



بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ



**SUDAN UNIVERSITY OF SCIENCE AND
TECHNOLOGY COLLEGE OF PETROLEUM
ENGINEERING AND TECHNOLOGY DEPARTMENT
OF PETROLEUM TRANSPORTATION AND REFINING**

تأثير الهواء الساخن علي إعادة تنشيط العامل الحفاز في وحدة التكسير الحفزي

**EFFECT OF HOT AIR ON REACTIVATION OF
CATALYST IN THE FLUIDIZED CATALYTIC
CRACKING PROCESS (RFCC)**

**A thesis submitted in partial fulfillment of the requirements
for the degree of B.Sc. Honors in petroleum and Refining
engineering**

BY:

1. ESRAA ABDEL RAHIM AI HUSSEIN
2. HATEM MHMOUD MOHAMED
3. TAMER OMER HASSEN OMER
4. KHBAB KAML MOHAMED ALI

Supervisor:

Dr. Mohammed Elmustafa A. A. Nasir

October 2018

بسم الله الرحمن الرحيم
الآية

قال تعالى:

{شهد الله انه لا إله إلا هو والملائكة وألو العلم قائما بالقسط لا إله إلا هو
العزیز الحكيم }

[العمران: الآية 18]

Dedication

We would like to dedicate this research to our Dear
parents.

To the people who paved our way of science and
knowledge.

To the taste of the most beautiful moments with our
friends.

Also we dedicate this research to our brothers and
sisters who spent their life to provide sufficient, Happiness and
love.

Finally we dedicate this research to our colleagues In
Transportation and refining department,

To all batch 23th petroleum engineering Students. And all
batch 5th refining engineering.

Acknowledgment

أرشدنا النبي صلي عليه وسلم الي مكافأه من أحسن النيات فإن لم تجد فإننا ندعو
جزاك الله خيرا.

روى ابو داوود(1672) عن عبدالله بن عمر رضي الله عنه قال:قال رسول الله
صلي الله عليه وسلم (من صنع اليكم معروفا فكافئوه فإن لم تجدوا ما تكافئونه فادعو
له حتي تروا أنكم قد كافأتموه).

صححه الالباني في إرواء الغليد(1617).

First of all, we would like to thank Great and Almighty
God who gave us the power to fulfill this study. Thanks should
be given to our supervisor's Dr. Mohammed Mustafa A. A.
Nasir and Mr.Adil Abbas and Eng. RAMAH AZHRY and
ENG.HOSSAM ELDIN MOSTAFA.

Thank you all

Abstract

The objective of this study is assess effect of air amount in regenerative process in Fluid catalytic cracking unit (FCCU by using ASPEN HYSYS simulation software.

The results showed that increase the amount of air present in the regenerator caused an increase in the regeneration of catalyst.

This study has shown the optimum amount to achieve carbon percentage of less than 0.05% on regeneration catalyst is **3400** Nm^3/min .

التجريد

الهدف من هذه الدراسة تقييم تأثير كميته الهواء في عملية التجديد في وحدة التكسير الحفزي باستخدام برنامج

(ASPEN HYSYS)

وأظهرت الدراسة أن زياده كميته الهواء في وحدة التجديد تؤدي الي زياده نشاطيه العامل الحفاز. وقد أظهرت هذه الدراسة أن كميته المثلي لتحقيق نسبه كربون أقل من 0.05% عند التجديد هي $3400Nm^3 /min$.

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SYMBOLS

SYMBOLS	Description	Unit
M_{cat}	Catalytic circulation	Kg/hr.
ρ_c	Catalyst density	Kg/ m ³
ρ_b	Bulk density of feed	Kg/m ³
V	volumetric flow rate of feed	m ³ /hr.
V_{av}	the average volumetric flow rate of feed in the riser,	m ³ /s
V_o	the volumetric flow rate at the out let of the riser	m ³ /s
V_i	the volumetric flow rate at the inlet of the riser	m ³ /s
U_{av}	the average linear velocity	m/s
U_o	the velocity at the inlet of the riser	m/s
U_i	the average at the outlet of the riser	m/s
A	cross section area	m ²
D	riser diameter	m
H	riser height	m
U_{av}	Average linear velocity	m/s
τ	Residence time in the riser	s
ΔP	Pressure drop	N/m ²
U_g^2	gas velocity through the riser	m/s
g_c	gravitational conversion factor,	kg.m/s ² .N
W_s	solid flux	kg/m ² .s
U_p	partial velocity	m/s
V	volume of the settler	m ³
D_o	diameter of riser	m
D_i	diameter of settler	m
L	height of settler	m
ρ	catalyst density in settler	kg/m ³
V_{ca}	volume of catalyst + coke	m ³
D_d	dense phase diameter	m
L_F	the fluidized bed height	m
m_{cat}	the mass flow rate of the catalyst	kg

t	the optimum residence time	min
W_{Ca}	the catalyst weight	kg
P	the density of the catalyst particles	Kg/m³
P1	- Dilute phase pressure	MPa
T1	Dilute phase temperature	k
T	thickness	m
Di	internal diameter	m
J	welded joint factor;	
Pi	internal pressure MPa	MPa
F	stress of material	N/mm²
M_{fg}	Mass flue gas	kg
M_{rca}	Mass of Regan. catalyst	kg
M_{SCa}	Mass of spent catalyst	kg
M_{air}	Mass of air	kg
M_p	Mass of product	kg
M_{so}	Mass of steam outlet	kg
M_F	Mass of feed	kg
M_{SI}	Mass of steam inlet	kg
FCC	fluid catalytic cracking	

Chapter (1)

1.1 Introduction

Global demand for transportation fuels will continue to grow and this demand will be met largely by gasoline and diesel fuels. The fluid catalytic cracking (FCC) process continues to play a key role in an integrated refinery as the primary conversion process of crude oil to lighter products. In the next two decades, the FCC process will be likely used for biofuels and possibly for reducing CO₂ emissions. For many refiners, the cat cracker is the key to profitability because the successful operation of the unit determines whether or not the refiner can remain competitive in today's market. (Sadeghbeigi, 2012)

The fluid catalytic cracking (FCC) unit is the essential transformation unit done numerous refineries and it is one of the most important and complex processes in the petroleum refining industry. It converts heavy material feeds consisting of high boiling points like gas oil into lighter and more valuable products like gasoline, liquefied petroleum gas (LPG), and olefins by using a zeolite catalyst and it helps to produce about half of the total gasoline output in a refinery. The FCC process vaporizes and breaks the long chain molecules of the high boiling hydrocarbon liquids into much shorter molecules by contacting the feedstock at high temperature and moderate pressure with a fluidized powdered catalyst. The heavy vacuum gas oil (VGO) has a boiling point range of 343- 565°C and an average molecular weight ranging from about 200 to 600 or higher. A wide range of feed stocks can be processed in the FCC unit such as cracked gas oils, deasphalted oils and hydro treated gas oil. (Ateya, 2016)

The modern FCC units are all continuous processes which operate 24 hours a day for as much as two to three years between shutdowns for routine maintenance. (Gary, 2001) The primary purpose of the FCC process has been to product gasoline, distillate, and C3/C4 olefin from low-value excess refinery gas oils and heavier refinery stream in this unit we use ZYULITE action to break the bonds. (Sadeghbeigi, 2012)

The modern RFCC unit can accept a broad range of feedstocks, a fact which contributes to RFCC's reputation as one of the most flexible refining processes in use today.

Examples of common feedstocks for conventional distillate feed FCC units are:

- Atmospheric gas oils
- Vacuum gas oils
- Thermally cracked gas oils
- Solvent deasphalted oils
- Lube extracts
- Hydrocracker bottoms

Products from the FCC and RFCC processes are typically as follows:

- Fuel gas (ethane and lighter hydrocarbons)
- C3 and C4 liquefied petroleum gas (LPG)
- Gasoline
- Light cycle oil (LCO)
- Fractionator bottoms (slurry oil)
- Coke (combusted in regenerator)
- Hydrogen Sulfide (from amine regeneration)

1.2 Problem Statement:

When cracking reactions occur, reduction in catalyst activity occurs due to carbon deposition on the catalytic surface and the decrease production rate.

1.3 Objectives:

- 1- Effect of hot air on reactivation catalyst in the fluidized catalytic cracking process
- 2- Increasing amount of gasoline production rate.

1.4. Scope:

- 1- Material balance around (Reactor and regenerator).
- 2- Simulation to unit by ASPEN HYSYS .
- 3- Design unit (reactor and regeneration).

Chapter (2)

Literature Review

2.1 Historical perspective about (FCC) UNIT:

Catalytic cracking was first commercialized in 1936 by Eugene Hurdy.

The fixed bed process was a major improvement over the thermal cracking processes it replaced due to the improved yield distribution and superior product properties. Multiple vessels were utilized that alternated between cracking, stripping, regeneration, and purge cycles. This configuration was quickly replaced by a moving bed reactor and a separate regenerator or kiln that first used a bucket lift to move the pelleted catalyst followed later by a pneumatic air lift system. The last of these units was built around 1960. (JONES†, 2006)

In 1936, a new cracking process opened the way to higher-octane gasoline; this process was catalytic cracking. The process is basically the same as thermal cracking but differs by the use of a catalyst, which is not (in theory) consumed in the process and directs the course of the cracking reactions to produce more of the desired higher-octane hydrocarbon products. (Speight, 2007)

Standard Oil of New Jersey developed their own cracking process rather than pay the large royalty being asked at the time.

They commercialized the fluid catalytic cracking (FCC) process in three years, starting in 1939 and culminating in 1942 with the start-up of PCLA#1 at their Baton Rouge, Louisiana refinery. The inherent superiority of the fluid process to transfer both heat and catalyst ultimately made it the catalytic cracking process of choice. (JONES†, 2006)

There has been continuous up gradation in catalytic cracking process from its incept of fixed bed technology to letter fluid bed catalytic cracking (FCC):

The fluid catalytic cracking (FCC) process is the heart of a modern refinery oriented toward maximum gasoline production. Within the entire refinery process, this process offers the greatest potential for increasing profitability; even a small improvement giving higher gasoline yields can result in a substantial economic gain. The FCC process increases the H/C ratio by carbon rejection in a continuous process and is used to convert the high - boiling, high - molecular - weight hydrocarbon fractions (typically, a blend of heavy straight -Run gas oil, light vacuum gas oil, and heavy vacuum gas oil) to more valuable gasoline, olefin gases, and other products. (John Wiley & Sons, 2011)

2.2 Flow diagram of (FCC) Unit:

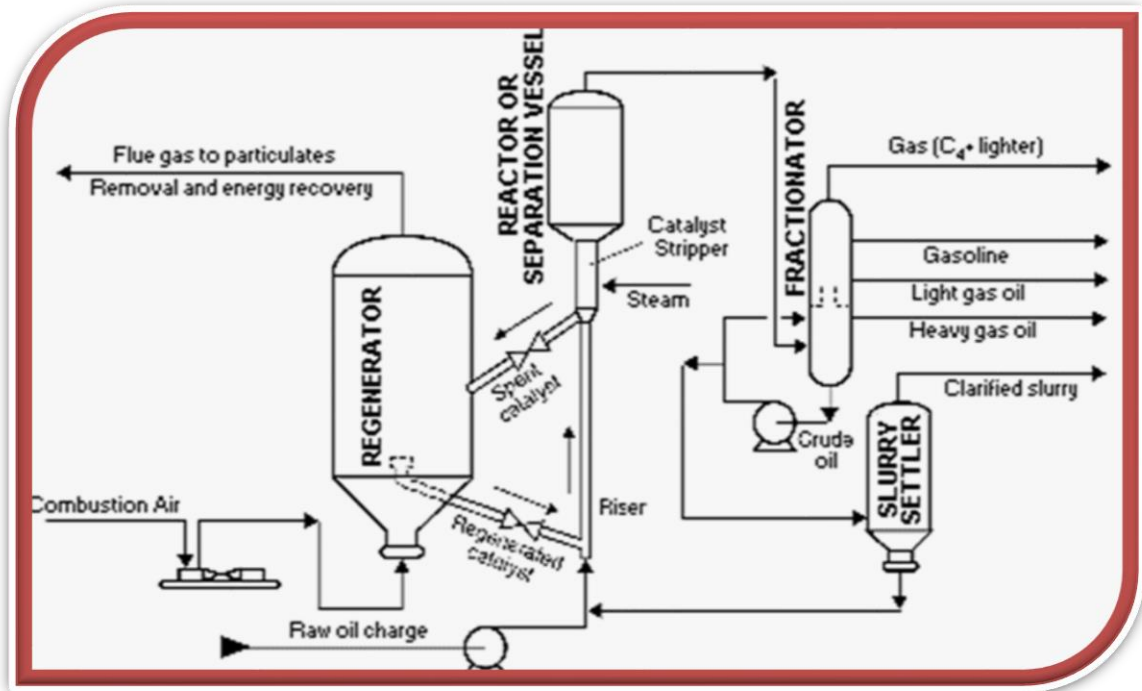


Fig. (2. 1) Schematic of the fluid catalytic cracking unit

2.3 Reactor:

Preheated fresh feedstock, plus any recycle feed, is charged to the base of the riser reactor. Upon contact with hot regenerated catalyst, the feedstock is vaporized and converted to lower-boiling fractions (light cycle oil, gasoline, C3 and C4 LPG, and dry gas).

Product vapors are separated from spent catalyst in the disengage cyclones and flow via the overhead line to the main fractionators and vapor recovery unit for quenching and fractionation. Coke formed during the cracking reactions is deposited on the catalyst, thereby reducing its activity. The coked catalyst, which is separated from the reactor products in the disengage cyclones, flows via the stripper and spent catalyst standpipe to the regenerator.

The discharge rate from the standpipe is controlled by the spent catalyst plug valve. In the regenerator, coke is removed from the spent catalyst by

combustion with air. Air is supplied to the regenerator air distributors from an air blower. Flue gas from the combustion of coke exits the regenerator through two-stage cyclones which remove all but a trace of catalyst from the flue gas. Flue gas is collected in an external plenum chamber and flows to the flue gas train. Regenerated catalyst, with its activity restored, is returned to the riser via the regenerated catalyst plug valve (MEYERS, 2002).

2.3.1 Major Components of the Reactor:

2.3.1.1 ATOMAX Feed Injection System

The catalyst then enters a feed injection cone surrounded by multiple, flat-spray, atomizing feed injection nozzles. The flat, fan-shaped sprays provide uniform coverage and maximum penetration of feedstock into catalyst, and prevent catalyst from bypassing feed in the injection zone. Proprietary feed injection nozzles, known as ATOMAX nozzles, are used to achieve the desired feed atomization and spray pattern while minimizing feed pressure requirements. The hot regenerated catalyst vaporizes the oil feed, raises it to reaction temperature, and supplies the necessary heat for cracking. The cracking reaction proceeds as the catalyst and vapour mixture flow up the riser. The riser outlet temperature is controlled by the amount of catalyst admitted to the riser by the catalyst plug valve. (MEYERS, 2002)

2.3.1.2 Riser Quench:

The riser quench system consists of a series of nozzles uniformly spaced around the upper section of riser. A portion of the feed or a recycle stream from the main fractionators is injected through the nozzles into the

riser to rapidly reduce the temperature of the riser contents. The heat required to vaporize the quench is supplied by increased fresh feed preheat or by increased catalyst circulation. This effectively increases the temperature in the lower section of the riser above that which would be achieved in a non-quenched operation, thereby increasing the vaporization of heavy feeds, increasing gasoline yield, olefin production and gasoline octane.

2.3.1.3 Spent Catalyst Stripping:-

Catalyst separated in the cyclones flows through the respective dip legs and discharges into the stripper bed. In the stripper, hydrocarbon vapors from within and around the catalyst particles are displaced by steam into the disengage dilute phase, minimizing hydrocarbon carry-under with the spent catalyst to the regenerator. Stripping is a very important function because it minimizes regenerator bed temperature and regenerator air requirements, resulting in increased conversion in regenerator temperature or air-limited operations. (MEYERS, 2002)

The catalyst entering the stripper is contacted by up flowing steam introduced through two steam distributors. The majority of the hydrocarbon vapors entrained with the catalyst are displaced in the upper stripper bed. The catalyst then flows down through a set of hat and doughnut baffles. In the baffled section, a combination of residence time and steam partial pressure is used to allow the hydrocarbons to diffuse out of the catalyst pores into the steam introduced via the lower distributor. (MEYERS, 2002) Stripped catalyst, with essentially all strippable hydrocarbons removed, passes into a standpipe, which is aerated with steam to maintain smooth flow. At the base of the standpipe, a plug valve

regulates the flow of catalyst to maintain the spent catalyst level in the stripper. (MEYERS, 2002).

2.4 Regenerator-Heat/Catalyst Recovery:

The spent catalyst entering the regenerator usually contains between 0.5 and 1.5 wt. % coke. Components of coke are carbon, hydrogen, and trace amounts of sulphur and organic nitrogen molecules. These components burn according to the reactions given in [Table \(2.1\)](#).

2.4.1 The regenerator has three main functions:

1. It restores catalyst activity.
2. It supplies heat for cracking reactions.
3. It delivers fluidized catalyst to the feed nozzles.

Air provides oxygen for the combustion of this coke and is supplied by one or more air blowers. The air blower provides sufficient air velocity and pressure to maintain the catalyst bed in a fluidized state.

The air/oxygen enters the regenerator through an air distribution system (Figure 2.2) located near the bottom of the regenerator vessel. The design of the air distributor is important in achieving efficient and reliable catalyst regeneration. (Speight, 2007)

Table (2. 1) The Main reaction of the coke Combustion reaction

	kcal/kg of C, H ₂ , or S	BTU/lb. of C, H ₂ , or S
$C + 0.5O_2 \rightarrow CO$	2200	3968
$CO + 0.5O_2 \rightarrow CO_2$	5600	10100
$C + O_2 \rightarrow CO_2$	7800	14100

$H_2 + 0.5O_2 \rightarrow H_2O$	28900	52125
$S + xO \rightarrow SO_x$	2209	3968
$N + xO \rightarrow NO_x$	-	-

Air distributors are often designed for a 1.0- to 2.0-psi (7_15kPa) pressure drop to ensure positive air flow through all nozzles.

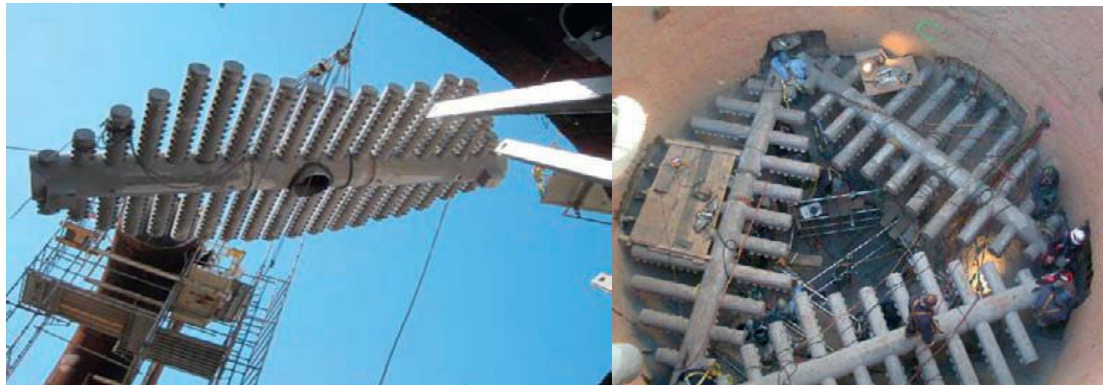


Fig. (2. 2) Examples of air distributor designs (Speight, 2007)

2.4.2 Partial Versus Complete Combustion:

Two distinctly different modes of regeneration are practiced partial combustion and complete combustion.

Complete combustion generates more energy and the coke yield is decreased; partial combustion generates less energy and the coke yield is increased. In complete combustion, the excess reaction component is oxygen, so more carbon generates more combustion. In partial combustion, the excess reaction component is carbon, all the oxygen is consumed, and an increase in coke yield means a shift from CO₂ to CO.

FCC regeneration can be further subdivided into low intermediate-, and high-temperature regeneration. In low Temperature regeneration (about 1,190_F or 640_C), complete Combustion is impossible. One of the

characteristics of low-temperature regeneration is. That at 1,190_F, all three components (O₂, CO, and CO₂) are present in the flue gas at significant levels. Low-temperature regeneration was the mode of operation that was used in the early implementation of the catalytic cracking process. (Speight, 2007)

In the early 1970s, high-temperature regeneration was developed. High-temperature regeneration meant increasing the temperature until all the oxygen was burned. The main result was low carbon on the regenerated catalyst. This mode of regeneration required maintaining, in the flue gas, either a small amount of excess oxygen and no CO or no excess oxygen and a variable quantity of CO.

If there was excess oxygen, the operation was in full burn. If there was excess CO, the operation was in partial burn.

With a properly designed air/spent catalyst distribution system and potential use of CO combustion promoter, the regeneration temperature could be reduced and still maintain full burn mode of catalyst regeneration.

(Table 2.2) contains a matrix summarizing various aspects of catalyst regeneration. Regeneration is either partial or complete at low, intermediate, or high temperatures. At low temperatures, regeneration is always partial, carbon on regenerated catalyst is high, and increasing combustion air results in after burn. At intermediate temperatures, carbon on regenerated catalyst is reduced. The three normal “operating regions” are indicated in (Speight, 2007)

2.5 Carbon concentration in the regenerated catalyst

The molecular sieve catalyst is very sensitive to the carbon concentration of the regenerated catalyst. The carbon concentration of the regenerated catalyst means the remaining coke content on the catalyst after regeneration. If the carbon content of the regeneration catalyst is too high, the activity and the selectivity of the molecular sieve catalyst will be decreased; therefore, the conversion yield will be decreased greatly, and the gasoline yield will also decrease, the bromine value will increase and the induction period will decrease. Adopting high-temperature regeneration can decrease the carbon concentration of the catalyst, normally, 0.1% carbon content decreasing, 2-3 units of the activity will be increased.

Table (2.2) Regeneration characteristic:

Operating Region Regenerator Combustion	Partial Combustion Mode	Full Combustion Mode
Low temperature (nominally 1,190F/640C)	Stable (small afterburning); O₂, CO, and CO₂ in the flue gas.	Not achievable
Intermediate temperature (nominally 1,275F/690C)	Stable (with combustion promoter).	Stable with combustion promote
High temperature (nominally 1,350F/730C)	tends to have high carbon on regenerated catalyst Stable Operation.	Stable operation

2.6.RFCC Catalysts:-

A catalyst is a substance that affects the rate of a reaction but emerges from the process unchanged. A catalyst usually changes a reaction rate by promoting a different molecular Path (“mechanism”) for the reaction (Fogler & F. Thurnau Professor , 2011).

Paralleling the significant improvements in RFCC unit design was a corresponding improvement in RFCC catalysts. The first catalysts used were ground-up amorphous silica alumina. Whether synthetic or naturally occurring, these catalysts suffered from low activity and poor stability relative to the catalysts available today. Additionally, they had poor fluidization characteristics. Often, fines had to be collected from the flue gas and returned to the unit to assist in maintaining smooth catalyst circulation. In 1946, spray-dried (micro spheroidal) synthetic silica-alumina catalysts were introduced. This type of catalyst, containing 10 to 13 percent alumina, was in general use until a more active and stable catalyst high in alumina (25 wt. % alumina) became available in the late 1950s. (Fogler & F. Thurnau Professor , 2011).

Zeolite is the key ingredient of the FCC catalyst. It provides product selectivity and much of the catalytic activity. The catalyst’s performance depends largely on the nature and quality of the zeolite. Understanding the zeolite structure, types, cracking mechanism, and properties is essential in choosing the “right” catalyst to produce the desired yields. (Speight, 2007) .

The resulting catalysts exhibited significantly higher activity and stability compared with catalysts available at the time. These crystalline catalysts were, and are, ideally suited for the short-contact-time riser

cracking concept. Besides being more active, these materials are more selective toward gasoline production which is the most important refinery product compared to the initial amorphous type. (Speight, 2007) .

Table (2. 2) Comparison of Amorphous and Zeolite Catalysts

	Amorphous	Zeolite
Coke, wt. %	4	4
Conversion, vol. %	55	65
C ₅ +gasoline, vol %	38	51
C ₄ 's, vol %	17	16
C ₃ gas, wt. %	7	6

Because a catalytic reaction occurs at the fluid–solid interface, a large interfacial area is almost always essential in attaining a significant reaction rate. In many catalysts, this area is provided by an inner porous structure (i.e., the solid contains many fine pores, and the surface of these pores supplies the area needed for the high rate of reaction). Sometimes pores are so small that they will admit small molecules but prevent large ones from entering. Materials with this type of pore are called molecular sieves. (Vennema, n.d.)

It has a well-defined lattice structure. Its basic building blocks are silica and alumina tetrahedral (pyramids). Each tetrahedron (Figure4.1) consists of a silicon or aluminium atom at the centre of the tetrahedron, with oxygen atoms at the four corners. The pore diameter of nearly all of today's FCC zeolite is 8.0 angstroms (Å). These small openings, with an internal surface area of roughly 600 m²/g. Zeolites employed in the manufacture of the FCC catalyst are synthetic versions of naturally occurring zeolites called faujasites.

The properties of the zeolite play a significant role in the overall performance of the catalyst. Understanding these properties increases our ability to predict catalyst response to changes in unit operation.

The zeolite must retain its catalytic properties under the hostile conditions of the FCC operation. The reactor/ regenerator environment can cause significant changes in chemical and structural composition of the zeolite. (Speight, 2007)

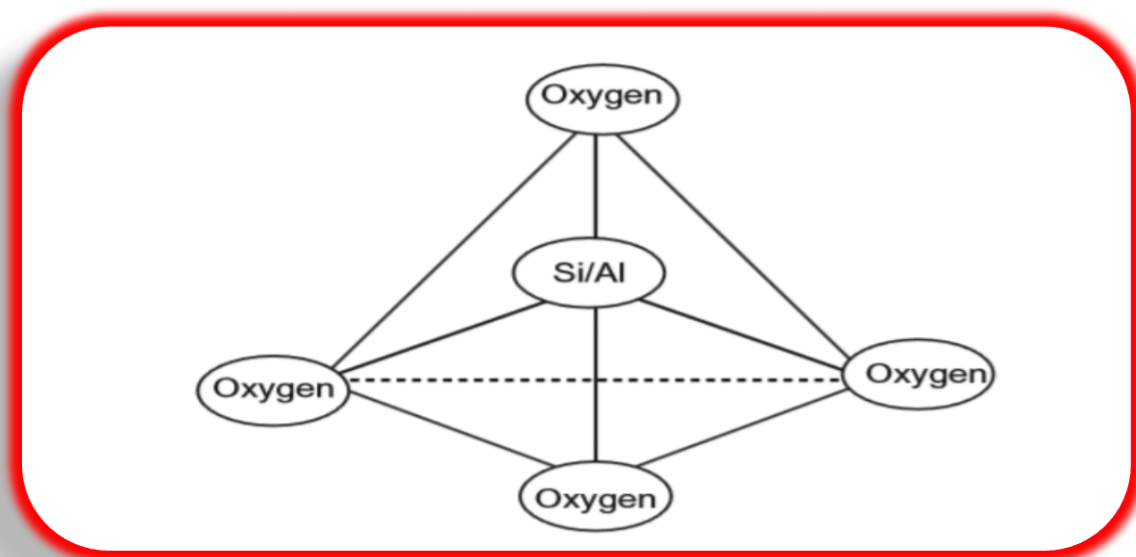


Fig. (2. 3) Silicon/aluminium-oxygen tetrahedron.

2.6.1 Additives:-

In some cases a catalyst consists of minute particles of an active material dispersed over a less active substance called a support. The active material is frequently a pure metal or metal alloy.

Such catalysts are called supported catalysts, as Distinguished from unsupported catalysts.

Analysts can also have small amounts of active ingredients added called promoters, which increase their activity. Examples of supported catalysts are the packed-bed catalytic converter in an automobile, the platinum-on-alumina catalyst used in petroleum reforming, and the vanadium pent oxide on silica used to oxidize sulfur dioxide in manufacturing sulphuric acid. (Speight, 2007).

2.6.2 Catalyst Deactivation:-

Most catalysts used in the chemical and petrochemical industries are strongly affected by one or another form of deactivation, leading to poor performances and reduced life.

Deactivation of catalysts can involve sintering, poisoning or fouling, and the last two of these involve the adsorption/deposition of various species on the catalyst.

Catalyst poisons tend to be selective, since they deactivate by strong adsorption. The major purpose of the material herein is to link the more fundamental aspects of catalyst deactivation by poisoning.

To those related problems which plague industrial practitioners. Thus we are primarily concerned with events which occur on an intermediate size scale. Catalyst foul ants are much less selective, coke formation in zeolite catalysts is a spatially demanding reaction and, as such, is particularly sensitive to zeolite pore structure.

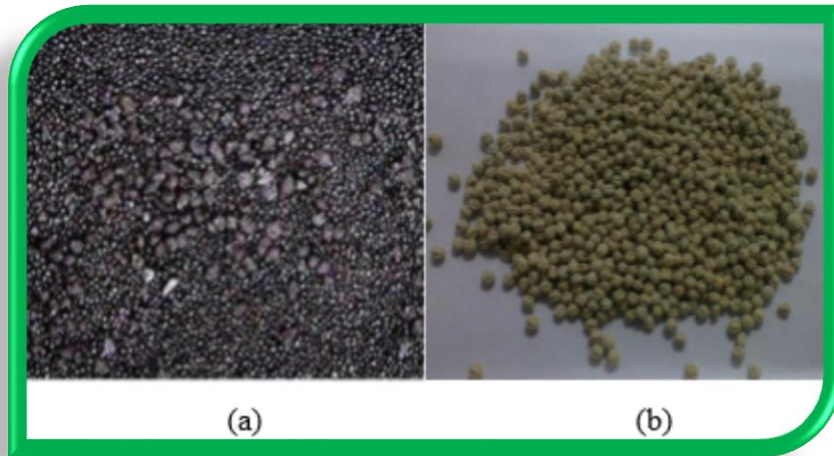


Fig. (2. 4) (a) Coked catalyst, (b) Fresh catalyst

But the nature of the reactions carried out over metallic or acidic catalysts is such that fouling is more likely over metallic or acidic catalysts. In general, fouling involves coke formation, or the deposition of inorganic materials on a catalyst.

The selection of a heterogeneous catalyst for a given action depends not only on the fact that the conversion of feedstock to desired products is high on the chosen catalyst, but also on the fact that the catalyst remains active for long periods under the particular conditions of operation Table (2.4): properties of Major synthetic Zeolites. (Figueiredo, 1981).

Table (2. 3) properties of Major synthetic Zeolites

Zeolite Type	Pore Size Dimensions (Å)	Silica to Alumina Ratio	Application
Zeolite A	4.1	2-5	Detergent manufacturing
Faujasit	7.4	3-6	Catalytic cracking and hydrocracking
ZSM-5	5.2*5.8	30-200	Xylene isomerization, benzene alkylation, catalytic cracking, catalyst methanol conversion

2.6.3 type of the catalyst:

Characterized by ultra-stable Y zeolite as active compound and contains vanadium resisting agent. It has high hydrothermal stability and capable of cracking heavy oil. It is a coke and light oil selective catalyst. The applications: (**Anon., 2013**)

- For processing residue and feeds difficult to be cracked.
- Feeds with high vanadium, sodium, calcium and basic nitrogen.
- For RFCC units required lower slurry yield.
- Higher activity and stability which allows RFCC to be operated at lower C/O ratio.

Chapter (3) Methodology

The main feed stream crude oil data from Nile blend from Central Petroleum Lap rotary (CPL) and data operation from (CDU-RFCC) Unit.

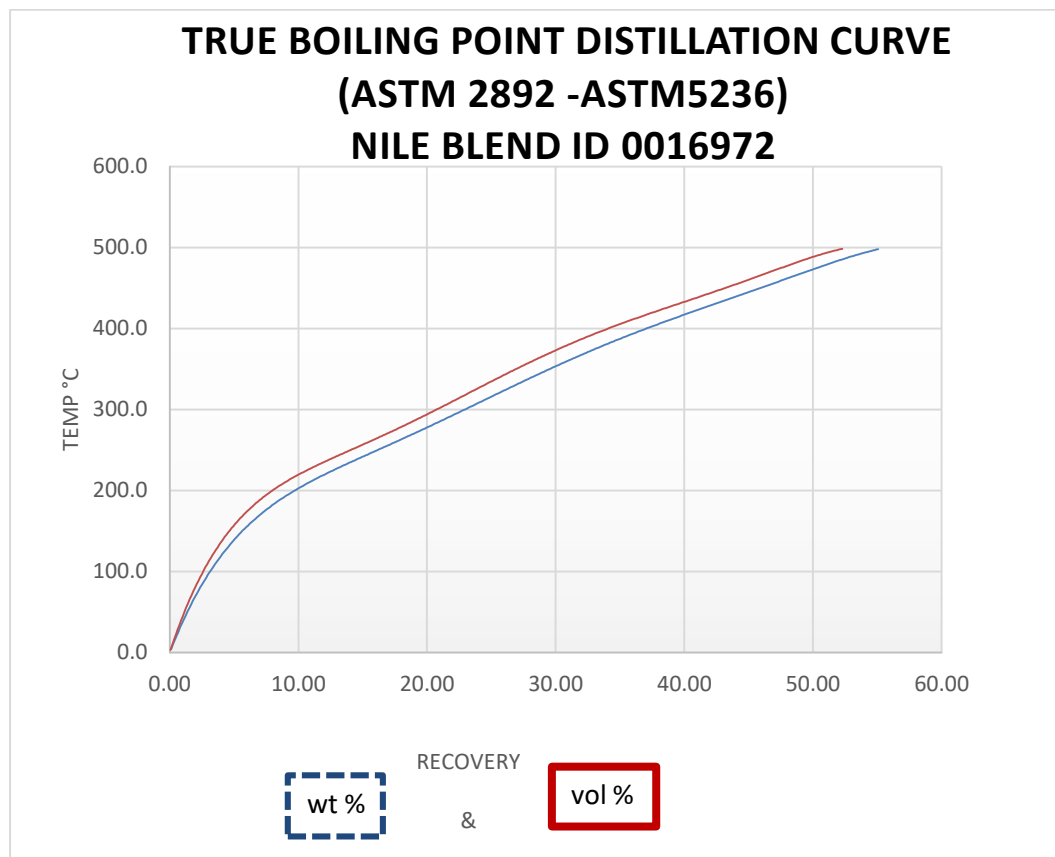


Fig. (3. 1) TBP petroleum assay

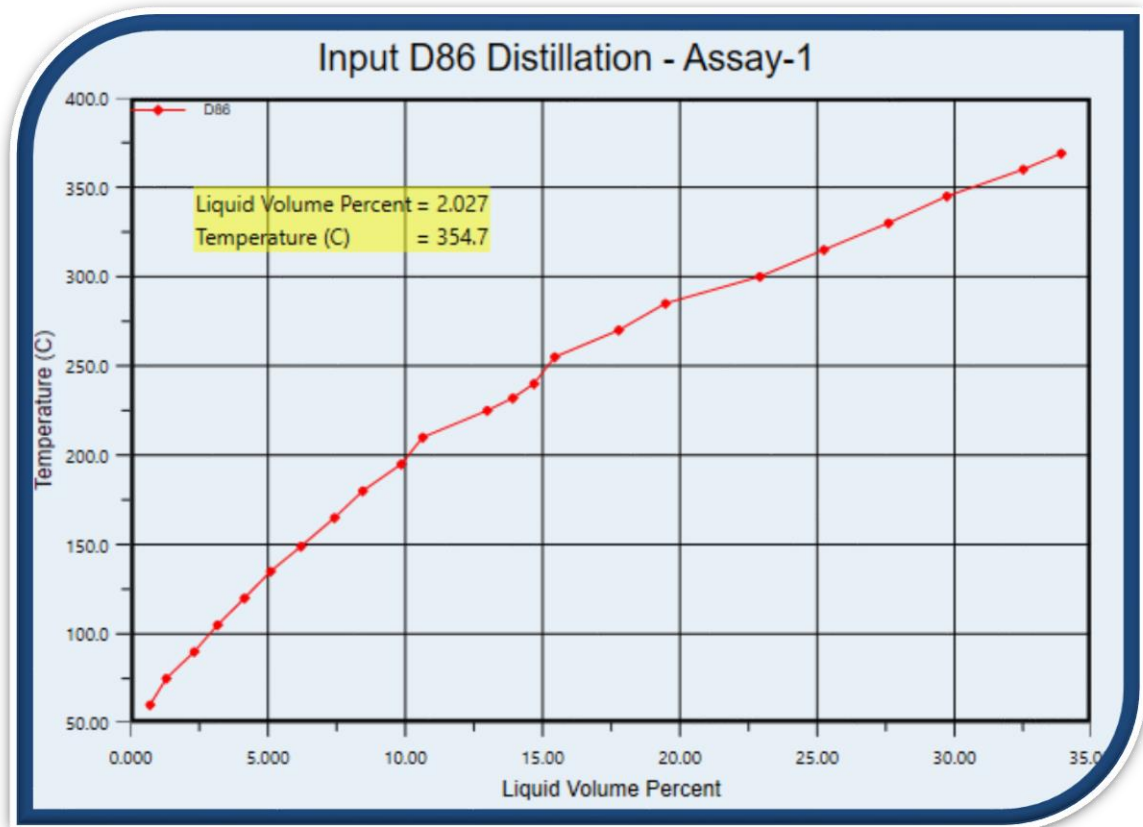


Fig. (3. 2) Input D86 Distillation-Assay-1

3.2. Case study:

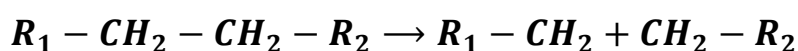
The effect of air volume in the regenerator was studied on the reactivation of the catalytic agent which in turn increased the production of gasoline by the unit RFCC. This study was applied to the simulation program.

3.3. Important Reactions Occurring in the FCC Unit:

3.3.1. Thermal cracking:

Before the advent of the catalytic cracking process, thermal cracking was the primary process available to convert low-value feedstocks into lighter products. Refiners still use thermal processes such as delayed coking and tiebreaking for cracking of residual hydrocarbons.

Thermal cracking is a function of temperature and time. The reaction occurs when hydrocarbons in the absence of a catalyst are exposed to high temperatures in the range of (800f-1,200F) (425c-650C). Equation (6.1) shows formation of a free radical when a paraffin molecule is thermally cracked



Free radicals are extremely reactive and short-lived. They can undergo alpha-scission, beta scission, and polymerization. (Alpha-scission is a break one carbon away from the free radical; beta-scission, two carbons away.). (Speight, 2007)

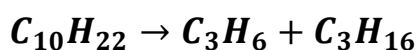
Once formed, carbenium ions can form a number of different reactions. The nature and strength of the catalyst acid sites influence the extent to which each of these reactions occur. (Sadeghbeigi, 2012)

The three dominant reactions of carbenium ions are:

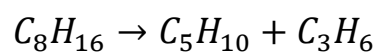
1. The cracking of a carbon bond
2. Isomerization.
3. Hydrogen transfer.

3.3.2. Cracking Reaction:

- a) Paraffin's cracking to olefin and smaller paraffin's.



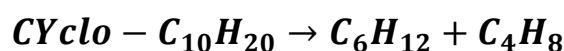
- B) Olefins cracking to smaller olefins.



- C) Aromatics side chain reactions.



D) Napthenes cracking to olefins and smaller rings



3.3.3. Isomerization Reactions.

Isomerization reactions occur frequently in catalytic cracking, infrequently in thermal cracking. In both, breaking of a bond is via beta-scission. However, in catalytic cracking, carbocation's tend to rearrange to form tertiary ions. Tertiary ions are more stable than secondary and primary ions; they shift around and crack to produce branched molecules. In thermal cracking, free radicals yield normal or straight-chain compounds. (Sadeghbeigi, 2012).

➤ **Some of the advantages of isomerization are as follows:**

1. Higher octane in the gasoline fraction. Isoparaffins in the gasoline boiling range have higher octane than normal paraffin's.
2. High-value chemical and oxygenate feedstock's in the C3/C4 fraction. Isobutylene and isoamylene are used for the production of MTBE and tertiary amyl methyl ether (TAME). MTBE and TAME can be blended into the gasoline to reduce auto emissions.
3. Lower cloud point in the diesel fuel. Isoparaffins in the LCO boiling range improve the cloud point



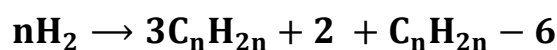
3.3.4. Hydrogen Transfer Reactions

Hydrogen transfer is more correctly called hydride transfer. It is a bimolecular reaction in which one reactant is an olefin. Two examples are the reaction of two olefins and the reaction of an olefin and a naphthene.

In the reaction of two olefins, both olefins must be adsorbed on active sites that are close together. One of these olefins becomes a paraffin and

the other becomes a cyclo-olefin as hydrogen is moved from one to the other. Cyclo-olefin is now hydrogen transferred with another olefin to yield a paraffin and a cyclodiolefin.

Cyclodiolefin will then rearrange to form an aromatic. The chain ends because aromatics are extremely stable. Hydrogen transfer of olefins converts them to paraffin's and aromatics. (Sadeghbeigi, 2012)



3.3.5. Other Reactions.

Cracking, isomerization, and hydrogen transfer reactions account for the majority of cat cracking reactions. Other reactions play an important role in unit operation. Two prominent reactions are dehydrogenation and coking. (Sadeghbeigi, 2012)

3.3.6. Dehydrogenation:

Under ideal conditions, i.e. a “clean” feedstock and a catalyst with no metals, cat cracking does not yield any appreciable amount of molecular hydrogen. Therefore, dehydrogenation reactions will proceed only if the catalyst is contaminated with metals such as nickel and vanadium. (Sadeghbeigi, 2012)

3.3.7. Coking:

Cat cracking yields a residue called coke. The chemistry of coke formation is complex and not very well understood. Similar to hydrogen transfer reactions, catalytic coke is a “bimolecular” reaction. It proceeds via carbenium ions or free radicals. In theory, coke yield should increase as the hydrogen transfer rate is increased. It is postulated that reactions producing unsaturated and multiring aromatics are the principal coke-forming compounds. Unsaturates such as olefins, diolefins, and multiring polycyclic olefins are very reactive and can polymerize to form coke. (Sadeghbeigi, 2012)

Table (3. 1) Some Thermodynamic Data for Idealized Reactions of Importance in Catalytic Cracking

1. Cracking:

Paraffin's cracked to olefins and smaller paraffin's

Olefins cracked to smaller olefins

Aromatic side-chain scission

Naphthenes (cycloparaffins) cracked to olefins and smaller ring compounds

2. Isomerization:

Olefin bond shift

Normal olefin to iso-olefin

Normal paraffin to isoparaffin

Cyclohexane to cyclopentane

3. Hydrogen transfer:

Cycloaromatization

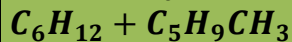
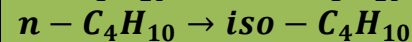
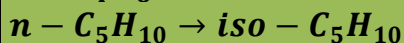
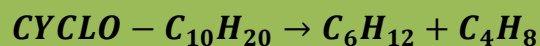
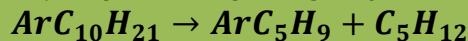
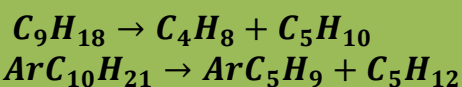
4. Trans alkylation/alkyl-group transfer

5. Cyclization of olefins to naphthenic

6. Dehydrogenation

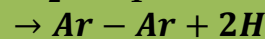
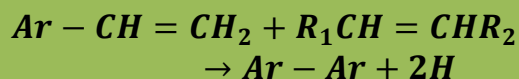
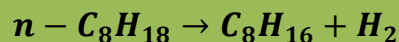
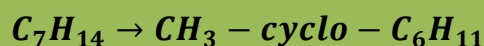
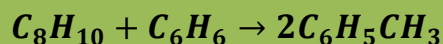
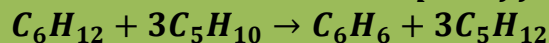
7. DE alkylation

8. Condensation



Naphthene + olefin

→ aromatic + paraffin



3.4 Processes description

Reaction and Regeneration Section:

The unit is designed to handle two kinds of feeding systems, hot feeding and cold feeding. Hot feedstock from the atmospheric distillation unit (CDU) and the delayed coking unit is directly fed to the feedstock surge drum while in cold feeding, the cold feedstock is drawn from unit tank farm using the feedstock pump to the surge drum and then drawn out using the feedstock pump or directly from the unit tank without passing through the surge drum and then heated to 150-200 c in the slurry /feed heat exchanger prior to being fed into the lower section in the riser. Antimony passivation solution is injected into the inlet header of feedstock using the pumps to suppress the action of the heavy metals contaminants and at the same injection point, anti-coke agent is injected.

The feedstock heated is divided into 4 flow valves and inject (atomized) into the riser and converted into fine droplet through 8 nozzle using atomizing steam at two location above each other where only 2 nozzle below and it 6 above. The atomizing steam rate is designed to be 6 to 8% of the feed stock mixes with seceding hot regenerated catalyst from the 2nd regenerator, it vaporizes and the catalyst and oil are accelerated in the upward direction in the cracking reaction take place during the residence time in the riser (2-4 sec) producing the cracked oil vapour which is mix light product as LPG. Gasoline and diesel as well as dry gas, slurry and coke that deposited on the catalyst. (Anon., 2013)

The hot regeneration catalyst enters the riser at the WYE section below the feed injection point and pushed up by left steam ring located at the bottom of the riser then 4 nozzles of left dry gas.

The specially designed feedstock injection nozzles guarantee the maximum conversion of the oil to light-end product, and minimize the coke formation. Coker naphtha nozzles were added as 2 below and 2 above the upper feedstock nozzles. Through 2 control valve 4 nozzles. Recycle oil is injected in the riser above the feed injection point to increase the conversion per cycle.

The riser is terminated by 4 quick cyclone separator spent catalyst is separated from the hydrocarbon vapours and dropped down through the dip legs to the stripping section, the dip legs of the cyclone are submerged inside the catalyst bed that is kept in fluidized state by the steam via steam rings . (Anon., 2013)

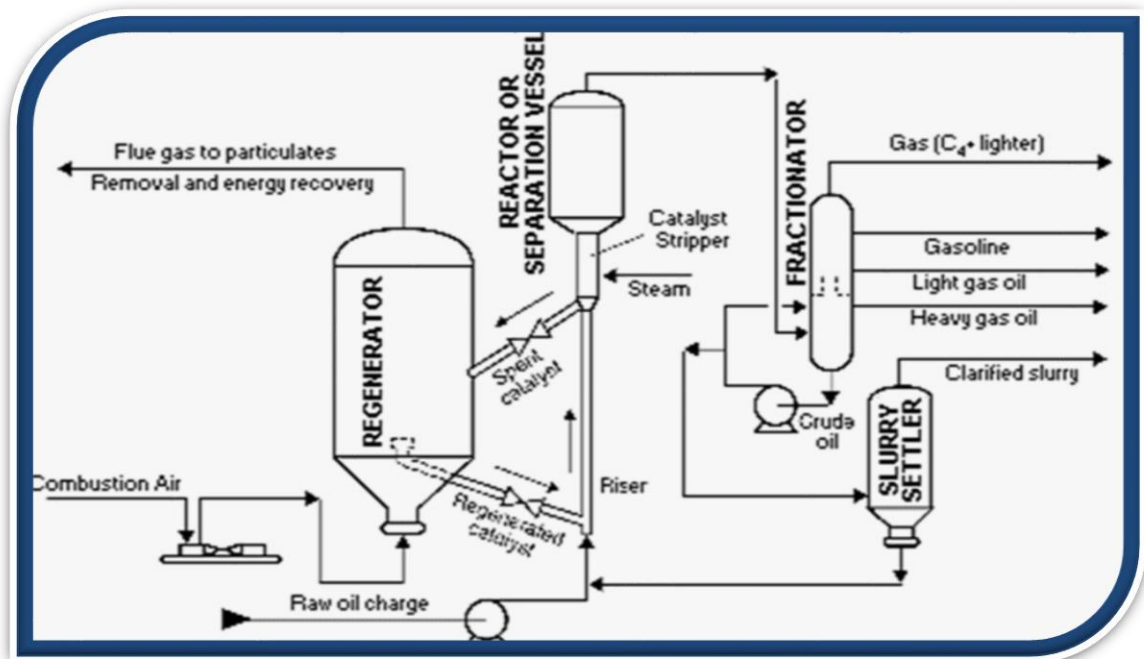


Fig. (3.3) Schematic of the fluid catalytic cracking unit (Speight, 2007)

3.5. ASPEN HYSYS simulator:

Provides an opportunity to check the feasibility of a process, to study and investigate the effect of various operating parameters on

various reactions. It is a strong tool for simulation studies and helps in analysing the outcome of a process. HYSYS offers a high degree of flexibility because there are multiple ways to accomplish specific tasks. This flexibility combined with a consistent and logical approach to how these capabilities are delivered makes HYSYS an extremely versatile process simulation tool. The usability of HYSYS is attributed to the following four key aspects of its design:

- 1-Event Driven operation
- 2-Modular Operations
- 3-Multi-flow sheet Architecture
- 4-Object Oriented Design

3.6. Overall balance:-

3.6.1. Flow sheet wide Mass balance:

Inlet Streams	Mass flow (tonne/hr.)	Outlet Streams	Mass flow (tonne/hr.)
Nile Blend	267.9	naphtha	26.41
Steam	2.145	water	2.102
-	-	Vapour product	380.2

3.6.2. Flow sheet wide energy balance:

Inlet Stream	Energy flow (Btu/hr.)	Outlet Streams	Energy flow (Btu/hr.)
--------------	-----------------------	----------------	-----------------------

Nile Blend	-4.250e+008	Q2	5.395e+005
q10	1.197e+008	naphtha	-5.246e+007
Steam	-2.575e+007	Q-Condenser	2.084e+007
Q-100	-1.227e+008	water	-3.130e+007
		Vapour product	-4.905e+008

3.7. Material and Energy Balance:

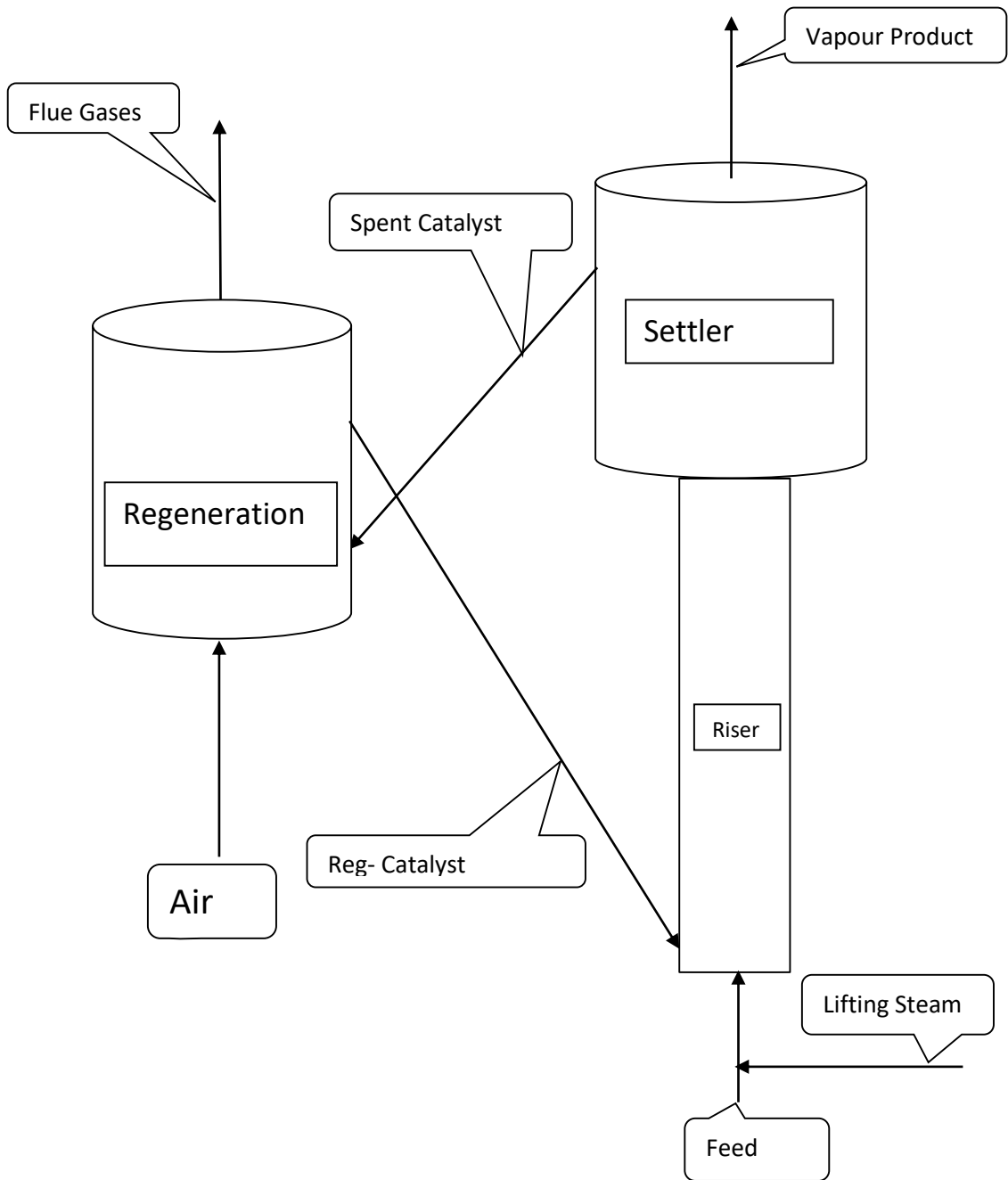


Fig. (3. 3) Input and output streams for reactor and regenerator in FCCU.

❖ To material and energy balance around the reactor and the Regenerator can be calculated by defining the input and output streams (Figure 3.2).

3.7.1 Reactor Material Balance:

- Assuming system is steady state.
- Assuming steam inlet doesn't condense.

➤ **Mass in**

Feed + steam inlet + Regenerated catalyst

➤ **Mass out**

Spent catalyst + steam out + Vapour Product

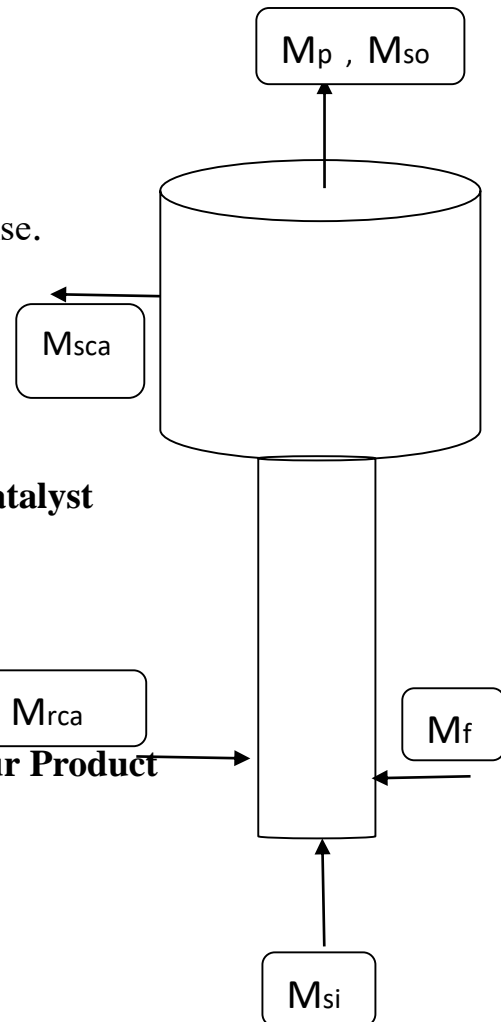
$$M_{sca} = M_{ock} + M_{rca}$$

✓ Over all material balance around reactor

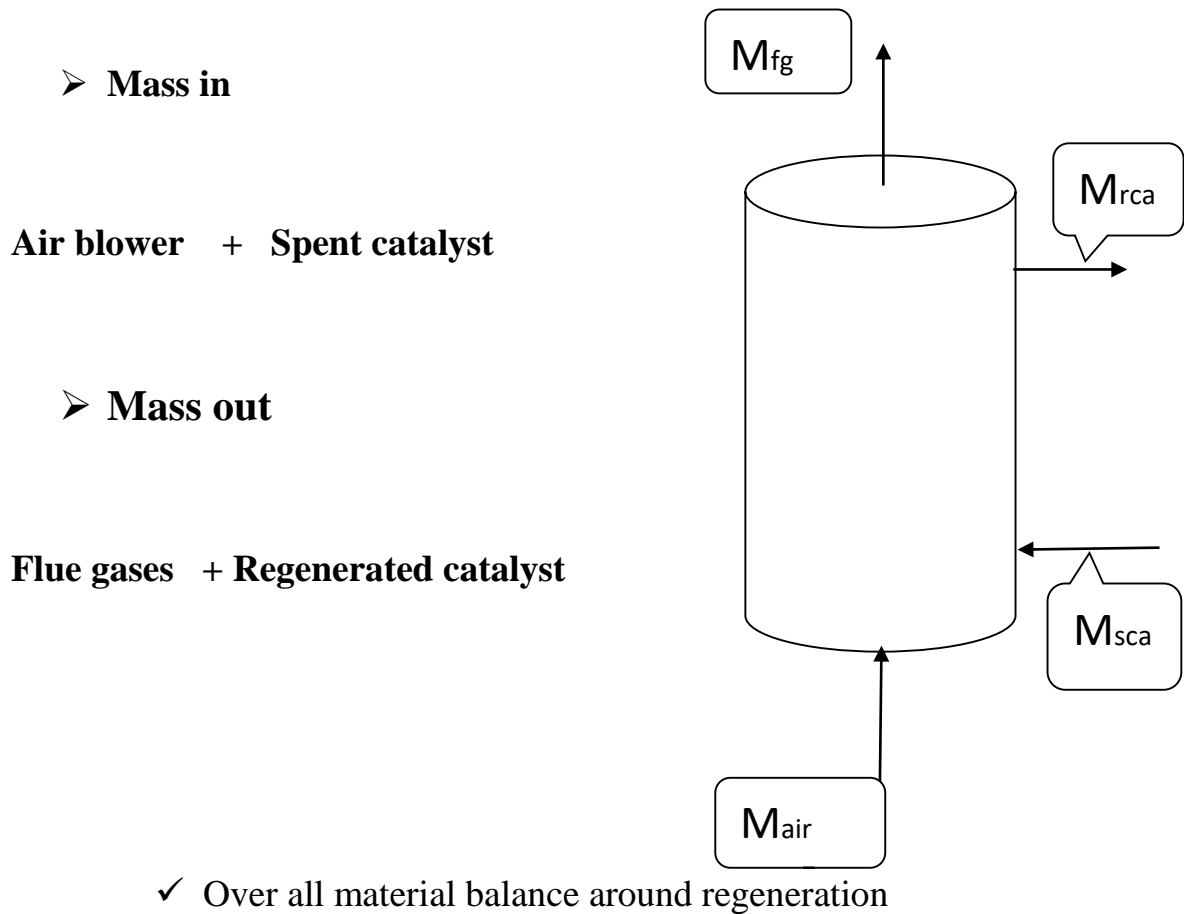
$$\text{Mass in} = \text{Mass out}$$

$$M_f + M_{si} + M_{rca} = M_{ock} + M_{eca} + M_{so} + M_p$$

$$M_f = M_{ock} + M_p$$



3.7.2 REGENERATOR MATERIAL BALANCE:



$$M_{air} + M_{sca} = M_{fg} + M_{rca}$$

3.8. Reactor Design:

In Khartoum refinery like in modern RFCC units, total riser reactor is applied, where reactions completely take place in the riser, the reactor consists of the following parts.

3.8.1- Riser:

It is a long vertical straight pipe where the desired reactions take place, quick separation of the catalyst from hydrocarbons vapor at the end of the riser important to give good result.

3.8.2. Riser Calculation:

First we must to calculate the volumetric flow rate of feed,

☒ *Volumetric flow rate of feed (V):*

The volumetric flow rate can be calculated by the following equation:

$$V = M_{cat} \left[\frac{1}{\rho_b} - \frac{1}{\rho_c} \right] \quad (\text{Anon., 2013})$$

The density of the bulk differs between the top and bottom of the riser, so the volumetric flow rate must be calculated at the both side.

i. *The volumetric flow rate at out let of the riser (V_o):*

☒ At the outlet of the riser we find:

$$M_{cat} = 1647498 \quad [\text{material balance}]$$

$$\rho_c = 780 \text{ kg/m}^3$$

$$\rho_b = 16 \text{ kg/ m}^3 \quad (\text{Anon., 2013})$$

$$V = 1647498 \left[\frac{1}{16} - \frac{1}{780} \right] = 10085.44 \text{ m}^3/\text{hr.} = 28 \text{ m}^3/\text{s}$$

ii. *the volumetric flow rate at the inlet of the riser (V_i):*

☒ At the inlet we have:

$$M_{cat} = 1647498 \quad [\text{material balance}]$$

$$\rho_c = 780 \text{ kg/m}^3$$

$$\rho_b = 160 \text{ kg/ m}^3 \quad (\text{Anon., 2013})$$

$$V = 1647498 \left[\frac{1}{160} - \frac{1}{780} \right] = 8187.69 \text{ m}^3/\text{hr.}$$

$$= 2.27 \text{ m}^3/\text{s}.$$

⇒ The average flow rate can be determine by the following equation:-

$$V_{av} = \frac{V_o - V_i}{\ln\left(\frac{V_o}{V_i}\right)}$$

☒ Where:-

V_{av}: the average volumetric flow rate of feed in the riser,

V_O: the volumetric flow rate at the out let of the riser which are calculated previous = 28 m³/s,

V_I : the volumetric flow rate at the inlet of the riser which also calculated previous = 2.27 m³/s.

$$V_{ac} = \frac{28 - 2.27}{\ln\left(\frac{28}{2.27}\right)} = 10.24 \text{ m}^3/\text{s}$$

The linear velocity through the riser:

The linear velocity of the bottom of the riser should be not less than (4.5 m/s), and at the top of the riser should be not less than (18 m/s) , so the average velocity must be calculated as follows:

$$U_{av} = \frac{U_o - U_i}{\ln\left(\frac{U_o}{U_i}\right)}$$

$$U_{av} = \frac{18 - 4.5}{\ln\left(\frac{18}{4.5}\right)} = 9.7 \text{ m/s}$$

☒ **Riser Diameter:**

The average volumetric flow rate

= cross section area * average linear velocity

$$V_{av} = A * U_{av}$$

$$A = V_{av}/U_{av}$$

$$A = \frac{10.24}{9.7} = 1.05m^2$$

☒ So riser diameter can be calculated from the following equation:

$$A = \frac{\pi}{4} * D^2$$

$$D^2 = 4 * A/\pi$$

$$D = \frac{\sqrt{4*1.05}}{3.14} = 1.16m$$

☒ **Riser Height:**

☒ Riser height can be calculated by the following equation:

Height (H) = average linear velocity (U_{av}) * residence time (τ)

$$H = U_{av} * \tau$$

H : riser height

U_{av} : Average linear velocity which calculated previous =9.7 m/s,

τ : Residence time in the riser = 5 s (Anon., 2013)

$$H = 9. \frac{7m}{s} * 5s = 48.5m$$

☒ *Pressure Drop through the Riser:*

Pressure drop can be calculated by the following equation:

$$\Delta P = 1.3 \left[\frac{U_g^2 \rho_g}{2 * g_c} + W * \frac{U_p}{g_c} \right]$$

Calculation of the solid flux (W):

☒ Solid flux (W) can be calculated as follows:

$$W_s = (\text{mass flow of the catalyst}) / (\text{cross section area of riser})$$

☒ But,

Mass flow of the catalyst = 1647498 kg/hr.

Cross section area of the riser = 1.16 m² [calculated previously]

$$W_s = \frac{1647498}{(3600) \left(\frac{\pi}{4} \right) (1.16^2)} = 433 \text{ kg/m}^2 \cdot \text{s}$$

☒ And we have,

$$U_g = U_p = 12.48 \text{ m/s} \quad (\text{Anon., 2013})$$

$$\rho_g = 16 \text{ kg/m}^3,$$

$$g_c = 1 \text{ kg.m/s}^2.\text{N}$$

☒ Now we can substitute these values in the main equation:

$$\Delta P = \left[\frac{(9.7)^2 * (16)}{2 * 1} + \frac{(433)(9.7)}{1} \right] = 6438.7 \text{ N/m} = 0.00644 \text{ Map}$$

3.8.3- Settler:

It is a vessel used to move the catalyst to the first regenerator

☒ *Settler Calculation:-*

Settler diameter:

At first settler volume must be calculated, this can be done as follows:

$$V = \frac{\pi}{4(D_o^2 - D_i^2)} * L \quad (\text{Anon., 2013})$$

It is found that the maximum level of the catalyst used to keep a good stripping is (L= 9)

Volume of settler can be calculated by other equation:

$$V = W_{ca} / \rho$$

☒ Where:

W_{ca} : Weight of catalyst,

ρ : catalyst density in settler = 700 kg/m³ (Anon., 2013)

The weight of catalyst = catalyst circulation * residence time of catalyst

☒ **But,**

- Catalyst circulation = 1671123 kg/hr. [Material balance]
- Residence time = 4.5 min (Anon., 2013)

So,

$$\begin{aligned} W_{ca} &= \frac{1671123}{60} \\ &= 12\,5334 \text{ kg} \end{aligned}$$

So,

$$\begin{aligned} V &= \frac{125334}{700} \\ &= 179m^3. \end{aligned}$$

$$D_i \text{ (riser diameter)} = 1.16 \text{ m} \quad [\textit{calculated previously}]$$

☒ **So, these values can be substituted in the main equation:**

$$V = \frac{\pi}{4} (D_0^2 - D_i^2) * L$$

$$179 = \frac{\pi}{4} (D_0^2 - (1.16^2)) * L$$

$$D_o^2 = \frac{4 * (174 + \frac{\pi}{4} (1.16)^2 * 9)}{\pi * 9}$$

$$D_o = \sqrt{\frac{4 * (174 + \frac{\pi}{4} (1.16)^2 * 9)}{\pi * 9}}$$

= 5.2 m

3.9. Regenerator Design:

3.9.1. The First Regenerator Design:

❖ Introduction:-

Catalyst leaving the reaction section contains a carbonaceous deposit on its surface. The carbon deposited on the catalyst surface occupies active catalyst sites along with other forms of coke, is burned in the regenerator. This restores the catalyst activity and provides the heat necessary for the cracking reaction.

Regenerators are large vessels where the catalyst and air are mixed efficiently.

RFCC regenerators are generally equipped with two stage cyclones. In these systems, the outlet duct of the first stage cyclone is coupled directly to the inlet duct of the second stage cyclone system. Most RFCC unit regenerators employ 4-16 parallel sets of primary and secondary cyclones.

☒ The dense phase diameter calculation:-

$$V = \frac{\pi}{4} D^2 L$$

$$V = W_{ca}/\rho$$

$$W = M_{cat} * t \quad [\text{Catalytic cracking of heavy petroleum}]$$

Where:-

m_{cat} = the mass flow rate of the catalyst (Kg)

t = the optimum residence time for the catalyst in the 1st regenerator
lays between (5-10 min), 5 min is selected.

$$m_{cat} = 1671123 \text{ kg/hr.} \quad (\text{Material balance})$$

$$t = 5 \text{ min} \quad [\text{Petroleum Refining}]$$

$$\rho = 780 \text{ kg/m}^3 \quad [\text{refinery manual}]$$

$$W = 1671123 * \frac{5}{60} = 139260.25 \text{ kg}$$

$$V = \frac{W}{\rho} = \frac{139260.25}{780} = 178.54 \text{ m}^3$$

$$\Rightarrow L = 11 \text{ m}$$

$$D = \sqrt{\frac{4V}{\pi * L}} = \sqrt{\frac{4 * 178.54}{\pi * 11}} = 4.5 \text{ m}$$

The dilute phase diameter calculations:

Table (3.2) Flue gas composition [KRC]

<i>Composition</i>	<i>Wt. %</i>	<i>Kg/hr.</i>	<i>M</i>	<i>Kmol/hr.</i>
CO	3.611	8530.987	28	304.678
CO2	10.942	25850.462	44	587.511
N2	71.658	169292.024	28	6046.144
O2	0.173	408.7125	32	12.7723
H2	13.616	32167.8	18	1787.1
Total	100	236250	-	8738.2

The dilute phase area = (Volume of the flue gas)/(Liner velocity)

[Catalytic cracking]

The volume of the gas V1:

From ideal gas law:

$$V_1 = \frac{P_0 V_0 n_1 T_1}{P_1 n_0 T_0}$$

Where:

P₀ = 1.01325 N/m²

P₁- Dilute phase pressure = 0.253 MPa

V₀ = 22.4 m³

T₁- Dilute phase temperature = 903 °K

n₀ = 1 kmol

n₁- 8738.2 kmol/hr.

T₀ = 273 °K

$$V = \frac{1.01325 * 22.4 * 8738.2 * 903}{0.253 * 10^6 * 1 * 273}$$

$$= 259293.2 \text{ m}^3/\text{hr} = 72.03 \text{ m}^3/\text{hr}$$

$$A = \frac{\text{Volume}}{\text{Linear velocity}}$$

Linear velocity = 1.9 m/s

[Catalytic cracking]

$$A = \frac{72.03}{1.9} = 37.90 \text{ m}^2$$

$$D = \sqrt{\frac{4A}{\pi}} = 6.9 \text{ m}$$

The dilute phase diameter = 6.9 m

☒ ***The thickness of cylinder wall:***

$$\frac{P_i D_i}{2f^*j - P_i} + C$$

[Chem. En. V6]

Where:

t: Thickness (m);

Di: internal diameter = 6.9 m;

F: stress of material = 90 N/mm²; from appendix

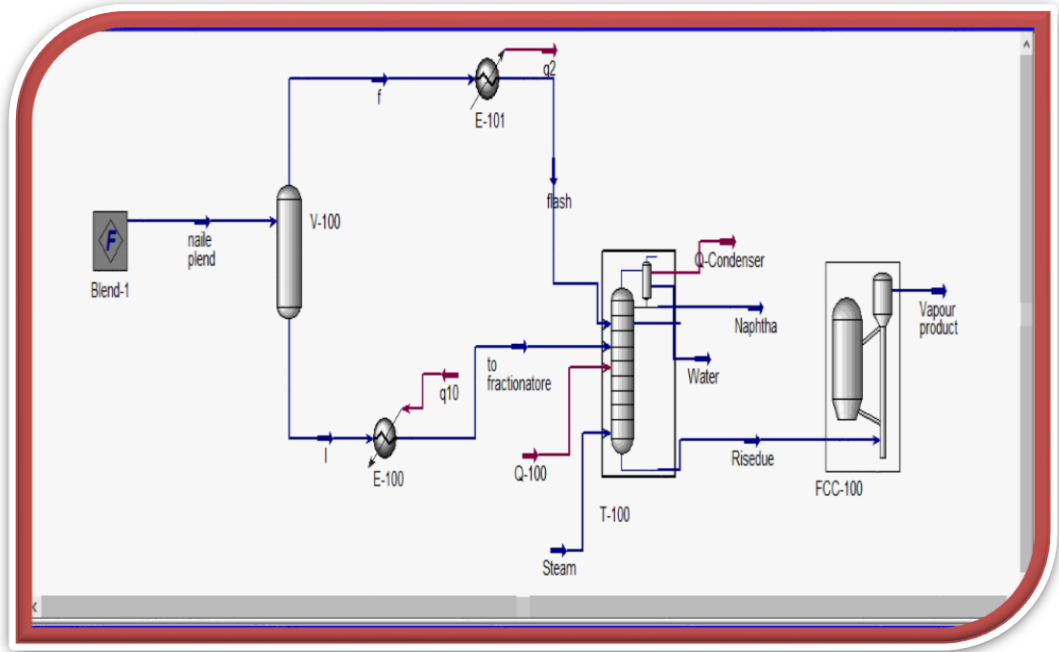
J: welded joint factor;

Pi: internal pressure = 0.253 MPa;

$$t = \frac{0.253 * 6.9}{2 * 90 - 0.253} = 0.09712 \text{ m} = 9.712 \text{ cm}$$

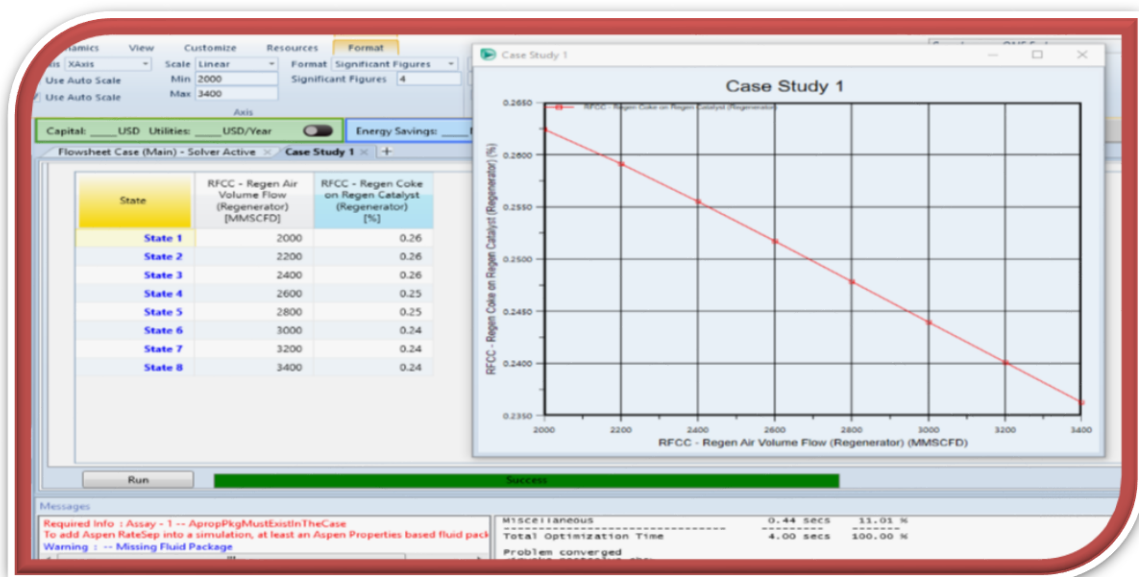
Chapter (4)

4.1. Result and discussion:



Fig(4.1) flow sheet simulation

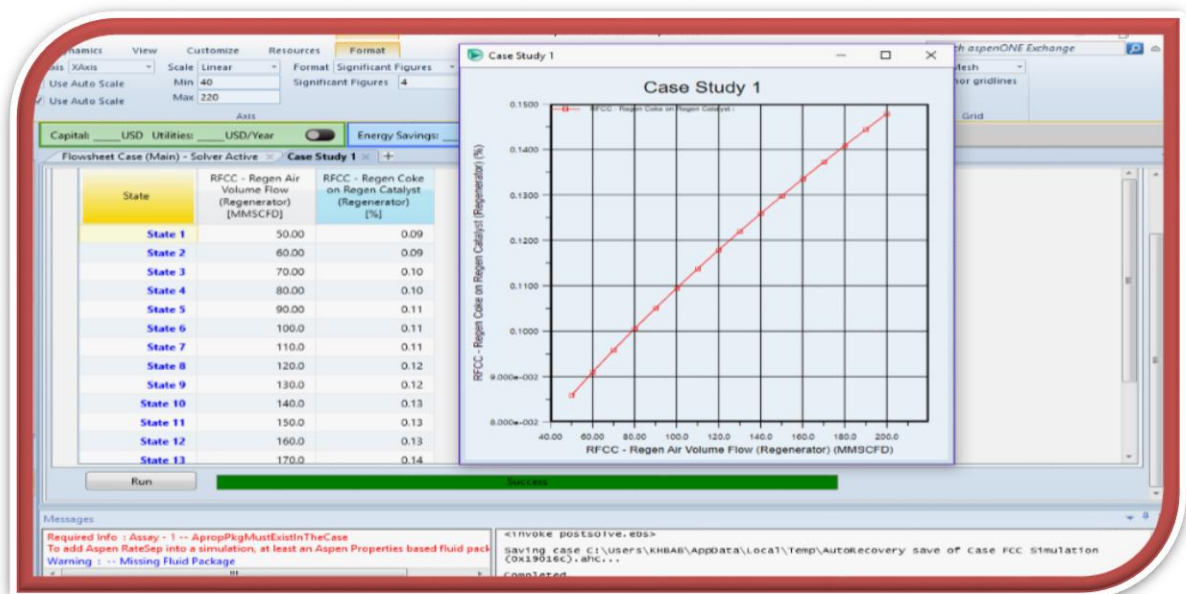
Case (1):-



Discussion OF Case (1):-

From this case that obtain of ASPEN HYSYS simulation appearing the amount of carbon removed in regeneration catalyst increases due to amount of air combustion increase.

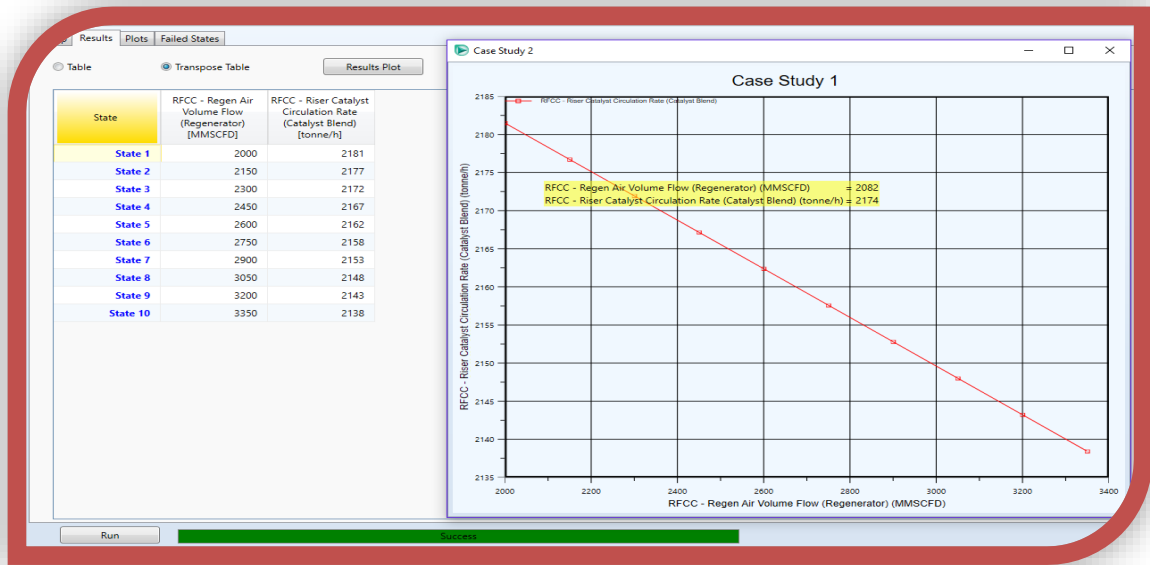
Case (2):-



Discussion OF Case (2):-

While the small amount of air combustion the amount of carbon is increase.

Case (3):-



Discussion OF Case (3):-

When amount of air combustion is increase catalyst circulation rate decrease.

Design riser Discussion

Catalyst circulation rate= 2.115e+006 Kg/h r [HYSYS Results]

Parameter design	Design in [KRC]	Calculation design
Average volume flow	10.24 m ³ /s	13.24 m ³ /s
Area	1.05m ²	1.36 m ²
Diameter	1.16m	0.839 m
high	48.5m	66.2 m

Chapter (5)

CONCLUSION & RECOMMENDATION

5.1 CONCLUSION:

In this project we have been study the effect of amount of air in regenerative catalyst in fluid catalytic cracking unit in Khartoum Refinery Company and we have been found the process of catalyst regenerative is effected by amount of air then. And has shown the optimum amount to achieve carbon percentage of less than 0.05% on regeneration catalyst is **3400 Nm³/min** .and design riser calculation Diameter is **0.839 m** and high is **66.2m**

5.2 Recommendation:

For further study of regeneration catalyst technology we recommended by:

- 1- Pretreatment to the feedstock of unit to reduce the amount of metals such as sodium.
- 2- check of carbon percentage on regeneration catalyst must be daily

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