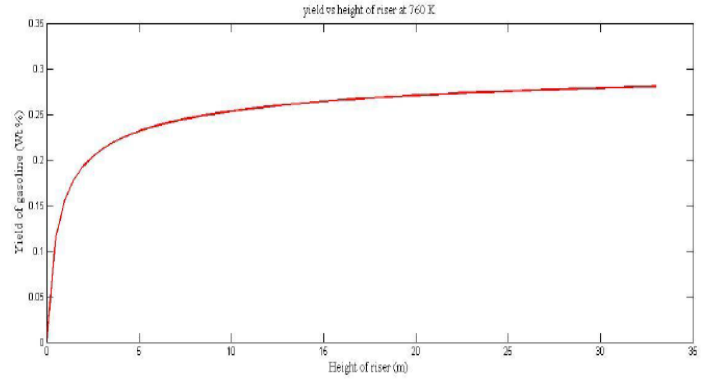


Figure 9: Gasoline yield at 760 °K

C. Effect of Catalyst to oil ratio (COR)

In order to study the effect of change of catalyst oil ratio on the yield of gasoline and this happens to be an important parameter for the FCC process. With increasing the COR at a constant

catalyst temperature, the catalyst hold up $(1 - \epsilon)$ increases with increasing of COR, leading to a higher conversion of the feedstock. Since due to cracking of the feedstock gasoil into lighter molecules leads to an increase in the interstitial velocity of the gas and catalyst particles, thus decreasing the residence time with further increase in value of COR. Figure 10, 11, 12 and 13 depict the yield of gasoline for different values of the catalyst oil ratio ranging from 3, 5, 7 and 13 respectively at an input catalyst temperature of 960 °K. As can be seen from the figures in increasing the value of COR from 3 to 5 the yield of gasoline increases and on further increasing the value of COR to 13 a decline in gasoline yield can be observed. This is because due to a higher rate of reaction due to an increase in COR the production of coke increases, thus deactivating the catalyst and hence resulting in a decrease in gasoline production at a later stage.

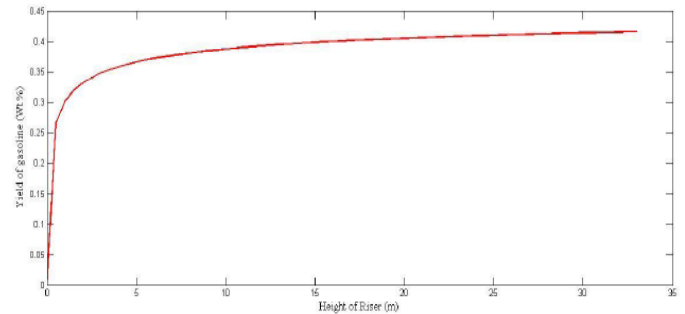


Figure 10: Yield of gasoline at COR = 3

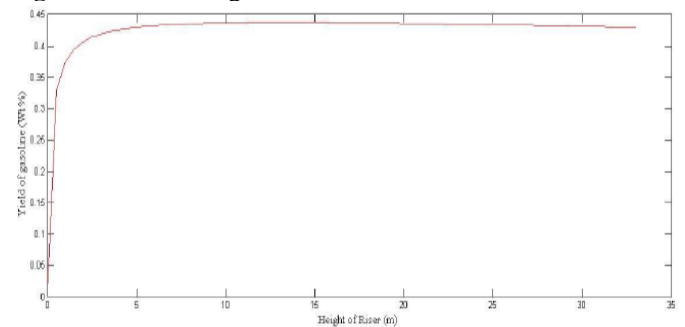


Figure 11: Yield of gasoline at COR = 5

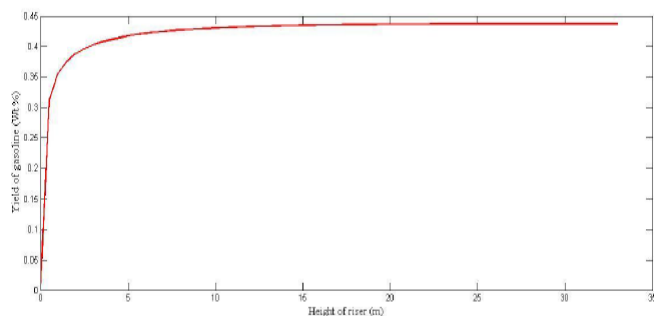


Figure 12: Yield of gasoline at COR = 7

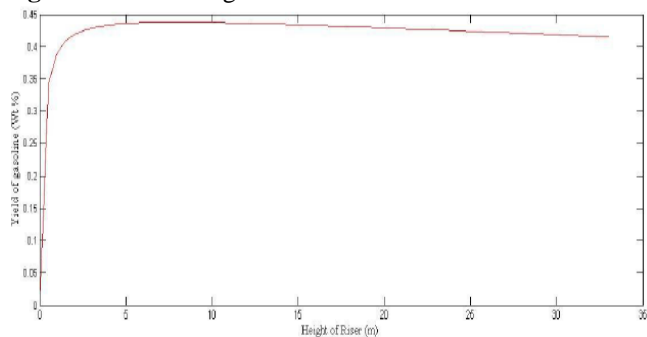


Figure 13: Yield of gasoline at COR = 13

CONCLUSION

In this work an adiabatic one-dimensional model of FCC unit, riser reactor was developed, that combines mass balance and riser hydrodynamic model for a four-lump kinetic scheme in order to predict the yield patterns. The yields predicted by the model were compared with four cases of plant data available and a good agreement between the industrial data and simulation result was observed. The temperature, pressure and axial profiles of products are also presented. The effects of input catalyst temperature to riser, catalyst to oil ratio (COR) and feed rate on yield of gasoline, is analyzed. A comparative study of the yield patterns for a riser reactor and a downer reactor is also given. It was observed that the yield of gasoline increases with an increase in catalyst temperature at the rate of reaction is known to decrease with a decrease in catalyst temperature. The yield of gasoline was found to increase with an increase in the catalyst oil ratio till it reaches a maximum value and starts decreasing because after a certain level the production of coke is increased and hence due to deactivation of catalyst the gasoline yield starts decreasing. It can be seen that the yield of gasoline for a downer reactor is more than that obtained for a riser reactor even though the reaction rate in the initial section of the riser reactor is more than that in the downer reactor. Also the yield of coke in downer is found to be less as compared to yield of coke in riser reactor due to reduced secondary reaction.

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APPENDIX

The values of kinetic parameters, thermodynamic properties are obtained from [17], and are given in the following tables.

TABLE 1: Kinetic parameters

	K_0	E (kJ/mol)	ΔH (kJ/kg)
Gas oil to Gasoline	1.15×10^3	59.66	393
Gas oil to light gases	7.36×10^3	47.82	795
Gas oil to coke	1.79	30.95	1200
Gasoline to light gases	4.26×10^2	68.83	1150
Gasoline to coke	5.99×10^4	57.74	151

TABLE 2: Industrial riser operating conditions used

	Case I	Case II	Case III	Case IV
Feed rate (kg/s)	19.95	25.7	26.9	23.6
Feed quality (API)	22.28	21.76	22.98	22.73
COR (kg/kg)	7.2	6.33	5.43	6.07
Inlet Pressure (kPa)	294	294	294	294
Feed Temperature (K)	494	494	494	494
Catalyst Inlet temperature (K)	960	1033	1004	1006
Steam (Wt %)	7.	5.5	5	5.75
Steam Temperature (K)	773	773	773	773

TABLE 3: Riser Dimensions

	Height (m)	Diameter (m)
Riser/downer reactor	33	0.8

TABLE 4: Riser Dimensions

Species	MW (kg/kmol)	C_p (kJ/kg.K)
Gas oil	333	2.67 (Liquid), 3.3 (Gas)
Gasoline	106.7	3.3
Light Gases	40	3.3
Coke	14.4	1.087
Steam	18	1.9
Catalyst	N/A	1.087

TABLE 5: Thermodynamic Properties of the Feed

Gas oil vaporization temperature	698 K
Viscosity of gas	1.4×10^{-5} N.s/m ²
Gas oil enthalpy of vaporization	190 kJ/kg