# SIMULATION OF FLUID CATALYTIC CRACKING UNIT (FCCU) FOR DIFFERENT FEEDSTOCK QUALITIES USING ASPEN HYSYS

**THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**
**OF**
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**RASHA HAITHAM KHUDHUR**

**A MASTER OF SCIENCE THESIS**
**IN**
**THE DEPARTMENT OF CHEMICAL ENGINEERING**
**AND APPLIED CHEMISTRY**

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**A THESIS SUBMITTED TO**

**THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

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**RASHA HAITHAM KHUDHUR**

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Approval of the Graduate School of Natural and Applied Sciences, Atılım University.

_______________________

Prof. Dr. Ali Kara

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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This is to certify that we have read the thesis “SIMULATION OF FLUID CATALYTIC CRACKING UNIT (FCCU) FOR DIFFERENT FEEDSTOCK QUALITIES USING ASPEN HYSYS” submitted by Rasha Haitham Khudhur and that in our opinion, it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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## ABSTRACT

### SIMULATION OF FLUID CATALYTIC CRACKING UNIT (FCCU) FOR DIFFERENT FEEDSTOCK QUALITIES USING ASPEN HYSYS

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Fluid catalytic cracking unit is the heart of the petroleum refinery because it converts low-value hydrocarbons with high boiling point and high molecular weight like heavy gasoil and residue to more valuable products such as gasoline and LPG by using a catalyst. FCCU is studied by using lumps strategy to describe cracking reactions such as cracking VGO to gasoline. In this work, 7-, 8-, and 10-lumps kinetics models are used. Each model has described a different feedstock quality. These models have been tested to design FCCU for both light and heavy feedstock under the same operating conditions with different riser diameters by using Aspen HYSYS (V.10). Results showed that the same FCCU cannot work with different feedstock quality. A large riser diameter is more suitable than a small one for a heavy feedstock quality due to the increased the residence time for the cracking reactions.

**Keywords:** Fluid catalytic cracking unit (FCCU), 7-, 8-, and 10-lumps kinetics model, Aspen HYSYS, feedstock quality, riser diameter.

# ÖZ

## AKIŞKAN KATALITIK PARÇALAMA UNITESININ (FCCU) FARKLI HAMMADDE KALITELERI İÇIN ASPEN HYSYS KULLANARAK SIMULASYONU

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Danışman: Doç. Dr. Nesrin E. Machin

Haziran 2019, 60 sayfa

Akışkan katalitik parçalama ünitesi (FCCU), petrol rafinerilerinin kalbidir. Çünkü yüksek molekül ağırlıklı ve kaynama noktalı değersiz hidrokarbonlar, katalizör kullanılarak benzin ve LPG gibi değerli ürünlere dönüştürülürler. Bu tezde, FCCU, parçalanma reaksiyonlarının yığın stratejisi kullanılarak çalışılmıştır. 7-, 8- ve 10 yığın kinetik modelleri kullanılmıştır.Her model, farkli bir hammadde kalitesini temsil etmektedir. Bu modeller, hem ağır, hem de hafif hammadde için, aynı koşullar altında farklı reaktor çapları için, Aspen HYSYS (V.10) kullanılarak test edilmiştir. Sonuçlar, aynı FCC ünitesinin farklı hammaddeler için çalıştırılamayacağını göstermiştir. Ağır hammaddelerin kullanıldığı durumda, reaktörde kalma süresini arttırdığı için, daha büyük çaplı reaktor kullanmanın daha uygun olduğu sonucuna varılmıştır.

**Anahtar Kelimeler:** Akışkan katalitik parçalama ünitesi (FCCU), 7-,8- ve 10 yığın kinetic modelleri, Aspen HYSYS, hammadde kalitesi, reaktor çapı

## DEDICATION

**With all my love**

I would like to dedicate this thesis to my grandfather (Khudhur Jadoo), my parents (Haitham Khudhur & Abtisam Ahmed), my uncles (Abd-al-Rahman Ahmed & Abd-al-Wadood Ahmed), brothers and sisters, who have supported me through this period of study.

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I would like to thank my supervisor Assoc. Prof. Dr. Nesrin E. Machin for her help to work on such a scientifically interesting project and I would like to express my sincere gratitude for her help, guidance, and support in this work. She always helps me with all technical and nontechnical issues during this research. Her encouragement and interest led to finish this study successfully.

I would like to appreciate all of those who support and encourage me to complete this thesis.

I would like to thank my friends for their help and support during this study.

Last, I would like to express my warmest regards to my parents and my family members for their unconditional love and support, without it which I could have never completed this thesis.

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| | |
|---|---|
| FCCU | Fluid Catalytic Cracking Unit |
| HGO | Heavy Gas Oil |
| VGO | Vacuum Gas Oil |
| ROT | Riser Outlet Temperature |
| AAD | Average Absolute Deviation |
| API | American Petroleum Institute |
| Ea | Activation Energy |
| K0 | Frequency Factor |

# CHAPTER 1
# INTRODUCTION

## 1.1 Introduction

Fluid catalytic cracking is a primary conversion process and many of the refineries have been considered catalytic cracker as the main unit that specifies the profits of a petroleum refinery. That is, it determines if refinery can compete with the market. Nearly 350 catalytic cracker units are operating worldwide and the providing capacity with these units are over 14.7 million barrels per day [1].

The main objective of FCC units is to convert low-value hydrocarbons with high boiling point range and high molecular weight like heavy gas oil and residue to more useful products such as gasoline and LPG by using a catalyst. The feedstock of FCC units is usually (HGO) from the crude distillation unit and (VGO) from the vacuum distillation unit. Heavy petroleum can also produce from another unit such as the delayed Coker or deasphalter, which can be a feedstock for FCCU ([1]-[7]).

A petroleum refinery consists of many handling units that transform heavy crude oil into applicable products. In short, it considers the workhorse of petroleum refinery and Figure 1.1 explains the role of this unit in the refinery ([1], [8]).

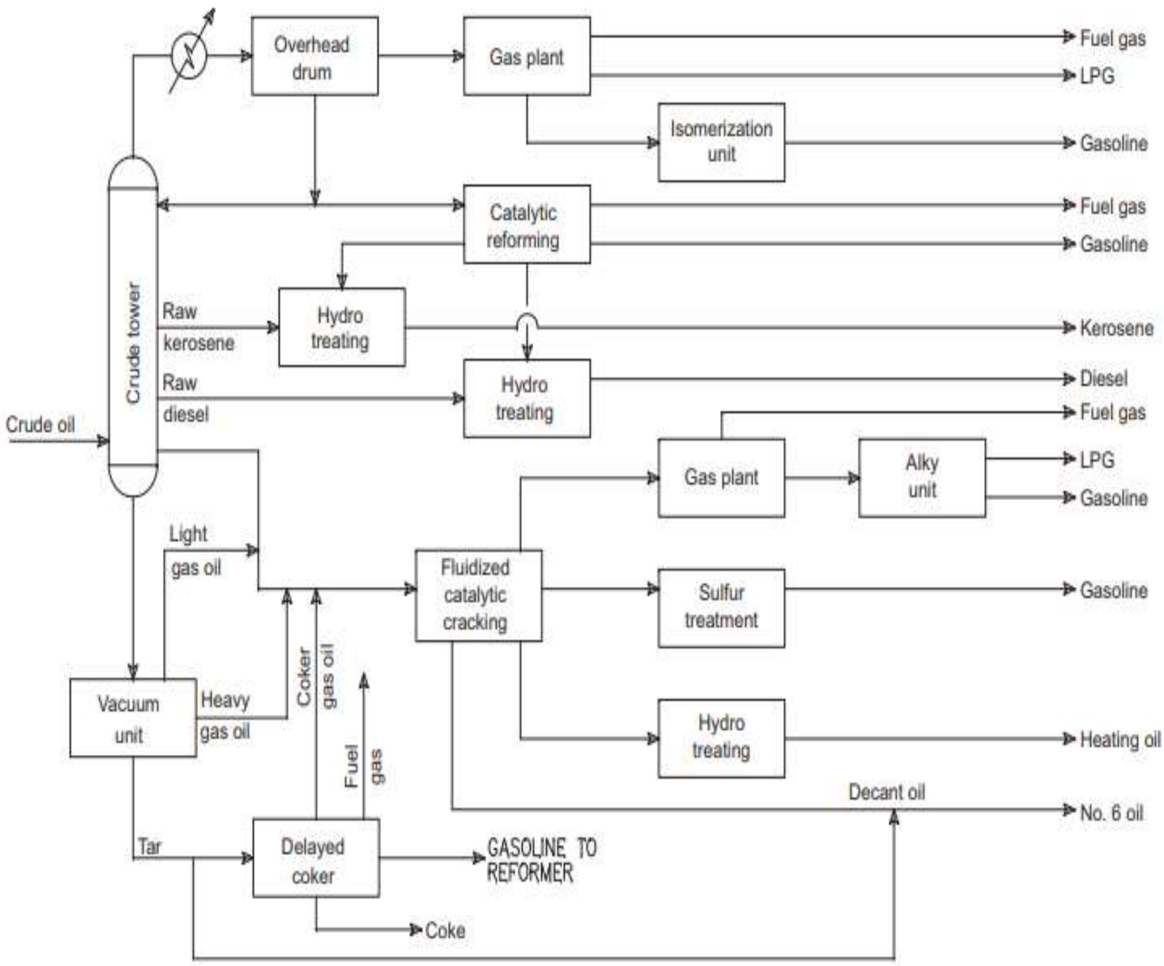



Figure 1.1 FCCU roles in petroleum refinery [8]

The core of modern petroleum refinery is FCCU [7]. It is one of the most important units in the petroleum refineries which has a remarkable history since 1942 when the first commercial FCCU was made [1], Evolution of FCCU can be shown in Table1.1 ([1], [2]).

Table 1.1 Evolution of FCCU [1]

| | |
|---|---|
| 1942 | The first commercial FCC unit started by processing 12,000 barrels per day. |
| 1947 | First Universal Oil Products (UOP)-stacked FCC unit was built. |
| 1948 | Microspheroidal FCC catalyst has been developed by the Davison Division of W.R. Grace & Co. |
| The 1950s | Evolution of bed cracking process designs. |
| 1954 | High alumina ($Al_2O_2$) catalysts were introduced. |
| 1956 | Shell invented riser cracking. |
| 1963 | The first Model I FCC unit was shut down after 22 years of operation. |
| 1972 | Amoco Oil invented high-temperature regeneration. |
| 1975 | Phillips Petroleum developed antimony for nickel passivation. |
| 1981 | TOTAL invented two-stage regeneration for processing residue. |
| 1994 | Coastal Corporation conducted a commercial test of ultrashort residence time, selective cracking (MSCC). |
| 1996 | ABB Lummus Global acquired Texaco FCC technologies. |

Several improvements have been made on FCCU in order to compete with the increasing demands in the markets of gasoline, diesel, and other products ([1], [9]). Approximately (45-50) wt% of all gasoline worldwide have been produced by this unit and auxiliary units, such as the alkylation unit ([1], [3]). Also, FCCU produces about 45 wt% of naphtha in the world [6].

## 1.2 Configuration Of FCCU

FCCU is a very complex process and consists of many parts. But, the most important parts are riser/reactor and regenerator which work as one part, as shown in Figure 1.2.

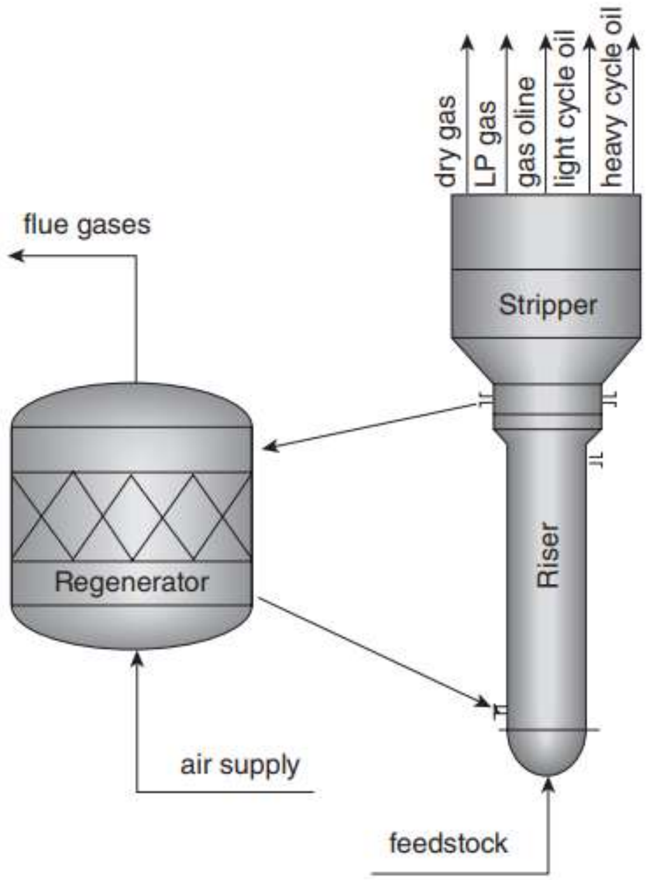



Figure 1.2 Configuration of FCCU

### 1.2.1 Riser/Reactor

As the FCCU is the core of any refinery, the riser-reactor/regenerator is the core of the FCC process. All the reactions of cracking take place in a very short time through 3.0 Sec or less. The catalyst and the products are separated in the reactor after the cracking reactions take place. The feed enters from the bottom of the riser where it contacts with the regenerated catalyst. The catalyst to oil ratio is actually between (4:1-9:1) by weight. The feedstock is heated to its required reactor temperature by using heat absorbed by the catalyst in the regenerator. The cracking reactions that occur in the riser are endothermic. The revolving catalyst between riser and regenerator give the energy required for reactions. The temperature of the regenerated catalyst is between (677°C - 732°C). The catalytic cracking reactions take place in the vapor phase and they start as soon as the feed vaporize. The main driving force which carries the catalyst up the riser is the expanding volume of the vapor that is generated. Catalyst and products are quickly separated by using cyclones [1].

Conversion of fluid catalytic cracking depends on the catalyst to oil ratio (C/O) and the quantity of catalyst loading [9]. The catalyst to oil ratio is an important factor because it determines the selectivity of the product [10].

### 1.2.2 Regenerator

Regenerating catalyst activity and providing the desired heat for cracking reaction in the riser are the main functions for the regenerator ([1], 11]). The temperature and pressure of regenerator are about 715°C and 2.41bar, respectively. A combustion reaction takes place in regenerator which is an exothermic reaction. The regenerated catalyst leaves the regenerator at about 715°C. The heat produced through combustion reactions is used for catalytic cracking process in the reactor, and this heat is carried to the reactor by catalyst as sensible heat. Regenerator with one or two-stage cyclones are used to return entrained catalyst from the flue gas before the hot flue gas exits the regenerator. The hot flue gases have been used for generating power [10]. The amount of coke on the spent catalyst depends on the quality of the feed. Coke is composed of carbon, hydrogen, and trace amounts of sulfur and nitrogen. Oxygen required to burn the coke is provided from the air by one or more air blowers. During regeneration, the coke level of the catalyst is typically reduced to 0.05 % [1].

## 1.3 Properties Of Feedstock In FCCU

The catalytic cracking operation has been identified by FCC feedstock characterization. Feed properties directly affect the unit's performance.

The gas oil is the main feedstock to FCCU and its boiling point ranges between (316 °C – 566 °C). Gas oil is mixtures of aromatic, naphthenic and paraffinic molecules and also it contains some contaminants such as sulfur, nitrogen, and metals with the varying amount, especially in the higher boiling fractions that affect the FCCU performance.

In the laboratory, some experiments are required to determine the quality of feedstock to FCCU. The most widely used properties are °API Gravity, distillation (TBP), aniline point (is the minimum temperature required to soluble of an oil sample in aniline), Refractive Index (RI), nitrogen content, metal content, and viscosity, as shown in Table 1.2 [8].

Table 1.2 Typical properties of the feedstock in FCCU [8]

| | Vacuum gas oil | Atmospheric residue |
|---|---|---|
| Specific gravity (15/4 C) | 0.896 | 0.889 |
| API | 26.3 | 27.5 |
| Gas oil fraction (GO), wt% (boiling point < 343 °C) | 7 | 4 |
| VGO fraction (VGO), wt% (boiling point 343–538 °C) | 88.5 | 52.5 |
| Vacuum residue fraction (VR), wt% (boiling point > 538 °C) | 4.5 | 43.5 |
| Conradson Carbon Residue (CCR), wt% | 0.2 | 4.2 |
| Sulphur, wt% | 0.4 | 0.11 |
| Nitrogen, wt% | 0.064 | 0.19 |
| Nickel (Ni), wppm | 0.26 | 17 |
| Vanadium (V), wppm | 0.15 | 0.5 |

## 1.4 Product Of FCCU

The yield of each product of FCCU has a certain limit, as shown in Table 1.3 [8]. But, the hydrodynamic designs of FCCU and operating conditions have a big impact on the yield of the product.

Table 1.3 Typical products of FCCU [8]

| Products | Characteristics | Yield (wt%) |
|---|---|---|
| Dry gas + $H_2S$ | $H_2S$ must be removed | 3-5 |
| LPG | Petrochemical feedstock | 8–20 |
| Gasoline | The main product, good octane number | 35–60 |
| Light cycle oil (LCO) | Rich in aromatics, high sulfur content, diluent for fuel | 12–20 |
| Heavy cycle oil (HCO) + slurry | Very rich in aromatics, a slurry of solids, (mainly catalyst coke) | 10–15 |
| Coke | Coke Consumed in regenerator | 3–5 |

## 1.5 Catalytic Cracking Reactions

The primary reaction taking place in FCCU is cracking of the paraffin, olefins, naphthenes and side chains in aromatic. As explained in Figure 1.3, the primary reactions lead to gasoline, LCO, and gases. In addition, gases, residue, and coke have been produced by the secondary catalytic cracking reaction. Additionally, the dehydrogenation reactions lead to coke formation which causes catalyst deactivation [8].

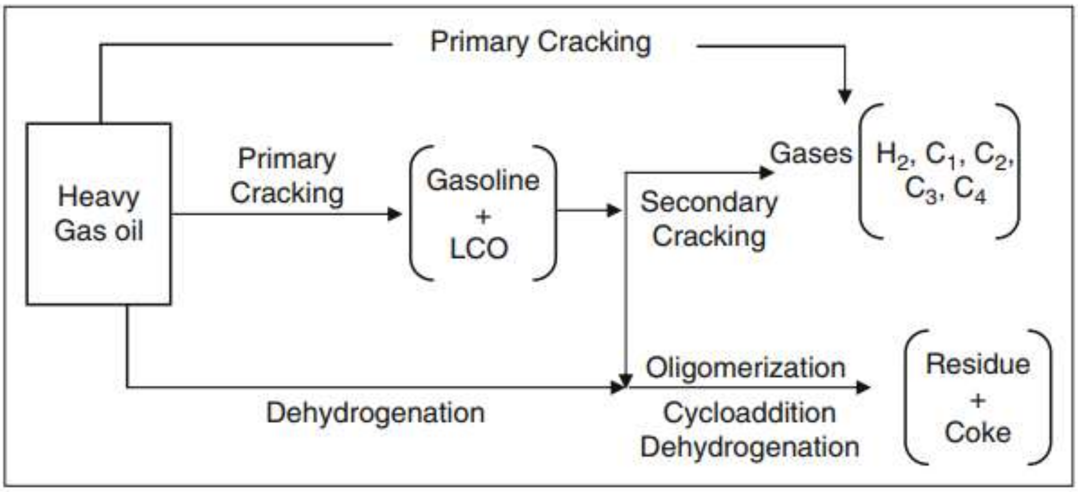



Figure 1.3 Reactions network in FCCU [8]

## 1.6 Catalysts Of FCCU

The greatest development in the history of the fluid catalytic cracking unit was the discovery of the zeolite catalyst which has higher activity, gasoline selectivity, and stability characteristics than silica-alumina catalyst ([12], [13]).

There are three types of commercial catalyst in FCCU:

1-Acid treated natural alumina-silicates.

2- Amorphous synthetic silica-alumina combinations.

3- Crystalline synthetic silica-alumina catalysts called zeolites or molecular sieve [10].

The typical catalyst of the fluid catalytic cracking unit consists of a mixture of an active matrix (alumina), an inert matrix (kaolin), a binder (silica or silica-alumina) and a Y zeolite. An important portion of the feedstock is converted into coke, during the FCC process [14]. The activity of the catalyst depends on the strength of acidic sites on its surface, zeolite content, and type at constant inactive matrix composition [15].

The critical point in the FCC operation and profitability is the regeneration of catalyst ([16], [17]). Solid catalyst has been circulated in one FCC unit about (40–50) tons of every minute. The catalyst loses its activity during the process because of the coke deposit [16]. The performance of the catalyst regenerator depends on burning efficiency and higher carbon content on a spending catalyst lead to an increase in the temperature of the regenerator. The ratio of the recycled-to-spent catalyst flow rate in the range (1.0–3.5) and temperatures of the spent catalyst in the range (703.15–803.15 °K) have effects on the general performance of the regenerator. The suitable superficial gas velocity and the spent catalyst flow rate are in the range of (4–7) m/s and (20–40) $kg/m^{-2}$ s, respectively [18].

### 1.7 Justifications Of These Simulation Models

#### 1.7.1 Statement Of The Problem

Iraq is a petrol rich country, yet there is no FFCU in refineries. The feedstock quality changes depending on the region the petrol are extracted, and it is one of the most important limitations for the hydrodynamic design of an FCCU. Designing an FCCU for a light feedstock is different than designing it for a heavy feedstock. This problem reported on the $10^{th}$ Arab Energy Conference by OPEC in Abu Dhabi, UEA in 2014.

In this work, the hydrodynamic design has been tested at different feedstock quality to see the effects on the product yield. Three kinetics models have been tested at the same industrial operating conditions with a different hydrodynamic design.

#### 1.7.2 Objective

1- To test the effect of different feedstock quality on the product yield in FCCU. Both light and heavy feedstock have been tested under the same operating conditions.

2- To find the most suitable riser diameter to achieve high yield both for light and heavy feedstock.

3- To test the yield for both light and heavy feedstock at the same FCCU, for a range of operating conditions (T, P, Flowrate, etc.).

**1.8 Scope Of The Thesis**

- Chapter 1 presents the introduction, process descriptions, statement of problem and objective.

- Chapter 2 presents a literature review about the types of kinetics model which are studied.

- Chapter 3 presents a simulation procedure, methodology, data of simulation models.

- Chapter 4 consists of two parts.

The first part of chapter 4 presents the results obtained from simulation models at different hydrodynamic design and compares them with an industrial plant data. These three models are:

Model I use the 7-lumps kinetics model to simulate feedstock with API=22.3 at 0.7m, 0.9m, 1m, 1.2m, and 1.5m riser diameter.

Model II uses the 8-lumps kinetics model to simulate feedstock with API=24.3 at 0.7m, 0.9m, 1m, 1.2m, and 1.5m riser diameter.

The model III uses 10-lumps kinetics model to simulate feedstock with API=27 at 0.7m, 0.9m, 1m, 1.2m, and 1.5m riser diameter.

These three models are chosen to describe the effect of a different feedstock quality with an API gravity (22.3, 24.3, and 27.6) because even if two-number shift in API gravity can have significant effects on yields [1]. But, riser diameters are tested for a large range to test its effect with light and heavy feedstock.

The second part of this chapter presents tested operating parameters in the hydrodynamic design of light feedstock in order to deal with heavy feedstock.

- Chapter 5 presents the conclusions of this thesis and future work in this field.

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Introduction

Cracking reactions in FCCU are studied by a lumping strategy which is grouped together with the chemical species with similar behaviors to form a smaller number of ″pseudo″ species [19].

The commercial feedstock of FCC is often composed of a wide boiling point range for its chemical species. Gasoline produces by cracking hydrocarbons with a wide molecular weight range ($C_1$ - $C_{20}$) [19]. Thus, a tractable exercise of the kinetics modeling can be made based on the lumping of species. Generally, the lumping of feedstock is based on two basic techniques.

The first technique is to examine the reactions between lumps molecules in different distillation cuts. Lumps such as gasoline, LCO, light gases, and coke are feedstock and final products.

The second technique is to lumps different products according to their main chemical families such as paraffin, naphthenes, olefins, and aromatics. With this technique stoichiometry and data of important reactions such as the reaction type (cracking, condensation, or hydrogen transfer) can be included. The different reaction pathways can be described by the second technique [20].

## 2.2 Lumping History

In (1970), the three lumps kinetics model was proposed by Weekman et al.and Nace et al. [21]. Later in the (1987), four lumps were proposed by modifying the three lumps, where gases and coke were separated by Yen et al. [22]. The 10-lumps kinetics model is the most complex and elaborated model in characterizing the feedstock and it was proposed by Jacob et al. (1976). This model has been developed because its rate constants did not depend on the feedstock composition [23].

In the (1987), a six lumps model was proposed by Coxson et al., which include the vacuum gas oil, gasoline, light gases, the heavy cyclic oil (HCO), the light cyclic oil (LCO), and the coke ([19], [24]).

In 1990, an eight lumps model was proposed by Kraemer et al., where he separated the feedstock into the light and heavy fractions: a) light paraffin, light naphthenes, and light aromatics and b) heavy paraffin, heavy naphthenes, and heavy aromatics. He assumed that the light oil lumps, gasoline, and light gases and coke produced from cracking heavy oil lumps [25].

In 1994, a model was developed by classifying lumps based on chemical family and boiling range or molecular weight by Pitault et al. The lighter gases, gasoline, LCO, and feedstock cuts have depended on this approach. This model has flexibility because of including important reactions such as hydrogen transfer and coking. Stoichiometry and reaction order of lumps reaction was specified and examined with experimental data [20].

In (1999), the four lumps model was expanded to five lumps model by Juarez et al. That is, he divided the gases into two different lumps (dry gas and liquefied petroleum gas) [26].

## 2.3 Kinetics Lumps Model Review

### 2.3.1 Three Lumps Kinetics Model

This model is composed of a feedstock lumps (VGO, or gas oil) and another two lumps are products such as (gasoline and light gases +coke). The gasoline lumps consists of hydrocarbons with a range between ($C_5$ - 220$^oC$). The (light gases + coke) lumps consists of fraction hydrocarbons between ($C_1$ - $C_4$ ) in addition to coke, as shown in Figure 2.1 ([24], [27]).

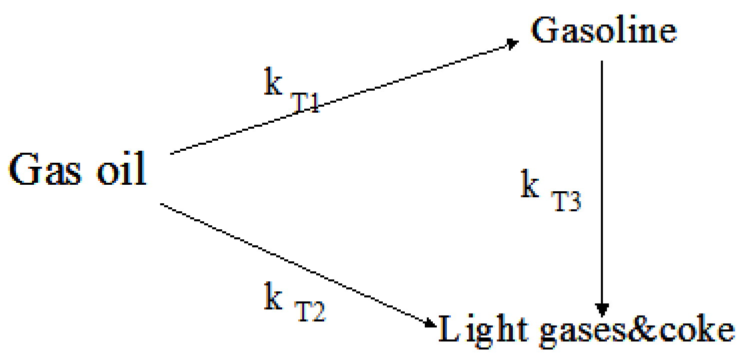



Figure 2.1 Three lumps kinetics model

### 2.3.2 Four Lumps Kinetics Model

The light gases + coke lumps was split into two lumps (light gases and coke) in order to form the four lumps kinetics model. Riser pilot plant data is used to determine the kinetics parameters and correlated according to the feedstock characteristics and operating conditions. The coke yield of VGO cracking in FCC pilot plants and commercial units predicted by this model, as shown in Figure 2.2 ([22], [27]).

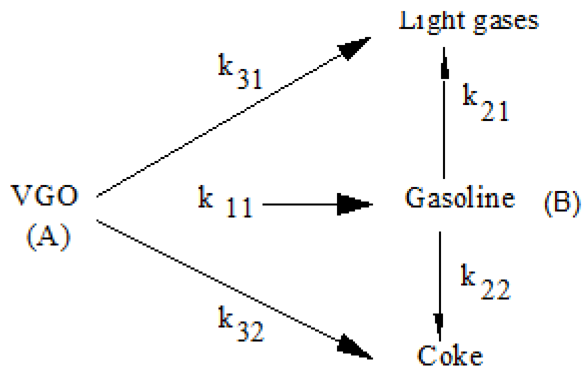



Figure 2.2 Four lumps kinetics model

### 2.3.3 Five lumps kinetics model

This model generated by extending four lumps kinetics model. The gases lumps was divided into two lumps (dry gas and liquefied petroleum gas). LPG can be produced either from gas, oil directly or it produces from over-cracking of gasoline as a secondary product. In contrast, dry gases can be produced either from gas oil directly or they produce from over-cracking of gasoline and LPG as a secondary product, as shown in Figure 2.3 ([26], [28]).

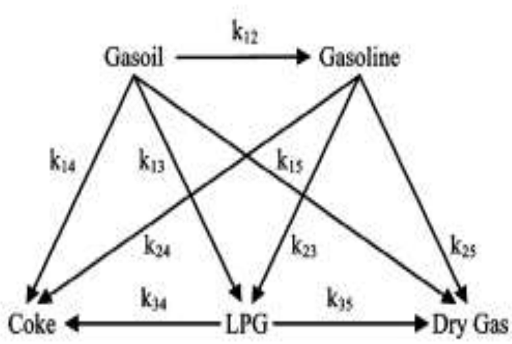



Figure 2.3 Five lumps kinetics model

### 2.3.4 Six Lumps Kinetics Model

This model composed of feedstock (VGO) and the most important products in the Fluid Catalytic Cracking Unit (FCCU): (1) gas oil (VGO), (2) gasoline ($C_5$ -220 °C), (3) propane and propylene ($C_3$), (4) butane, i-butane and butylene ($C_4$), (5) dry gases (H2, C1 -C2), (6) coke and, as shown in Figure 2.4 ([29]-[31]).

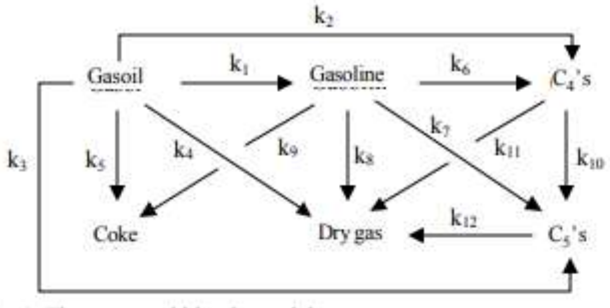



Figure 2.4 Six lumps kinetics model

### 2.3.5 Seven Lumps Kinetics Model

Seven lumps model was proposed to predict the behavior of the commercial RCC units. The feedstock based on the type of crude oils and its pretreatment is divided into (1) VR (vacuum residue, >500 °C), (2) VGO (vacuum gas oil, 350-500 °C), (3) LFO (light fuel oil, 200-350 °C), (4) G (gasoline, C5-200 °C), (5) $S_1$ (LPG), (6) $S_2$ (dry gases), and (7) C (coke), as shown in Figure 2.5 ([32], [33]).

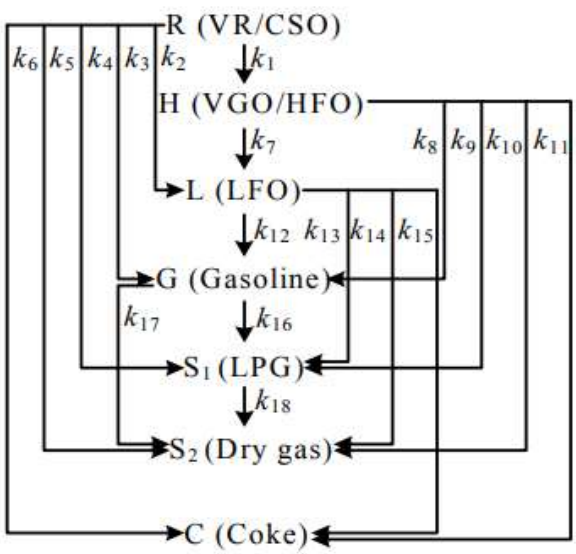



Figure 2.5 Seven lumps kinetics model

### 2.3.6 Nine Lumps Kinetics Model

Nine lumpsed kinetics models were proposed as a new complex reaction network by the aromatization reaction of FCC gasoline. In this model network, the aromatization reaction species were lumpsed into (1) n-paraffins, (2) i-paraffins, (3) olefins, (4) aromatics, (5) coke, (6) butene ($C^{=}_{4}$), (7) butane($C^{0}_{4}$), (8) ethylene & propylene ($C^{=}_{2-3}$), and (9) methane, ethane, & propane ($H_2 + C^{0}_{1-3}$).

paraffin dehydrogenation, cyclization, paraffin isomerization and cracking to low carbon hydrocarbon are the main three type reactions among nine lumpsed components, which were considered in the aromatization reaction network. The less important reactions and some reactions seldom take place were eliminated from this network to simplify it. This model has been studied by considering the reaction mechanism, as shown in Figure 2.6 [34].

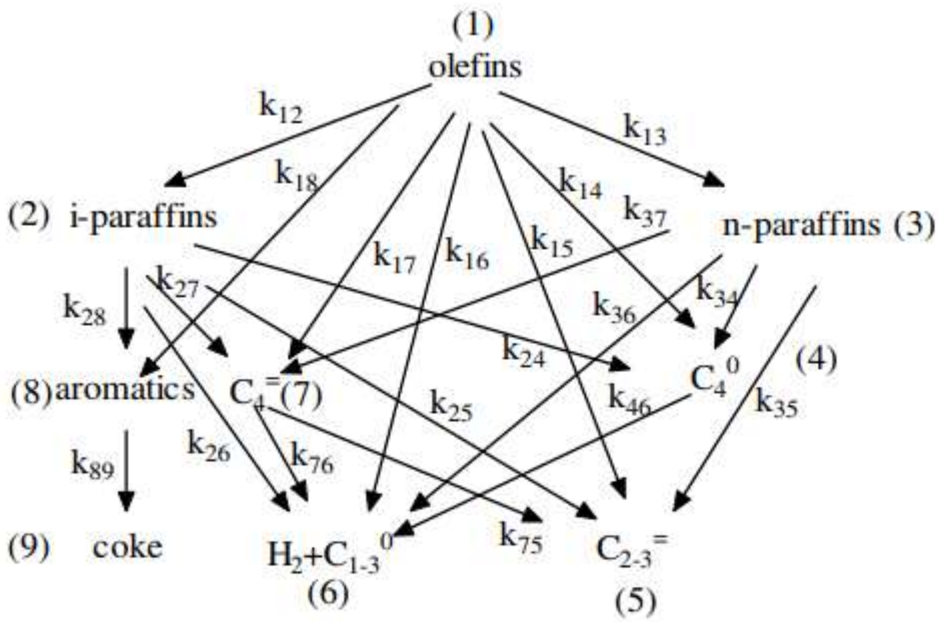



Figure 2.6 Nine lumps kinetics model

### 2.3.7 Twenty-One Lumps Kinetics Model

This model is based on the popular 10-lumps model. Both these models follow the same pathways and basic structure in terms of grouping lumps according to the boiling point range of each chemical type. Moreover, the 10-lumps model has not been dealt with ranges of boiling point (< 510 °C). But, this model has been developed to deal with heavy feedstock. Aromatic lumps are separated into lumps containing side chains and multiple rings. Coke lumps in this model has been separated into two lumps: (a) kinetics coke is produced by cracking reactions and (b) metal coke is produced from metal content activity, as shown in Figure 2.7 ([35]-[37]).

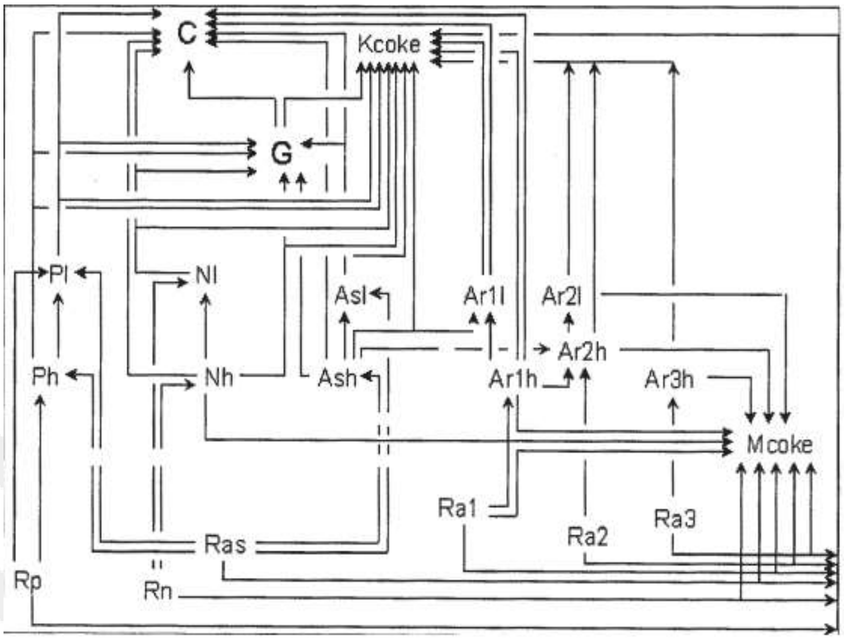



Figure 2.7 Twenty-one lumps kinetics model

Table 2.1 Abbreviations of 21- lumps kinetics model

| | Lumps | Boiling point range |
|---|---|---|
| 1 | Light gas | <$C_5$ |
| 2 | Gasoline | $C_5$-221 °C |
| 3 | Light paraffin (PL) | |
| 4 | Light naphthene (NL) | |
| 5 | Light aromatic with side chains (ALs) | 221-343 °C (VGO) |
| 6 | One-ring light aromatic (ALr1) | |
| 7 | Two-ring light aromatic (ALr2) | |
| 8 | Heavy paraffin (PH) | |
| 9 | Heavy naphthene (NH) | |
| 10 | Heavy aromatic with side chains (AHs) | 343-510 °C (heavy VGO) |
| 11 | One-ring heavy aromatic (AHr1) | |
| 12 | Two-ring heavy aromatic (AHr2) | |
| 13 | Three-ring heavy aromatic (AHr3) | |
| 14 | Residue paraffin (PR) | |
| 15 | Residue naphthene (NR) | |
| 16 | Residue aromatic with side chains (ARs) | <510 °C (residue) |
| 17 | One-ring residue aromatic (ARr1) | |
| 18 | Two-ring residue aromatic (ARr2) | |
| 19 | Three-ring residue aromatic (ARr3) | |
| 20 | Kinetics coke | Produced by the reaction scheme |
| 21 | Metal coke | Produced by metal activity on the catalyst |

## 2.4 Deactivation Of Catalyst

Deactivation of catalyst in FCCU happens by losing its shape and mass because of high temperatures and attrition. The catalyst is poisoned because of the impurities in the feedstock such as sulfur, nitrogen, oxygen, nickel, and vanadium ([38]-[40]). The catalyst loses its activity because the active sites of the catalyst are covered by coke during the cracking reactions.

## 2.5 Catalyst Activity Decay

Modeling the deactivation of the catalyst is based on two approaches. The content of coke in the catalyst is the first approach. The relationship between the deactivation of the catalyst and time-on-stream (TOS) is the second approach ([41], [42]).

### 2.5.1 The Content Of Coke

The first approach to model the catalyst decay is related to the catalyst deactivation function ($\phi$) with its coke content $C_c$, as shown in relationships below [43].

$$\varphi = \exp(-\delta C_c) \qquad (a)$$

$$\varphi = 1/(1+\delta C_c) \qquad (b)$$

$$\varphi = (1-\delta C_c)^2 \qquad (c)$$

$$\varphi = 1/(1+\delta C_c)^2 \qquad (d)$$

$$\varphi = 1-\delta C_c \qquad (e)$$

where $\delta$ is a constant for the catalyst decay, and determined by the experiments.

### 2.5.2 Time-On-Stream

The second approach to model catalyst decay is (TOS). The rate of coke is independent of the composition of reactant, and a space velocity of hydrocarbons in this approach [44].

The following two relations employed to describe the deactivation of the catalyst by Weekman (1968) [45].

1- Power decay law $\varphi = t^{-n}$

2 - Exponential decay law $\varphi = \exp(-\alpha t)$

where: t stands for catalyst time-on-stream,

$\alpha$ and n are rate constants of the catalyst decay function

# CHAPTER 3
# RESEARCH METHODOLOGY

## 3.1 Introduction

In this work, three kinetics models have been tested by using Aspen HYSYS (Version10) simulation program. These models are 7-lumps kinetics model, 8-lumps kinetics model, and 10-lumps kinetics model. We run each one of these simulation kinetics models under the same industrial operating conditions and commercial catalyst (Y-zeolite). But, kinetics models run at different feedstock quality. All cracking reactions are defined in Aspen HYSYS according to their activation energy and the frequency factor. The number of the cracking reactions changes depending on the lumps number. For example,

- 18 cracking reactions occur among seven lumps in the 7-lumps kinetics model.
- 27 cracking reactions occur among eight lumps in the 8-lumps kinetics model.
- 25 cracking reactions occur among ten lumps in the 10-lumps kinetics model.

We get all the parameters of the reaction from the literature ([53], [57], [58]).

## 3.2 Aspen HYSYS

In aspen ONE, Aspen Plus and Aspen HYSYS process simulators are used in the modeling and analysis of the process. Aspen HYSYS process simulator is a powerful tool used to improve and simplify petroleum refining simulations and optimization of hydrocarbons. Many oil and gas producers, refineries and engineering companies use Aspen HYSYS for optimization of process and design, energy and utility optimization ([46], [47]).

### 3.3 Components Of FCCU Model In Aspen HYSYS

Petroleum Refining FCCU model is available as one unit in Aspen HYSYS, as shown in Figure 3.1 [48]. But, this unit relies on a series of sub-models which they represent the entire operating units through simulating of the main model, as shown in Figure 3.2 [50]. Minimum sub-models require in a simulation is listed in Table 3.1 ([35], [49]).

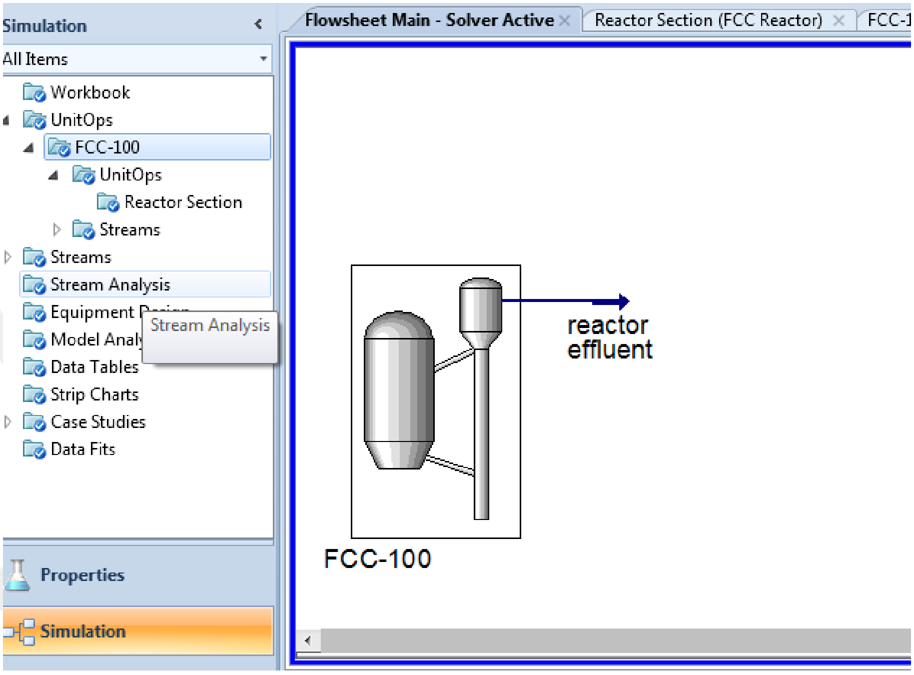



Figure 3.1 FCCU in Aspen HYSYS

Table 3.1 Sub-models required in FCCU simulation ([49]-[51])

| No. | Sub-model | Unit operation | Purpose |
|---|---|---|---|
| 1 | Riser | PFR | Crack heavy gasoil into more valuable products. |
| 2 | Reactor/Stripper | Bubbling-bed reactor with two phases | Complete cracking feed and separate product from the catalyst |
| 3 | Regenerator | Bubbling-bed reactor with two phases | Combust coke and regenerate the catalyst. |
| 4 | Regenerator freeboard | PFR | Complete coke combustion |
| 5 | Cyclones | Splitter of component | Separate the catalyst from the reactor effluent |
| 6 | Delumpser | | Convert lumps composition to TBP suitable for fractionator. |

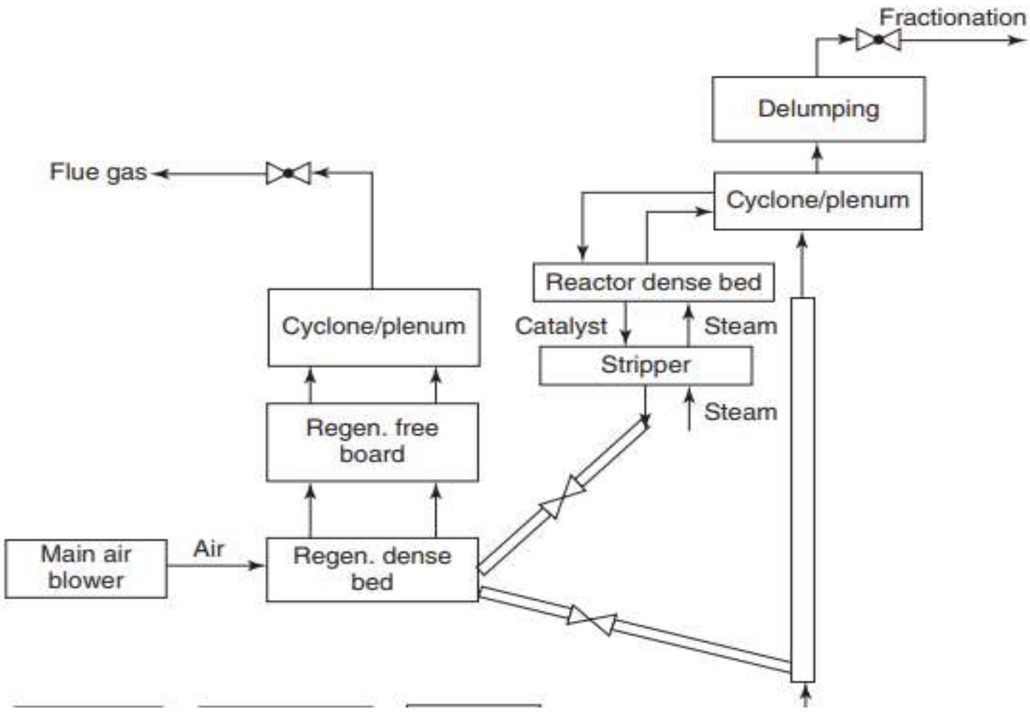



Figure 3.2 Petroleum Refining FCCU Sub-models in the Aspen HYSYS ([49]-[51])

### 3.4 Steps Of Modeling And Simulation Of FCCU In Aspen HYSYS

1- Properties Environment

- As a first step to build FCCU in Aspen HYSYS, we need to determine the components in properties environment. Therefore, the list of components is imported from the program (FCCU components Celsius. CML ), as shown in Figure 3.3 ([48]-[50]).

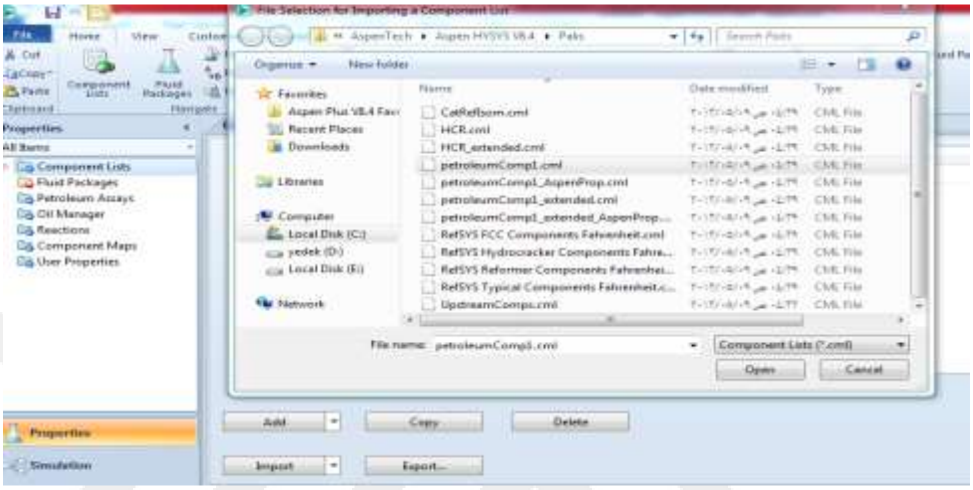


Figure 3.3 Petroleum component list

- Secondly, we have to select a fluid package which can deal with pseudo-component (hypothetical component). The recommended fluid package is Peng–Robinson, as shown in Figure 3.4 ([48]-[50]). In addition, Redlich-Kwong Soave have been tried because it can deal with hydrocarbon systems as well.

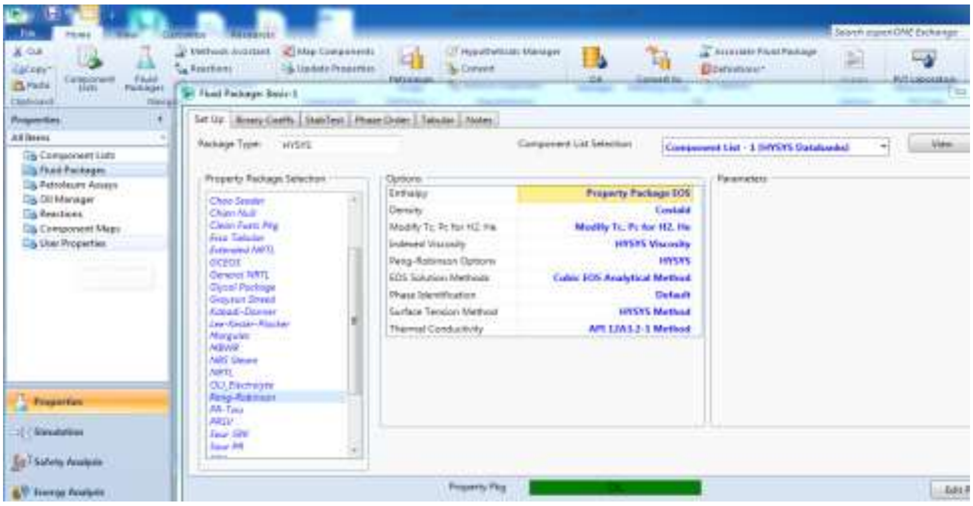


Figure 3.4 Thermodynamic of Fluid package

- The final step in this environment is to add reactions between the component according to activation energy and its frequency factor.

2- Simulation Environment

- When the required input is given in properties environment, we switch to the simulation environment. As the first step in this environment, FCCU model is selected from the models and streams palette > refining > FCCU and in this case, we have to choose either “Read an Existing FCCU Template” option or "configure a new FCCU unit"  option, as shown in Figure 3.5 ([48]-[50]).

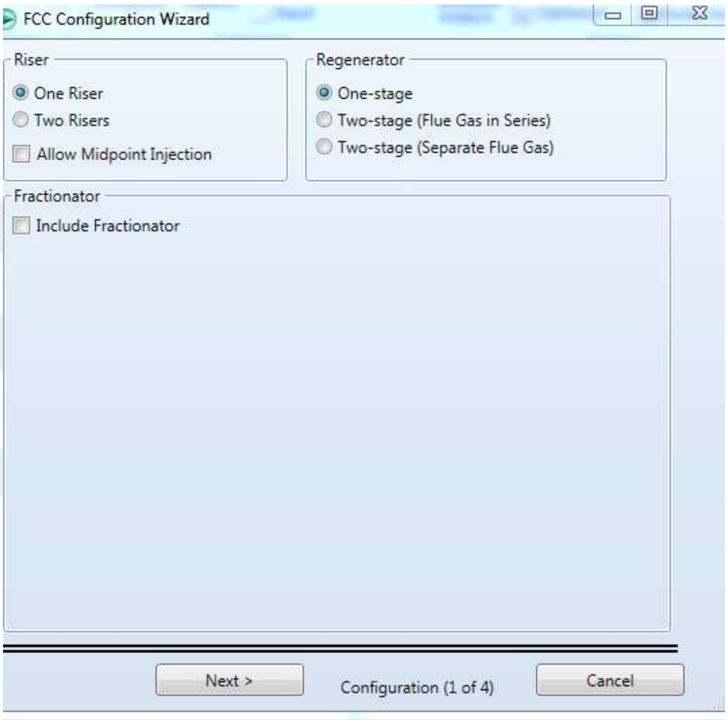



Figure 3.5 Selecting FCCU configuration

- Secondly, we have to determine which kind of FCCU we need to simulate in terms of risers numbers, stages of the regenerator, and with or without fractionators. After that, the geometric dimensions of FCCU have been entered, as shown in Figure 3.6 ([48]-[50]).

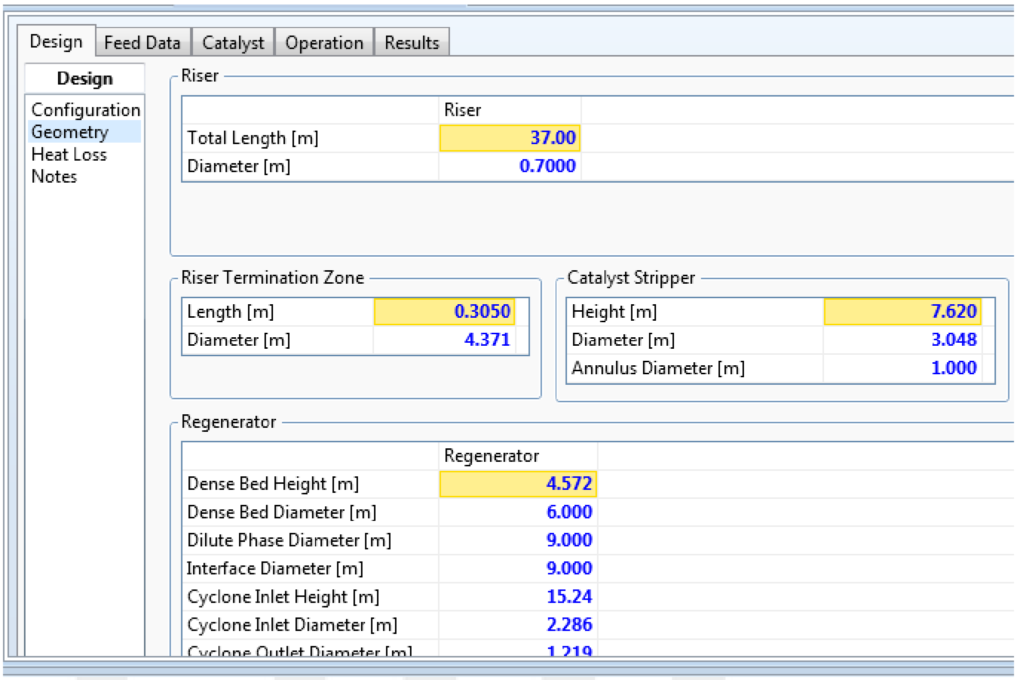



Figure 3.6 Geometric dimensions of Riser & Regenerator

- As a third step, under the design window, we have to define the feed stream of the reactor in the connection tab and specify the composition and properties of the catalyst in the Catalyst Blend tab, as shown in Figure 3.7 ([48]-[50]).

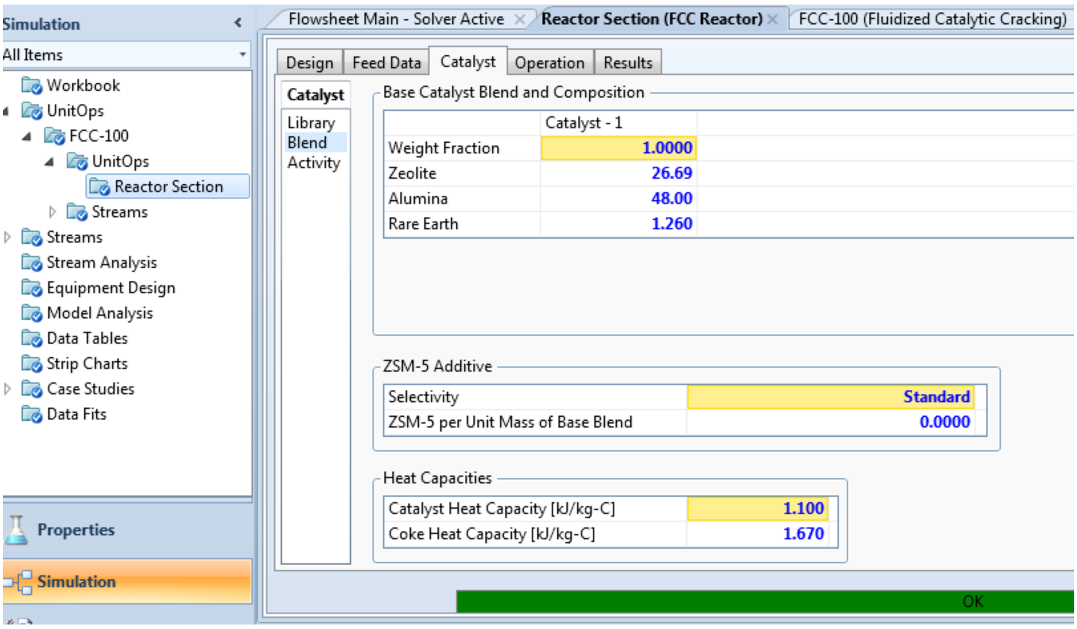
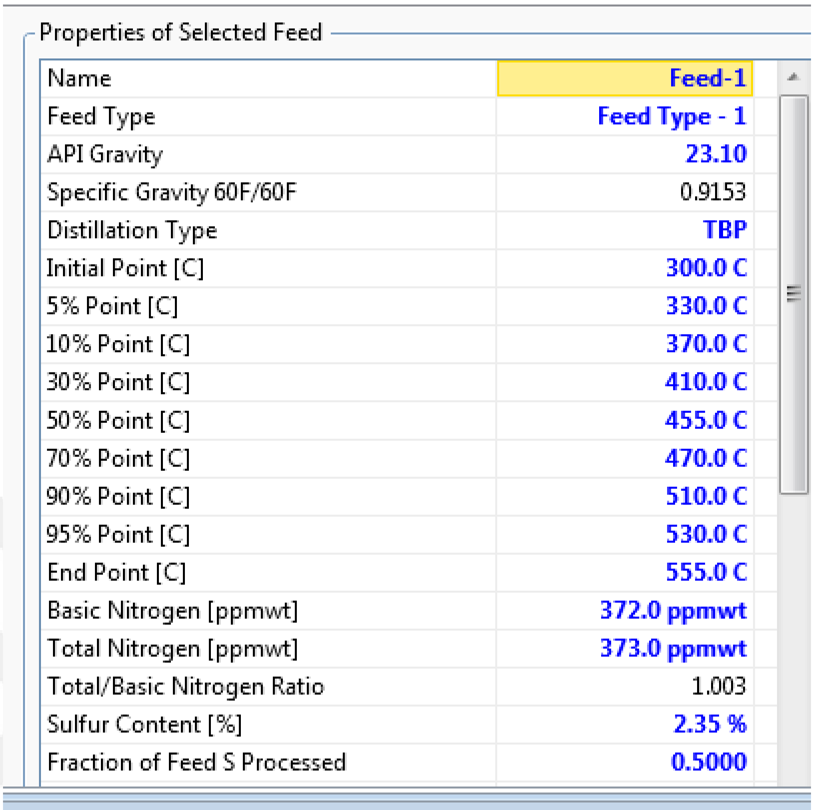



Figure 3.7 Catalyst properties

- Under Feed Data, we have to specify the type of feed in the library tab and enter the properties of the feed in the properties tab, as shown in Figure 3.8.


Properties of Selected Feed

| | |
|---|---|
| Name | Feed-1 |
| Feed Type | Feed Type - 1 |
| API Gravity | 23.10 |
| Specific Gravity 60F/60F | 0.9153 |
| Distillation Type | TBP |
| Initial Point [C] | 300.0 C |
| 5% Point [C] | 330.0 C |
| 10% Point [C] | 370.0 C |
| 30% Point [C] | 410.0 C |
| 50% Point [C] | 455.0 C |
| 70% Point [C] | 470.0 C |
| 90% Point [C] | 510.0 C |
| 95% Point [C] | 530.0 C |
| End Point [C] | 555.0 C |
| Basic Nitrogen [ppmwt] | 372.0 ppmwt |
| Total Nitrogen [ppmwt] | 373.0 ppmwt |
| Total/Basic Nitrogen Ratio | 1.003 |
| Sulfur Content [%] | 2.35 % |
| Fraction of Feed S Processed | 0.5000 |

Figure 3.8 Feed properties

- Under Reactor Section, we have to define the operating conditions such as feed flow, temperature, pressure, location, sulfur processed, and steam parameters in the feed tab. Also, we have to define metals content and catalyst inventory in the Catalyst Activity tab. Moreover, we have to define the temperature of the reactor and stripping steam parameters in the Riser/Reactor tab and specify parameters of ambient air, oxygen content in flue gas, discharge temperature of air blower in the Regenerator tab, as shown in Figure 3.9 ([48]-[50]).

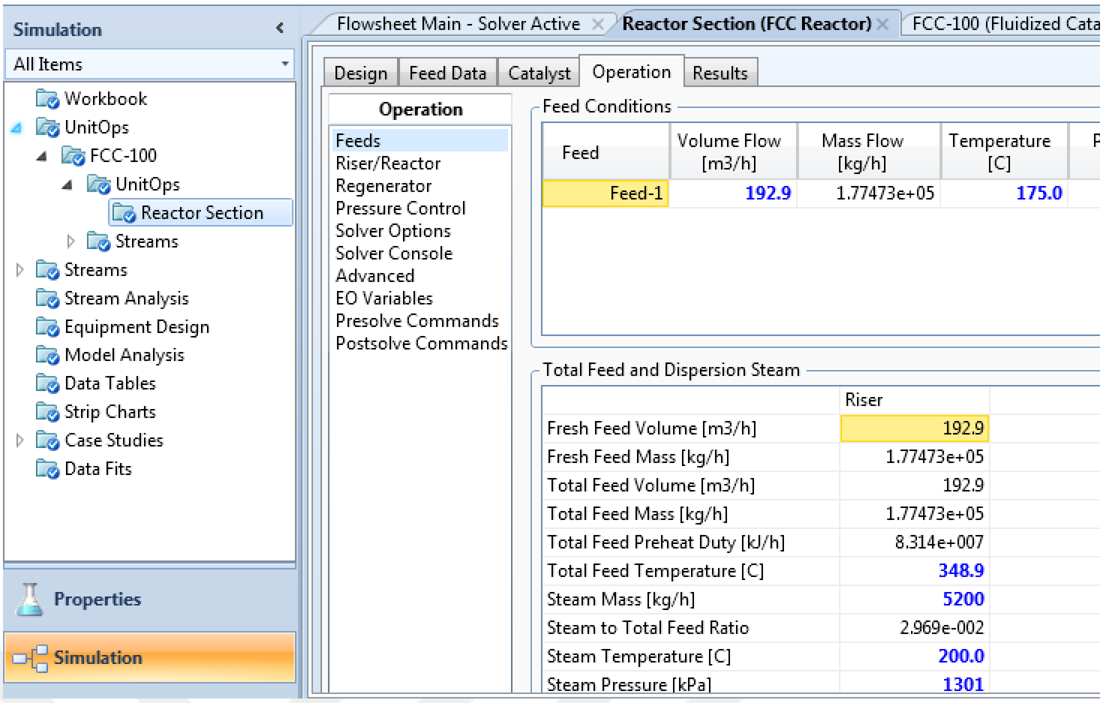
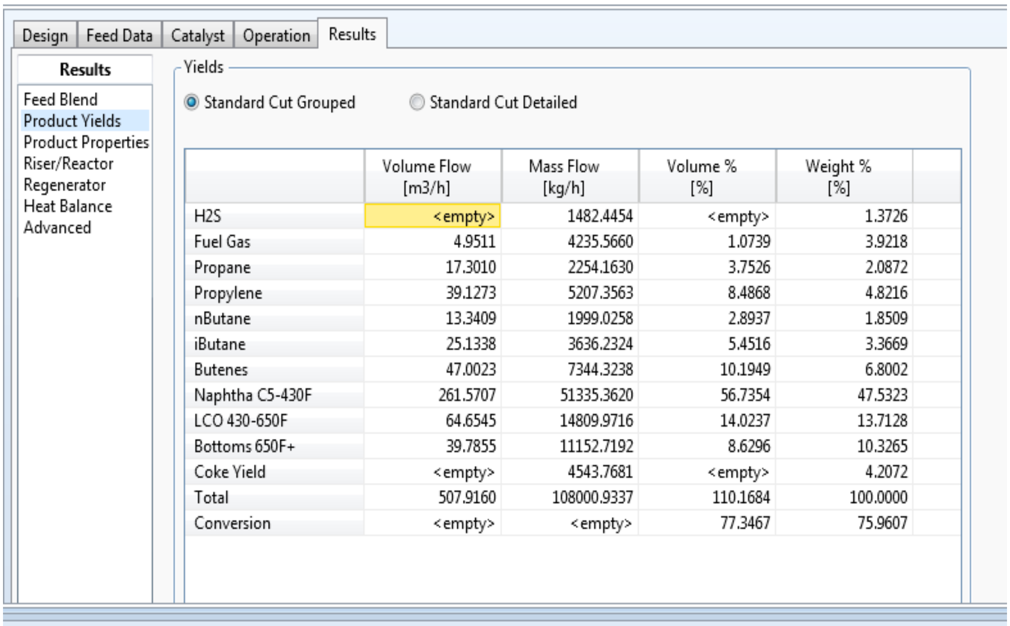



Figure 3.9 Operating conditions

- Finally, when all the required parameters are finished, Results are available in Feed Blend, Product Yields, Product Properties, Riser/Reactor, and Regenerator tabs under Results, example as shown in Figure 3.10 ([48]-[50]).




| | Volume Flow [m3/h] | Mass Flow [kg/h] | Volume % [%] | Weight % [%] |
|---|---|---|---|---|
| H2S | <empty> | 1482.4454 | <empty> | 1.3726 |
| Fuel Gas | 4.9511 | 4235.5660 | 1.0739 | 3.9218 |
| Propane | 17.3010 | 2254.1630 | 3.7526 | 2.0872 |
| Propylene | 39.1273 | 5207.3563 | 8.4868 | 4.8216 |
| nButane | 13.3409 | 1999.0258 | 2.8937 | 1.8509 |
| iButane | 25.1338 | 3636.2324 | 5.4516 | 3.3669 |
| Butenes | 47.0023 | 7344.3238 | 10.1949 | 6.8002 |
| Naphtha C5-430F | 261.5707 | 51335.3620 | 56.7354 | 47.5323 |
| LCO 430-650F | 64.6545 | 14809.9716 | 14.0237 | 13.7128 |
| Bottoms 650F+ | 39.7855 | 11152.7192 | 8.6296 | 10.3265 |
| Coke Yield | <empty> | 4543.7681 | <empty> | 4.2072 |
| Total | 507.9160 | 108000.9337 | 110.1684 | 100.0000 |
| Conversion | <empty> | <empty> | 77.3467 | 75.9607 |

Figure 3.10 Example of simulation result

### 3.5 Modeling With 7-Lumps In Aspen HYSYS

7-lumps kinetics model has been described as a heavy feedstock kinetics model with 22.3 API gravity. This model has been considered as sour gas, as shown in the Figure 3.11[52]. It is composed of the following lumps:

(1) Feedstock (VGO)

(2) Gasoline

(3) Cyclic oils

(4) LPG

(5) Light gases

(6) Sour gas ($H_2S$)

(7) Coke

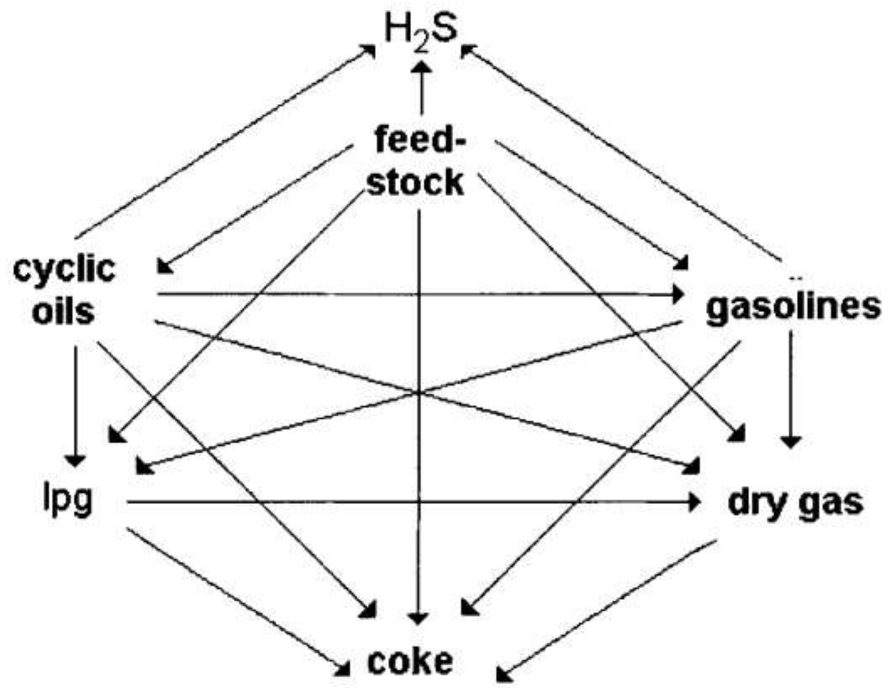



Figure 3.11 Seven lumps kinetics model [52]

The 7-lumps kinetics model has been entered to Aspen HYSYS (V.10) according to its boiling point and molecular weight, as shown in Table 3.2 [23]. Moreover, the properties of feedstock and kinetics parameters of reaction have been used in the simulation, and reported in the Table 3.3 and Table 3.4, respectively ([52]-[54]).

Table 3.2 Boiling Range of 7-lumps and their molecular weight [23]

| No. | Lumps | Boiling Point (°C) | Molecular weight (g/mol) |
|---|---|---|---|
| 1 | VGO | 420 | 386 |
| 2 | LCO | 280 | 226 |
| 3 | Gasoline | 125 | 117.8 |
| 4 | LPG | -42 | 46.7 |
| 5 | Sour gas | -60.7 | 34.08 |
| 6 | Dry gas | -162 | 18.4 |
| 7 | Coke | 700 | 12 |

Table 3.3 Properties of feedstock in the 7-lumps kinetics model ([52]-[54])

| | |
|---|---|
| Specific gravity | 0.92 |
| 10 (wt%) | 346 °C |
| 30 (wt%) | 412 °C |
| 50 (wt%) | 422 °C |
| 70 (wt%) | 476 °C |
| 90 (wt%) | 501 °C |
| Rambsbotton C (ppm) | 0.2 |
| Ni(ppm) | 380 |
| V(ppm) | 440 |
| Fe(ppm) | 750 |
| Cu(ppm) | 2.5 |

Table 3.4 Reaction parameters of activation energy and its frequency factor in the 7-lumps kinetics model ([52]-[54])

| Reaction path | K° | Activation energy (kJ/mole) |
|---|---|---|
| 1 (Feedstock → cycle oils) | 240 | 70 |
| 2 (Feedstock → gasoline) | 380 | 70 |
| 3 (Feedstock → LPG) | 70.5 | 70 |
| 4 (Feedstock → dry gas) | 217.5 | 80 |
| 5 (Feedstock → sour gas) | 2400 | 70 |
| 6 (Feedstock → coke) | 0.4 | 50 |
| 7 (Cycle oils →gasoline) | 24 | 60 |
| 8 (Cycle oils →LPG) | 30 | 60 |
| 9 (Cycle oils → dry gas) | 217.5 | 60 |
| 10 (Cycle oils → sour gas) | 600 | 70 |
| 11 (Cycle oils → coke) | 0.6 | 50 |
| 12 (Gasoline → LPG) | 1 | 50 |
| 13 (Gasoline → dry gas) | 145 | 70 |
| 14 (Gasoline → sour gas) | 300 | 70 |
| 15 (Gasoline → coke) | 0.5 | 50 |
| 16 (LPG → dry gas) | 261 | 40 |
| 17 (LPG → coke) | 0.4 | 40 |
| 18 (Dry gas → coke) | 1.3 | 40 |

### 3.6 Modeling With 8-Lumps In Aspen HYSYS

The 8-Lumps kinetics model has been used to describe heavy gas oil with 24.3 API gravity by using Aspen HYSYS (V.10). The simulation of this model is run according to molecular weight and boiling point of lumps, as shown in Table 3.5 [57]. The 8-lumps model is composed of the following lumps, as shown in the Figure 3.12 ([55]-[57]):

(1) Feedstock (VGO)

(2) Diesel and gasoline

(3) LPG (i.e. C3-C4)

(4) Butylenes (i.e. C4 and i-C4)

(5) Propylene (i.e. C3)

(6) Ethylene (i.e. C2)

(7) Light gases (i.e. C1-C2)

(8) Coke

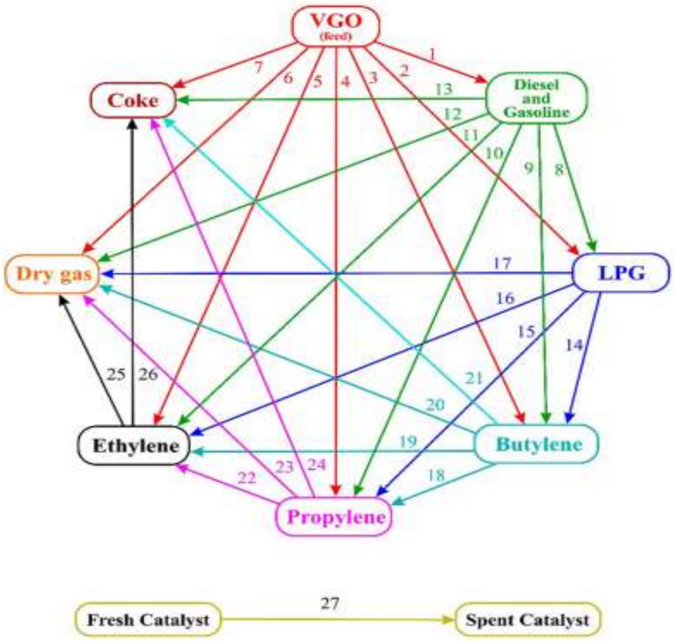



Figure 3.12 Eight lumps kinetics model network

Table 3.5 Boiling range of 8-Lumps and their molecular weight [57]

| No. | Lumps | Boiling Point (°C) | Molecular weight (g/mol) |
|---|---|---|---|
| 1 | VGO | 422 | 386 |
| 2 | Gasoline | 125 | 117.8 |
| 3 | LPG | -42 | 46.7 |
| 4 | Butylene | -6.252 | 56 |
| 5 | Propylene | -47.75 | 42 |
| 6 | Ethylene | -103.8 | 28 |
| 7 | Dry gas | -162 | 18.4 |
| 8 | Coke | 700 | 12 |

The properties of the feedstock in this model are presented in the Table 3.6 ([35], [58]) and reaction parameters among lumps reported in the Table 3.7 [56].

Table 3.6 Properties of feedstock gas oil in the 8-lumps kinetics model ([35], [58])

| | |
|---|---|
| Specific gravity | 0.9082 |
| 10 (wt%) | 354 °C |
| 30 (wt%) | 412 |
| 50 (wt%) | 447 |
| 70 (wt%) | 476 |
| 90 (wt%) | 539 |
| Sulfur (wt%) | 0.69 |
| Rambsbotton C (wt%) | 0.28 |
| Aniline point (°C) | 85 |
| Paraffins (wt%) | 12.5 |
| Naphthenes (wt%) | 26.6 |
| Aromatics (wt%) | 60.9 |

Table 3.7 Reaction parameters of activation energy and its frequency factor in 8-lumps kinetics model [56]

| Reaction path | Frequency factor(1/s) | Activation energy (kJ/mole) |
|---|---|---|
| 1 | 6221.91 | 61.74 |
| 2 | 0.70 | 14.12 |
| 3 | 192.52 | 56.39 |
| 4 | 1488.07 | 67.51 |
| 5 | 26242704077.41 | 194.01 |
| 6 | 330.80 | 65.88 |
| 7 | 307.48 | 59.40 |
| 8 | 122726.33 | 123.06 |
| 9 | 67.12 | 42.23 |
| 10 | 132.96 | 132.96 |
| 11 | 47182250.91 | 199.9 |
| 12 | 1912.41 | 107.38 |
| 13 | 65942690.90 | 190.64 |
| 14 | 3324.59 | 70.87 |
| 15 | 24877575574.11 | 190.98 |
| 16 | 250457547109.65 | 199.32 |
| 17 | 61821942560.00 | 198.56 |
| 18 | 18777.24 | 99.3 |
| 19 | 465045616.48 | 164.58 |
| 20 | 18.56 | 78.01 |
| 21 | 3994459.22 | 156.29 |
| 22 | 4705616207.33 | 175.02 |
| 23 | 811578783.81 | 186.46 |
| 24 | 89097.70 | 94.26 |
| 25 | 143185584.81 | 147.80 |
| 26 | 0.04 | 10.00 |

### 3.7 Modeling With 10-Lumps In Aspen HYSYS

There are two classifications in this model. One model has been based on molecular weight and molecular structure of the feedstock of gas oil. This model is composed of the following lumps: -

1- The light gas oil (LGO) components with boiling points from (222°C to 342°C) are each classified in four lumps: paraffin, naphthenes, aromatics, and aromatics with substituent branches.
2- The heavy gas oil (HGO) contains the same four lumps and every lumps has a boiling point (> 342°C).
3- Gasoline contains ($C_5$ - 222°C).

4- The "C" lumps contains coke and light gases ($C_1 - C_4$), as shown in Figure 3.13 below ([23], [59]).

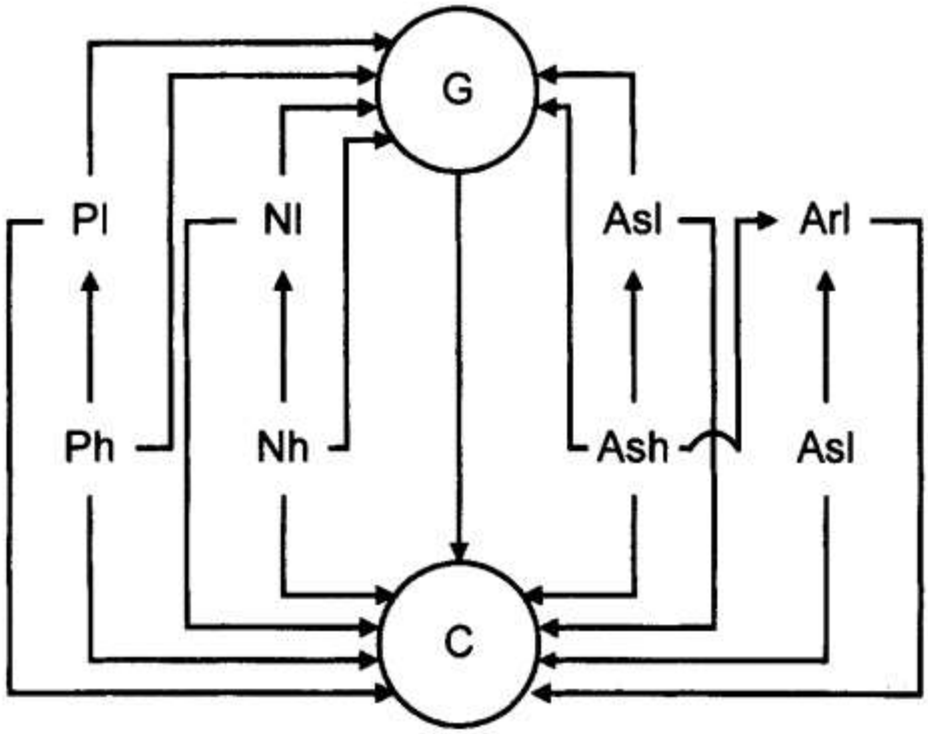



Figure 3.13 Ten lumps kinetics models network ([23], [59])

Table 3.8 Abbreviations of 10- lumps kinetics model ([23], [59])

| Lumps | Description |
|---|---|
| $P_h$ | Heavy Paraffinic molecules |
| $N_h$ | Heavy Naphthenic molecules |
| $A_{sh}$ | Heavy Aromatic substituent molecules |
| $A_{rh}$ | Heavy Carbon atoms among aromatic rings |
| $P_l$ | Light Paraffinic molecules |
| $N_l$ | Light Naphthenic molecules |
| $A_{sl}$ | Light Aromatic substituent molecules |
| $A_{rl}$ | Light Carbon atoms among aromatic rings |
| G | Gasoline |
| C | Coke + light gases |

In this study, the second classification of this model has been used which is composed of four lumps (gasoline, dry gas, LPG and coke) and six lumps of the light and heavy fractions of paraffin, naphthenes, and aromatics, as shown in Figure 3.14 [60].

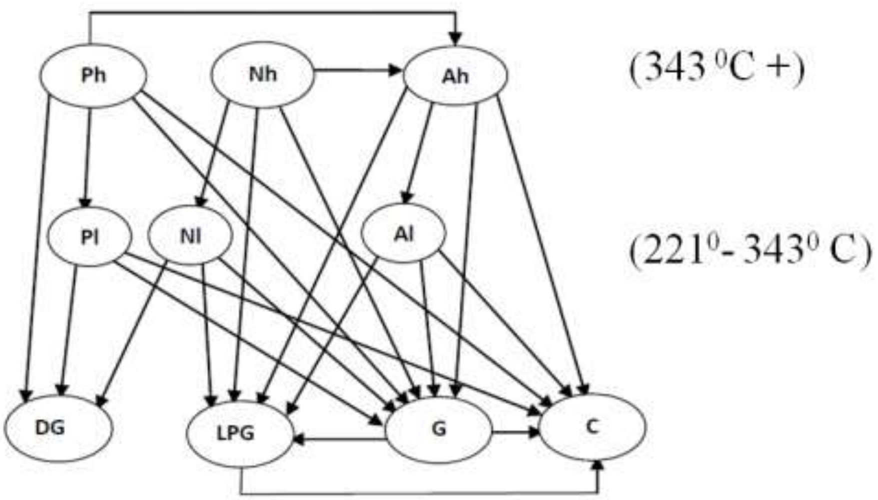



Figure 3.14 Ten lumps kinetics model network [60]

This model has been used to describe light gas oil with 27.6 API gravity by using Aspen HYSYS (V.10). Lumps have been entered to Aspen HYSYS according to boiling point for each lumps and its molecular weight, as shown in Table 3.9. The properties of feedstock and reaction parameters are shown in Table 3.10 and Table 3.11, respectively [60].

Table 3.9 Boiling Range of 10-lumps and their molecular weight [60]

| No. | Lumps | Boiling Point (°C) | Molecular weight (g/mol) |
|---|---|---|---|
| 1 | Heavy paraffin (Ph) | $343^+$ | 339 |
| 2 | Heavy naphthenes (Nh) | $343^+$ | 339 |
| 3 | Heavy aromatics (Ah) | $343^+$ | 339 |
| 4 | Light paraffins (Pl) | 221- 343 | 240 |
| 5 | Light naphthenes (Nl) | 221- 343 | 240 |
| 6 | Light aromatics (Al) | 221- 343 | 240 |
| 7 | Gasoline(G) | 125 | 117.8 |
| 8 | Liquefied Petroleum Gas (LPG) | 42 | 46.7 |
| 9 | Dry Gas (DG) | -162 | 18.4 |
| 10 | Coke (C) | 700 | 12 |

Table 3.10 Properties of feed in 10-lumps kinetics model [60]

| | |
|---|---|
| Specific gravity | 0.8896 |
| 0 (wt%) | 288 °C |
| 5 (wt%) | 370 °C |
| 10 (wt%) | 386 °C |
| 30 (wt%) | 425 °C |
| 50 (wt%) | 450 °C |
| 70 (wt%) | 483 °C |
| 90 (wt%) | 530 °C |
| 95 (wt%) | 542 °C |
| 100 (wt%) | 546 °C |
| Sulfur (wt%) | 0.5 |
| Basic Nitrogen | 307 |
| Total Nitrogen | 900 |
| CCR (wt%) | 0.15 |
| V (ppm) | <0.2 |
| Ni (ppm) | <0.2 |
| Fe (ppm) | 0.36 |
| Cu (ppm) | <0.2 |

Table 3.11 Reaction parameters of activation energy and its frequency factor in 10-lumps model [60]

| Reaction path | Frequency factor(1/s) | Activation energy (kJ/mole) |
|---|---|---|
| 1 (Ph → Ah) | 0.54 | 10207 |
| 2 (Ph → Pl) | 9.19 | 11374 |
| 3 (Ph → G) | 0.45 | 21583 |
| 4 (Ph → DG) | 0.33 | 8743 |
| 5 (Ph → Coke) | 1.96 | 15725 |
| 6 (Nh → Ah) | 1.92 | 8038 |
| 7 (Nh →Nl) | 0.85 | 15015 |
| 8 (Nh → G) | 0.80 | 16210 |
| 9 (Nh→ LPG) | 2.00 | 44570 |
| 10 (Ah → Al) | 0.90 | 19473 |
| 11 (Ah → G) | 0.40 | 8119 |
| 12 (Ah → LPG) | 0.35 | 14286 |
| 13 (Ah → Coke) | 0.59 | 43132 |
| 14 (Pl → G) | 3.73 | 19239 |
| 15 (Pl → DG) | 0.33 | 22925 |
| 16 (Pl → Coke) | 0.45 | 22332 |
| 17 (Nl → G) | 1.70 | 21532 |
| 18 (Nl → LPG) | 0.30 | 26919 |
| 19 (Nl → DG) | 0.10 | 13253 |
| 20 (Al → G) | 1.57 | 25049 |
| 21 (Al → LPG) | 0.56 | 28050 |
| 22 (Al → Coke) | 0.19 | 25549 |
| 23 (G →LPG) | 0.29 | 37330 |
| 24 (G → Coke) | 0.49 | 33808 |
| 25 (LPG → Coke) | 0.35 | 24103 |

### 3.8 Catalyst

Unique characteristics of zeolite, such as thermal stability, acidity, and shape selectivity, make it the preferred catalyst in petroleum industries [61].

Zeolite Y is stable at a higher temperature, so it is the main zeolite component in FCCU catalyst. Moreover, it is very efficient when the smaller FCCU feed molecules enter through its microspores ([62], [63]). Therefore, the greatest yield of gasoline at the high octane with the greatest degree of catalytic stability is provided by zeolite Y [64]. The simulations of three models have been done by using Aspen HYSYS (V.10) at the same commercial catalyst. The properties of catalyst have been used in these simulation are given in the Table 3.12 ([56], [58]).

Table 3.12 Properties of catalyst ([56], [58])

| Particle size (μm) | |
|---|---|
| 0-20 | 0 wt% |
| 0-40 | 6 wt% |
| 0-80 | 60 wt% |
| Average particle diameter (μm) | 75 |
| Bulk density (g/cm$^3$) | 0.94 |
| BET surface area (g/cm$^2$) | 205 |
| Composition | |
| Cu | 10 ppm |
| Ni | 270 ppm |
| V | 1200 ppm |
| Fe | 0.35 wt% |
| Na | 0.17 wt% |
| C | 0.10 wt% |
| $Al_2O_3$ | 48.0 wt% |
| ReO | 1.26 wt% |

### 3.9 Operating Conditions

The 7-lumps kinetics model, 8-lumps kinetics model, and 10-lumps kinetics model have been simulated by using Aspen HYSYS (V.10) at the same industrial operating conditions, as shown in Table 3.13 [60].

Table 3.13 Operating conditions [60]

| | |
|---|---|
| Feed rate (kg/s) | 49.3 |
| Feed Preheat (K) | 621.9 |
| Reactor outlet temperature (K) | 767.3 |
| Cat/Oil | 4.6 |
| Cat circulation rate (kg/sec) | 225 |
| Catalyst density (kg/m$^3$) | 817 |
| Reactor pressure (kpa) | 229.5 |
| Regenerator pressure (kpa) | 256.9 |
| Regenerator dense phase temperature (K) | 938 |
| Regenerator dilute phase temperature (K) | 958.2 |
| Riser height (m) | 37 |
| Riser diameter (m) | 0.7 |

### 3.10 Overall Strategy Of Modeling

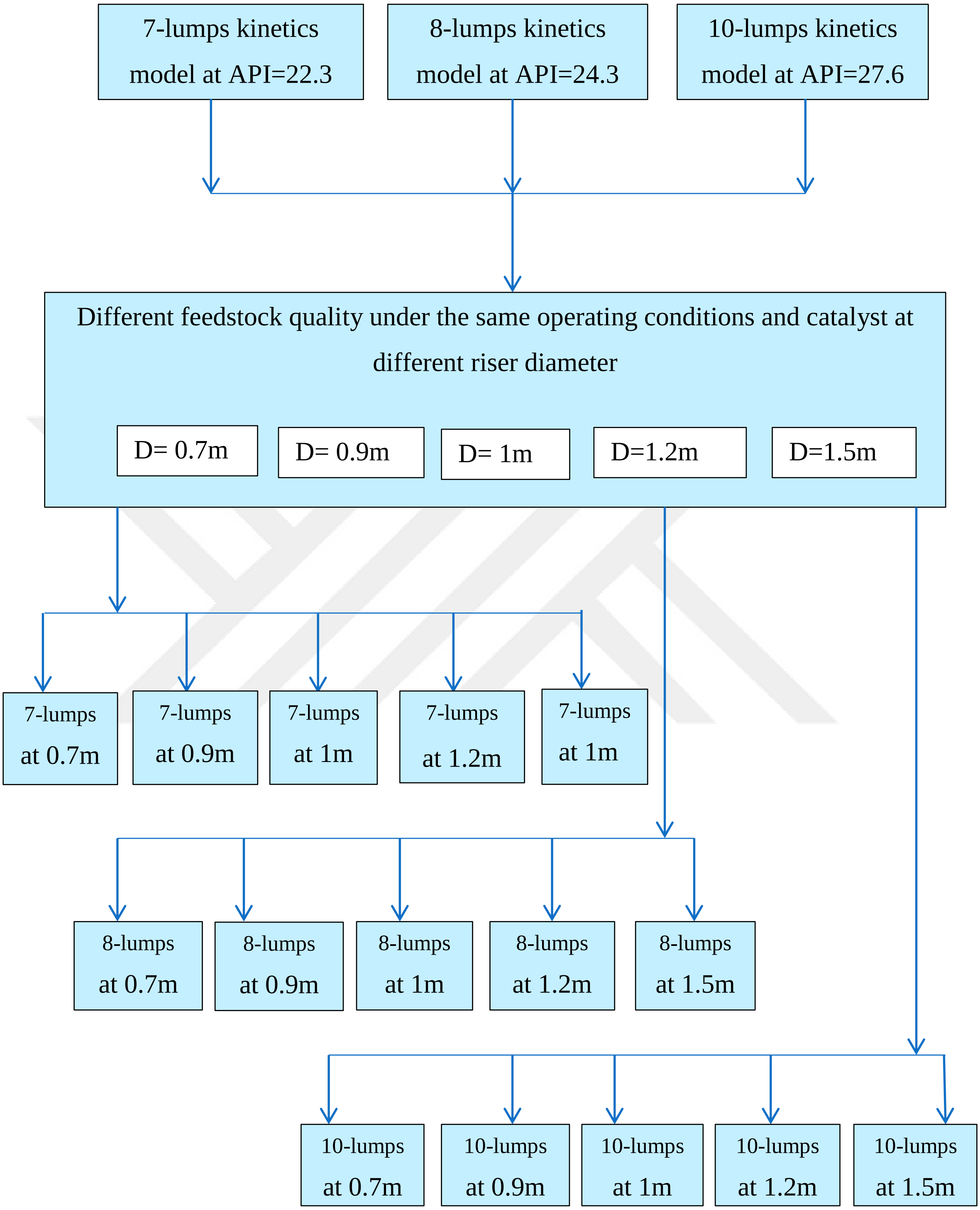



Figure 3.15 Overall strategy of modeling

# CHAPTER 4
# RESULT AND DISCUSSION

## 4.1 Introduction

FCCU have been studied by dividing feedstock and products as kinetics lumps such as (three lumps, four lumps, five lumps, six lumps, etc.). Additionally, there are two methods in order to determine the kinetics parameters in model network. The first method is to experimentally measure the compositions of the products, and make a calibration by using Aspen HYSYS [51]. The second method is to use the reaction kinetics (frequency factor and activation energy) in each reaction and predict the product yield ([56], [52], [60]). The second method has been considered in this work, because we do not have experimental data.

7-, 8-, and 10-lumps kinetics models have been considered because their quality changes from heavy to light feedstock. These models have been considered at the same catalyst and operating conditions. Then, they have been tested at different hydrodynamic design (Riser Diameter). First, different feedstock qualities have been tested at different riser diameter, and the predicted results have been compared with industrial plant data. In the following part the most important operating conditions were shown for the heaviest feedstock.

**Part I**

In this part, the feedstock qualities have been tested at different riser diameter and the predicted results have been compared with industrial plant data. That is, each model has been tested at a riser diameter of 0.7m, 0.9m, 1m, 1.2m and 1.5m and the most suitable riser diameter have been specified according to the deviation percent between real and predicted result for each feedstock quality.

## 4.2 Validations Of The Kinetics Models

### 4.2.1 Validation Of Model I (7-Lumps Kinetics Model)

The predicted results in 7-Lumps kinetics model at different riser diameters are presented in Table 4.1.

The predicted results in this kinetics model match closely with commercial FCCU yields at 1.5m riser diameter, with average absolute deviation of 2.93%. But, the average absolute deviation is 8.74% at 0.7 m riser diameter because the feedstock quality in this model is heavy. Therefore, it requires a large riser diameter in order to get a higher yield of gasoline. Meanwhile, LPG is over-predicted because the secondary reactions of gasoline took place in the case of a large riser diameter. Moreover, LPG yield of heavy feedstock has not matched with industrial plant data of light feedstock, even with an increased riser diameter. On the other hand, gasoline yield has increased at large riser diameter, due to increased residence time that convert LCO and bottoms into gasoline. Superficial velocity changes from 8 to 4.11 m/s for 0.7 to 1.5m riser diameter. This is also an indication of an increasing in the residence time. The comparison of industrial plant data with simulation results of 7-lumps kinetics model are shown in Figure 4.1.

Table 4.1 Comparison of 7-Lumps kinetics model simulation results with industrial plant data

| Parameters | Industrial plant data [60] | 7-Lumps simulation results | | | | |
|---|---|---|---|---|---|---|
| | | D=0.7m | D=0.9m | D=1m | D=1.2m | D=1.5m |
| Dry Gas ( wt %) | 1.5 | 0.98 | 1.08 | 1.1 | 1.2 | 1.3 |
| LPG (wt %) | 11.4 | 10.9 | 12.37 | 13.2 | 14.3 | 15.9 |
| Gasoline (C5 - 221°C) (wt %) | 51.5 | 26.4 | 31.2 | 33.5 | 37.3 | 41.3 |
| LCO( 221 -343) (°C) | 17.2 | 23.9 | 22.3 | 21.4 | 20 | 18.4 |
| Bottom (343+) (°C) | 14.5 | 32.5 | 27.2 | 24.9 | 20.7 | 16. |
| Coke (wt %) | 4 | 2.4 | 2.8 | 3 | 3.4 | 4 |
| Conversion (wt%) | | 43.5 | 50.4 | 53.7 | 59.2 | 65.5 |
| Ave. abs.dev. (AAD%) | | 8.74 | 6.78 | 5.97 | 4.5 | 2.93 |

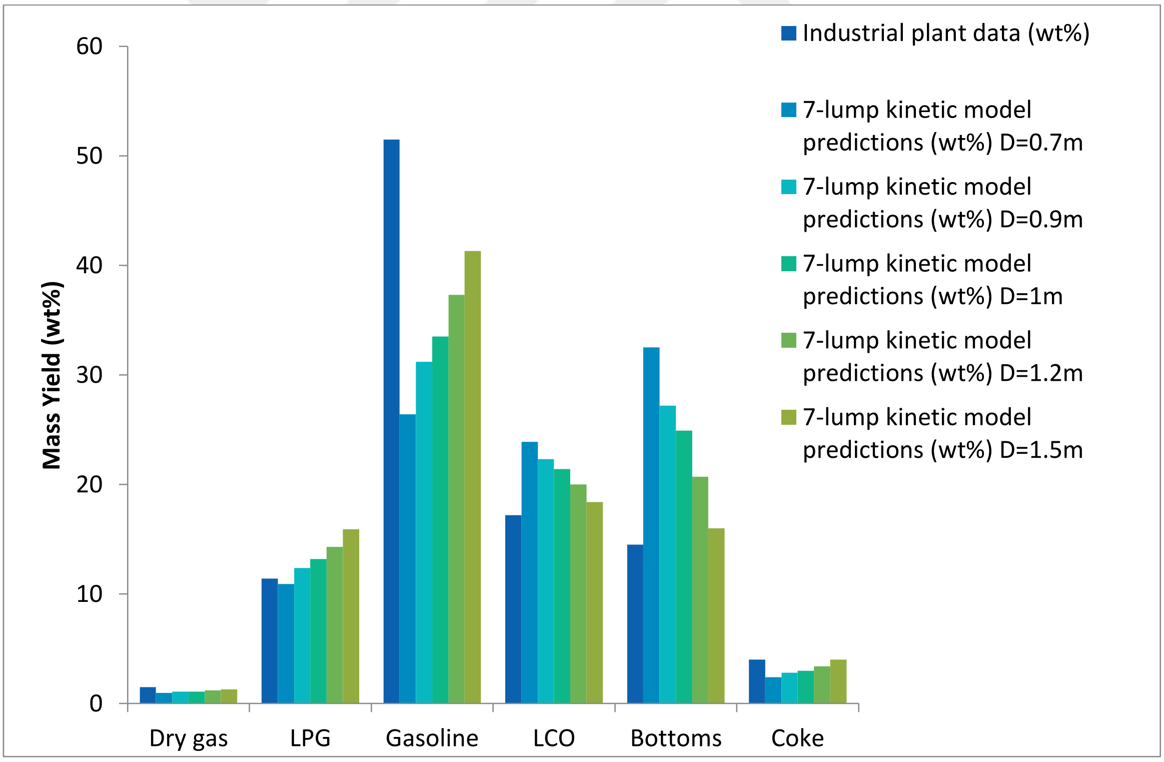



Figure 4.1 Comparison of 7-Lumps kinetics model predictions with industrial plant data

### 4.2.2 Validation Of Model II (8-Lumps kinetics model)

The results obtained in 8-Lumps kinetics model at different riser diameters are presented in Table 4.2.

The predicted results of this kinetics model match closely with commercial FCCU unit yields at 1.5m riser diameter, with average absolute deviation 2.25%. But, we can see clearly the average absolute deviation is 8.41% at 0.7 m riser diameter. Feedstock quality of this model is heavy. Therefore, large riser diameter is required because small riser diameter is not suitable for this kind of feedstock. Additionally, LPG yield increased because of the secondary reactions of gasoline, LCO, and bottoms at large riser diameter 1.5m. Therefore, a large riser diameter produced overcracking of gasoline, LCO, and bottoms. Superficial velocity changes from 7.6 to 3.83 m/s for 0.7 to 1.5m riser diameter. This is also an indication of an increasing in the residence time. The comparison of industrial plant data with simulation results of 8-lumps kinetics model is shown in Figure 4.2.

Table 4.2 Comparison of 8-Lumps kinetics model simulation results with industrial plant data

| Parameters | Industrial plant data [60] | 8-Lumps simulation results | | | | |
|---|---|---|---|---|---|---|
| | | D=0.7m | D=0.9m | D=1m | D=1.2m | D=1.5 m |
| Dry Gas ( wt %) | 1.5 | 1 | 1.1 | 1.2 | 1.3 | 1.4 |
| LPG (wt %) | 11.4 | 11.3 | 13 | 13.9 | 15.4 | 16.8 |
| Gasoline (C5 - 221°C) (wt %) | 51.5 | 28.2 | 33.7 | 36.2 | 40.6 | 45.4 |
| LCO( 221 -343) (°C) | 17.2 | 23.1 | 21 | 20.1 | 18.3 | 16.3 |
| Bottom (343+) (°C) | 14.5 | 32.8 | 27 | 24.3 | 19.7 | 14.5 |
| Coke (wt %) | 4 | 1.64 | 2 | 2.1 | 2.5 | 3 |
| Conversion (wt%) | - | 44 | 51.9 | 55.5 | 62 | 69.2 |
| Ave. abs.dev. (AAD%) | - | 8.41 | 6.35 | 5.45 | 3.82 | 2.25 |

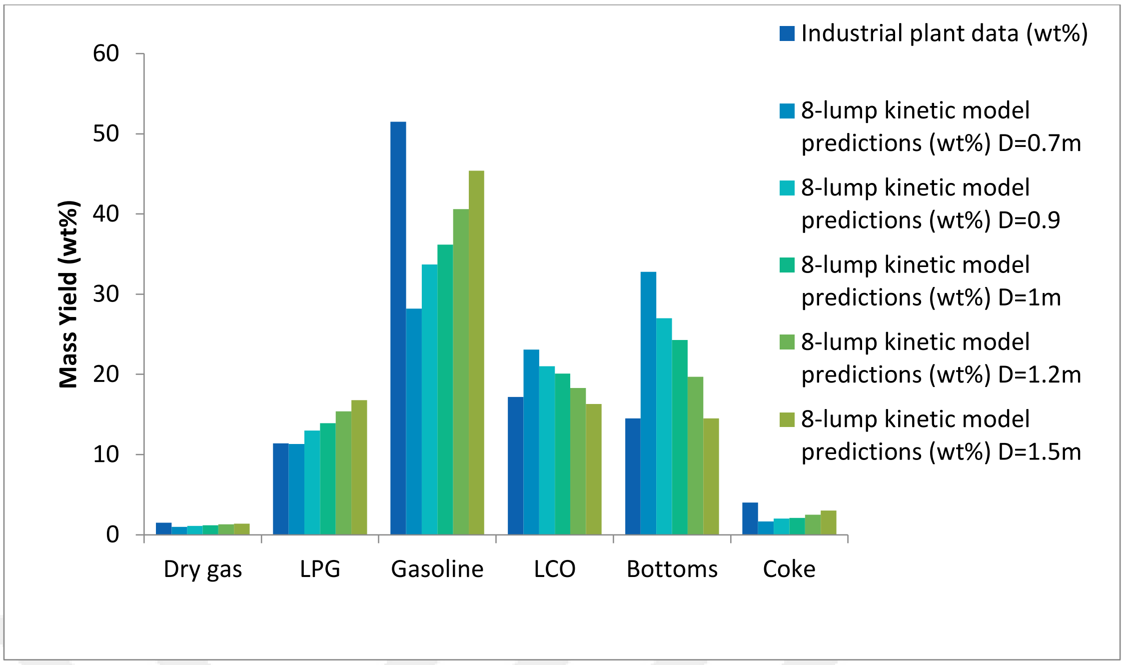



Figure 4.2 Comparison of 8-Lumps kinetics model predictions with industrial plant data

### 4.2.3 Validation Of Model III (10-Lumps Kinetics Model)

The results obtained in 10-Lumps kinetics model at different riser diameters are presented in Table 4.3.

The predicted results in this model have good agreement with commercial FCCU unit yields at 0.7 riser diameter, with average absolute deviation 1.66%. But, these results did not match closely at 1.5m riser diameter because the feedstock quality is light in this model. Therefore, LCO and bottoms lumps have been produced less than industrial result. Meanwhile, gasoline and LPG have been produced more than industrial result, because small riser diameter is more suitable than large riser diameter in case of light feedstock quality. Superficial velocity changes from 5.6 to 3 m/s for 0.7 to 1.5m riser diameter. This is also an indication of an increasing in the residence time.The comparison of industrial plant data with simulation results of 10-lumps kinetics model, as shown in Figure 4.3.

Table 4.3 Comparison of 10-Lumps kinetics model simulation results with industrial plant data

| Parameters | Industrial Plant data [60] | 10-Lumps simulation results | | | | |
|---|---|---|---|---|---|---|
| | | D=0.7m | D=0.9m | D=1m | D=1.2m | D=1.5m |
| Dry Gas ( wt %) | 1.5 | 1.1 | 1.06 | 1.22 | 1.3 | 1.34 |
| LPG (wt %) | 11.4 | 13.6 | 13 | 15 | 15.9 | 16.7 |
| Gasoline (C5 - 221 °C) (wt %) | 51.5 | 46.2 | 50.2 | 51.8 | 54.3 | 56.7 |
| LCO( 221 -343) (°C) | 17.2 | 17.5 | 15.5 | 14.6 | 13.2 | 11.4 |
| Bottom (343+) (°C) | 14.5 | 16 | 12.2 | 10.7 | 8.4 | 6.3 |
| Coke (wt %) | 4 | 3.7 | 4.1 | 4.3 | 4.7 | 5.2 |
| Conversion (wt%) | | 66.6 | 72 | 74.7 | 78.5 | 82.4 |
| Ave. abs.dev. (AAD%) | | 1.66 | 1.74 | 1.83 | 3.05 | 4.31 |

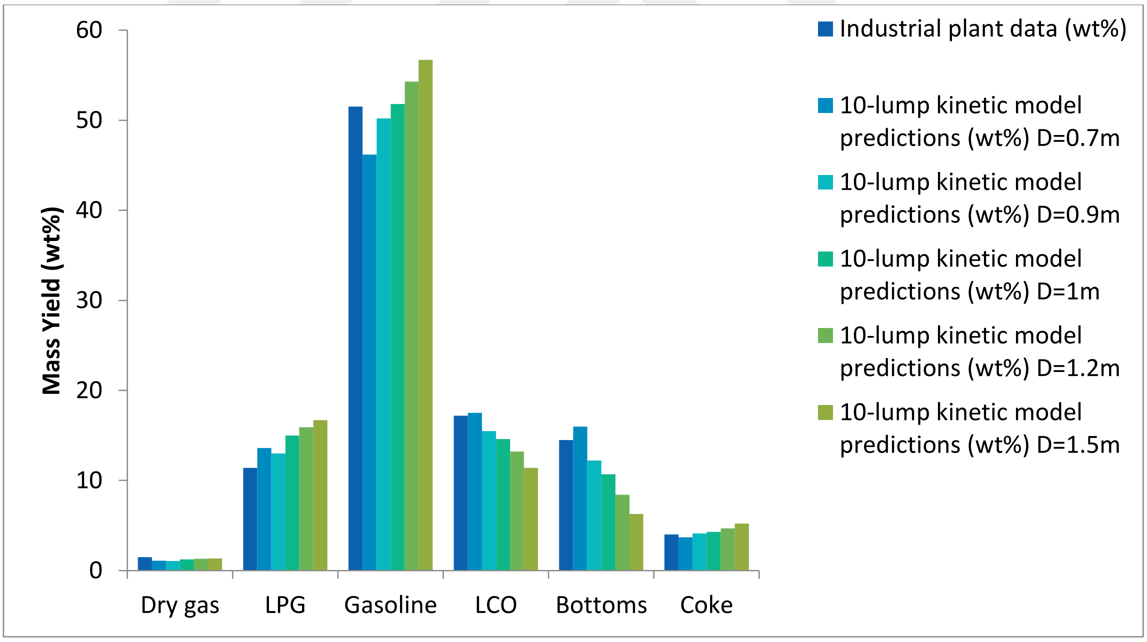



Figure 4.3 Comparison of 10-Lumps kinetics model predictions with industrial plant data

## Part II

In the first part, light and heavy feedstock qualities have been considered in 7-, 8-, and 10-lumps kinetics model respectively. In this part, the effects of some operating parameters and riser length have been studied. The feedstock in 7-lumps kinetics model has been considered, because it is the heaviest one, and presents Iraqi feedstock better. This feedstock has been tested in order to determine the effect of the riser length, riser outlet temperature, feedstock flow rate, and the dispersion steam flow rate on the desired product yield.

### 4.3 Riser Length

Residence time is increased by increasing the riser length. When the riser length is increased from 34 to 42 m, the residence time only increased from 1.2 to 1.55 Sec, as shown in Figure 4.4. As a result, gasoline yield increased from 25 wt% to 30 wt%, as shown in Table 4.4. Meanwhile LCO yield decreased from 25 wt% to 23wt%. Also, fuel gas and coke yield increased as well, as shown in Figure 4.5.

Table 4.4 Gasoline yield as a function of riser length

| Constant parameters | Riser Length range (m) | Gasoline Yield (wt%) |
|---|---|---|
| Riser diameter 0.7m<br>ROT,<br>Feed flow rate,<br>Dispersion steam flow rate | 33 | 25.2 |
| | 34 | 25.5 |
| | 35 | 25.8 |
| | 36 | 26.1 |
| | 37 | 26.4 |
| | 38 | 26.7 |
| | 39 | 27.0 |
| | 40 | 27.3 |
| | 41 | 27.6 |
| | 42 | 27.9 |
| | 43 | 28.1 |

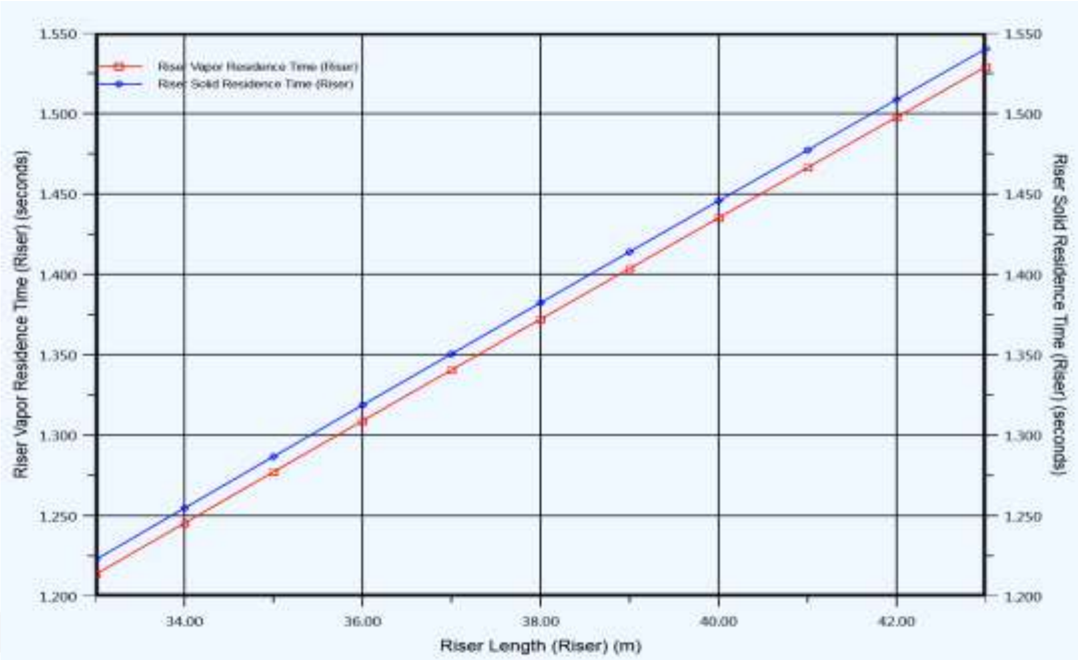



Figure 4.4 Residence time as a function of the Riser Length (m) in the 7-lumps kinetics model at 0.7m riser diameter

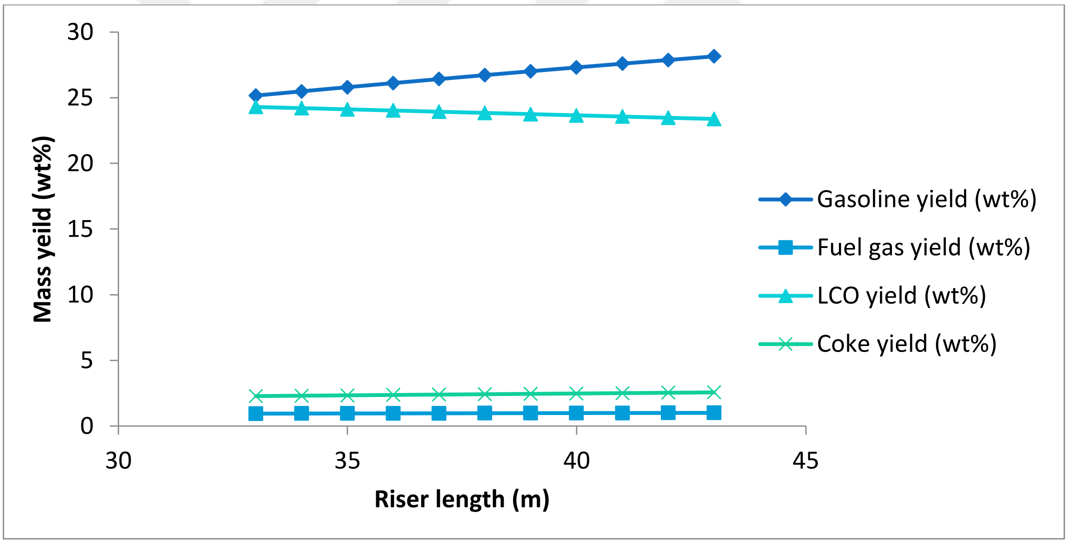



Figure 4.5 Mass yield (wt%) as a function of the Riser Length (m) in the 7-lumps kinetics model at 0.7m riser diameter

### 4.4 Riser Outlet Temperature

The yield of gasoline has been increased from 23 wt% to 39 wt% while LCO yield decreased from 25 wt% to 15 wt% by increasing ROT between 480- 560 °C as shown in Table 4.5. This is thought to be due to the increased reaction rate. But, after 560°C, the gasoline yield decreased to 25wt%, because it starts decaying into coke and fuel gas. Therefore, the yield of fuel gases and coke are increased, as shown in Figure 4.6.

Table 4.5 Gasoline yield as a function of ROT

| Constant parameters | ROT (°C) | Gasoline Yield (wt%) |
|---|---|---|
| Riser diameter 0.7m<br>Riser length,<br>Feed flow rate,<br>Dispersion steam flow rate | 480 | 23.1 |
| | 490 | 25.0 |
| | 500 | 27.0 |
| | 510 | 29.2 |
| | 520 | 31.6 |
| | 530 | 34.3 |
| | 540 | 37.2 |
| | 550 | 39.4 |
| | 560 | 39.5 |
| | 570 | 35.5 |
| | 580 | 25.3 |

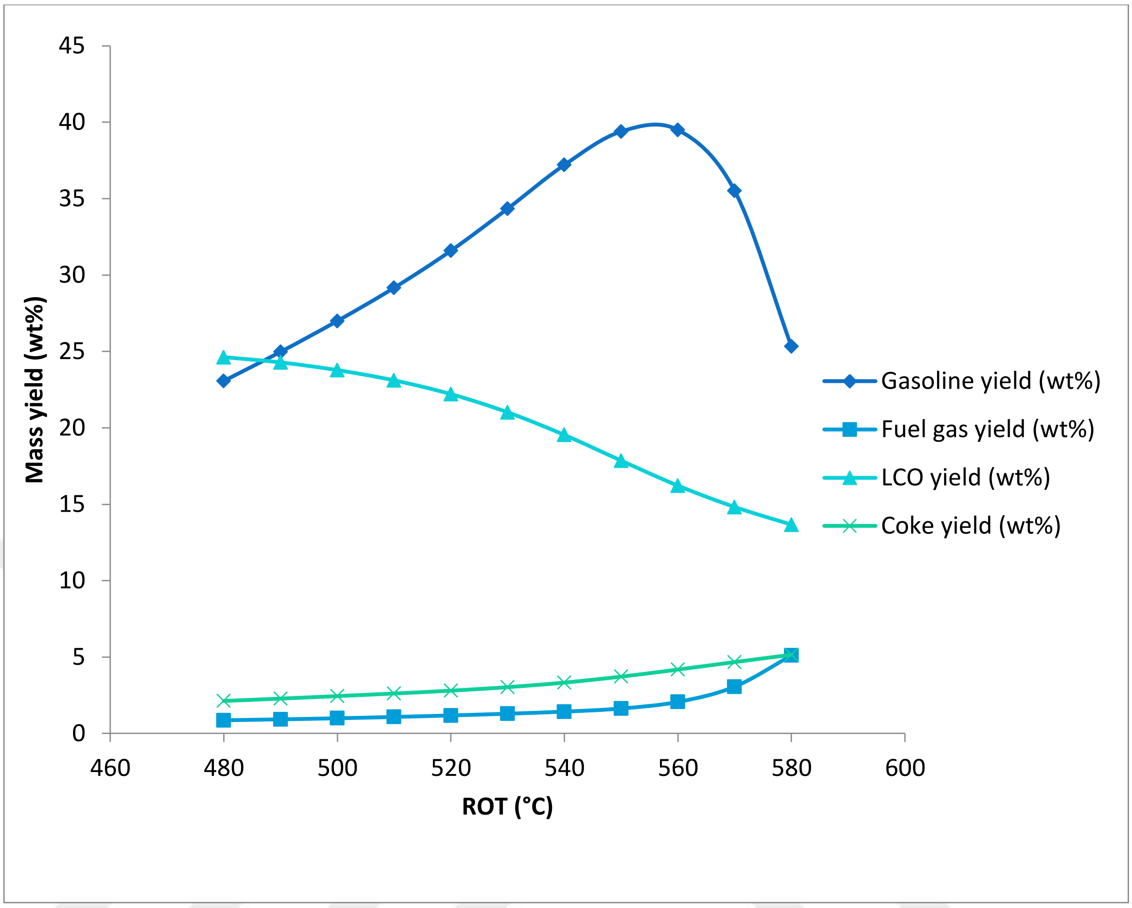



Figure 4.6 Mass yield (wt%) as a function of the ROT (°C) in 7-lumps kinetics model at 0.7m riser diameter

### 4.5 Flow Rate Of Feedstock

The yield of gasoline increased from 28 wt% to 33 wt% by decreasing the flow rate of the feedstock, as shown in Table 4.6. Meanwhile, the yield of LCO decreased, while coke and fuel gas yield increased, as shown in Figure 4.7. Residence time decreased from 1.75 sec to 1.2 sec with increased flow rate, as shown in Figure 4.8. On the other hand, the residence time increased from 1.2 to 5 sec when the riser diameter is increased from 0.7 to 1.6 m, as shown in Figure 4.9. As a result, the residence time increase by increasing the riser diameter is larger, compared to the increase in residence time by decreasing the feedstock flowrate. Moreover, when the feed flow rate is decreased, C/O ratio is increased that lead to increase in the yield, as shown in Figure 4.10.

Table 4.6 Gasoline yield as a function of feed flow rate

| Constant parameters | Feedstock flow rate (m3/hr) | Gasoline Yield (wt%) |
|---|---|---|
| Riser diameter 0.7m<br>Riser length,<br>ROT,<br>Dispersion steam) | 125 | 33.4 |
| | 135 | 32.7 |
| | 145 | 32.0 |
| | 155 | 31.4 |
| | 165 | 30.8 |
| | 175 | 30.3 |
| | 185 | 29.8 |
| | 195 | 29.3 |
| | 205 | 28.8 |
| | 215 | 28.4 |
| | 225 | 28.0 |

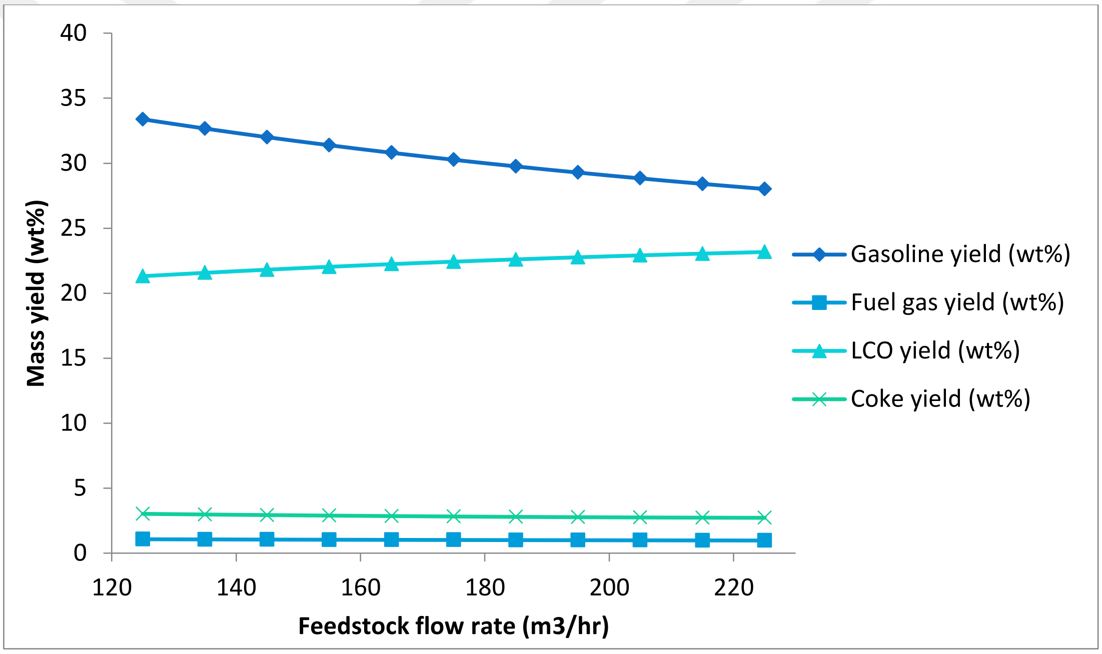



Figure 4.7 Mass yield (wt%) as a function of the Feedstock flow rate ($m^3$/hr) in the 7-lumps kinetics model at 0.7m riser diameter

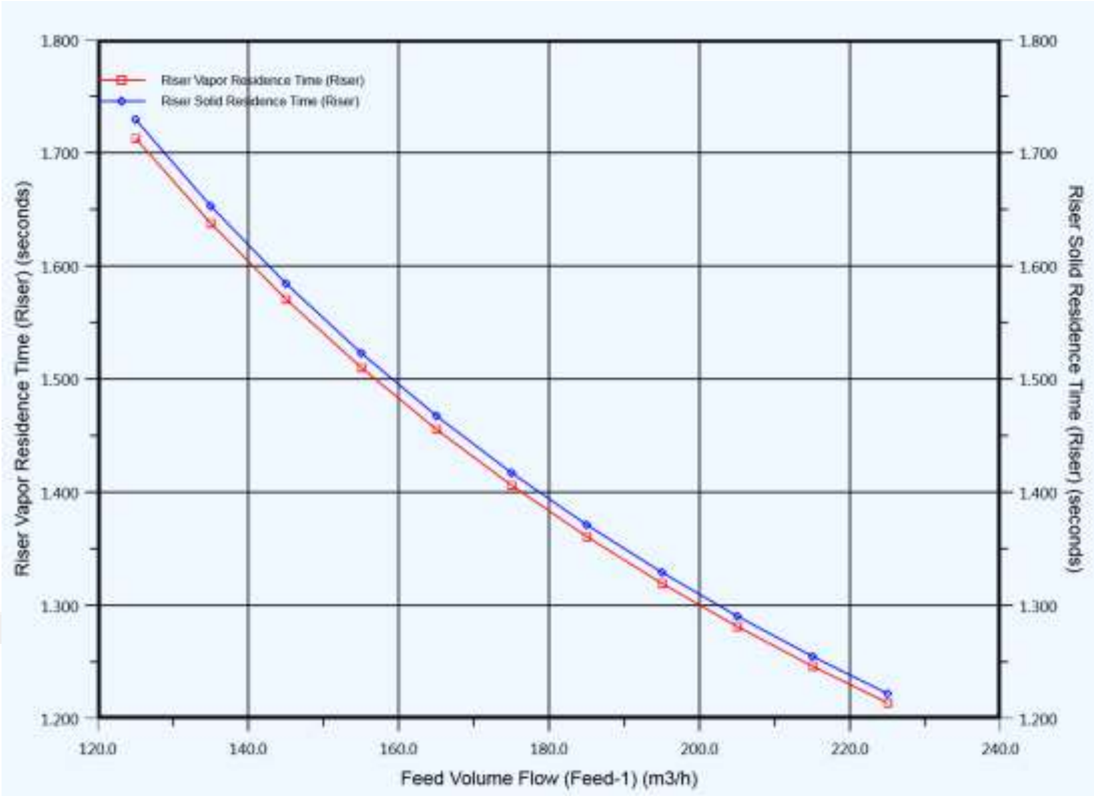



Figure 4.8 Residence time as a function of the Feedstock flow rate ($m^3$/hr) in the 7-lumps kinetics model at 0.7m riser diameter

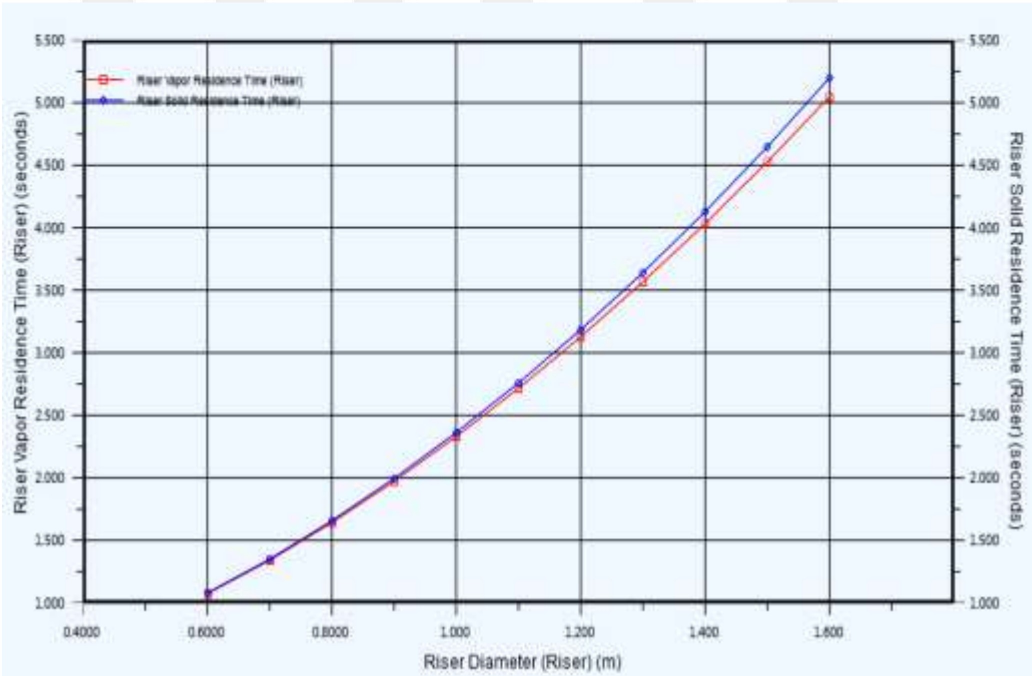



Figure 4.9 Residence time as a function of the Riser diameter (m) in the 7-lumps kinetics model at 0.7m riser diameter

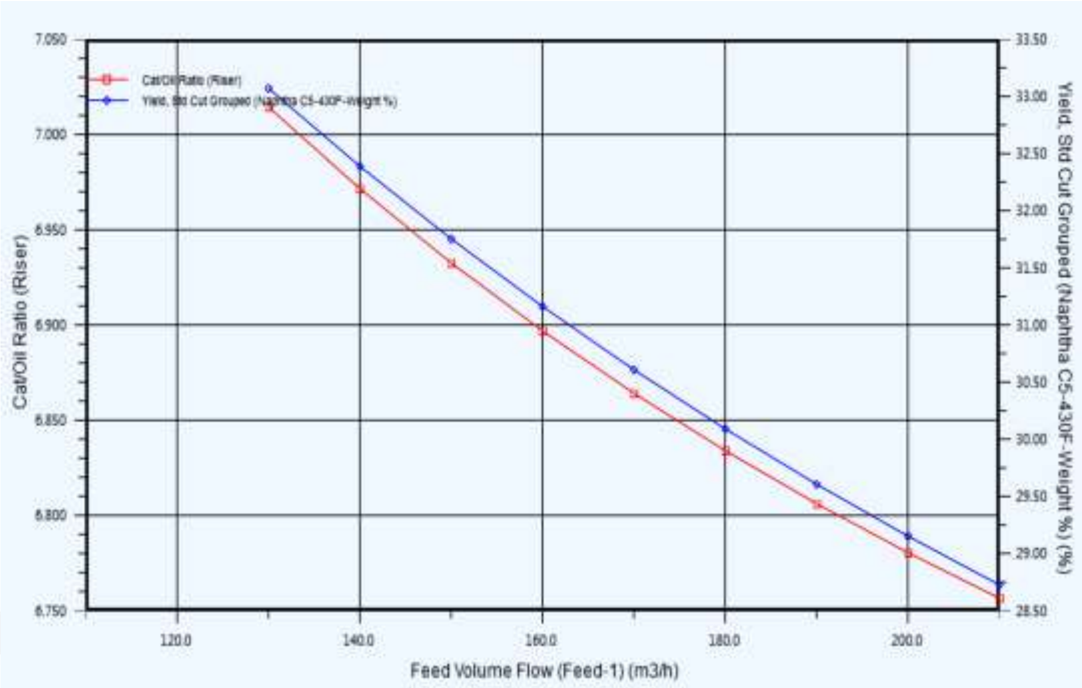



Figure 4.10 C/O ratio and as a function of the Feedstock flow rate ($m^3$/hr) in the 7-lumps kinetics model at 0.7m riser diameter

### 4.6 Dispersion Steam Flow Rate

Dispersion steam has been used in order to atomize the feed. Smaller feed droplets increase the availability of feed (adsorbed feed droplets in the pores of catalyst) at the reactive catalyst acid sites [1]. But, when the dispersion steam flow rate increase, the acid sites on the catalyst adsorb more steam which causes a decrease in the number available active sites for reactions. Therefore, the gasoline yield decrease, as shown in Figure 4.11 [58].

Table 4.7 Gasoline yield as a function of dispersion steam feed flow rate

| Constant parameters | Dispersion steam flow rate (kg/hr) | Gasoline Yield (wt%) |
|---|---|---|
| Riser diameter 0.7m<br>Riser length,<br>ROT,<br>Feed flow rate, | 4000 | 27.2 |
| | 4200 | 27.1 |
| | 4400 | 26.9 |
| | 4600 | 26.8 |
| | 4800 | 26.7 |
| | 5000 | 26.5 |
| | 5200 | 26.4 |
| | 5400 | 26.3 |
| | 5600 | 26.2 |
| | 5800 | 26.0 |
| | 6000 | 25.91 |

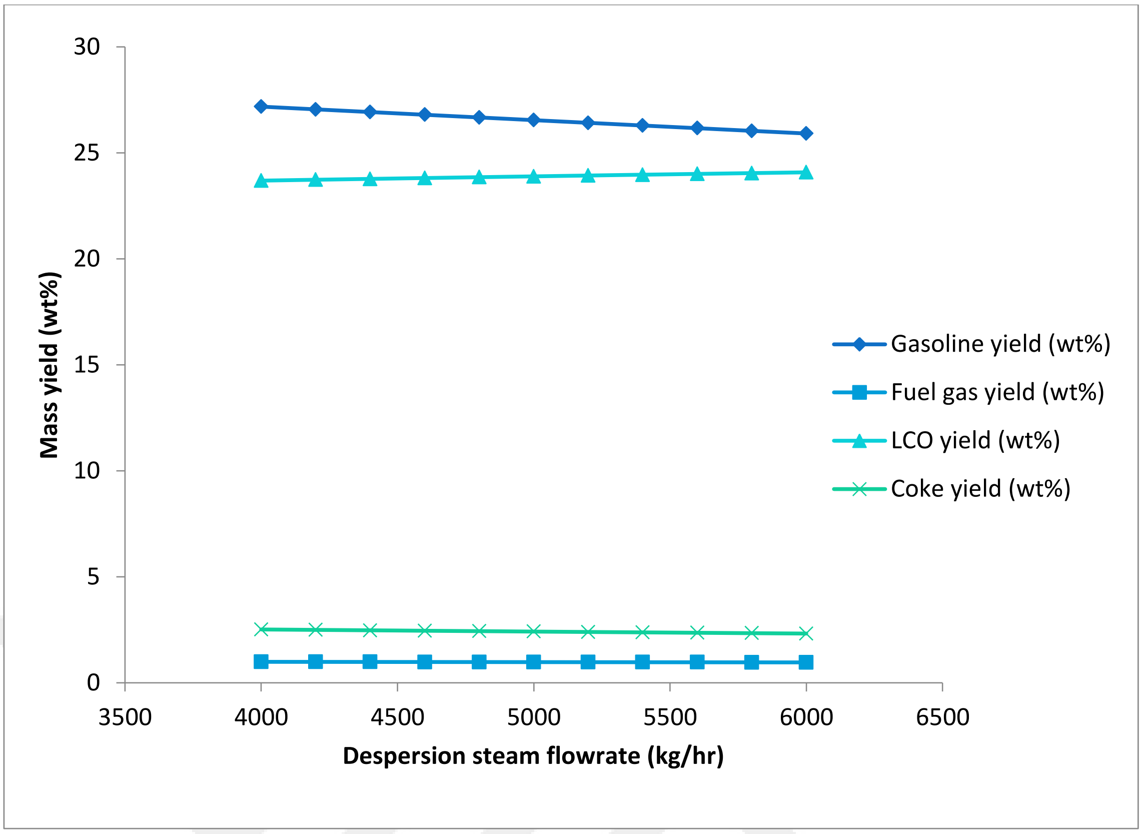



Figure 4.11 Mass yield (wt%) as a function of the dispersion steam flow rate (kg/hr) in the 7-lumps kinetics model at 0.7m riser diameter

# CHAPTER 5
# CONCLUSIONS AND FUTURE WORK

## 5.1 Conclusions

In this study, three kinetics models have been used in order to design FCCU for different feedstock qualities. Each model has been used to consider different feedstock quality under at the same industrial operating conditions.

In part I, the three kinetics models have been tested at 0.7m, 0.9m, 1m, 1.2m and 1.5m riser diameter.

- Model I (7-Lumps kinetics model) has been used to describe feedstock with API gravity 22.3. To conclude, large riser diameter is more suitable than small one when API gravity of feedstock is low (heavy feedstock). As a result, when riser diameter is increased, gasoline yield and conversion of feedstock are increased.
- Model II (8-Lumps kinetics model) has been used to describe feedstock with API gravity 24.3. To conclude, large riser diameter increases gasoline yield and conversion of feedstock when the API gravity of feedstock increases.
- Model III (10-Lumps kinetics model) has been used to describe feedstock with API gravity 27.6. To conclude, small riser diameter is more suitable than large one because of increasing coke yield to the maximum value which is around 5.2wt%.

In part II, range of some parameters have been tested in order to design FCCU for light and heavy feedstock. Riser length, riser temperature, feedstock flow rate, and dispersion steam flow rate have been tested because they have a strong effect on gasoline yield. To conclude, riser temperature has more effect than other parameters. But, riser temperature also does not have the same effect compared with riser diameter. That is, the product yield produced by large riser diameter for heavy feedstock is more than yield produced when riser temperature has been increased. Moreover, it affects adversely when it increases more than 560 °C because the secondary cracking reactions of gasoline and LCO to fuel gases, LPG, coke and residue.

## 5.2 Recommendations For The Future Work

Several steps need to be taken in a future work, in order to develop and design FCCU such as:

- Macro-activity test (MAT) unit can be used as a first step in designing FCCU because this unit has been used for evaluating the activity of the catalyst with feedstock. As a result, FCCU can be designed more accurately.
- The compositions and properties of both the feedstock and products can be analyzed and determined from the operation units in order to optimize the operating parameters that lead to maximization of the desired product.

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