# SIMULATION STUDIES ON FLUID CATALYTIC CRACKING RISER REACTOR

*A Dissertation Report Submitted*
*in partial fulfillment of the requirement for*
*the award of degree of*

**MASTER OF TECHNOLOGY**

**IN**

**CHEMICAL ENGINEERING**

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**JUNE 2013**

***Dedicated to my mother***

# CERTIFICATE

This is to certify that the dissertation entitled **"Simulation Studies on Fluid Catalytic Cracking Riser Reactor"** is an authentic record of my own work carried out as per requirements for the award of degree of **M.Tech. (Chemical Engineering)** at Thapar university , Patiala, under the guidance of **Dr. Raj Kumar Gupta,** Associate Professor, Department of Chemical Engineering, Thapar University, Patiala during July 2012 to June 2013.

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# ABSTRACT

The fluid catalytic cracking unit(FCC) is of great importance in petroleum refining industry as it treats heavy fractions from various process units to produce light ends (valuable products). The main units of FCC are riser, catalyst stripper and regenerator. Riser reactor is the most important part of this unit as the cracking reactions take place in the riser.

Modeling and simulation of riser helps in understanding the complex physical phenomena taking place in FCC riser unit. Modeling difficulties in FCC riser unit includes complex hydrodynamics, unknown hydrocarbons in the FCC feed and involvement of different type of simultaneous reactions. There has been lot of progress in the modeling of riser reactor. Most of the researchers have taken four to five lump model to avoid complexities in determining reaction rates. These models are easy to integrate with the material and energy balance equations. In the literature two phase hydrodynamics models are used by many authors, heat and mass transfer resistances are ignored in many studies and exponential catalyst deactivation model is used in most works.

In this work, FCC riser is simulated solving the material and energy balance equations considering four lump reaction kinetics, deactivation based on coke concentration on catalyst, 2 phase hydrodynamics and interphase mass transfer phenomena. A computer program is developed in C for the model solution. A base case model for the FCC riser is solved assuming constant cluster size of 6mm.Various cluster size correlations are used in base model to predict the product yields. The predicted cluster size varies considerably for different correlations. The results show significant variation in conversion, gasoline, and coke for these correlations. The correlations that predict larger cluster predict low overall conversion as compared to the correlations that predict smaller size clusters. Coke yield prediction is most influenced by the cluster size.

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# NOMENCLATURE

| | |
|---|---|
| $a_{pi}$ | Solid–gas inter-phase area, $m^2$ |
| $A$ | Cross sectional area of riser, $m^2$ |
| $C_{Pfl}$ | Specific heat of liquid feed, KJ/Kg K |
| $C_{Pfv}$ | Specific heat of vaporized feed, KJ/Kg K |
| $C_{Pcat}$ | Specific heat of catalyst, KJ/Kg K |
| $C_{coke}$ | Coke concentration on catalyst, wt% of catalyst |
| $C_d$ | Drag coefficient |
| $d_p$ | Particle diameter, m |
| $D_{cl}$ | Cluster diameter, m |
| $E_j$ | Activation energy for $j^{th}$ reaction, Kcal/Kmol |
| $G$ | Gravitational acceleration, $m/s^2$ |
| $H_r$ | Heat of reaction, KJ/Kg |
| $k_m$ | Mass transfer coefficient of $j^{th}$ component, $s^{-1}$ |
| $k_j$ | Reaction kinetic constant of reaction $j$, $m^3r/(m^3cat.s)$ |
| $m_j$ | Rate of mass transfer of component $j$, Kg/s |
| $M_{coke}$ | Mass of coke, Kg |
| $M_{cat}$ | Mass flow rate of catalyst, Kg/s |
| $MW_{VGO}$ | Molecular weight of VGO, (382 Kg/Kmol) |
| $MW_{gasoline}$ | Molecular weight of gasoline, (120 Kg/Kmol) |
| $MW_{gas}$ | Molecular weight of gas, (45 Kg/Kmol) |
| $MW_{coke}$ | Molecular weight of coke, (12 Kg/Kmol) |
| $M_{gas}$ | Mass flow rate of hydrocarbon feed, Kg/s |
| $P$ | Pressure, atm |
| $r_j$ | Rate of production of component $j$, $Kg/(s.m^3cat)$ |
| $R$ | Gas constant, Kcal/(Kmol K) |
| $T$ | Temperature of riser, K |
| $T_v$ | Vaporization temperature, K |
| $T_f$ | Temperature of feed, K |
| $T_{cat}$ | Temperature of catalyst, K |

| | |
|---|---|
| $u$ | Gas superficial velocity, m/s |
| $u_c$ | Cluster velocity, m/s |
| $u_g$ | Gas actual velocity, m/s |
| $u_t$ | Terminal velocity, m/s |
| $U_d$ | Local average superficial solid velocity, m/s |
| $U_g$ | Local average superficial gas velocity, m/ s |
| $U_{mf}$ | Incipient fluidization velocity, m/s |
| $V_{cat}$ | Volume of solid particles, $m^3$ |
| $y_c$ | Mass fraction components in cluster phase |
| $y_g$ | Mass fraction components in gas phase |

***Greek letters***

| | |
|---|---|
| $\delta_c$ | Cluster holdup fraction |
| $\varepsilon$ | Local average voidage for local flow |
| $\varepsilon_c$ | Cluster phase voidage |
| $\varepsilon_d$ | Average voidage for dilute phase,(.995) |
| $\varepsilon_{mf}$ | Voidage at incipient fluidization, (.45) |
| $\phi$ | Catalyst activity factor |
| $\lambda$ | Latent heat of vaporization, KJ/Kg |
| $\rho_c$ | Cluster density, $Kg/m^3$ |
| $\rho_g$ | Gas phase density, $Kg/m^3$ |
| $\rho_{go}$ | VGO vapour density, $Kg/m^3$ |
| $\rho_p$ | Particle density, $Kg/m^3$ |
| $\rho_{sus}$ | Suspension density of clusters, $Kg/m^3$ |
| $\mu_g$ | Gas phase viscosity, Kg/(ms) |

## CHAPTER 1

# INTRODUCTION

Fluid Catalytic Cracking (FCC) technology has been a part of the petroleum industry since the 1940’s. Yet, despite being a very mature technology, continued development is vital, especially as many refiners move their FCC operations from fuels production to higher value products. The fluid catalytic cracking (FCC) unit can be said to be a major conversion unit in the petroleum refining process. It upgrades heavy petroleum fractions to more valuable lighter products by cracking, and is a primary producer of gasoline in refineries being sometimes referred to as the heart of the refinery. The performance of the FCC units seemingly depends largely on the riser reactor. Any improvement in its operation is expected to result in dramatic economic benefits. This improvement can be achieved by the development of an accurate model which can be used to study the process in order to possibly obtain a more optimum and profitable operation.

A typical FCC unit is shown in Fig.1. The unit comprises two interconnected fluidized bed reactors: the riser reactor, in which almost all endothermic cracking reactions occur, as well as coke deposition in the catalyst pores, and the regenerator, in which air is used to consume the coke deposits by burning. The heat produced is carried by the catalyst from the regenerator to the riser. The process is very complex, one of the reasons being the interaction between operating variables from both reactors. Furthermore, the cracking reaction and the catalyst deactivation – by coke deposition – kinetics are not well known.

FCC Riser reactor is the most important part of this unit as the catalytic cracking reactions take place in the riser. Modern FCC units use short diameter risers (0.8-1.2 m) with lengths varying from 30-40 m. The Vacuum gas oil (feedstock) has an initial boiling point of 340°C or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 or higher. In the riser reactor, the contact time between the gas oil and the catalyst is very short (less than 5 seconds). At the bottom of the riser, the gas oil feed comes in contact with the hot regenerated catalyst coming from the regenerator and instantaneous vaporization occurs. As a result, the cracking reactions start and the density of the oil decrease causing an increase in the velocity of the vapor/gas phase. The increasing gas phase velocity accelerates the velocity of the catalyst and the riser behaves as a transport bed reactor. The cracking reaction's by product (coke) gets deposited on the catalyst surface and decreases its activity as the catalyst moves toward the exit of the riser. At the riser exit, the deactivated (spent) catalyst is separated from the hydrocarbon products vapor through specially designed riser termination device and sent to the regenerator for burning off the coke from its surface. The product vapors are sent to the main fractionators for recovery.

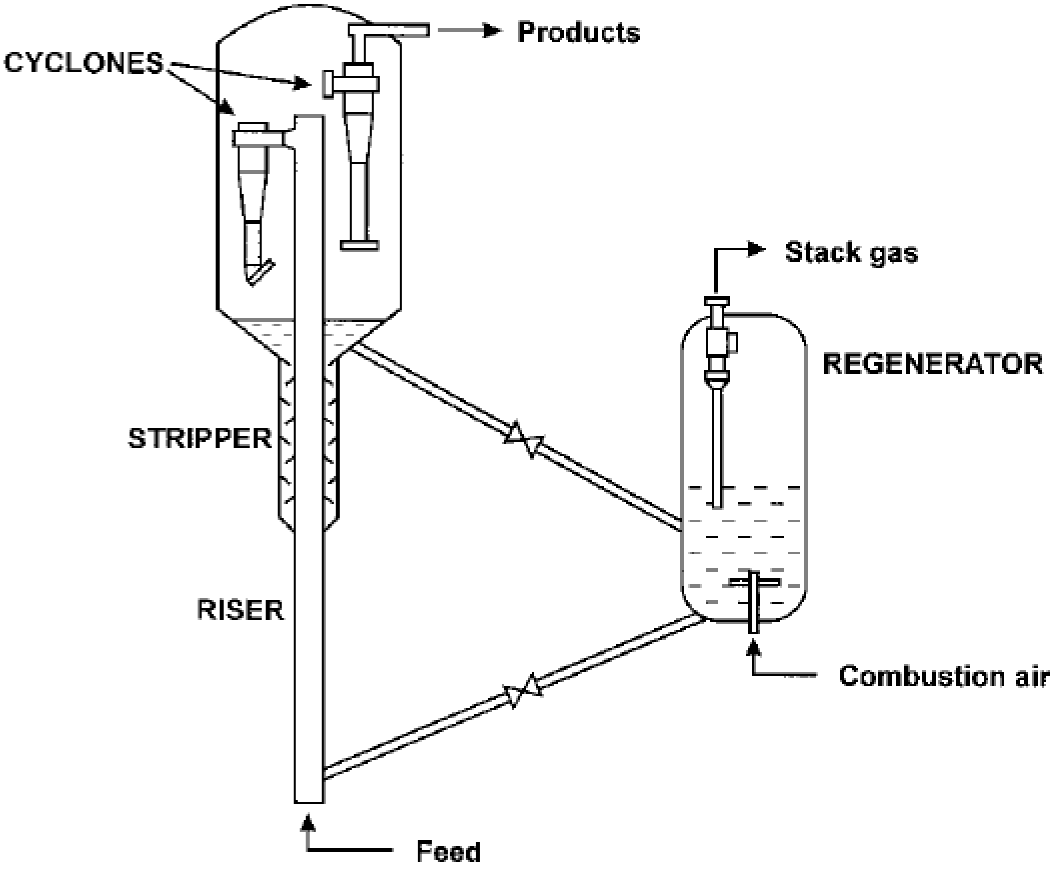

**Fig. 1:** Typical FCC unit (Michalopoulos et al., 2001)

As of 2006, FCC units were in operation at 400 petroleum refineries worldwide and about one-third of the crude oil refined in those refineries were processed in an FCC in order to produce high octane gasoline and fuel oils. During 2007, the FCC units in the United States processed a total of 5,300,000 barrels (834,300,000 liters) per day of feedstock (U.S. Dept. of Energy, 2012) and FCC units worldwide processed about twice that amount.

## 1.1. History of fluid catalytic cracking

The first commercial catalytic cracking process was developed by Eugene Houdry in 1920s. This process was an outgrowth of his experiments on catalysts for removing sulfur from oil vapors. These catalysts became deactivated due to the buildup of a carbonaceous deposit from the oils. Houdry discovered that this deposit could be burned off with air, and the catalyst activity can be restored. This discovery made a commercial viable process possible.

In 1922, a French mechanical engineer named Eugene Jules Houdry and a French pharmacist named E.A. Prudhomme set up a laboratory near Paris to develop a catalytic process for converting lignite coal to gasoline. Supported by the French government, they built a small demonstration plant in 1929 that processed about 60 tons per day of lignite coal. In 1931, the Vacuum Oil Company merged with Standard Oil of New York (Socony) to form the Socony-Vacuum Oil Company. In 1933, Houdry and Socony-Vacuum joined with Sun Oil Company in developing the Houdry process. In 1937, Sun Oil began operation of a new Houdry unit processing 12,000 barrels per day (1,900 $m^3$/d) in their Marcus Hook refinery in Pennsylvania. The Houdry process at that time used reactors with a fixed bed of catalyst and was a semi-batch operation involving multiple reactors with some of the reactors in operation while other reactors were in various stages of regenerating the catalyst.

By 1938, when the Houdry process was publicly announced, Socony-Vacuum had eight additional units under construction. Licensing the process to other companies also began and by 1940 there were 14 Houdry units in operation processing 140,000 barrels per day (22,000 $m^3$/d). The next major step was to develop a continuous process rather than the semi-batch Houdry process. That step was implemented by advent of the moving-bed process known as the Thermal Catalytic Cracking (TCC) process which used a bucket conveyor-elevator to move the catalyst from the regeneration kiln to the separate reactor section. A small demonstration TCC unit was built in Socony-Vacuum's Paulsboro refinery in 1941 and operated successfully. Then a full-scale commercial TCC unit processing 10,000 barrels per day (1,600 $m^3$/d) began operation in 1943 at the Beaumont, Texas refinery of Magnolia Oil Company, an affiliate of Socony-Vacuum. By the end of World War II in 1945, the processing capacity of the TCC units in operation was about 300,000 barrels per day (48,000 $m^3$/d).

The first commercial fluid catalytic cracking unit (known as the Model I FCC) began processing 13,000 barrels per day (2,100 $m^3$/d) of petroleum oil in the Baton Rouge refinery on May 25, 1942, just four years after the CRA consortium was formed and in the midst of World War II. A little more than a month later, in July 1942, it was processing 17,000 barrels per day (2,700 $m^3$/d). In 1963, that first Model I FCC unit was shut down after 21 years of operation and subsequently dismantled. In the many decades since the Model I FCC unit began operation, the fixed bed Houdry's units have all been shut down as have most of the moving bed units (such as the TCC units) while hundreds of FCC units have been built. During those decades, many improved FCC designs have evolved and cracking catalysts have been greatly improved, but the modern FCC units are essentially the same as that first Model I FCC unit.

## 1.2 Process description

FCC units used in industries are usually of two types:

i. Side by side reactor

ii. Stacked type reactor

In side by side reactor, reactor and regenerator are separated from each other and placed side by side. In case of stacked type reactor rector and regenerator are mounted together.

All modern FCC units consists of two basic components, a riser reactor in which the catalyst is brought in contact with the feed (gas oil), and a regenerator in which the coke deposited on the catalyst during the cracking reactions is burned off for regenerating the catalyst. Other auxiliary units such as feed preheat and flue gas systems are also required for control and optimal operation of this unit. The FCC process is very complex. For clarity, the process description has been broken down into the following separate sections as Feed preheat, Feed nozzles—riser, Catalyst separation, Stripping section, Regenerator—heat/catalyst recovery.

### 1.2.1 Feed Preheat

The refinery produced gas oil and supplemental feed stocks are generally combined and sent to a surge drum which provides a steady flow of feed to the FCC unit's charge pumps. This drum can also serve as a device to separate any water or vapor that may be present in the feed stocks. From the surge drum, the feed is normally heated to a temperature of 270-375 $^0$C (550-700 $^0$F). This is usually done by heat exchange with intermediate heat removal pumparound from the main fractionators as shown in Fig.2. The figure represents FC(flow control), LC(level control), TC(temperature control), LCO(light cycle oil). While feed preheat system may differ greatly from unit to unit, the feed is normally heated by exchange with the light cycle oil, heavy cycle oil, or bottom pumparound. This raises the feed temperature to 150-260 $^0$C (300-500 $^0$F) which is generally sufficient for most FCCUs. In some cases, however, fired heaters are also used to preheat the feed.

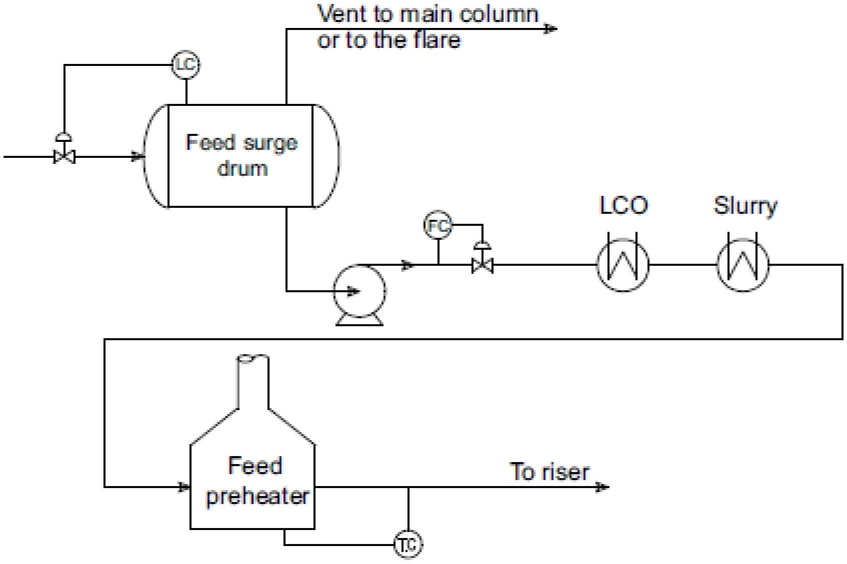

**Fig. 2:** Typical feed preheat system (Sadeghbeigi, 2012).

### 1.2.2 Feed nozzles—riser

The reactor-regenerator is the heart of the FCC process. In today's cat cracking, the riser is the reactor for a typical riser wye feed section as shown in Fig.3. Efficient contacting of the feed and regenerated catalyst is critical for achieving the desired cracking reactions. Feed nozzles are used to atomize the feed with the help of dispersion or atomizing steam.

Smaller oil droplets increase the availability of feed at the reactive acid sites on the catalyst. With high-activity zeolite catalyst, virtually all of the cracking reactions take place in 3 seconds or less. In most FCC units, the feed nozzles are an "elevated" type, in which they are located about 15-40 ft (5-12 m) above the base of the riser. Depending on the FCC feed rate and riser diameter, the number of feed nozzles can range from 1 to 15.The cracking reactions ideally occur in the vapor phase. Cracking reactions begin as soon as the feed is vaporized by the hot regenerated catalyst. The expanding volume of the vapors is the main driving force that is used to carry the catalyst up the riser.

The hot regenerated catalyst will not only provide the necessary heat to vaporize the gas oil feed and bring its temperature to the desired cracking temperature, but also compensate for the "internal cooling" that takes place in the riser due to endothermic heat of reaction. Depending on the feed preheat, regenerator bed, and riser outlet temperatures, the ratio of catalyst to oil is normally in the range of 4:1 to 10:1 by weight. The typical regenerated catalyst temperature ranges between 1,250 $^0$F and 1,350 $^0$F (677-732 $^0$C).

The cracking or reactor temperature is often in the range of 925-1050 $^0$F (496-565 $^0$C). The riser is often a vertical pipe. Typical risers are 2 to 7 feet (61 to 213 cm) in diameter and 75 to 120 feet (23 to 37 meters) long. The ideal riser simulates a plug flow reactor, where catalyst and vapor travel the length of the riser, with minimum back mixing. Some risers are fully external, in which they are mostly cold-wall design with 4- to 5-in. (10-13 cm) thick internal refractory lining, for insulation and abrasion resistance. The section of the riser that is internal to the reactor vessel is of a hot-wall design, often having 1-in. (2.5 cm) thick internal refractory lining.

The material of construction for the cold-wall riser is carbon steel and low chrome alloy for the hot-wall design. Risers are normally designed for an outlet vapor velocity of 40-60 ft/s (12-18 m/s). The average hydrocarbon and catalyst residence times are about 2 and 3 s, respectively (based on riser outlet conditions). As a consequence of the cracking reactions, a hydrogen-deficient material called "coke" is deposited on the catalyst, reducing catalyst activity.

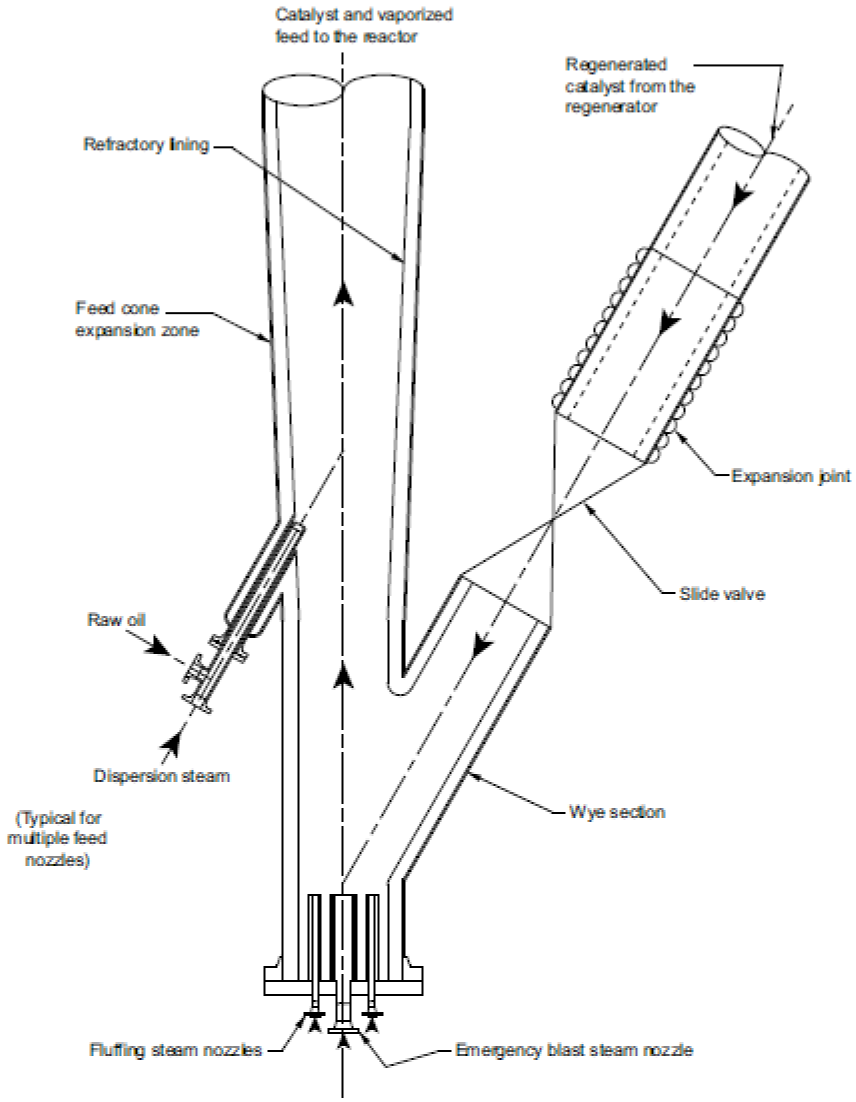

**Fig. 3:** Typical riser wye feed section (Sadeghbeigi, 2012).

### 1.2.3 Catalyst separation

After exiting the riser, catalyst enters the reactor vessel. In today’s FCC operations, the reactor vessel serves as housing for the cyclones and/or a disengaging device for catalyst separation. In the early application of FCC, the reactor vessel provided further bed cracking, as well as being a device used for additional catalyst separation.

Nearly every FCC unit employs some type of inertial separation device connected on the end of the riser to separate the bulk of the catalyst from the vapors. A number of units use a deflector device to turn the catalyst direction downward. On some units, the riser is directly attached to a set of cyclones. The term “rough cut” cyclones generally refers to this type of arrangement.

Most FCC units employ either single- or two-stage cyclones as shown in Fig.4, to separate the remaining catalyst particles from the cracked vapors. The cyclones collect and return the catalyst to the catalyst stripper via the diplegs and flapper/trickle valves. The product vapors exit the upper cyclones and flow to the main fractionator tower. The efficiency of a typical riser termination device and upper cyclone system is often 99.999+%.

It is important to separate catalyst and vapors as soon as they enter the reactor, especially if the cracking temperature is >950$^0$F (510$^0$C). If not, the extended contact time of the vapors with the catalyst in the reactor housing will allow for nonselective catalytic recracking of some of the desirable products. The extended residence time also promotes thermal cracking of the desirable products. These recracking reactions can be extensive if the reactor temperature is more than 950$^0$F (510$^0$C). Most refiners have modified their riser termination devices to minimize these reactions.

**Fig. 4:** A typical two-stage cyclone system (Sadeghbeigi, 2012).

### 1.2.4 Stripping Section

The "spent catalyst" entering the catalyst stripper has hydrocarbons that are adsorbed on the surface of the catalyst; there are hydrocarbon vapors that fill the catalyst's pores, and hydrocarbon vapors that are entrained with the catalyst. Stripping steam is used primarily to remove the entrained hydrocarbons between individual catalyst particles. The stripping steams does not often address hydrocarbon desorption or the hydrocarbons that have filled the catalyst's pores. However, cracking reactions do continue to occur within the stripper. These reactions are driven by the reactor temperature and the catalyst residence time in the stripper. The higher temperature and longer residence time allow conversion of adsorbed hydrocarbons into "clean lighter" products. Shed trays, disk/donut baffles, and structural packing are the most common devices in commercial use for providing contact between down-flowing catalyst and upflowing steam (for stripper example, Fig.5). An efficient catalyst stripper design provides the intimate contact between the catalyst and steam. Reactor strippers are commonly designed for a steam superficial velocity of about 0.75 ft/s (0.23 m/s) and a catalyst mass flux rate at approximately 700 lb/min/ft$^2$ (3,418 kg/min/m$^2$). At too high a flux rate, the falling catalyst tends to entrain steam, thus reducing the effectiveness of stripping steam. A typical stripping steam rate is in the range of 2-5 lb of steam per 1,000 lb (2-5 kg per 1,000 kg) of circulating catalyst.

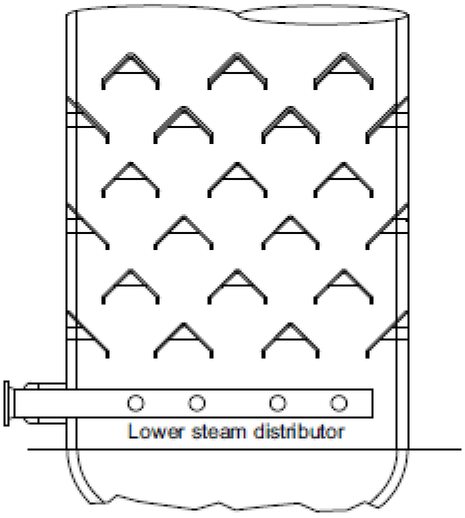

**Fig. 5:** An example of a catalyst stripper (Sadeghbeigi, 2012).

## CHAPTER 2

# LITERATURE REVIEW

A brief review of the literature on fluid catalytic cracking riser unit is presented in paragraphs below.

## 2.1 Hydrodynamics:-

A fluid catalytic cracking riser unit has a very complex hydrodynamics, due to interaction of multiple phases in the riser column and due to several other flow parameters. In literature there have been several modeling efforts in order to employ different mathematical formulations to predict the relationship between solid concentration, operating conditions, and riser geometry. Harris and Davidson (1994) classified the models in the literature that have strong significance into three broad groups: - (i) It includes those models that only predict the axial variation of the solids suspension density (Li and Kwauk, 1980; Yang et al., 1998; Choi et al., 1991; Mori et al., 1991); (ii) It include those models that assume two or more regions, such as core annulus or clustering annular flow models to predict the radial variation and the high average slip velocities (Horio et al., 1988; Horio and Takei, 1991; Berruti and Kalogerakis, 1989;Rhodes, 1990) and ;(iii) It include those models that predict the two phase gas-solid flow by using the fundamental equations of fluid dynamics (Adewumi and Arastoopour ,1986, Yasuna et al., 1994, Dasgupta et al., 1994, Gidaspow et al., 1992). Every model has certain significance and can be applied according to the application. Model of the type (i) and type (ii) are best suited to investigate the effect of operating conditions and riser dimensions on the riser flow structure. These models can be easily coupled with the reaction kinetic models to simulate the performance of CFB risers (Pugsley et al., 1992; Pugsley and Berruti, 1994). Type (iii) models are suitable to investigate the local flow structure and the impact of geometry in CFB risers.

Pugsley and Berruti (1996) proposed a type (ii) predictive model to describe and characterize all the time-averaged key parameters of both the axial and radial flow structure in circulating fluidized bed (CFB) risers. There model postulates the existence of a core-annulus type of flow structure and is based on both fundamental principles and empirical relationships.

Flinger et al. (1994) developed a two-phase heterogeneous model for riser reactors operating in pneumatic transport. The model consists of a dispersed cluster phase which contains all the catalyst and where the bulk of the catalytic reactions occur, and a continuous oil phase with mass transfer between the phases. The proposed model also provides a basis to determine the incentives for improving the mass transfer between the two phases in the riser by making hardware modifications. In the work presented by Godfroy et al. (1999) they compared ten different hydrodynamic models with a set of experimental data that covered a wide range of operating conditions and showed reasonable to poor overall agreement. Herein, they describe the model that gave the best overall agreement with the experimental data.

Gao et al. (2001) in their hydrodynamic model focused on feed injection zone and studied the effect of changing spray droplet diameter, volumetric concentration and temperature of the feed. Gupta and Subba Rao (2001) discussed the effect of feed droplet size on the conversion and yield patterns, catalyst temperature, catalyst holdup, and catalyst activity in their hydrodynamics model of the riser reactor. Related to their work they also predicted the effect of feed atomization on regenerator temperature and on carbon on spent catalyst in their simulator for the entire FCC unit (Gupta and Subba Rao, 2003). Berry et al. (2004) described the riser hydrodynamics by the two- dimensional model of Malcus and Pugsley (2002). The hydrodynamic model was modified to make it predictive by incorporating the slip factor for calculation of the cross-sectional averaged voidage. The model was validated against industrial riser data from three literature sources and found to agree within 10-20%. You et al. (2009) in their work developed a generic modeling approach which can fully incorporate multiphase flow hydrodynamics with FCC process. The emphasis of this model was to develop a framework to simultaneously simulate the multiphase flow hydrodynamics, cracking reaction and their inter-coupling characteristics in riser reactor. This modeling approach opened up a new dimension for making generic models suitable for the analysis and control studies of FCC units.

Several new scientific techniques have been used by many researchers to understand the complex phenomenon taking place in riser section of circulating fluidized bed (CFB). Computational fluid dynamics (CFD) is proved to be a powerful tool that enables an in-depth analysis and understanding of the complex phenomena that take place in a riser catalytic cracking reactor and especially in the feed injection area where the cracking reactions are initiated. Two different classes of CFD models are found to be used: Eulerian-Eulerian models and Eulerian-Lagrangian models. Eulerian-Eulerian models consider both gas and solid phases as continuous and fully interpenetrating. Eulerian-Lagrangian models solve the Newtonian equations of motion for each individual particle, taking into account the effects of particle collisions and forces acting on the particle by the gas. Theologos & Markatos (1993) and Theologos, Nikou, Lygeros & Markatos (1997) incorporated an atomization modeling scheme into a CFD model to evaluate atomization effects on feedstock vaporization rates, cracking reactions initiation, reactor selectivity and overall reactor performance. Theologos et al. (1999) worked on the same lines and simulated cracking reactions using a simplified 3-lump model. In this work the atomization modeling scheme takes into account the initial droplet size of liquid feedstock at nozzle's exit, as well as droplet size reduction along with vaporization, incorporating experimental data from the literature. This model predicts the area where feedstock vaporization takes place inside the reactor. Nayak et al. (2005) presented a model considering heat transfer from the gas phase as well as from the solid particles for simulating evaporation of a drop. The model relates the evaporation rate of droplet with rate of collisions of solid particles, specific heat capacities of solid and liquid, latent heat of vaporization, relative velocity of gas and liquid and temperatures of three phases. A commercial CFD code, FLUENT using Eulerian–Lagrangian approach was employed to simulate simultaneous evaporation and cracking reactions occurring in FCC riser reactors.

Zimmermann et al. (2005) used computational fluid dynamics (CFD) to simulate the hydrodynamics and reaction kinetics of gas-solid fluidized beds containing fluid catalytic cracking (FCC) particles. The CFD modeling used in this work of fluidized-bed hydrodynamics shows that the drag models of Gidaspow and Syamlal- O’Brien are not applicable in their original forms for simulating FCC particles classified as Geldart A particles within the examined range. Gao et al. (2008) simulated the hydrodynamic characteristics in bubbling fluidized beds (FCC Strippers) were by using computational fluid dynamics (CFD) code. Gao et al. (2009) presented an experimental and computational study on the hydrodynamic characteristics of FCC particles in a turbulent fluidized bed. Based on the Eulerian/Eulerian model, they presented a computational fluid dynamics (CFD) model incorporating a modified gas-solid drag model, and the model parameters were examined by using commercial CFD software. Wang et al. (2012) simulated the Flow behavior of particles in the riser using a computational fluid dynamics

(CFD). Conservation equations of mass and momentum for solid phase were solved on the basis of kinetic theory of rough spheres (KTRS). The fluctuation kinetic energy of particles was introduced to characterize the random motion of particles as a measure of the translational and rotational velocities fluctuations. Peng et al. (2012) proposed a new approach to specify the inlet boundary conditions that considering the inlet air jet effect simulates gas-solid two-phase flows in circulating fluidized bed (CFB) risers more accurately. A computational fluid dynamics (CFD) model based on Eulerian-Eulerian approach coupled with kinetic theory of granular flow was adopted to simulate the flow using the proposed inlet boundary conditions.

## 2.2 Cracking kinetics

Weekman and Nace (1970) developed a 3 lump kinetic model as show in Fig. 6, which was able to predict the gasoil conversion and gasoline yield in isothermal condition in a fixed, moving and fluid bed reactor. This 3 lump model was further studied for different aspects of FCC unit modeling by many researchers (Lee et al.1989 and Theologos and Markatos, 1993).

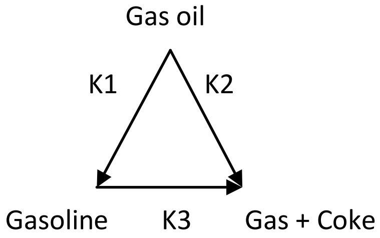

**Fig. 6:** Three lump kinetic scheme (Weekman and Nace, 1970).

After this discovery number of lumps were studied for either product yield or cracking kinetics with or without use of deactivation model. Other researchers studied lumps as, a 4 lump model as shown in Fig. 7 (Lee, Chen, & Huang, 1989; Pitault, Forissier, & Bernard, 1995), 10 lump model as shown in Fig. 8 (Jacob, Gross, Voltz, & Weekman, 1976) and 19 lump model (Pitault, Nevicato, Forissier, & Bernard, 1994), to explain the kinetic, material and energy balance equations.

Weekman (1979) has provided a comprehensive overview of lumping from both practical as well as theoretical viewpoints. He pointed out some of the problem areas, of which some were dealt by Coxson et al. (1987). They presented some of the techniques of cluster analysis to provide a basis for analyzing large quantities of empirical data to provide a rational way to lump them into fewer groups, which was one of the problems. Subsequently, the Mobil 10-lump catalytic cracking model was further lumped by this technique into groupings. Feng et al. (1993) developed a fundamental kinetic model of catalytic cracking on zeolite catalysts. The complete network of elementary steps of the carbenium ion reaction intermediates were generated by means of an algorithm based on Boolean relation matrices. Single-event rate parameters were estimated for the cracking of paraffin's, accounting for the thermodynamic constraints.

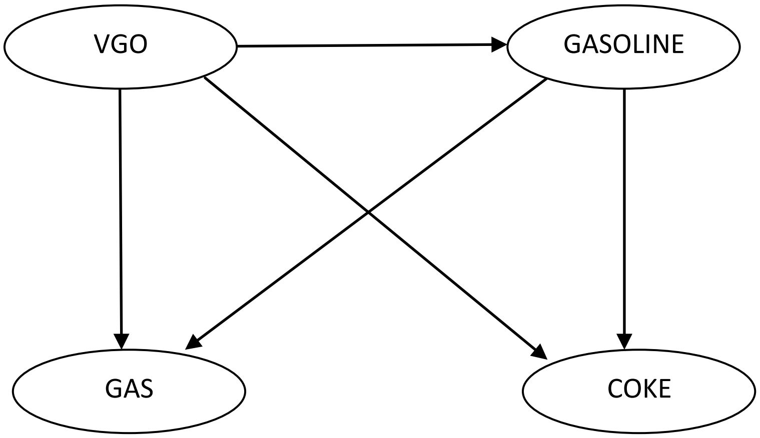

**Fig. 7:** Reaction scheme for four lump kinetic model (Lee et al., 1989).

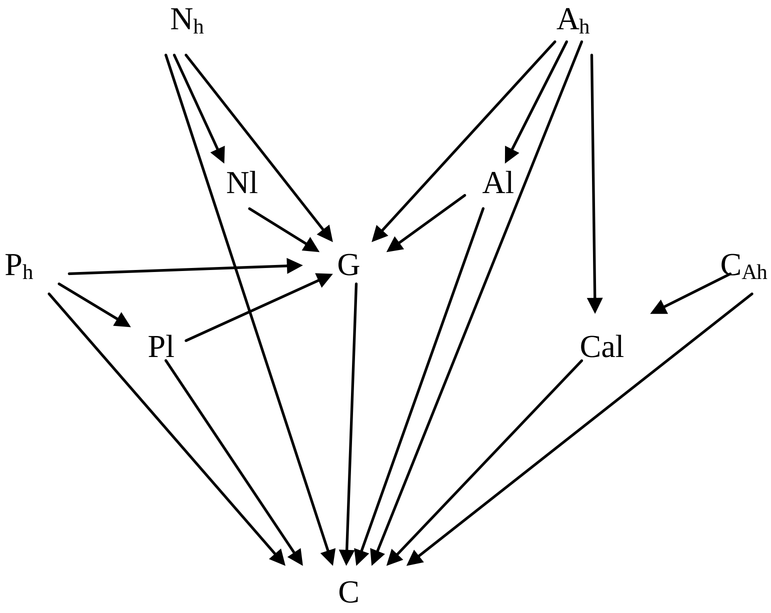

**Fig. 8:** Ten lump kinetic scheme (Jacob et al., 1976).

Flinger et al. (1996) model consists of a dispersed cluster phase which contains all the catalyst and is where the bulk of the catalytic reactions occur and a continuous oil phase with mass transfer between the phases. This model used a simple three component kinetic model was used to describe the rates of reaction which occur in the cluster phase. The model was able to determine the average concentration of any component at any axial or radial position in the riser by the density-weighted average of the cluster phase and the oil phase at that position using experimental values for the radial density distribution.

Arbel et al. (1995) used a 10 lump kinetic model to study Dynamics and Control of Fluidized Catalytic Crackers. The model allows one to study realistically both the steady state and dynamic control of a fluidized catalytic cracker. The model was structured in a way that users can substitute their own kinetic models.

Gupta and Subba Rao (2001) used a 4 lump kinetic model in their work evaluate the performance of FCC riser reactor. Gupta et al. (2007) developed a new kinetic model for the fluid catalytic cracking (FCC) riser. This new kinetic scheme was based on pseudo components cracking and developed a semi-empirical model for the estimation of the rate constants of the resulting reaction network. Fifty pseudo components (lumps) were considered in this scheme resulting in more than 10,000 reaction possibilities. This approach eliminated the need of determining a large number of rate constants required for conventional lumped models. The model was found to be more versatile than the existing models and opens up a new dimension for making generic models suitable for the analysis and control studies of FCC units. Novia et al. (2007) developed a model to simulate the 3-lump reaction kinetics in FCC riser reactor.

Recently authors employed user defined function (UDF) approach in computational fluid dynamics (CFD) in order to model FCC riser reactor. Trujillo et al. (2010) evaluated the application of a rotating fluidized bed in a static geometry to fluid catalytic cracking by means of computational fluid dynamics (CFD) simulations using an Eulerian-Eulerian model and the kinetic theory of granular flow. Gan et al. (2011) conducted numerical simulations in which the fluid flow was coupled to cracking reactions to verify the performance of a novel multiregime gas-solid fluidized reactor for heavy-oil catalytic pyrolysis. This process demonstrated its superiority over other catalytic cracking/pyrolysis process. The numerical work provided more detailed insights into the cracking process: (i) The catalyst distribution of the changing-diameter riser was better than that of the traditional riser; various fluidized regimes could be integrated in a single reactor. (ii) The multiregime gas-solid reactor provided better control of fast reaction systems, especially for heavy-oil catalytic cracking. (iii) The cracking reactions mainly took place in the feed mixing section; hence, optimizing the oil and catalyst contact in this region was found to be of vital importance.

## 2.3 Interphase heat and mass transfer

In FCC riser, interphase heat transfer is a very important phenomenon taking place. As in riser inlet instantaneous vaporization takes, all feed gets vaporized and exothermic cracking reactions starts. Since, the temperature influences the reaction rates the prediction of inter-phase heat transfer becomes important. From heat transfer point of view, very early models assumed isothermal riser. Most of the riser models assume instantaneous thermal equilibrium between the vapor and solid phases at the riser inlet. Theologos et al. (1999) developed a 3-D mathematical model that predicts the two-phase flow, heat transfer and chemical reaction in catalytic cracking riser reactor. They used a correlation of Nusselt number as a function of Reynolds number. Gupta and Subba Rao (2001) also presented a model using interphase heat transfer in all 3 phases.

In literature studied it was found that in most of the works on FCC riser modeling external mass transfer resistances in the riser are neglected by many researchers (Corella and Frances, 1991a; Ali et al., 1997; Theologos et al., 1999; Das et al., 2003, Berry et al., 2004; Gupta et al., 2007, Gupta and Kumar, 2008). However, considering mass transfer resistance between the phases helps in predicting the concentration of the reacting species at the catalyst surface. Flinger et al. (1994) in their model considered mass transfer to occur between the two phases. Gupta and Subba Rao (2001) and Nayak et al. (2005) modeled the inter-phase mass transfer using the correlation for Sherwood number proposed by Ranz and Marshall (1952).

## 2.4 Particle clustering

Particle clustering in fluidized beds has been proposed for since 1948(Wilhelm et al., 1948). A lot of work is done in field of fluid catalytic cracking riser considering constant cluster size in the whole column. A lot of work is presented in literature using constant cluster size such as (Gupta and Subbarao, 2001; Bollas et al., 2002;Gupta et al., 2007; Fernandes et al., 2007;Wang et al., 2008). Fernandes et al., (2003), showed clustering effect in the conversion and slip factor at the riser reactor by taking different values of the cluster diameter along the riser height and used mass, momentum and energy balances in their 6 lump model.

Several correlations have been developed for the estimation of the cluster diameter. Among those are:

Xu and Li (1998) derived a simple equation for local equivalent diameter $d_{cl}$ of cluster in the energy-minimization multi-scale (EMMS) model (Li et al., 1988; Li and Kwauk, 1994).

$$\frac{D_{cl}}{d_p} = \frac{A}{\left(\frac{\rho_{sus}}{\rho_P}\right)^n} \tag{1}$$

Here *A* and *n* were derived as follows for gas-solid flow before the occurrence of the so-called accumulative choking defined by Bi et al. (1993) where:-

$$n = \frac{2Q_1 + Q_2}{2Q_1 - 4M_2} \tag{2}$$

$$A = \frac{2(M_1 - M_2)}{(Q_1 - 2M_2)}\left(\frac{(1-\varepsilon_{mf})(\rho_p - \rho_g)}{2\rho_p}\right)^n \tag{3}$$

Computations from the EMMS model were conducted and it was found that above is valid for a wide range of gas-solid systems. Among various literature correlations for cluster size (Yerushalmi et al., 1976; Subbarao, 1986; Horio and Takei, 1990; Horio et al., 1992; Zou et al., 1994; Horio and Ito, 1997) above equation also takes a relatively simple formulation with respect to the dense phase fraction *f* (or the local average voidage $\varepsilon$), which seems convenient for use in hydrodynamic modeling of heterogeneous gas-solid flow.

Xu and Kato (1999) gave a correlation by simplifying the hydrodynamic correlation for equivalent cluster diameter given by Xu and Li (1998) as:-

$$\frac{D_{cl}}{d_P} = \frac{A\rho_P}{\rho_{sus}} \tag{4}$$

Where, $Q_1 = \frac{(\rho_P - \rho_g)g}{\rho_P}\left[u_g + \frac{U_d\varepsilon_{mf}}{(1-\varepsilon_{mf})} + \frac{1}{4}u_t\varepsilon_{mf}^{4.7}\right]$ (5)

$$A = \frac{(3333U_d g - M_2)(1-\varepsilon_{mf})(\rho_P - \rho_g)}{(Q_1 - 2M_2)\rho_P} \tag{6}$$

$$M_2 = \left(U_{mf} + \frac{U_d \varepsilon_{mf}}{(1-\varepsilon_{mf})}\right) g \tag{7}$$

Zou et al. (1994) gave a correlation based on the above techniques:

$$\frac{D_{cl}}{d_p} = 1.8543 \left[\frac{(1-\varepsilon)^{.25}\varepsilon^{-1.5}}{(\varepsilon-\varepsilon_{mf})^{2.41}}\right]^{1.3889} + 1 \tag{8}$$

On the same lines Gu and Chen (1998) gave a correlation:

$$\frac{D_{cl}}{d_p} = 1 + \left(0.027/d_p - 10\right)(1-\varepsilon) + 32\,(1-\varepsilon)^6/d_p \tag{9}$$

Harris et al. (2002) reviewed the literature on cluster sizes and proposed a correlation for cluster size as

$$D_{cl} = \frac{(1-\varepsilon)}{40.8-94.5(1-\varepsilon)} \tag{10}$$

Subbarao (2010) found that this equation does not reflect the dependence of cluster size on gas and particle properties as well as column diameter, improvising which he gave a correlation

$$D_{cl} = \left[\frac{\frac{(1-\varepsilon)}{(1-\varepsilon_C}}{1-\frac{(1-\varepsilon)}{(1-\varepsilon_C)}}\right]^{1/m} D_v + d_p, \tag{11}$$

Here ‘$m$’ is a constant and having a value ‘3’ for spherical clusters.

Subbarao (2010) used void diameter as 10 mm since void size for most of the particles used in the various investigations on risers is around 10 mm.

## 2.5 Conclusions

In literature studied it has been found out that there are many researchers who extensively investigated cluster size variation in circulating fluidized bed (CFB), which has an immense effect on hydrodynamics of riser section of CFB reactor (Wilhelm and Kwauk, 1948; Arena et al., 1989; Horio et al., 1992a; Jin,1992 ; Horio and Kuroki ,1994). The occurrence of clusters is one of the most characteristic features of dense gas-solid flow in the riser section of a circulating fluidized bed (CFB). In a fluidized bed solids do not move independently but as aggregates called clusters. Each single particle is attached to a solid aggregate in the dense bed and moves with it until the solid aggregate breaks-up. The continuous formation and destruction of clusters influences particle hold-up, pressure drop, heat transfer at the wall, and mixing. Therefore, knowing the hydrodynamic properties of these clusters (i.e., size, voidage and velocity) is important for providing an accurate estimation of performance of fluidized bed reactors such as riser.

Many efforts have been found in literature giving several correlations for the variation of cluster size in circulating fluidized beds (Zou et al., 1994; Gu and Chen, 1998; Xu and Li, 1998; Xu and Kato, 1999; Harris et al., 2002; Lu et al., 2008; Subbarao 2010). In literature there is no work reported to be using the modeling efforts of these researchers on cluster size to model the fluid catalytic cracking riser unit (Flinger, 1994; Gupta and Subbarao, 2001; Gupta and Subbarao, 2003; Gupta et. al., 2007, Baudrez et al., 2009).

Flinger has estimated the cluster size using the relationship developed by Yerushalmi (1976), and predicted 6 mm and 2 mm size clusters for different conditions. Most of the riser models available in literature, that have calculated axial catalyst holdup using momentum balance on clusters, used constant cluster size (Gupta and Subbarao, 2001; Bollas et al., 2002;Gupta et al., 2007; Fernandes et al., 2007;Wang et al., 2008). However, the local flow conditions influences the cluster size. Also, in the riser reactor cluster size may not be constant due to expansion in the gas phase. The correlations available in literature can be used for predicting cluster size as a function of local flow conditions.

## CHAPTER 3

# FCC RISER MODEL

In this chapter the mathematical model of the FCC riser used in this work is discussed. The model incorporates several correlations of cluster size in a four lump kinetic model considering two-phase flow, effect of cracking on phase velocities, catalyst deactivation and variable cluster size.

## 3.1 Riser model assumptions:-

The following, commonly used, assumptions are made in this model:

1. Instantaneous vaporization of liquid feed occurs when it come in contact with the hot regenerated catalyst at the riser inlet. The catalyst and the gas phase then attain thermal equilibrium.
2. Riser is adiabatic. The temperature inside the riser falls due to endothermic cracking reactions taking place.
3. The gas phase behaves ideally.
4. Both phases are in plug flow condition hence back mixing is neglected.
5. Catalyst activity is varying with coke concentration on catalyst.

## 3.2 Model equations

### 3.2.1 Material balance

In the present work riser section of FCC unit is divided into several compartments along the riser height. Plug flow is assumed in the riser section. VGO gets cracked inside the riser column to give products gasoline, gas and coke. Mass of each element formed or consumed in each compartment is calculated.

Mass balance for gas phase over $i^{th}$ compartment:

Mass in from $(i\text{-}1)^{th}$ compartment - Mass out from $i^{th}$ compartment = mass consumed/formed in $i^{th}$ compartment

$$M_{j,(i-1)} - M_{j.i} = r_{j.i} \qquad j=VGO,\ gasoline\ and\ gas \qquad (12)$$

Mass balance for solid over $i^{th}$ compartment:

Mass out from $i^{th}$compartment – Mass in from $(i\text{-}1)^{th}$ compartment = coke formed in $i^{th}$ compartment

$$M_{j,i} - M_{j.(i-1)} = r_{j.i} \qquad j=coke \tag{13}$$

### 3.2.2 Riser hydrodynamics

Hydrodynamics controls the performance of FCC riser unit as whole of the catalyst deactivation scheme is controlled by this phenomenon. In our work riser hydrodynamics is modeled by using a force balance, to calculate solid holdup fraction along the riser height. Force balance for clusters fluidized by gas gives us an equation:-

$$\frac{-d\delta_c}{dz} = \frac{A\rho_c}{M_{cat}u}\delta_c^2(1-\delta_c)\left(\frac{3}{4}\left(\frac{C_D}{D_{cl}}\right)\left(\frac{\rho_g}{\rho_c}\right)\left(u_g - \frac{M_{cat}}{A\rho_c\delta_c}\right)^2 - g\right) \tag{14}$$

The velocity of clusters and gas is calculated inside the riser section as follows.

$$u_c = \frac{M_{cat}/\rho_c}{A\delta_c} \tag{15}$$

Actual gas velocity is

$$u_g = \frac{M_g/\rho_g}{A(1-\delta_g)} \tag{16}$$

Density of gas is calculated using average molecular weight of gas as shown below.

$$\rho_g = \frac{PMW_{g,avg}}{R\,T_i} \tag{17}$$

### 3.2.3 Reaction kinetics

The reaction scheme for the four lump kinetic model is shown in Fig.9 .The four lumps are VGO (feedstock), gasoline, gas and coke. VGO is cracked to gasoline, gas and coke. There is secondary cracking of gasoline also to gas and coke.

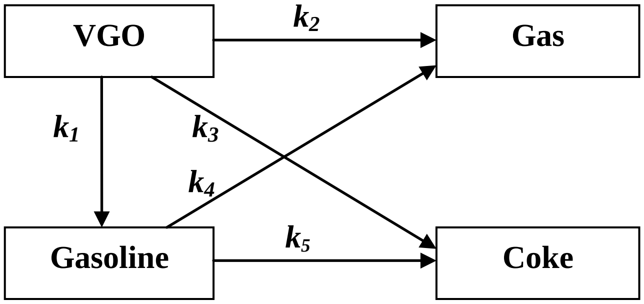

**Fig. 9:** Reaction scheme for four lump kinetic model.

The rates of production of the lumps (Kg/s) per unit of catalyst volume in the '$i^{th}$' compartment can be expressed as:-

For VGO:

$$r_{VGO,i} = -\phi_i(k_1 + k_2 + k_3)\frac{\left(\rho_{gi} y_{C_{1,i}}\right)^2}{\rho_{VGO}} V_{cat,i} \tag{18}$$

Gasoline:

$$r_{gasoline,i} = -\phi_i \left( k_1 \frac{\left(\rho_{gi} y_{C_{1,i}}\right)^2}{\rho_{VGO}} - (k_4 + k_5)\rho_{gi} y_{C_{2,i}} \right) V_{cat,i} \tag{19}$$

Gas:

$$r_{gas,i} = -\phi_i \left( k_2 \frac{\left(\rho_{gi} y_{C_{1,i}}\right)^2}{\rho_{VGO}} + k_4 \rho_{gi} y_{C_{2,i}} \right) V_{cat,i} \tag{20}$$

Coke:

$$r_{coke,i} = -\phi_i \left( k_3 \frac{\left(\rho_{gi} y_{C_{1,i}}\right)^2}{\rho_{VGO}} + k_5 \rho_{gi} y_{C_{2,i}} \right) V_{cat,i} \tag{21}$$

The dependence of kinetics on temperature is described by a modified Arrhenius expression shown as.

$$k_j(T_i) = k_{j,756K} exp\left[-\frac{E_j}{R}\left(\frac{1}{T_i} - \frac{1}{756}\right)\right] \tag{22}$$

Different types of catalyst deactivation schemes are reported in the literature. Non-selective deactivation of catalyst is assumed in the current model. The activity factor $\phi$ is based on the coke concentration on catalyst (Pitault et al., 1995).

$$\phi_i = \frac{B+1}{B+\exp\left(A.C_{coke,i}\right)} \tag{23}$$

Where, A= 4.29 and B= 10.4, and where,

**Table 1:** Kinetic constants reported by (Pitault et al., 1995)

| **Kinetic constant** | **Value at 756 K** |
|---|---|
| $K_{r1}$ | 68.30 |
| $K_{r2}$ | 17.15 |
| $K_{r3}$ | 2.32 |
| $K_{r4}$ | 0.20 |
| $K_{r5}$ | 0.55 |

**Table 2:** Activation energy for cracking reactions reported by (Lee et al., 1989)

| Cracking reactions | Activation energy $E_j$ ,Kcal/Kmol |
|---|---|
| VGO → gasoline | 16328 |
| VGO → gas | 21344 |
| VGO → coke | 15449 |
| Gasoline →gas | 12612 |
| Gasoline →coke | 27621 |

### 3.2.4 Enthalpy balance

At the inlet of the reactor temperature is calculated assuming instant vaporization of feed oil and assuming thermal equilibrium of both phases after vaporization of feed:

Heat lost by the catalyst = sensible heat gained of the liquid feed + heat required to vaporize the feed oil + sensible heat gain of the vaporized feed oil

$$M_{cat}C_{P_{cat}}(T_{cat}-T_{in}) = M_{feed}C_{P_{fl}}(T_{cat}-T_{in}) + \lambda_f M_{feed} + M_{feed}C_{P_{fv}}(T_{in}-T_v) \tag{24}$$

In riser section the temperature of the catalyst and gas decreases due to the endothermic cracking reactions. It is assumed that in first section itself whole liquid feed gets vaporized due to which there are only two phases solid phase and gas phase. It is assumed that both phases move upward in thermal equilibrium with each other. Heats of reactions used in the present model are shown in Table 3.

**Table 3:** Heat of reactions data

| Cracking Reactions | Heat of reactions | Source |
|---|---|---|
| VGO → gasoline | 525 KJ/Kg | Gupta and Subbarao, 2001 |
| VGO → gas | 525 KJ/Kg | Gupta and Subbarao, 2001 |
| VGO → coke | 525 KJ/Kg | Gupta and Subbarao, 2001 |
| Gasoline →gas | 353.5 KJ/Kg | Dave and Saraf, 2003 |
| Gasoline →coke | 353.5 KJ/Kg | Dave and Saraf, 2003 |

Heat of reaction for every element of the FCC riser is calculated as:

$$H_r = H_{r,VGO\rightarrow gasoline}\left[\phi_i k_1 \frac{\left(\rho_{gi} y_{C_{1,i}}\right)^2}{\rho_{VGO}} V_{cat,i}\right] + H_{r,VGO\rightarrow gas}\left[\phi_i k_2 \frac{\left(\rho_{gi} y_{C_{1,i}}\right)^2}{\rho_{VGO}} V_{cat,i}\right] + H_{r,VGO\rightarrow coke}\left[\phi_i k_3 \frac{\left(\rho_{gi} y_{C_{1,i}}\right)^2}{\rho_{VGO}} V_{cat,i}\right] + H_{r,gasoline\rightarrow gas}\left[\phi_i k_4\, \rho_{gi}\, y_{C_{2,i}} V_{cat,i}\right] + H_{r,gasoline\rightarrow coke}\left[\phi_i k_5\, \rho_{gi}\, y_{C_{2,i}} V_{cat,i}\right] \tag{25}$$

$$T_{i+1} = T_i - \frac{H_r}{(Mcat\ C_{P_{cat}} + M_g C_{P_g})} \tag{26}$$

### 3.2.5 Mass transfer

Mass transfer in FCC riser unit takes place from bulk gas to cluster phase.In the cluster phase, VGO concentration decreases as it cracks while the concentration of the products builds up. This develops the concentration gradient between gas phase and cluster phase and results in the mass transfer of VGO from gas phase to cluster phase and the products  gasoline and gas) from cluster phase to gas phase. Coke is a solid product and remains in cluster phase as a deposit on catalyst particles. The rate of mass transfer of component in each compartment may be written as

$$m_{j,i} = k_{m,i} a_{P_i} (y_{g_{j,i}} - y_{c_{j,i}}) \tag{27}$$

The Solid–gas inter-phase area can be estimated as

$$a_{P_i} = \frac{6A\Delta z \delta_C (1-\varepsilon_c)}{D_{cl}} \tag{28}$$

In our model correlation given by Ranz and Marshall (1952) for single particle provides a reasonable estimate of solid to gas mass transfer coefficients. Diffusion coefficient is assumed to be constant and the same for all the components.

$$Sh = 2 + 0.6(Re)^{1/2}(Sc)^{1/3} \tag{29}$$

### 3.2.6 Solution of material balance equations

The material balance equations can be combined with kinetics and mass transfer models and solved for concentrations in cluster phase.

For VGO, a quadratic equation can be obtained as follows:

$$a_i\, y^2_{C_{VGO,i}} + b_i y_{C_{VGO,i}} + c_i = 0 \tag{30}$$

Where,

$$a_i = \frac{(k_{1,i} + k_{2,i} + k_{3,i}) V_{cat,i} \phi_i (\rho_{gi}/\rho_{VGO})}{a_{pi} k_{m,i}} \tag{31}$$

$$b_i = \frac{M_g}{M_g + k_{m,i} a_{P_i} \rho_{gi}} \tag{32}$$

$$c_i = \frac{-M_g \times y_{g_{1,i-1}}}{M_g + k_{m,i} a_{P_i} \rho_{gi}} \tag{33}$$

*Gasoline:*

$$y_{C_{2,i}} = \frac{\frac{M_g \times y_{g_{2,i-1}}}{M_g + k_{m,i} a_{P_i} \rho_{gi}} + \frac{k_{1,i} V_{cat,i} \phi_i \left(\frac{\rho_{gi}}{\rho_{VGO}}\right)}{a_{pi} k_{m,i}}}{\frac{(k_{4,i} + k_{5,i}) V_{cat,i} \phi_i}{a_{pi} k_{m,i}} + \frac{M_g}{M_g + k_{m,i} a_{P_i} \rho_{gi}}} \tag{34}$$

*Gas:*

$$y_{C_{2,i}} = \frac{\frac{M_g \times y_{g_{3,i-1}}}{M_g + k_{m,i} a_{P_i} \rho_{gi}} + \frac{\left(k_{1,i} y_{C_{1,i}}^2 \left(\frac{\rho_{gi}}{\rho_{VGO}}\right) + k_{4,i} y_{C_{2,i}}\right) \phi_i V_{cat,i}}{a_{pi} k_{m,i}}}{\frac{M_g}{M_g + k_{m,i} a_{P_i} \rho_{gi}}} \tag{35}$$

## CHAPTER 4

# RESULTS AND DISCUSSION

In this chapter the FCC riser is simulated solving the material and energy balance equations considering four lump reaction kinetics, deactivation based on coke concentration on catalyst, 2 phase hydrodynamics and interphase mass transfer phenomena. A computer program is developed in C for the model solution. A base case model for the FCC riser is solved assuming constant cluster size of 6mm. Various cluster size correlations are then used in base model to predict different yields and conversions.

## 4.1 Validations of the Base case model

Firstly for the validation of the base model of FCC riser, using constant 6mm cluster diameter the results are compared with the plant data reported by Ali et al. (1997) as shown in Fig. 10 and Fig. 11. The results were found to match well with the reported plant data. The parameters used in the simulations are shown in the Tables 4, 5 and 6.

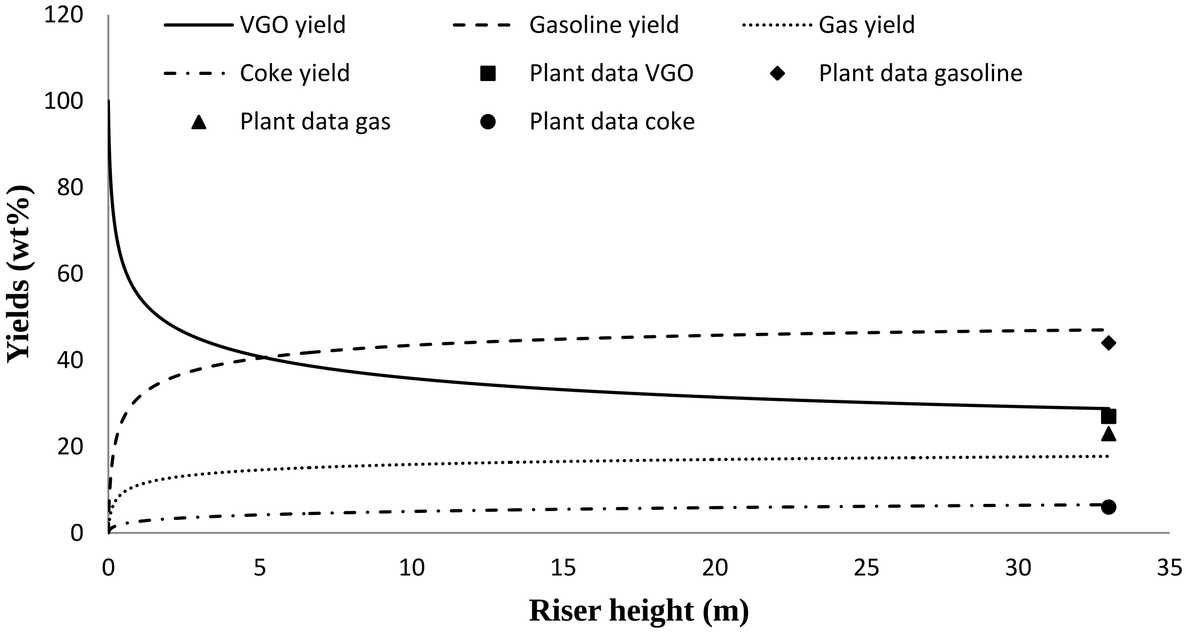

**Fig. 10:** Products Yield for the base model compared with plant data

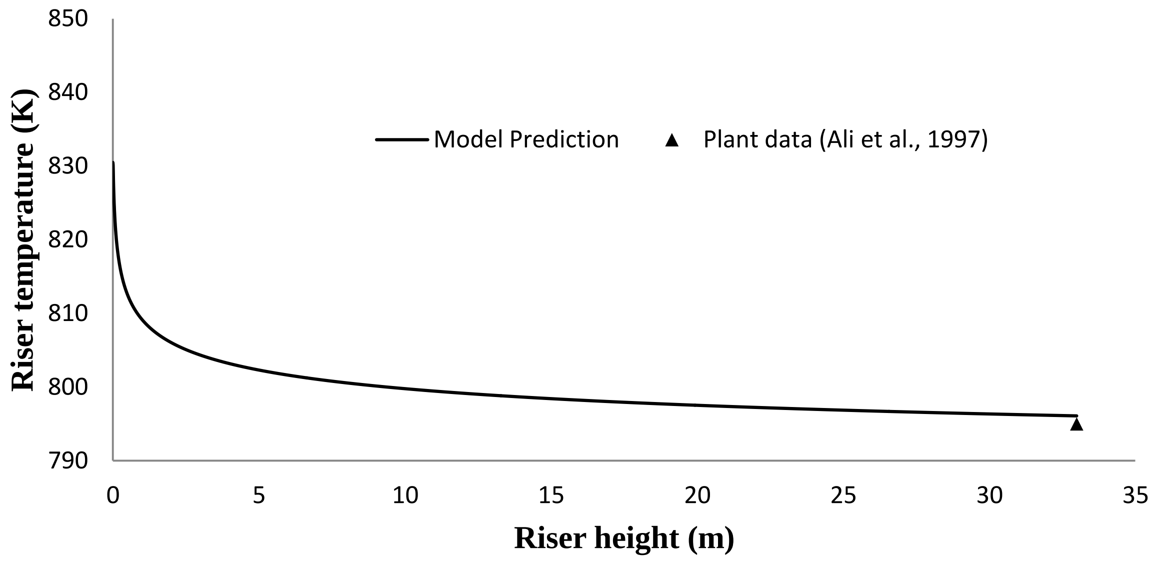

**Fig. 11:** Riser temperature for the base model compared with plant data

**Table 4:** Properties of hydrocarbon feed/products (Gupta and Subba Rao, 2001)

| **Parameter** | **Value** |
|---|---|
| Sp. heat of liquid VGO | 2.67 KJ/Kg.K |
| Sp. heat of gas, and vapor VGO | 3.3 KJ/Kg.K |
| Latent heat of feed vaporization | 96 KJ/Kg |
| Vaporization temperature | 700 K |
| Density gas phase | $1.3 \times 10^{-5}$ Kg/m.s |
| Gas phase conductivity | $3.15\times10^{-5}$ Kw/m.K |
| Diffusivity | $1.0 \times 10^{-5}$ $m^2/s$ |

**Table 5:** Industrial FCC riser data used in model (Ali et al., 1997)

| **Parameter** | **Value** |
|---|---|
| Riser diameter | 0.8 m |
| Catalyst flow rate | 144 Kg/s |
| Catalyst inlet temperature | 960 K |
| Riser pressure | 2.9 atm |
| Riser height | 33m |
| Feed flow rate | 20 Kg/s |
| Feed inlet temperature | 494 K |

**Table 6:** Catalyst properties (Gupta and Subba Rao, 2001)

| **Parameter** | **Value** |
|---|---|
| Particle density | 1200 $Kg/m^3$ |
| Average particle diameter | 75µm |

## 4.2 Riser simulations using various correlations for cluster size

After validation of base model, the various cluster size correlations, reported in literature are used in the model for the prediction of cluster size as a function of local conditions in the riser. Different correlation depends on different parameters such as average voidage, holdup fraction, gas velocities and void diameter. For the simulations the constant cluster size in the base case model is replaced with a cluster size correlation. The cluster size predicted by various correlations is shown in Fig. 12.

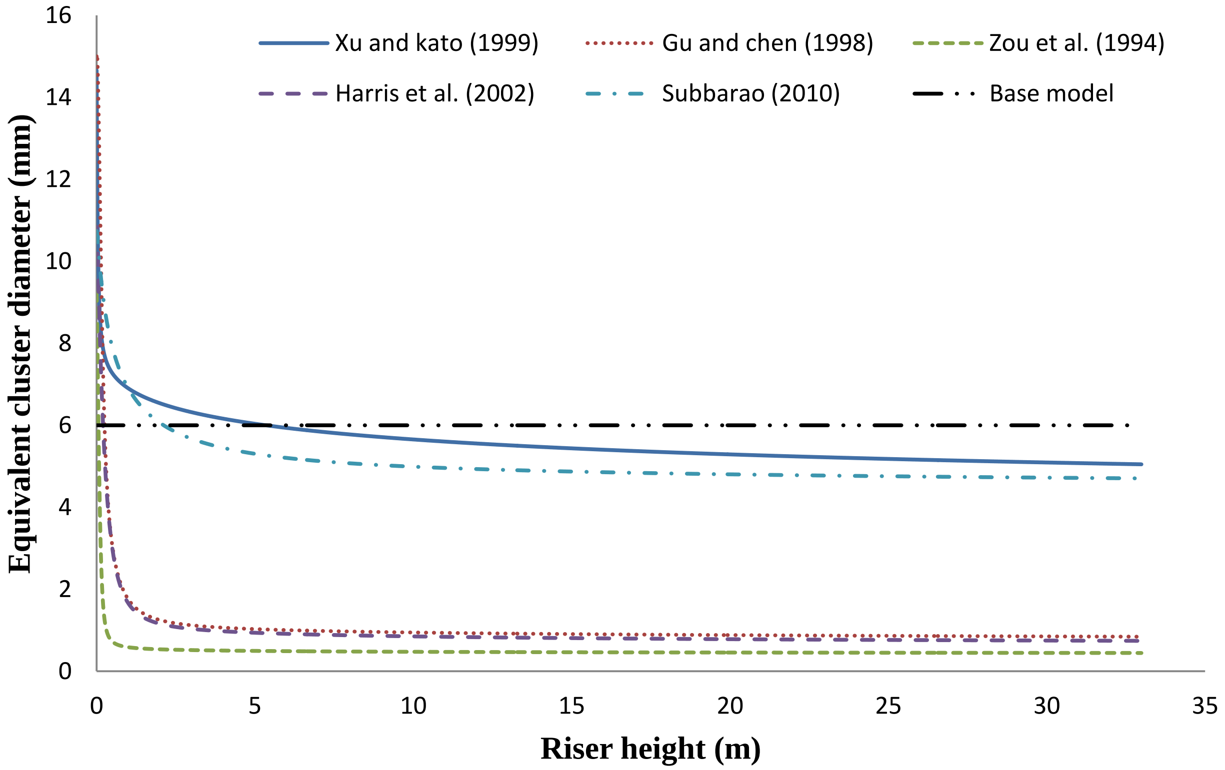

**Fig. 12:** Cluster size along the riser height predicted by various correlations

The figure shows that the correlations of Xu and Kato (1999), Gu and Chen (1998) and Subbarao (2010) predicted initial cluster size of about 15 mm, whereas, the initial cluster size predicted by the correlations of Zou et al. (1994) and Harris et al. (2002) is 10 mm. Correlations of Xu and Kato (1999) and Subbarao (2010) predicted gradual change in cluster size to 5 and 6 mm respectively. Other correlations predicted very sharp initial decline in cluster size, and constant size (< 1 mm) after first 2-3 m of riser height.

Due to variation in cluster size along the riser height for different correlations there is a considerable effect on yield, conversions, phase velocities and temperature which is shown in the figures below. The most important product of the FCC riser unit is gasoline. The plot of gasoline yield (Fig. 13) shows considerable variation in predicted yields by different correlations. Effect of cluster size variation on gas yield is shown in Fig. 14. It is interesting to note that the coke yield is maximum (Fig. 15), for the Subbarao's correlation. This may be due to the higher residence time of bigger size clusters in the inlet zone where the catalyst activity is high.

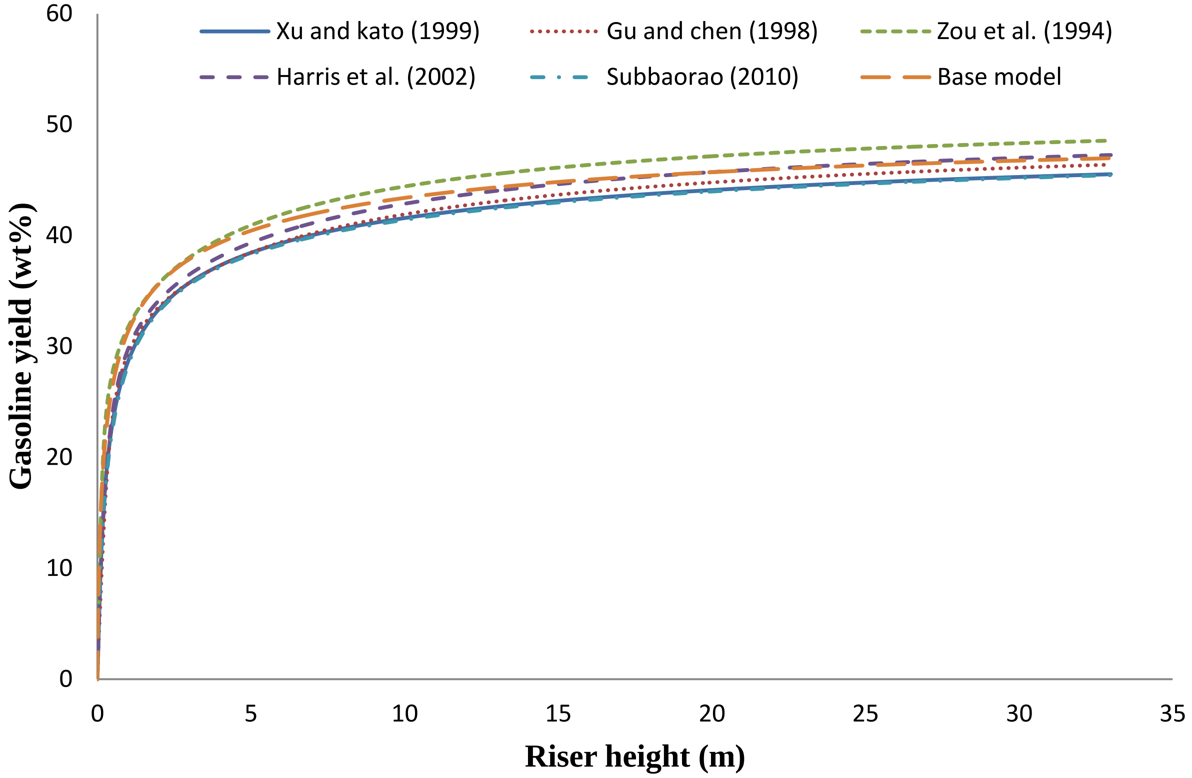

**Fig. 13:** Gasoline yield profiles predicted by various correlations

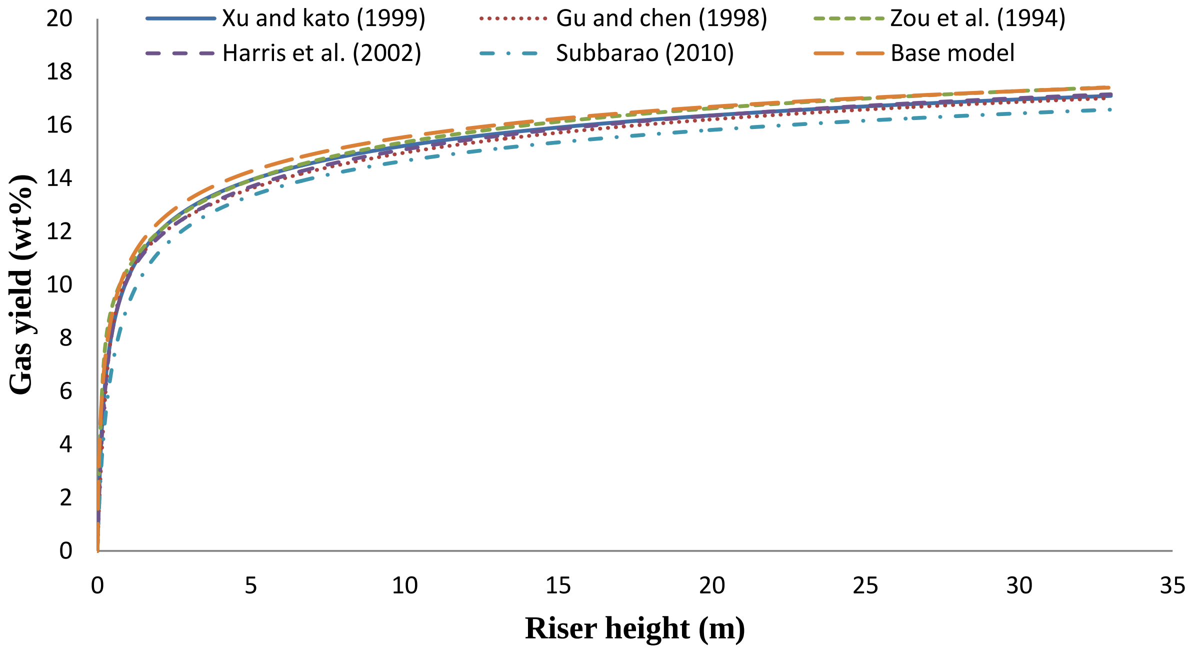

**Fig. 14:** Gas yield profiles predicted by various correlations

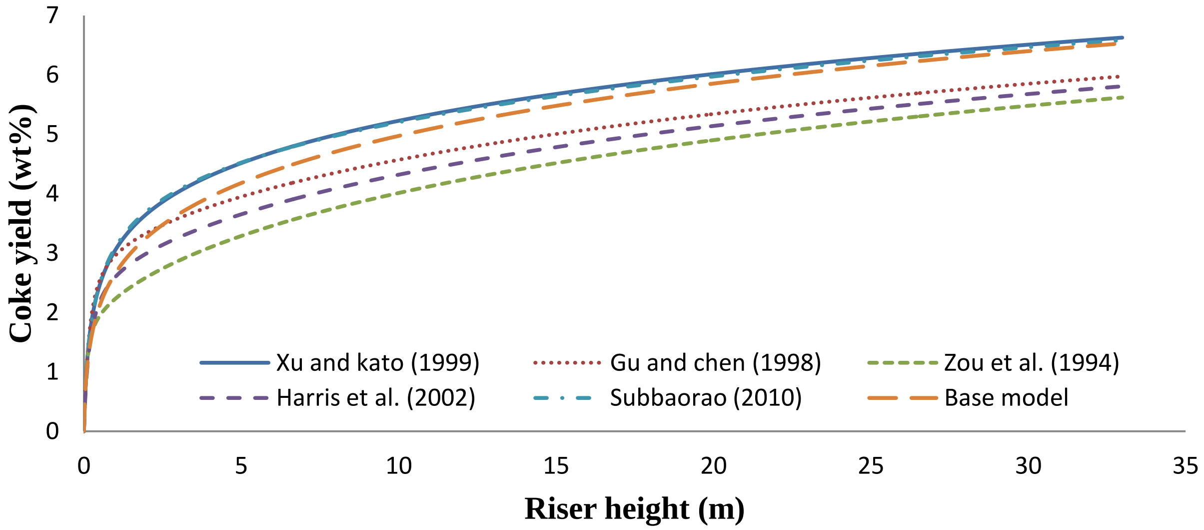

**Fig. 15:** Coke yield profiles predicted by various correlations

A considerable variation was found in gas velocities and cluster velocities along the riser height. Fig. 16 and Fig. 17 shows the predicted gas and cluster velocities for different correlations. Correlation of Zou et al. (1994) gives minimum gas and maximum cluster velocity profiles since the size of clusters predicted decreases sharply due to which clusters moves with higher velocity compared with other size clusters. Comparison of cluster sizes (Fig. 12) and clusters velocities

(Fig. 17) show that large clusters move slower than the small ones. Catalyst fractional holdup variation along the riser height is shown in Fig. 18.

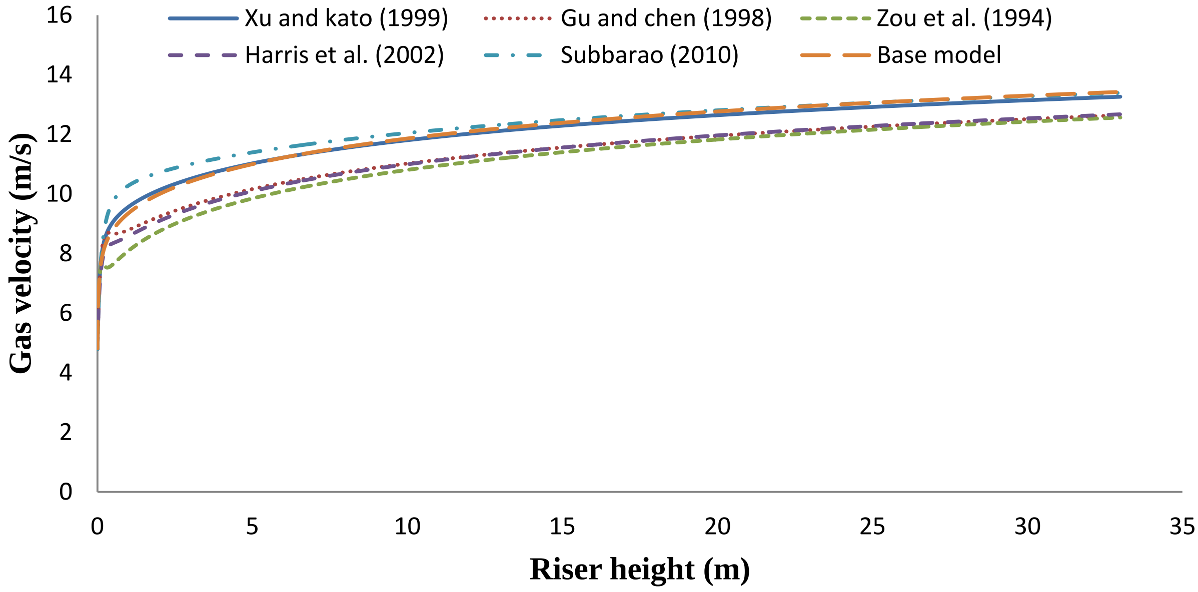

**Fig. 16:** Gas velocity predicted by various correlations

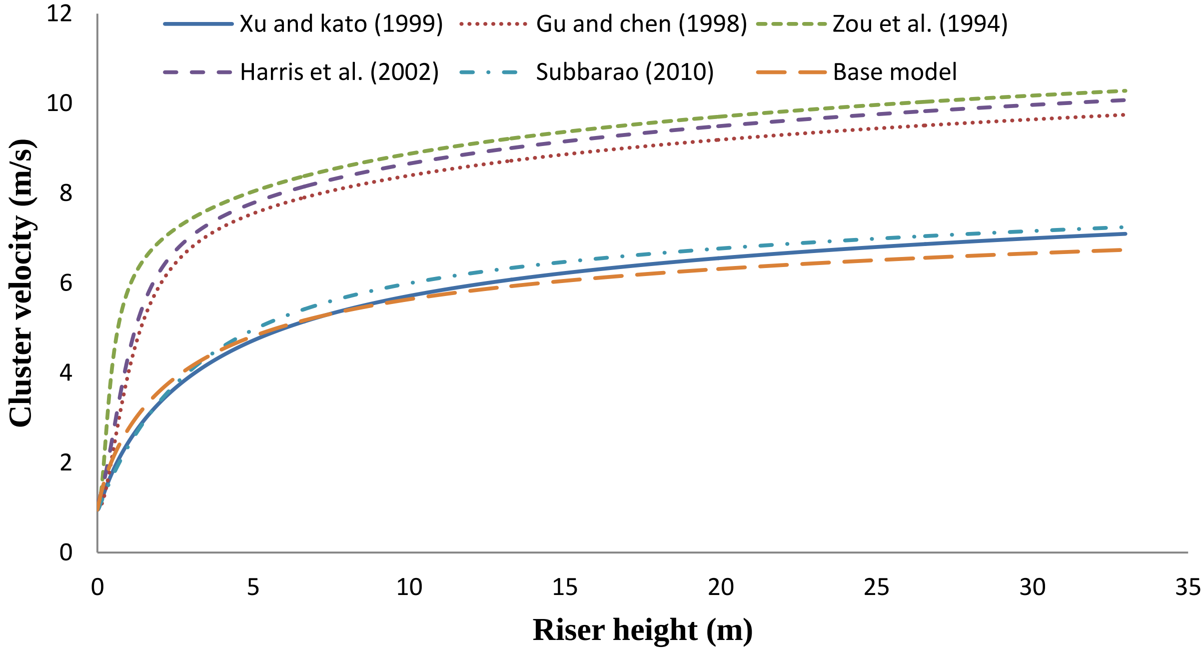

**Fig. 17:** Cluster velocity predicted by various correlations

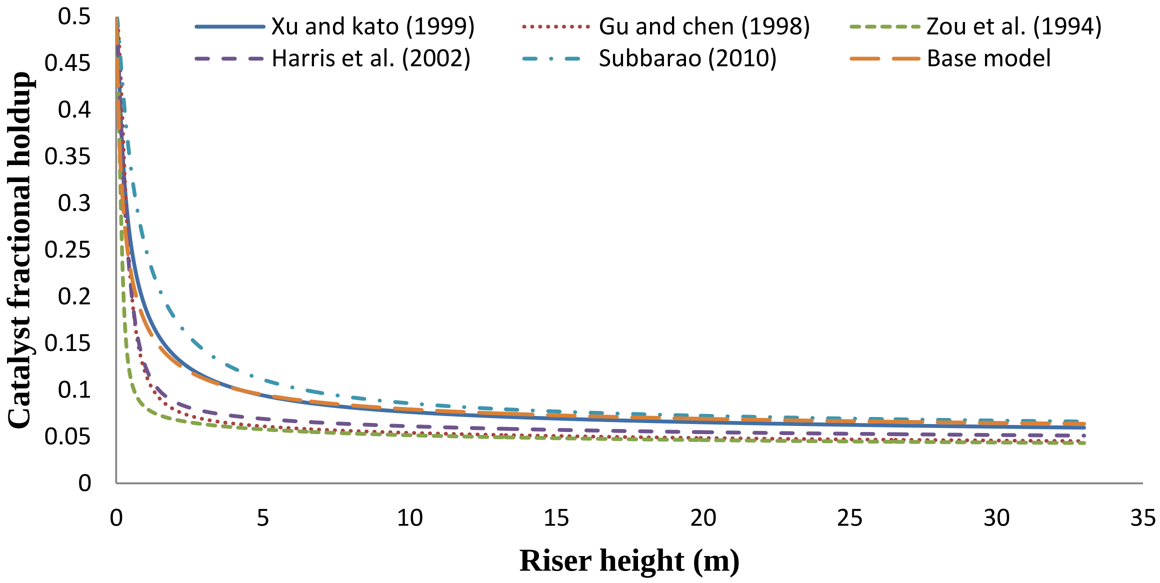

**Fig. 18:** Cluster fractional holdup variations for various correlations.

Catalyst activity along the riser height is presented in Fig. 19. The activity decrease, in the riser entry zone, is faster for the larger clusters. This can be attributed to the higher residence time of bigger size clusters in the inlet zone, where the catalyst activity is high. This leads to faster catalyst deactivation.

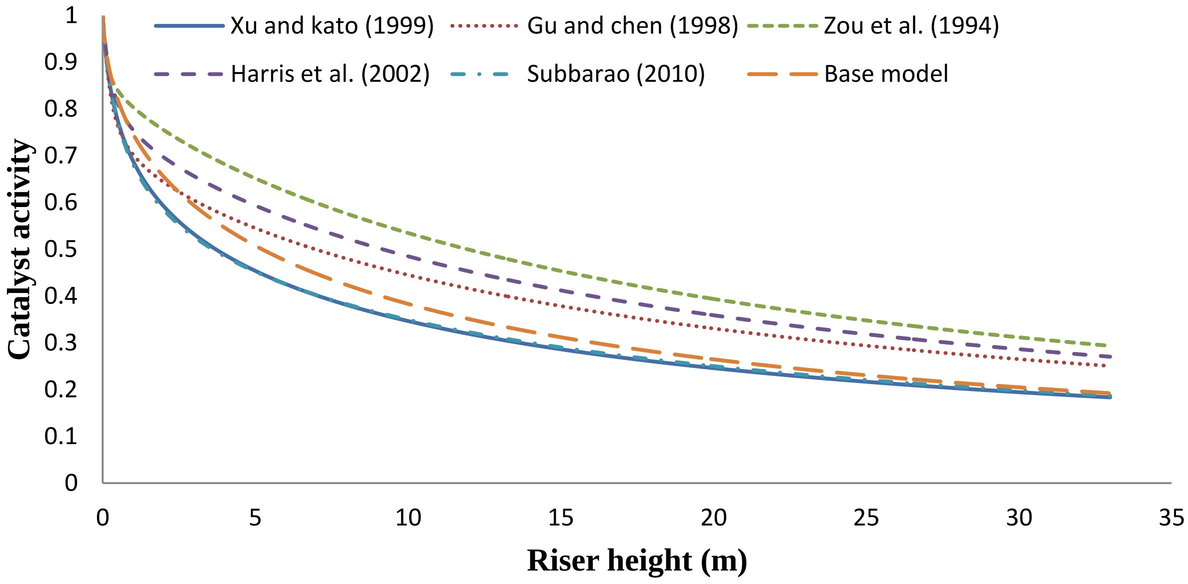

**Fig. 19:** Catalyst activity along the riser height predicted by various correlations

Fig. 20 shows the conversion (wt%) predicted for various correlations. The minimum conversion predicted by Subbarao's correlation is due to the fact that the big size clusters spend more time in the entry zone and thus catalyst deactivation is more, leading to lesser overall conversion. Maximum conversion predicted by the correlation of Zou et al. (1994) is due to short residence time in the entry zone (minimum cluster size) coupled with higher mass transfer rates.

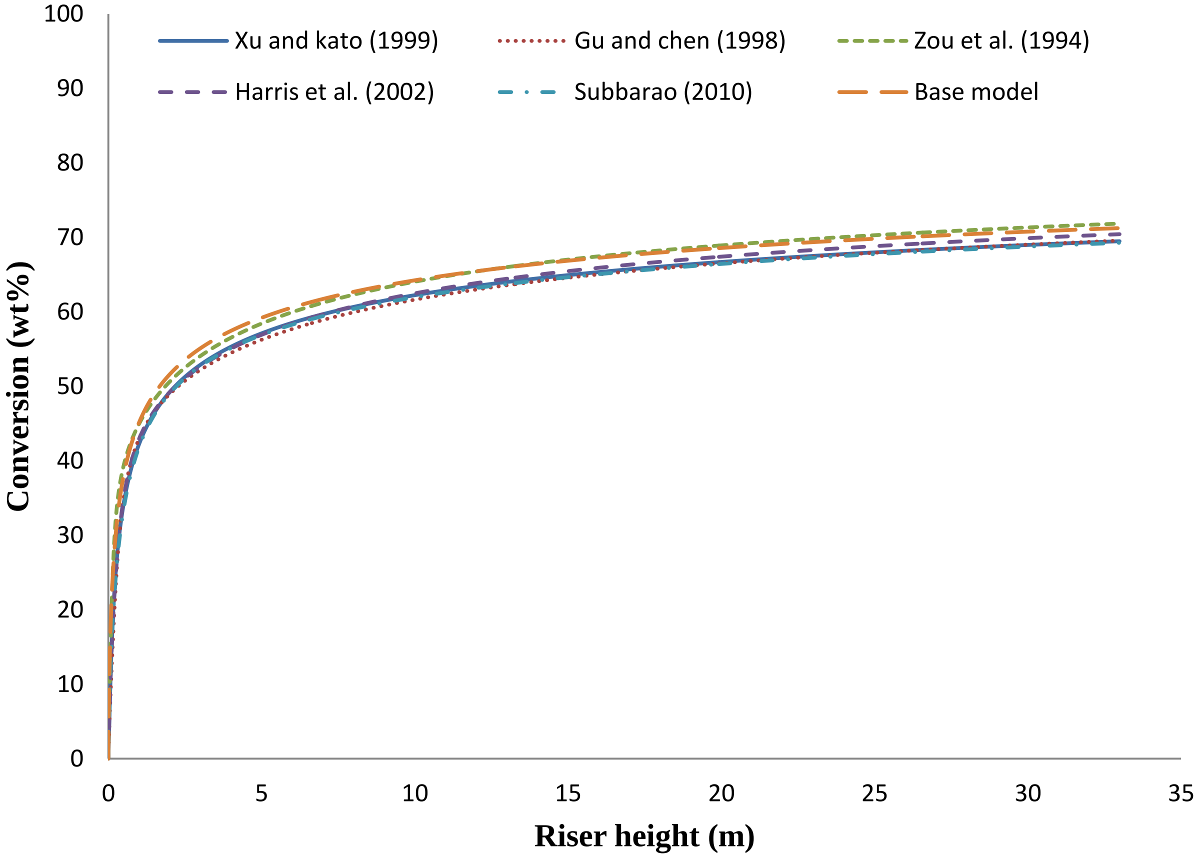

**Fig. 20:** Overall conversion predicted by various correlations

Fig. 21 shows the temperature profile predicted by various correlations. After instantaneous vaporization the riser temperature falls gradually along the riser height due to cracking reactions taking place in the column.

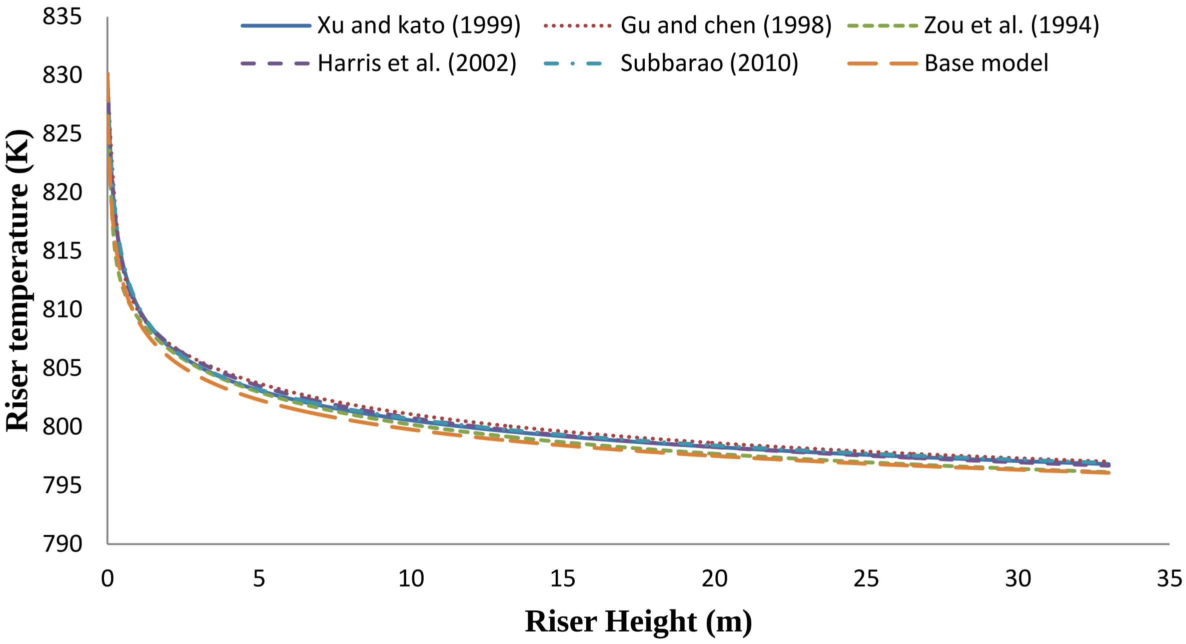

**Fig. 21:** Riser temperature predicted by various correlations

The product yields predicted at the riser exit for different cluster size correlations are shown in Table 7. It is evident that the cluster size has significant effect on the product yields; thus, a reasonable estimate of cluster size is important for model simulations.

**Table 7:** Predictions of product yields at riser exit for various cluster sizes correlations

| **Correlations used** | **Product yield (wt %)** | | |
|---|---|---|---|
| | **Gasoline** | **Gas** | **Coke** |
| **Xu and Kato (1999)** | 45.535681 | 17.300658 | 6.624279 |
| **Gu and Chen (1998)** | 46.390843 | 17.187853 | 5.970358 |
| **Zou et al. (1994)** | 48.556021 | 17.676845 | 5.616911 |
| **Harris et al. (2002)** | 47.256678 | 17.374162 | 5.805431 |
| **Subbarao (2010)** | 45.435381 | 17.248408 | 6.584337 |
| **Base Model (Constant cluster size, 6mm)** | 46.981034 | 17.713325 | 6.528778 |

## CHAPTER 5

# CONCLUSIONS AND FUTURE RECOMMENDATIONS

## Conclusions

The predicted cluster size varies considerably for different correlations. The results show significant variation in conversion, and yields of VGO, gasoline, gas and coke for these correlations. The correlations that predict larger cluster predict low overall conversion as compared to the correlations that predict smaller size clusters. Coke yield prediction is most influenced by the cluster size.

## Future recommendations

- In the present work cluster correlations are applied to estimate the performance of FCC riser unit. This approach can be extended to FCC riser and regenerator unit model to know the effect of cluster size correlations on its performance.
- CFD models can be used to capture the complex phenomena of the FCC riser unit using cluster size approach.

# PUBLICATION

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# REFERENCES

**Ali, H., and Rohani, S. (1997)**. Dynamic modeling and simulation of a riser-type fluid catalytic cracking unit, *Chemical Engineering and Technology*, 20, 118-130.

**Ancheyta, J.J., Lopez, I.H., Aguilar, R.E., and Moreno, M.J. (1997)**. A strategy for kinetic parameter estimation in the fluid catalytic cracking process. *Industrial and Engineering Chemistry Research*, 36, 5170-5174.

**Arbel, A. Huang, Z., Rinard, I.H., Shinnar, R., and Sapre, A.V. (1995)**. Dynamics and control of fluidized catalytic crackers. Modeling of the current generation FCC. *Industrial and Engineering Chemistry Research*, 34, 1228-1243.

**Baudrez, E., Heynderickx, G. J., Marin, G. B. (2010).** Steady-state simulation of fluid catalytic cracking riser reactors using a decoupled solution method with feedback of the cracking reactions on the flow, *Chemical Engineering Research and Design*, 88, 290-303.

**Benyahia, S., Ortiz, A.G., and Paredes, J.I.P. (2003).** Numerical analysis of a reacting gas/solid flow in the riser section of an industrial fluid catalytic cracking unit, *International Journal of Chemical Reaction Engineering*, Volume 1, Article A41.

**Berry, T.A., McKeen, T.R., Pugsley, T.S., and Dalai, A.K. (2004)**. Two-dimensional reaction engineering model of the riser section of a fluid catalytic cracking unit. *Industrial and Engineering Chemistry Research*, 43, 5571-5581.

**Berruti, F., Chaouki, J., Godfroy, L., Pugsley, T.S., and Patience, G.S. (1995).** Hydrodynamics of circulating fluidized bed risers: a review, *The Canadian Journal of Chemical Engineering*, 73, 579-602.

**Bi, H.T. (2002).** Some issues on core-annulus and cluster models of circulating fluidized bed reactors, *The Canadian Journal of Chemical Engineering*, 80, 809-817.

**Bollas, G.M., and Vasalos, I.A. (2002).** Modeling Small-Diameter FCC Riser Reactors. A Hydrodynamic and Kinetic Approach. *Industrial and Engineering Chemistry Research***,** 41, 5410-5419.

**Corella, J. (2004)**. On the modeling of the kinetics of the selective deactivation of catalysts. Application to the fluid catalytic cracking process. *Industrial and Engineering Chemistry Research*, 43, 4080-4086.

**Corella, J., Bilbao, R., Molina, J.A., and Artigas, A. (1985)**. Variation with time of the mechanism, observable order, and activation energy of the catalyst deactivation by coke in the FCC process. *Industrial and Engineering Chemistry Research*, 24, 625-636.

**Corella, J., Fernandez, A., and Vidal, J.M. (1986)**. Pilot plant for the fluid catalytic cracking process: Determination of the kinetic parameters of deactivation of the catalyst. *Industrial and Engineering Chemistry Research*, 25, 554-562.

**Corella, J., and Menedez, M. (1986)**. The modeling of the kinetics of deactivation of mono functional catalysts with and acid strength distribution in their non homogeneous surface. Application of the deactivation of commercial catalysts in the FCC process. *Chemical Engineering Science*, 41, 1817-1826.

**Coxon, P.G., and Bischoff, K.B. (1987)**. Lumping Strategy, 1. Introduction techniques and application of cluster analysis. *Industrial and Engineering Chemistry Research*, 26, 1239-1248.

**Das, A.K., Martin, G.B., and Heynderickx, G.J. (2003)**. Three-dimensional simulation of a fluid catalytic cracking riser reactor. *Industrial and Engineering Chemistry Research*, 42, 2602-2617.

**David, S.J., Jones and Peter, P. P. (2006).** Handbook of Petroleum Processing (1st ed.), *The Netherlands, Springer.*

**Dave, D.J., and Saraf, D.N. (2003).** Model suitable for rating and optimization of industrial FCC units, *Indian Chemical Engineer*, Section A, Vol. 45, No. 1.

**Fernandes, J. L., Pinheiro, C. I. C., Oliveira N. and Ramoa Ribeiro F. (2003).** Modeling and Simulation of an Operating Industrial Fluidized Catalytic Cracking (FCC) Riser. *2nd and 4th Mercosur Congress on Process Systems Engineering.*

**Feng, W., Vynckier, E., and Froment, G.F. (1993).** Single event kinetics of catalytic cracking, *Industrial and Engineering Chemistry Research*, 32, 2997-3005.

**Fligner, M., Schipper, P.H., Sapre, A.V., and Krambeck, F.J. (1994)**. Two phase cluster model in riser reactors: Impact of radial density distribution on yields. *Chemical Engineering Science*, 49, 5813-5818.

**Fogler, H.S. (1992)**. Elements of Chemical Reaction Engineering (2nd edition, pp.62). *New Delhi: Prentice-Hall of India.*

**Gao, J., Xu, C., Lin, S., Yang, G., and Guo, Y. (1999)**. Advanced model for turbulent gas-solid flow and reaction in FCC riser reactor. *AIChE J.*, 45, 1095-1113.

**Gao, J., Xu, C., Lin, S., Yang, G., and Guo, Y. (2001)**. Simulation of gas-liquid-solid 3-phase flow and reaction in FCC riser reactors. *AIChE J.*, 47, 677-692.

**Gianetto, A., Faraq, H., Blasetti, A., and de Lasa, H. (1994).** FCC catalyst for reformulated gasoline. Kinetic modeling, *Industrial and Engineering Chemistry Research*, 33, 3053-3062.

**Godfroy, L., Patience, G.S., and Chauki, J. (1999**). Radial hydrodynamics in risers, *Industrial and Engineering Chemistry Research*, 38, 81-89.

**Gu, W.K., and Chen, J.C. (1998).** A model for solid concentration in Circulating Fluidized Beds, in *Fluidization IX*, L.S. Fan and T.M. Knowlton, Eds., *Engineering Foundation*, New York, NY,501-508.

**Gupta, A., and Subba Rao, D. (2001)**. Model for the performance of a fluid catalytic cracking (FCC) riser reactor: Effect of feed atomization. *Chemical Engineering Science*, 56, 4489-4503.

**Gupta, A., and Subba Rao, D. (2003)**. Effect of feed atomization on FCC performance: simulation of entire unit. *Chemical Engineering Science*, 58, 4567-4579.

**Gupta, R.K., Kumar, V., and Srivastava, V.K. (2005)**. Modeling and simulation of fluid catalytic cracking unit. *Reviews in Chemical Engineering*, 21(2), 95-131.

**Gupta, R.K., Kumar V., and Srivastava V.K. (2007).** A new generic approach for the modeling of fluid catalytic cracking (FCC) riser reactor, *Chemical Engineering Science*, 62, 4510-4528.

**Gupta R.K., and Kumar V.K. (2008).** Fluid catalytic cracking riser modeling in heat transfer mode, *Chemical Product and Process Modeling*, Volume 3, Issue 1, Article 11.

**Gupta R.K., Kumar V., and Srivastava V.K. (2010).** Modeling of fluid catalytic cracking riser Reactor: A Review, *International journal of chemical reactor Engineering*, Volume 8, Review R6.

**Han, I.S., Chung, C.B., and Riggs, J.B. (2000)**. Modeling of fluidized catalytic cracking process. *Computer and Chemical Engineering*, 24, 1681-1687.

**Horio, M., and Kuroki, H. (1994).** Three-dimensional flow visualization of dilute dispersed solids in bubbling and circulating fluidized beds. *Chemical Engineering Science,* Vol. 49. No. 15, pp. 2413-2421.

**Hiroyuki, I., Nakajima, T., and Horio, M. (1989).** The Clustering annular flow model of circulating fluidized beds. *Journal of Chemical Engineering of Japan*, Vol 22, No. 5.

**Hoomans, B.P.B., Kuipers, J.A.M., and Van Swaaij W.P.M. (1998).** Granular dynamics simulation of cluster formation in riser flow. *Third International Conference on Multiphase Flow, ICMF'98 Lyon, France*.

**Huilin, S.Q, Yurong, Yongli, J., and Ding, Li. (2005).** Numerical study of particle cluster flow in risers with cluster-based approach. *Chemical Engineering Science*, 60, 6757 – 6767.

**Jacob, S.M., Gross, B., Voltz, S.E., and Weekman, V.W., jr. (1976)**. A lumping and reaction scheme for catalytic cracking. *AIChE J.*, 22, 701-713.

**Lu, H., Wang, S., He, Y., Ding, J., Liu, G., and Hao, Z. (2008).** Numerical simulation of flow behavior of particles and clusters in riser using two granular temperatures. *Powder Technology*, 182, 282–293.

**Michalopoulos, J., Papadokonstadakis, S., Arampatzis G. And Lygeros A. (2001).** Modeling of an industrial fluid catalytic cracking unit using neural networks, *Chemical Engineering Research and Design*, 79A, 137-142.

**Novia, N., Ray, M. S., and Pareek, V. (2007).** Three-dimensional hydrodynamics and reaction kinetics analysis in FCC riser reactors, *Chemical Product and Process Modeling*, Volume 2, Issue 2, Article 4.

**Nayak, S. V., Joshi, S. L., and Ranade, V. V. (2005).** Modeling of vaporization and cracking of liquid oil injected in a gas–solid riser, *Chemical Engineering Science*, 60, 6049 – 6066.

**Park, J.Y. (2002).** The clustered dense phase model for group A fluidization: I. Dense phase hydrodynamics. *Chemical Engineering Science*, 58,193 – 202.

**Pekediz, A., Kraemer, D., Blasetti, A., and de Lasa, H. (1997)**. Heats of catalytic cracking. Determination in a riser simulator reactor. *Industrial and Engineering Chemistry Research*, 36, 4516-4522.

**Pugsley, T.S., and Berruti, F. A. (1996)**. Predictive hydrodynamic model for circulating fluidized bed risers. *Powder Technology*, 89, 57-69.

**Sadeghbaigi, R. (2012).** Fluid catalytic cracking handbook , 3rd edition, Butterworth-Heinemann publications.

**Sundaresan, S. (2000)**. Modeling the hydrodynamics of multiphase flow reactors: Current status and challenges. *AIChE J.*, 46, 1102-1105.

**Subbarao, D. (2008)**. A cluster model for mass transfer in risers. *Journal of Engineering Science and Technology Vol. 3*, No. 2, 131 – 137.

**Subbarao, D. (2010)**. A model for cluster size in Risers, *Powder Technology*, 199, 48-54.

**Theologos, K.N., Lygeros, A.I., and Markatos, N.C. (1999)**. Feedstock atomization effects on FCC riser reactors selectivity. *Chemical Engineering Science*, 54, 5617-5625.

**Trujillo, W. R., and Wilde, J.D. (2010).** Computational Fluid Dynamics Simulation of Fluid Catalytic Cracking in a Rotating Fluidized Bed in a Static Geometry. *Industrial and Engineering Chemistry Research*, 49, 5288–5298.

**U.S. Dept. of Energy. (2012).** U.S. Downstream Processing of Fresh Feed Input by Catalytic Cracking Units. *Energy Information Administration*.

**Wang, L., G., Xu., and S.D. (2008).** Numerical Predication of Cracking Reaction of Particle Clusters in Fluid Catalytic Cracking Riser Reactors. *Chinese Journal of Chemical Engineering*, 16, 670-678.

**Wang, L., Yang, B., and Wang, Z. (2005)**. Lumps and kinetics for the secondary reactions in catalytically cracked gasoline. *Chemical engineering Journal*, 109, 1-9.

**Weekman, V.W., Jr. (1968)**. A model of catalytic cracking conversion in fixed, moving, and fluid-bed reactors. *Industrial and Engineering Chemical Process Design Development,* 7, 90-95.

**Weekman, V.W., Jr. (1979)**. Lumps, models, and kinetics in practice. *AIChE Monograph Series,* 11, 75, 3-29.

**Weekman, V.W., Jr., and Nace, D.M. (1970)**. Kinetics of catalytic cracking selectivity in fixed, moving, and fluid bed reactors. *AIChE J*., 16, 397-405.

**Wilhelm, R.H., Kwauk, M. (1948).** Fluidization of solid particles. *Chemical Engineering Progress*. 44, 201.

**Xu, G.W., and Li, J.H. (1998).** Analytical solution of the energy minimization multi-scale model for gas–solid two-phase flow. *Chemical Engineering Science*, 53, 1349–1366.

**Xu, G., and Kato, K. (1999).** Hydrodynamic equivalent diameter for clusters in heterogeneous gas–solid flow, *Chemical Engineering science*, 1837-1847.

**Yerushalmi, J., Turner, D. H., and Squires, A. M. (1976).** The fast fluidized bed, *Industrial and Engineering Chemistry Process Design and Development*, 15, 47-53.

**Zheng, Y. Y. (1994)**. Dynamic modeling and simulation of a catalytic cracking unit. *Computer and Chemical Engineering*, 18, 39-44.

**Zhou, J., Grace, J.R., Qin, S., Brereton, C.M.H., Lim, C.J., and Zhu, J. (1994)**. Voidage profiles in a circulating fluidized bed of square cross-section. *Chemical Engineering Science*, 49, 3217-3226.

**Zimmermann, S., and Taghipour, F. (2005).** CFD modeling of the hydrodynamics and reaction kinetics of FCC fluidized-bed reactors, *Industrial and Engineering Chemistry Research*, 44, 9818–9827.