

Modeling and Simulation of Fluid Catalytic Cracking Riser Reactor

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ACKNOWLEDGEMENT

DECLARATION

I hereby declare that thesis entitled “**Modeling of Fluid Catalytic Cracking Riser Reactor**” is an authentic record of my work carried out as per the requirements for the award of degree of **M.Tech. (Chemical Engineering)** at **Thapar University, Patiala**, under the guidance of **Dr. Raj Kumar Gupta**, (Assistant Professor) and **Mr. Parminder Singh**, (Assistant Professor) **Department of Chemical Engineering**, Thapar University, Patiala during **July 2010 to July 2011**. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.

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This is to certify that above declaration made by the student concerned is correct to the best of our knowledge and belief.

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ABSTRACT

A Fluid Catalytic Cracking Unit mainly consists of a riser reactor, a catalyst stripper, and a regenerator. Riser reactor is the most important part of this unit as the cracking reactions take place in the riser. 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 and the cracking reactions start. The reactions' 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 fractionator for recovery.

Modeling of riser helps in understanding the complex physical phenomena of this process. Complex hydrodynamics, unknown hydrocarbons in the FCC feed and involvement of different type of simultaneous reactions make riser modeling difficult. 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 or three phase flow hydrodynamics is used by various authors, heat and mass transfer resistances are ignored in most studies, and exponential catalyst deactivation model is used in most works.

The present work incorporates a four lump kinetic model having two-phase flow with cluster based approach (considering pressure drop inside the riser). The effect of cracking on phase velocities, and catalyst deactivation model based on concentration of coke on catalyst is also considered. For the solution of the model, the riser is divided into a number of small volume elements along the height. Material and energy balance equations are solved in each volume element. Product yields, riser temperature, catalyst activity, phase velocities, and riser pressure profiles are plotted and discussed. The model predictions matches well with the data reported in the literature. Simulations are also done for various cluster sizes and the effect of cluster size on cluster velocity and product yields is presented.

CONTENTS

	Page No.
Declaration	i
Acknowledgement	ii
Abstract	iii
List of Figures	vi
List of Tables	vii
CHAPTER-1 INTRODUCTION	1-10
1.1 Process description	2
1.1.1 Feed preheat	3
1.1.2 Riser reactor	4
1.1.3 Regenerator–heat/catalyst recovery	7
CHAPTER-2 LITERATURE REVIEW	11-17
2.1 Riser modeling	11
2.1.1 Hydrodynamics	11
2.1.2 Cracking kinetics	13
2.1.3 Heat transfer and mass transfer	14
2.1.4 Catalyst deactivation	15
2.2 Concluding remarks	17
CHAPTER-3 FCC RISER MODEL	18-25

3.1 Riser Model	18
3.1.1 Model equations	18
CHAPTER-4 RESULTS AND DISCUSSION	26-33
CONCLUSIONS AND FUTURE RECOMMENDATIONS	34
NOMENCLATURE	35-36
REFERENCES	37-42

LIST OF FIGURES

	Title	Page no.
Figure 1	Schematic of FCC unit	3
Figure 2	Two stage stripper	6
Figure 3	Air distributor	7
Figure 4	Schematic of a volume element in the riser	19
Figure 5	Schematic for four lump kinetic model	22
Figure 6	Conversion/ product yield along riser height	28
Figure 7	Temperature drop along riser height	29
Figure 8	Phase velocities along riser height	30
Figure 9	Catalyst activity along riser height	31
Figure 10	Pressure drop along the riser height	32
Figure 11	Effect of cluster size on cluster phase velocity	33

LIST OF TABLES

	Title	Page no.
Table 1	Main features of some FCC riser models	16
Table 2	Molecular weight of various lumps	20
Table 3	Stoichiometric coefficients	24
Table 4	Heat of reaction data	25
Table 5	Plant data used for riser simulation	26
Table 6	Parameters used for riser simulations	26
Table 7	Kinetic parameters used in the model	27
Table 8	Model predictions of product yields at riser exit for different cluster sizes	33

Chapter 1

Introduction

Fluid catalytic cracking unit (FCCU) converts heavy hydrocarbon petroleum fractions into more usable products such as gasoline, middle distillates, and light olefins. Fluid catalytic cracking (FCC) is considered the primary conversion process in an integral refinery. 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 is processed in an FCC to produce high-octane gasoline and fuel oils (Speight, 2006). Most of the existing FCC units have been designed or modified by six major technology licensors:

1. ABB Lummus Global
2. Exxon Research and Engineering (ER&E)
3. Kellogg Brown & Root—KBR (formerly The M.W. Kellogg Company)
4. Shell Oil Company
5. Stone & Webster Engineering Corporation (SWEC)
6. UOP (Universal oil products)

Although the mechanical configuration of individual FCC units may differ, their common objective is to upgrade low-value feedstock to more valuable products. Worldwide, about 45% (Reza, 2000) of all gasoline comes from FCC and ancillary units, such as the alkylation unit. Since the start-up of the first commercial FCC unit in 1942, many improvements have been made. These improvements have enhanced the unit's mechanical reliability and its ability to crack heavier, lower value feed stocks. The FCC has a remarkable history of adapting to continual changes in market demands.

FCCU mainly consists of a riser reactor, a catalyst stripper, and a regenerator. Riser reactor is the most important part of this unit as the cracking reactions take place in the riser. Modern FCC units have 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 reactions' 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 fractionator for recovery.

1.1 Process description

The FCC unit uses a micro-spheroid catalyst, which behaves like liquid when properly aerated by gas. The main purpose of the unit is to convert high-boiling petroleum fractions called *gas oil* to high value, high-octane gasoline and heating oil. Gas oil is the portion of crude oil that commonly boils in the 650°F to 1,050°F (330° to 550°C) range. Before proceeding, it is helpful to examine how a typical catalyst cracker fits into the refinery process (Figure 1). A petroleum refinery is composed of several processing units that convert raw crude oil into usable products such as gasoline, diesel, and jet fuel. The crude unit is the first unit in the refining process. Here, the raw crude is distilled into several intermediate products: naphtha, kerosene, diesel, and gas oil. The heaviest portion of the crude oil, which cannot be distilled in the atmospheric tower, is heated and sent to the vacuum tower where it is split into gas oil and tar.

The FCC process is very complex. For clarity, the process description has been broken down into three separate sections:

- Feed Preheat.
- Riser Reactor
- Regenerator—Heat/Catalyst Recovery.

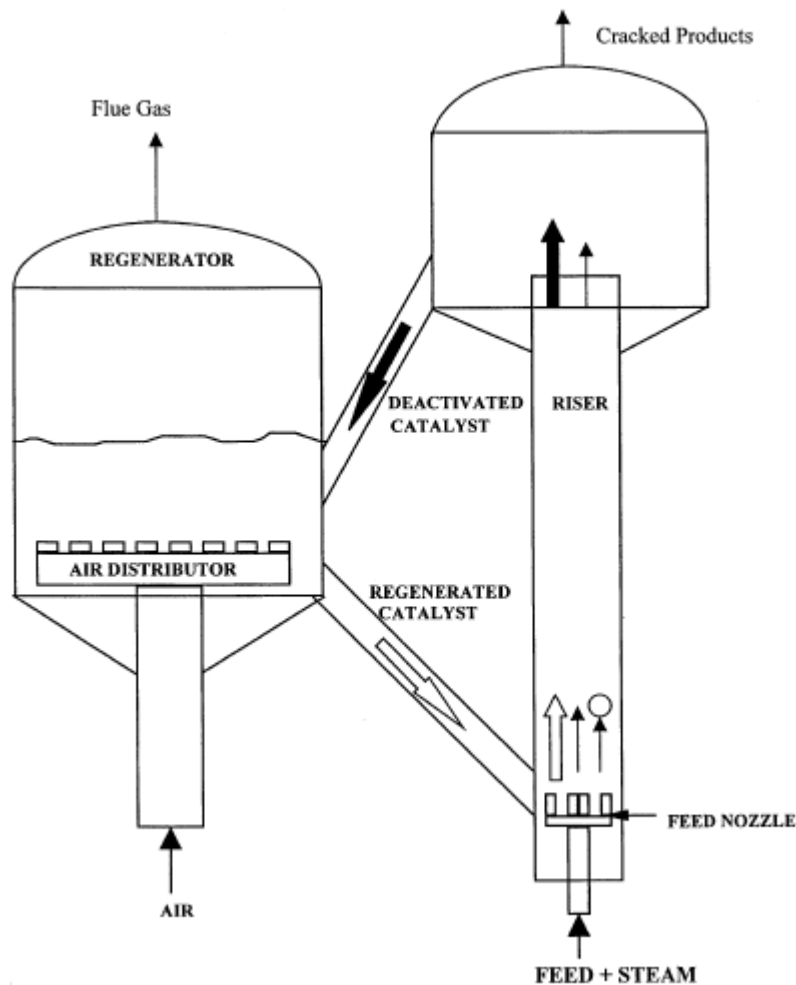


Figure 1: Schematic of FCC unit (Source: Gupta et al., 2003)

1.1.1 Feed preheat

The feed is normally heated to a temperature of 500°F to 700°F (260°C to 370°C). The main fractionator bottoms pump-around and/or fired heaters are the 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 product, and bottoms pump-around are commonly used. Removing heat from the main fractionator is at least as important as preheating the feed. Most FCC units use fired heaters for FCC feed final preheat. Feed temperature is raised to 300-500° F (150-260°C) which is generally sufficient for most of the FCCUs.

1.1.2 Riser reactor

The riser reactor is the heart of the FCC process. In a modern catalyst cracking units, 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 (Figure 1). The ratio of catalyst to- oil is normally 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 the reaction occurring in the riser is endothermic (i.e., it requires energy input). The circulating catalyst provides this energy. The typical regenerated catalyst temperature ranges between 1250°F to 1350°F (677°C to 732°C).

Catalytic reactions occur in the vapor phase. After vaporization of feed cracking reactions starts. 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. A number of refineries are modifying the riser termination devices to minimize these reactions. The riser is a vertical pipe. It usually has 4 to 5 inch (10 to 13 cm) thick refractory lining for insulation and abrasion resistance. Typical risers are 2 to 6 feet (60 to 180 cm) in diameter and 75 to 120 feet (25 to 30 meters) 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 the 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. With high-activity zeolite catalyst, virtually all of the cracking reactions take place in three seconds or less. Risers are normally designed for an outlet vapor velocity of 50 ft/sec to 75 ft/sec (15.2 to 22.8 m/sec). The average hydrocarbon residence time is about two seconds (based on outlet conditions). As a consequence of the cracking reactions, a hydrogen-deficient material called coke is deposited on the catalyst, reducing catalyst activity.

After exiting the riser, catalyst entrained by the vapors is separated in the cyclone separators. Most FCC units employ either single or two-stage cyclones to separate the remaining catalyst particles from the cracked vapors. The cyclones collect and return the catalyst to the stripper through the dip-legs and flapper/trickle valves. The product vapors exit the cyclones and flow to

the main fractionator for recovery. It is important to separate catalyst and vapors as soon as they enter the reactor. Otherwise, the extended contact time of the vapors with the catalyst in the reactor housing will allow for non-selective catalytic re-cracking of some of the desirable products. The extended residence time also promotes thermal cracking of the desirable products.

Stripping section:

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 with the catalyst also fall into the stripper. Stripping steam, at a rate of 2 to 5 lbs per 1,000 lbs (2 kg to 5 kg per 1,000 kg) is primarily used to remove the entrained hydrocarbons between catalyst particles. Stripping steam does not address hydrocarbon desorption and hydrocarbons filling the catalyst pore. However, reactions continue to occur in 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. A two stage stripper design (Figure 2) is used in commercial work. An efficient stripper design generates intimate contact between the catalyst and steam. Reactor strippers are commonly designed for a steam superficial velocity of 0.75 ft/sec (0.23 m/sec) and a catalyst flux rate of 500 to 700 lbs per minute per square foot (2.4 kg to 3.4 kg per minute per square meter).

At too high a flux, 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/liquid have a higher hydrogen-to-carbon ratio than the coke on the catalyst.

The drawbacks of allowing these hydrogen rich hydrocarbons to enter the regenerator are as follows:

Loss of liquid product: Instead of the hydrocarbons burning in the regenerator, they could be recovered as liquid products.

Loss of throughput: The combustion of hydrogen to water produces 3.7 times more heat than the combustion of carbon to carbon dioxide. The increase in the regenerator temperature caused by excess hydrocarbons could exceed the temperature limit of the regenerator internals and force the unit to a reduced feed rate mode of operation.

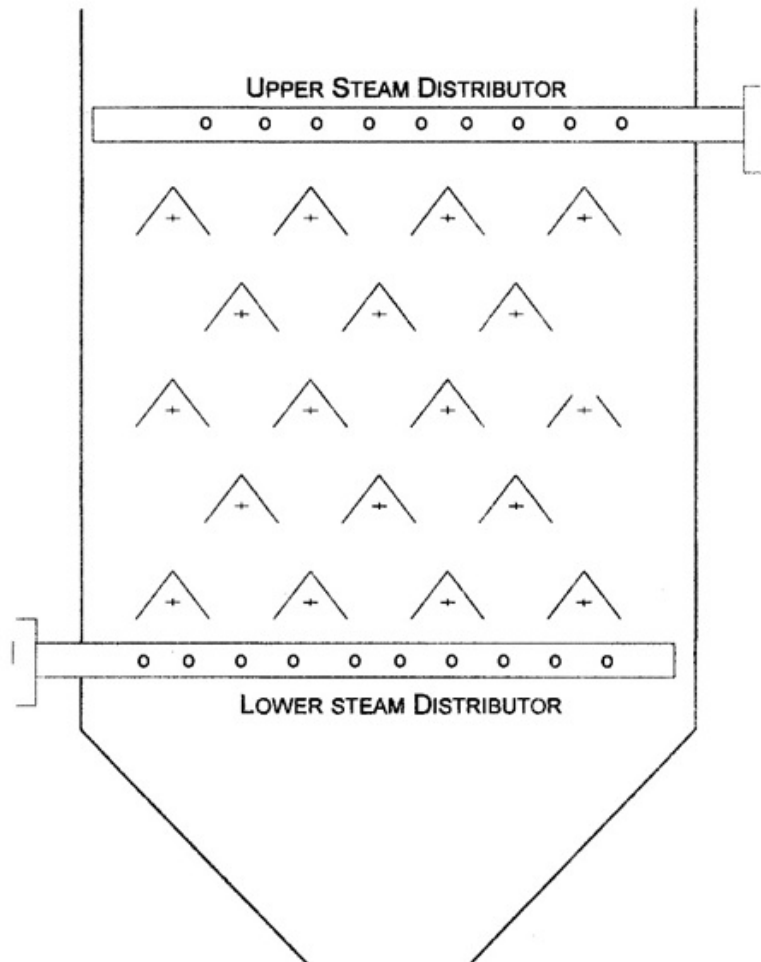


Figure 2: Two stage stripper

Loss of catalyst activity: The higher regenerator temperature combined with the formation of steam in the regenerator reduces catalyst activity by destroying the catalyst's crystalline structure. The flow of spent catalyst to the regenerator is typically controlled by a valve that slides back and forth. This slide valve is controlled by the catalyst level in the stripper. The catalyst height in the stripper provides the pressure head, which allows the catalyst to flow into the regenerator. The exposed surface of the slide valve is usually lined with refractory to withstand erosion. In a number of earlier FCC designs, lift air is used to transport the spent catalyst into the regenerator.

1.1.3 Regenerator–heat/catalyst recovery

The regenerator has two main functions: it restores catalyst activity and supplies heat to crack the feed. The spent catalyst entering the regenerator contains between 0.4 wt% and 2.5 wt% coke, depending on the quality of the feedstock. Components of coke are carbon, hydrogen, and trace amounts of sulfur and nitrogen.

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 the bottom of the vessel.

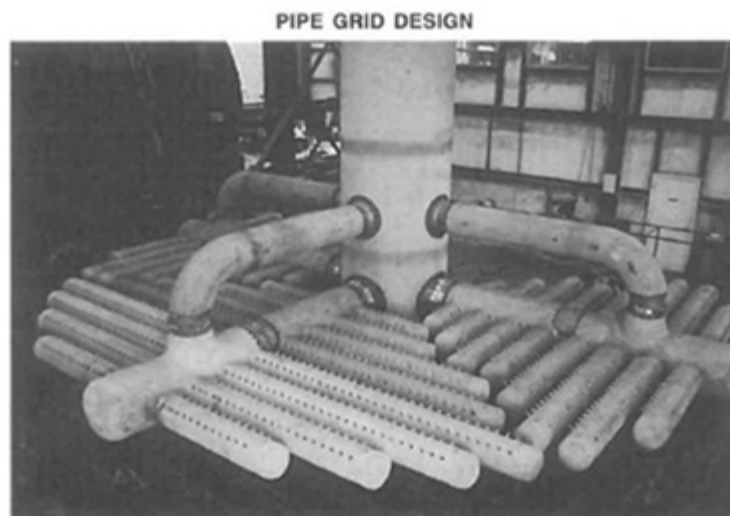


Figure 3: Air distributor

The design of an air distributor is important in achieving efficient and reliable catalyst regeneration (Figure 3). Air distributors are typically designed for a 1.0 psi to 2.0 psi (7 to 15 Kpa) pressure drop to ensure positive air flow through all nozzles. There are two regions in the regenerator: the dense phase and the dilute phase. At velocities common in the regenerator, 2 ft/sec to 4 ft/sec (0.6 to 1.2 m/sec), the bulk of catalyst particles are in the dense bed immediately above the air distributor. The dilute phase is the region above the dense phase up to the cyclone inlet, and has a substantially lower catalyst concentration.

Standpipe/slide valve:

During regeneration, the coke level on the catalyst is typically reduced to 0.05%. From the regenerator, the catalyst flows down a transfer line commonly referred to as a standpipe. The standpipe provides the necessary pressure to circulate the catalyst around the unit. Some standpipes extend into the regenerator, and the top section is often called a catalyst hopper. The hopper, internal to the regenerator, is usually an inverted cone design. In units with "long" catalyst standpipes, external withdrawal hoppers are often used to feed the standpipes. The hopper provides sufficient time for the regenerated catalyst to be "de-bubbled" before entering the standpipe. Standpipes are typically sized for a flux rate in the range of 100 to 300 lb/sec/ft² (500 to 1,500 kg/sec/m²) of circulating catalyst. In most cases, sufficient flue gas is carried down with the regenerated catalyst to keep it fluidized. However, longer standpipes may require external aeration to ensure that the catalyst remains fluidized. A gas medium, such as air, steam, nitrogen, or fuel gas, is injected along the length of the standpipe. The catalyst density in a well-designed standpipe is in the range of 35 to 45 lb/ft³ (560 to 720 kg/m³). The flow rate of the regenerated catalyst to the riser is commonly regulated by either a slide or plug valve. The operation of a slide valve is similar to that of a variable orifice. Slide valve operation is often controlled by the reactor temperature. Its main function is to supply enough catalyst to heat the feed and achieve the desired reactor temperature.

Catalyst separation:

As flue gas leaves the dense phase of the regenerator, it entrains catalyst particles. The amount of entrainment largely depends on the flue gas superficial velocity. The larger catalyst particles, 50microns-90microns diameter, fall back into the dense bed. The smaller particles, 0microns-50microns diameter, are suspended in the dilute phase and carried into the cyclones. Most FCC unit regenerators employ 4 to 16 parallel sets of primary and secondary cyclones. The cyclones are designed to recover catalyst particles greater than 20 microns diameter. The recovered catalyst particles are returned to the regenerator via the diplegs. The distance above the catalyst bed at which the flue gas velocity has stabilized is referred to as the transport disengaging height (TDH). At this height, the catalyst concentration in the flue gas stays constant; none will fall back into the bed. The centerline of the first-stage cyclone inlets should be at TDH or higher. Otherwise, excessive catalyst entrainment will cause extreme catalyst losses.

Flue gas heat recovery schemes:

The flue gas exits the cyclones to a plenum chamber in the top of the regenerator. The hot flue gas holds an appreciable amount of energy. Various heat recovery schemes are used to recover this energy. In some units, the flue gas is sent to a CO boiler where both the sensible and combustible heat is used to generate high-pressure steam. In other units, the flue gas is exchanged with boiler feed water to produce steam via the use of a shell/tube or box heat exchanger. In most units, about two-thirds of the flue gas pressure is let down via an orifice chamber or across an orifice chamber. The orifice chamber is vessel containing a series of perforated plates designed to maintain a given backpressure upstream of the regenerator pressure control valve. In some larger units, a turbo expander is used to recover this pressure energy. To protect the expander blades from being eroded by catalyst, flue gas is first sent to a third-stage separator to remove the fines. The third-stage separator, which is external to the regenerator, contains a large number of swirl tubes designed to separate 70% to 95% of the incoming particles from the flue gas.

From the expander, the flue gas goes through a steam generator to recover thermal energy. Depending on local environmental regulations, an electrostatic precipitator (ESP) or a wet gas scrubber may be placed downstream of the waste heat generator prior to release of the flue gas to the atmosphere. Some units use an ESP to remove catalyst fines in the range of 5microns-20mocrons from the flue gas. Some units employ a wet gas scrubber to remove both catalyst fines and sulfur compounds from the flue gas stream.

Catalyst handling facilities:

Even with proper operation of the reactor and regenerator cyclones, catalyst particles smaller than 20 microns still escape from both of these vessels. The catalyst fines from the reactor collect in the fractionator bottoms slurry product storage tank. The recoverable catalyst fines exiting the regenerator are removed by the electrostatic precipitator or lost to the environment. Catalyst losses are related to:

- The design of the cyclones
- Hydrocarbon vapor and flue gas velocities
- The catalyst's physical properties
- High jet velocity

- Catalyst attrition due to the collision of catalyst particles with the vessel internals and other catalyst particles

The activity of catalyst degrades with time. The loss of activity is primarily due to impurities in the FCC feed, such as nickel, vanadium, and sodium, and to thermal and hydrothermal deactivation mechanisms. To maintain the desired activity, fresh catalyst is continually added to the unit. Fresh catalyst is stored in a fresh catalyst hopper and, in most units, is added automatically to the regenerator via a catalyst loader. The circulating catalyst in the FCC unit is called equilibrium catalyst, or simply E-cat. Periodically, quantities of equilibrium catalyst are withdrawn and stored in the E-cat hopper for future disposal. A refinery that processes residue feedstock can use good-quality E-cat from a refinery that processes light sweet feed. Residue feedstock contains large quantities of impurities, such as metals and requires high rates of fresh catalyst. The use of a good-quality E-cat in conjunction with fresh catalyst can be cost-effective in maintaining low catalyst costs.

The present work incorporates a four lump kinetic model, two-phase flow with cluster based approach (considering pressure drop inside the riser). The effect of cracking on phase velocities, and catalyst deactivation model based on concentration of coke on catalyst is also considered. The feed oil vaporization is assumed to be instantaneous and heat and mass transfer resistances are ignored. For the solution of the model, the riser is divided into a number of small volume elements along the height. Material and energy balance equations are solved in each volume element. Fligner et al. (1994) proposed a cluster model approach to explain experimentally observed high slip factors. The authors used a cluster size of 6 mm. In the present work, simulations are done to see the effect of cluster size on the cluster velocity and product yields.

Chapter 2

Literature review

In this chapter a brief review of the work done on the riser modeling is presented. A more detailed review of the FCC riser modeling is given by Gupta et al. (2005, 2010). A detailed review on riser hydrodynamics is given in Berruti et al. (1995).

2.1 Riser modeling

Modeling of riser reactor is very complex due to complex hydrodynamics, unknown multiple reactions coupled with mass transfer and heat transfer resistances. Moreover, the conditions keep changing all along the riser height due to cracking which causes molar expansion in the gas phase and influences the axial and radial catalyst density in the riser. In the literature, numerous models of FCC riser are available with varying degrees of simplifications and assumptions.

2.1.1 Hydrodynamics

When vaporization of feed occurs, only solid phase (catalyst & coke) and vapor phase (steam, hydrocarbon feed and product vapor) are left. The simplest hydrodynamic models assume plug flow for both the phases. However, there is considerable back mixing in the solid phase because of slip between the solid and vapor phase which makes the prediction of solid velocity profile difficult.

CFB (Circulating Fluidized Bed) risers, employs different mathematical formulations to predict the relationship between solid concentration, operating conditions, and riser geometry. Harris and Davidson (1994) proposed three broad categories of these models: (i) the models that predict the axial variation of the solid suspension density, but not the radial variation; (ii) the models that predict the radial variation and the high average slip velocities by assuming two or more regions, such as core-annulus or clustering annulus flow models; and (iii) the models which are based on the numerical modeling of the conservation equations for mass, momentum, and energy for gas and solid phases.

Particular kind of model selection depends on its intended application. Models of 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). Type (iii) models are suitable to investigate the local flow structure and the impact of geometry in CFB risers.

Pugsley and Berruti (1995) modified the model of Wirth (1991) by considering the solids flow in core and annulus regions and calculated the core-to-annulus solids interchange coefficient. In another work (Pugsley and Berruti, 1996) they proposed a type (ii) predictive model based on fundamental principles and empirical relations. Theologos and Markatos (1993) proposed a three dimensional mathematical model considering two phase flow, heat transfer, and three lump reaction scheme in the riser reactor. The authors developed the full set of partial differential equations that describes the conservation of mass, momentum, energy and chemical species for both phases, coupled with empirical correlations concerning inter-phase friction, inter-phase heat transfer, and fluid to wall frictional forces. The model can predict pressure drop, catalyst holdup, inter-phase slip velocity, temperature distribution (in both phases) and yield distribution all over the riser. Theologos et al. (1997) coupled the model of Theologos and Markatos (1993) with a ten lump reaction scheme to predict the yield pattern of the FCC riser reactor. Theologos et al. (1999) accounted for feed atomization effect on riser performance in their model. Gao et al. (1999) developed a model that predicted three-dimensional, two-phase flow inside the riser-type reactor.

Gupta et al. (2007) predicted the phase velocities and increase in molar flux of gas all along the riser height. Malay et al. (1999) and Han and Chung (2001b), in their FCC riser simulations, have also predicted similar phase velocity profiles. Also, density, viscosity, and void fraction change due to modifications in the operating conditions (temperature and pressure) and because of mole generation (Leon-Becerril et al. 2004).

A two phase 2-D flow model was presented using transient Eulerian approach with a simple three lumps kinetic scheme (Benyahia et al. 2003). Zimmermann and Taghipour (2005) simulated the hydrodynamics and reaction kinetics of gas-solid fluidized beds containing

fluid catalytic cracking (FCC) particles. The authors included the kinetic term in an additional transport equation for modeling the reaction kinetics. Nayak et al. (2005) used the Eulerian–Lagrangian approach to simulate simultaneous evaporation and cracking reactions occurring in FCC riser reactors. Eulerian–Lagrangian approach was used for the simulation of gas-solid flow in FCC process (Wu et al. 2010). Novia et al. (2007) developed a model to simulate the 3-D hydrodynamics and reaction kinetics (3-lump) in FCC riser reactor. Baurdez et al. (2009) proposed a method for steady-state/transient, two- phase gas–solid simulation of a FCC riser reactor. Authors used a simple four lump kinetic model to demonstrate the feasibility of the method. Kumar and Reddy (2011) carried out CFD simulations and demonstrated that most of the reaction occurs in the first 10 m height of FCC riser.

2.1.2 Cracking kinetics

For modeling of cracking kinetics, Weekman and Nace (1970) divided the FCC feed stock and products into three lumps: feedstock lump, gasoline lump, and dry gas and coke lump. The kinetic parameters of the model were evaluated using the experimental data. Lee et al. (1989) proposed a four lump kinetic model by separating the coke from the three lump model of Weekman and Nace (1970). The model is still popular because of its simplicity and ease of formulation and solution of kinetic and material and energy equations. This simple lumping approach for kinetic modeling was further extended by various researchers by increasing the number of lumps in their models. Following are the other kinetic models proposed by various workers: five lump models (Larocca et al., 1990; Ancheyta-Juarez et al., 1999), six lump model (Coxson and Bischoff, 1987; Takatsuka et al., 1987), ten lump model (Jacob et al., 1976), eleven lump model (Mao et al., 1985), twelve lump model (Oliveira et al., 1987), thirteen lump model (Sa et al., 1995), and nineteen lump model (Pitault et al., 1994).

Jacob et al. (1976) included the chemical nature of the feed in their ten lump kinetic model. This model is used by Arbel et al. (1995), Ellis et al. (1998), and Nayak et al. (2005) for their FCC modeling studies.

Gupta et al. (2007) proposed a new kinetic scheme 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) are considered in this scheme resulting in more than 10,000 reaction possibilities. The model can be easily used to incorporate other aspects of the riser modeling. This kinetic model is used by Gupta and Kumar (2008) and Ruqiang et al. (2008) for their works on FCC modeling.

2.1.3 Heat transfer and mass transfer

When complete vaporization of feed droplets occurs, a vapor phase (hydrocarbons and steam) and a solid phase (catalyst particles) exist in the riser. There is considerable temperature difference in these phases near the bottom of the riser. 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.

External mass transfer resistances in the riser are neglected in most of the works on FCC riser modeling (Corella and Frances, 1991a; Martin et al., 1992; Ali et al., 1997; Derouin 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). Intra-pellet mass transfer has the effect of decreasing the reactant concentration within the pellet. Consequently, the average rate will be less than what it would be in the absence of internal concentration gradient (Smith, 1981). Pruski et al. (1996) determined adsorption coefficients for four lumps, while cracking gas oil. Bidabehere and Sedran (2001) developed a model to study the effects of diffusion, adsorption, and reaction at high temperature inside the particles of commercial FCC catalysts and experimentally studied the relative importance of these phenomena. Dupian

et al. (2006) have discussed the external and internal mass transfer correlations used for modeling the FCC riser.

2.1.4 Catalyst deactivation

Deactivation of FCC catalyst occurs due to the deposition of coke on the catalyst surface during cracking reactions. Most of the popular theories on deactivation are based on the time-on-stream concept. Various models for time dependent catalyst decay have been proposed for different lengths of contact time (Weekman, 1968, Nace et al., 1971; Paraskos et al., 1976; Shah et al., 1977). Froment and Bischoff (1990) proposed a mechanistic based model considering catalyst decay rate as a function of the fraction of active sites and the concentration of the reactants. Corella and Menendez (1986) developed a model in which the catalyst surface was assumed to be non-homogeneous with acidic sites of varying strength. Corella and Monzon (1988) developed a model for deactivation and coking kinetic relations between activity, concentration of coke and time on stream for four different mechanisms of coke formation and growth. Corella (2004) developed a selective deactivation kinetic model for the commercial FCC catalysts and feed-stocks.

Different empirical equations have been used by various researchers to fit their experimental data. However, there are two functions that fit the experimental data quite well: power function and exponential function. The exponential function is more widely used. Larocca et al. (1990) reported that the catalyst deactivation can be represented by both an exponential decay function and a power decay function with an average exponent of 0.1 to 0.2. Kraemer et al. (1991) used the data from two different experimental reactors and showed that exponential decay function or power law function could equally represent the data; however, the power law assumes the unrealistic limits of infinite catalyst activity at zero time-on-stream and requires two parameters to describe deactivation. They further concluded that the simple first order decay function is an effective equation for describing the catalyst activity decay for short reaction times (less than 20 seconds).

The main features of some of the riser models available in literature are given in Table 1.

Table 1: Main features of some FCC riser models

	Paraskos et al. 1976	Corella and Frances 1991	Theologous et al. , 1993	Gupta et al., 2001	Gupta et al., 2007	Baudrez et al., 2009
Vaporization	Instantaneous	Instantaneous	Instantaneous	Considered	Instantaneous	Instantaneous
Temperature variation	Isothermal	Adiabatic	Adiabatic	Adiabatic	Adiabatic	Adiabatic
Molar expansion	Not considered	Considered	Not considered	Considered	Considered	Considered
Axial catalyst holdup	Slip factor 1	Slip factor varied from 1.15 to 1.05 along the riser height	CFD model	Calculated using momentum balance on clusters ignoring pressure drop in the riser	Calculated using momentum balance on clusters considering pressure drop in the riser	CFD model
Mass transfer resistance	Not considered	Not considered	Not considered	Considered	Not considered	Considered
Kinetic model	Three lump	Five lump	Three lump	Four lump	Fifty lump (Pseudo component based approach)	Four lump
Deactivation	Non-selective, based on the coke concentration on catalyst	Non-selective, based on the time-on-stream of catalyst	Non-selective, based on the time-on-stream of catalyst	Non-selective, based on the coke concentration on catalyst	Non-selective, based on the coke concentration on catalyst	Non-selective, based on the coke concentration on catalyst

2.2 Concluding remarks

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. Four lump kinetic model is used by various authors in their work (Lee et al., 1989; Gianetto et al., 1994; Pitault et al., 1995; Blasetti and de lasa, 1997; Oliveira and Biscaia 1989; Anchetya et al. 1997; Berry et al., 2004; Gupta and Subba Rao 2001, 2003; Nayak et al., 2005, Baurdez et al 2009). In the literature two phase or three phase flow hydrodynamics is used by various authors, heat and mass transfer resistances are ignored in most studies, and exponential catalyst deactivation model is used in most works.

In this work, a four lump kinetic model, two phase hydrodynamic model, and exponential catalyst deactivation model is used to simulate the FCC riser.

FCC Riser Model

In this chapter the mathematical model of the FCC riser used in this work is discussed. The model incorporates a four lump kinetic model, two-phase flow with cluster based approach (including pressure drop inside the riser), effect of cracking on phase velocities, and catalyst deactivation model based on concentration of coke on catalyst.

3.1 Riser Model

For the solution of the model, the riser is divided into a number of small volume elements along the height. Volume elements are denoted with the symbol ' i ' starting from bottom of the riser (feed inlet). Two phases (gas and solid) are considered in each volume element. The following assumptions are made in this model:

- 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.
- Catalyst particles are assumed to move as clusters to account for the observed high slip velocities.
- Riser is adiabatic. The temperature inside the riser falls due to endothermicity of cracking reactions.
- The gas phase behaves ideally.
- Heat and mass transfer resistances are assumed as negligible.
- Both phases are in plug flow condition hence back mixing is neglected.

3.1.1 Model equations

Material balance:

The riser reactor of FFCU is divided into i number of compartments along its height . Each compartment is assumed to have two phase flow, gaseous and solid phase flow. At the inlet of riser liquid feed is instantaneously evaporated. Moreover inlet riser conditions are known to us (Mass of feed, temperature of feed, components present etc). Mass and moles of each element

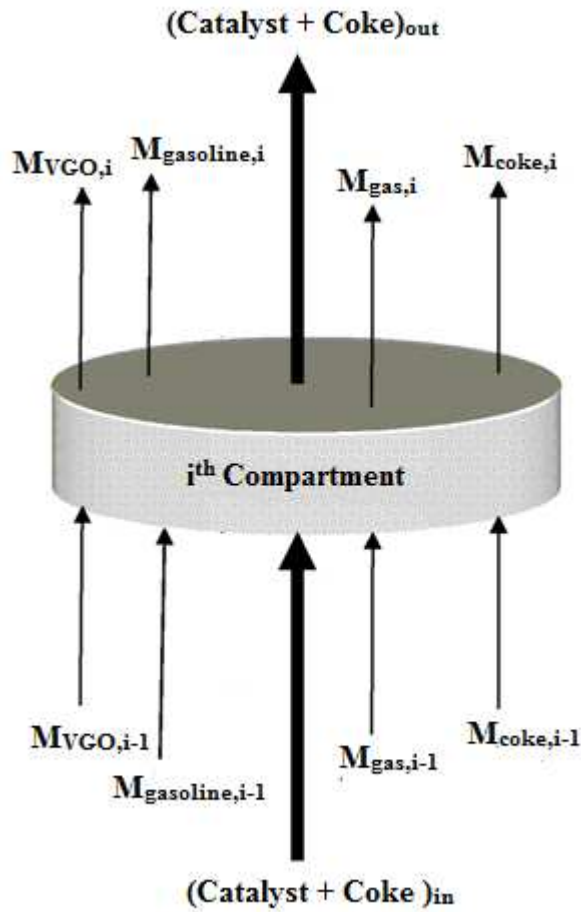


Figure 4: Schematic of a volume element in the riser

formed or consumed in i^{th} compartment is calculated from the cracking reactions occurring inside that particular compartment (Figure 4). Average molecular weight, velocity of gas, cluster velocity, pressure and vapor density which changes along the height of riser are calculated in that particular compartment. Generally, outlet conditions for $(i-1)$ compartment are inlet conditions for next compartment i.e. i^{th}

Vacuum gas oil cracks in presence of catalyst to give gasoline , gas and coke. gasoline further cracks to give gas and coke. Coke formed is deposited on the surface of catalyst, which decreases the activity of the catalyst. Coke is later burned off from the surface of catalyst in regenerator to achieve its activity.

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

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

$$M_{j,(i-1)} - M_{j,i} = r_{j,i}MW_j \quad \text{for } j = 1 \text{ to } 3 \quad (1)$$

Mass balance over solid phase in i^{th} compartment:

$$\begin{aligned} \text{Rate of mass out from } i^{\text{th}} \text{ compartment} - \text{rate of mass in from } (i-1)^{\text{th}} \text{ compartment} \\ = \text{coke formed in } i^{\text{th}} \text{ compartment} \end{aligned}$$

$$(F_{rgc} + M_{4,(i-1)}) - (F_{rgc} + M_{4,i}) = r_{j,i}MW_4 \quad (2)$$

Table 2: Molecular weight of various lumps (Gupta and Subba Rao, 2001):

j	1	2	3	4
component	VGO	Gasoline	Gas	Coke
Mol. Wt.	382	120	45	12

Riser hydrodynamics:

As instantaneous vaporization of the gas oil is assumed a two phase riser hydrodynamic model is used. Riser hydrodynamics is modeled on the lines of the model used by Gupta et al. (2007). The catalyst particles are assumed to move as clusters.

Initial cluster volume fraction is assume to be 0.2, and cluster voidage is assumed to be 0.5 (Gupta and Subba Rao, 2001).

Value of cluster volume holdup for each compartment is calculated as follows :

$$\delta_{ci} = \frac{(F_{rgc} + M_{coke i})}{(\rho_c * A_{ris} * v_{ci})} \quad (3)$$

Gas volume fraction is calculated by following expression:

$$\delta_{gi} = 1 - \delta_{ci} \quad (4)$$

Solid phase momentum balance proposed by Tusso and Gidaspow, (1990) is applied assuming the change in the mass of solids along the riser height as negligible :

$$\rho_c \delta_c v_c \frac{dv_c}{dz} = C_f (v_g - v_c) + \frac{2f_s \delta_c \rho_c v_c^2}{D} - \epsilon_c \rho_c g \quad (5)$$

Frictional forces per unit volume is calculated by following expression (Markatos and Shinghal, 1982):

$$F = 0.5C_D A_p \rho_g |v_g - v_c| (v_g - v_c) = C_f (v_g - v_c) \quad (6)$$

Drag coefficient is calculated on the basis of Reynolds number:

$$C_D = \frac{24}{Re} (1 + 0.15Re^{0.687}) \text{ for } Re < 1000, \quad (7)$$

$$C_D = 0.44 \text{ for } Re \geq 1000 \quad (\text{Arastoopour and Gidaspow, 1979}) \quad (8)$$

Reynolds number is calculated using following expression:

$$Re = \frac{\rho_g \delta_g |v_g - v_c| d_c}{\mu_g} \quad (9)$$

Pressure drop along the riser height is estimated using on the lines of Pugsley and Berruti (1996).

Authors have proposed the following four main components for pressure drop along the height of riser reactor.

$$\left(\frac{dP}{dz}\right)_{Total} = \left(\frac{dP}{dz}\right)_s + \left(\frac{dP}{dz}\right)_{acc} + \left(\frac{dP}{dz}\right)_{fs} + \left(\frac{dP}{dz}\right)_{fg} \quad (10)$$

Where pressure drop due to hydrostatic head of solids is represented as:

$$\left(\frac{dP}{dz}\right)_s = \rho_c g \delta_c \quad (11)$$

Pressure drop due to solids acceleration is given as:

$$\left(\frac{dP}{dz}\right)_{acc} = \frac{\rho_c \delta_c \Delta v_c^2}{2\Delta z} \quad (12)$$

Pressure drop due to solid friction, defined as frictional force per unit volume between solids and wall of the riser reactor:

$$\left(\frac{dP}{dz}\right)_{fs} = \frac{2f_p \rho_c \delta_c v_c^2}{D} \quad (13)$$

Pressure drop due to gas friction, defined as frictional force per unit volume between gas and solids:

$$\left(\frac{dP}{dz}\right)_{fg} = \frac{f_g \rho_g v_g^2}{D} \quad (14)$$

Gas friction factor is calculated from Blasius friction factor expressed as

$$f_g = 0.316Re^{-1/4} \quad (15)$$

Solids friction factor is calculated from Konno's expression

$$f_p = 0.0025v_c^{-1} \quad (16)$$

Pressure in the next volume element is calculated as

$$P_i = P_{i-1} - \left(\frac{dP}{dz} \right)_{Total} \Delta z \quad (17)$$

Gas phase density is calculated using ideal gas law

$$\rho_{gi} = \frac{(P_i * MW)}{(R * T_i)} \quad (18)$$

Velocity of solid phase can be calculated using the following expression

$$v_{ci} = \frac{F_{rgc}}{(A_{ris} * \rho_c * \delta_{ci})} \quad (19)$$

and gas velocity is calculated by

$$v_{gi} = \frac{M_{gasi}}{(A_{ris} * \rho_{gi} * \delta_{gi})} \quad (20)$$

Superficial gas velocity is

$$v_i = \frac{M_{gasi}}{(\rho_{gi} * A_{ris})} \quad (21)$$

Reaction kinetics:

Four lump kinetic model is used in most of the FCC riser models due to its simplicity and ease of integrating it with material and energy balance equations. Four lump kinetic model is used by various researchers in their work (Lee et al., 1989; Gianetto et al., 1994; Pitault et al., 1995; Blasetti and de lasa, 1997; Berry et al., 2004; Gupta and Subba Rao 2001, 2003; Nayak et al., 2005; Baurdez et al., 2010). A four lump reaction kinetics model (Figure 5) is used in the present work also.

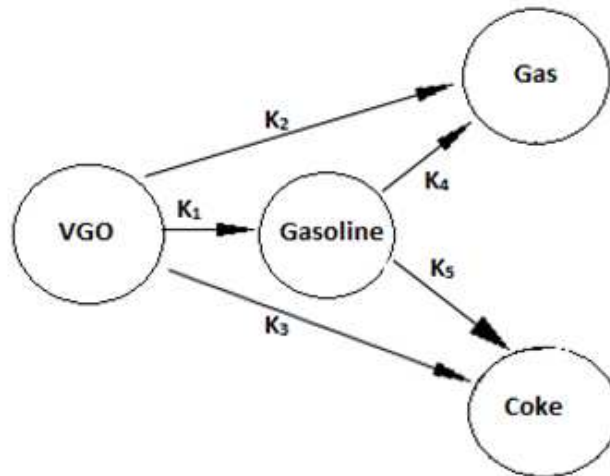


Figure 5: Schematic for four lump kinetic model.

The rate of formation of the lumps (kmol/s) in the i^{th} compartment are expressed as:

For VGO

$$r_{1,i} = -\phi_i(1 - \delta_g)\rho_c(K_1 + K_2 + K_3)C_{1,i-1}^2(A_{ris}\Delta Z) \quad (22)$$

For gasoline

$$r_{2,i} = \phi_i(1 - \delta_g)\rho_c(a_1K_1C_{1,i}^2 - (K_4 + K_5)C_{2,i-1})(A_{ris}\Delta Z) \quad (23)$$

For gas

$$r_{3,i} = \phi_i(1 - \delta_g)\rho_c(a_2K_2C_{1,i}^2 + a_4K_4C_{2,i})(A_{ris}\Delta Z) \quad (24)$$

For coke

$$r_{4,i} = \phi_i(1 - \delta_g)\rho_c(a_3K_3C_{1,i}^2 + a_5K_5C_{2,i})(A_{ris}\Delta Z) \quad (25)$$

Initial concentrations of the lumps at the inlet of riser are calculated using the following expressions:

gasoil:

$$C_1 = \left(\frac{M_f}{(MW_1 * v * A_{ris})} \right) \quad (26)$$

gasoline:

$$C_2 = 0 \quad (27)$$

gas:

$$C_3 = 0 \quad (28)$$

coke:

$$C_4 = \left(\frac{(C_{coke} * F_{rgc})}{(MW_{coke} * v * A_{ris})} \right) \quad (29)$$

Kinetic constants are predicted from Arrhenius expression:

$$K = K_0 \exp(-E/RT) \quad (30)$$

Catalyst activity is calculated by the following expression (Pitault et al., 1995)

$$\phi_i = \frac{B+1}{B + \exp(A * C_{coke i})} \quad (31)$$

where, A= 4.29 and B= 10.4, and

$$C_{coke\ i} = 100 * \left(\frac{M_{coke\ i}}{F_{rgc}} \right) \quad (32)$$

Stoichiometric coefficient used in rate equations for various lumps are given in Table 3 .

Table 3: Stoichiometric coefficients

Reaction	Stoichiometric coefficient	a _i
VGO to gasoline	380/120	a ₁
VGO to gas	380/45	a ₂
VGO to coke	380/12	a ₃
Gasoline to gas	120/45	a ₄
Gasoline to coke	120/12	a ₅

Energy 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

$$F_{rgc} * Cp_{cat} * (T_{cat} - T_{in}) = M_{feed} * Cp_{fl} * (T_v - T_f) + \lambda_f * M_{feed} + M_{feed} * Cp_{fv} * (T_{in} - T_v) \quad (33)$$

In the riser the temperature of the catalyst and gas decreases due to the endothermic cracking reactions. The heat of reaction data is given in Table 4.

Heat lost by the catalyst and gas in a volume element = \sum Heat of cracking of component j * moles of component j cracked

$$\left(M_{gas} * Cp_{fv} + F_{rgc} * Cp_{cat} \right) * (T_{i-1} - T_i) = \sum_{j=1}^3 H_{rj} * r_j \quad (34)$$

using the above equation temperature for the next element is calculated as:

$$T_i = T_{i-1} - \frac{\left(\sum_{j=1}^3 H_{rj} * r_j \right)}{\left(\left(M_{gas\ i} * Cp_{fv} + F_{rgc} * Cp_{cat} + M_{coke} * Cp_{coke} \right) \right)} \quad (35)$$

Table 4: Heat of reaction data (Source: Dave and Saraf, 2003)

Reaction	H_r (kJ/kmol)
VGO to gasoline	45000
VGO to gas	159315
VGO to coke	159315
Gasoline to gas	42420
Gasoline to coke	42420

Chapter 4

Results and discussion

In this chapter the FCC riser is simulated and validated against industrial data. The simulations are done using MATLAB. Plant data given in Table 5 reported by Ali et al. (1997) is used for the validation. The parameters used for the simulations are given in Table 6.

Table 5: Plant data used for riser simulation given by Ali et al. (1997)

Parameter	Value
Feed flow rate	20 kg/s
Catalyst flow rate	144 kg/s
Riser diameter	0.8 m
Riser pressure	2.9 atm
Catalyst inlet temperature	960.0 K
Riser height	33 m

Table 6: Parameters used for riser simulations

Parameter	Value	Source
Specific heat of VGO (Liquid)	2.67 kJ/kg.K	Ali et al., 1997
Specific heat of VGO (vapor)	3.3 kJ/kg.K	Ali et al., 1997
Latent heat of vaporization	96 kJ/kg	Gupta and Subba Rao, 2001
Gas phase viscosity	1.3×10^{-5} kg/m.s	Gupta and Subba Rao, 2001
Catalyst Particle density	1200 kg/m ³	Gupta et al., 2008
Catalyst particle diameter	75 microns	Gupta and Subba Rao, 2001
Specific heat of catalyst	1.15 kJ/kg.K	Ali et al., 1997

The yields of gasoline, gas, coke, and VGO conversion are shown as a function of riser height in Figure 6. The simulation results are matching well with the plant data. The values of kinetic parameters were adjusted to match the model results with the plant data (Table 7). The riser temperature profile is shown in Figure 7. The initial instant drop in the temperature is due the assumption of instantaneous vaporization and bringing the hydrocarbons in thermal equilibrium with the catalyst. The exit temperature predicted by the simulation deviates about 6% from the plant data. This deviation may be attributed to the variation in the values of heats of cracking.

Table 7: Kinetic parameters used in the model

Reaction	Pre exponential factor ($m^6/kgcat.kmol.s$)	Activation energy (kJ/kmol) (Gupta and Subba Rao, 2001)
VGO to gasoline	946	68316
VGO to gas	11878	89303
VGO to coke	72	64638
Gasoline to gas	0.42043	52768
Gasoline to coke	0	115566

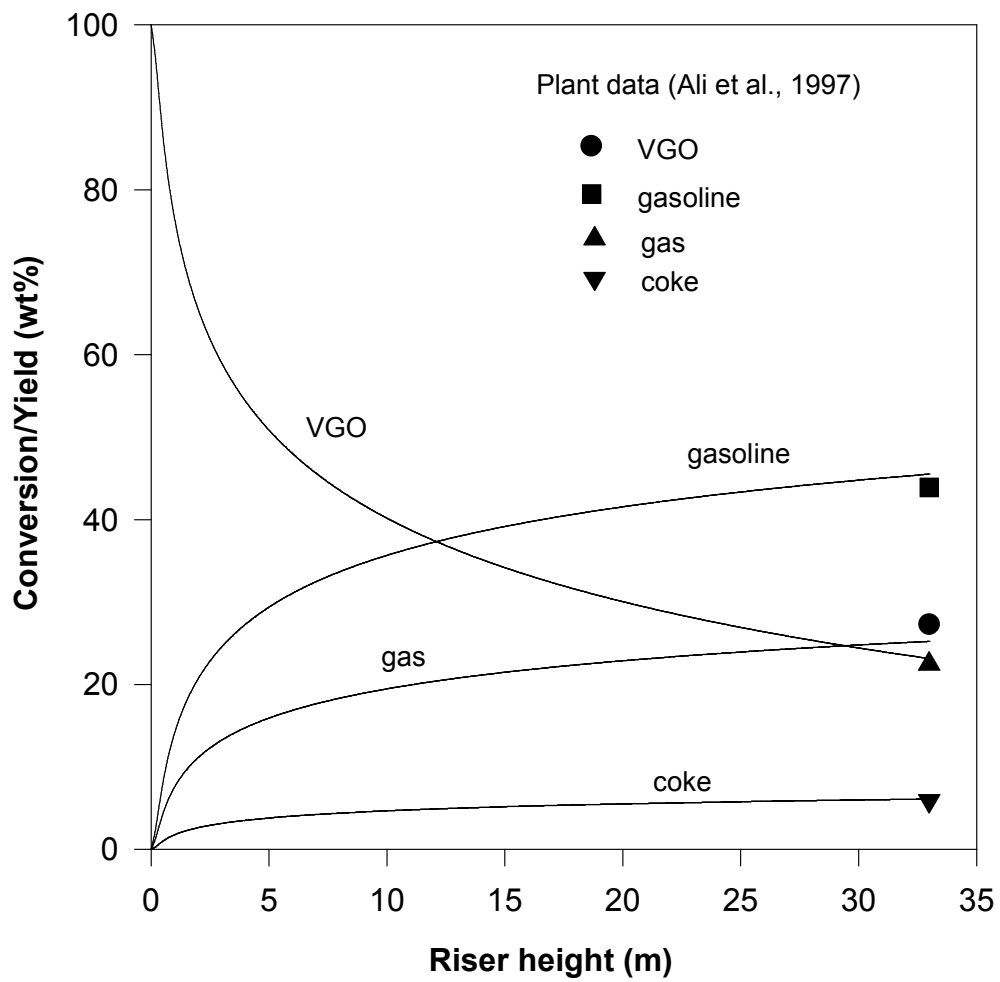


Figure 6: Conversion/ product yield along riser height

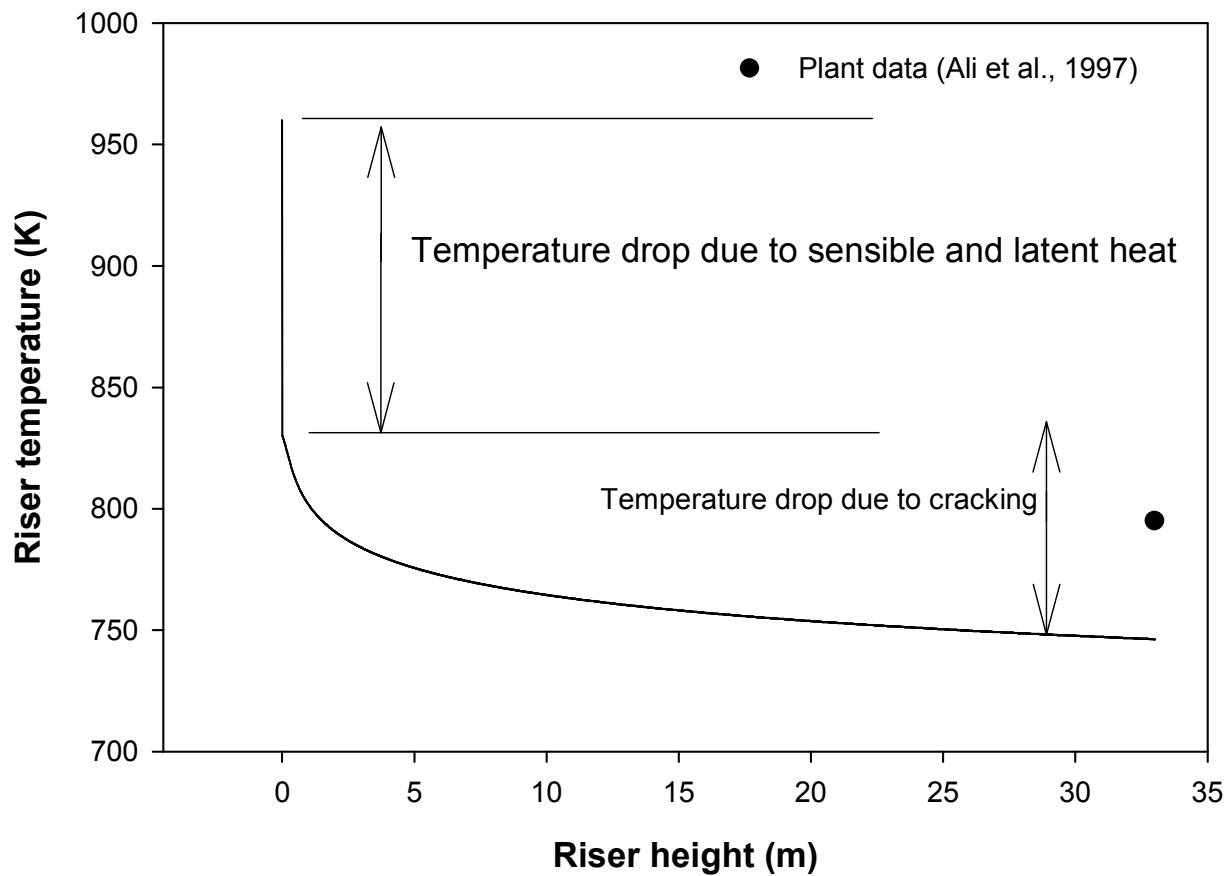


Figure 7: Temperature drop along riser height

Figure 8, 9 and 10 presents phase velocities, catalyst activity, and riser pressure respectively along the riser height. The profiles of phase velocities and catalyst activity match well with the literature predictions. The slip factor, defined as ratio of gas velocity to particulate velocity, is changing from about 1.4 at the inlet to about 2 at the outlet of the riser.

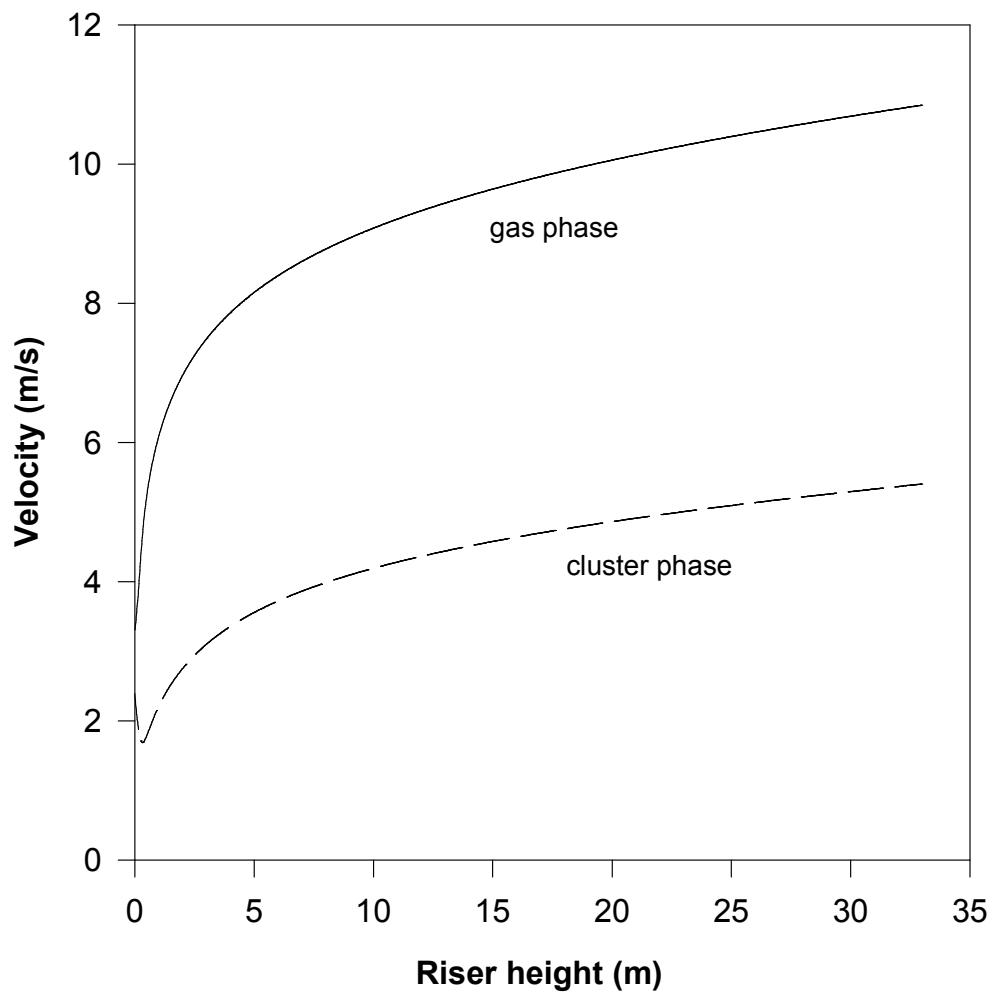


Figure 8: Phase velocities along riser height

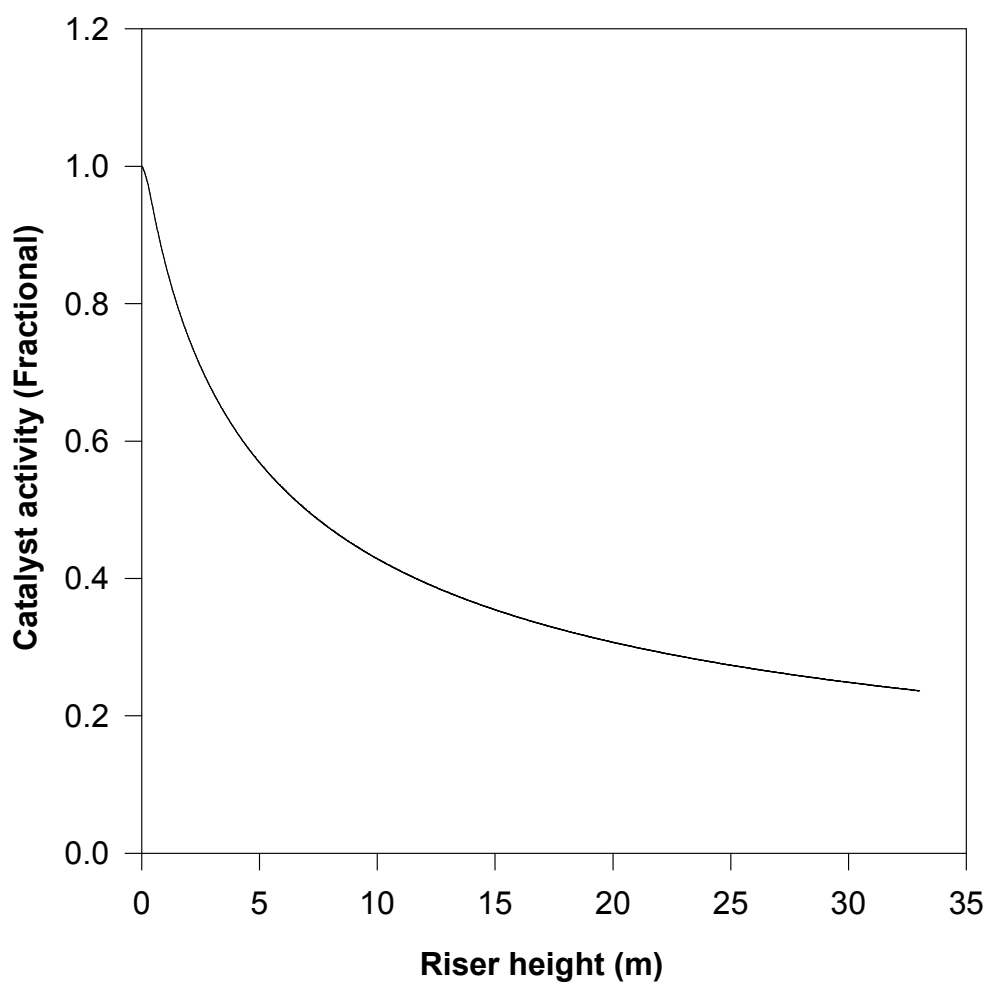


Figure 9: Catalyst activity along riser height

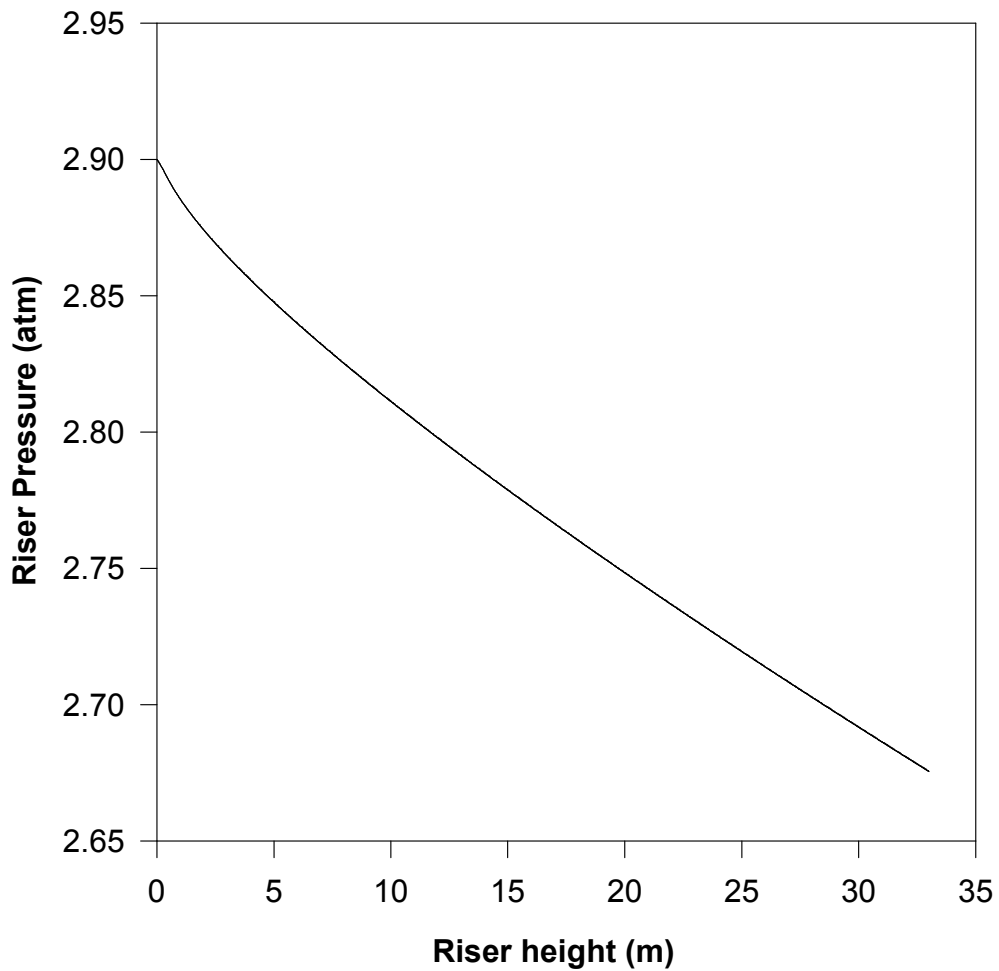


Figure 10: Pressure drop along the riser height

Fligner et al. (1994) proposed a cluster model approach to explain experimentally observed high slip factors. The model simulations are done for various cluster sizes to study the effect of cluster size on the model predictions. The results are shown in Figure 11. The simulations are done for cluster sizes of 3 mm, 6 mm, 9 mm, and 12 mm. The results of cluster velocity show that the large clusters move slowly and spend more time in the riser. The product yields predicted at the riser exit for different cluster sizes are shown in Table 8.

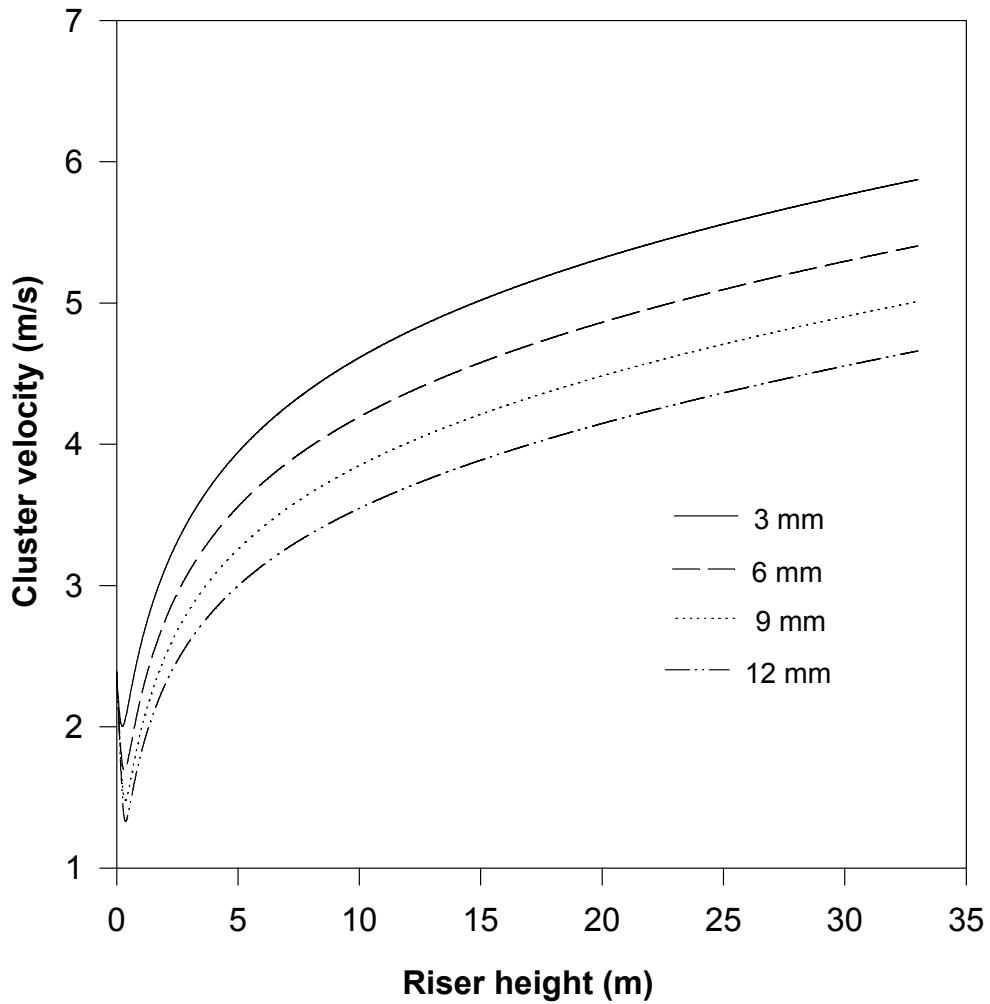


Figure 11: Effect of cluster size on cluster phase velocity

Table 8: Model predictions of product yields at riser exit for different cluster sizes

Product Yield (wt %)	Cluster diameter			
	3mm	6mm	9mm	12mm
gasoline	39.7	45.29	49.58	53.14
gas	21.61	25.23	28.20	30.69
coke	5.5	6.28	6.88	7.39

Conclusions and Future Recommendations

Conclusions

The FCC riser reactor is simulated using MATLAB. The model incorporates two phase hydrodynamics, and a four lump kinetic model with catalyst deactivation as exponential function. The simulation results are matching very closely with the plant data. The effect of variation in cluster size on cluster phase velocity and products yields is also presented.

Recommendations

While modeling of riser reactor range of kinetic parameters of the lumps seems to vary a lot in the literature. The causes for this variation is the lumped nature of the kinetic parameters and their dependency on the catalyst and feed used for generating these parameters. Work should be done on the evaluation of these kinetic parameters for various lumped schemes. CFD models can be used to capture the complex phenomena at the riser inlet where most of the conversion takes place.

Nomenclature

a	Stoichiometric coefficient
$A_p = 1.5 (\epsilon_c/d_c)$	Projected area per unit volume.
A_{ris}	Area of riser (m^2)
$C_{coke,i}$	Coke on regenerated catalyst (wt %)
C_D	interphase friction coefficient between two phases
$C_{p_{cat}}$	specific heat of catalyst (kJ/kg.K)
$C_{p_{coke}}$	specific heat of coke (kJ/kg.K)
$C_{p_{fl}}$	specific heat of liquid feed (kJ/kg.K)
$C_{p_{fv}}$	specific heat of vapor feed (kJ/kg.K)
d_c	Cluster diameter (m)
dz	Height increment (m)
E	Activation energy (kJ/kmol)
F_{rgc}	Catalyst circulation rate (kg/s)
g	Acceleration due to gravity (m/s)
H_r	Heat of reaction (kJ/kmol)
K_j	Kinetic rate constant ($m^6/kg_{cat}.kmol.s$)
K_o	Pre exponential rate constants ($m^6/kg_{cat}.kmol.s$)
$M_{j,i}$	Mass of j^{th} element in i^{th} compartment (kg/s)
M_{coke}	Mass of coke formed (kg/s)
M_f	Mass of feed (kg/s)
MW_j	Molecular weight of j^{th} element (kg/kmol)
P_i	Pressure in i^{th} compartment (atm)
$r_{j,i}$	rate of j^{th} element in i^{th} compartment (kmol/s)
R	Universal gas constant (kJ/kmol.K)
Re	Reynolds number
T_{cat}	Temperature of regenerated catalyst (K)
T_i	Temperature in i^{th} compartment (K)
T_{in}	Temperature of reaction mixture at inlet (K)
v_c	Velocity of cluster (m/s)

v_g

Velocity of gas phase (m/s)

Greek symbols

λ_f

Latent heat of vaporization (kJ/kg)

$\delta_{c,i}$

Cluster volume holdup for i^{th} compartment

$\delta_{g,i}$

Gas volume holdup for i^{th} compartment

ρ_g

Density of gas (kg/m^3)

ρ_c

Density of cluster (kg/m^3)

Θ_i

Catalyst activity in i^{th} compartment

μ_g

viscosity of gas (kg/m.s)

References

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

Ancheyta-Juarez J., Lopez-Isunza F., Aguilar-Rodriguez E., "A strategy for kinetic parameter estimation in the fluid catalytic cracking process", *Applied Catalysis A: General*, 1999, 177, 227-235.

Ancheyta-Juarez Jorge, Felipe Lopez-Isunza, Enrique Aguilar-Rodrique and Juan C. Moreno-Mayorga", *A Strategy for kinetic parameter Estimation in the Fluid Catalytic Cracking Process"*, *Industrial and Engineering Chemistry Research*, 1997, 36, 5170-5174.

Arastoopour H., and Gidaspow D., "Vertical pneumatic conveying using four hydrodynamics Models", *Industrial and Engineering Chemistry Fundamentals* 1979, 18, 123-130.

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

Baudrez E., Heynderickx G. J., Marin G. B. "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*, 2009, 88, 290-303.

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

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

Berry T.A., McKeen T.R., Pugsley T.S., and Dalai A.K., "Two-dimensional reaction engineering model of the riser section of a fluid catalytic cracking unit", *Industrial and Engineering Chemistry Research*, 2004, 43 (18), 5571-5581.

Bidabehere C.M., and Sedran U., "Simultaneous diffusion, adsorption, and reaction in fluid catalytic cracking catalysts", *Industrial and Engineering Chemistry Research*, 2001, 40, 530-535.

Blasetti, A., de Lasa, H., "FCC riser unit operated in the Heat- Transfer Mode: Kinetic Modeling", *Industrial and Engineering Chemistry Research*, 1997, 36, 3223-3229.

Corella J. and Frances E., M. L. Occelli Ed., "Analysis of the riser reactor of a fluid cracking unit: Model based on kinetics of cracking and deactivation from laboratory tests", in *Fluid*

catalytic cracking-II: Concepts in catalyst design, ACSsymposium series, American Chemical Society, Washington 1991a, 452, 165–182,.

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

Corella J., and Menedez M., “The modelling of the kinetics of deactivation of monofunctional 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*, 1986, 41, 1817-1826.

Corella J., and Monzon, A., “Deactivation and coking kinetic relations between activity, concentration of coke and time-on-stream for different mechanisms of formation and growth of the coke”, *Ann. Quim.*, 1988, 84, 205-220.

Coxson P.G., and Bischoff K.B., “Lumping Strategy, 1. introduction techniques and application of cluster analysis”, *Industrial and Engineering Chemistry Research*, 1987, 26, 1239-1248.

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

Dave J. Dhaval, and Deoki N. Saraf, "Model suitable for rating and optimization of industrial FCC units", *Indian Chemical Engineer, Section A*, January-March 2003, Vol. 45, No. 1.

Derouin C., Nevicato D., Forissier M., Wild G., and Bernard J.R., “Hydrodynamics of riser units and their impact on FCC operation”, *Industrial and Engineering Chemistry Research*, 1997, 36, 4504-4515.

Ellis R.C., Li X., and Riggs J.B., “Modeling and optimization of a model IV fluidized catalytic cracking unit”, *AIChE Journal*, 1998, 44, 2068-2079.

Flinger M., Schipper P. H., Sapre A. V., Krambeck F. J., “Two phase cluster in riser reactors: impact of radial density distribution on yields”, *Chemical Engineering Science*, 1994, 49, 5813-5818.

Froment G.F., and Bischoff K.B., “Chemical reactor analysis and design”, *Wiley Series in Chemical Engineering*, 2nd edition, 1990, John Wiley, New York.

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

Gianetto Arturo, Hany I. Farag, Alberto P. Blasetti, and Hugo I.de Lasa, "Fluid catalytic cracking catalyst for reformulated gasoline's. Kinetic Modeling ", *Industrial and Engineering Chemistry Research*, 1994, 33, 3053-3062.

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

Gupta Ajay, and D. Subba Rao, "Effect of feed atomization on FCC performance: Simulation of entire unit", *Chemical Engineering Science*, 2003, 58, 4567-4579

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

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

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

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

Han I.S., and Chung, C.B., "Dynamic modeling and simulation of a fluidized catalytic cracking process. Part II: Property estimation and simulation", *Chemical Engineering Science* 2001(b), 56, 1973-1990.

Harris B. J., Davidson J. F. and Xue Y., A. A. Avidan Ed., "Axial and radial variation of flow in circulating fluidized bed risers". In *Circulating Fluidized Bed Technology IV*, American Institute of Chemical Engineers, New York, 1994, 103-110.

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

James. G. Speight (2006). *The Chemistry and Technology of Petroleum* (4th ed.). CRC Press.
Kraemer D., Larocca M., and de Lasa H.I., "Deactivation of cracking catalyst in short contact time reactors: alternative models", *The Canadian Journal of Chemical Engineering*, 1991, 69, 355-360.

Kumar V., and Reddy A.S.K., "Why FCC riser is taller than model predictions", *AIChE Journal*, 2011, 57 (onlinelibrary.wiley.com/doi/10.1002/aic.12499/pdf).

Larocca M., Ng S., and de Lasa H., "Catalytic cracking of heavy gas oils: modelling coke deactivation", *Industrial and Engineering Chemistry Research*, 1990, 29, 171-180.

Lee L., Chen Y., Huang T., and Pan W., "Four lump kinetic model for fluid catalytic cracking process", *The Canadian Journal of Chemical Engineering*, 1989, 67, 615-619.

Leon-Becerril E., Maya-Yescas R., and Salazar-Sotelo D. "Effect of modelling pressure gradient in the simulation of industrial FCC risers", 2004, 100, 181-186.

Malay P., Rohani S., and Milne B. J., "The modified dynamic model of a riser type fluid catalytic cracking unit", The Canadian Journal of Chemical Engineering, 1999, 77, 169-179.

Mao X., Weng H., Zhu Z., Wang, S., and Zhu K., "Investigation of the lumped kinetic model for catalytic cracking: III. Analyzing light oil feed and products and measurement of kinetic constants", Acta Pet. Sin. (Pet. Process Sect.), 1985, 1, 11.

Markatos, N.C., Shinghal, A.K., "Numerical analysis of one-dimensional, two phase flow in a vertical cylindrical passage. Advance Engineering Software" , 1982, 4, 99.

Martin M.P., Derouin P.T., Forissier M., Wild G. and Bernard J.R., "Catalytic cracking in riser reactors. Core-annulus and elbow effects", Chemical Engineering Science, 1992, 47, 2319-2324.

Nace D.M., Voltz S.E., and Weekman V.W. Jr., "Application of a kinetic model for catalytic cracking. Effects of charge stocks", Industrial and Engineering Chemistry Process Design and Development, 1971, 10, 530-537.

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

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

Oliveira L. Laura, and Evaristo C. Biscaia, Jr., "Catalytic Cracking Kinetic Models. Parameters Estimation and Model Evaluation", Industrial and Engineering Chemistry Research, 1989, Vol. 28, No. 3.

Oliveira, L.L., "Estimacao de Parametros e Avaliacao de Modelos de Craqueamento Catalitico", M.Sc. Thesis (in Portuguese), 1987, University Federal do Rio de Janeiro, Brazil.

Paraskos J.A., Shah Y.T., McKinney J.D., and Carr N.L., "A kinetic model for catalytic cracking in a transfer line reactor", Industrial and Engineering Chemistry Process Design and Development, 1976, 15, 165-169.

Pitault I., Nevicato D., Forissier M., and Bernard J.R., "Kinetic model on a molecular description for catalytic cracking of vacuum gas oil", Chemical Engineering Science, 1994, 49, 4249-4262.

Pitault, I., Forissier, M., Bernard, J.R., 1995. Determination de constantes cinetiques du craquage catalytique par la modelisation du test de microactivite (MAT). The Canadian Journal of Chemical Engineering 73, 498-503.

Pruski J., Pekediz A., and de Lasa H. I., "Catalytic cracking of hydrocarbons in a novel Riser Simulator: lump adsorption parameters under reaction conditions", *Chemical Engineering Science*, 1996, 51, 1799-1806.

Pugsley T. S., and Berruti F., "A core-annulus solids interchange model for circulating fluidized bed and FCC risers", in "Fluidization VIII" preprints, 1995, 449-455.

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

Pugsley T. S., Patience G. S., Berruti F., and Chaouki J., "Modeling the oxidation of n-butane to maleic anhydride in a circulating fluidized bed reactor", *Industrial Engineering Chemistry Research*, 1992, 31, 2652-2660.

Ranz W.E., Marshall W.R., "Evaporation from drops", *Chemical Engineering Progress*, 1952, 48, 141-146.

Reza Sadeghbeigi, "Fluid Catalytic Cracking Handbook (2nd ed.)", 2000, Gulf Publishing.

Ruqiang W., Chufu L., Xiaorong H., and Bingzhen C., "A novel close-loop strategy for integrating process operations of fluidized catalytic cracking unit with production planning optimization", *Chinese Journal of Chemical Engineering*, 2008, 16, 6, 909-915.

Sa, Y., Liang, X., Chen, X., and Liu, J., "Study of 13-lump kinetic model for residual catalytic cracking", *Selective papers in memorial of 30th anniversary of fluid catalytic cracking process*, Petrochemical Engineering Corporation, 1995, 145, Luoyang, China.

Shah Y.T., Huling G.T., Paraskos J.A., and Mckinney J.D., "A kinematic model for an adiabatic transfer line catalytic cracking reactor", *Industrial and Engineering Chemistry Process Design and Development*, 1977, 16, 89-94.

Smith J.M., "Chemical Engineering Kinetics", 1981, McGraw-Hill, New York.

Takatsuka T., Sato S., Morimoto Y., and Hashimoto H., "A reaction model for fluidized-bed catalytic cracking of residual oil", *Institute of Chemical Engineers*, 1987, 27(1), 107-116.

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

Theologos K.N., and Markatos N.C., "Advanced modeling of fluid catalytic cracking riser-type reactors", *AIChE Journal*, 1993, 39, 1007-1017.

Theologos K.N., Nikou I.D., Lygeros A.I., and Markatos N.C., "Simulation and design of fluid catalytic cracking riser-type reactors", *AIChE Journal*, 1997, 43, 486-493.

Tsuo, Y.P., Gidaspow, D., Computation of flow patterns in circulating fluidized beds. A.I.Ch.E. Journal, 1990, 36, 885–896.

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

Weekman V.W., Jr., and Nace D.M., “Kinetics of catalytic cracking selectivity in fixed, moving, and fluid bed reactors”, AIChE Journal, 1970, 16, 397-404.

Wirth K. E., “Fluid mechanics of circulating fluidized beds”, Chemical Engineering and Technology, 1991, 14, 29-38.

Wu C., Cheng Y., Ding Y., and Jin Y., “CFD–DEM simulation of gas–solid reacting flows in fluid catalytic cracking (FCC) process”, Chemical Engineering Science, 2010, 65, 542 – 549.

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