MODELLING AND SIMULATION OF A REFINERY FLUID CATALYTIC CRACKING UNIT RISER

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MENG/SEET/2008/1898

CHEMICAL ENGINEERING DEPARTMENT

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NOVEMBER, 2012

DECLARATION

I hereby declare that this thesis titled: **Modelling and Simulation of a Refinery Fluid Catalytic Cracking Unit Riser** .Is a collection of my original research work and it has not been presented for any other qualification anywhere. Information from other sources (published or unpublished) has been duly acknowledged.

30/01/2013

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CERTIFICATION

The thesis titled: **Modelling and Simulation of the Fluid Catalytic Cracking Unit Riser** by: MOHAMMED, Halima Allurawa MENG/SEET/2008/1898 meets the regulations governing the award of the degree of Masters of Engineering of the Federal University of Technology, Minna and it is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

I dedicate this project to GOD Almighty who made this work possible and to my husband Mr. Moses Hamman and my son Jeremiah and to my late first son. I love you all so much.

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My profound gratitude goes to Almighty GOD for giving me the strength and ability to go through this program.

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ABSTRACT

The purpose of this work is to model and simulate the Fluid Catalytic Cracking Unit (FCCU) riser of a refinery having Kaduna Refining and Petrochemical Company (KRPC) Kaduna as a study. The unit's operation is cracking of heavy gasoil (VGO) to light weight oils in the presence of catalyst (zeolite). The method employed involves the collection of operating conditions, feed stock stream analysis data from the refinery which was processed in order to obtain mass fractions of the representative specie involved in the cracking reactions. A model equation was obtained and simulated using Comsol Multiphysics software. Furthermore mass and energy balance were carried out. The results of the simulation of the model showed a good agreement with the experimental results. In addition to gases and oils, gasoline obtained was 54% by weight fraction. The result obtained from the simulation was close to the data obtained from KRPC as well as results from other researchers. Thus the model obtained can be used for the simulation of crudes other than the Nigerian crude and the computational software used is recommended for the optimization of process units.

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CHAPTER ONE

1.0 INTRODUCTION

The merits of the fluid catalytic cracking unit are, firstly, that as a result of the overall speeding up of the process, the cracking temperature can be lowered somehow and the process can be conducted at a low pressure and secondly, which is most important, the selective action of the catalyst accelerates reactions that lead to the accumulation in the cracking, gasoline of arenes, iso-alkanes and iso-alkenes possessing high octane numbers (Erikh *et al.*, 1988).

The features of the catalytic cracking mechanism in comparison with thermal cracking sharply affect the composition and properties of the gas and gasoline. The gas contains less low-molecular components, but much more isobutene. The gasolines are enriched in isoalkanes and arenes (Erikh., *et al* 1988).

The need for products derived from crude oil is essential in all facets of life whether in the developed, developing or underdeveloped countries. This has led to the search for more oil reservoirs by the geologists and geophysicists and subsequent refining of this crude oil by chemical engineers and engineers from other related fields of engineering. The fluid catalytic cracking unit (FCCU) in the refinery is where feed oil (heavy hydrocarbon chain oil) from the crude distillation unit (CDU) and atmospheric distillation unit (ADU) are cracked into lighter molecules of hydrocarbons. The feed oil is contacted with catalyst in the presence of very hot air in the riser reactor which is now sent to the fractionators to give gasoline of high octane number, light gas oil, heavy gas oil, feed for petrochemical unit and coke. The coke is sent to the regenerator to be burnt off and the catalyst recycled for another operation.

Among the products of the FCCU, gasoline is the most important, in that it is used to run most motor vehicles, generators to give power and used as solvent in some industries and road side mechanics.

The reactor used in the FCCU is the most important equipment of the unit as it is the central processing unit where physical fluids or solids are converted to desired products taking into consideration the residence time in which the reaction is expected to take place in an economically viable way. In view of this, modelling of the riser reactor is important in order to achieve maximum yield of gasoline and other FCCU products.

1.1 Aim and Objectives of the Work

The aim of this work is to model and simulate the cracking reactions that occur in the riser reactor and this will be achieved using the following objectives.

1 To develop a mathematical model that describes the reactions of interest that takes place in the reactor system.

2 To investigate the influence of the riser to give light end products with high octane number.

3 To simulate the developed model using a computer programme and compare the simulated results with the experimental results.

1.2 Scope and Limitation of the Study

This work is limited to the riser of the FCCU of Kaduna refining and petrochemical company (KRPC). The study focuses its attention on the riser reactor and all the cracking reactions responsible for the heavy gasoil conversion into lighter petroleum fractions.

The simulation would be done with the use of COMSOL Multi physics software to run the energy and mass balances with the data collected from Kaduna Refining and Petrochemical Company (KRPC). These data are operating conditions, reactor dimensions, catalyst properties and feedstock composition.

1.3 Justification for the work

The justification of this work is based on the fact that petroleum refining operations is presently responsible for about 70-85% of world energy and the FCCU is an important unit in the refinery, knowing that the chief product is gasoline. Model equation developed will help to predict the behaviour and performance of riser reducing volume of laboratory experimentation and tedious calculations. The problem sometimes envisaged with industrial plant is in the changing of some variables in order to obtain better yield of product but this work intends to discover through modelling and simulation of riser on how to enhance better yield of light products. The use of COMSOL Multiphysics software version 3.4 is reasonable because it has in the Comsol Engineering Lab an environment where mass and energy balances and also chemical reactions can be simulated.

CHAPTER TWO

2.0 LITERATURE SURVEY

The fluid catalytic cracking unit in the refinery is one of the primary conversion process used to crack heavy gas oils to light weight oils in the presence of catalyst at low temperature and pressure to get gasoline that have high octane numbers which are useful to car engines. Other products are olefinic gases and coke which is sent to the regenerator to be burned off.

Crude oil is distilled in an atmospheric distillation unit to produce LPG, naphtha, kerosene and diesel oil. The residue from the atmospheric distillation unit is fed to the vacuum distillation unit where it is separated into vacuum gas oils and vacuum residue. The heavy vacuum gas oil, which normally constitutes 25-30% of the total crude oil volume, is fed to the FCCU where it is converted into lighter products (Gupta, 2006).

2.1 Process Description

2.1.1 Riser Reactor-Stripper

Most modern fluid catalytic cracking units (FCCU) have, as the most important component a riser reactor in which the catalyst contacts the feed and a cracking takes place and a regenerator where the spent catalyst is burnt off and recycled back to the reactor for another round of operation. In a modern catalytic cracker virtually all reactions take place between 1.5 to 3 seconds before the catalyst and products are separated in the reactor (Sadeghbeigi., 2000).

From the pre-heater the feed enters the riser near the base where it contacts the regenerated catalyst .The ratio of catalyst to oil is 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 1,250 ^{o} F to 1,350 ^{o} F (677 ^{o} C to 732^{o} C). Figure 2.1 shows a typical FCCU.

The catalytic reactions occur in the vapour phase. Cracking reactions begin as soon as the feed is vaporized. The expanding volumes of the vapours that are regenerated 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 a 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 vapour 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 sites on the catalyst. With high activity zeolite catalyst, virtually all the cracking reactions take place in three seconds or less (Sadeghbeigi., 2000).

Risers are normally designed for an outlet vapour 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 (Sadeghbeigi., 2000). One of the most important process differences in FCC units relates to the location and control of the cracking reaction. Until about 1965, most units were designed with a discrete dense-phase fluidized-catalyst bed in the reactor vessel. The units were operated so most of the cracking occurred in the reactor bed. The extent of cracking was controlled by varying reactor bed depth (time) and temperature. Although it was recognized that cracking occurred in the riser feeding the reactor because the catalyst activity and temperature were at their highest there, no significant attempt was made to regulate the reaction by controlling riser conditions. After the more reactive zeolite catalysts were adopted by refineries, the amount of cracking occurring in the riser (or transfer line) increased to levels requiring operational changes in existing units. As a result, most recently constructed units have been designed to operate with a minimum bed level in the reactor and with control of the reaction being maintained by a varying catalyst circulation rate (Gary and Handwerk 2001).Figure 2.1 shows a simple diagram of a modern refinery with the riser as a vertical pipe.

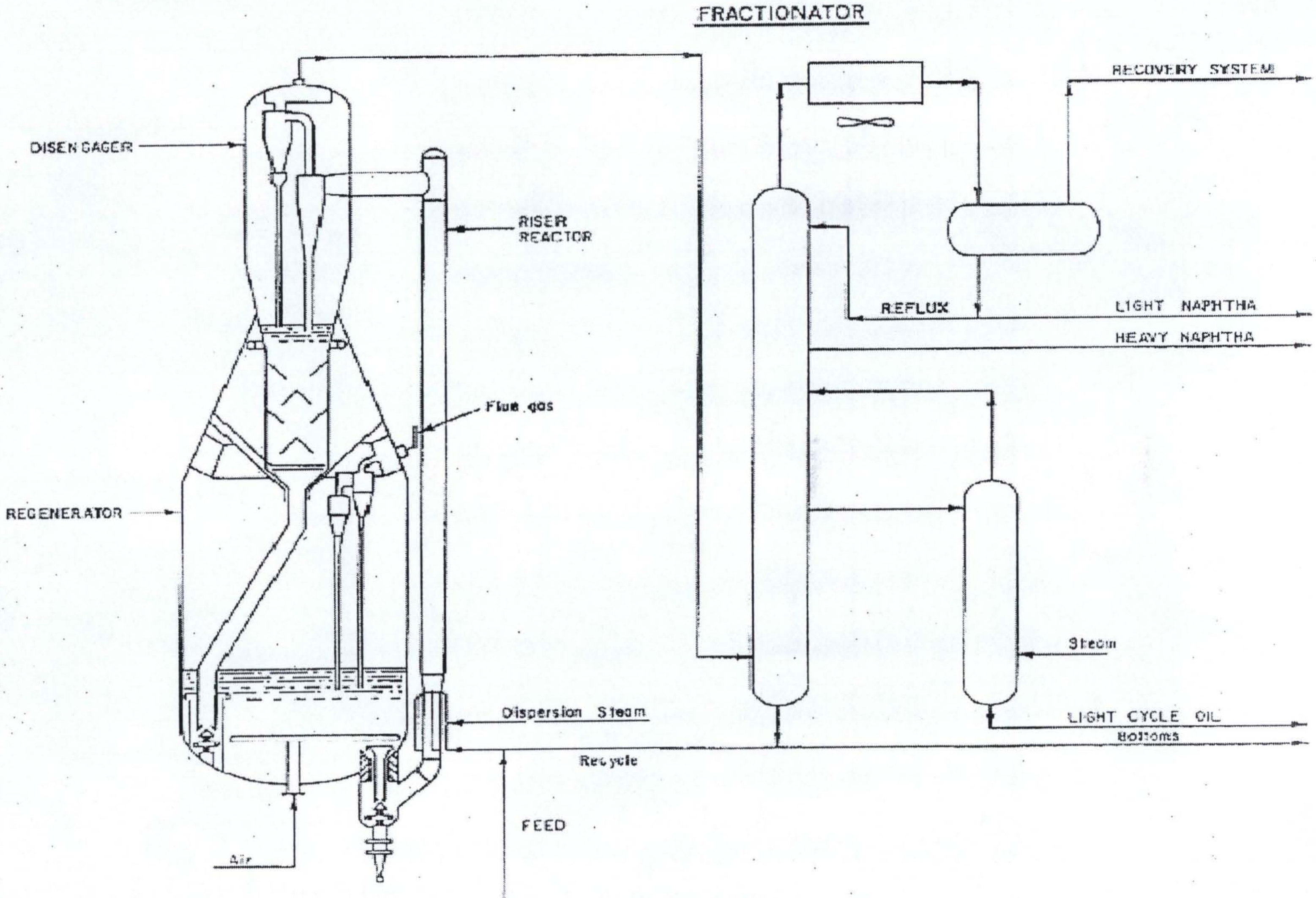


Figure 2.1: FCC UNIT

2.1.2 Regenerator

The catalyst is moved from the reactor to the regenerator by the flue gases and from the regenerator to the reactor by hot air. The bottom part of the gas (air) lift called a batcher helps the catalyst get into the stream of gas. The regenerator is an apparatus with a square cross section of 3×3m and 27m high made from carbon steel with an internal lining of refractory bricks (Sadeghbeigi., 2000).

2.2 Catalysts and Reactions in Catalytic Cracking

A catalyst can be defined as a substance that increases the rate of a chemical reaction without itself undergoing any change. Thus, the use of fine catalyst is employed in cracking reactions in different forms. Commercial cracking catalyst can be divided into three classes (Gary and Handwerk 2001).

i. Acid- treated aluminosilicates,
ii. Amorphous synthetic silica-alumina combinations, and
iii. Crystalline synthetic silica-alumina catalyst called zeolites or molecular sieves.

The advantages of the zeolites catalyst over the natural and synthetic amorphous catalysts are:

i. Higher activity
ii. Higher gasoline yield at a given conversion.

iii. Production of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons.

iv. Lower coke yield (and therefore usually a larger through put at a given conversion level)

v. Increased isobutane production.

vi. Ability to go to higher conversions per pass without over cracking (Gary and Handwerk 2001).

2.2.1 **Catalyst Deactivation**

A feature of catalytic cracking catalyst is their rapid deactivation. The catalyst pores become clogged with coke after 10-15 minutes of operations. Therefore cracking constantly has to be alternated with catalyst regeneration. Catalytic processes with frequent change of the cycles of operation and regeneration are called cyclic ones (Erikh *et al.*,1988).

Catalyst can also be deactivated by fouling whereby coke and / or metals deposit can block the catalyst pores and thereby limit the mass transfer.

Reversible deposits (nitrogen coke) are removed during regeneration. If we assumed that the poisoning effect will increase with concentration then the poisoning effect will be inversely proportional to the catalyst - to – oil ratio (CTO) and therefore will be dependent on the coke selectivity of the catalyst. Irreversible catalyst poisons (metals) on the other hand, will build up and continue to interact with the catalyst.

in (liquid) eutectic melts on the surface of the catalyst particles, which can be block the important entrance pores and even glaze catalyst surface completely (O'Connor, 2001).

2.3 Mechanisms in catalytic cracking

2.3.1 Carbonium ion theory

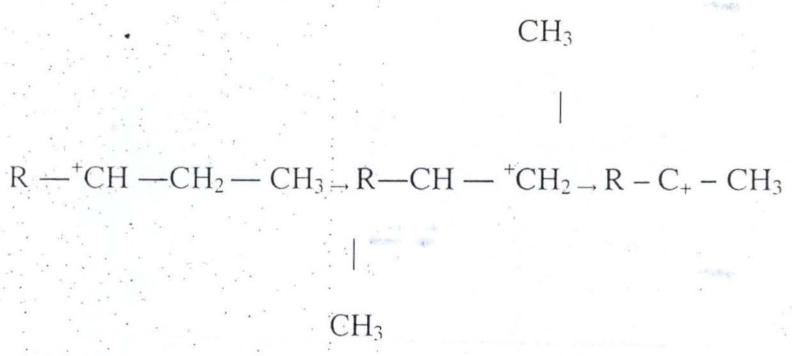
Carbonium ions are similar to their ammonium counterparts and contain a trivalent positively charged carbon atom. They form the easiest when in a proton of the catalyst reacts with an alkene.

$$R - CH = CH_2 + H^+ \rightarrow R - {}^{+}CH - CH_3$$

The unstable carbonium ions tend to acquire more stable forms by internal regrouping or reaction with other molecules. They are distinguished by a very high reactivity and can enter into the most diverse reactions.

The following transformations are the most typical of carbonium ions.

1. Regrouping of the atom in a molecule with the relocation of hydrogen or methyl group, i.e. in other words, skeleton isomerization leading to the formation of an isomer ion.



$$R-{}^{+}CH-CH_2-CH_3 \rightarrow R-\underset{\displaystyle CH_3}{\underset{|}{CH}}-{}^{+}CH_2 \rightarrow R-\overset{\displaystyle CH_3}{\overset{|}{C_{+}}}-CH_3$$

2. Reaction with neutral molecules with the formation of new carbonium ions and new saturated or unsaturated molecules.

$$R-{}^{+}CH-CH_3+C_4H_{10}\rightarrow C_4H_9^{+}+R-CH_2-CH_3$$

$$R-{}_{+}CH-CH_3+C_4H_8\rightarrow C_4H_9^{+}+R-CH=CH_2$$

Consequently, a carbonium ion can either detach a proton from other molecules or transfer its proton to alkenes and transform into a stable alkene.

3. A carbonium ion with a large number of carbon atoms generally decomposes along a 2nd position bond, counting from the charged carbon atom. The decomposition products are an alkenes and carbonium ion with a smaller number of carbon atoms.

$$CH_3-{}_{+}CH-CH_2-R\rightarrow CH_3-CH=CH_2+R^{+}$$

Carbonium ion cracking mechanism produces a higher yield of a much more desirable gasoline than thermal cracking. While thermally cracked gasoline is quite olefinic, catalytically cracked gasoline contains a large amount of aromatics and branched compounds which is beneficial for the gasoline octane numbers (RON and MON) (O'Connor).

2.3.2 Alkanes

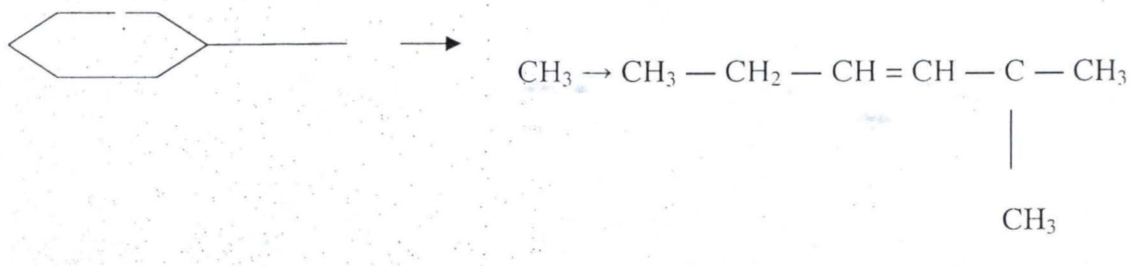
The alkane when cracked decomposes into an alkene and alkane of a lower molecular mass. One possible reaction might be:

$$\underset{}{C_{15}H_{32}} \rightarrow \underset{\text{Ethene}}{C_2H_4} + \underset{\text{propene}}{C_3H_6} + \underset{\text{octane}}{C_8H_{18}}$$

2.3.3 Alkenes

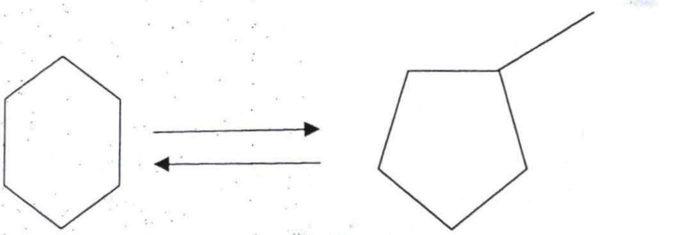
In addition to decomposition, the alkenes enter into reaction of polymerization – depolymerisation, isomerisation, hydrogen redistribution and cyclization. The isomerisation reactions are especially diverse. They include structural regroupings, migration of a double bond along the chain, and sometimes also cis – and trans-isomerisation.

1) **Decomposition Reaction**

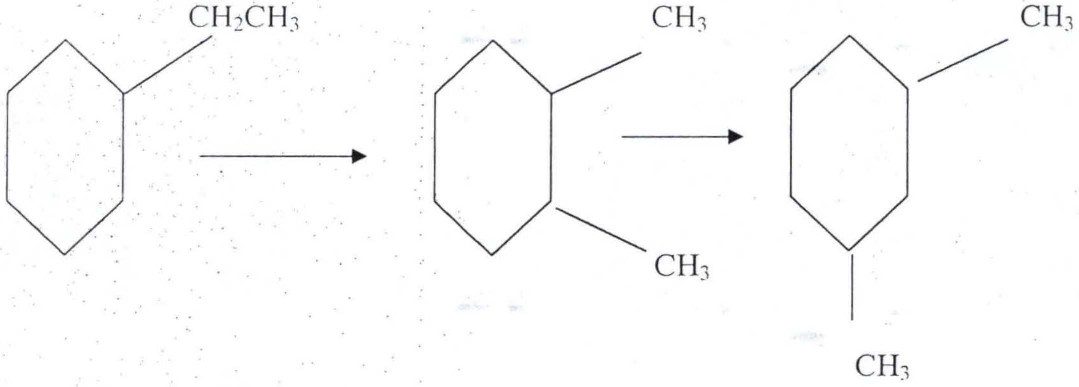


$$\longrightarrow CH_3 \rightarrow CH_3 - CH_2 - CH = CH - \underset{\displaystyle CH_3}{\underset{|}{C}} - CH_3$$

2) **Ring Isomerisation**

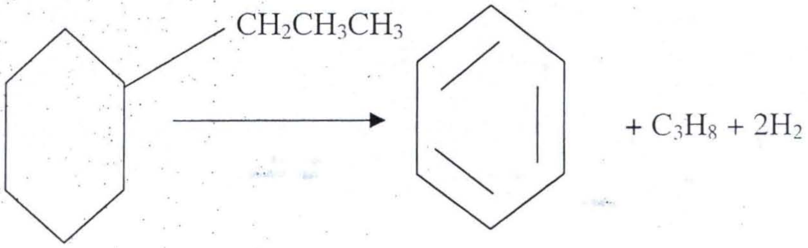


3) **Side chain redistribution (migration of substitutes)**



4) **Dehydrogenation and Dealkylation** of cycloalkanes proceed with redistribution of the hydrogen. As a result, arenes and alkenes accumulate in the cracking products.

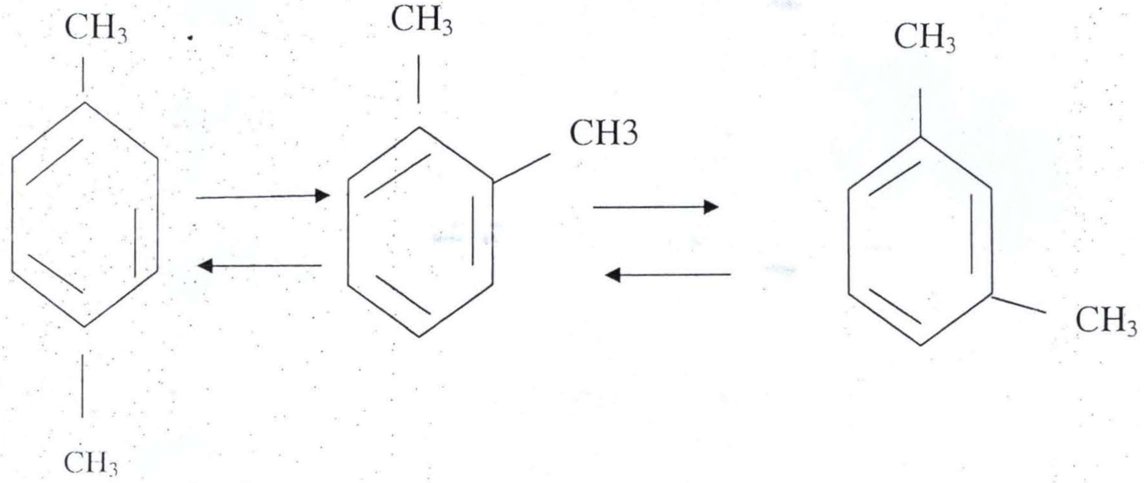
For example:

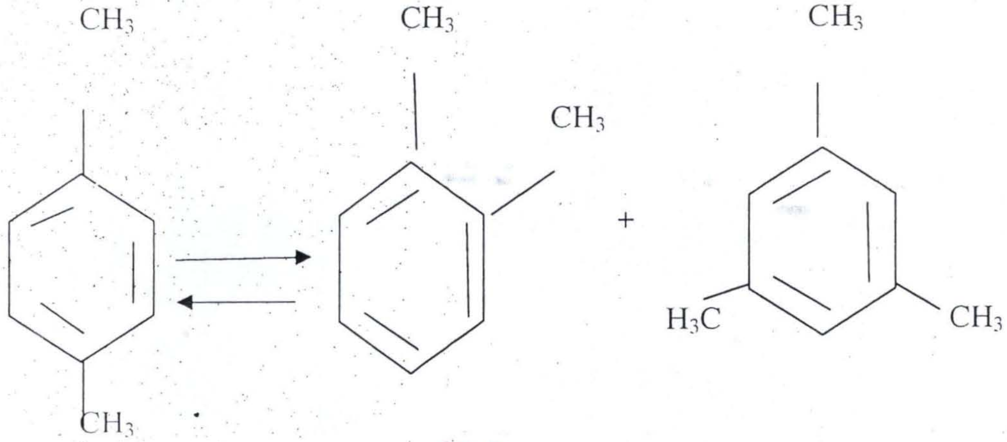


2.3.4 Arenes

Benzene homologues generally lose their side chains completely, which lead to the accumulation of benzene.

Polymethylated benzene homologues are readily isomerised with the redistribution of the methyl groups. Thus, in the cracking of P-xylene, the reaction products were found to contain toluene, trimethyl benzene and O-xylenes.





2.4 Hydrocarbon Types

2.4.1 Normal Paraffins: These crack mostly to olefins and paraffins and give fair yields of very light gasoline (mostly C_5 and C_6 hydrocarbons). The normal paraffins are fairly difficult to crack (Bollas and Vasalos 2004).

The reaction rates and products of paraffin cracking are determined by the molecular size and structure. Paraffinic molecules containing tertiary carbon atoms crack most readily, where as quaternary carbon atoms are more resistant to cracking.

2.4.2 Naphthenes and Iso-paraffins tend to crack about the same rate but the product distributions are much different. Naphthenes produce relatively little gas and give excellent yields of gasoline, of better quality than that from paraffin cracking and contain appreciable quantities of aromatics, resulting from dehydrogenation of the naphthene ring (Bollas and Vasalos 2004).

2.4.3 Aromatics crack in several ways. The benzene ring is practically impossible to crack. Condensed ring aromatics without side chains are converted to a limited extent, but almost entirely to coke. Alkyl aromatics with side chains containing at least three carbon atoms crack extensively by shearing off the entire side chain. With long side chains, secondary reactions will occur, resulting in products similar to those from the cracking of olefins and paraffins. Generally, more aromatic feeds give poorer FCC yields. A contributing factor to this general trend is that, as the number of ring structures in the feed increases, the likelihood increases that dehydrogenation from contaminant metals will cause multi-ring aromatics to form, leading to condensation and coking of the catalyst. The molecular structure of the aromatic hydrocarbons is another important issue regarding their crackability. The distribution of aromatics among the degree of condensation clearly affects the rate of cracking. As the number of rings in polynuclear aromatic molecules increases, the rate of cracking decreases although the aromatic content appears to remain the same.

The net result of the catalyst cracking of aromatic hydrocarbons is moderate yields of gas, very little gasoline, large quantities of very aromatic cycle stock and high coke yields (Bollas and Vasalos 2004).

2.4.4 Olefins seldom appear in catalytic cracking feeds but their reactions are of interest because they are the primary products of other cracking reactions. Olefins heavier than about C_6 are extremely reactive. The products of olefin cracking are primarily propylene and butenes, along with butanes from secondary reactions, since polymerization and cyclization takes place in olefin cracking to produce a small amount of cycle stock and fairly high coke yields (Bollas and Vasalos 2004).

2.5 Lumps Development

The catalytic cracking kinetics is also of great importance for the correct prediction of mass fraction concentrations at the riser's output section. Just like it was shown for the fluid flow, there are many kinetic models in the literature for modelling of the cracking reactions in a FCC riser reactor. The important thing to be considered in a simulation is to recognize what is the main goal of the work and then select the most appropriate kinetic model for the specific use (Souza., *et al* 2007).

2.5.1 Total Lumping of Petroleum Fractions

Total lumping may be viewed as a limiting case of partitioned based lumping. There one is primarily interested in the overall behaviour of a petroleum fraction. For instance, refiners would very much like to be able to predict how the overall behaviour (e.g. HDS level) changes as feeds vary. Process developers want to know how different reactor types affect the overall behaviour and it is important for catalyst developments to rank exploratory catalyst based on their activities for the overall conversion of the feed (Ho, 1995).

2.6 COMSOL Multiphysics

The COMSOL Multiphysics engineering simulation software environment facilitates all steps in modeling process defining the geometry, meshing, specifying physics, solving and then visualizing the result.

Model set-up is quick, thanks to a number of predefined physics interfaces for applications ranging from fluid flow and heat transfer to structural mechanics and electromagnetic analysis. Material properties, source terms and boundary conditions can all be arbitrary functions of the dependent variables and predefined multiphysics application templates solve many common problem types (COMSOL, 2007).

2.6.1 COMSOL Reaction Engineering Lab

The COMSOL Reaction Engineering Lab® is a tool that uses reaction formulas to create models of reacting systems. In this context, a model means the material, energy, and momentum balances for a system. The Reaction Engineering Lab not only defines these balances, it can also solve the material and energy balances for space-independent models, balances, it can also solve the material and energy balances for space-independent models, that is, for models where the composition and temperature in the reacting system vary only in time. For space-dependent models, the Reaction Engineering Lab offers a direct coupling to the Chemical Engineering Module, the MEMS Module, and the Earth Science Module. This direct link enables you to create models involving material, energy, and momentum balances in COMSOL Multiphysics® directly from a set of reaction formulas. Included in these models are the kinetic expressions for the reacting system, which are automatically or manually defined in the Reaction Engineering Lab. You also have access to a variety of ready-made expressions in order to calculate a system's thermodynamic and transport properties.

In addition to the formulation and solution of models from reaction formulas, the Reaction Engineering Lab also lets you perform parameter estimation calculations. Using this feature you can readily extract kinetic parameters from experimental data. Furthermore, in combination with COMSOL Script, the Reaction Engineering Lab can implement parametric studies and custom post preprocessing (COMSOL 2007).

CHAPTER THREE

3.0 METHODOLOGY

3.1 Materials

1. Plant Stream Analysis

2. Operating conditions and Plant data for KRPC (Table 3.3)

3. Comsol Multiphysics Software version 3.4

3.2 Feed Stream Analysis

The feedstock used is vacuum gas oil (VGO) and is characterized from carbon number C_1-C_{40}.The plant stream gotten from KRPC see appendix A was analyzed by plotting the individual boiling points in to a True Boiling Point (TBP) graph (Figure 4.1) using Microsoft Excel.

From this graph, the volume fractions of the feed stream constituents were obtained and also the representative specie for each lump was selected. Each types of hydrocarbon react under catalytic cracking conditions in certain definite ways. The major difference among hydrocarbons of a particular type is in their "crackability" or extent of conversion for a given set of operating conditions (Bollas et al 2004).

3.3 The Lumping Strategy

In modelling crude fractions that are a mixture of many hydrocarbons with a wide range of carbon numbers and physiochemical characteristics, modellers have found it helpful to group hydrocarbon species with similar properties into new representative species with averaged properties in an attempt to capture the entire crude fractions to arrive at a model that is easier to handle. This strategy employed is referred to as Lumping of the overall feedstock in to smaller groups or categories.

However, it is left at the modeller's discretion on how 'accommodating' or how large a lump should be. The smaller and more critical a lump is, the better its quality. In refineries, each lump quality is governed by the operating conditions and characteristics of the main fractionators. As a consequence, the number of lumps established in most kinetic models is commonly related with the number of boiling point cuts considered in the fractionators (Hernandez-Barajas *et al.*, 2008).

The modified six lump model is used in this work. It is defined by the following cuts: heavy cycle oil (C_{21}+), light cycle oil (approximately C_{15} – C_{21}), heavy naphtha (approximately C_{13} – C_{14}), light naphtha (approximately C_5- C_{12}), butane- butylenes (C_4) and light gases (C_1-C_3). These definitions refer to approximate boiling point cuts through the range of boiling points depending on each operating case (Hernandez – Barajas *et al.*, 2008).This is shown in Table 3.1

TABLE 3.1 CUTS DERIVED FROM BOILING POINTS

CUTS	BOILING POINT RANGE (K)	NAMES
C_{21}+	641.8^{+}	Heavy Cycle oil (HCO)
$C_{15} - C_{21}$	543.8 – 629.7	Light Cycle oil (LCO)
$C_{13} - C_{14}$	508.62 – 526.23	Heavy Naphtha (HN)
$C_4 - C_{12}$	309.21 – 489.47	Light Naphtha (LN)
C_4	266.89	Butane – Butylenes (BB)
$C_1 - C_3$	111.67 – 231.05	Light Gases (LG)

Source of Boiling Points: Handbook of Chemistry and Physics.87th Edition David R.Lide

TABLE 3.2 REPRESENTATIVE SPECIE FOR EACH CUT AND ITS EXTENT OF CRACKING

LUMP NO.	RANGE	PRESENCE IN FEED	TYPE	EXTENT OF CRACKING	REP. SPECIE	MW (g/mol)
1	C_{21}+	Yes	P,O, N, A	Yes	P_{30}	422
2	C_{15}- C_{21}	Yes	P,O, N, A	Yes	P_{18}	254
3	C_{13}-C_{14}	Yes	P, O, N, A	Yes	P_{14}	198
4	C_5-C_{12}	Yes	P, O, N, A	Yes	P_8	114
5	C_4	Yes, very few	P, O	Yes, very well	O_4	54
6	C_1–C_3	No	P, O	Yes	P_2	28

P – Paraffin; O – Olefin; N – Naphthene, A – Aromatic

Table 3.2 shows the representative species for each lump and their presence in the feed. The representatives for each lump is selected as the member in the 'middle' because it was observed in the TBP graph (Figure 4.1) that fairly equal volume percents exist amongst members of both the 1st and 2nd lump. Hence, it is assumed that there will be equal representation as they crack into members of the rest of the lumps.

TABLE 3.3 THE OPERATING CONDITIONS OF A REFINERY (KRPC)

OPERATING PARAMETERS	VALUE
Preheat feed temperature (K)	593
Riser inlet temperature (K)	793
Riser outlet temperature (K)	773
Feed flow rate of liquid feed (m^3/s)	0.0230556
Length of Riser (m)	27.5
Diameter of riser (m)	1.35
Catalyst to oil ratio	6

3.4 Development of Modelling Technique

To model a riser using a batch reactor model, the following assumptions are observed.

1. The reacting fluid is gas which is assumed to behave as an ideal gas.
2. Perfectly mixed system was taken into consideration.
3. The system is assumed to be an adiabatic one.
4. A batch reactor is used for the work.
5. Instant vaporization occurs at the inlet of the riser.
6. The reaction is an endothermic one.
7. One dimensional fluid flow is considered.

The rate constants used for the model are obtained from literature (Hernandez – Barajas *et al.*, 2008) as shown in Table 3.4 and the number of kinetic constants and reaction pathways are obtained using empirical correlations which are shown in appendix B.

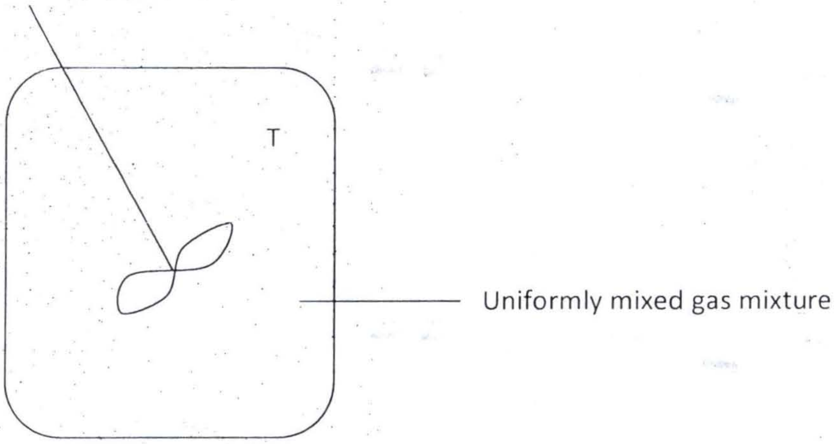


Figure 3.1 A Simple Batch Reactor

The variables to be used for the model equations are;

i = specie (compound)

j = reaction

N = highest number of reactions

M = highest number of species

c_i = specie molar concentration (mol/m^3)

c_{rate} = rate of concentration change ($mol/m^3.s$)

V = model reactor volume (m^3)

n = order of reaction j.

r = reaction rate ($mol/m^3.s$)

k_j = reaction constant for reaction j ($[m^3$ of gas/(g of catalyst s)$][m^3$ of gas/mol$]^{n-1}$)

$C_{p,i}$ = heat capacity for specie i (J/mol.K)

sf = scaling factor (unity)

ρ = density of catalyst (g/m^3)

ΔH = enthalpy (J/mol.s)

Q_j = Heat effect due to reaction j. (J/s)

Q_{rate} = rate of energy change (J/s)

3.4.1 Mass Balance

For a simple reactor, the conservation of mass principle for a constant volume is:

{rate of accumulation of specie within reacting volume} = {rate of specie input into system} - {rate of specie output from system} ± {rate of generation/consumption of specie within system} 3.1

$$\Delta c_{rate-i} = c_{i,\ rate\text{-}in} - c_{i,\ rate\text{-}out} \pm c_{i,\ rate\ \text{-}generation/\mathrm{Consumption}} \quad 3.2$$

With the assumption that for our closed batch reactor, there is no rate of specie input c_{in} or rate of specie output c_{out} through the boundaries, 3.2 reduces to;

$$\Delta c_{rate-i} = \pm\, c_{rate\ \text{-}generation/Consumption} \quad 3.3$$

In the batch reactor, generation or consumption is due to reaction of species. The molar rate of reaction for a batch which is given as;

$$\mathrm{r_i} V = \pm\, dc_i\, /dt \quad 3.4$$

And for the non-elementary reactions in catalytic cracking, the reaction rate is given as;

$$dc_{i,j}\, /dt \;=\; k_j\, c_{i,j}^{\;n,\,j} \quad 3.5$$

Substituting equation 3.5 into equation 3.4 the following is obtained

$$\mathrm{r_i} V \;=\; k_j\, c_{i,j}^{\;n,\,j} \quad 3.6$$

Now, to account for the $c_{rate\ \text{-}generation/Consumption}$, substitute equation 3.6 into equation 3.2;

$$\Delta c_{rate\text{-}i,j} = k_j \, c_{i,j}^{\;n,j} \qquad 3.7$$

Summing up all reactions j for where specie i appear gives as a final mass balance equation per specie;

$$\Delta c_{rate-i} = \sum_{i,j}^{N} [k_j \, c_{i,j}^{\;n,j}] \text{ (mol/kg of catalyst. s)} \qquad 3.8a$$

To convert the unit of the above equation into an overall unit to account for what is going in the reactor, a scaling factor (sf) and the catalyst density (ρ) are used to account for the 'diffused rate' when the reaction is scaled throughout the entire reactor and for the fractional volume occupied by the catalyst respectively. When applied, this converts equation 3.7 to:

$$\Delta c_{rate-i} = \frac{sf}{\rho} \sum_{i,j}^{N} [k_j \, c_{i,j}^{\;n,j}] \qquad \text{(mol/m}^3\text{ of reactor. s)} \qquad 3.8b$$

3.4.2 Heat of Reaction.

The Standard heat of reaction is defined as the energy absorbed by the system when the products after reaction are restored to the same temperature as the reactant. The variation of heat of reaction with temperature depends on the difference in molal heat capacities of the products and reactants (Smith., 1981).

$$\Delta H_{Tj} = \Delta H_{T_0} + \int_{T_0}^{T} \Delta C_{pi} dT \qquad 3.9$$

This equation relates ΔH at any temperature T to the known value at the base temperature T_0.

However, what is of interest in this work is heat of reaction at any temperature as the reaction is not carried out at standard temperature of 298K. Comsol Multiphysics allows the use 0K as the base or reference temperature. Hence this reduces ΔH_{T_0} to zero (i.e the enthalpy of any substance at absolute zero).

Therefore, equation 3.8 for any given reaction per mole reduces to ;

$$\Delta H_{Tj} = \int_{T_0}^{T} C_{pi} dT \qquad 3.10$$

According to NASA polynomial (2005) analysis, the heat capacity of specie at any temperature is given by a Fourier series of 5 constant coefficients;

$$C_{pi} = \mathrm{R}\ (\mathrm{a}_1 + \mathrm{a}_2\mathrm{T} + \mathrm{a}_3\mathrm{T}^2 + \mathrm{a}_4\mathrm{T}^3 + \mathrm{a}_5\mathrm{T}^4) \qquad 3.11$$

Hence substituting 3.11 into 3.10;

$$\Delta H_T = \mathrm{R} \int_{T_0}^{T} (\mathrm{a}_1 + \mathrm{a}_2\mathrm{T} + \mathrm{a}_3\mathrm{T}^2 + \mathrm{a}_4\mathrm{T}^3 + \mathrm{a}_5\mathrm{T}^4) \qquad 3.12$$

Integrating and factorizing out T now gives:

$$\Delta H_{Ti} = \mathrm{RT}\ (\mathrm{a}_1 + 0.5\ \mathrm{a}_2\mathrm{T} + 0.33\ \mathrm{a}_3\mathrm{T}^2 + 0.25\ \mathrm{a}_4\mathrm{T}^3 + 0.20\ \mathrm{a}_5\mathrm{T}^4 + \mathrm{a}_6) \qquad 3.13$$

N/B: The additional coefficient a_6 is the constant of integration

Therefore at any given temperature, the enthalpy of reaction will always be calculated as:

$$\Delta H_{Tj} = \sum (\ \Delta H_{Products}) - \sum(\ \Delta H_{Reactants}) \qquad 3.14$$

The rate of enthalpy change in the reacting system is a cumulative of all heat addition/consumption effects of all the reactions. This is given as;

$$Q_{\text{rate -generation/Consumption}} = \sum_{j}^{N} (\Delta H_{Tj} * r_j) \qquad 3.15$$

Where Q j is heat source of reaction, we then have;

$$Q_{\text{rate -generation/Consumption}} = \sum_{j}^{N} (Q_j) \qquad 3.16$$

3.4.3 Energy balance

To ascertain the quantity of heat required for the cracking reaction, an energy balance is given using the basic equation thus;

{Rate of accumulation of energy within the system} =

{Rate transfer of energy into system through system boundary} - {Rate of transfer of energy out of system through system boundary} + {Rate of energy generation/consumption within system} 3.17

$$\Delta Q_{rate-System} = Q_{\text{rate-}in} - Q_{rate\text{-}out} \pm Q_{rate\text{-}eneration/Consumption} \qquad 3.18$$

With the assumption that for an adiabatic batch reactor, there is no rate of energy input Q_{in} (i.e stirring work, W_s) or rate of energy output Q_{out} (i.e expansion work, PdV) through the boundaries, 3.16 reduces to;

$$\Delta Q_{rate-System} = \pm \mathrm{Q}_{rate\text{-}Generation/Consumption} \qquad 3.19$$

Substituting equation 3.15 into equation 3.18

$$\Delta Q_{rate-System} = \sum_{j}^{N} (\mathrm{Q}_{j}) \qquad 3.20$$

This is the overall energy balance and the model equation for the simulation.

The effect of the rate of heat absorbed by or desorbed from a system, $\Delta Q_{rate-System}$ in (J/s) can be quantified with the traditional definition of molar heat capacity being;

$$\Delta Q_{rate-System} = \sum_{i} \mathrm{c}_{i}\, \mathrm{C}_{p,i} \frac{dT}{dt} \qquad 3.21$$

Substituting this into equation 3.19, we have:

$$\sum_{i} \mathrm{c}_{i}\, \mathrm{C}_{p,i} \frac{dT}{dt} = \sum_{j}^{N} (\mathrm{Q}_{j}) \qquad 3.22$$

3.5 Reaction pathways / Rate constants.

The maximum number of reaction pathways and consequently of rate constants can be calculated as thus (Hernandez – Barajas., *et al* 2008);

$$\text{Number of pathways} = \frac{N!}{2!(N-2)!} = \frac{N(N-1)}{2} \qquad 3.23$$

Calculations are in Appendix C

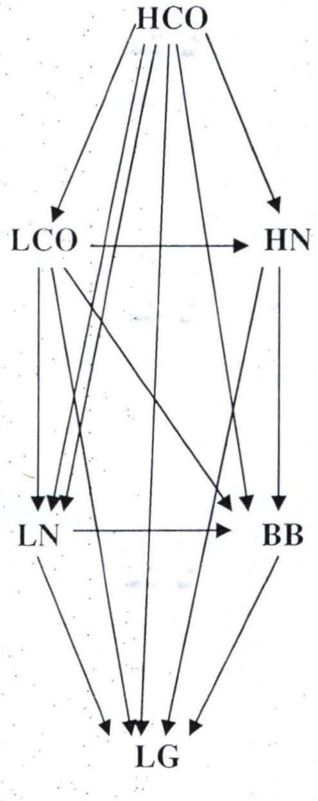


Figure 3.2 The Kinetic Network

3.6 The Kinetic Constants

The kinetic constants in Table 3.4 used for this model is versatile as it possesses the following properties;

1. It is temperature insensitive; hence, the temperature dependence of the Arrhenius equation is not required.
2. The kinetic constants which were derived from experimental works were calculated for a limited range of temperatures which is the operating temperature ranges of the FCCU unit, hence, these kinetic parameters could not be used for initial temperatures well below 790K.
3. The unit of the kinetic constants was expressed in per catalyst volume basis; hence, this allows us to use this model for any other catalyst to feed ratios in FCCU operations.

TABLE 3.4 Kinetic Constants for the six lumps used for the Simulation.

kHCO,LCO = 8.24E_1	kHCO,HN = 3.01E_1	kHCO,LN = 3.78E_1
kHCO,BB = 7.22E_4	kHCO,LG = 3.87E_4	kLCO,HN = 1.67E_1
kLCO,LN = 3.81E_1	kLCO,BB = 8.67E_4	kLCO,LG = 4.76E_4
kHN,LN = 5.42E_1	kHN,BB = 1.09E_1	kHN,LG = 6.15E_2
kLN,BB = 2.61E_4	kLN,LG = 3.11E_4	kBB,LG = 2.51E_2

$$r_j = \sum v_{ij} . k_{ij} c_i^{n2} - \sum k_{ji} c_j , \quad j = 1, 2 \ldots N \qquad 3.24$$

Equation 3.24 can be written to describe the disappearance and generation of the heaviest lump to the lightest lump thus as shown in Table 3.5

TABLE 3.5 Generation and Disappearance of Species.

Lump g	Generation	Disappearance
r_1	$= 0$	$- (k_{1,2} + \ldots + k_{1,N}) c_1^{n1}$
r_2	$= v_{1,2} k_{1,2} c_1^{n1}$	$- (k_{2,3} + \ldots + k_{2,N}) c_1^{n2}$
:	:	:
:	:	:
:	:	:
r_{N-1}	$= v_{1,N-1} k_{1,N} c_1^{n1} + \ldots + v_{N-2,N-1} k_{N-2,N-1} c_{N-2}^{nN-2}$	$- (k_{N-1,N}) c_{N-1}^{nN-1}$
r_N	$= v_{1,N} k_{1,N} c_1^{n1} + \ldots + v_{N-1,N} k_{N-1,N} c_{N-1}^{nN-1}$	0

Table 3.5 shows that the reaction rate for lump 1, r_1 includes only disappearance of species and no generation because it is the biggest lump and hence can only be cracked and not cracked into. Conversely, the smallest lump N has its reaction rate r_N as only including generation terms and no disappearance since it is the smallest lump.

k_{ji}, k_{ij} = reaction rate constants (m^3 of gas/kg of catalyst) [m^3 of gas/kg mol]$^{n-1}$

v_{ij} = stoichiometric coefficient

M = molecular weight

n = order of reaction

g = lump

The stoichiometric coefficients are calculated using $v_{ij} = M_i/M_j$ as shown in appendix B

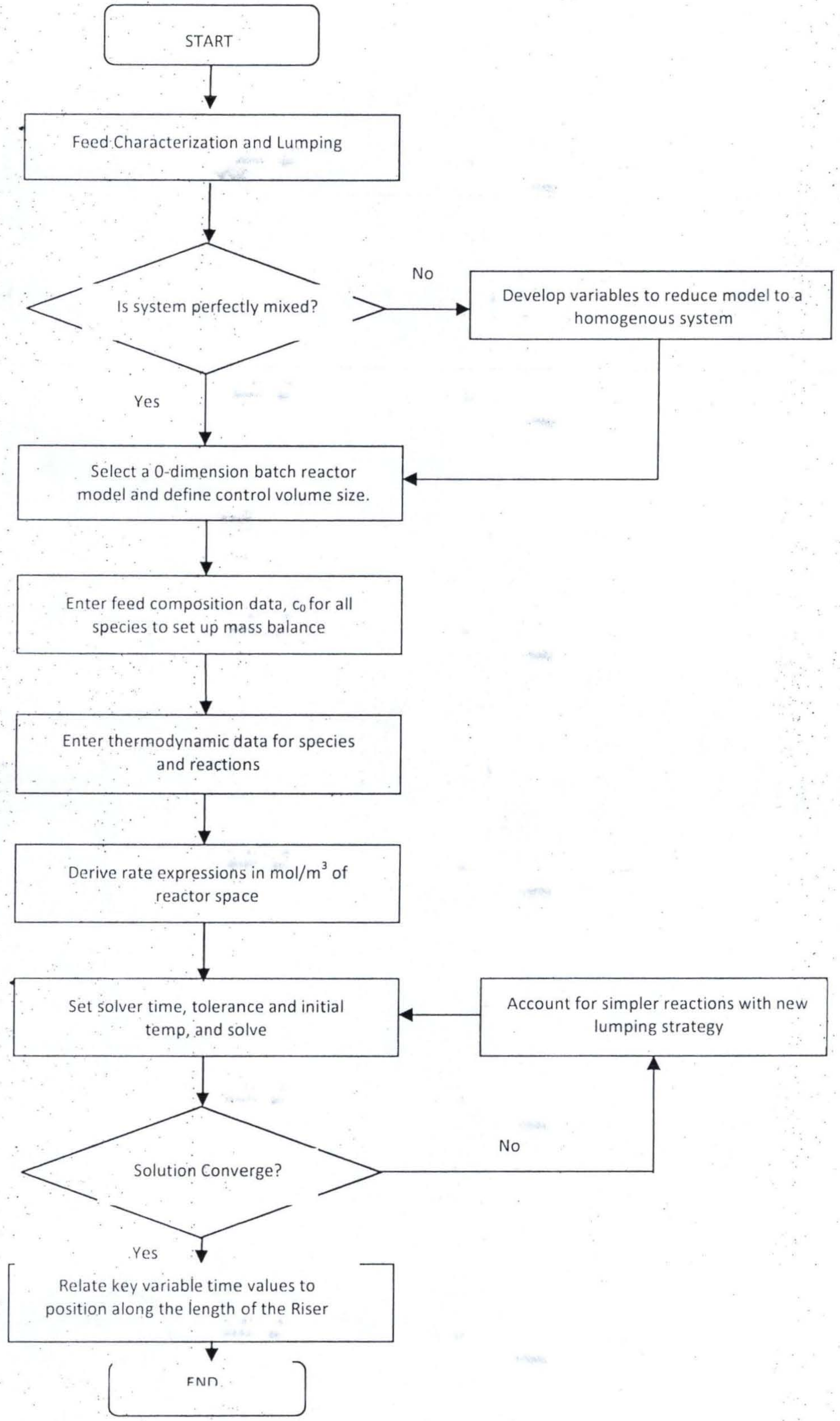


Fig 3.3 Simulation Flow Chart for FCCU Riser Model

3.7 Steps for Gathering Data for Model Input

1. Analysis from the TBP graph was carried out to determine the percentage volumetric cuts of the 6 carbon number lumps.
2. The average molecular mass of the crude was determined.
3. The gaseous volumetric feed flow rate from plant data and molecular mass were calculated.
4. Relate percentage volumetric cuts from TBP graph for present carbon lumps in feed to calculate their various volumetric flow rates.
5. A static sample volume for analysis with the assumption of a perfectly mixed and homogenous flow through the riser was selected; this sample volume will be used for a batch analysis in the Comsol Multiphysics software.

3.8 Inclusion of Mass and Energy Balance into Comsol Engineering Lab

The Procedure for including Mass and Energy balance into COMSOL Reaction Engineering Lab is as follows:

a. Click on the **Comsol Reaction Engineering Lab** icon on the desktop
b. Select 'New' from the **Model Navigator** dialog box.

The *Comsol Reaction Engineering Lab* interface opens

c. Follow the command path **Model** > **Model Setting**. The dialog box will open.

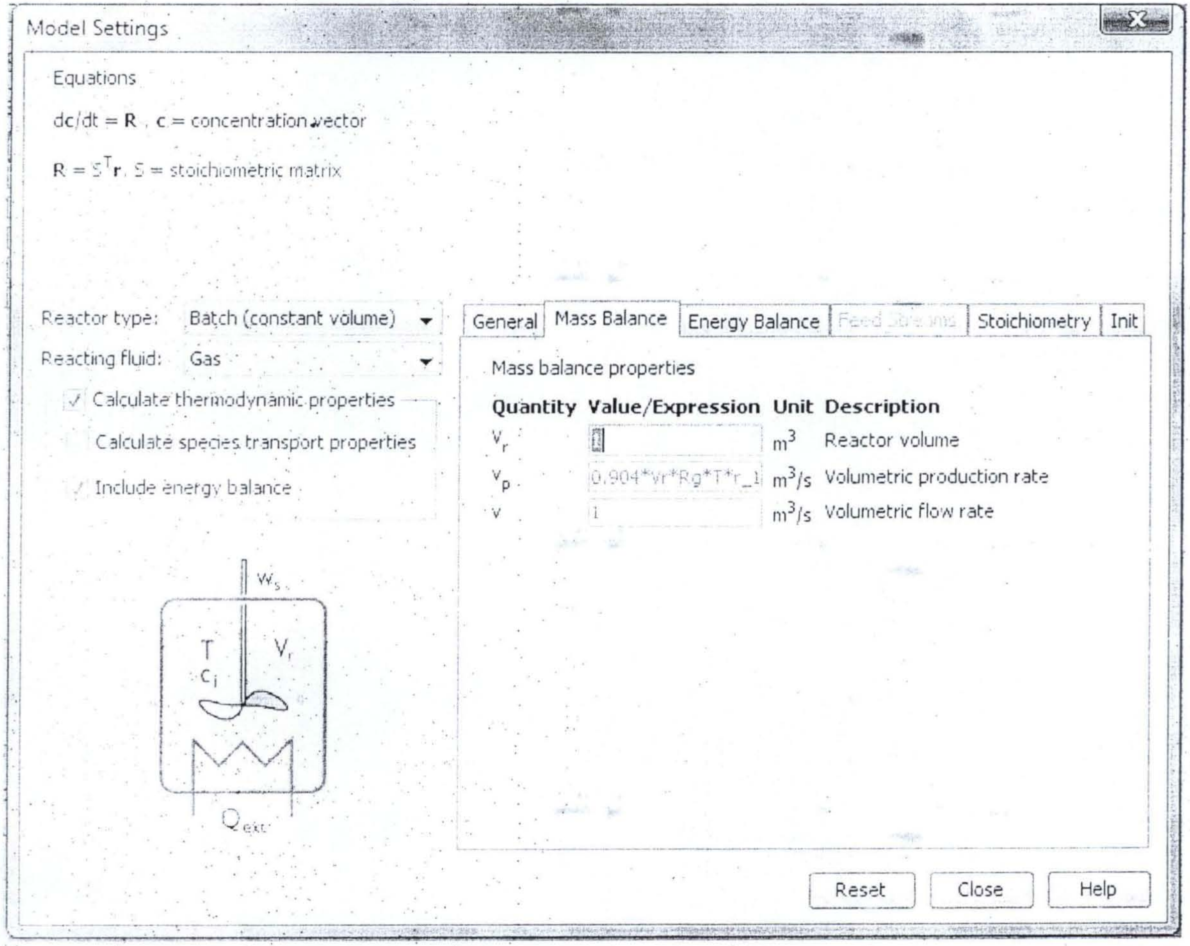
d. In the **Model Settings** dialog box, select 'Batch reactor (constant volume)' in the **Reactor type** field box.

e. Select 'Gas' from the **Reacting fluid** field box.

f. Enter into the **Pressure** text box: $R_g*T*(c_{HCO}+c_{LCO}+c_{HN}+c_{LN}+c_{BB}+c_{LG})$

g. Click the **Mass balance** Tab.

h. Type in '1' in the reactor volume text box. This sets the control volume/sample volume of the model to $1m^3$.



Model Settings

Equations

dc/dt = **R** , **c** = concentration vector

R = S^T**r**, S = stoichiometric matrix

Reactor type: Batch (constant volume)

Reacting fluid: Gas

☑ Calculate thermodynamic properties

☐ Calculate species transport properties

☑ Include energy balance

Mass balance properties

Quantity	Value/Expression	Unit	Description
V_r	1	m^3	Reactor volume
v_p	0.904*Vr*Rg*T*r_1	m^3/s	Volumetric production rate
v	1	m^3/s	Volumetric flow rate

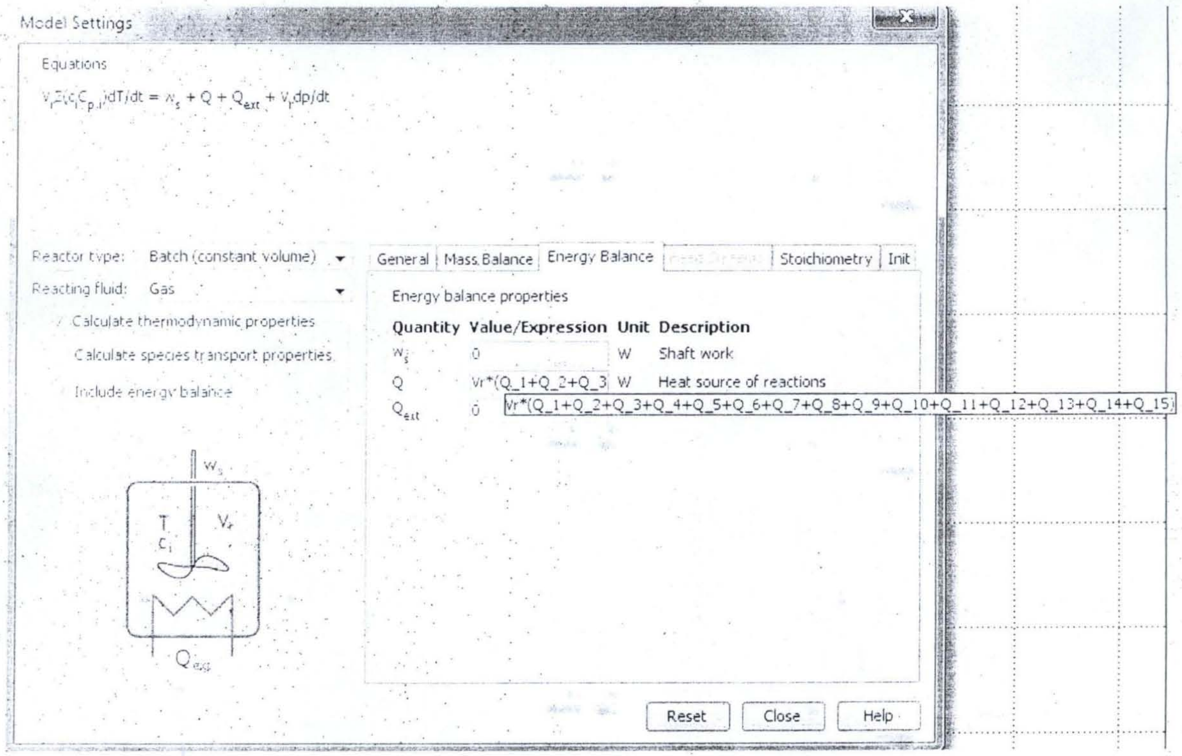
Figure 3.4 Mass balance setting in the COMSOL reaction engineering interface

i. Check the **Thermodynamic properties** and **Energy balance** checkboxes to enable an Energy balance.

j. Select the **Energy Balance** tab. Leave Shaft Work (w_s) and External heat source (Q_{ext}) text boxes at their default values of zero.

k. Enter the cumulative heat source for all 15 reactions in the Heat Source of Reactions (Q) (i.e: Q_1+Q_2+Q_3+Q_4+Q_5+Q_6+Q_7+Q_8+Q_9+Q_10+ Q_11+Q_12+Q_13+Q_14+Q_15).

l. Go to the **Init tab**, type 793 into the **Initial temperature** text box.



Model Settings

Equations

$V_r\Sigma(c_iC_{p,i})dT/dt = w_s + Q + Q_{ext} + V_r dp/dt$

Reactor type: Batch (constant volume)

Reacting fluid: Gas

☑ Calculate thermodynamic properties

☐ Calculate species transport properties

☐ Include energy balance

Energy balance properties

Quantity	Value/Expression	Unit	Description
w_s	0	W	Shaft work
Q	Vr*(Q_1+Q_2+Q_3	W	Heat source of reactions
Q_{ext}	0		

Vr*(Q_1+Q_2+Q_3+Q_4+Q_5+Q_6+Q_7+Q_8+Q_9+Q_10+Q_11+Q_12+Q_13+Q_14+Q_15)

Figure 3.5 Energy balance setting in the COMSOL reaction engineering interface

Now, the reaction kinetics will be incorporated into the model via the Reaction Settings dialogue box.

a. Follow the command path on the menu bar; **Model > Reaction settings**. The **Reaction Settings** dialogue box opens.

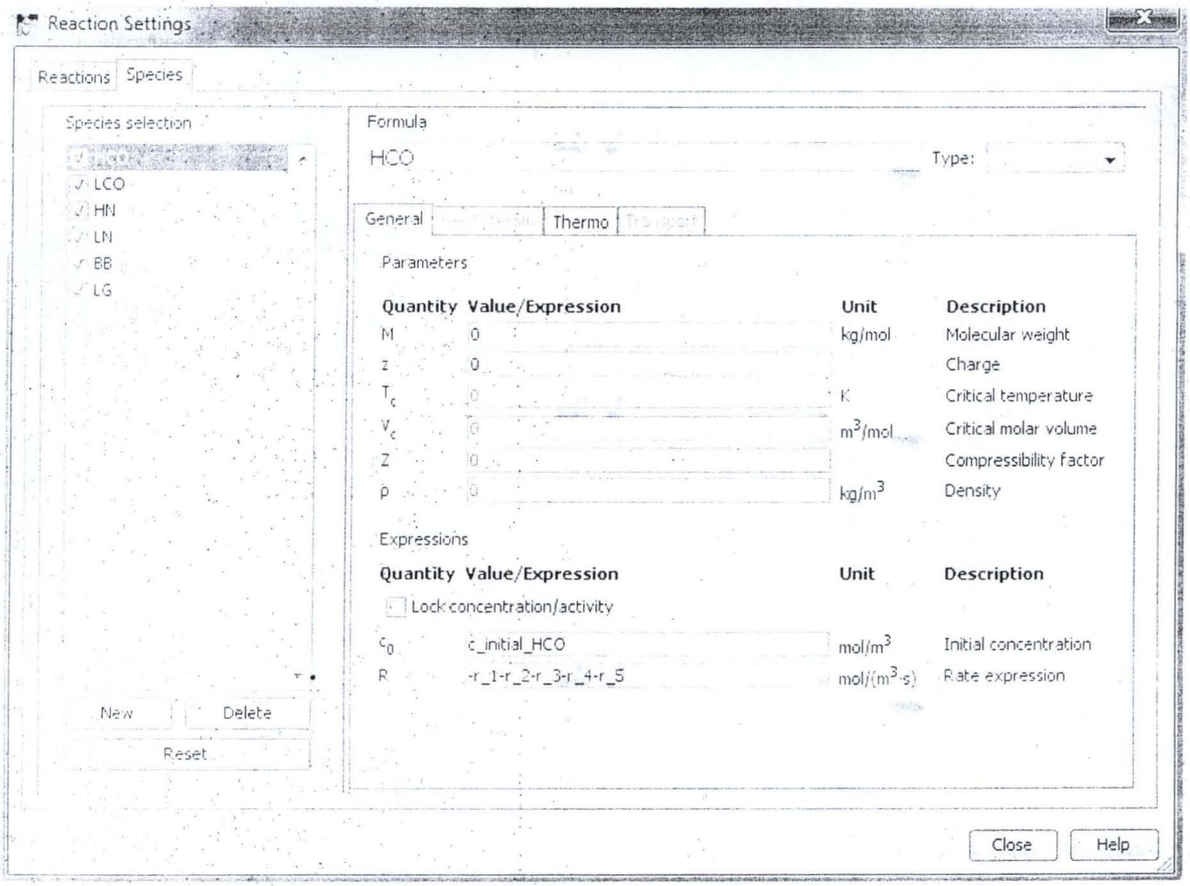
b. Click **Species** tab

c. Click **New** to enter a New specie.

d. Type the lump (e.g HCO) into the **Formula** text box and press *Enter* when done.

e. Enter the initial concentration into the **Initial concentration** text box.

f. Enter in the cumulative rate expression into the **Rate expression** for the specie disappearance (e.g: for *dHCO/dt = -r1-r2-r3-r4-r5*)



Formula: HCO
Type:

Parameters

Quantity	Value/Expression	Unit	Description
M	0	kg/mol	Molecular weight
z	0		Charge
T_c	0	K	Critical temperature
V_c	0	m^3/mol	Critical molar volume
Z	0		Compressibility factor
ρ	0	kg/m^3	Density

Expressions

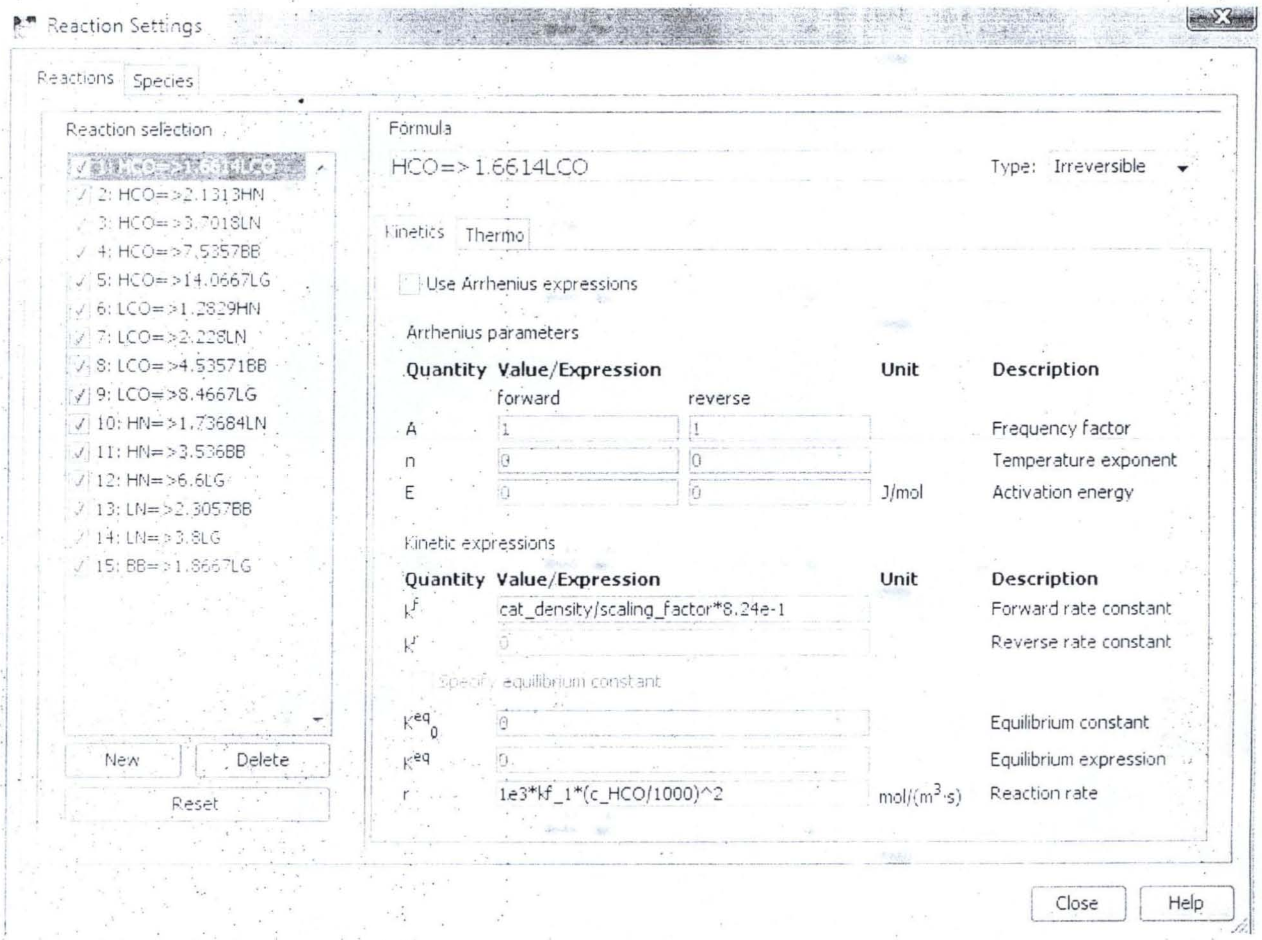
Quantity	Value/Expression	Unit	Description
☐ Lock concentration/activity			
c_0	c_initial_HCO	mol/m^3	Initial concentration
R	-r_1-r_2-r_3-r_4-r_5	$mol/(m^3 \cdot s)$	Rate expression

Figure 3.6 Specie edit page in the COMSOL reaction engineering interface

Repeat this for the remaining 5 lumps.

Next, the reaction kinetic parameters are entered.

a. Click **Reactions** tab
b. Click **New** to enter a New reaction.
c. Select **Irreversible** from the type drop down list.
d. Type the reaction (e.g HCO => 1.6614LCO) into the **Formula** text box and press *Enter* when done. The reaction becomes numbered as *Reaction 1*
e. Type in the value of *k* into the **Forward rate constant** text box.
f. Type in the reaction rate for the reaction (i.e: $cat\_density/scaling\_factor * k * c_{HCO}^{2}$)
g. Repeat this for the remaining 14 reactions with the appropriate data.



Reaction Settings

Reactions | Species

Reaction selection

- ☑ 1: HCO=>1.6614LCO
- ☑ 2: HCO=>2.1313HN
- ☑ 3: HCO=>3.7018LN
- ☑ 4: HCO=>7.5357BB
- ☑ 5: HCO=>14.0667LG
- ☑ 6: LCO=>1.2829HN
- ☑ 7: LCO=>2.228LN
- ☑ 8: LCO=>4.535718B
- ☑ 9: LCO=>8.4667LG
- ☑ 10: HN=>1.73684LN
- ☑ 11: HN=>3.536BB
- ☑ 12: HN=>6.6LG
- ☑ 13: LN=>2.3057BB
- ☑ 14: LN=>3.8LG
- ☑ 15: BB=>1.8667LG

Formula: HCO=> 1.6614LCO

Type: Irreversible

Kinetics | Thermo

☐ Use Arrhenius expressions

Arrhenius parameters

Quantity	Value/Expression forward	reverse	Unit	Description
A	1	1		Frequency factor
n	0	0		Temperature exponent
E	0	0	J/mol	Activation energy

Kinetic expressions

Quantity	Value/Expression	Unit	Description
k^f	cat_density/scaling_factor*8.24e-1		Forward rate constant
k^r	0		Reverse rate constant
	☐ Specify equilibrium constant		
K^{eq}_0	0		Equilibrium constant
K^{eq}	0		Equilibrium expression
r	1e3*kf_1*(c_HCO/1000)^2	mol/(m³·s)	Reaction rate

Figure 3.7 Reaction edit page in the COMSOL reaction engineering interface

Finally, we post process and solve the set of model equations entered;

a. Follow the command path **Simulation > Solver Parameters**. The Solver parameter setting box opens.

b. In the times text box, enter '*0 100*'. This solves the reaction from 0 to 100 seconds.

c. Click Apply and click OK.

d. Follow the command path **Simulation > Solve** problem to solve problem.

e. The results are displayed.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

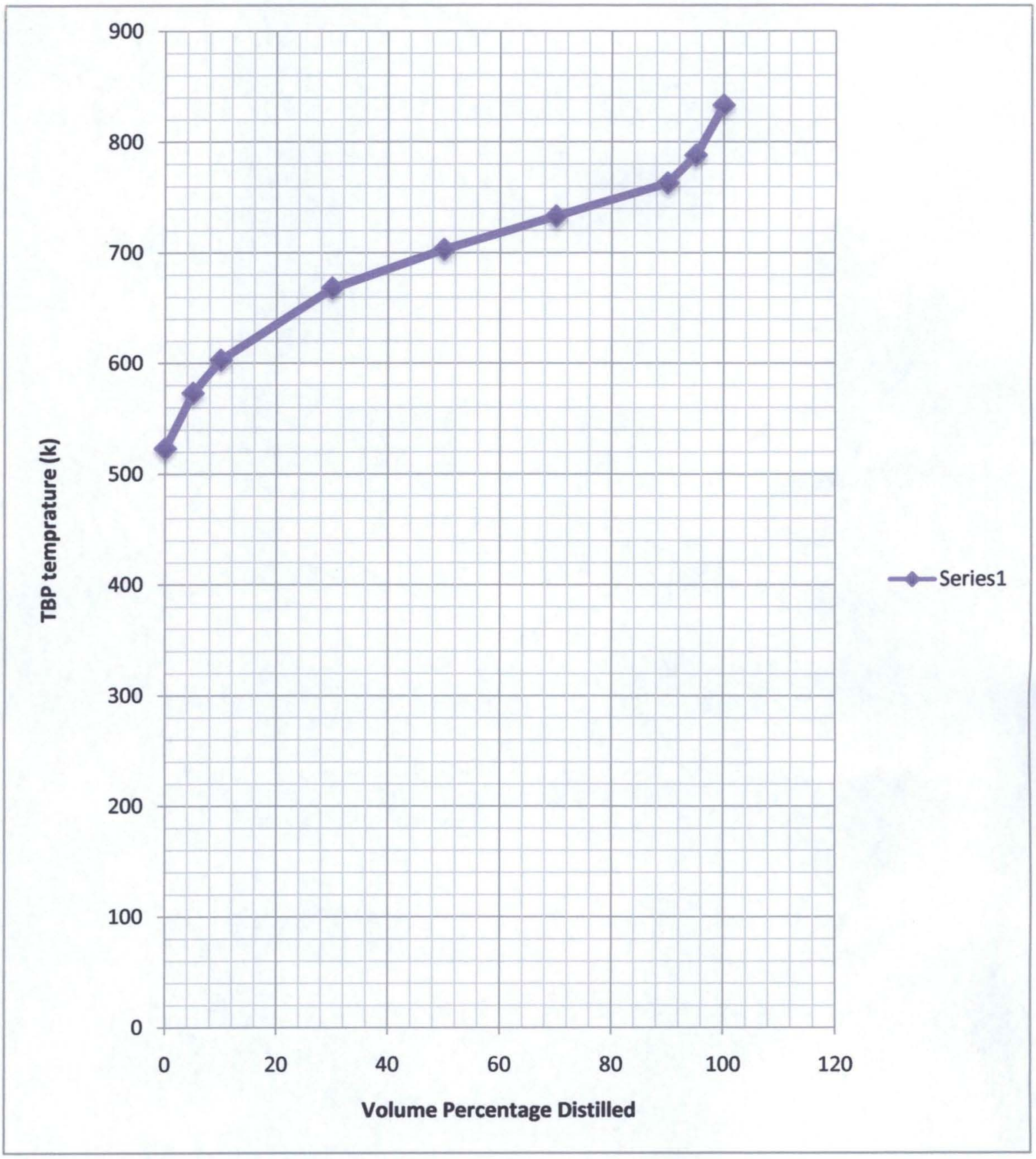


Figure 4.1 True Boiling Point graph for the FEEDSTOCK

Figure 4.1 shows the true boiling points of the feedstock used which was obtained from Kaduna Refining and Petrochemical Company as shown in appendix A. This feed stream was plotted so as to obtain the mole fractions of the lumps used. The results of the simulation of the model are presented in the next pages.

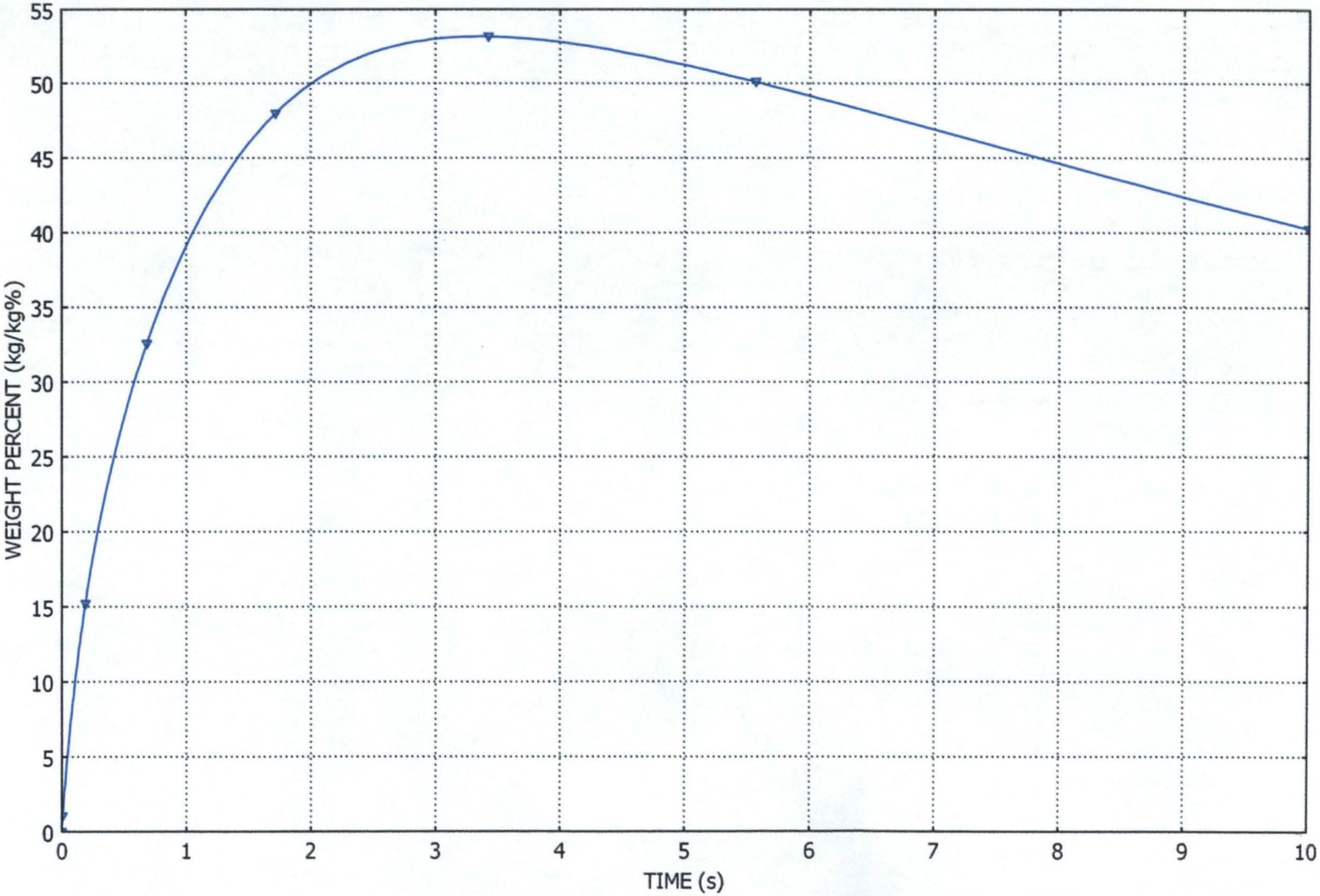


Fig 4.2: Weight Percent Conversion of Gasoline versus time

Figure 4.2 shows that the production of gasoline being the chief component of the FCCU simulated at the operating conditions shown in Table 3.3 reached a maximum value at 3.5 seconds at 54% of gasoline. The result obtained agrees with the plant data and other works such as Hernández Barajas et al (2008) which stated that the reaction time is between 3 – 5 seconds. However, the gasoline production continues beyond this point, so it would be wise to allow the reaction to still run for a longer period, say up to 7 seconds. Furthermore, from simulation result for gasoline production is close to that of the plant data hence suggesting that the model used is valid.

The fractions on the graph are made up of

Gasoil (c_HCO + c_LCO + c_HN) / (c_HCO + c_LCO+c_HN+c_LN+c_BB+c_LG)*100

Gasoline (c_LN+c_BB) / (c_HCO + c_LCO+c_HN+c_LN+c_BB+c _LG)*100

Gases (c _LG) / (c_HCO + c_LCO+c_HN+c_LN+c_BB+c _LG)*100

c_ means concentration.

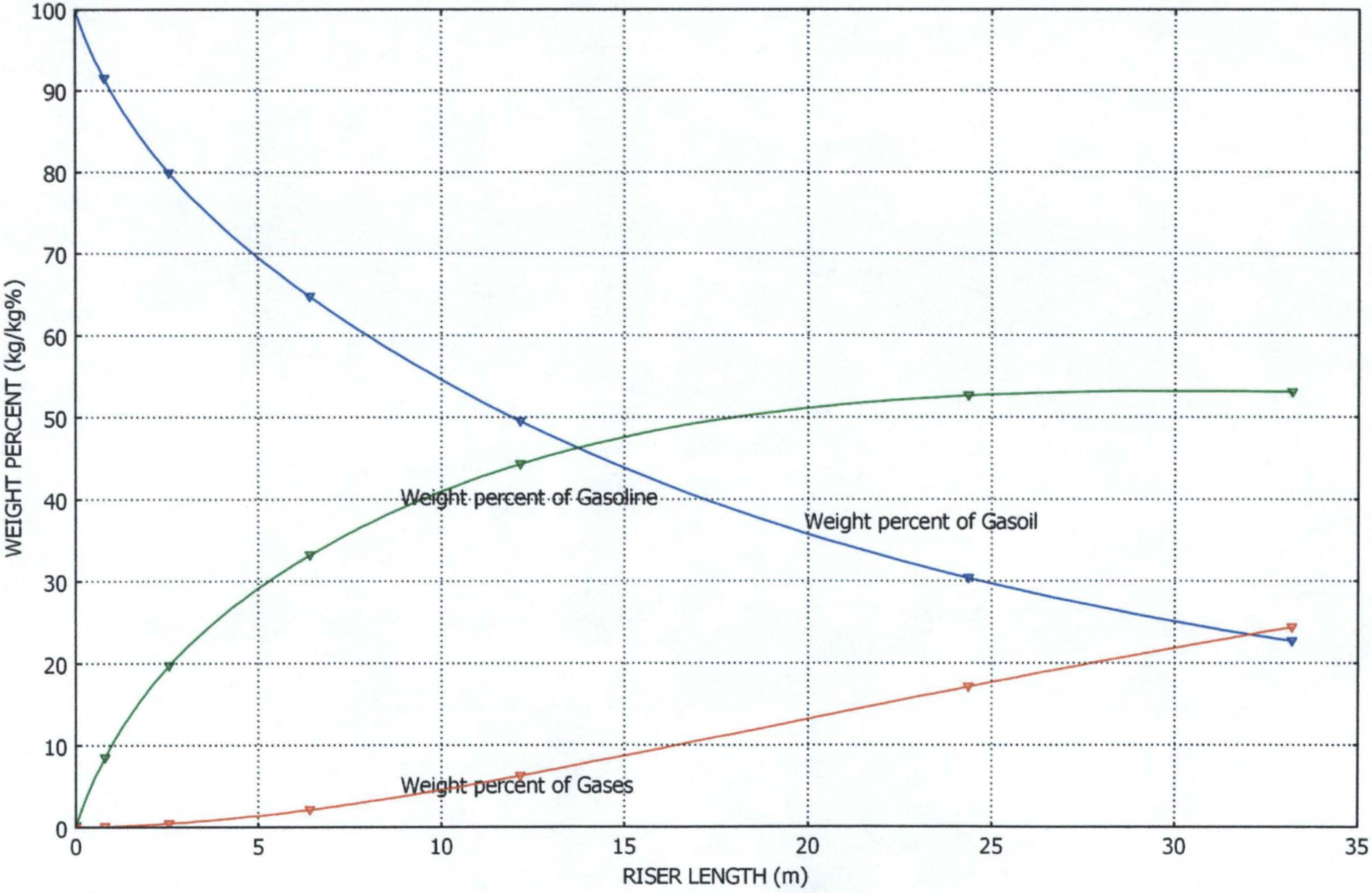


Figure 4.3 Weight Percent Conversions of FCCU Products versus Riser Length

Figure 4.3 shows the yield in weight percent for all the FCCU products. There was about 75% conversion of the feed at the riser outlet which is an optimum conversion.

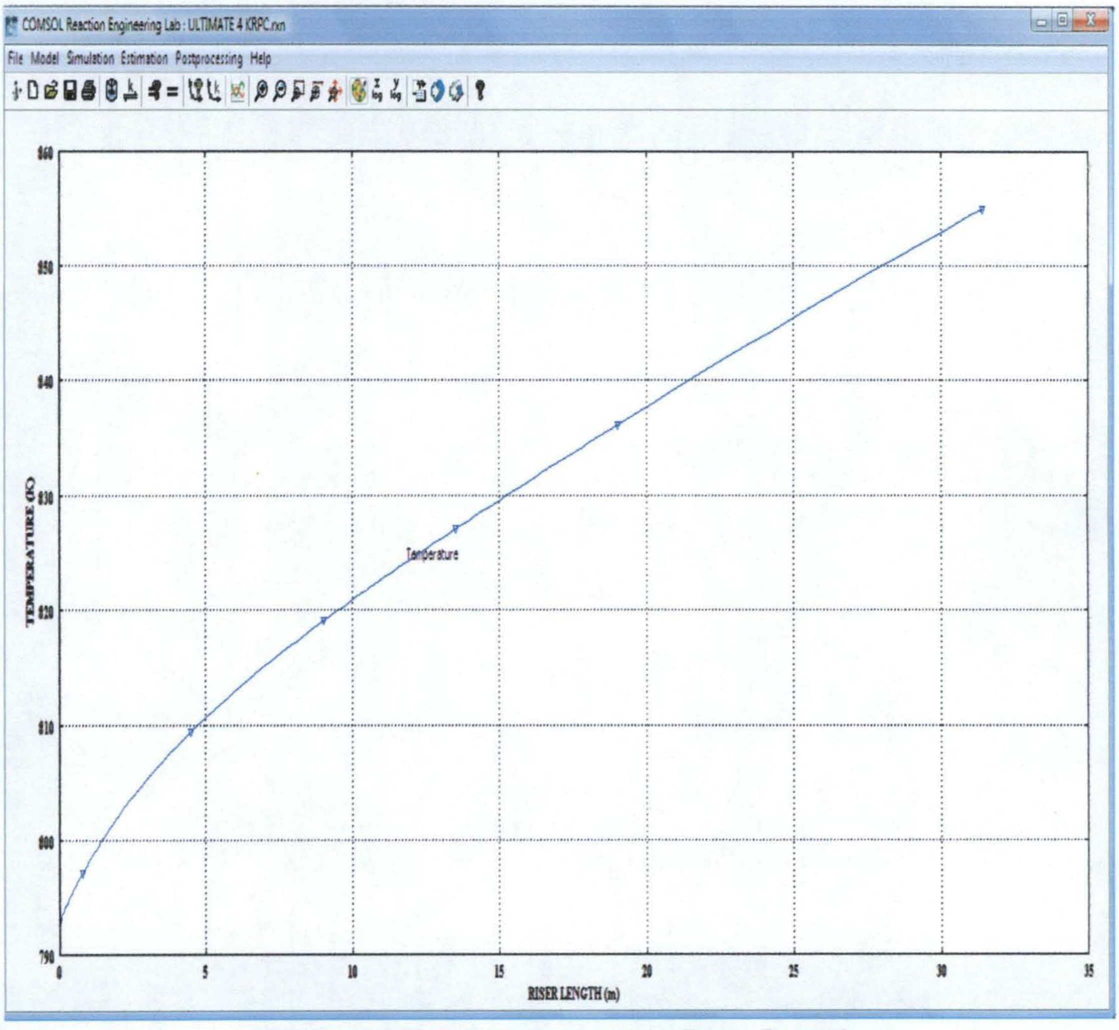


Figure 4.4 Temperature versus Riser Length

Figure 4.4 shows that see there is a rapid increase of the temperature profile from 793K to 857.5K. This is due to the high exothermicity of reactions 1, 2, 3, 5, 6, 7, 9, 10, 12, 14, 15. These reaction represent the cracking of heavy FCC feed components into smaller paraffinic components ('paraffinic cracking'). However, reactions 4, 8, 11 and 13 which represent the hydrocracking of higher species into the only olefin lump, BB (Olefinic Cracking) are endothermic. It is therefore obvious that the energy release rate by paraffinic cracking dominates throughout the entire course of the reaction the energy absorption of the olefinic cracking, yielding a net exothermicity with a temperature gain of 64.5K.

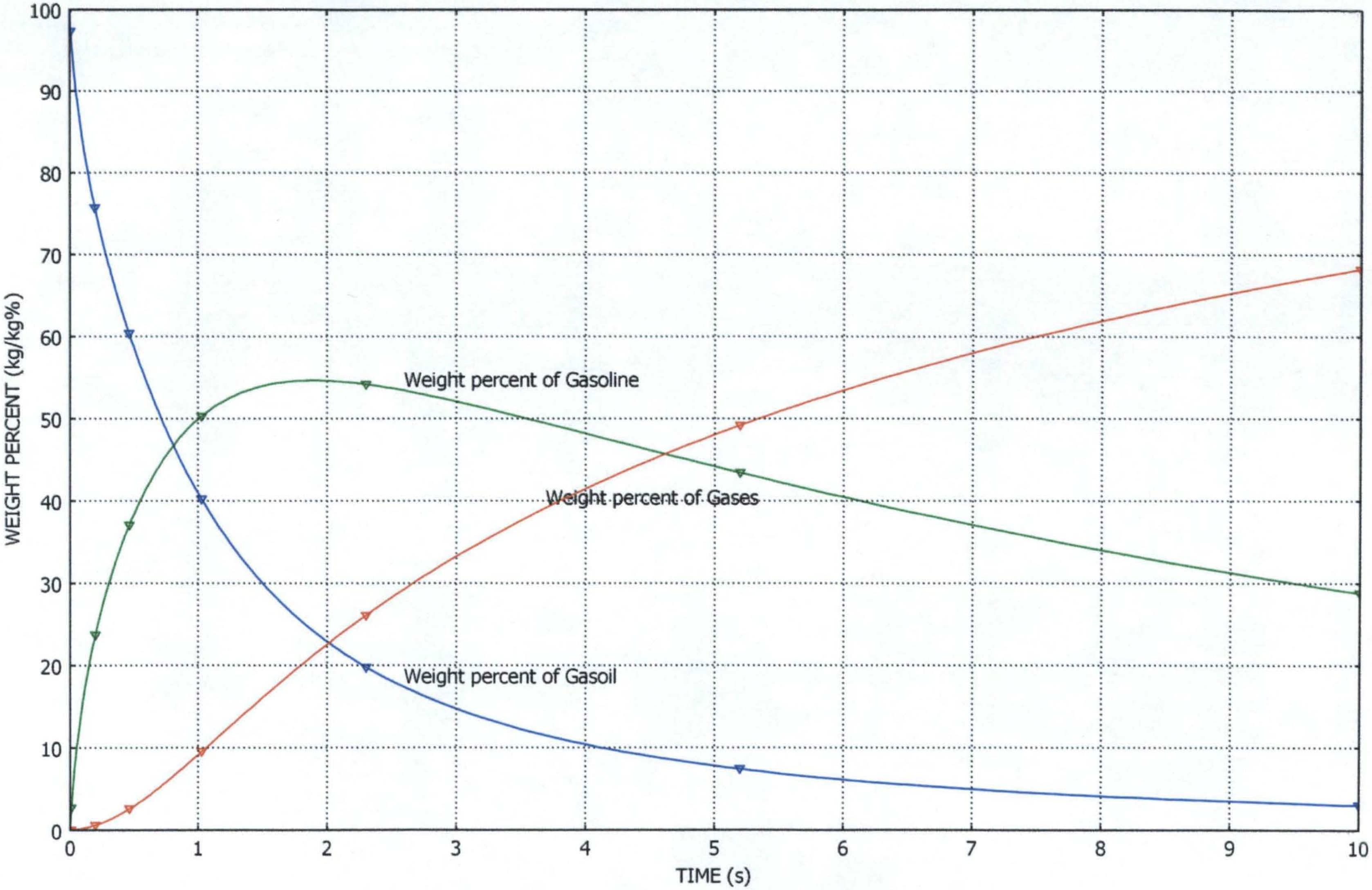


Fig 4.5: Weight percent variation of FCCU products against time
Hernández-Barajas et al (2008)

Figure 4.5 shows a graph with the result of the simulation carried out on the work of Hernández Barajas et al (2008) using comsol multiphysics with the lumping strategy used for this research but the operating conditions of the author. This shows 54% yield of gasoline at 1.8 second suggesting that the model used for this work is valid though with difference in time of maximum yield of the gasoline production.

The difference between this project and that of Hernández Barajas et al (2008) is the use different crude oils having different characteristics and operating conditions in the cracking of the fractions.

TABLE 4.1 THE VALUES OF THE PARAMETERS OBTAINED

PARAMETER	KRPC PLANT DATA	Hernández Barajas et al (2008)	Quintana-Solo´rzano et al (2009)	SIMULATED RESULT
FCC Yields				
Gasoline	61.4 %	51.6%	55.05%	54%
Gases	21.5%	19.4%	11.6%	22%
Gasoil	17.1%	29%	33.3	25%
Operating Condition				
Inlet temperature (K)	793	810	N/A	793
Outlet temperature (K)	773	810	754.9	798
Pressure (KPa)	161.8	193	193	161.8
Catalyst to oil ratio	6	8	6	6

Table 4.1 is a summary of the results obtained, the industrial data from KRPC and the work of two published authors. A deviation of 16%, 10.3%, and 11.5% was noticed between the data obtained from KRPC and the works of Hernández Barajas et al (2008),Quintana-Solo´rzano et al (2009) and the simulated results this could be as a result of the use of different feedstock and operating conditions.

Table 4.2 EFFECT OF VARIATION OF OPERATING CONDITIONS ON PRODUCT YIELD

PARAMETER	OLD VALUE	NEW VALUE	GASOLINE	GASES	GASOIL
Temperature (K)	793	813	53%	21%	26%
Pressure (KPa)	161.8	300	60%	20%	20%
Catalyst-oil-ratio	6	9	54%	21%	25%

From Table 4.2 the operating conditions were varied and run with the same model which shows that an increase in temperature and Catalyst-oil-ratio do not have a marked difference in the yield of products.

However an increase in pressure shows an increase in gasoline production. Only the maximum yield of 60% was obtained at 1.3seconds suggesting that an increase in pressure increases yield of gasoline at a shorter residence time as long as temperature is constant.

Table 4.3: MASS BALANCE FOR FCCU RISER SPECIES

LUMP	Mol. Wt (g/mol)	Molar Conc. IN (mol/m^3)	Molar Conc. IN (g/m^3)	Molar Conc. OUT (mol/m^3)	Molar Conc. OUT (g/m^3)
HCO	422	18.6136	7854.939	2.8681	1210.3382
LCO	254	5.4660	1388.364	8.0938	2055.8252
HN	198	0.4770	94.446	6.4657	1280.2086
LN	114	0	0	37.2317	4244.4138
BB	54	0	0	1.4633	79.0812
LG	28	0	0	16.7062	467.7736
Total		**25.185**	**9337.749**	**72.161**	**9337.6406**

Table 4.3 shows a balanced mass content for each of the six species per m^3 of model reactor therefore proving that mass was conserved during the entire process despite concentration changes

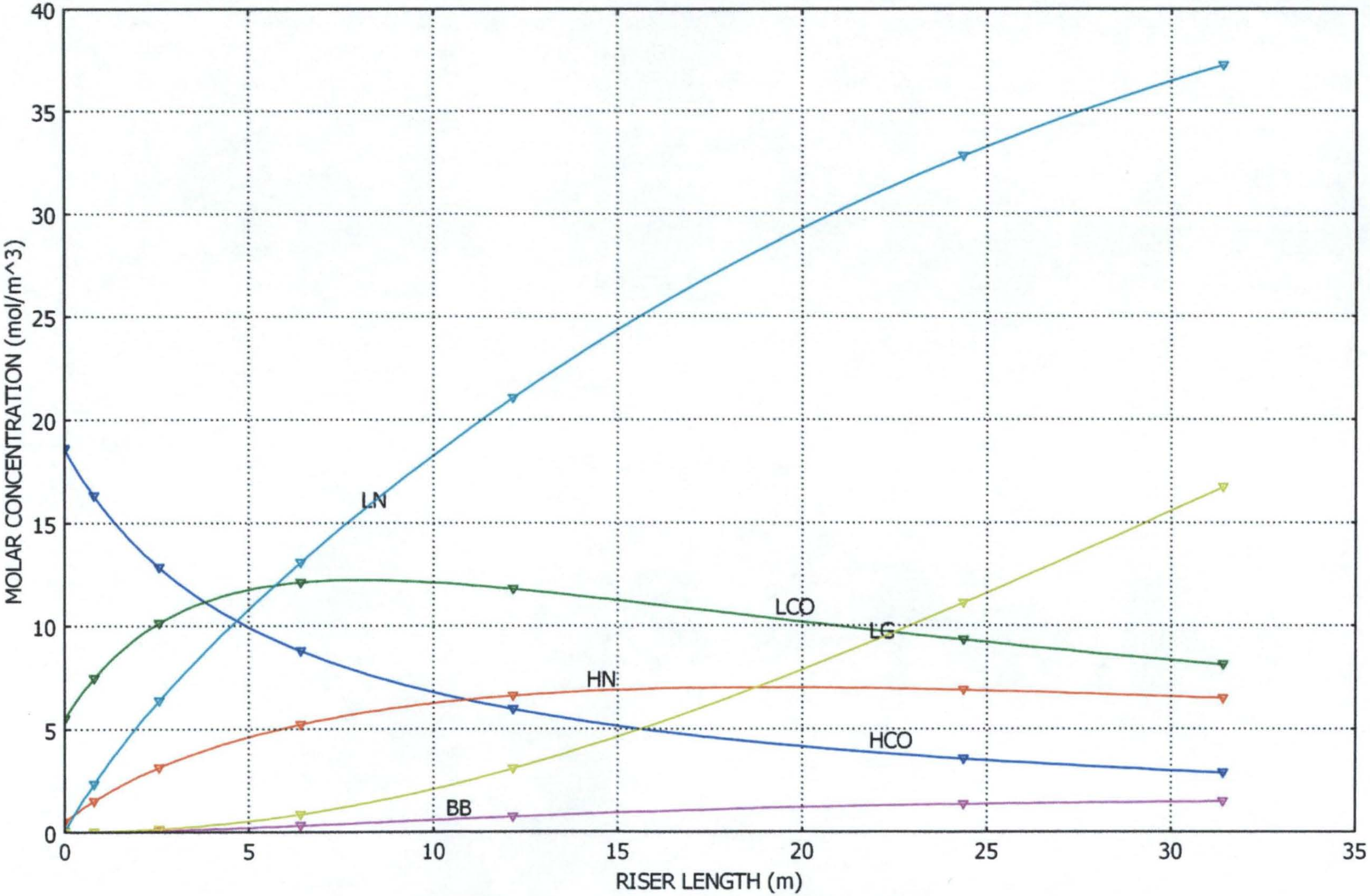


Figure 4.6: Molar concentration of Species versus Riser Length

Figure 4.6 shows that the simulation is in favour of the production of Light Naphtha (LN) at 37% which is the chief constituent of the gasoline fraction and its production begins at the inlet of the riser suggesting that instant vaporization begins at the inlet of the riser thus the production of gasoline begins at the inlet of the riser. The heavy Cycle Oil (HCO), light Cycle Oil (LCO) and Heavy Naphtha (HN) show a marked depletion coming to 2.8%, 8% and 6.5% at the end of the riser length respectively.

Moreover the production of Butane – Butylenes (BB) stand at 1.5% and Light Gases (LG) 16.7% its production was gradual then it soared on towards the end of the riser length this shows that LG are a sought of by product at the end of the reaction.

Table 4.4: ENERGY BALANCES FOR FCCU RISER SPECIES

	SPECIE	Mol frac. IN m_{in} (mol)	Mol. frac. OUT m_{out} (mol)	Av Cp in-out (Cp @ 793K)	m_{in} Cp_{av} In	m_{out} Cp_{av} Out
	HCO	18.6136	2.8681	1401.400	26085.099	4019.355
	LCO	5.4660	8.0938	856.440	4681.301	6931.854
	HN	0.4770	6.4657	678.482	3.0841	41.8052
	LN	0.000	37.2317	391.860	0.000	14589.6154
	BB	0.000	1.4633	174.990	0.000	256.063
	LG	0.000	16.7062	109.133	0.000	1823.1977
TOTAL					30769.484	27661.890

Heat of Reaction$\sum \Delta H = \sum(m_{out}\ Cp_{av}\ \Delta T_{out} - m_{in}\ Cp_{av} \Delta T_{in})$

[27661.890 * (855-0)] – [30769.484 * (793-0)]

[27661.890 - 30769.484]* (855-793)

-3107.594 * 62

-192670.82 of J/mol

Table 4.4 shows a negative resultant heat effect, hence this is an exothermic reaction.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

This study is focus on the modelling and simulation of a refinery fluid catalytic cracking unit riser. From the simulated result obtained it can be drawn that operating pressure positively affects the gasoline yield. The following conclusion can also be drawn from the study based on the simulated results obtained:

1. The simulation of the developed model compared favourably with that of the actual plant data with about 7% difference.
2. The software package (Comsol Multiphysics) used in this study will reduce the time spent in tedious calculations of some parameters such as the rate constants, enthalpy of reaction, heat capacity e.t.c.

5.2 RECOMMENDATIONS

In view of the results obtained and discussed, the following recommendations were made.

1. A Computational software such as Comsol Multiphysics is recommended for this work and probably for other equipment not only in the oil industry but other chemical process industries in that it takes care of both mass and energy balance provided the relevant data are provided and entered in the correct units.

2. A riser reactor of a longer length is recommended for the feed quality given seeing that product yield of gasoline runs for a longer period beyond the length given though there would be cost involved in shut down of the plant in for installation and repairs.

3. The pressure employed can be increased during operation though not at once but increment can be done gradually in that a marked increase and shorter residence time is experienced.

4. The model should be employed for simulation of crudes of good quality other than Nigerian crude (Escravos).

5. Computational software such as Comsol Multiphysics is recommended for the optimization of process units.

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KRPC LTD. PLANT STREAM ANALYSIS AREA 1-CDU-1
HEM. LAB. (REF)
TIME 14:00HRS DATE 24-04-

SAMPLE NAME	~~PRE-NAPHTHA~~	~~WHOLE NAPHTHA~~ VGO	KERO	DLGO.	DHGO	S/R	MP	LP	02
ANALYSIS									
SG @ 15/4 °C		0·9114				0,9639			
DIST. IBP °C		260							
5%		310							
10%		335							
30%		390							
50%		430							
70%		455							
90%		500							
95%		520							
EBP °C		550							
REC. %VOL.		98							
FLASH PT. °C		168							
CLOUD PT. °C									
POUR PT. °C									
VISC. @ 82.2°C									
pH							10,28	10,88	4,74
BS&W % SiO2							21·32	28·33	
~~SALT~~ (ptb). CCR		0·39							
COLOUR ASTM		5.0							
COLOUR SAYBOLT									

SHIFT LEADER........ 24/04

APPENDIX B

STOCHIOMETRIC COEFFICIENTS FOR THE FIFTEEN (15) REACTIONS

REACTION	Vij=Mi/Mj	STOICHIOMETRIC COFFICIENT
HCO=>LCO	422/254	1.6614
HCO=>HN	422/198	2.1313
HCO=>LN	422/114	3.7018
HCO=>BB	422/54	7.8148
HCO=>LG	422/28	15.0714
LCO=>HN	254/198	1.2829
LCO=>LN	254/114	2.2281
LCO=>BB	254/54	4.7037
LCO=>LG	254/28	9.0714
HN=>LN	198/114	1.7368
HN=>BB	198/54	3.6667
HN=>LG	198/28	7.0714
LN=>BB	114/54	2.1111
LN=>LG	114/28	4.0714
BB=>LG	54/28	1.9286

APPENDIX C

Number of pathways = $\frac{N!}{2!(N-2)!} = \frac{N(N-1)}{2}$

N= Number of lumps used/considered in a kinetic model

$$\frac{N!}{2!(N-2)!} = \frac{N(N-1)}{2}$$

$$\frac{6!}{2!\,(N-2)!} = \frac{6(6-1)}{2}$$

$$= 15$$

Hence; 15 reaction pathways/kinetics are used for the work.

APPENDIX D

Calculations for Cross Sectional Area and Velocity Using Feed Flow Rate

Cross sectional area $A = \pi r^2$

Diameter of riser (m) = 1.35

Radius = 1.35/2=0.675

$$A = 3.14 * 0.675^2$$

$$= 1.4307\text{m}^2$$

Linear velocity (V) = Feed flow rate /Cross sectional area

12.837 /1.4307

V = 8.9727m/s

The velocity is used to relate the time profile of any variable to its corresponding position in the riser reactor.