A
MAJOR PROJECT REPORT ON

To Develop a Kinetic Model for a FCC Riser

For the partial fulfillment of Bachelor of Technology

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To Develop a Kinetic Model for a FCC Riser

A dissertation submitted in partial fulfillment of the requirement for the Degree of

Bachelor of Technology

By

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UNIVERSITY OF PETROLEUM & ENERGY STUDIES

Certificate

This is to certify that the work contained in this dissertation titled **"To Develop a Kinetic Model for a FCC Riser"** has been carried out by **Gaurav Arya** (R010205016) and **Nirbhik Sinha** (R010205037) under my supervision and has not been submitted elsewhere for a degree.

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Executive Summary

Fluid Catalytic Cracking Unit is one of the most important units of the refinery. FCC is a catalytic conversion process for converting HGO, namely vacuum distillates into more valuable products such as LPG, gasoline, cycle oils, olefin rich light hydrocarbons that may be further processed to even more valuable products and fuel oils. It is a low pressure, intermediate to high temperature process.

The study on various aspects of FCCU deals with their Modeling, Simulation, Kinetics, Optimization and Control. The Traditional and global approach of modeling of cracking kinetics is based on lumping of compounds. In the kinetic lumping approach, the reaction kinetics considered is that of 'conversion' of one lump to another and not the 'cracking' of an individual lump. The Proposed model is a 5 Lump scheme consisting of **Gas Oil, Gasoline, LPG, Dry Gas and Coke.**

The Riser is modeled as a vertical tube comprising of a no. of equal sized compartments (or Volume element) of circular cross-section. The height of a typical volume element is considered to be z_j which is 1/1000 time of riser height. The FCC riser is modeled as a steady state plug flow reactor. The mass balance and heat balance riser calculations are performed by integrating the values along riser height using Runge-Kutta numerical technique for obtaining the Riser Top Temperature and the yields of the various lumps involved in the reaction.

A C++ program has been developed for obtaining the final result.

Table of Contents

Contents

List of Figures

List of Tables

1.1 **Objective:** To develop a Kinetic Model for a FCC Riser.

2.1 Introduction:

2.1.1 Fluid Catalytic Cracking:

Fluid Catalytic Cracking (FCC) is a Refinery Process in which the heavy hydrocarbon molecules such as Gas Oil are converted into lighter and more valuable fractions like middle distillate, gasoline, LPG and some by-products like dry gas and coke.

The FCC unit consists of a Reactor/Riser, Stripper, Catalyst Regenerator, Cyclone Separator and fractionators.

The hydrocarbon feed enters a transport bed tubular reactor (riser) through feed atomizing nozzles and comes in contact with the hot catalyst coming from the regenerator. The liquid feed gets vaporized and cracks down to the lighter hydrocarbons as it travels upward along with the catalyst. As a result of cracking the velocity of the vapors increase along the riser height. Coke, the byproduct of cracking reaction gets deposited on the catalyst surface causing the catalyst to loose its activity. The cracked hydrocarbon vapors are separated from the de-activated catalyst in a cyclone separator; the vapors adsorbed onto the surface of the catalyst are also stripped off using steam in the catalyst stripper. The cracked hydrocarbon vapors are sent to the main fractionation column for further separation into various fractions, and the de-activated catalyst flows into the regenerator. In the regenerator, the coke deposited on the catalyst surface is burned off to regenerate the catalyst. The catalyst becomes hot during regeneration process. This hot regenerated catalyst is recycled back to the riser reactor. Thus, the catalyst also acts as a heat carrier and provides the heat required for the endothermic cracking reactions in the riser as well as heat required for the vaporization of the feed. Cracking reactions take place on the surface of the catalyst particles in vapor phase.

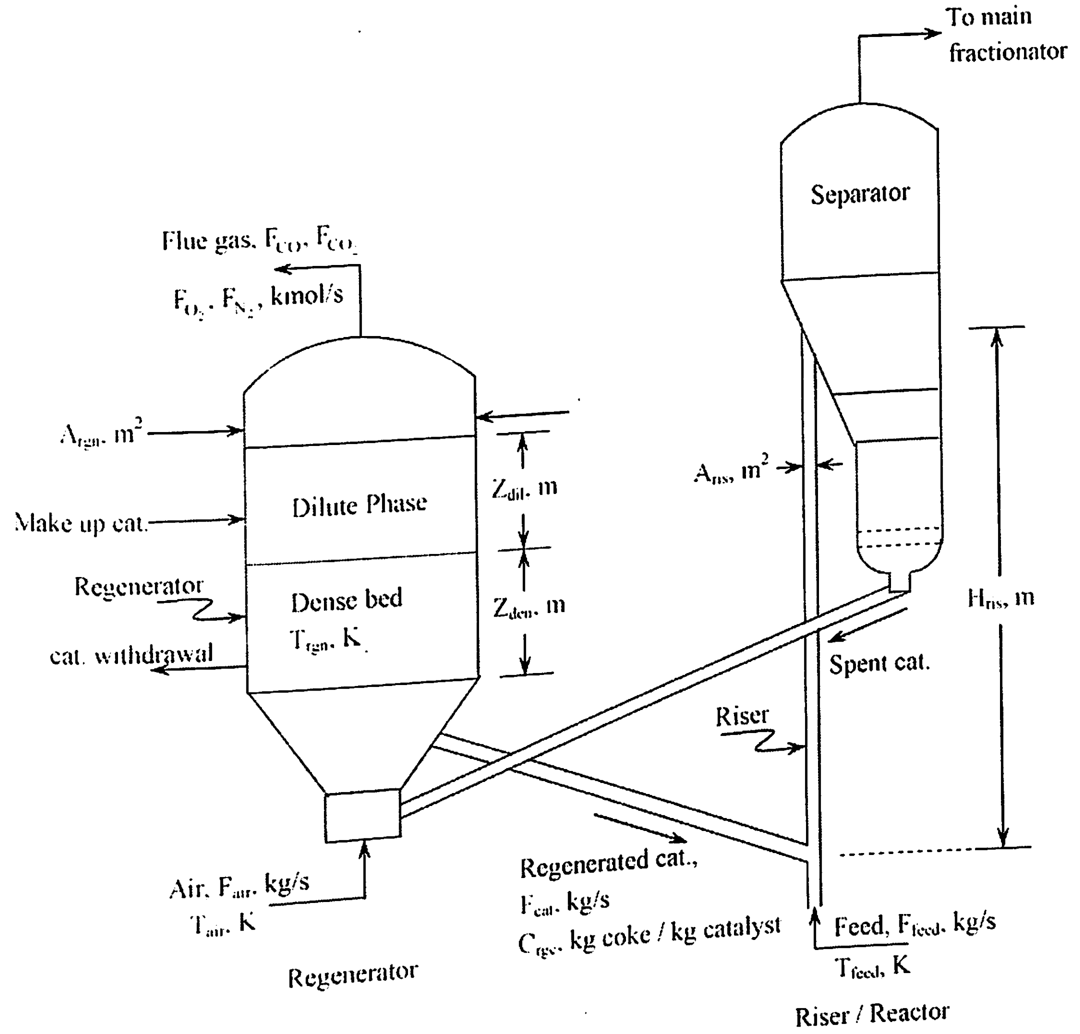

Figure 1- Fluidized Bed Catalytic Cracking Unit

The FCC process description has been broken down into four sections:-

- Feed Preheat Section
- Riser, Reactor, Stripper Section
- Regeneration- Heat/Catalyst Recovery Section
- Main Fractionation Section

2.1.1.1 Feed Preheat Section:

The refinery produced Gas Oil and any supplemental FCC feed stock are generally combined and sent to a surge drum which provides a steady flow of feed to the charge pumps. This drum can also separate any water or vapor that may be in the feed stocks. From the surge drum, the feed is normally heated to the temperature of 500^0F to 700^0F. The main fractionator bottom pump-arounds and or fired heaters are usual sources of heat. The feed is first routed through heat exchangers using hot streams from the main fractionator. The main fractionator top pump-around, light cycle oil and bottoms pump-around are commonly used. Most FCC units use fired heaters for FCC feed final pre-heat. The feed pre-heater provides control over the catalyst to oil ratio. In units where air blower is constrained, increasing pre-heat temperature allows increased throughput.

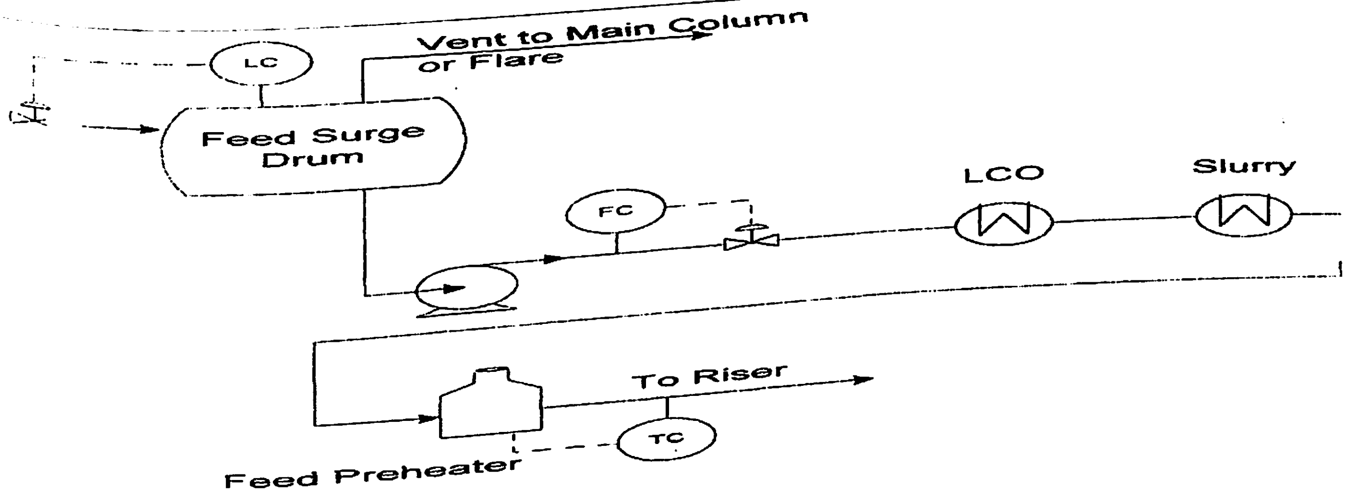

Figure 2- Feed Pre-heat System

2.1.1.2 Riser, Reactor, Stripper Section:

The Riser Regenerator is the heart of the FCC process. In a modern catalytic cracker, virtually all the reactions occur in 1.5 to 3.0 seconds before the catalyst and the products are separated in the reactor.

From the pre-heater, the feed enters the riser near the base where it contacts the regenerated catalyst. The ratio of catalyst to oil is nearly in the range of 4:1 to 9:1 by weight. The heat absorbed by the catalyst in the regenerator provides the energy to heat the feed to its desired reactor temperature. The heat of reaction occurring in the riser is endothermic. The circulating catalyst provides this energy. The catalytic reactions occur in the vapor phase. Cracking reactions begins as soon as the feed is vaporized. The expanding volumes of the vapors that are generated are the main driving force to carry the catalyst up the riser. Catalyst and products are quickly separated in the reactor. However, some thermal and non-selective catalytic reactions continue.

The riser is a vertical pipe. It usually has a 4 to 5 inch thick refractory lining for insulation and abrasion resistance. Typical risers are 2 to 6 ft in diameter and 75 to 120 ft long. The ideal riser simulates a plug flow reactor, where the catalyst and the vapor travel the length of the riser with minimum back mixing. Efficient contacting of feed and catalyst is critical for achieving the desired cracking reactions. Steam is commonly used to atomize the feed. Smaller oil droplets increase the availability of feed at the reactive acid sites on the catalyst. All the cracking reactions take place in 3 seconds or less with high activity zeolite catalyst. The average hydrocarbon residence time is about 2 seconds in the riser.

After exiting the riser, catalyst enters the reactor vessel. The reactor serves as housing for the cyclones. The cyclones are employed to separate the remaining catalyst particles from the cracked vapors.

The cyclone collects and returns the catalyst to the stripper through the diplegs and flapper/trickle valves. The product vapors exits the cyclone and flow to the main fractionator for recovery. It is important to separate catalyst and vapors as soon as they enter the reactor, otherwise non-selective catalytic re-cracking of some of the hydrocarbons would take place. The extended residence time also promotes thermal cracking of some of the desirable products.

As the spent catalyst falls into the stripper, hydrocarbons are adsorbed on the catalyst surface, hydrocarbon vapors fill the catalyst pores and the vapors entrained within the catalyst also fall into the stripper. Stripping steam at a rate of 2 to 5 lbs per 1000 lbs is primarily used to remove the entrained hydrocarbon between catalyst particles. The reactions in the stripper are driven by the reactor temperature and catalyst residence time in the stripper. The higher temperature and longer residence time allow conversion of adsorbed hydrocarbons into clean lighter products. At too high a flux, the falling catalyst tends to entrain steam, thus reducing the effectiveness of stripping steam. It is important to minimize the amount of hydrocarbon vapors carried through to the regenerator but not all the hydrocarbon vapors can be displaced from the catalyst pores in the stripper. A fraction of them are carried with the spent catalyst into the regenerator. These hydrocarbon vapors have high hydrogen-to-carbon ratio than the coke on the catalyst. The flow of spent catalyst in the regenerator is controlled by a valve which in turn is controlled by the catalyst level in the stripper.

The draw-backs of allowing these hydrogen rich hydrocarbons to enter the regenerator are as follows:-

1. Loss of liquid products.
2. Loss of throughput.
3. Loss of catalyst activity.

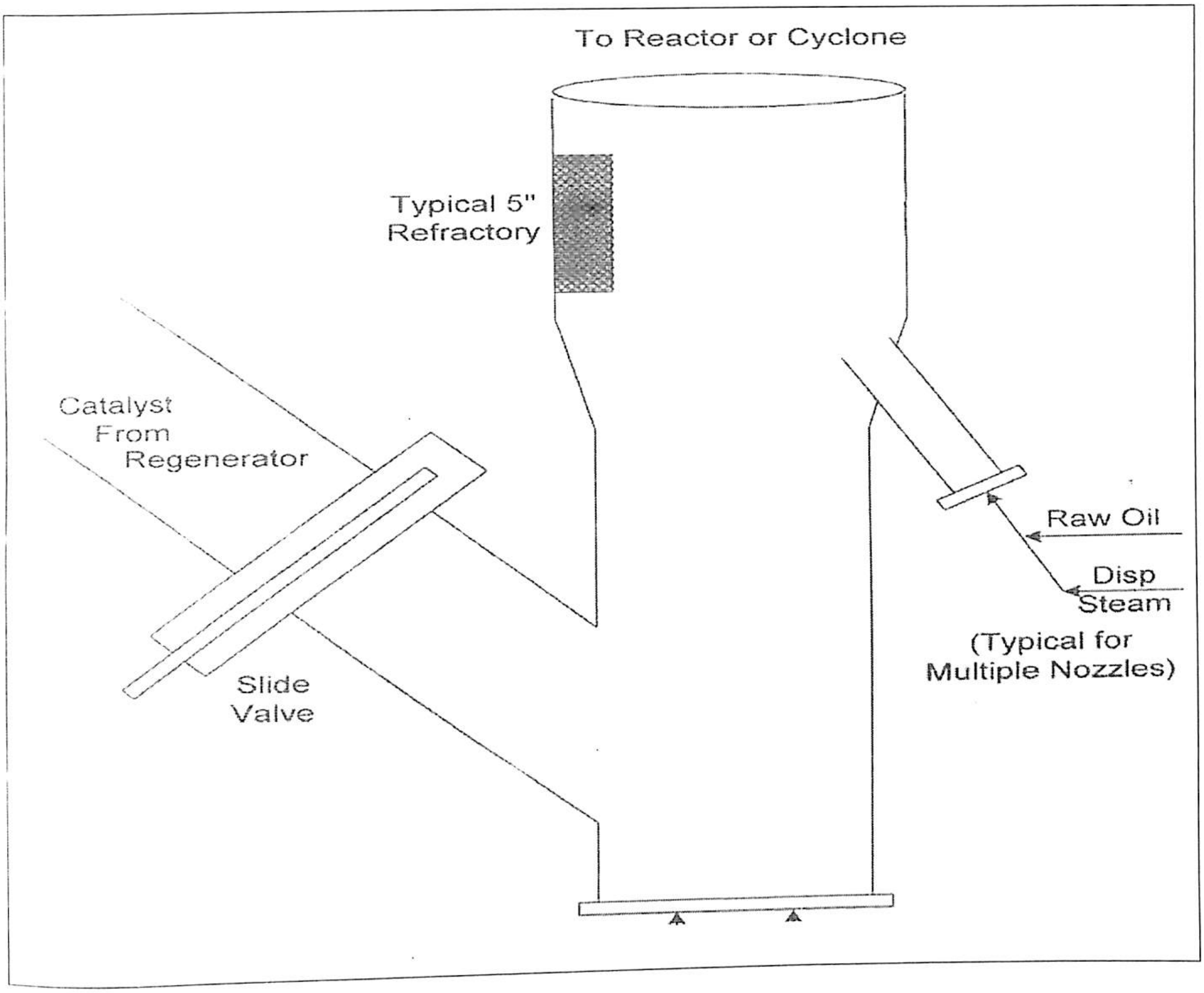

Figure 3- FCC Riser

2.1.1.3 Regeneration Section:

The Regenerator has two main functions-

- It supplies heat to crack the feed
- It restores catalyst activity.

The spent catalyst entering the regenerator contains between 0.4 wt. % and 2.5 wt. % of coke depending on the quality of feed-stock. Components of coke are carbon, hydrogen and trace amount of sulphur and nitrogen which burns according to the following reactions,

$C + \frac{1}{2} O_2 \rightarrow CO$

$CO + \frac{1}{2} O_2 \rightarrow CO_2$

$C + O_2 \rightarrow CO_2$

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

$S + xO \rightarrow SO_X$

$N + xO \rightarrow NO_X$

Air provides oxygen for the combustion of coke and is supplied by one or more air blowers. The air blower provides sufficient air velocity and pressure to maintain the catalyst bed in a fluid state. The air enters the regenerator through an air distributor located near bottom of the vessel. During regeneration the coke level on the catalyst is reduced to 0.05%. From the regenerator catalyst flows down a transfer line referred to as a Stand pipe. The Stand pipe provides the necessary pressure to circulate the catalyst around the unit. Some stand-pipes extend into the regenerator, and the top section is often called a catalyst-hopper. The hopper internal is usually an inverted cone design. The hopper provides sufficient time for the regenerated catalyst to be de-bubbled before entering the stand pipe. There are two regions in the regenerator, the dense phase and the dilute phase. The region immediately above the air distributor is the dense phase. The dilute phase is the region above the dense phase up to the cyclone inlet. A cyclone separator is employed in the regenerator to recover the catalyst particles entrained in the flue gases leaving the dense phase region. The hot flue gas exiting the cyclones to the plenum chamber in the top of the regenerator holds an appreciable amount of energy. Various heat recovery schemes are used to recover this energy. The catalyst in the regenerator can be regenerated by two modes of regeneration scheme; the partial combustion scheme, the complete combustion scheme. Complete combustion generates more amount of energy than partial combustion when coke yield is increased. In complete combustion scheme the excess reaction component is oxygen. In partial combustion scheme the excess component is carbon.

Advantages of full combustion,

- Energy efficient.
- Heat-balances at low coke yield.
- Minimum hardware (no CO boiler).
- Better yields from clean feed.

Disadvantages of full combustion,

- Narrow range of coke yields unless some heat removal system is incorporated
- Greater after burn, particularly with a spent catalyst distribution section.

With clean feed, complete combustion scheme is adopted and with low quality feed or residue, partial combustion is done.

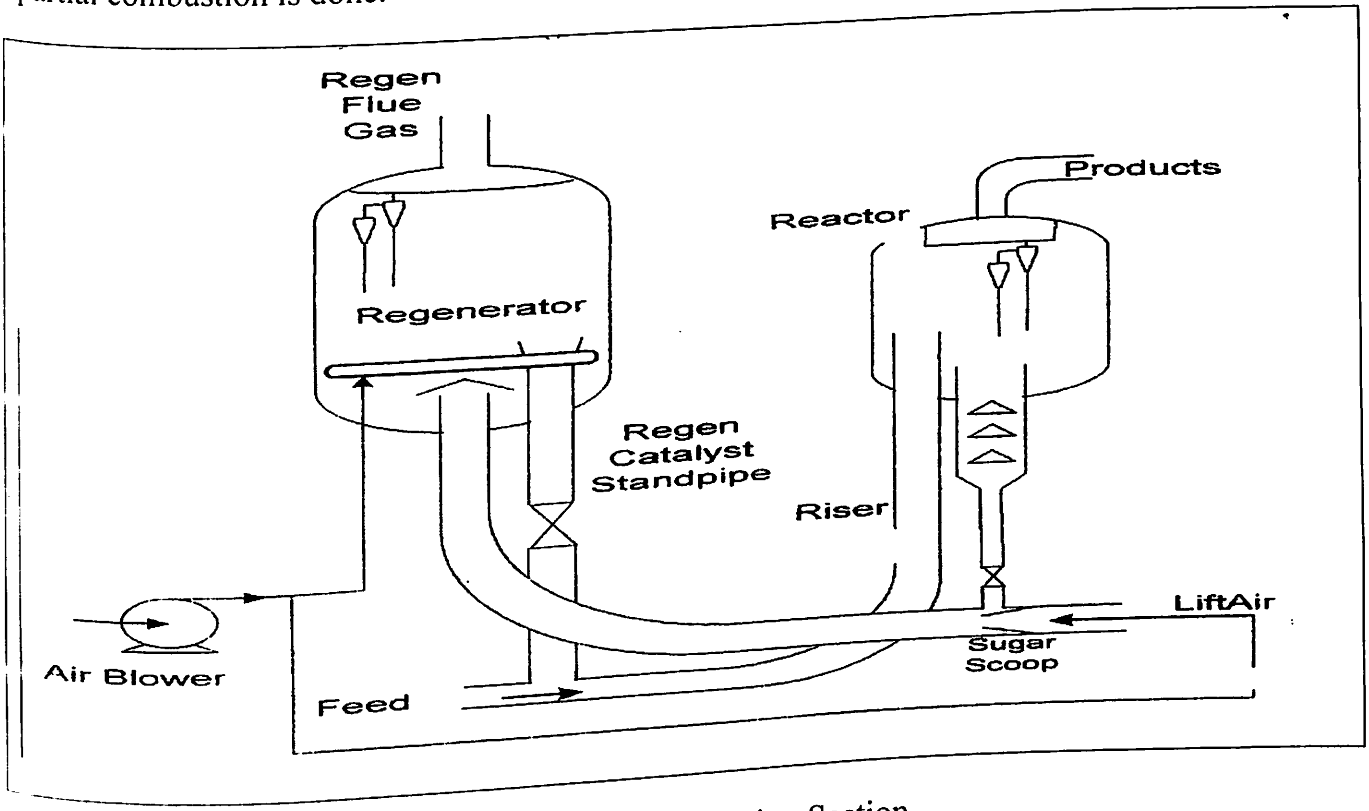

Figure 4- Regeneration Section

2.1.1.4 Main Fractionation Section:

The purpose of the main fractionator or main column is to de-superheat and recover liquid products from the reactor vapours. The hot product vapours from the reactor flow into the main fractionator near the base. Fractionation is accomplished by condensing and re-vaporizing hydrocarbon components as the vapour flows upward through trays in the tower. In the fractionator, the reactor effluent vapours must be cooled before any fractionation begins. The overhead reactor vapour is de superheated and cooled by a pump-around stream. Pump-around also serves as a scrubbing medium to wash down catalyst fines entrained in the vapours. The recovered heat from the column bottom is commonly used to pre-heat the fresh feed or generate steam. The heaviest bottom product from the main column is commonly called slurry or Decant oil. High quality Decant oil can be used for carbon black feed stocks. The carryover of catalyst to the main column results in catalyst losses. It can be controlled by two ways:

Firstly, high recycle rates should be used to return slurry to the reactor. Secondly, the slurry products should be returned through slurry settlers, either gravity or centrifugal to remove catalyst fines.

Above the bottoms product, the main column is designed for three possible cuts,

- Heavy Cycle Oil (HCO) - used as a pump-around stream, sometimes as recycle to the riser but rarely as product.
- Light Cycle Oil (LCO) – used as a pump-around stream, sometimes as absorption oil in the gas plant and stripped as a product for diesel blending.
- Heavy Naphtha – used as a pump-around stream, sometimes as absorption oil in the gas plant and possible blending in the gasoline pool.

2.1.2 FCC Feed Characterization:

Feed Characterization is the process of determining the physical and chemical properties of the feed. Two feeds with similar boiling point ranges may exhibit dramatic differences in cracking performance and product yield. Feed characterization relates products yield and qualities to feed quality. Knowing the effect of feedstock on unit yields, a refiner can purchase the feedstock that maximizes profitability.

The two primary factors that affect feed quality are:-

- Hydrocarbon classification
- Impurities

2.1.2.1 Hydrocarbon Classification-

The hydrocarbon types in the FCC feed are broadly classified as paraffin, olefin, naphthenes and aromatics.

2.1.2.1.1 Paraffin:-

Paraffins are straight or branched chain hydrocarbons having the chemical formula C_nH_{2n+2}. FCC feeds are predominantly paraffinic. The paraffinic carbon content is typically between 50 wt. % to 65 wt. % of the total feed. Paraffinic stocks are easy to crack and normally yield the greatest amount of total liquid products. They make the most gasoline and the least fuel gas, but also the lowest octane no:

2.1.2.1.2 Olefins:-

Olefins are unsaturated compound with a chemical formula C_nH_{2n}. Compared to paraffins, olefins are unstable and can react with themselves or with other compounds. Olefins do not occur naturally; they show up in the FCC feed as a result of pre-processing the feeds elsewhere. These processes include thermal cracking and other catalytic cracking operations. Olefins are not the preferred stocks to an FCC unit as they often polymerize to form undesirable products such as slurry and coke. The typical olefin content of FCC feed is less than 5 wt. %.

2.1.2.1.3 Naphthenes:-

Naphthenes (C_nH_{2n}) have same chemical formula as olefins but their characteristics are significantly different. Naphthenes are desirable FCC feed-stocks because they produce high-octane gasoline. The gasoline derived has more aromatics and is heavier than gasoline produced from cracking of paraffins.

2.1.2.1.4 Aromatics:-

Aromatics are not a preferred feed-stock because few of the molecules will crack. The cracking of aromatics mainly involves breaking off the side chains resulting in the excess fuel gas yields. In comparison with cracking paraffins, cracking aromatic stocks results in lower conversion, lower gasoline yield, and less liquid volume gain but with higher gasoline octane.

2.1.2.1.5 Feed-stock Physical Properties:-

Characterizing an FCC feed-stock involves determining both their physical and chemical properties. Because sophisticated analytical techniques such as mass spectrometry are not practical on a daily basis, physical properties are used. They provide qualitative measurement of the feed's composition.

The most widely used properties are:-

1. ^{0}API gravity
2. Distillation
3. Aniline point
4. Refractive index
5. Bromine no: and bromine index
6. Viscosity
7. Conradson, Ramsbottom

2.1.2.2 Impurities-

Nowadays, FCC feed-stocks are generally heavier and contain higher level of impurities. The most common contaminants are,

1. Nitrogen
2. Sulfur
3. Nickel
4. Vanadium
5. Sodium

2.1.3 FCC Catalyst:

The Zeolite catalyst is more active and more selective as compared to amorphous silica-alumina catalyst. The higher activity and selectivity translate to more profitable liquid product yields and additional cracking capacity.

FCC Catalysts are in the form of fine powders with an average particle size in the range of 75 microns. A modern catalytic cracking catalyst has four major components:

- Zeolite
- Matrix
- Binder
- Filler

2.1.3.1 Zeolite:

Zeolite or more properly 'faujasite' is the key ingredient of the FCC catalyst. It provides product selectivity and much of the catalytic activity. The catalyst's performance largely depends on nature and quality of the zeolite catalyst.

2.1.3.1.1 Zeolite Structure:

Zeolite is sometimes called 'molecular sieves'. It has a well defined lattice structure. Its basic building blocks are silica and alumina tetrahedral (pyramids). Each tetrahedron consists of a silicon or aluminum atom at the centre of the tetrahedron, with oxygen atoms at the four corners. Zeolite lattices have a network of very small pores. The pore diameter of FCC zeolite is approximately 8.0 angstorms (^{0}A).

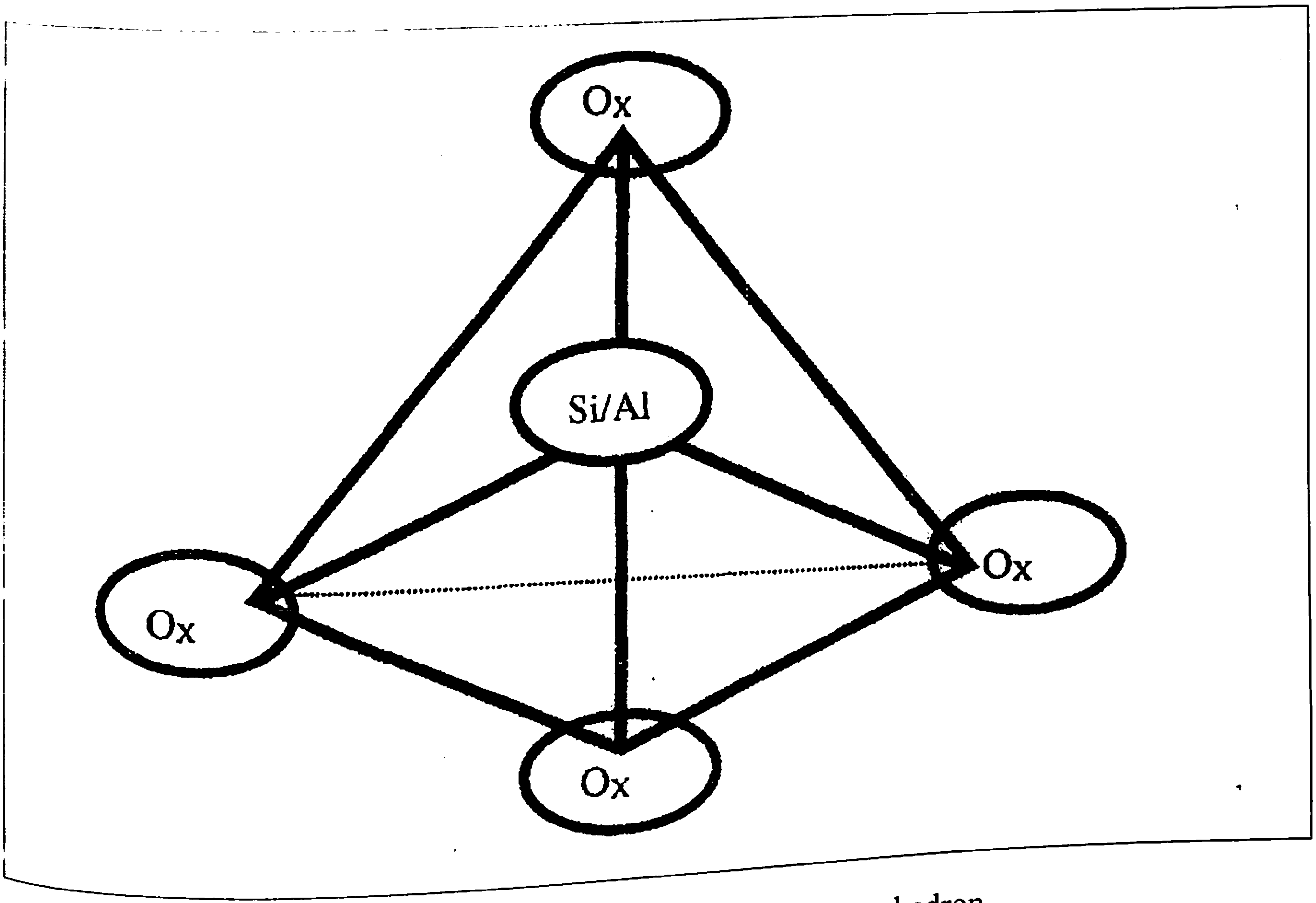

Figure 5- Silicon/aluminum-Oxygen tetrahedron

2.1.3.1.2 Zeolite Types:

Zeolites employed in the manufacture of FCC catalyst are synthetic versions of naturally occurring zeolites called 'faujasites'. The zeolites with application to FCC are Type X, Type Y and ZSM-5. Both X and Y zeolites have essentially the same crystalline structure. The X zeolite has a lower silica-alumina ratio than the Y zeolite. The X zeolite also has a lower thermal and hydrothermal stability than the Y zeolite. All of today's catalyst contains Y zeolite.

ZSM-5 is a versatile zeolite that increases olefin yields and octane.

2.1.3.2 Matrix:

Matrix means components of the catalyst other than zeolite and the term active matrix means the component of the catalyst other than zeolite having catalytic activity. Alumina is the source for an active matrix. Most active matrices used in FCC catalysts are amorphous. However, some of them also have a crystalline structure. An active matrix provides the primary cracking sites. The acid sites located in the catalyst matrix are not as selective as the zeolite sites, but are able to crack larger molecules that are hindered from entering the small zeolite pores. The active matrix pre-cracks heavy feed molecules for further cracking at the internal zeolite sites. The active matrix can also serve as a trap to catch some of the vanadium and basic nitrogen which poisons the catalyst.

2.1.3.3 Fillers and Binders:

The filler is clay incorporated in the catalyst to dilute its activity. Kaoline $[Al_2(OH)_2, Si_2O_5]$ is the most common clay used in the FCC catalyst.

The Binder serves as a glue to hold the zeolite, matrix and filler together. Binder may or may not have catalytic activity. The importance of the binder becomes more prominent with catalyst that contains high concentration of zeolite.

The function of the filler and binder are to provide physical integrity (density, attrition resistance, particle size distribution etc), a heat transfer medium and a fluidizing medium in which the more important and expensive zeolite component is incorporated.

The study on various aspects of FCCU deals with their Modeling, Simulation, Kinetics, Optimization and Control.

The study of the kinetics can be discussed in two ways:-

- Separate study for kinetics of the reactor and kinetics of the regenerator.
- Integrated models for the Reactor-Regenerator systems.

2.1.4 Lumping of Compounds:

The Traditional and global approach of modeling of cracking kinetics is based on lumping of compounds. Mathematical models dealing with riser kinetics can be categorized into two main types. In one category, the lumps are made on the basis of boiling range of feed stocks and corresponding products in the reaction system. This kind of model has an increasing trend in the number of lumps of the cracked components. The other approach is that in which the lumps are made on the basis of molecular structure, characteristics of hydrocarbon group composition in reaction system. These both categories of models do not include chemical data such as type of reaction and reaction stoichiometry. The number of kinetic constants in these models increases very rapidly with the number of lumps. All these models assume that FCC feed and products are made of a certain number of lumps, and kinetic parameters for these lumps are estimated empirically considering conversion of one lump to the other.

In the advanced model of FCC riser three lump, four lump or five lump kinetic schemes are used to avoid the mathematical complexities as the number of cracking constants increases rapidly with the number of lumps.

The 10 or 12 lump kinetic model requires a detailed feed characterization which calls for use of sophisticated analysis tools like mass spectroscopy, gas chromatography, silica gel precipitation etc, which is not practical on a routine basis. Moreover, for a given refinery unit if it is assumed that composition of the feed to FCCU does not change too often the entire feed can be grouped into one kinetic lump with the products lumped into 2,3 or 4 groups. This type of grouping compromises with the rigor but is very simple to use and hence more popular.

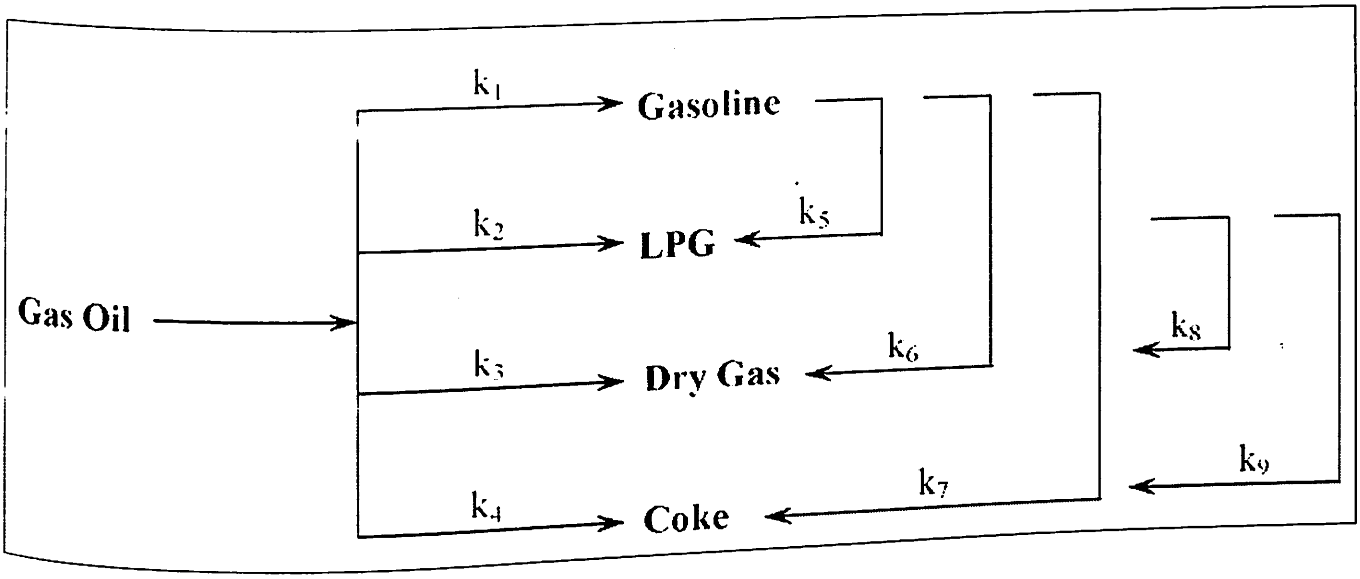

Figure 6- The Five Lump Kinetic Scheme

3.1 Description of the Project:

The modeling of cracking kinetics is based on lumping of compounds. Lumping of compounds is an approach in which the feeds and the products are characterized and grouped in terms of their similar nature and each of these groups are taken to behave as a single kinetic entity called kinetic lump. The no: of kinetic constants in the model increases rapidly with the no: of lumps as, the rate constants are highly dependent upon the feed composition. In the kinetic lumping approach, the reaction kinetics considered is that of 'conversion' of one lump to another and not the 'cracking' of an individual lump. The pure components in the lumped kinetic model are grouped as Pseudo components. All these components are collectively called as pseudo components and abbreviated as PCs. Apart from these components a separate coke lump is also considered which is formed as a byproduct of the cracking reactions.

4.1 Methodology:

4.1.1 Riser Model:

The Riser is modeled as a vertical tube comprising of a no. of equal sized compartments (or Volume element) of circular cross-section. Volume elements are designated by symbol 'n' and no. of volume elements are done from bottom (inlet) to top (outlet). Each volume element is assumed to contain two phases (i) solid phase (catalyst and coke) and (ii) gas phase (vapors of feed and product hydrocarbon and steam). It is assumed that known amount of reactants enter the

nth volume element, the ith cracking reactions takes place in the elements for a period equal to the residence time of the hydrocarbons in the element. The concentration of the reacting mixture at the outlet of the nth volume element serve in defining the feed for the (n+1)th volume element. The height of a typical nth volume element is considered to be z_j which is 1/1000 time of riser height.

The Proposed model will discuss the Kinetics of the process by taking into consideration the study of rate constants of the chemical equations. The lumps formed, are on the basis of their molecular weight and are designated by the symbol 'j'.

The Proposed model is a 5 Lump scheme consisting of **Gas Oil, Gasoline, LPG, Dry Gas and Coke** where the rate constants depends on feed composition and needs to be determined afresh for each feed.

The FCC riser is modeled as a steady state plug flow reactor with the following assumptions:

- The Slip factor in the reactor is considered to be 1.
- Gas Oil cracking is a second order reaction but the cracking of Gasoline and LPG are first order reactions.
- Dry Gas produces no coke.
- The heat capacities and densities are constant through length of the reactor.

The Reactions involved would be:-

i	Rate Constant	Reactions	Frequency factor*	Activation Energy(kj/kmol)	Heat of reaction(kj/kmol)
1	k_1	Gas Oil → Gasoline	18579.90	57540	45000
2	k_2	Gas Oil → LPG	3061.10	52500	159315
3	k_3	Gas Oil → Dry Gas	532.14	49560	159315
4	k_4	Gas Oil → Coke	39.04	31920	159315
5	k_5	Gasoline → LPG	65.40	73500	42420
6	k_6	Gasoline → Dry Gas	0.00	45360	42420
7	k_7	Gasoline → Coke	0.00	66780	42420
8	k_8	LPG → Dry Gas	0.32	39900	2100
9	k_9	LPG → Coke	0.19	31500	2100

Table-1:

*(m^3_g/(kg catalyst)(kmol gas oil)(s)) for reactions 1to 4.

(m^3_g/(kg catalyst)(s)) for reactions 5 to 9.

4.1.1.1 Mass Balance:-

The Mass Balance across the differential element of the Riser can be written as:

$$\frac{dF_j}{dh} = A_{ris}H_{ris}(1-\varepsilon)\,\rho c \sum_{i=1}^{9} \alpha_{ij} r_i \qquad j=1,2.............5 \qquad (1)$$

Where, j =1to 5 represents Gas Oil, Gasoline, LPG, Dry Gas and Coke

i =1 to 9 represents the reactions as shown in Table-1

$$h \quad \frac{z}{H_{ris}} \tag{2}$$

$$M_{Wg} = \sum_{j=1}^{5} X_j M_{Wj} \tag{3}$$

$$\rho_v = (P_{ris} M_{Wg})/RT \tag{4}$$

$$\varepsilon = \frac{F_{feed}/\rho_v}{\frac{F_{feed}}{\rho_v} + \frac{F_{rgc}}{\rho_c}} \tag{5}$$

α_{ij} = stoichiometric coefficients = $\frac{M_{Wi}}{M_{Wj}}$ for I going to j. (6)

The Rate Equations in (kmol) / ((kg cat) (s)) are given by the following expressions:

$$r_1 = k_{o,i}\, exp\left(\frac{-E_i}{RT}\right) C_1^{\,2} \varphi \qquad for\ i = 1,2,3,4 \tag{7}$$

$$r_2 = k_{o,i}\, exp\left(\frac{-E_i}{RT}\right) C_2\, \varphi \qquad for\ i = 5,6,7 \tag{8}$$

$$r_3 = k_{o,i}\, exp\left(\frac{-E_i}{RT}\right) C_3\, \varphi \qquad for\ i = 8,9 \tag{9}$$

Where C_1, C_2, C_3 are concentrations of Gas Oil, Gasoline and LPG respectively.

$$\varphi = (1+51C_c)^{-2.78} \tag{10}$$

C_C = Coke on catalyst

4.1.1.2 Enthalpy Balance:-

The Enthalpy Balance across the differential element of the Riser can be written as:

$$\frac{dT}{dH} = \frac{A_{ris}\, H_{ris}\, \rho_c\, (1-\varepsilon)}{F_{rgc}\, C_{pc} + F_{feed}\, C_{pfv}} \sum_{i=1}^{9} r_i\, (-\Delta H_i) \tag{11}$$

The Riser bottom temperature is calculated as follows:

$$T\,(h = 0) = \frac{F_{rgc} C_{pc}\, (T_{rgn} - 10) + F_{feed}\, C_{fl} T_{feed} - \Delta H_{evp}\, F_{feed} - Q_{loss.ris}}{F_{rgc}\, C_{pc} + F_{feed}\, C_{pfv}} \tag{12}$$

5.1 Procedure:

The reactor calculations are performed to obtain a value of final riser temperature and coke on catalyst. Equations 1-11 will be integrated along the riser height with fractional step length of 0.001 using Runge-Kutta numerical method technique. Riser bottom temperature is calculated using equation 12.

The values of different parameters used in the calculations work are provided in Table 1, 2 and 3.

A C++ program has been developed for obtaining the final result.

The C++ code developed for iteration is mentioned in Appendix-A.

6.1 Results and Discussions:

The Activation Energy, Frequency factor and Heat of reaction of all the reactions involved in the kinetic scheme are provided in Table-1. The Thermodynamic and other parameters used in the C++ code are included in Table-5. Table-6 gives the design data for the FCC Unit used in the project.

Table-4 shows a comparison of model predicted yield with the measured ones for two different data sets. There has been a slight variation between the measured and the predicted values due to initial assumptions and unavailability of certain data. Although, the concentration and the temperature profile as shown in Figure-6 and Figure-7 are matching with the concerned profile of the FCC riser model.

7.1 Conclusion:

An Industrial FCC Riser-Reactor has been successfully modeled using a five-lump kinetic scheme. The calculated yields and conversion are in partial agreement with available scanty plant data for a FCC Unit. This can perhaps be attributed to imprecise assumptions of the values of the constants involved in the Voorhies Equation.

From Table-4 it is seen that the calculated Gasoline and LPG yields are closer to those obtained in the plant data, but there is a large difference between Dry Gas and Coke yields. These discrepancies are due to unavailability of certain data which were bound to be assumed.

Step Length	Gas-Oil (kmol/m^3)	Gasoline (kmol/m^3)	LPG (kmol/m^3)	Dry Gas (kmol/m^3)	Coke (kmol/m^3)
0	100	0	0	0	0
100	72.6244	22.295	4.10565	0.654	0.319
200	66.863	26.943	4.7969	0.809	0.404
300	63.611	29.558	5.47391	0.900708	0.455
400	61.391	31.341	5.811	0.964	0.492
500	59.729	32.673	6.06	1.01	0.52
600	58.415	33.725	6.264	1.051	0.543
700	57.337	34.588	6.428	1.083	0.5622
800	56.428	35.315	6.566	1.111	0.578
900	55.645	35.94	6.685	1.134	0.592
1000	54.962	36.486	6.789	1.155	0.605

Table-2: **Concentration variation of various lumps**

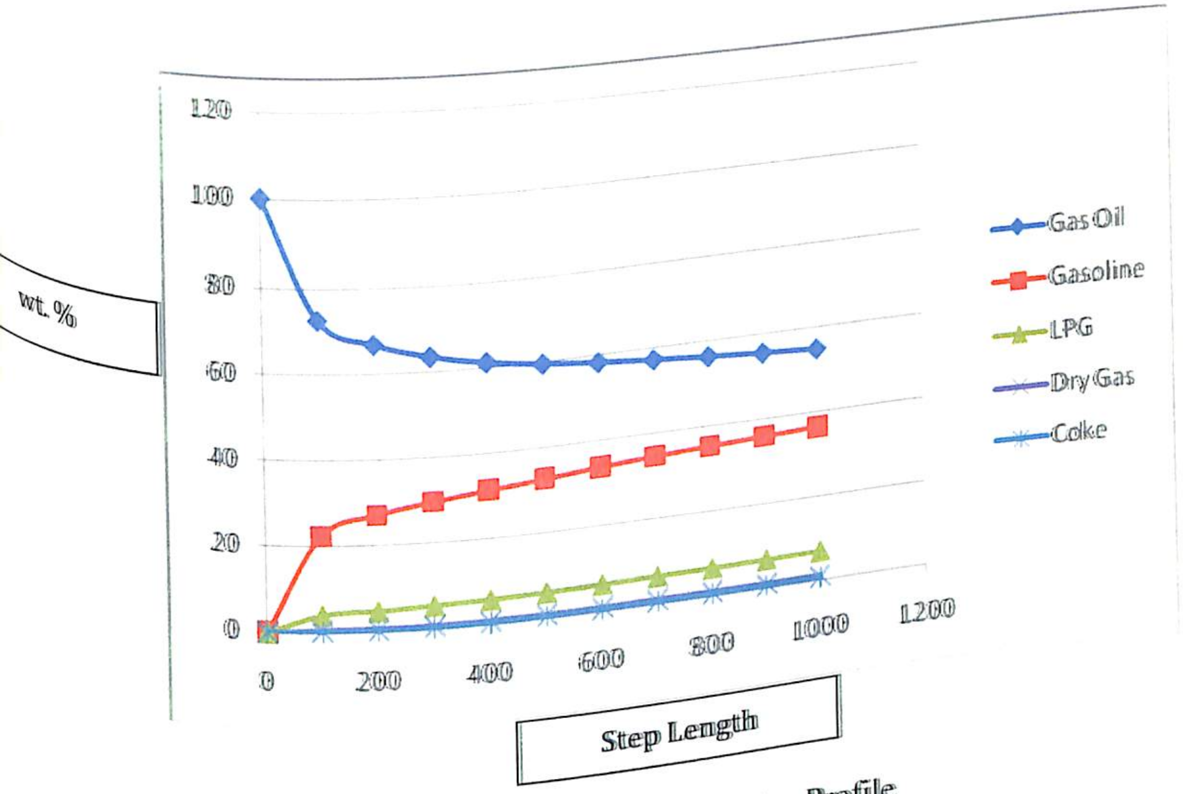

Figure 7- Concentration Profile

Step Length	Temperature variation (K)
0	820
100	792.01
200	786.139
300	782.808
400	780.527
500	778.816
600	777.46
700	776.345
800	775.404
900	774.594
1000	773.885

Table-3: **Temperature variations**

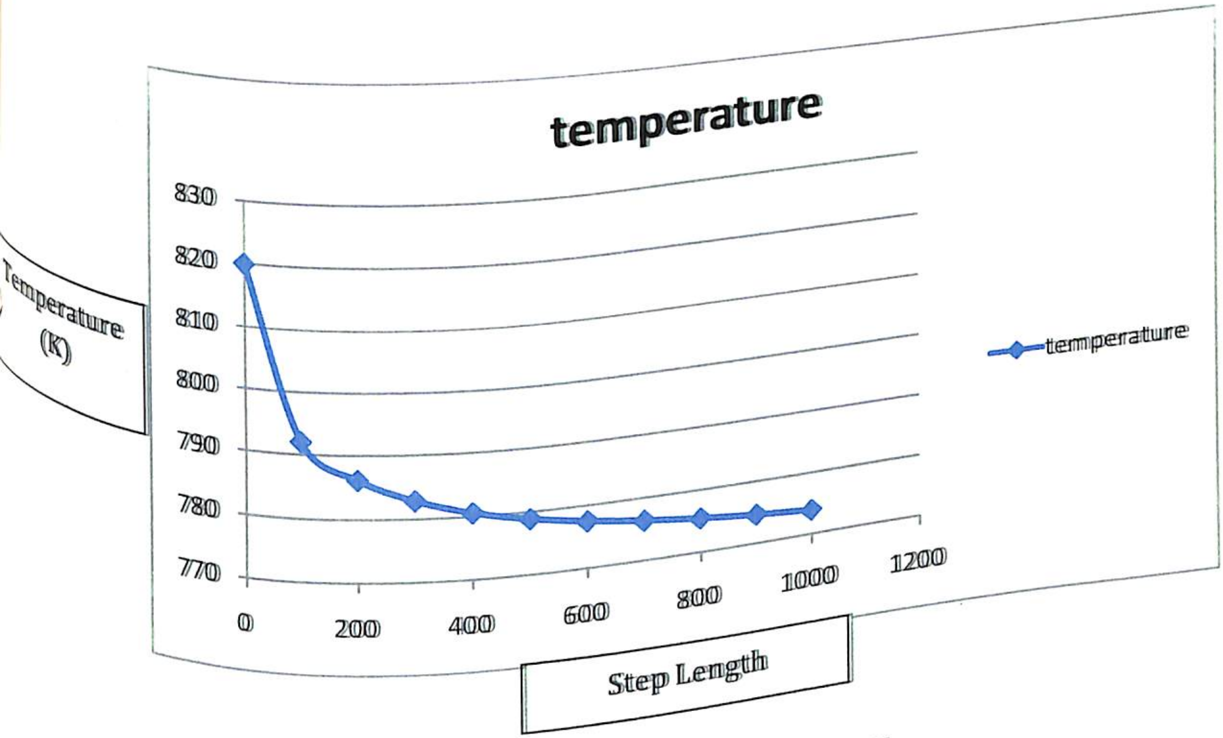

Figure 8- Temperature Profile

	Data Set-1		**Data Set-2**	
	Measured	Predicted	Measured	Predicted
Feed flow rate (kg/sec)	31.47	31.47	32.11	32.11
Catalyst flow rate (kg/sec)	208.33	208.33	205.00	205.00
Riser top Temp. (K)	765.5	773.2	766.66	762.3
Riser Pressure (atm.)	2.457	2.457	2.506	2.506
Gas Oil (%)	48.1	54.96	44.1	53.90
Gasoline (%)	32.6	36.48	35.2	37.14
LPG (%)	12.1	6.78	12.6	7.042
Dry Gas (%)	3.1	1.15	3.8	1.148
Coke (%)	4.1	0.60	4.3	0.770

Table-4:

8.1 Nomenclature:

A_{ris} – Riser cross sectional area, (m^2)

C_{pc} = Catalyst heat capacity, (kj/kg K)

C_{pfl} = Liquid feed heat capacity, (kj/kg K)

C_{pfv} = Vapor feed heat capacity, (kj/kg K)

E_i = activation energy of i^{th} cracking reaction in the riser.

F_j = molar flow rate of j^{th} lump, (kmol/s)

F_{rgc} = Regenerated catalyst flow rate, (kg/s)

F_{feed} = Oil feed flow rate, (kg/s)

h – Dimensionless riser height

H_{ris} = Riser height, (m)

ΔH_{evp} = Heat of vaporization of oil feed, (kj/kg)

ΔH_i = Heat of cracking of lump 'i', (kj/kmol)

$K_{o,i}$ = frequency factor for i^{th} reaction in the riser.

M_{Wj} = Molecular weight of j^{th} lump, (kg/kmol)

M_{Wg} = Average molecular weight of Gas Oil feed, (kg/kmol)

P_{ris} = Riser pressure, (atm)

r_i = Rate of i^{th} reaction, (kmol/kg.cat.s)

T – Position dependent riser or dilute phase temperature, (K)

T_{feed} = gas oil feed temperature, (K).

T_{rgn} = regenerator dense bed temperature,(K).

$T_{ris,top}$ = riser top temperature,(K).

x_j = Mole fraction of j^{th} component

z – Axial height from entrance of riser, (m)

ρ_v = Oil vapor density,(kg/m^3)

ρ_c – Catalyst density, (kg/m^3)

φ = Catalyst activityα_{ij} = stoichiometric coefficient of jth species in ith reaction.

ε = riser or regenerator void fraction.

9.1 References:

1. Dave, D., & Saraf, D. N. (2003) "Model suitable for rating and optimization of industrial FCC units", Indian Chemical Engineer, 45, 7.
2. Gupta, A., &Subba Rao D (2001) "Model for the performance of a FCC riser reactor: effect for feed atomization", Chemical Engineer Science, vol. 56, pp. 4489-4503 (26 ref.).
3. Ahari, J.S., & Farshi, A. (2008) "A Mathematical Modeling of the Riser-Reactor in industrial FCC Unit", Development Department-Research Institute of Petroleum Industry (RIPI), Tehran 18745-4163, Iran University of Science & Technology.
4. Sadeghbeigi, Reza, FCC Handbook, Houston, Texas.

Parameter	Numerical value
$C_{p.c}$ (kj/kg K)	1.003
$C_{p.fl}$ (kj/kg K)	3.430
$C_{p.fv}$ (kj/kg K)	3.390
$C_{p.N2}$ (kj/kg K)	30.530
$C_{p.O2}$ (kj/kg K)	32.280
$C_{p.H2O}$ (kj/kg K)	36.932
$C_{p.CO}$ (kj/kg K)	30.850
$C_{p.CO2}$ (kj/kg K)	47.400
ΔH_{evp} (kj/kg)	350.0
H_{CO} (kj/kmol)	1.078×10^5
H_{CO2} (kj/kmol)	3.933×10^5
H_{H2O} (kj/kmol)	2.42×10^5
X_{pt}	0.10
ρ_c (kg/m^2)	1089.0

C_H (kg H_2/kg coke)	0.165
D_p (ft)	2.0×10^{-4}
$MW_{gas\ oil}$	350
$MW_{gasoline}$	114
MW_{LPG}	58
$MW_{dry\ gas}$	30
MW_{coke}	12

Table-5:

Design data for FCC Unit

Parameter	Value
Riser length (m)	36.965
Riser diameter (m)	0.684
Regenerator length (m)	19.344
Regenerator diameter (m)	4.522
Catalyst hold up in the regenerator (vol. %)	40.0

Table-6:

10.1 Appendix- A:

```
//.....................................c++ code to solve the kinetic model of FCC
riser.....................................//

#include<iostream.h>

#include<conio.h>

#include<fstream.h>

#include<math.h>

void main()

{       int i,j,k,n;

        // ...........................value of the activation energy and frequency
constant..............................//

        double ki[9],ei[9];

        ki[0]=18579.90,ki[1]=3061.10,ki[2]=532.14,ki[3]=39.04;

        ki[4]=65.40,ki[5]=0,ki[6]=0,ki[7]=.32,ki[8]=.19;

        ei[0]=57540,ei[1]=52500,ei[2]=49560,ei[3]=31920,ei[4]=73500;

        ei[5]=45360,ei[6]=66780,ei[7]=39900,ei[8]=31500;

        double hl[9];

        hl[0]=45000,hl[1]=159315,hl[2]=159315,hl[3]=159315;

        hl[4]=42420,hl[5]=42420,hl[6]=42420,hl[7]=2100,hl[8]=2100;

        double ph,phi;

        double R,T;

        //..............................value of different input data for solving.................................//
```

```
double Pris,MWg=350,pv,C1=.036517,C2=0,C3=0,F1,F2,F3,F4,F5;

R=8.314,T=820,F1=.089914285,F2=0,F3=0,F4=0,F5=0;

Pris=248.955;

double e,Ffeed,pc,Frgc,c;

Ffeed=31.47,pc=1089,Frgc=208.33;


double mw[5];

//.............................value of different lumps used in the model..............................//

mw[0]=350,mw[1]=114,mw[2]=58,mw[3]=30,mw[4]=12;

double hris,cpc,cpfv,aris=(3.14*.342*.342);

hris=36.965,cpc=1.003,cpfv=3.390;

double y,cc=.002,sum1,o,p,a,b;

double r[9],r1[9],r2[9],r3[9],r4[9],r5[9];

double k1[4],l1[4],m1[4],n1[4],o1[4],p1[4],yy,m=.015,rt=.006;

double pv1,pv2,pv3,v1,v2,v3,h=.001,z,w,x[5],x1[5],xj[5],sum,tm;

//.....................................loop for solving in the 1000
steps.............................................//

for(w=0;w<1000;w++)

{

double f1=F1;

double f2=F2;

double f3=F3;
```

```
    double f4=F4;

    double f5=F5;

    double t=T;

    double hh=h;

    //..........................loop solving the runge kutta fourth order
method.................................//

    for(j=0;j<4;j++)

    { tm=f1+f2+f3+f4+f5;

            x[0]=f1;

            x[1]=f2;

            x[2]=f3;

            x[3]=f4;

            x[4]=f5;

     sum=0;

     for(i=0;i<5;i++)

     {      xj[i]=x[i]/tm;

            x1[i]=xj[i]*mw[i];

            sum=sum+x1[i];

     }

     MWg=sum;

     z=hh*hris;

     pv=(Pris*MWg)/(R*t);

     e=((Ffeed/pv)/((Ffeed/pv)+(Frgc/pc)));
```

```
y=aris*36.965*(1-e)*pc;

ph=(1+(51*cc));

phi=pow(ph,-2.78);

for(i=0;i<4;i++)

{       o=((-(ei[i])/(R*t))/2.303);

        p=pow(10,o);

        r[i]=ki[i]*p*pow(C1,2)*phi;

}

sum1=0;

for(i=0;i<9;i++)

{       a=mw[i+1]/mw[0];

        b=r[i]*-a;

        sum1=sum1+b;

}

k1[j]=sum1*y*.001;


for(i=0;i<9;i++)

{       if(i==0)

        { o=((-(ei[i])/(R*t))/2.303);

                p=pow(10,o);

                r1[i]=ki[i]*p*pow(C1,2)*phi;

        }

        if(i==4)
```

```
        {       o=((-(ei[i])/(R*t))/2.303);
                p=pow(10,o);
                r1[i]=ki[i]*p*C2*phi;
        }
}
sum1=0;
for(i=0;i<9;i++)
{       if(i==0)
        {       a=1;
                b=r1[i]*a;
                sum1=sum1+b;
        }
        if(i==4)
        {       a=mw[2]/mw[1];
                b=r1[i]*-a;
                sum1=sum1+b;
        }
}
l1[j]=sum1*y*.001;

for(i=0;i<9;i++)
{       if(i==1)
        {       o=((-(ei[i])/(R*t))/2.303);
```

```
            p=pow(10,o);
            r2[i]=ki[i]*p*pow(C1,2)*phi;
        }
        if(i==4)
        {       o=((-(ei[i])/(R*t))/2.303);
            p=pow(10,o);
            r2[i]=ki[i]*p*C2*phi;
        }
        if(i==7)
        {       o=((-(ei[i])/(R*t))/2.303);
            p=pow(10,o);
            r2[i]=ki[i]*p*C3*phi;
        }
        if(i==8)
        {       o=((-(ei[i])/(R*t))/2.303);
            p=pow(10,o);
            r2[i]=ki[i]*p*C3*phi;
        }
}
sum1=0;
for(i=0;i<9;i++)
{       if(i==1)
        {       a=1;
```

```
            b=r2[i]*a;
            sum1=sum1+b;
        }
        if(i==4)
        {   a=1;
            b=r2[i]*a;
            sum1=sum1+b;
        }
        if(i==7)
        {   a=mw[3]/mw[2];
            b=r2[i]*-a;
            sum1=sum1+b;
        }
        if(i==8)
        {   a=mw[4]/mw[2];
            b=r2[i]*-a;
            sum1=sum1+b;
        }
    }
    m1[j]=sum1*y*.001;

    for(i=0;i<9;i++)
    { if(i==2)
```

```
        {       o=((-(ei[i])/(R*t))/2.303);
                p=pow(10,o);
                r3[i]=ki[i]*p*pow(C1,2)*phi;
        }
        if(i==7)
        {       o=((-(ei[i])/(R*t))/2.303);
                p=pow(10,o);
                r3[i]=ki[i]*p*C3*phi;
        }
}
sum1=0;
for(i=0;i<9;i++)
{       if(i==2)
        {       a=1;
                b=r3[i]*a;
                sum1=sum1+b;
        }
        if(i==7)
        {       a=1;
                b=r3[i]*a;
                sum1=sum1+b;
        }
}
```

```
n1[j]=sum1*y*.001;


for(i=0;i<9;i++)
{       if(i==3)
        {       o=((-(ei[i])/(R*t))/2.303);
                p=pow(10,o);
                r4[i]=ki[i]*p*pow(C1,2)*phi;
        }
        if(i==8)
        {       o=((-(ei[i])/(R*t))/2.303);
                p=pow(10,o);
                r4[i]=ki[i]*p*C3*phi;
        }
}
sum1=0;
for(i=0;i<9;i++)
{ if(i==3)
        {       a=1;
                b=r4[i]*a;
                sum1=sum1+b;
        }
        if(i==8)
        {       a=1;
```

```
            b=r4[i]*a;
            sum1=sum1+b;
        }
    }
    o1[j]=sum1*y*.001;

    yy=((aris*36.965*pc*(1-e))/((Frgc*cpc)+(Ffeed*cpfv)));
    for(i=0;i<9;i++)
    { if(i<4)
        {   o=(-(ei[i])/(R*t))/2.303;
            p=pow(10,o);
            r5[i]=ki[i]*p*pow(C1,2)*phi;
        }
        if(i==4||i==5||i==6)
        {   o=(-(ei[i])/(R*t))/2.303;
            p=pow(10,o);
            r5[i]=ki[i]*p*C2*phi;
        }
        if(i==7||i==8)
        {   o=(-(ei[i])/(R*t))/2.303;
            p=pow(10,o);
            r5[i]=ki[i]*p*C3*phi;
        }
```

```
}
sum1=0;
for(i=0;i<9;i++)
{ b=r5[i]*(-hl[i]);
        sum1=sum1+b;
}
p1[j]=sum1*yy*.001;
if(j==0)
{
t=T+(.5*p1[j]);
f1=F1+(.5*k1[j]);
f2=F2+(.5*l1[j]);
f3=F3+(.5*m1[j]);
f4=F4+(.5*n1[j]);
f5=F5+(.5*o1[j]);
hh=h+(.5*.001);
}
if(j==1)
{
t=T+(.5*p1[j]);
f1=F1+(.5*k1[j]);
f2=F2+(.5*l1[j]);
f3=F3+(.5*m1[j]);
```

```
f4=F4+(.5*n1[j]);
f5=F5+(.5*o1[j]);
hh=h+(.5*.001);
}
if(j==2)
{
t=T+p1[j];
f1=F1+k1[j];
f2=F2+l1[j];
f3=F3+m1[j];
f4=F4+n1[j];
f5=F5+o1[j];
hh=h+001;
}
pv1=((Pris*MWg)/(R*t));
v1=((f1*350)/pv1);
C1=f1/v1;
pv2=((Pris*114)/(R*t));
v2=((f2*114)/pv2);
C2=f2/v2;
pv3=((Pris*58)/(R*t));
v3=((f3*58)/pv3);
C3=f3/v3;
```

```
        cc=(m*pow(rt,.5));


}

        //................................... calculation after runge kutta at each
step.....................................//

        F1=F1+((k1[0]+(2*k1[1])+(2*k1[2])+k1[3])/6);

        F2=F2+((l1[0]+(2*l1[1])+(2*l1[2])+l1[3])/6);

        F3=F3+((m1[0]+(2*m1[1])+(2*m1[2])+m1[3])/6);

        F4=F4+((n1[0]+(2*n1[1])+(2*n1[2])+n1[3])/6);

        F5=F5+((o1[0]+(2*o1[1])+(2*o1[2])+o1[3])/6);

        T=T+((p1[0]+(2*p1[1])+(2*p1[2])+p1[3])/6);

        h=h+.001;

        rt=rt+.006;
}

// ...............................................values of final
result..........................................................//

        cout<<"\n value of F1:"<<F1;

        cout<<"\n value of F2:"<<F2;

        cout<<"\n value of F3:"<<F3;

        cout<<"\n value of F4:"<<F4;

        cout<<"\n value of F5:"<<F5;

        cout<<"\n value of temperature:"<<T;

        cout<<"\n value of gasoil:"<<((F1*350)/31.47);
```

```
        cout<<"\n value of gasoline:"<<((F2*114)/31.47);
        cout<<"\n value of LPG:"<<((F3*58)/31.47);
        cout<<"\n value of dry gas:"<<((F4*30)/31.47);
        cout<<"\n value of coke:"<<((F5*12)/31.47);
        getch();
}
```