بسم □ الرَّحْمَنِ الرَّحِيمِ

Sudan University of Science & Technology

College of Petroleum Engineering & Technology

Petroleum Transportation & Refining Engineering Department

***Graduation Project about*:**

MODELING AND DESIGN OF FLUIDIZED CATALYTIC CRACKING RISER

نمذجة وتصميم مفاعل وحدة التكسير الحفزي

Submitted to College of Petroleum Engineering & Technology in Sudan University partial fulfillment for one of requirement to take the degree of B.Sc. in Petroleum Transportation & Refining Engineering Department.

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هذا المشروع مقدم إلى كلية هندسة وتكنولوجيا النفط –جامعة السودان للعلوم والتكنولوجيا كإنجاز جزئي لأحد المتطلبات الأساسية لنيل درجة البكالوريوس مرتبة الشرف في هندسة نقل وتكرير النفط.

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الإستهلال

قل تعالي:

" يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ
دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ "

سورة المجادلة الآية رقم 11.

Dedication

To our parents

we just want to thank you for all the sacrifices you have made, all the support you have given us, all the guidance you have given when we needed it most and molding into persons we have become today.

We love you with all our hearts and we are proud to be yours

our brothers and sisters

our friends

our teachers

In memory of AMAR DIRAR. You left fingerprints of grace on our lives, you shan't be forgotten.

Thank you all

ACKNOWLEDGMENTS

In the name of ALLAH, the Most Beneficent, the Most Merciful.

First of all, praise be to Allah almighty for his welfare, kindness and great mercy. We are pleased to seize this opportunity to express our gratitude to everyone who supported us throughout this project. We would like to express our acknowledgment to College of Petroleum Engineering for giving us an opportunity to do this research Work and providing all materials and facilities.

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Abstract

In the present research, Material and Energy balance, and modeling for the fluid catalytic cracking was developed to obtain conversion 92% by using Runge-kutta order implemented in MATLAB with suitable zeolite weight. And also, comparison between them in the yield of gasoline, light gases, and coke was made. The riser of the fluid catalytic cracking was considered as a plug flow reactor incorporating the four lumps model for kinetics of cracking reactions. The model which consisted of ordinary differential equations was solved in order to get the yield patterns. Also, partial design of FCC take into account.

التجريد

في هذا البحث المقدم، تم عمل موازنة مادة وطاقة ونمذجة لوحدة التكسير الحفزي لهدف الوصول الي تحويل 92% بإستخدام أمر رانج-كوتا المطبق في الماتلاب. وأيضا تم عمل مقارنة بينهم بالنسبة لمنتوج البنزين ،الغازات الخفيفة، والفحم. كما تم إعتبار المفاعل مثالي (plug flow reactor) وأن التفاعل يكون بين هذه المكونات فقط وهي التغذية (Feed) ، الغازات الخفيفة (Light Gases) ، البنزين (Gasoline) ،والفحم (Coke). يحتوي النموذج على معادلات تفاضلية من الدرجة الأولى تم حلها لإيجاد المنتوج. كما تم عمل تصميم جزئي لوحدة التكسير الحفزي.

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NOMENCLATURES

m_f	*oil feed*
s_{in}	*injection steam*
m_{cat} m_{scat}	*regenerated catalyst* *spent catalyst circulation rate*
s_{out}	*steam presented in cracked products*
p	*total number at vapor products*
m_{air}	*air for coke burning*
n_i	*flue gases*
Q_f	*heat of feed oil*
Q_s	*heat of steam in injected*
Q_{cat}	*heat of regenerated catalyst*
Q_p	*heat of vapor product*
$Q_{s,out}$	*heat of exit steam*
Q_{scat}	*heat of spent catalyst*
q_{coke}	*heat of coke combustion*
Q_{fg}	*heat of flue gas*
Y_1	*weight fraction of vacuum gas oil*
Y_2	*weight fraction of gasoline*
Y_3	*weight fraction of light gases*
Y_4	*weight fraction of coke*

E_j	*activation energy*
K_{oj}	*frequency factor*
T R	*reactor temperature*
d_p	*gas constant*
u_{mf}	*particle diameter*
u_t	*minimum fluidization velocity*
d_b	*terminal velocity*
u_b	*bubble diameter*
f_b f_c	*bubble rise velocity*
f_w	*fraction occupied by the bubble*
f_e	*fraction occupied by the cloud*
	fraction occupied by the wake
	fraction occupied by the emulsion

Greeks

μ	*feed viscosity*
ε_{mf}	*porosity at minimum fluidization*
τ	*space time*
ρ_p	*feed density*
φ	*deactivation*

Abbreviation

FCC	*Fluidized Catalytic Cracking*
VGO	*Vacuum Gas Oil*
RFCC	*Residue Fluidized Catalytic Cracking*
DCC	*Deep Catalytic Cracking*
HPLC	*High-Pressure Liquid Chromatography*
NIR	*Near-infrared spectroscopy*
ASTM	*American Society for Testing Materials*
PNA_s	*Poly-nuclear Aromatics*
HCO	*Heavy Cycle Oil*
LCO	*Light Cycle Oil*
KRC	*Khartoum Refinery Company*
LV	*Target conversion*
LPG	*Liquefied petroleum gas*
ODE	*Ordinary Deferential Equation*

Chapter 1

Introduction

1.1. Background

Fluid catalytic cracking (FCC) technology is a technology with more than 60 years of commercial operating experience. The process is used to convert higher-molecular-weight hydrocarbons to lighter, more valuable products through contact with a powdered catalyst at appropriate conditions. The primary purpose of the FCC process has been to produce gasoline, distillate, and C3/C4 olefins from low-value excess refinery gas oils and heavier refinery streams. FCC is often the heart of a modern refinery because of its adaptability to changing feedstocks and product demands and because of high margins that exist between the FCC feedstocks and converted FCC products. As oil refining, has evolved over the last 60 years, the FCC process has evolved with it, meeting the challenges of cracking heavier, more contaminated feedstocks, increasing operating flexibility, accommodating environmental legislation, and maximizing reliability. In the environmental protection field, FCC unit-play a significant role by producing the gasoline. Refineries use fluid catalytic cracking to correct the imbalance between the market demand for gasoline and the excess of heavy high boiling range products resulting from the distillation of crude oil.(Meyers, 2004)

The fluid catalytic cracking (FCC) unit consists of a reaction section and a fractionating section that operate together as an integrated processing unit. The reaction section includes two reactors, the riser reactor, where almost all the endothermic cracking reactions and coke deposition on the catalyst occur, and the regenerator reactor, where air is used to burn off the accumulated coke. The regeneration process provides, in addition to reactivating the catalyst powders, the heat required by the endothermic cracking reactions, (Figure 1.1).

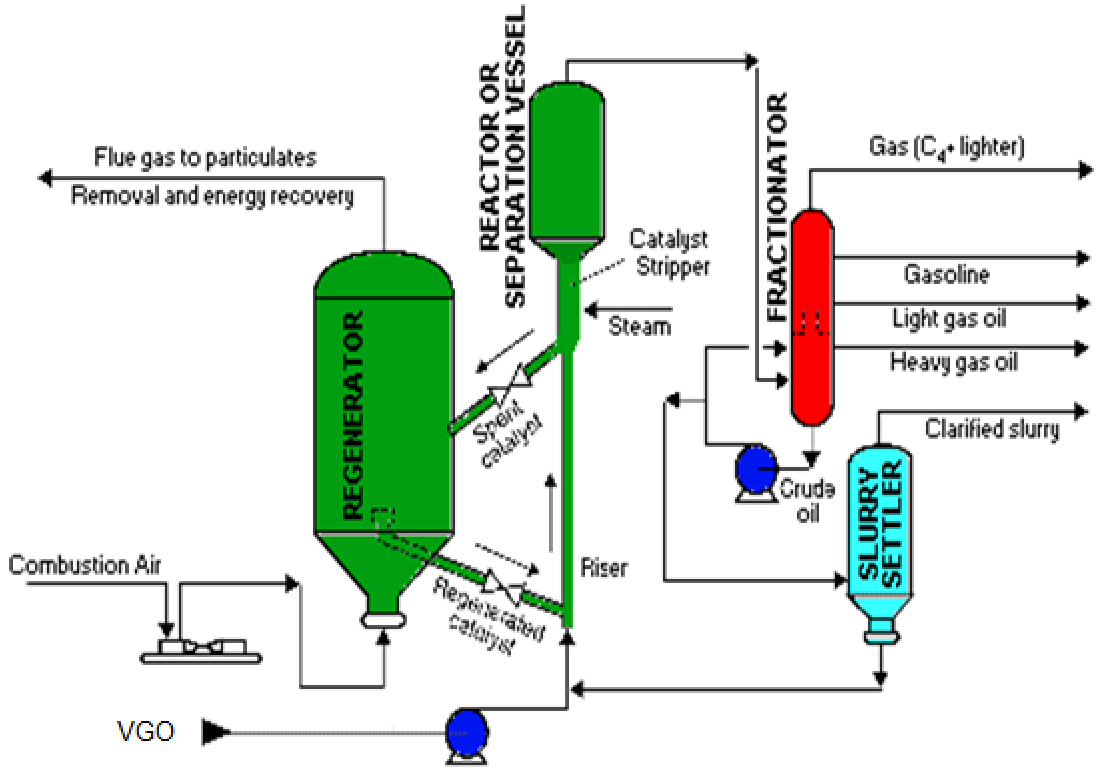


Figure (1.1) Fluid Catalytic Cracking Unit

A modern FCC unit comprises different sections such as a riser reactor, a stripper, a disengager, a regenerator, a main fractionator, catalyst transport lines (spent catalyst standpipe and regenerated catalyst standpipe) and several other auxiliary units such as: cyclones, air blower, expander, wet gas compressor, feed pre-heater, air heater, catalyst cooler, etc. The proprietary new designs and technologies that have been developed by the major FCC designers and licensors.(Fernandes et al., 2005)

Because of the importance of FCC unit in refining, a construction of mathematical model that can describe the dynamic behavior of FCC unit equipment's in steady state is very important. Accurate model can be used as a powerful tool to study the effect of process variables on the performance and productivity of the system.(Fernandes et al., 2005).

Simulation studies also provide guidance in the development of new processes and can reduce both time and investment.(Rao et al., 2004). The effective simulation of the fluid catalytic cracking operation requires knowledge of reaction kinetics, fluid dynamics, feed and catalyst effects.(Bollas et al., 2007).

The riser reactor is probably the most important equipment in a FCC unit. The modeling of a riser reactor is very complex due to complex hydrodynamics and unknown multiple reactions, coupled with mass transfer resistance, heat transfer resistance and deactivation kinetics. A complete model of the riser reactor should include all the important physical phenomena and detailed reaction kinetics(Gupta et al., 2010).

1.2. Project Objectives

The main objectives of the present work are:

- A short literature review of previous FCC riser modeling and simulation studies.
- Formulation of a mathematical model that can describe the reaction kinetics in the riser section of FCC unit by using four lump model to get suitable catalyst weight that leads to target conversion.
- Description of the physical properties of flow in the riser of the reactor.

Chapter 2

Literature review

2.1. Fluidized Catalytic Cracking

2.1.1. Introduction

The fluidized catalytic cracking (FCC) unit is the heart of the refinery and is where heavy low-value petroleum stream such as vacuum gas oil (VGO) is upgraded into higher value products, mainly gasoline and C3/C4 olefins, which can be used in the alkylation unit for production of ultraclean gasoline (C7-C8 alkylates). The FCC process has been in operation for over 60 years during which, a great deal of developments has occurred. Major developments have occurred in two areas: new catalysts and new reactor and regenerator designs. Recently, new processes have been developed, such as petro-FCC, residue FCC (RFCC) and olefin production, by a variety of means, including deep catalytic cracking (DCC). The original FCC has also been developed to improve yield, emission control and adaptability for different crude. The FCC unit mainly depends on circulating a zeolite catalyst with the vapor of the feed into a riser-reactor for a few seconds. The cracked products are disengaged from the solids and taken out to a distillation column for separation of the desired products. The catalyst is circulated back into the regenerator where coke is burned and the catalyst regenerated. The combustion of the coke generates the heat required to carry out the generally endothermic reaction in the riser(Fahim et al., 2009).

2.1.2. FCC Feed Characterization

Refiners process many different types of crude oil. As market conditions and crude quality fluctuate, so does cat cracking feedstock. Often the only constant in FCC operations is the continual change in feedstock quality. Feed characterization is the process of determining the physical and chemical properties of the feed. Two feeds with similar boiling point ranges may exhibit dramatic differences in cracking performance and product yields. FCC feed characterization is one of the most important activities in monitoring the cat cracking operation. Understanding feed properties and knowing their impact on unit performance are essential. Troubleshooting, catalyst selection, unit optimization, and subsequent process evaluations all depend on the feedstock. Feed characterization relates product yields and qualities to feed quality. By knowing the effects of a feedstock on unit yields, a refiner can purchase the feedstock that maximizes profitability. It is not uncommon for refiners to purchase raw crude oils or FCC feedstock's without knowing their impact on unit operations. This lack of knowledge can be expensive. Sophisticated analytical techniques, such as mass spectrometry, high-pressure liquid chromatography (HPLC), near-infrared spectroscopy (NIR), and chemometrics, can be used to measure aromatic and saturate contents of the FCC feedstock.. Unfortunately, only a few refinery laboratories either directly or indirectly use any of the methods to characterize their FCC feedstock. This is largely because these analysis techniques are time consuming, costly, and do not provide practical insight that a unit can use on a daily basis to evaluate and improve its performance. Consequently, simpler empirical correlations are more often used. They require only routine tests commonly performed by the refinery's laboratory. These empirical correlations are good alternatives to determine total paraffin, naphthene, and aromatic molecules, plus they provide practical tools for monitoring the FCC unit's performance. As with the sophisticated analytical techniques, the empirical correlations assume an olefin-free feedstock.(Sadeghbeigi, 2012)

The two primary factors that affect feed quality are:

- Hydrocarbons Classification
- Impurities

2.1.2.1. Hydrocarbons Classification

- **Paraffin’s**

Paraffin’s are straight- or branched-chain hydrocarbons having the chemical formula C_nH_{2n+2}. The name of each member ends with _ ane; examples are propane, isopentane, and normal heptane’s.(Sadeghbeigi, 2012)

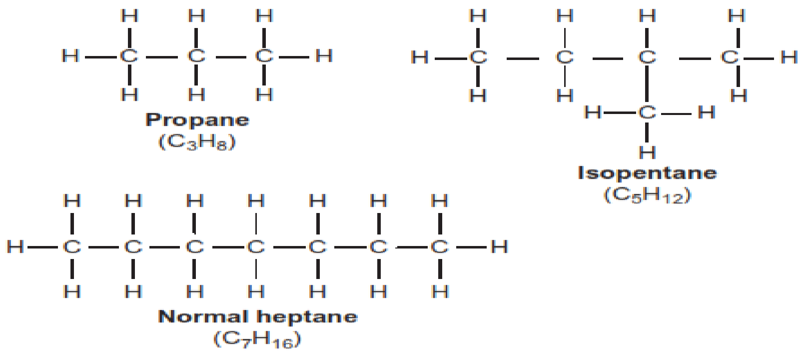


Figure (2.1) Examples of Paraffin’s

- **Naphthenes**

Naphthenes (C_nH_{2n}) have the same formula as olefins, but their characteristics are significantly different. Unlike olefins, which are straight-chain compounds, naphthene’s are paraffin’s that have been “bent” into a ring or a cyclic shape. Naphthenes, like paraffin’s, are saturated compounds. Examples of naphthene’s are cyclopentane, cyclohexane, and methylcyclohexane.(Sadeghbeigi, 2012)

- **Aromatic**

Aromatics (C_nH_{2n-6}) are similar to naphthene’s, but they contain a resonance-stabilized unsaturated ring core. Aromatics are compounds that contain at least one benzene ring. The benzene ring is very stable and does not crack to smaller components. Aromatics are not a preferred feedstock because few of the molecules will crack. The cracking of aromatics mainly involves breaking off the side chains resulting in excess fuel gas yield. In addition, some of the aromatic compounds contain several rings (polynuclear aromatics, PNAs) than can “compact” to form what is commonly called “chicken wire.” illustrates three examples of a PNA compound. Some of these compacted aromatics will end up on the catalyst as carbon residue (coke), and some will become slurry product. In comparison with cracking paraffin’s, cracking aromatic stocks results in lower conversion, lower gasoline yield, and less liquid volume gain, but with higher gasoline octane.(Sadeghbeigi, 2012)

- **Olefins**

Olefins are unsaturated hydrocarbons with a formula of $C_n H_{2n}$. The names of these compounds end with _ene, such as ethane (ethylene) and propene (propylene).
(Figure 2.2) shows typical examples of olefins. Compared to paraffin's, olefins are unstable and can react with themselves or with other compounds such as oxygen and bromine solution. Olefins do not occur naturally; they show up in the FCC feed as a result of preprocessing the feeds elsewhere. These processes include thermal cracking and other catalytic cracking operations. Olefins are not the preferred feedstocks to an FCC unit. This is not because olefins are inherently bad, but because olefins in the FCC feed indicate thermally produced oil. They often polymerize to form undesirable products such as slurry and coke. The typical olefin content of FCC feed is less than 5 wt.%, unless un-hydrotreated cocker gas oils are being charged.(Sadeghbeigi, 2012)

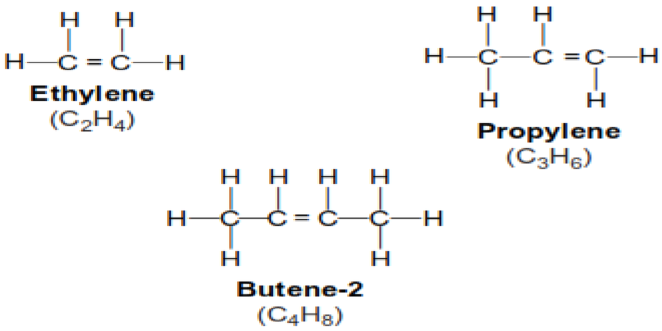


Figure (2.2) Examples of Olefins

- **Impurities**

The concentration of impurities in the FCC feedstock largely depends on the crude oil quality, gas oil EP, and the severity of hydrotreating. The cat cracker, as the main conversion unit, is designed to handle a variety of feedstock's. However, these impurities have negative effects on unit performance. Understanding the nature and effects of these contaminants is essential in feed and catalyst selection as well as troubleshooting the unit.

Most of the impurities in the FCC feed exist as components of large organic molecules. The most common contaminants are:

- Nitrogen
- Sulfur
- Metals (nickel, vanadium, potassium, iron, calcium, copper).

2.1.3. FCC Products

The cat cracker converts less valuable gas oil feedstock to a more valuable product. A major objective of most FCC units is to maximize the conversion of gas oil to gasoline and LPG, though recently the trend has been in maximizing diesel production. The typical products produced from the cat cracker are:

- Dry gas (hydrogen, methane, ethane, ethylene)
- LPG (propane, propylene, isobutane, normal butane, butylene’s)
- Gasoline
- LCO
- HCO (in few FCC units)
- Decanted (or slurry) oil
- Combustion coke.

Table shows the FCC products and the percentages of its yield

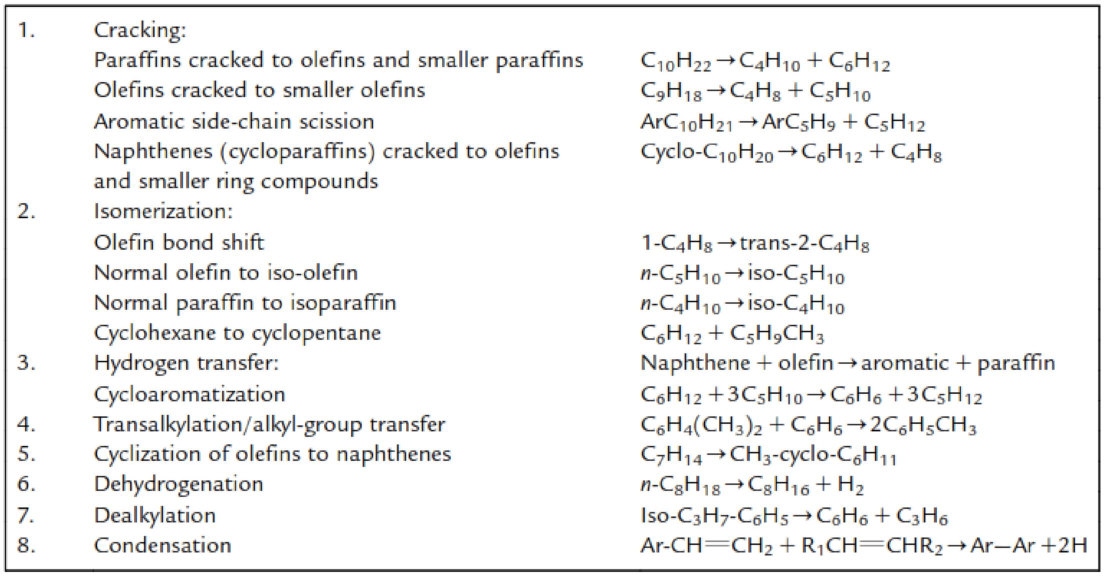
Table (2.1) FCC products

Product	Characteristics	Yield (wt%)
Dry gas + H2S $(C_1+C_2+C_3+H_2)+H_2S$	H2S must be removed	3-5
LPG: C_3, C_3’’, C_4, C_4’’	Petrochemical feedstock	8-20
Gasoline	Main product, good octane number	35-60
Light cycle oil (LCO)	Rich in aromatics & High sulfur content	12-20
Heavy cycle oil (HCO)+ Slurry	Very rich in aromatics	10-15
Coke	Consumed in regenerator	3-5

2.1.4. FCC Reactions

The main reaction in the FCC is the catalytic cracking of paraffin, olefins, naphthene's and side chains in aromatics. A network of reactions occurring in the FCC is illustrated in The VGO undergoes the desired 'primary cracking' into gasoline and LCO. A secondary reaction also occurs, which must be limited, such as a hydrogen transfer reaction which lowers the gasoline yield and causes the cycloaddition reaction. The latter could lead to coke formation (needed to provide heat for catalyst regeneration).(Fahim et al., 2009)

Table (2.2) Typical thermodynamic data for idealized reactions of importance in catalytic cracking



1.	Cracking:	
	Paraffins cracked to olefins and smaller paraffins	$C_{10}H_{22} \rightarrow C_4H_{10} + C_6H_{12}$
	Olefins cracked to smaller olefins	$C_9H_{18} \rightarrow C_4H_8 + C_5H_{10}$
	Aromatic side-chain scission	$ArC_{10}H_{21} \rightarrow ArC_5H_9 + C_5H_{12}$
	Naphthenes (cycloparaffins) cracked to olefins and smaller ring compounds	Cyclo-$C_{10}H_{20} \rightarrow C_6H_{12} + C_4H_8$
2.	Isomerization:	
	Olefin bond shift	1-$C_4H_8 \rightarrow$ trans-2-C_4H_8
	Normal olefin to iso-olefin	*n*-$C_5H_{10} \rightarrow$ iso-C_5H_{10}
	Normal paraffin to isoparaffin	*n*-$C_4H_{10} \rightarrow$ iso-C_4H_{10}
	Cyclohexane to cyclopentane	$C_6H_{12} + C_5H_9CH_3$
3.	Hydrogen transfer:	Naphthene + olefin → aromatic + paraffin
	Cycloaromatization	$C_6H_{12} + 3C_5H_{10} \rightarrow C_6H_6 + 3C_5H_{12}$
4.	Transalkylation/alkyl-group transfer	$C_6H_4(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5CH_3$
5.	Cyclization of olefins to naphthenes	$C_7H_{14} \rightarrow CH_3$-cyclo-$C_6H_{11}$
6.	Dehydrogenation	*n*-$C_8H_{18} \rightarrow C_8H_{16} + H_2$
7.	Dealkylation	Iso-C_3H_7-$C_6H_5 \rightarrow C_6H_6 + C_3H_6$
8.	Condensation	$Ar\text{-}CH{=}CH_2 + R_1CH{=}CHR_2 \rightarrow Ar{-}Ar + 2H$

2.1.5. FCC Catalyst

The main catalyst which is used in a FCC reactor is the zeolite type. Compared to amorphous silica-alumina catalyst, the zeolite catalysts are more active and more selective. The higher activity and selectivity translates to more profitable liquid product yields and additional cracking capacity.(Fahim et al., 2009)

2.1.5.1. Catalyst Components

FCC catalysts are in the form of fine powders with a typical particle size of 75 µm. A modern cat cracking catalyst has four major components:

- ## Zeolite

Zeolite is in a powder-form with an average particle size of 75 mm and an average surface area of 800 m2/g. It has a crystalline structure of aluminosilicates. A matrix is added to the zeolite which acts as a binder and filler. The main active component in the catalyst is the Y-Zeolite. It is a crystalline structure of aluminosilicates which has the Y-faujasite structure. The highest pore size in the Y-faujasite structure is 8°A which is called the super cage. It can allow some C18-C25 mono-, di- and tri-nuclear aromatics present in the VGO to pass. In the cracking of long chain paraffin's, another type of high silica zeolite is added. This zeolite is called ZSM-5 and is used to improve octane number.

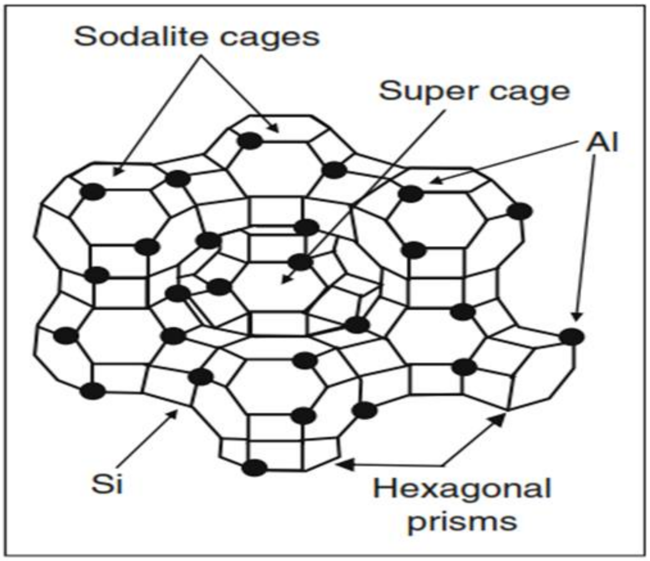


Figure (2.3) Structure of Y-faujasite

- ## Matrix

Matrix refers to the catalyst binder. It means components of the catalyst other than zeolite, and the term active matrix means the components of the catalyst other than zeolite having catalytic activity. Alumina is the source for an active matrix. Most active matrices used in FCC catalysts are amorphous. However, some of the catalyst suppliers incorporate a form of alumina that also has a crystalline structure.

- ## Filler and Binder

The filler is a clay incorporated into the catalyst to dilute its activity. Kaoline [$Al_2(OH)_2$, SI_2O_5] is the most common clay used in the FCC catalyst. One FCC catalyst manufacturer uses kaoline clay as a skeleton to grow the zeolite in situ. The binder serves as a glue to hold the zeolite, matrix, and filler together. Binder may or may not have catalytic activity. The importance of the binder becomes more prominent with catalysts that contain high concentrations of zeolite. The functions of the filler and the binder are to provide physical integrity, a heat transfer medium, and a fluidizing medium in which the more important and expensive zeolite component is incorporated.

In summary, zeolite will affect activity, selectivity, and product quality. An active matrix can improve bottoms cracking and resist vanadium and nitrogen attacks. But a matrix containing very small pores can suppress strippability of the spent catalyst and increase hydrogen yield in the presence of nickel. Clay and binder provide physical integrity and mechanical strength.

2.2. Models of FCC

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

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 interphase friction, interphase heat transfer, and fluid to wall frictional forces. The model can predict pressure drop, catalyst holdup, interphase slip velocity, temperature distribution in both phases, and yield distribution all over the riser.

An integrated dynamic model for the complete description of the fluid catalytic cracking unit (FCC unit) was developed by Bollas et al. (2002); the model simulates successfully the riser and the regenerator of FCC and incorporates operating conditions, feed properties and catalyst effects.

Erthal et al. (2003), developed a one dimensional, mathematical model, they considered in their model gas-solid flow that occurs in FCC risers, two equations of momentum conservation applied to the compressible gas flow and solid flow respectively, the model considers also the drag force and heat transfer coefficient between two phases; four lump model used for cracking reactions description.

Souzaa et al. (2003), combined a 2-D fluid flow field with a 6- lumps kinetic model and used two energy equations (catalyst and gas oil) to simulate the gas oil cracking process inside the riser reactor.

Das et al. (2003), performed the three-dimensional simulation of an industrial-scale fluid catalytic cracking riser reactor using a novel density based solution algorithm. The particle-level fluctuations are modeled in the framework of the kinetic theory of granular flow. The reactor model includes separate continuity equations for the components in the bulk gas and inside the solid phase.

Osman et al. (2010) developed a kinetic model to simulate the riser of a residue fluid catalytic cracking unit (RFCC) at steady state. The model based on combination the material and energy balance equations with seven lump model and a modified two-dimensional hydrodynamic model. Simulation has been performed based on the data from an operating unit at Khartoum Refinery Company (KRC). MATLAB environment has been used to solve and analyze the kinetic model and process variables.

Ali et al. (1997); Arbel et al. (1995); Han et al. (2001), developed a mathematical model of an industrial FCC unit, includes one dimensional mass, energy, and species balance; their models were based on the assumption of instantaneous and complete vaporization of the feed when contacted with hot regenerated catalyst assuming modern high efficiency feed injection systems. These types of modeling are normally simple to formulate and to solve. They are more suitable when the interest is to explore the influence of operating conditions, test a kinetic model or when the simulation includes not only the riser, but also other equipment’s like the regenerator and the stripper. The simplest kind of these models is the homogeneous version, where both the vapor phase (hydrocarbon feed & products vapors) and the solid phase (catalyst & coke) are moving at the same velocity. The heterogeneous version considers different velocities for the two phases, resulting in different residence times for each phase inside the riser.

The simplest hydrodynamic models assume steady state ideal plug flow reactor. Ali et al. and Han et al. used the four-lump kinetic models to describe the behavior of cracking reactions, while Arbel et al. used more complex ten-lump model.

An integrated dynamic model for the complete description of the fluid catalytic cracking unit (FCC unit) was developed by Bollas et al. (2002); the model simulates successfully the riser and the regenerator of FCC and incorporates operating conditions, feed properties and catalyst effects.

Berry et al. (2004), modified the two-dimensional hydrodynamic model to make it predictive by incorporating the slip factor for the calculation of the cross-sectionally averaged voidage. The model has been coupled with the four-lump kinetic model to predict the effect of operating conditions on profiles of conversion, yield, temperature and pressure in the riser.

Hassan (2005), developed Material and energy balance calculations todesign Fluidized catalytic cracking (FCC) unit from Iraqi crude oil. She used the visual basic program in her work.

With regard to reaction and kinetics, Xu et al. (2006) proposed aseven-lump kinetic model to describe residual oil catalytic cracking, in which products especially coke was lumped separately for accurate prediction. Because in recent studies, kinetics was developed accounting for coke formation leading to catalyst deactivation. The reactor block is modeled as a combination of an ideal Plug Flow Reactor (PFR) and a Continuously Stirred Tank Reactor (CSTR).

On the other hand, Krishnaiah et al. (2007), a steady state simulation for the fluid cracking was investigated, the riser reactor was modeled as a plug flow reactor incorporating four lump model for cracking reactions; they studied the effect of the operating variables on FCC unit performance, a catalyst to oil ratio, air rate and gasoil inlet temperature have been chosen as operating variables.

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.

Ahari et al. (2008), a one dimensional adiabatic model for riser reactor of FCC unit was developed, the chemical reaction was characterized by a four-lump kinetic model, in their study, four cases of industrial riser operating conditions have been adopted and the modified kinetic parameters are used to eliminate the deviations between calculated and real values, also simulation studies are performed to investigate the effect of changing process variables.

Based on Ahari et al. (2008) study, Heydari et al. (2010) performed an excessive analysis to gasoline yield throughout the riser with respect to different inlet mixing temperatures, different feed rates and different catalyst to oil ratios.

Shakoor (2010) developed a computer program using MATLAB 7software to determine the rate constants of FCC unit cracking reactions represented by six lump model and at any certain temperature.

Baurdez et al. (2010) 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.

A control system of a fluidized-bed catalytic cracking unit has been developed by AL-Niami (2010). In this work the dynamic and control system based on basic energy balance in the reactor and regenerator systems have been carried out. For the control system, the important input variables were chosen to be the reactor temperature and the regenerator temperature.

Chapter 3

Methodology

3.1. Introduction

In this chapter, a mathematical model for the riser of an industrial FCC is developed, based on the reactor/regenerator configuration presented in the (Figure 3.1). Feed and steam are mixed and injected through the feed nozzles distributors. At the distributors, the riser diameter increases to allow for the expansion of hydrocarbon vapors as the oil is vaporized when it meets the catalyst. As a result of feed vaporization, the cracking reactions start and the density of the oil decreases 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 Gasoil is converted to gasoline range hydrocarbons, light gases and coke. 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. Because the riser volume is small, it limits the contact time between the catalyst and hydrocarbon to 5 seconds or less, and prevents over cracking of the feed.

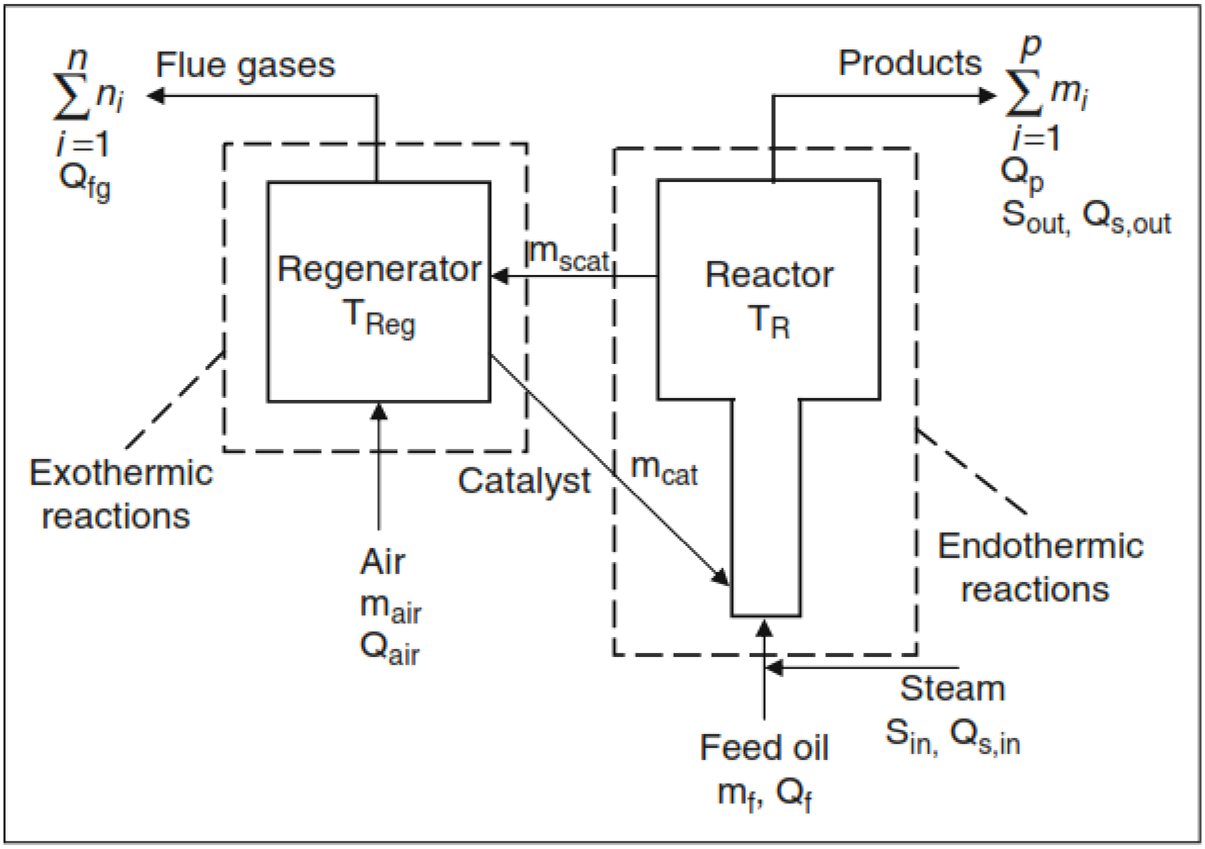


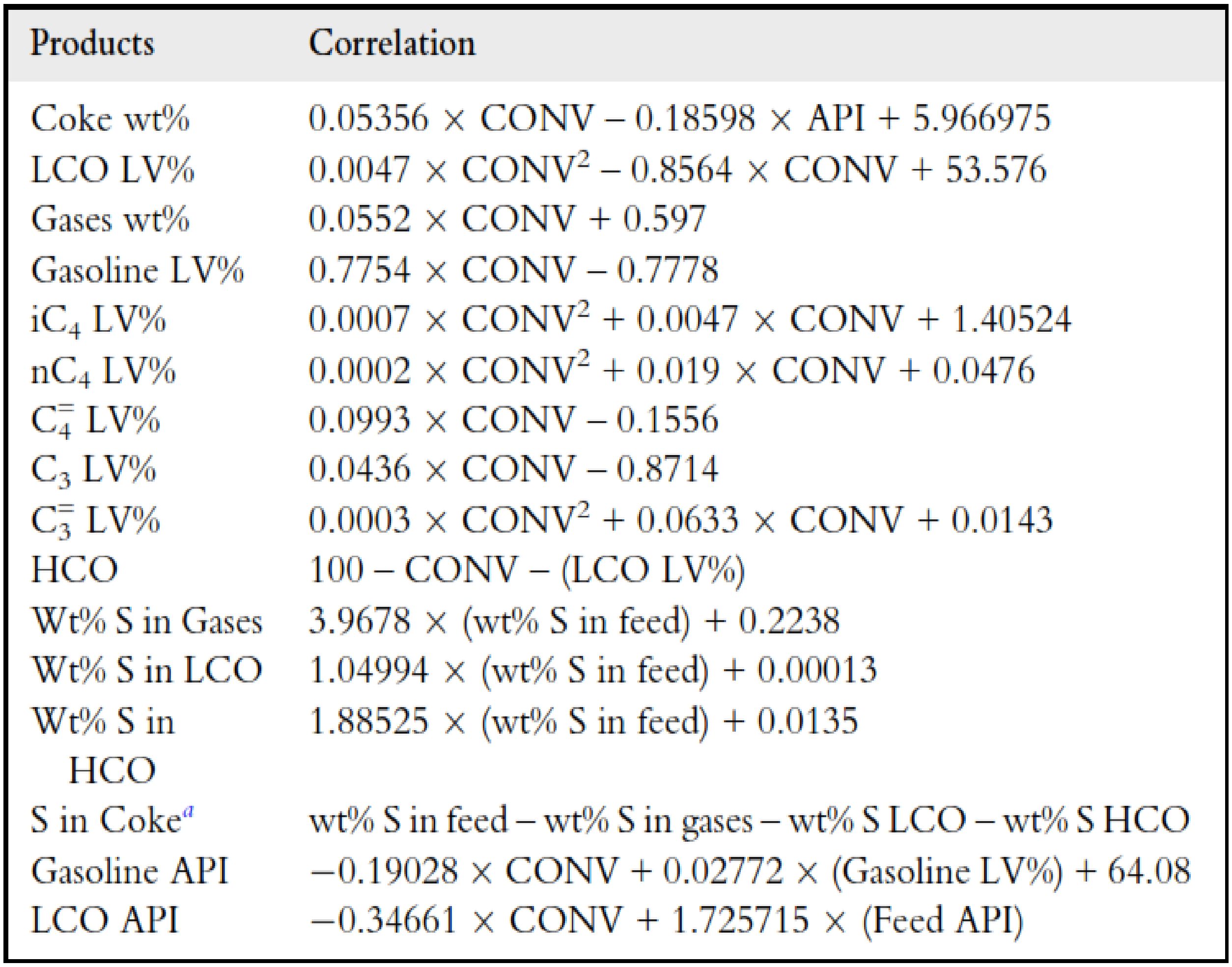
Figure (3.1) Input and output streams for reactor and regenerator in FCC unit

3.2. FCC Yield Correlations

The yields of the products involved in fluid cracking are obtained by the regression of plant data. The correlations given in Table (3.1) require target conversion (LV%), feed API and Sulphur in the feed. Conversion is defined as the percentage of the oil fed that has been cracked into lighter fractions than gasoline and lighter products:

$$CONV\% = \left(\frac{Volume\ of\ oil\ feed\ -\ Volume\ of\ cycle\ stock}{Volume\ of\ oil\ feed}\right) * 100 \qquad \textbf{(3.1)}$$

Table (3.1) FCC Yield Correlations



Products	Correlation
Coke wt%	$0.05356 \times CONV - 0.18598 \times API + 5.966975$
LCO LV%	$0.0047 \times CONV^2 - 0.8564 \times CONV + 53.576$
Gases wt%	$0.0552 \times CONV + 0.597$
Gasoline LV%	$0.7754 \times CONV - 0.7778$
iC_4 LV%	$0.0007 \times CONV^2 + 0.0047 \times CONV + 1.40524$
nC_4 LV%	$0.0002 \times CONV^2 + 0.019 \times CONV + 0.0476$
$C_4^=$ LV%	$0.0993 \times CONV - 0.1556$
C_3 LV%	$0.0436 \times CONV - 0.8714$
$C_3^=$ LV%	$0.0003 \times CONV^2 + 0.0633 \times CONV + 0.0143$
HCO	100 – CONV – (LCO LV%)
Wt% S in Gases	3.9678 × (wt% S in feed) + 0.2238
Wt% S in LCO	1.04994 × (wt% S in feed) + 0.00013
Wt% S in HCO	1.88525 × (wt% S in feed) + 0.0135
S in Coke[a]	wt% S in feed – wt% S in gases – wt% S LCO – wt% S HCO
Gasoline API	−0.19028 × CONV + 0.02772 × (Gasoline LV%) + 64.08
LCO API	−0.34661 × CONV + 1.725715 × (Feed API)

3.3. Material and Energy Balances

The material and energy balance around the reactor and regenerator can be calculated by defining the input and output streams.

3.3.1. Material Balance

3.3.1.1. Reactor Material Balance

The input and output streams to the reactor (Figure 3.1) are:

Reactor input:

- Oil feed (VGO) to the riser: F (BPD) or m_f (Ib/h)
- Injection steam: S_{in} (Ib/h)
- Regenerated catalyst: m_{cat}(Ib/h)

Reactor output:

- Masses of products m as calculated from FCC yield correlations. These correlations require some feed properties such as: API, Sulphur content and degree of severity expressed as conversion.
- Spent catalyst circulation rate: m_{scat}(Ib/h)
- Steam present in cracked products: S_{out}(Ib/h)

Thus, a material balance around the reactor is

$$m_f + S_{in} + m_{cat} = \sum_{i=1}^{p} m_i + S_{out} + m_{scat} \qquad (3.2)$$

where p is the total number of vapor products and assuming Sin does not condense and is present in the exiting vapor products at the same rate ($S_{in} = S_{out}$). M_i is the mass of each product that can be calculated using the FCC correlations. The produced coke is present in spent catalyst. Thus

$$m_{coke} = m_{scat} - m_{cat} \qquad (3.3)$$

3.3.1.2 Regenerator Material Balance

Regenerator input:

- Spent catalyst circulation rate m_{scat} (Ib/h)
- Air for cock burning m_{air}(Ib/h)

Regenerator output:

- Flue gases n_i (Ib/h)
- Regenerated catalysts m_{cat} (Ib/h)

Thus, the material balance around the regenerator produces:

$$m_{\mathrm{air}} + m_{\mathrm{scat}} = \sum_{i=1}^{N} n_i + m_{\mathrm{cat}} \tag{3.4}$$

where n_i is the mass of each gas produced from the coke burning which may contain CO_2, CO, H_2O, SO_2, N_2 and O_2 (from excess air).

3.3.2. Energy Balance

3.3.2.1. Reactor Heat Balance

Heat input:

- Heat of feed oil Q_F (Btu/h) at inlet feed temperature (T_F)
- Heat of steam injected Q_s (Btu/h) at T_S
- Heat of regenerated catalyst Q_{Cat} (Btu/h) at regenerator outlet temperature (T_{Reg})

Heat output:

- Heat in vapor products Q_p (Btu/h) at reactor outlet temperature (T_R)
- Heat of spent catalyst Q_{Scat} (Btu/h) at (T_R)
- Heat of exit steam $Q_{S,\ OUT}$ (Btu/h) at (T_R)

Then the energy balance can be expressed as

$$\begin{aligned} & m_{\mathrm{f}} C_{\mathrm{p,f}} (T_{\mathrm{f}} - T_{\mathrm{o}}) + m_{\mathrm{f}} (-\Delta H_{\mathrm{R}}) + m_{\mathrm{cat}} C_{\mathrm{P,cat}} (T_{\mathrm{Reg}} - T_{\mathrm{o}}) + S_{\mathrm{in}} C_{\mathrm{ps}} (T_{\mathrm{s}} - T_{\mathrm{o}}) \\ & = (T_{\mathrm{R}} - T_{\mathrm{o}}) \sum m_i C_{\mathrm{P},i} + m_{\mathrm{scat}} C_{\mathrm{P,scat}} (T_{\mathrm{R}} - T_{\mathrm{o}}) + S_{\mathrm{out}} C_{\mathrm{ps}} (T_{\mathrm{R}} - T_{\mathrm{o}}) \end{aligned} \tag{3.5}$$

3.3.2.2. Regenerator Heat Balance

Heat input:

- Heat of spent catalyst Q_{Scat} (Btu/h) at (T_R)
- Heat of input air for coke burning Q_{Air} (Btu/h) at (T_{Air})
- Heat of coke combustion q_{coke} (Btu/h)

Heat output:

- Heat of flue gas Q_{fg} (Btu/h) at (T_{Rg})
- Heat of regenerated catalyst Q_{Cat}(Btu/h) at (T_R)

Thus, the heat balance around the regenerator can expressed as

$$\begin{aligned} m_{\mathrm{air}} C_{\mathrm{p,air}} (T_{\mathrm{air}} - T_{\mathrm{o}}) + m_{\mathrm{coke}} C_{\mathrm{P,coke}} (T_{\mathrm{R}} - T_{\mathrm{o}}) + q_{\mathrm{coke}} \\ = (T_{\mathrm{Reg}} - T_{\mathrm{o}}) \sum n_i C_{\mathrm{P,gi}} + m_{\mathrm{cat}} C_{\mathrm{P,cat}} (T_{\mathrm{Reg}} - T_{\mathrm{R}}) \end{aligned} \quad (3.6)$$

3.4. Riser Model

For numerical computation, riser is divided into equal sized segments of thickness (dz), forming sequential equal sized volume elements (see Figure 3.4).

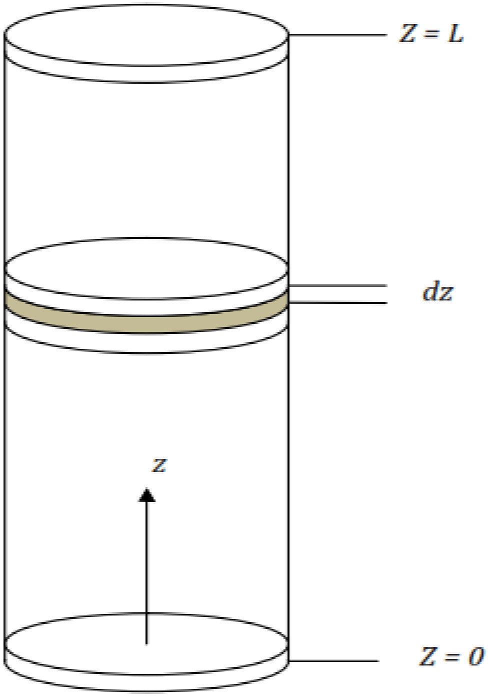


Figure (3.2) A volume element in the riser reactor

3.4.1. Model Assumptions

In order to develop a mathematical model for the riser reactor, the following assumptions are introduced:

- One dimensional transported plug flow reactor prevails in the riser without radial and axial dispersion
- Steady state operation
- The riser wall is adiabatic.
- Viscosities and heat capacities for all components in vapor phase are constant along the riser.
- The coke deposited on the catalyst does not affect the fluid flow.
- Catalyst activity constant along the riser.

3.4.2. Cracking Reactions Kinetics

The FCC process involves a network of reactions producing a large number of compounds. Therefore, lumping models can be used to describe the reaction system in terms of the feed and a defined number of products, the agglomeration of many chemical compounds into a single compound (called a lump), should exhibit some or several common properties (i.e. boiling point, molecular weight, reactivity). In this work four lump model scheme has been selected (Figure 3.4). This scheme consists of (VGO feed, Light gases, Gasoline, and Coke), it is more realistic and simple to solve, with more lumps, the mathematic becomes more complicated.

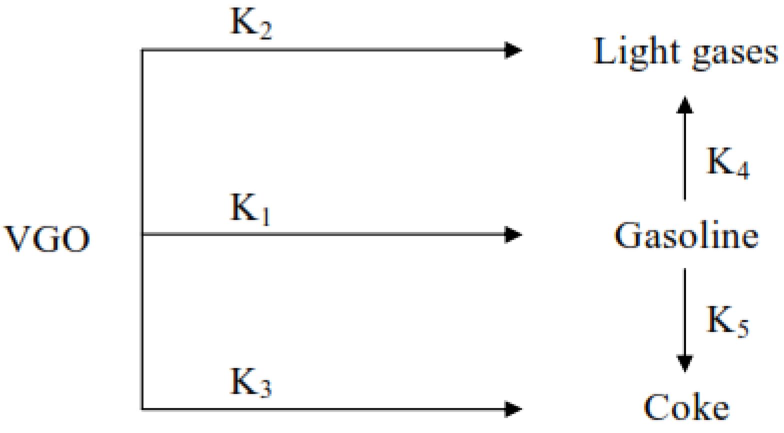


Figure (3.3) Schematic of four lumped reactions

According to this scheme, a part of gasoline is also converted to light gases and coke. It is assumed that cracking reaction rate is second order with respect to Gasoil, and first order with respect to Gasoline, and the reactions take place only in the vapor phase. Rate constants (Kj) for cracking reactions follow the Arrhenius dependence on temperature (equation 3.6).

$$K_j = K_{oj} e^{\left(\frac{-E_j}{RT}\right)} \tag{3.7}$$

In order to fit the predicted gasoline, yield with industrial gasoline yield, the selected frequency factors can be scaled linearly by dividing each one by the modified frequency factor (Ko1) of the reaction feedstock → gasoline:

3.4.3. Concentration, and Coking Time Profiles in The Riser

In order to calculate the concentration profile for each lump throughout the riser height, a differential material balance can be applied along the riser, the following set of equations is:

For VGO lump:

$$\frac{dY_1}{d\tau} = -(k_{12} + k_{13} + k_{14})\phi Y_1^2 \tag{3.8}$$

For gasoline lump:

$$\frac{dY_2}{d\tau} = k_{12}\phi\, Y_1^2 - (k_{23} + k_{24})\phi Y_2 \tag{3.9}$$

For light gases lump:

$$\frac{dY_3}{d\tau} = k_{13}\phi\, Y_1^2 + k_{23}\phi Y_2 \tag{3.10}$$

For coke lump:

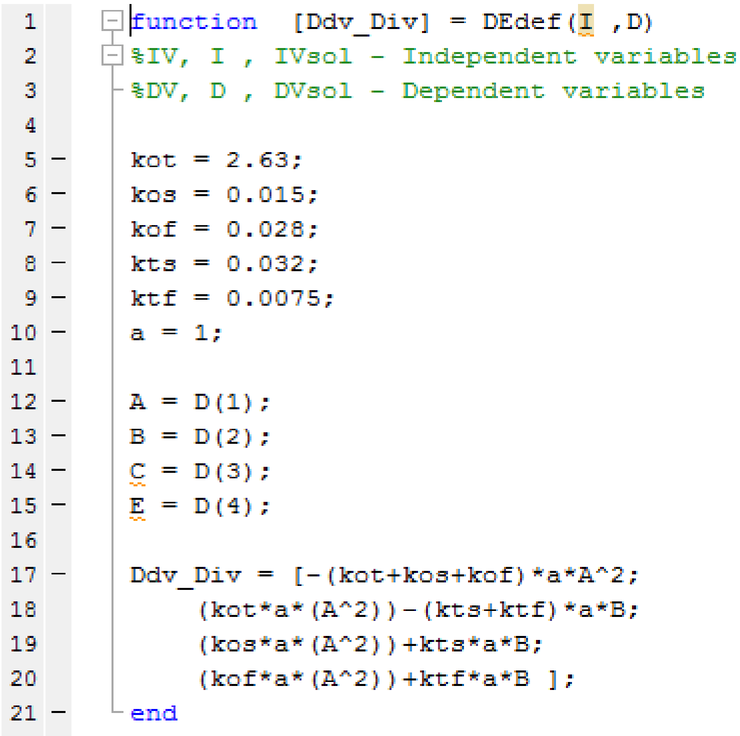
$$\frac{dY_4}{d\tau} = k_{14}\phi\, Y_1^2 + k_{24}\phi Y_2 \tag{3.11}$$

where Y is the weight fraction and subscripts 1, 2, 3, and 4 correspond to the pseudo components as the Gas Oil, gasoline, gases, and coke, and Ꞇ indicates residence time W/F (Weight of Catalyst/feed rate) and Φ is the deactivation factor of the catalyst.

3.4.4. Model Solution

MATLAB software version 7 used for solve presented model, based on the scorned order Runge – Kutta method numerical technique; and a sequential approach has been chosen in this solution. the sequence of calculation steps is listed below, and the model results and discussions are presented in chapter four.

- **Step 1:** Create the m.file 1



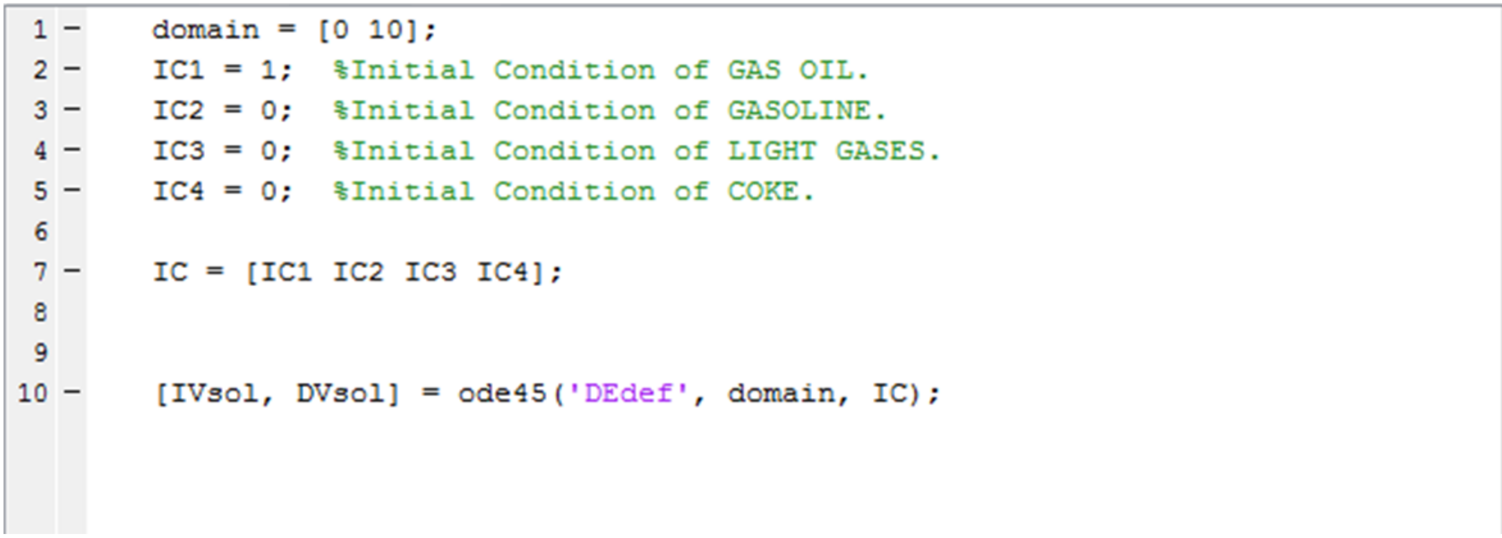
```
function   [Ddv_Div] = DEdef(I ,D)
%IV, I , IVsol - Independent variables
%DV, D , DVsol - Dependent variables

kot = 2.63;
kos = 0.015;
kof = 0.028;
kts = 0.032;
ktf = 0.0075;
a = 1;

A = D(1);
B = D(2);
C = D(3);
E = D(4);

Ddv_Div = [-(kot+kos+kof)*a*A^2;
    (kot*a*(A^2))-(kts+ktf)*a*B;
    (kos*a*(A^2))+kts*a*B;
    (kof*a*(A^2))+ktf*a*B ];
end
```

- **Step 2:** Create the m.file 2



```
domain = [0 10];
IC1 = 1;  %Initial Condition of GAS OIL.
IC2 = 0;  %Initial Condition of GASOLINE.
IC3 = 0;  %Initial Condition of LIGHT GASES.
IC4 = 0;  %Initial Condition of COKE.

IC = [IC1 IC2 IC3 IC4];


[IVsol, DVsol] = ode45('DEdef', domain, IC);
```

- **Step 3**: Use the ODE45 function in the command window

[IVsol, DVsol] = ode45('DEdef', domain, IC);

- **Step 4**: plot the results

3.5. FCC Design

• Data and Assumption

☒ The bubbles are all of one size.
☒ The solids in the emulsion phase flow smoothly downward, essentially in plug flow.
☒ The emulsion phase exists at minimum fluidizing conditions. The gas occupies the same void fraction in this phase as it had in the entire bed at the minimum fluidization point.
☒ $\psi = 0.33$, $\rho_p = 2500$ kg m^{-3}, Dp = 0.05 mm = 0.05*10^{-3}m, $\alpha = 0.6$,
$D_m = 0.14$ m^2 h^{-1} = 0.4*10^{-4} m^2 S^{-1}, $\mu_f = 1.44$ kg h^{-1} m^{-1}

- The Porosity at minimum fluidization ε_{mf}:

$$\varepsilon mf = \left[\frac{0.071}{\psi}\right]^{\frac{1}{3}} \qquad \textbf{(3.12)}$$

$$= (0.071/0.33)^{1/3} = \boxed{0.6}$$

- The minimum fluidization velocity is obtained from Equation

$$u_{mf}^2 + \frac{150(1-\epsilon_{mf})\mu_f}{1.75\rho_f d_p'}u_{mf} - \frac{g(\rho_p - \rho_f)\epsilon_{mf}^3 d_p'}{1.75\rho_f} = 0 \qquad (3.13)$$

$u_{mf} = 0.005$ m/s

- The terminal velocity U_T

$$u_t = \eta d_p^2 / 18\mu \qquad (3.14)$$

Where:

$\eta = g\ (\rho_p - \rho_f)$

$\eta = g\ (\rho_p - \rho_f) = 9.81\ (2500 - 899) = 1601$

$U_t = 0.31\ m\ s^{-2}$

- The bubble diameter, d_b

$$d_b/\text{cm} = 0.853[1 + 0.272(u_{fl} - u_{mf})]^{1/3}(1 + 0.0684x)^{1.21} \qquad (3.15)$$

$D_b = 0.001$ cm

- The bubble rise velocity, U_b

$$U_{br} = (0.71)\ (gd_b)^{1/2} \qquad (3.16)$$

$$U_b = U_o - U_{mf} + (0.71)\ (gd_b)^{1/2} \qquad (3.17)$$

$U_{br} = 0.71 * (9.81*0.1)^{1/2} =$ **$0.704\ m\ S^{-1}$**

$U_b = 0.2 - 0.005 + (0.71)\ (9.81*0.1) =$ **$0.9\ m\ S^{-1}$**

- The region fractions in the reactor bed

☒ Fraction occupied by bubbles f_b

$$\mathbf{F_b = u_0/u_b} \qquad \mathbf{(3.18)}$$

$$F_b = 0.2/0.9 = \boxed{\mathbf{0.222}}$$

☒ Fraction occupied by cloud f_c

$$f_c = \frac{3u_{mf}f_b}{\epsilon_{mf}\ u_{br} - u_{mf}} \qquad \mathbf{(3.19)}$$

$$F_c = \frac{3*0.005*0.222}{0.6*0.704-0.005} = \boxed{\mathbf{0.007}}$$

☒ Fraction occupied by wake f_w

$$F_w = \alpha f_b$$

$$F_w = 0.6*0.222 = \boxed{\mathbf{0.133}} \qquad \mathbf{(3.20)}$$

☒ Fraction occupied by Fraction occupied by emulsion f_e

$$\mathbf{f_e = 1- f_b - f_c - f_w} \qquad \mathbf{(3.21)}$$

$$f_e = 1- 0.222 - 0.007 - 0.133 = \boxed{\mathbf{0.638}}$$

Chapter 4

Results and Discussions

4.1. Introduction

As discussed in previous chapter, the material and energy balance equations were combined with reaction kinetics equations to obtain a model capable to predicting the yield pattern along the riser height. Model results are plotted in the following figures with a brief discussion. An Excel worksheet and MATLAB software was developed for modeling.

4.2. Case Study

For model validation, commercial FCC unit (5008 TPSD) designed to handle hydrotreated VGO feed was selected. The unit operates for maximum gasoline mode, therefore, no recycle occurs at normal operation. (Table 1.1) shows the kinetic parameters for cracking reactions with adjustable frequency factors utilizing the productivity of studied case.

Table (1.1) Kinetic parameters with Modified frequency factors used in present model

	Frequency factor k_{oj}	Activation energy E_j (kJ/kmol)
Gas oil to gasoline	$7.978 * 10^6$	-68,250
Gas oil to gases	$4.549 *10^6$	-89,216
Gas oil to coke	$3.765 *10^4$	-64,575
Gasoline to gases	$3.255 *10^3$	52,718
Gasoline to coke	$7.957 *10^3$	63,458

4.2.1 Feed and process Data

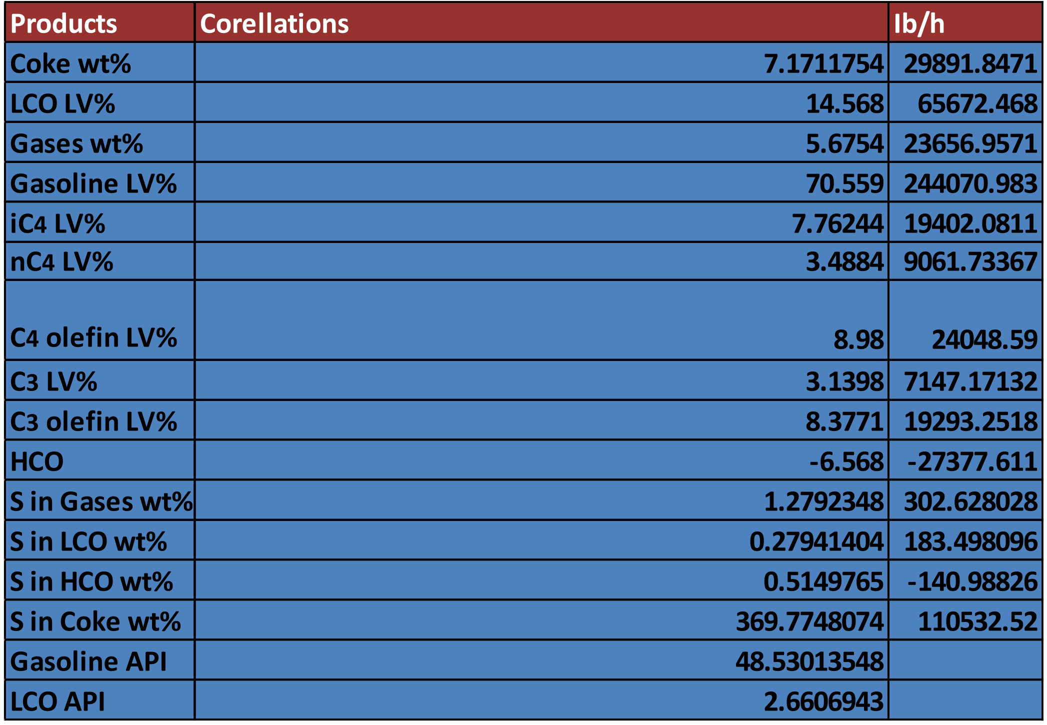
Table (4.2) Feed and Process Data used in the present model

Feed API	20.02
Sulfur in feed wt%	0.266
Conversion %	75
Specific Gravity of feed	0.9339
Feed Temperature (K◦)	850
Regenerator Temperature (K◦)	973
Reactor Temperature (K◦)	823
Steam Temperature (K◦)	518
Air Temperature (K◦)	473
-ΔH (kj/kmol)	393000
Steam In (ton/h)	2500

4.3. Material and Energy Balance Results

4.3.1. Yield Correlation Results

Table (4.3) Yield Results from excel software



Products	Corellations	Ib/h
Coke wt%	7.1711754	29891.8471
LCO LV%	14.568	65672.468
Gases wt%	5.6754	23656.9571
Gasoline LV%	70.559	244070.983
iC4 LV%	7.76244	19402.0811
nC4 LV%	3.4884	9061.73367
C4 olefin LV%	8.98	24048.59
C3 LV%	3.1398	7147.17132
C3 olefin LV%	8.3771	19293.2518
HCO	-6.568	-27377.611
S in Gases wt%	1.2792348	302.628028
S in LCO wt%	0.27941404	183.498096
S in HCO wt%	0.5149765	-140.98826
S in Coke wt%	369.7748074	110532.52
Gasoline API	48.53013548	
LCO API	2.6606943	

4.3.2. Material Balance Results

Table (4.4) Reactor Material Balance Results from excel

Reactor Side	
M_f (lb/h)	416833.3
M_{cat} (lb/h)	166733.32
M_{coke} (lb/h)	29891.84707
$\sum M_i$ (lb/h)	384975.6252
M_{scat}	196625.1671
S_{in}	208416.65

Table (4.5) Regenerator Material Balance Results from excel

Regenerator Side	
M_{air} (lb/h)	141982.9
$\sum n_i$ (kmol/h)	141982.9

4.3.3. Energy Balance Results

Table (4.6) Reactor Energy Balance Results from excel software

Reactor Side		
Hydrocarbons	API°	Cp (Btu / lb.F)
Feed	20.01515152	0.885548852
Gasoline	48.53013548	0.905595741
LCO	2.6606943	0.873348148
i_{c4}	121.1785714	0.956669771
n_{c4}	111.6271478	0.949954834
C_4 olefin	104.3333333	0.944827063
C_3	145.9509804	0.974085518
C_3 olefin	142.7248062	0.971817421

Table (4.7) Regenerator Energy Balance Results from excel

Regenerator Side	
$C_{p,co2}$ (Kj/Kmol.k)	46.9
$C_{p,N2}$ (Kj/Kmol.k)	32.6
$C_{p,air}$ (kj/kmol.k)	28.84
coke (kmol/h)	1129.127
$C_{p,cat}$ (kj/kg.k)	1.11
q (kj/h)	443746911
$C_{p,s}$ (KJ/Kg.K)	2.182

4.4. Model Results

In order to validate the model, the results obtained by solving the model by using the given data from the plant. The results obtained and the deviation in the results is reported in the next figures. By trial and error, we get the suitable weight of catalyst that give conversion 92%.

Figure (4.1) shows the consumption of gasoline and the yields of gasoline, light gases, and coke in the riser reactor. Where Space time (Ꞇ) represented by T.

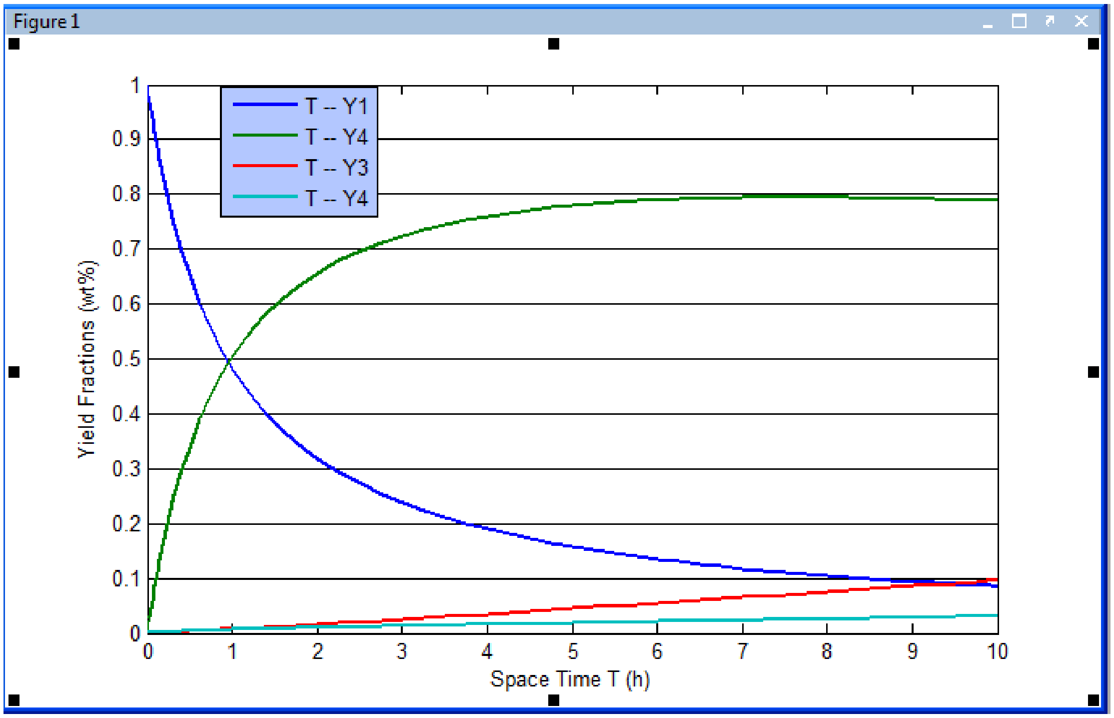


Figure (4.1) Space time Vs. weight fractions

Table (4.8) Comparison of the yield between the Modeling & Material Balance

	Weight fraction from Material Balance (wt.%)	**Weight fraction from Modeling (wt.%)**	**Deviation**
Gasoline	71	78	+7%
Gases	5.6	4	-1.6%
Coke	7	9	+2%

And figures (4.2), (4.3), (4.4) show the yields of gasoline, light gases, and coke respectively.

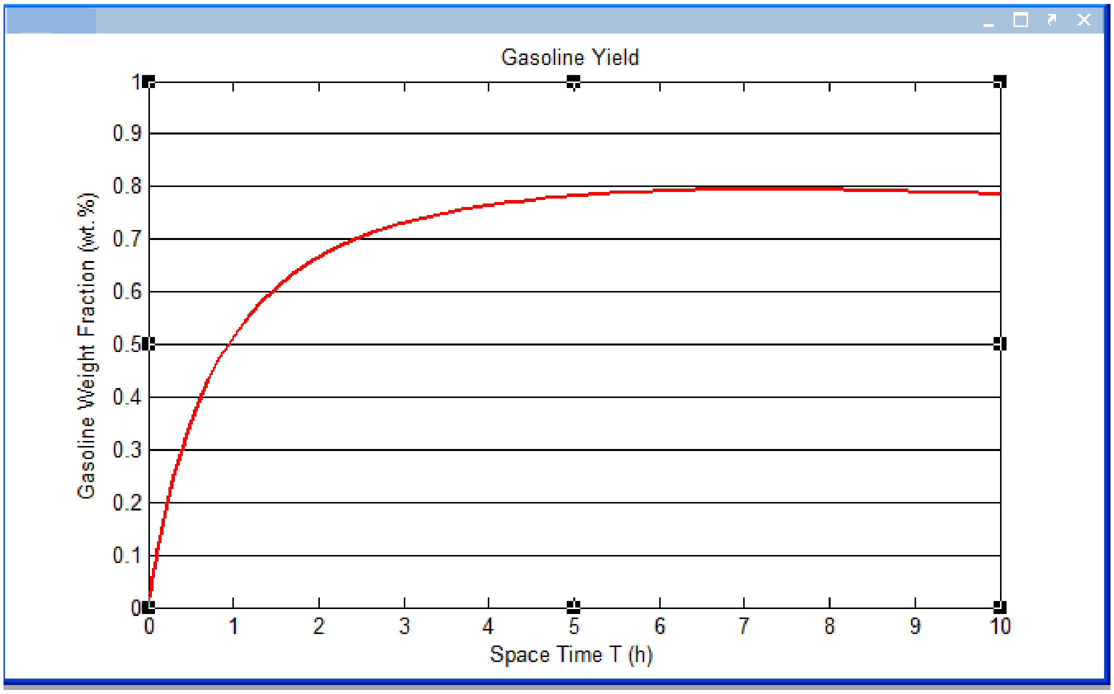


Figure (4.2) Yield of Gasoline

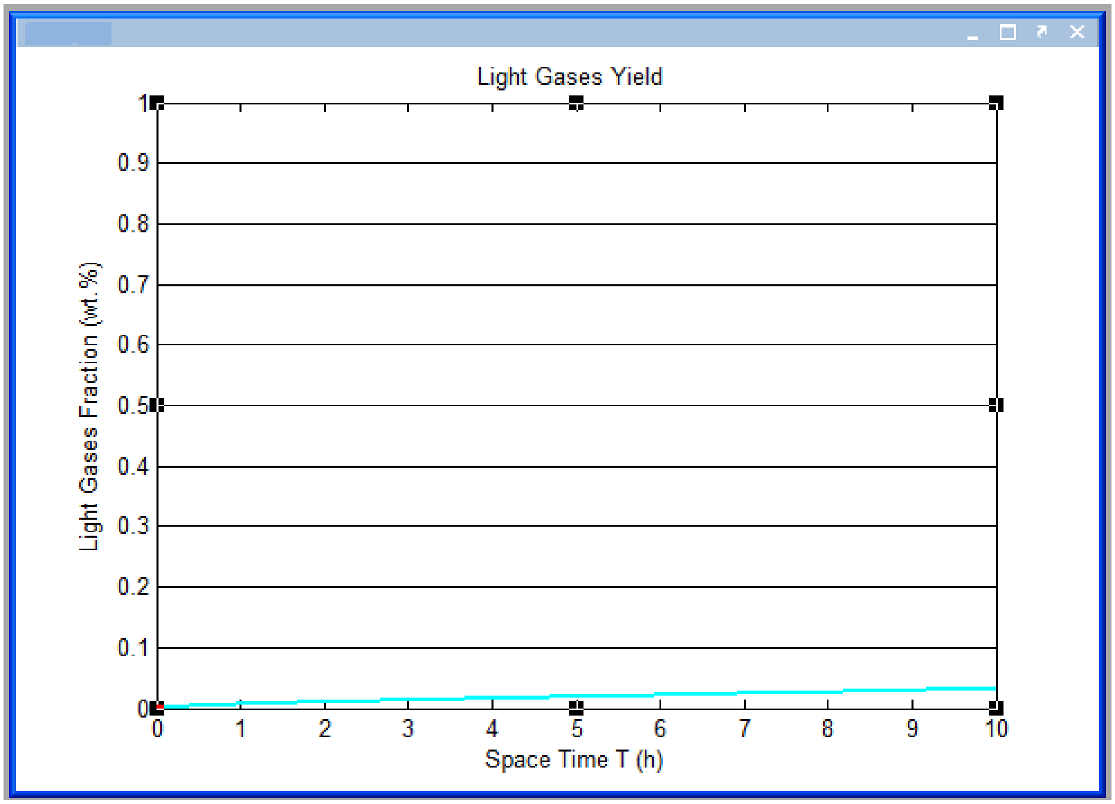


Figure (4.3) Yield of Light gases

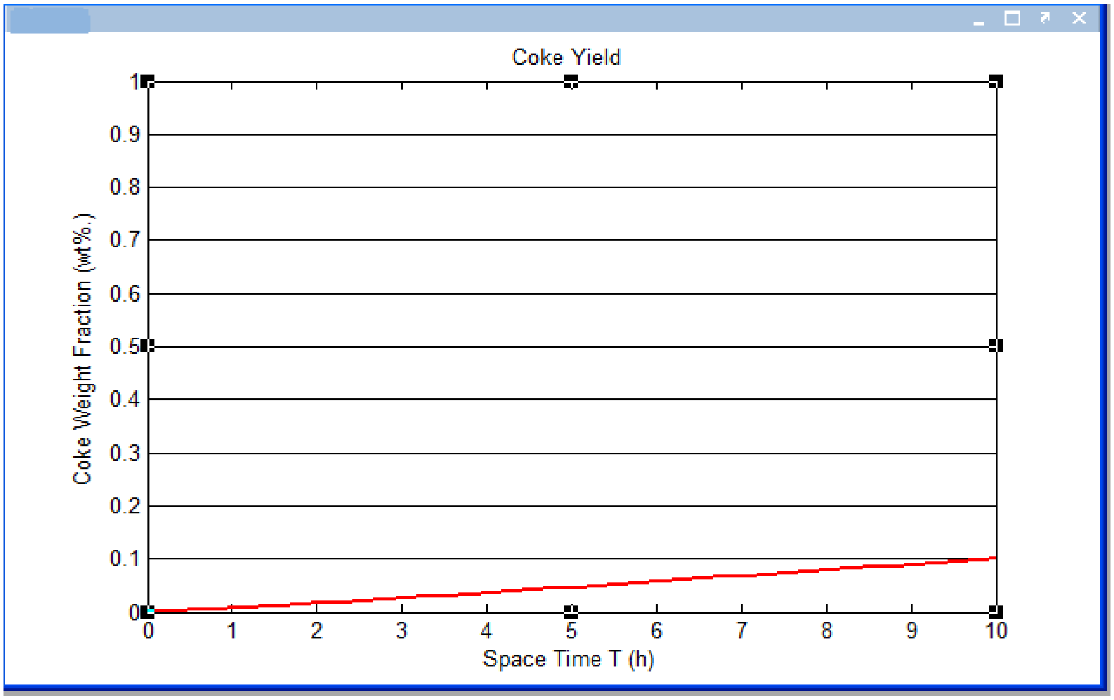


Figure (4.4) Yield of Coke

Chapter 5

Conclusion and Recommendations

5.1. Conclusion

In this work an Isothermally model for FCC unit riser reactor was developed, that combines material and heat balance of model for a four- lump kinetic scheme in order to predict the yield patterns. It was observed that the yield of gasoline increases with an increase in catalyst temperature as the rate of reaction is known to decrease with a decrease in catalyst temperature. After a certain level the production of coke is increased and hence due to deactivation of catalyst the gasoline yield starts decreasing.

5.2. Recommendations for Future Work

The following suggestions for future work can be considered:

- Developing the model to include the cyclone, VSS, and regenerator performance as well.
- Developing the model using more lumps for kinetics, multi- dimensions for the riser, and multi-phase system.
- Developing the model to taking account the friction effects between phases with the wall of the riser and between phases itself.
- Study the effect of change of any operating conditions variables on unit performance, i.e. feed temperature, feed type and C/O ratio.

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