

**FEED QUALITY AND ITS EFFECT ON PERFORMANCE OF THE
FLUID CATALYTIC CRACKING UNIT. A CASE STUDY OF
PORT-HARCOURT REFINERY COMPANY.**

BY

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DECLARATION

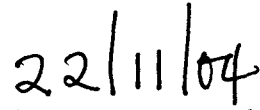
I, Samuel Aduku Monday, declare that this research work has not been presented for the award of Bachelor of Engineering degree anywhere. All literatures cited have been duly acknowledged.



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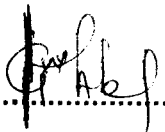
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CERTIFICATION

This is to certify that Samuel Aduku Monday of Chemical Engineering Department, School of Engineering and Engineering Technology, Federal University of Technology, Minna carried out this research on "Feed Quality and its Effect on the Performance of Fluid Catalytic Cracking Unit. A Case Study of Port-Harcourt Refining Company". This is in partial fulfillment of the requirement for the award of Bachelor of Engineering Degree in chemical engineering department.

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DEDICATION

To my Father in heaven in whose image I am perfectly made and by Him I became a part of the adorable family of Mr and Mrs Samuel Unubi.

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ABSTRACT

A study of the feed quality and its effect on the performance of the fluid catalytic cracking unit was carried out using the Port-Harcourt Refinery Company (PHRC) as a case study. The important feed qualities used are the hydrocarbon content and a hydrotreated feed. Data on the feed properties used in PHRC were collected and a product mass balance was carried out on the fluid catalytic cracking unit. Conversion and gasoline yield of the unit were 73.43 vol% and 52.07 vol% respectively. On comparison with cracking of aromatic feed, from literature, with 61.3 vol% conversion and 45.64 vol% gasoline yield, the feed is said to be paraffinic because of its higher conversion and gasoline yield. On comparison with that collected for hydrotreated feed, 80.62 vol% conversion and 63.9 vol% gasoline yield, it is concluded that feed hydrotreating increases conversion and gasoline yield by a significant amount.

CHAPTER ONE

1.0 INTRODUCTION

1.1 GENERAL BACKGROUND

Catalytic cracking has emerged as the most widely used refining process in the world today with about 10.6 mega million barrels of crude oil being processed daily. Two major factors that have increased the need for cracking are the depletion of old, light crude and the increasing demand for gasoline (the most important refinery product, a blend of hydrocarbons with boiling ranges from ambient temperatures to about 400⁰F). Over the years, demand for gasoline has increased in contrast with its availability. The fluid catalytic cracking unit (FCCU) is used for gasoline production. Production of gasoline as well as other important products depends to a large extent on the performance of the FCCU (Jones, 1995). Various parameters can be manipulated to improve the performance of the FCCU. A good example is the feed. The feed, being a starting material, gives an excellent base for manipulation to improve product yield. For almost every refining process unit, feed quality is the basic factor in determining yields and economics. In fluid catalytic cracking feed quality is primarily important since it impacts on the heat balance and the ultimate cracking intensity in addition to the fundamental effects on the natural crackability of the molecular structures.

Some important aspects of feed qualities are:

- i. type of hydrocarbon contained in the feed
- ii. hydrotreating (pretreating) of the feed

Hydrocarbons are organic compounds of carbon and hydrogen atoms that may include from 1- 60 carbon atoms (Dazeley, 1969). The simplest type of hydrocarbon is methane (CH₄). Hydrocarbons can either be saturated or unsaturated. Saturated hydrocarbons have all the carbon atoms satisfied. That is the hydrocarbon chain carries the full complement of hydrogen atoms.

Crude oil is a dark-viscous fluid which is complex mixture of hydrocarbons and non hydrocarbon derivatives (over 90% hydrocarbon by weight) found trapped in certain porous geological strata (Dazeley, 1969). Examples of saturated hydrocarbons found in gas oil are paraffins and naphthenes. Paraffins (methane, ethane and so on) have the general formula C_nH_{2n+2}, while naphthenes have the general formula of C_nH_{2n} and are arranged in the form of closed rings(cyclic) and are found in all fractions of crude oil except the very lightest. They are characterized by high octane number. Octane number is a measure for grading gasoline and for expressing the anti-knock rating of a fuel (Dazeley, 1969). Unsaturated hydrocarbons are those with deficiency in hydrogen atoms; unsatisfied carbon atoms. They are ring type (cyclic) compounds which react readily because of their deficiency in hydrogen. They contain at least one benzene ring (C₆H₆). They are also known as aromatics.

In addition to the hydrocarbon content, there are often small quantities of sulphur, nitrogen and oxygen compounds and sometimes metals such as nickel, vanadium and iron. These impurities, if not removed, can have detrimental effect on the equipment, the catalyst, and even the finished product. Hydrotreating offers an excellent feed pretreatment for the

removal of these impurities which would otherwise poison the cracking catalyst and reduce its efficiency. Typically, hydrotreating of feed is carried out prior to catalytic reforming. It may also be done prior to catalytic cracking to reduce sulphur and improve product yield as well as upgrading middle-distillate petroleum fractions such as kerosene, and diesel. It is also intended to prevent the catalyst from contamination.

This research work takes a close look at the Port-Harcourt Refining Company limited in order to determine how these stated feed qualities influence the performance of the fluid catalytic cracking unit of the company.

1.2 PORT-HARCOURT REFINERY COMPANY LIMITED (PHRC).

The Port-Harcourt Refining Company limited is a subsidiary of the Nigerian National Petroleum Corporation (NNPC) which comprises of a premier refinery usually referred to as the Old Port Harcourt refinery (OPHR) with a processing capacity of 60,000 barrels of crude oil per stream day and the new refinery has a processing capacity of 150,000 barrels of crude oil per stream day. Combined, they produce premium and regular gasoline, dual-purpose kerosene, diesel oil, liquefied petroleum gas (LPG) and fuel gas.

The company is located at Alesa-Eleme, some 25 kilometers east of Port-Harcourt, the Rivers state capital and occupies an area of about 900 hectares.

1.3 OBJECTIVES

This research project, among other things is intended to;

- determine the nature of the feed used in PHRC fluid catalytic cracking unit
- determine the difference between the effects of paraffinic and aromatic feeds on the fluid catalytic cracking unit performance
- determine the difference in feed and product yield between that used in PHRC and that obtained from hydrotreated feed in order to quantify their effects on the fluid catalytic cracking unit.

1.4 JUSTIFICATION

Parameters such as temperature, catalyst and space velocity, as well as material and energy balance have all been used to characterize the performance of the fluid catalytic cracking unit.

This project is investigating further the effects which the feed quality has on the performance of the fluid catalytic cracking unit using the feed quality and product mass balance as a measure.

CHAPTER TWO

2.0 LITERATURE REVIEW

Most industrial reactions are catalytic and one of the largest scale catalytic processes in practice is cracking. Cracking is the conversion of large petroleum molecules into smaller hydrocarbons, primarily in the gasoline range. Cracking processes were first carried out in the absence of catalysts but in the last four decades a series of continuously improved cracking catalysts has been applied, all of them solid acids.

2.1.0 DEVELOPMENTAL HISTORY OF FCCU

The idea of cracking large hydrocarbon molecules into smaller ones began in the late 1800s when it was found that the large molecules broke into smaller molecules at high temperatures. The rapid increase in the demand for kerosene to fuel kerosene lamps also played a major part in this advent. However, as a result of advancement in technology which in turn led to the invention of automobile, electricity and its equipment, the desire for petroleum products shifted from kerosene to gasoline in the early 1900s. This began the development of thermal cracking bringing about the first commercialized cracking process known as the Burton process which went on line in 1913. Development of cracking units revolutionized the refinery industry which led to a rapid change in thinking about petroleum processing. During this revolution, an important discovery was encountered. It was discovered that an aluminium chloride catalyst made

the process easier by operating at low temperatures and pressures. Then the McAfee process, a unit that utilized the aluminium chloride catalyst, came on line in 1915, just two years after the Burton process.

Catalytic cracking was pursued as a desirable process over thermal cracking for two major reasons:

- i. catalytic cracking gives more control over the products by breaking large hydrocarbons more towards the middle minimizing the yield of light hydrocarbons and maximizing gasoline yield
- ii. The gasoline produced in catalytic cracking is of much higher quality, namely a higher octane number. This is due to the skeletal isomerization, dealkylation of aromatics and dehydrogenation reactions that take place in the reactor. (Jones, 1995)

2.1.1 FIXED BED CATALYTIC CRACKING

A major drawback to the McAfee process was the loss of the expensive catalyst due to coking on the catalyst surface. Thus, a catalyst regeneration system was next step in developing a better cracking unit.

In mid 1920s, Eugene Houdry, a French mechanical engineer and a race car enthusiast, became interested in gasoline quality. After screening numerous catalyst formulations using trial and error, Houdry discovered that acid activated clay (mixture of silica and alumina) was a more effective catalyst for cracking heavy oil to lighter products particularly high octane gasoline.

In 1931, Houdry, in conjunction with Socony-vacuum, now mobil, founded the Houdry process company to develop the Houdry fixed bed catalytic cracking process. The Houdry process developed was a cyclic in which four time-phased reactors, each of which is cycled through a sequence of steps as given below:

- a. Hot heavy oil is cracked by contact with fixed bed catalyst
- b. The reactor is purged to remove hydrogen
- c. Coke deposited on the catalyst is burned off using air
- d. The combustion gases are expended from the reactor and the reactor is ready to begin the next cracking cycle.

The first commercialized Houdry catalytic cracking process was at Marcus Hook refinery in 1937. As a result of further studies and advancement in the catalytic cracking process, interest in the Houdry process declined after 1941. (Dubbs, 1988).

2.1.2 THERMOFOR CATALYTIC CRACKING (TCC)

- The next advancement in catalytic cracking was the development of a continuous moving bed catalyst. Pellets continuously move through the reactor to the regenerator vessel and are then returned to the reactor. The key to the TCC process was the thermofor kiln used to regenerate the spent catalyst. Originally, the kiln was developed to burn off coke of fuller earth used to filter lube oil.

In the TCC process, regenerated catalyst flows by gravity from a surge vessel elevate above the reactor into the vessel where the catalyst contacts the hot oil and the cracking reaction takes place. The environment of the

catalyst surge vessel is buffed from the hydrocarbon environment of the reactor by steam injected into the catalyst transfer line. Both the hydrocarbon vapour and the catalyst flow down through the reactor to a lower section where the cracked products exit the reactor through separation pipes.

The steam stripping zone also serves to provide a barrier between air in the regenerator and hydrocarbon in the reactor. The hot regenerated air is mechanically conveyed back up to the catalyst vessel surge by bucket elevator, latter units employed pneumatic or lift systems to transfer the regenerated catalyst back to the vessel.

Socony-vacuum was the principal developer of the TCC process and the first commercialized unit started operations at the Paulsboro refinery in 1941.

TCC units were licensed and operated by Socony-vacuum and others from 1941 to 1955 when the TCC gave way for the more versatile

Fluid catalytic cracking process

(Dubbs, 1988)

2.2.0 FLUID CATALYTIC CRACKING

The need for a better cracking unit arises as a result of the need for catalyst regeneration. Thus, the fluid catalytic cracking process was developed. It uses the principle of fluidized bed operations. Researchers found that a finely powdered catalyst would act like a fluid when mixed with vapour from vapour oil. This idea made it possible to circulate catalysts through a regenerator and a reactor. Then, in 1930s Exxon took a leading role in producing the first fluid catalytic cracking unit (FCCU). It was

commercialized in 1942. This was encouraged by the need for high-octane aviation during World War II. It went on stream in Standard oil of New Jersey refinery, Baton Rouge, Louisiana in May, 1942. This design, model I or "up flow" was quickly improved with model II or "down flow" design. A total of 31 units were designed and built. Though engineered by different organizations, these units were similar in concept because the technology came from the same pool, a result of wartime cooperative efforts. Of these first units, several remain today. The principal features of the model II unit included a reactor vessel near ground level with the catalyst regenerator offset and above it (Gary and Handwerk, 2001)

Following the war, the "stacked" FCC design, which featured a low-pressure reactor stacked directly above a higher-pressure regenerator, was commercialized. This design was a major step towards shifting the cracking reaction from the dense phase of the catalyst bed to the dilute phase of the riser. In the mid 1960s, the "straight riser" or "side-by-side" design was introduced. In this unit, the regenerator was located near ground level with the reactor to the side in an elevated position. Regenerated catalysts, fresh and recycled feed were directed to the reactor by means of a long straight riser located directly below the reactor. Product yields and selectivity were substantially improved compared with those of earlier designs. A major breakthrough in catalyst technology occurred in the mid 1960s with the development of zeolite catalysts. These sieve catalysts demonstrated vastly superior activity, gasoline selectivity, and stability characteristics compared with the amorphous silica-alumina catalysts initially used. The availability of the zeolite catalysts served as the basis for most of the process innovations

that have been developed in recent years as many companies have developed their own FCC process and there are numerous varieties in unit configuration.

(Dubbs, 1988)

2.2.1 FCC PROCESS DESCRIPTION

The modern fluid catalytic cracking unit is a large and complex process for cracking heavy gas oils to lighter hydrocarbon fractions. In its simplest form, the process consists of a reactor, a catalyst regenerator and a product separation section as shown in figure 2. For the purpose of simplicity, the unit will be divided into four sections for description. The main features of this unit are that UOP FCC has been designed to have all riser cracking reactor and a complete CO combustion high efficiency regenerator. The four sections are:

I. Reactor-regenerator-feed preheat section

This is where the heavy feed is cracked to products ranging from oil, which is heavier than the feed, to light fuel gas. The catalyst is continuously regenerated by burning off coke deposited during the cracking reaction. Raw oil charge is preheated by circulating naphtha, main column bottoms and products.

II. Flue gas section

Hot flue gas from the regenerator is passed through the flue gas cooler. The flue gas cooler is used to recover the heat energy from the gas via steam regeneration.

III. Fractionation section

The main column cools the reactor product vapours and begins the separation process. Heavy fuel oils come off the tower as bottom products while gasoline and lighter materials leave the top of the tower together.

IV. Gas concentration and recovery section

The main column overhead material is separated into gasoline, LPG and fuel gas. The composition of each stream is controlled for maximum product value and to meet the specifications. (PHRC)

In general, a typical FCC process involves mixing a preheated hydrocarbon charge with hot, regenerated catalyst as it enters the riser leading to the reactor. The charge is combined with a recycle stream within the riser, vapourised and raised to the reactor temperature by the hot catalyst. As the mixture travels up the riser, the charge is cracked at 10-30 psi in a dilute phase. In the more modern FCC units, all cracking takes place in the riser. The "reactor" no longer functions as a reactor; it merely serves as a holding vessel for cyclones. This cracking continues until the oil vapours are separated from the catalyst in the reactor cyclone. The resultant product stream (cracked product) is then charged to a fractionation column where it is separated into fractions and some of the heavy oil is recycled to the riser. Spent catalyst is regenerated to get rid of coke that collects on the catalysts during the process. Spent catalyst flows through the catalyst stripper to the regenerator where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed. With the use of special

catalysts, all the carbon monoxide in the flue gas is combusted to carbon dioxide in the regenerator. Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process.

(OSHA)

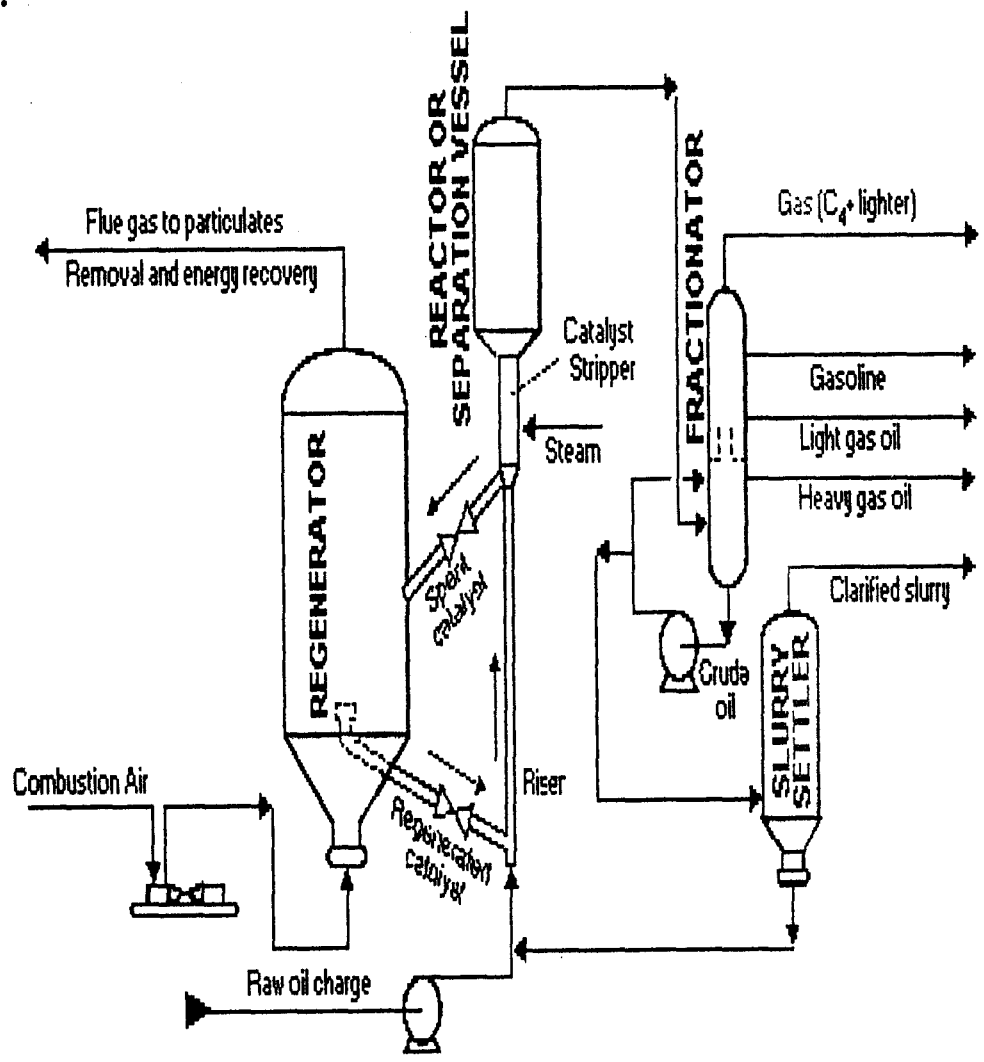


FIGURE 2.1 FLUID CATALYTIC CRACKING LAYOUT

2.2.2 FCC PROCESS PARAMETERS

The FCCU is very flexible with the ability to crack feedstock from naphtha to pretreated residues. The process variables that enable the FCCU to be flexible are catalyst activity, temperature, catalyst to oil ratio, space velocity, and contact time. Feedstock to the FCCU typically includes the heavy gas oil fraction with boiling point ranging from 640-980oF. The range of feedstock fed to the FCCU is limited by the upper boiling point because of high metal content in the heavier streams. Four major influences of feedstock that affect the FCCU are Conradson carbon residue (CCR), metals, sulphur and nitrogen content. CCR gives a high yield of coke, which decreases the catalyst activity. Metals and nitrogen in the feed also reduce catalyst activity. Sulphur is released as SO₂, H₂S, and sulphur in distillate. Modern catalyst technology has helped make catalytic cracking the most used process in the refining industry today. High yields of high-octane gasoline are obtained in today's FCCU using a high activity zeolite-based catalyst held in a matrix of amorphous silica-alumina. The pore diameters of the zeolite catalyst prevent large hydrocarbons from passing through until cracked, giving a high conversion of the feedstock. The pore size governs the conversion of feedstock to specific fractions. Within normal operation increasing the reaction temperature, catalyst/oil ratio, catalyst activity and contact time will yield a higher conversion of feedstock. An increase in the space velocity will decrease conversion.

Table 2.1: Parameters for FCC

Reactor space velocity (lb/hr/lb)	1.1-13.4
Catalyst/oil ratio (v/hr/lb)	5-16
Recycle/fresh feed	0-0.5
Catalyst requirement (lb/bbl feed)	0.15-0.25
Catalyst circulation rate (ton cat/bbl total feed)	0.9-1.5
On-steam efficiency	96-98
Reactor temperature (oF)	885-950
Regenerator temperature (oF)	1200-1500
Reactor pressure (psi)	8-30
Regenerator pressure (psi)	15-30
Research octane number (RON)	92-99
Motor octane number (MON)	80-85

(Adopted from Gary and Handwerk, 2001)

2.3 FEEDSTOCK

Before the introduction of residues, vacuum distillates were solely used as feedstock to load the cracker fully. These days, even residues are used to load the cracker. The term used for this type of configuration is long residue catalytic cracking complex. The only modification or addition needed is a residue desalter and a bigger and more heat resistant reactor (Hengstebeck, 1959). However, the feedstock for catalytic cracking is normally obtained from vacuum distillation or solvent deasphalting. In this way, the feed is virtually free of asphaltic materials and metals. Asphaltic materials tend to cause excessive coke formation. The metals, which deposit on the catalyst and cannot be removed from it, have their own undesirable catalytic effect, which leads to increased formation of coke and light gases at the cost of gasoline. As in catalytic reforming, the objective of catalytic cracking is to obtain a high yield of gasoline with low coke production. The best feedstocks for catalytic cracking are also naphthenic (light and heavy gas oils). In refineries, which have coking plants, the coking gas oil is generally sent to catalytic cracking (KRPC).

2.4 PRODUCT

The products or yields of a catalytic cracker are influenced, not only by the quality of the feedstock and by variables (temperature, pressure, e.t.c), but also by other variables which exercise just as complex effect on the progress of

the reactions and, therefore, on the product distribution. The valuable products from the FCCU are:

- Fuel gas (ethane and lighter hydrocarbons)
- Liquefied petroleum gas-LPG (C₃ and C₄)
- Gasoline (C₅-C₆)
- Light cycle oil (LCO)
- Slurry oil

Although gasoline is typically the desired product of the FCCU in Nigeria and everywhere in the world, operating variables are still being adjusted to maximize other products. The three main aims are to maximize gasoline, LPG and sometimes LCO production.

2.5 CATALYST

The catalysts used in fluid catalytic cracking are made up of natural or synthetic earths. The principal catalyst base is made up of silica (SiO₂) and alumina (Al₂O₃). It is known that silica and alumina, taken separately, cannot function as catalyst, but combined in certain proportions they show catalytic properties.

A fresh catalyst, not yet used, has a very large surface area (up to 600-800 m²/g) and a high porosity (up to 0.6-0.8 cm³/g). As the catalyst is used, surface and porosity diminish, and its activity diminishes in proportion until it reaches a "balanced activity" which is maintained by the continuous or intermittent addition

of fresh catalyst. The deactivation of the catalyst is caused by three principal factors:

- I. The high temperatures reached during regeneration process,
- II. The steam used for "steam seals",
- III. Stripping in the reactors.

And the presence of certain poisons which can be:

a. Temporary poisons

The coke deposited on the catalyst impedes the contact between hydrocarbons and "active centers". Once the coke has been burnt in the catalyst regeneration phase, the catalyst returns to its balanced activity.

b. Permanent poisons

Some metallic compounds, which, concentrated in the heavy fractions during the atmospheric and vacuum distillation, can, in the end, reach (in very small but still noxious quantities) the cracking plant. The most noxious (poisonous) elements are:

- Iron, Fe^{2+}
- Copper, Cu^{2+}
- Sodium, Na^{+}

In conclusion, coke reduces the catalyst activity, while the permanent poisons alter the selectivity. Coke is eliminated by the regeneration process (combustion by air blown from outside in a quantity sufficient to eliminate it almost entirely from the catalyst surface). The permanent poisons are mainly eliminated first by

occlusion on the catalyst surface and finally by attrition that reduces the catalyst to almost minute dust particles, which are dispersed in the atmosphere.

(KRPC)

2.6 ADVANTAGES OF FCC

A. It gives higher control over the products by breaking large hydrocarbons more towards the middle minimizing the yield of light hydrocarbons and maximizing gasoline yield

B. The gasoline produced in the catalytic cracking is of much higher quality, namely a higher octane number.

2.7 DISADVANTAGES OF FCC

A. Explosive concentrations of catalyst dust could result during recharge or disposal

B. Because of the presence of heaters in catalytic cracking units, the possibility exists for fire due to leak or vapour release

2.8 HYDROGEN CONTENT

Basically, vacuum gas oils can vary greatly in hydrogen content from below 12.0 wt% in aromatics to over 14.0 wt% in paraffinic feeds. Taking

ordinary benzene, for example, with empirical formula C_6H_6 , hydrogen wt% is 7.7. But its compatriot in the paraffin family in terms of carbon atoms, hexane (C_6H_{14}), has hydrogen wt% of 16.23. This depends largely on crude source.

2.9 API GRAVITY

API (American Petroleum Institute) gravity is a universally acceptable means of defining petroleum. The higher the API gravity, the lighter the oil. For example, light petroleum has high API gravity and low specific gravity. Gas oil with low carbon, high hydrogen, and high API gravity are usually rich in paraffin and tend to yield greater proportions of gasoline and light petroleum products while those with high carbon, low hydrogen, and low API gravity are usually rich in aromatics and tend to yield lesser products (OSHA, 2002).

Because aromatics have higher density and contain less hydrogen than paraffins, the API gravity of the oil decreases with decreasing hydrogen content.

2.10 ANILINE POINT

Aniline point is a measure of the temperature at which oil becomes miscible with aniline. Aniline is an amine derivative of benzene. It is also known as amino benzene, phenyl benzene or cyanol with structural formula $C_6H_5NH_2$. Since aniline is an aromatic structure, more aromatic gas oils tend to be able to mix with aniline at a lower temperature thereby reducing the amount of gas oil that will reach the highest temperature for separation. This reduces the yield. (Perry, 1998)

2.11 K-FACTOR

This is the feed crackability characteristics factor as stipulated by UOP.

Table 2b gives a detailed summary of K-Factor for various feeds from which the paraffinic feed type possesses a fine cracking expectation.

Table 2.2 K-factor

Range of characteristics factor - k	Relative crackability	Feed type
>12.0	High	Paraffinic
11.5-11.6	Intermediate	Naphthenic
<11.3	Refractory	Aromatic

(Dubbs, 1988)

2.12 HYDROTREATING

The feed pretreatment involved is basically hydrotreating which is about 95% desulphurization. Hydrotreating uses a mild catalyst process of adding hydrogen to improve the quality of petroleum fractions by removing sulphur, nitrogen and metals from them. Hydrotreating carried out is about 95% desulphurization. Hydrotreating selectively hydrogenates these contaminants without destroying the aromatic portions (Adebayo, 1991). Typically, hydrotreating comprise of the following processes

Process	Primary Benefits
Demetallation	removal of metals like vanadium, nickel
Hydrocracking	reduction of bpt by decreasing mwt
Hydrodenitrogenation	removal of nitrogen
Hydrodeoxygenation	removal of oxygen
Hydrodesulphurization	removal of sulphur
Hydrogenation	addition of hydrogen, saturates aromatics
Hydroprocessing	removal of sulphur, nitrogen & lowers bpt

Hydrotreating is effected by hydrogen partial pressure, process temperature and contact time.

- By increasing the hydrogen pressure, a better removal of undesirable materials and a better rate of hydrogenation is achieved.

- Contact time is set to give adequate treatment without exceeding the point of excessive hydrogen usage and undue coke formation.
- Excessive temperature increases the formation of coke, thus temperature is maintained within the operating range.

2.12.1 HYDROTREATING PROCESS

The feed mixed with make up and recycled hydrogen is preheated to temperature of about 750°F. The mixture is then passed through a packed bed reactor vessel where the viscosity index improvement and decolourization are obtained. The bottom product from the reactor is cooled and then fed to a high pressure separator where a hydrogen rich gas is separated and recycled to the reactor and some collected for use in other reactions. After separation of hydrogen, the product stream is fed to a stripping column for stabilization. The light ends and residual hydrogen sulphide in the top stream from the stripper are removed and hydrotreated. Desulphurized product is then obtained.

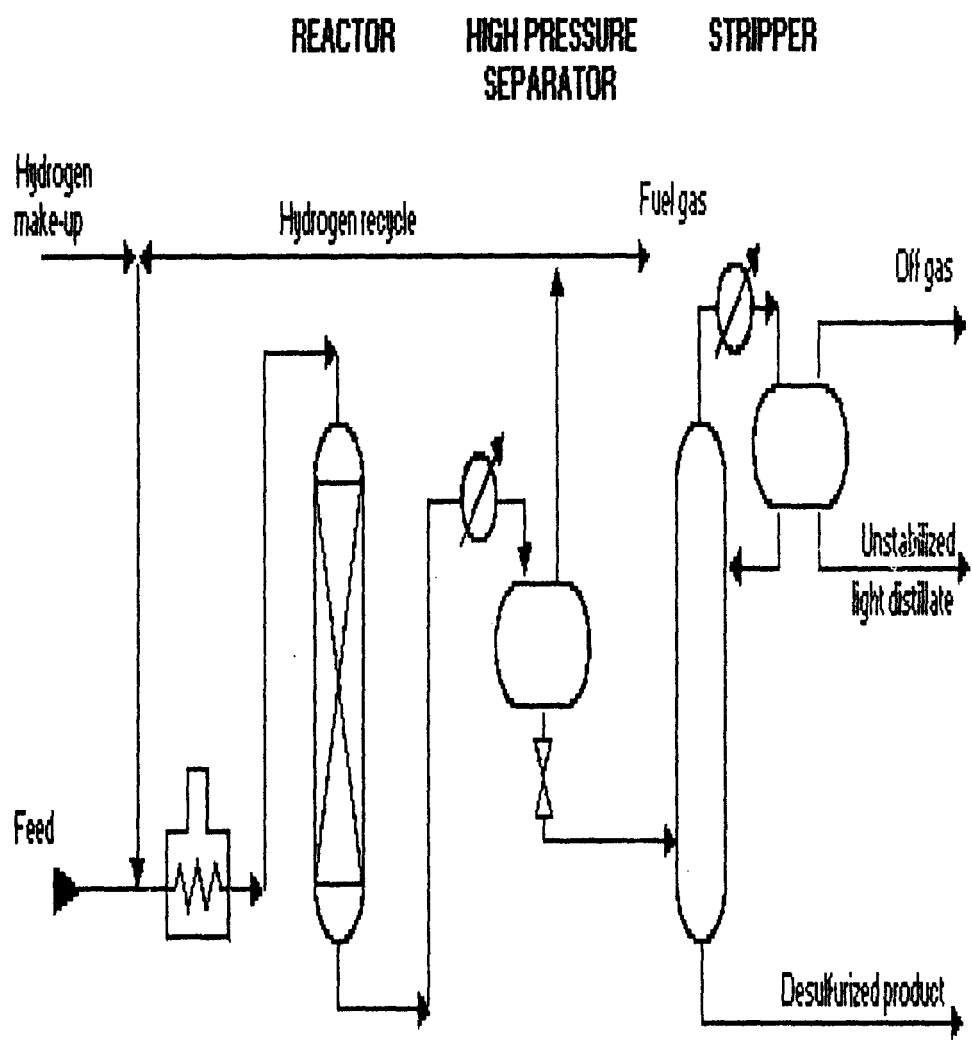


FIGURE 2.2: FLOW DIAGRAM FOR HYDROTREATING PROCESS

CHAPTER THREE

3.0 METHODOLOGY

3.1 COLLECTION OF DATA

Data on the feed and product were sourced for and documented. These sources include various textbooks, handbooks, journals, operating manuals and internet sites. Data collected from PHRC include mass flow rates for both feed and products, corrected mass flow rates for feed and products, feed and product specific gravities and constants for feed and product charge.

3.2 DATA UTILIZATION

Some of the data collected were used to carry out the mass balance calculations as presented in Appendix A. Thus, a mass balance was generated as presented in table 3.4.

3.3 METHOD OF ANALYSIS

The method used in determining the effect of the feed quality on the fluid catalytic cracking unit performance involves comparing the yields obtained from the mass balance calculations with those collected from the cracking of aromatic and hydrotreated feeds. The measures used for quantifying are the conversion and yields for gasoline, liquefied petroleum gas, light cycle oil, bottoms and coke.

Table 3.1 Mass balance for FCC yields in PHRC (operative)

IN	lb/hr	Wt%	Ft3/hr	Vol%
Feed	436334.39		477.39	
OUT				
Gasoline	201862.41	48.37	266.27	52.07
LPG	5238	12.56	94.58	18.50
LCO	85940	20.60	91.27	17.85
Bottoms	37420	8.97	35.59	6.95
Flue gas	16334.97	3.90	23.69	4.63
Coke	23317.8	5.6	-	-
Total	417273.18	100	511.4	100

Table 3.2 FCC yield for cracking of aromatic feed

Conversion, vol%	61.3
Gasoline, vol%	45.64
LPG, vol%	11.83
LCO, vol%	14.79
Bottoms, vol%	7.92
Coke, vol%	5.6

(Wilcox and Kowalczyk, 2000)

Table 3.3: Feed properties for PHRC and Aromatic feed

	PHRC	Aromatic
Specific Gravity	0.914	0.934
Sulphur, wt%	0.98	2.04
Nitrogen, wt%	0.17	0.38
K-Factor	12.54	11.67
Aniline point	228	176

Table 3.4: Differences in feed quality between hydrotreated and PHRC feed

	Hydrotreated	PHRC	Change
Specific gravity, at 15°C	0.905	0.914	-0.09
Sulphur, wt%	0.17	0.98	-0.81
CCR, wt%	0.09	0.27	-0.18
Nitrogen, wt%	0.08	0.17	-0.09
K factor	12.89	12.54	0.35
Aniline point, °F	238	228	10

Table 3.5 FCC yields for hydrotreated feed

Conversion, vol%	80.2
Gasoline, vol%	63.9
LPG, vol%	28.5
LCO, vol%	12.8
Bottoms, vol%	5.02
Coke, wt%	4.79

(Campgna et al, 2001)

CHAPTER FOUR

4.0 RESULTS

Table 4.1 Differences in FCC yields between PHRC feed and aromatic feeds

	PHRC	Aromatic	Change
Conversion, vol%	73.43	61.3	12.13
Gasoline, vol%	52.07	45.64	7.42
LPG, vol%	18.50	11.83	6.67
LCO, vol%	17.85	14.79	3.06
Bottoms, vol%	6.95	7.92	-0.96
Coke, wt%	5.6	5.6	0

Table 4.2 Differences in FCC yields between hydrotreated and PHRC feeds

	Hydrotreated	PHRC	Change
Conversion, vol%	80.2	73.43	6.77
Gasoline, vol%	63.9	52.07	11.83
LPG, vol%	28.5	18.50	10.0
LCO, vol%	12.8	17.85	-5.05
Bottoms, vol%	5.02	6.95	-1.93
Coke, wt%	4.79	5.6	-0.81

4.1 DISCUSSION

Looking through table 4.1, yields from cracking of PHRC feed gives a conversion of 73.43 vol% and a gasoline yield of 52.07 vol% with a total LPG yield of 18.50 vol%. Yields from cracking of aromatic feeds were 61.3 vol% conversion, 45.64 vol% gasoline and 11.83 vol% LPG. It follows that as the feed hydrogen content decreases so does the conversion level, gasoline and LPG yields. The lower conversion achieved when cracking aromatic feed could be due to the fact that the presence of high percentage of nitrogen compounds in oils are in ring structures so that aromatic gas oils tend to have higher nitrogen contents. Since these nitrogen compounds are basic (or can become basic on cracking), they can poison the acidic FCC catalyst resulting in lower FCC conversions. Another contributing factor is that as the number of ring structures increases, there is an increase in the chance that dehydrogenation from contaminant metals will cause multi-ring aromatics to form leading to condensation and coking on catalyst (Campagna et al, 2001). Another very interesting observation on the effect of feed hydrogen content is in the ratio of LCO to bottoms. For aromatic feed we have LCO: bottoms ratio of 14.79:7.92 vol% while for PHRC feed we have LCO: bottoms ratio of 17.85: 6.96 vol%. This could be due to the fact that as the percentage of aromatics in the feed increases, there is a significant rise in the number of molecules (or molecular fragments) that simply cannot be cracked (Jones, 1995)

On comparison of hydrotreated feed quality with that of PHRC, hydrotreated feed has lower specific gravity of 0.09 numbers, lower sulphur content by 0.81 wt%, lower Conradson carbon residue (CCR) by 0.18 wt%, lower nitrogen content by 0.09 wt%, higher K-factor by 0.35, higher aniline point by 10.0. The reduced specific gravity increases the API gravity thus improving the crackability of the feed (OSHA). This is indicated by the increment in the K-factor. Sulphur compounds are highly objectionable in commercial products on account of their unpleasant smell or bad odour. It also corrodes iron and steel used in refinery process equipment, piping and tanks (Adebayo, 1991). The lower sulphur content reduces the possibility of formation of sulphurous compounds which could cause corrosion or can be harmful to the unit or environment. It reduces the level of sulphurous compounds emitted from the FCC significantly, thus eliminating the need for the use of sulphurous compound reducing agents or the installation of flue gas scrubber. Since aniline point is the temperature at which petroleum fractions become miscible with aniline, thus at higher temperature basic knowledge indicates that less amount of the gas oil will be lost to aniline. Table 4.2 presents the difference in FCC yields between hydrotreated and PHRC (assumed unhydrotreated) feeds. For hydrotreated feed, FCC conversion is higher by 6.77 vol%, gasoline yield is higher by 11.83 vol%, LPG is higher by 10.0 vol%, LCO is lower by 5.05 vol%, bottoms is lower by 1.93 vol% and coke is lower by 0.81 wt%. The decrease in LCO and bottoms and increased gasoline and LPG can be linked with the side reactions of hydrocracking and

hydroprocessing. Gary and Handwerk (2001) reported that hydrocracking and hydroprocessing decrease the boiling point of the feed by decreasing the molecular weight. A decrease in boiling point as a result of decrease in molecular weight gives rise to lighter fractions which can easily be cracked into more desired products as manifested in the increased gasoline and LPG yields. The decrease in the coke weight percent can be linked with the saturation of aromatics by hydrogenation. This reduces the extent of coking on the catalyst.

CHAPTER FIVE

5.0 CONCLUSION

The existence of numerous variables which have markedly important impact on the FCCU performance cannot be ignored. However, since performance is characterized by efficiency and conversion is basically a proof of the efficiency of a unit, Far more than any other single variable, FCC feed qualities greatly impact on FCCU performance. For straight run VGO feeds, hydrogen content is an excellent indicator of the conversion and yields that can be expected from the FCCU. Hydrotreating greatly improves the intrinsic qualities of FCCU feeds, thus improving their crackability as shown in the form of a higher conversion of 80.62 vol%.

5.1 RECOMMENDATION

- I.** Before any process of fluid catalytic cracking is carried out, intensive laboratory analysis should be performed on the feed. This is to determine the nature of hydrocarbon contained in the feed. The more paraffinic one should be used since it provides less unsatisfied carbon atoms which could cause the formation of excess coke that will poison the catalyst surface thereby reducing its efficiency and life span as well as increasing the cost of regenerating the catalyst
- II.** Since paraffinic gas oil has high wax yield as by-product, it should be the main choice of any refiner so as to create room for maximum utilization of the feed.

III. Two major importance of feed hydrotreating are:

- a. better FCC yields and gasoline octane
- b. no need for flue gas scrubbing to remove SO_x

With these advantages, it is expected that feed hydrotreating would be an obvious choice for refiners, but most refiners are opting for product treating due to lower capital cost involved and lower hydrogen consumption. However understandable this is, consideration should be taken on the disadvantages of product treating which are mainly in the reduction in gasoline yield and lower gasoline octane number due to further destruction of aromatics. Since cost is a short term effect, this should be overlooked because in the long run the cost involved would not match the gains attached.

IV. Where the cost of hydrogen is low, feed hydrotreating should be chosen in place of product treating.

V. As specifications for amount of sulphur compounds to be flared into the atmosphere keeps improving by the day, refiners wishing to meet the future very low sulphur content standard should take a giant step towards putting in place a hydrotreating unit for pretreatment of feed for the FCCU.

VI. In Port-Harcourt Refinery, the most important refinery in Nigeria today, gasoline production is definitely not matching the amount of crude oil available. Therefore, apart from total and regular turn around maintenance required by the FCCU as well as the entire plant for optimum performance, efforts should be

made to set up a means of hydrotreating of feed for FCCU so that gasoline yield can be improved to meet or keep up with its ever increasing demand by the Nigerian populace.

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APPENDIX

MASS BALANCE

In generating the mass balance as presented in table 3.1 the following equations were used:

$$Q_m = \frac{Q_{cm}K(G_f)^{0.5}}{S_g} \quad (\text{lb/hr})$$

$$Q_v = \frac{Q_m}{S_g \times 10^3} \quad (\text{ft}^3/\text{hr})$$

Where:

Q_m – corrected mass flow rate

Q_{cm} – average mass flow from computer

K – Constant for feed charge

G_f – flow gravity = $S_g \times \text{VCF}$

S_g – specific gravity

VCF – volume correction factor

Q_v – volumetric flow rate

Thus for:

- **VGO Feed**

At 399.2°F, $S_g = 0.914$, $\text{VCF} = 0.9849$

$G_f = 0.914 \times 0.9849 = 0.9$

$Q_{cm} = 194773 \text{ kg/hr} \Rightarrow 429400 \text{ lb/hr}$

$$Q_m = 429400 \times 0.979 \times \frac{(0.9)^{0.5}}{0.914}$$

$$Q_m = 436334.739 \text{ lb/hr}$$

$$Q_v = \frac{436334.739}{0.914 \times 10^3}$$

$$Q_v = 477.39 \text{ ft}^3/\text{hr}$$

- Gasoline

At 89°F, K = 0.8817, Sg = 0.7581, VCF = 0.9784

$$G_r = 0.9784 \times 0.7581 = 0.7417$$

$$Q_{cm} = 91414 \text{ kg/hr} \Rightarrow 201533.3724 \text{ lb/hr}$$

$$Q_m = 201533.3724 \times 0.8817 \times \frac{(0.7417)^{0.5}}{0.7581}$$

$$Q_m = 201862.41 \text{ lb/hr}$$

$$Q_v = \frac{201862.41}{0.7581 \times 10^3}$$

$$Q_v = 266.27 \text{ ft}^3/\text{hr}$$

- Liquefied petroleum gas (LPG)

At 94°F, K = 0.7671, Sg = 0.554, VCF = 0.956

$$G_r = 0.554 \times 0.956 = 0.529$$

$$Q_{cm} = 23600 \text{ kg/hr} \Rightarrow 52029.09 \text{ lb/hr}$$

$$Q_m = 52029.09 \times 0.7671 \times \frac{(0.529)^{0.5}}{0.554}$$

$$Q_m = 52398 \text{ lb/hr}$$

$$Q_v = \frac{52398}{0.554 \times 10^3}$$

$$Q_v = 94.58 \text{ ft}^3/\text{hr}$$

- Light cycle oil (LCO)

At 88°F, K = 0.9882, Sg = 0.9416, VCF = 0.9895

$$G_f = 0.9895 \times 0.9416 = 0.9317$$

$$Q_{cm} = 38481 \text{ kg/hr} \Rightarrow 84836.08 \text{ lb/hr}$$

$$Q_m = 84836.08 \times 0.9882 \times \frac{(0.9317)^{0.5}}{0.9416}$$

$$Q_m = 85940 \text{ lb/hr}$$

$$Q_v = \frac{85940}{0.9416 \times 10^3}$$

$$Q_v = 91.27 \text{ ft}^3/\text{hr}$$

- Bottoms

At 174°F, Sg = 1.0514, K = 1.0582, VCF = 0.9614

$$G_f = 1.0514 \times 0.9614 = 1.0108$$

$$Q_{cm} = 16774 \text{ kg/hr} \Rightarrow 36980.34 \text{ lb/hr}$$

$$Q_m = 36980.34 \times 1.0514 \times \frac{(1.0108)^{0.5}}{1.0514}$$

$$Q_m = 37420 \text{ lb/hr}$$

$$Q_v = \frac{37420}{1.0514 \times 10^3}$$

$$Q_v = 35.59 \text{ ft}^3/\text{hr}$$

- Fuel gas

At 111.974°F = 317.43 k, pressure = 13.603 kg/hr

$$= 13.603 + 1.023 = 14.626 \text{ A,}$$

$$Q_f = 9.0 \text{ KNm}^3/\text{hr}$$

$$M_w = \text{mm} \times \text{mol}\%$$

$$= \text{H}_2(2.02 \times 0.1569) + \text{N}_2(28 \times 0.009) + \text{CH}_4(16.032 \times 0.427) + \text{C}_2\text{H}_6(30.48 \times 0.298) + \text{C}_3\text{H}_8(44.064 \times 0.004) + \text{isoC}_4\text{H}_{10}(58.08 \times 0.0141) + \text{nC}_4\text{H}_{10}(58.08 \times 0.007) + \text{C}_4\text{H}_8(56.064 \times 0.0003) + \text{isoC}_5\text{H}_{12}(72.096 \times 0.0001) + \text{C}_6\text{H}_{14}(86.122 \times 0.0004)$$

$$= 0.3160 + 2.772 + 6.845 + 8.9212 + 0.1762 + 0.8189 + 0.0406 + 0.0168 + 0.0360 + 0.00072 + 0.0344$$

$$M_w = 19.9787 \text{ g}$$

Therefore,

$$S_g = \frac{M_w \text{ gas}}{M_w \text{ air}}$$

$$= \frac{19.9787}{28.97}$$

$$S_g = 0.6896$$

For vapour,

$$\begin{aligned} Q_{cmv} &= Q_f K (P_f/T \times Sg)^{0.5} \\ &= 9 \times 4.1092 \times (14.626/317.47 \times 0.6896)^{0.5} \\ &= 9.559 \text{KNm}_3/\text{hr} \end{aligned}$$

$$\text{Flow for inert} = \% N_2 \times Q_f \times \text{Mw of } N_2 \times 10^3 \times \frac{1}{22.4 \times 0.4536}$$

$$= 0.099 \times 9 \times 28 \times 10^3 \times \frac{1}{22.4 \times 0.4536}$$

$$= 2455.39 \text{ lb/hr}$$

Mass flow of vapour

$$Q_{mv} = Q_{cmv} \times k \times S \times 10^3 \times \frac{1}{0.4536}$$

$$= 9.559 \times 1.293 \times 0.6896 \times 10^3 \times \frac{1}{0.4536}$$

$$= 18790.36 \text{ lb/hr}$$

Corrected mass flow for fuel gas

$$Q_m = Q_{mv} - \text{inert flow}$$

$$= 18790.36 - 2455.39$$

$$= 16334.97 \text{ lb/hr}$$

$$Q_v = \underline{16334.97}$$

$$0.6896 \times 10^3$$

$$= 23.69 \text{ ft}^3/\text{hr}$$

- Coke

Flow rate of regeneration air

$$K = 1.293, S_g = 1.0, Q_{cm} = 137.87 \text{ KNm}^3/\text{hr}$$

$$Q_{mra} = \frac{137.87 \times 1.293 \times 1.0 \times 10^3}{0.4536}$$

$$Q_{mra} = 393020.67 \text{ lb/hr}$$

mols/hr:

$$\text{Wet air} = \frac{Q_{mra}}{K} = \frac{393020.67}{28.4} = 13,838.76 \text{ lbmol wet air/hr}$$

$$\text{Dry air} = \frac{393020.76}{29.87} = 13157.70 \text{ lbmol dry air/hr}$$

Assuming 3% humidity,

$$Q_m \text{ H}_2\text{O} = 13838.76 - 13157.70$$

$$= 681.06 \text{ lbmol/hr}$$

Composition of flue gas

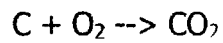
CO₂ – 13.80%

N₂ – 83.0%

O₂ – 3.2%

$$\begin{aligned} \text{Moles of flue gas} &= \frac{\text{N}_2 \text{ fraction in air} \times \text{mols dry air}}{\text{N}_2 \text{ fraction in flue gas}} \\ &= \frac{0.79 \times 13157.70}{0.83} \\ &= 12523.59 \text{ lbmol/hr flue gas} \end{aligned}$$

Coke production



1 : 1

$$\begin{aligned} \text{Moles of CO}_2 \text{ in flue gas} &= \text{mole fraction} \times \text{moles of flue gas} \\ &= 0.138 \times 12523.59 \\ &= 1728.26 \text{ mol of CO}_2 \end{aligned}$$

From equation of C + O₂,

$$\text{Moles of carbon that reacted} = 1728.26 \text{ mols}$$

By O₂ balance,

$$\text{O}_2 \text{ in inlet air} = \text{excess O}_2 \text{ in flue gas} + \text{O}_2 \text{ reacted to CO}_2$$

$$\text{O}_2 \text{ in inlet air} = \text{air flow rate} \times \text{CO}_2 \text{ fraction}$$

$$= 13157.7 \times 0.21$$

$$= 2762.97 \text{ mols}$$

$$\text{O}_2 \text{ excess in flue gas} = 0.032 \times 12523.59 = 400.76 \text{ mols}$$

$$\text{O}_2 \text{ reacted to CO}_2 = 1728.26 \text{ mols}$$

$$\text{Therefore, O}_2 \text{ reacted to H}_2\text{O} = \text{O}_2 \text{ in air} - (\text{O}_2 \text{ reacted to CO}_2 + \text{O}_2 \text{ excess})$$

$$= 2762.97 - (1728.2 + 400.76)$$

$$= 634.01 \text{ mols}$$

If 1 mol of O_2 reacts with 2 mols of H_2 , thus 634.01 mols of O_2 reacts with

$$634.01 \times 2 = 1268.02 \text{ mols of } H_2$$

From carbon,

$$1728.26 \times 12.01 = 20756.40$$

From hydrogen,

$$1268.02 \times 2.02 = 2561.40$$

$$\text{Total coke} = 20756.40 + 2561.40$$

$$= 23317.8 \text{ lb/hr}$$

- Conversion

Conversion was calculated based on volumetric flow rate as given below

$$\text{Conversion} = \frac{\text{Feed} - (\text{LCO} + \text{Bottoms})}{\text{Feed}} \times 100\% \text{ vol}$$

$$= \frac{477.39 - (91.27 + 35.59)}{477.39} \times 100$$

$$= 350.53 \times 100$$

477.39

= 73.43 vol%