INVESTIGATION OF THE PERFORMANCE OF THE FLUID CATALYTIC CRACKING UNIT OF PORTHARCOURT REFINERY

BY

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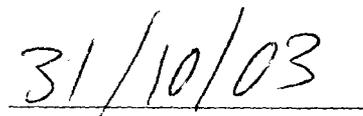
OCTOBER, 2003

DECLARATION

I Idachaba Onuche declare that this research work has not been presented in whole or in part for the award of Bachelor of Engineering degree anywhere. All literature cited have been duly acknowledged in the reference.

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CERTIFICATION

This is to certify that Idachaba Onuche of Chemical Engineering Department, School of Engineering and Engineering Technology, Minna carried out this work on "Investigation of the performance of the fluid catalytic cracking unit of the Port Harcourt Refinery" in partial fulfillment of the requirement in chemical engineering.
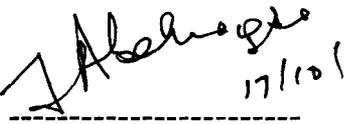

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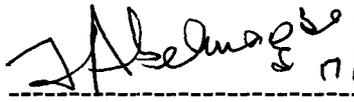
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External Examiner   Date

DEDICATION

I wish to dedicate this work first and foremost to Jesus Christ, the lover of my soul and to my parents Mr. And Mrs. J. U. Idachaba.

ACKNOWLEDGEMENT

ABSTRACT

A performance evaluation of the fluid catalytic cracking unit of the Port Harcourt Refinery has been undertaken. The evaluation was carried out in order to determine whether the unit is operating in accordance with the design specifications.

Material and energy balances were used to determine the values of the performance variables. The performance variables considered include conversion, gasoline yield, material loss, catalyst/oil ratio; coke lay down, regeneration efficiency and catalytic cracking efficiency. The vital performance variables are the catalytic cracking efficiency and regenerator efficiency. The operating catalytic cracking efficiency was 70.3% and the design value is 76.75%. The operating regenerator efficiency was 75% and the design value is 62%.

The results obtained show a decrease in the units' performance efficiency. The decrease in efficiency was mainly due to a faulty reactor catalyst control valve, faulty regenerator cyclone and overdue turn around maintenance.

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CHAPTER ONE

1.0 INTRODUCTION

Fluid catalytic cracking is one of the processes in petroleum refining. It involves the breakdown of heavy gas oil (60 carbon atom hydrocarbons) into lighter, more valuable products. These products include gasoline, olefinic liquefied petroleum gas (LPG), Fuel oil [light cycle oil (LCO), main column bottom (MCB)], fuel gas and steam. Catalyst such as Zeolite catalyst and amorphous silica alumina (handbook,1988)[11].

The fluid catalytic cracking process evolved as a result of the high fees required to license the Houdry cracking process, diffusion and heat limitations associated with both the Houdry cracking process and thermofor catalytic cracking process and the increased demand for high octane aviation fuel brought on by World War II[11].

The first catalysts used in the fluid catalyst-cracking unit were amorphous silica alumina as stated by (handbook,1988)[11]. The synthetic and natural types suffered from low activity, poor selectivity and poor stability. The most significant breakthrough in catalyst technology occurred in the 1960's with the development of the Zeolite catalyst. (Handbook,1988)[11]. This new catalyst was more active, had greater stability, improved fluidization

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characteristics and greater selectivity for gasoline. It is presently the catalyst used in modern fluid catalyst cracking units. (Handbook,1988)[11]

The fluid catalyst-cracking unit produces large volume of high-octane gasoline, olefinic liquefied petroleum gas (LPG), fuel oil [light cycle oil (LCO), and main column bottom (MCB)], fuel gas and steam (handbook,1988)[11]. The yields are primarily determined by process variables such as feedstock, operating conditions and catalyst type. Process variable have varying degrees of interdependence and may frequently produce changes in the yield structure of the products. An all-encompassing performance test is recommended weekly by operation manuals to evaluate the effect of process variables on yield. This is not fully carried out at the Port Harcourt refining. This investigation looks at whether the required specifications for products are attained and if not why the deviations exist?

1.1   OBJECTIVES

The objectives of this investigation is to determine the performance of the fluid catalyst cracking unit of the Port Harcourt refining company and suggest possible means of improving the plant performance.

The evaluation is done by collection data from the running plant then performance of material and energy balances are done to obtain the operating value for the performance variables. The values obtained are analyzed and

compared with design values obtained from operation manuals. This in turn gives a clear and vivid picture of the plant performance.

Subsequently, recommendations are made on how to improve the unit performance.

1.2   JUSTIFICATION

The fluid catalytic cracking unit is the heart of most modern day petroleum refineries. This is due to the fact that it can be adapted to changing feedstocks and product demand.

The performance evaluation is carried out in order to determine the operating level of the unit at that particular time, identify areas of fault and eventually suggest solution for these faults and recommend ways of still improving production. The evaluation acts as the basis for optimization of unit operations.

Performance evaluations are therefore an intricate and unavoidable aspect of plant operation.

CHAPTER TWO

2.1.0 LITERATURE REVIEW

The advent of the petroleum refining industry can be traced to the rapidly increasing demand for kerosene to fuel kerosene lamps in the later half at the 1800s. With the invention of electric and automobile in the early 1900s, the more desirable product of petroleum refining shifted from kerosene to gasoline. The increasing demand for gasoline soon out stripped the availability of straight run gasoline from crude distillation. This shortage of gasoline produced the impetus for the development of technology for increasing the gasoline yield from a barrel of crude oil[10].

2.1.1 DEVELOPMENT TRENDS OF FCCU (HISTORY)

The first thermal conversion process was the Burton process first practiced commercially in 1913 by standard oil of Indiana. In the original Burton process oil was exposed batch wise to high temperature at elevated pressure to achieve to high achieve thermal conversion of lighter products. Due to the batch nature of the Burton process commercial units contained a large number at individual cracking stills in order to achieve acceptable daily throughput.[10]

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Following the commercialization of Burton process the Dubbs thermal cracking process was developed and patented in 1915 (UOP). The Dubbs process was a continuous process of the thermal conversion of oil to lighter products at elevated temperatures and pressures. This was widely used in refineries through the 1920s and into the 1930s.[10]

2.1.2 FIXED BED CATALYTIC CRACKING

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

In 1931 Houdry, in partnership with Socony-vaccum (now Mobil) founded the Houdry process Company to develop Houdrys fixed bed catalytic cracking process. The Houdry process was a cyclic process, which typically used four time-phased reactors, each of which cycled through a sequence of steps outlined below.

i. Hot heavy oil is cracked by contact with a fixed bed catalyst.

ii. The reactor is purged to remove hydrogen.

iii. Coke deposited on the catalyst is burned off with air.

iv.   The combustion gases are purged from reactor and the reactor is ready to begin the next cracking cycle.

The Houdry catalyst cracking process was first commercialized at the sun-Marcus Hook refinery in 1937. Interest in the Houdry process however declined after 1941 due to further advances in the catalytic cracking process.

2.1.3 THERMOFOR CATALYTIC CRACKING (TCC)

The next advance 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 referred to the reactor. The key to the TCC process was the thermofor Kiln used to regenerate the spent catalyst. (The kiln had been originally developed to burn coke off of fuller earth used to filter lub oil).

In the TCC process, regenerated catalyst flows by gravity from a surge vessel elevated above the reactor, into the reactor vessel where the catalyst contacts the hot oil and the cracking reaction take place. The air environment of the catalyst surge vessel is buffed from the H – C environment of the reactor by steam injected into the catalyst transfer line. Both the H – C 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 H – C in the reactor. The hot regenerated catalyst is mechanically conveyed back up to the catalyst surge vessel by bucket elevator later units employed pneumatic or lift systems to transfer the regenerated catalyst back to the vessel.

Socony-vacum was the principle developer of the TCC process and the first commercialized unit started up at the Paulsboro refinery in 1941. TCC units where licensed and operated by Socony-vacuum and other from 1941 to about 1955 when the TCC gave from to the more versatile fluid catalyst cracking.

2.1.4 FLUID CATALYTIC CRACKING

Early developments of fluid catalytic cracking process took place in the late 1930's. There were a number of motivations behind the development of FCC process. Among these were the high fees required to license the Houdry Cracking process, the diffusion and heat transfer limitation associated with both the Houdry fixed bed and the TCC process (both used large size catalyst pellets) and the increasing demand for high octane aviation gasoline brought on by World War II.(fluid catalytic cracking process,1988).

Initial FCC development efforts were led by standardized oil of New Jersey (now Exxon) in association with two researchers from the Massachusetts

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institute of Technology, Warren Lems and Edwin Gilliland. These researchers found out that under the proper aeration conditions, finely divided solid particles could flow through pipes and in many respects act similarly to liquids. This was the advent of fluidization. The use of finely divided cracking catalyst offered a means of overcoming the diffusion and heat transfer limitations encountered with the large size catalyst pellets used in the earlier catalytic cracking processes.

2.1.5 MODERN FCC

During the 1940s military requirements resulted in wide spread commercialization following this period UOP was in the forefront with commercialization of the "stacked" FCC design, which features a low presence reactor stacked directly above a high pressure regenerator. The stacked design not only met the economic needs of small refineries, it was a major step towards shifting the cracking from the dense phase of the catalyst bed to the dilute phase of the riser. In the mid 1950s UOP introduced the "straight riser" or "side-by-side" design. In this limit the regenerator was located near the ground level with the reactor to the side in an elevated position. The regenerated catalyst, fresh feed and recycle were directed to the reactor by means of a long straight riser located directly below the reactor. Compared to earlier designs product yields and selectivity was substantially improved.

The next major improvement in FCC technology was the development of catalytic and regenerator system for complete internal combustion of carbon monoxide (CO) to carbon dioxide (CO_2). In 1973, an existing UOP unit was revamped to include a new combustor concept in regeneration technology to achieve direct conversion of CO within the unit. This was followed by the start-up in 1974 of a New FCC unit specifically designed to incorporate the combustor regenerator technology.

The development in regeneration design and operating techniques resulted in reduced coke yields, lower CO emission which satisfy environmental standards and higher circulating catalyst activity that improved product distribution and quality.

2.1.6 FCC PROCESS DESCRIPTION

Reactor Section

The reactor can be said to be the heart of the unit. The feed is preheated with MCB, Naptha before it is cut into the reactor. The raw oil, which has been preheated, is contacted with steam so as to reduce its partial pressure, the steam serves also to atomize the raw oil to enable adequate oil catalyst contact. The catalyst in this case is a mixture of regenerated and fresh catalyst whose temperature has attained the prescribed value. The raw oil is sprayed through a nozzle, which further atomizes the raw oil. Preceding this point the raw oil

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makes contact with the hot catalyst at the bake of the riser. On contact cracking begins to occur. The pressure heat and force of the reaction takes approximately 60 seconds within the riser. The dis-engager or cyclones at the top of the reactor quenches the cracking reaction by catalyst. The spent catalyst drops down into the stripping section of the reactor where steam is used to remove oil from the spent catalyst. Stripping is done in order to prevent the oil from reaching the regenerator and causing explosions. When the spent catalyst is up to the required level the pressure exerted by it will result in its movement to the regenerator. The vapour oil that leaves the top of the reactor is cooled initially by an air fan cooler after which four heat exchangers are used to cool the mixture. The result is a mixture of water, hydrocarbon and gas, which are sent to other units for further treatment.

2.1.7 REGENERATOR SECTION

The regenerator is a vital part of the unit because it functions as the life giver to the spent catalyst. The spent catalyst from the reactor is brought to the regenerator for treatment. The regenerator has attached to it, a direct-fired air heater, which supplies heat to the air in the regenerator. The poisoned catalyst drops into the regenerator through the spent catalyst slide valve into the regenerator. The coke deposited on the catalyst during the reaction is burned off the catalyst by the hot air from the axial air blower through the heater at the
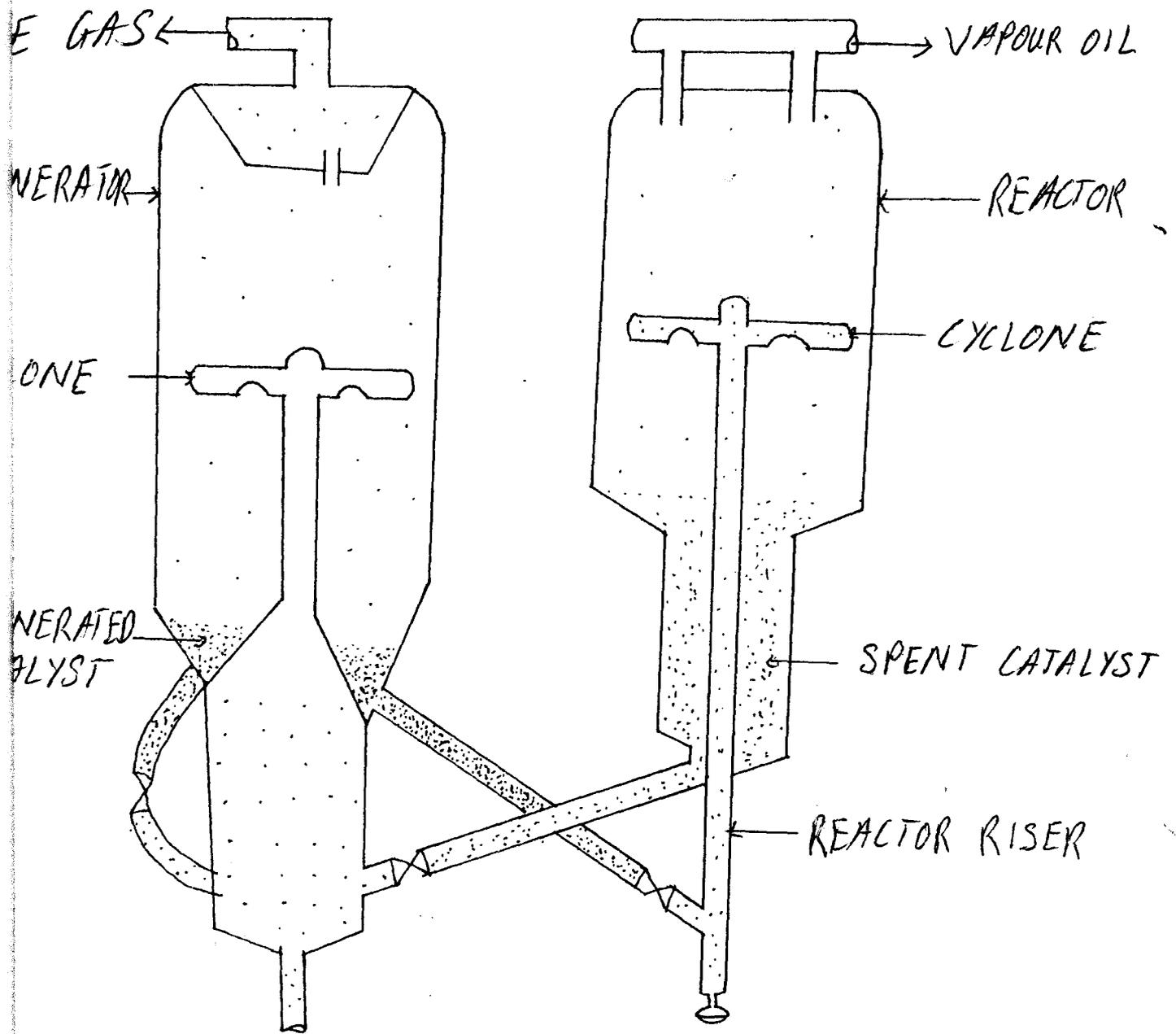
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E GAS ←

VAPOUR OIL →

NERATOR →

REACTOR

ONE

CYCLONE

NERATED
ALYST

SPENT CATALYST

REACTOR RISER

Fig 1 SIDE BY SIDE FCC

base of the regenerator. This is a new development in catalyst regeneration systems as it produces complete combustion of CO to CO_2 in the regenerator. This reduces coke yields, lower CO emissions and a high circulating catalyst activity that improves product distillation and quality. The catalyst is then separated from the flue gas by a two-stage cyclone. The regenerator pressure is about $4kg/cm^2$, which is higher than that of the reactor. This aids the movement of catalyst from regenerator to the reactor. The regenerated catalyst is sent back to the reactor through the regenerated catalyst slide valve. The burning of coke off the catalyst generates large amounts of heats, which is sent to the flue gas cooler.

2.1.8 FLUE GAS SECTION

In the fluid catalytic cracking unit very little is wasted. Due to the complete combustion in the regenerator the flue gas consist mainly of very little CO, light entrained catalyst, Sulphur compound and temperatures ranging from $650 - 700^{o}c$. Such heat would be harmful to the environment and also a waste of energy. To avoid release of the flue gas directly into the atmosphere it is passed through the flue gas cooler.

The flue gas from the regenerator first passes through the orifice chamber where its velocity and pressure is greatly reduced by the arrangement of the plates in the chamber. The gas then moves into the first section of the flue gas

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cooler called the super heater section. If then moves to the vaporizer then finally to the economizer. On leaving the flue gas cooler into the stack, the flue gas temperature is at about 200°c. The coolant used is boiler feed water which is turned into superheated steam. The steam is dried and used as instrument air. The steam produced is sent to the steam header as high pressure steam.

2.1.9 FRACTIONATION SECTION

The vapour coming from the reactor, together with small quantities of catalyst, which have not been separated by the cyclones, is sent to the bottom of the fractionator.

The condensed oil known as slurry oil or MCB because it contains the catalyst which escaped from the reactor is cooled by passing it through a steam generator. Cooled MCB is then delivered to the top of the desuperheating section of the fractionator to bring about the desuperheating of the reactor overhead vapour in this section and also to wash entrained catalyst back into the bottom of the column.

The MCB oil can be cooled and then run down as product or it could used as recycle material. Recycling the whole of the MCB product is undesirable, because this results in excessive coke deposits. A better alternative is to concentrate most of the catalyst into part of the of the MCB stream and to recycle only part of the MCB stream to the reactor for catalyst recovery. This

can be done by means of settlers or hydrocarbons. The other part of the "slurry" having a very low catalyst content is known as clarified oil.

The top part of the fractionators operates as a normal distilling column. Two side-streams are withdrawn and fed into side-strippers. The higher and lighter stream constitutes the light cycle oil (LCO), while the lower and heavier stream constitutes the heavy cycle oil the combination of light, heavy cycle oil and slurry oil production proportions is known as total cycle oil.

Between the two side-streams there is an intermediate reflux and above the lateral light stream there is the top reflux, which is for naphtha. The vapour at the top of the fractionators is uncondensable within the fractionators. It is therefore passed to a light product recovery system where the separation into gasoline and lighter products occurs (c_1, c_2, c_3, and c_4 fractions) [Text – Process and Operating Manual Port Harcourt Refinery Project].

2.2.0 RAW MATERIAL

2.2.1 FEEDSTOCK

2.2.2 EFFECT OF FEED ON PERFORMANCE

The feed–stocks for the FCC process are complex mixtures of hydrocarbons of various types and sizes ranging from small molecules like gasoline up to large complex molecules of perhaps 60 carbon atoms. These feedstocks have a relatively small content of contaminant materials such as

organic sulphur, nitrogen compounds and organ metallic compounds. The relative proportion of all these materials vary with geographical origin of the crude and the particular boiling range of FCC feedstocks. However, feedstock can be ranked according to their crackability, or ease with which they can be converted in an FCC unit. Crackability is a function of the relative proportions of paraffinic, naphthanic and aromatic species in the feed.

The general crackability of FCC feedstock can be correlated against some simple parameters like feed stock hydrogen content or the UOP characterization factor K.

$$K = \frac{\sqrt[3]{T_B}}{S_g}$$

Where T_b = average boiling point of the feedstock

°R and S_g is its specific gravity.

A large amount of experimental data can be classified as shown below the catalyst.

2.2.2.1 FEEDSTOCK CRACKABILITY

Range of characteristics factor K	Relative crackability	Feedstock type
> 12.0	High	Paraffinic
11.5 – 11.6	Intermediate	Naphthanic
< 11.3	Refractory	Aromatic

Sulphur compounds do not seriously affect crackability. The cracked sulphur compounds are distributed into the liquid products, thus creating a need for product clean up before final use. In addition, sulphur also exists from the FCC unit in the form of H_2S and sulphur oxides, the later posing a potential air pollution problem.

The organometallic compounds are deposited on the circulating catalyst and after regeneration almost all the metals in the feedstock remain deposited on the catalyst. These deposited metals have two rather serious deleterious effects. They affect product distribution by causing more light gas formation, especially hydrogen. They also deactivate catalyst. To counteract these effects more fresh catalyst must be added to maintain its activity level.

The modern FCCU accepts a broad range of feedstock, a fact which contributes to catalytic cracking reputation as one of the most flexible refining process.

Examples of common feedstocks are:

- Atmospheric gas oil (AGO)

- Vacuum gas oil (VGO)

- Coker gas oil

- Thermal cracked gas oils

- Solvent – deasphalted oils

- Lube extracts

- Hydro cracker bottoms.

The feedstock considered in this case is vacuum gas oil (VGO). It is the product of vacuum distillation of the atmospheric residue from the initial distillation.

[Handbook of Petroleum Refining Processes, 2nd Edition]

2.2.2.2 Feedstock Quality

The quality of the feedstock is base on its compliance with environmental laws, improvement of yields, increasing conversion of crude and minimizing residue. Hydrotreatment is an effective way to improve all areas.

Feed properties

Type	Hydrotreated VGO	Unhydrotreated VGO
Sulphur Pct wt	0.17	3.02
Conradson carbon	0.17	0.81
Nickel, ppm	0.03	0.20
Vanadium, ppm	0.17	1.20
UOP K	11.95	11.60
$C_{Aromatic}$	12.20	18.80
$C_{parafinse}$	59.60	52.60
$C_{naphthenic}$	28.10	28.60

2.2.2.3 Yield change

Type	Hydrotreated VGO	Unhydrotreated VGO
Capacity	3400	3200
Gasoline	57.30	49.00
Coke	5.20	5.50
Conversion $445^{o}F$	78.7	74.4

2.2.3 Product properties

Type	Hydrotreated VGO	Unhydrotreated VGO
RON	90.90	91.60
MON	79.40	79.90
Paraffins	7.10	6.10
Olefins	27.70	25.00
Naphthanes	43.20	44.00
Aromatics	22.00	24.90

As expected RON and MON of hydrotreated feedstocks are reduced due to less aromatics and more olefins.

[Text – Katalystiks, Fluid Catalyst Cracking Symposium]

2.2.4 CATALYST

The second major feed to the reactor is the catalyst. It is made up of natural or synthetic clays, characterized by the presence of "active centers" where conversion reactions occur. The catalyst activity depends on its acidity. The principal catalyst base in made up of silica and alumina (Al_2O_3). It is known that silica and alumina show acidic characteristics only when they are joined together.

The first catalyst used in the FCC where granulated amorphous silica alumina. The synthetic and natural type suffered from low activity and poor selectivity compared to present day catalyst. They also had poor fluidization characteristics.

A spray-dried (microsperoidal) synthetic silica–alumina catalyst was introduced. It contained 10 to 13wt% more alumina and 25 wt% alumina was later achieved. The activity and stability of the catalyst was improved so also the fluidization characteristics were improved.

The most significant catalyst development occurred when molecular sieves were introduced into the catalyst. The resulting catalyst was more active, had greater stability and was more selective toward gasoline production.

A wide variety of catalyst can be used in an FCC unit ranging from low activity amorphous catalyst to high activity-Zeolite containing catalyst. The

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table below summarizes the pilot plant results from processing the same feedstock at identical condition over various catalyst.

Table 2.2.4   Effect of catalyst Activity

	Amorphous	Low Activity sieve	Moderate activity sieve	High Activity sieve
Conversion LV%	63.00	67.90	76.50	78.90
Gasoline, LV%	45.10	57.60	55.40	57.60
RON	93.30	92.60	92.30	92.30

Basis: Middle East sour gas oil, $23^{\circ}F$ API g ($S_g = 0.912$) 11.84 UOP K factor, 2.48%wt sulfur.

2.2.4.1 Amorphous and Zeolite catalyst

The initial cracking reactions are essentially the same for both amorphous and zeolite catalysts. There is a difference, however in the composition of the final products. The gasoline products of a zeolite catalyst are substantially higher in paraffin and aromatics. An amorphous catalyst produces a mixture, which has more naphthenas, and olefins than a zeolite catalyst would. This difference can be explained by a hydrogen transfer mechanism.
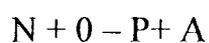
$$N + O - P + A$$

Where N, O, P, A are naphthanes, olefins, paraffin's and aromatics respectively. The transfer is one that uses the catalyst as a transfer medium. The stability of the aromatics and the branched paraffin would be one driving force

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for this type of reaction. Another would be the ease of formation of carbonium ions from olefins, especially the large olefins. With an amorphous catalyst, the hydrogen transfer reaction must compete with the large gas oil molecules for active sites. The zeolities provides a regular inner surface, which would be ideal for transfer reactions. An affinity for absorption by the sieves tends to favour hydrogen transfer over cracking because transfer is a binocular process. The stability of the species formed also inhibits further cracking.

Initial cracking produces cycle oil, gasoline and light gases. A high activity zeolite with short contact time inhibits the zeolite cracking time may also be beneficial from the standpoint of limiting hydrogen transfer from some of the lighter olefins.

2.2.4.2 Coke Formation

Coke is a mixture of carbon and hydrogen with traces amount of Sulphur, nitrogen and metals. It deactivates the catalyst by covering the active sites or by blocking the catalyst pores. Dehydrogenation (degradation reactions) of polynuclear aeronautics or olefins reaction is probably the major source of coke. Hydrogen transfer from an olefin to another molecule will raise its C/H ratio. The olefin may also undergo condensation reactions with aromatics or other olefins. These reactions will split off the light hydrocarbon with low C/H content, leaving the species on the active site even heavier. Eventually it

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becomes coke a non-volatile material, which blocks the acid site. If the condensation reaction leads to a bulky product, the pore itself is closed because the large molecules cannot diffuse out of the pore. Other reactive molecules are effectively kept out of the active area. Oxidation in the regenerator converts the coke to carbon dioxide, carbon monoxide and water vapour. These small gas molecules leave the pores easily and the catalyst is reactivated.

[Reaction Chemistry. Text: - FCC process technology UOP]

2.5.0 PRODUCT

The valuable products from the FCCU are:

- Fuel gas (i.e. ethane and lighter hydrocarbons)

- Liquefied petroleum gas (LPG. i.e. C_3 and C_4)

- Gasoline (i.e. $C_5 - C_6$)

- Light cycle oil (LCO)

- Slurry oil

Although gasoline is typically the desired product from FCCU in Nigeria, operating variables can be adjusted to maximize other products. The three principle modes of FCC operations are maximum gasoline production, maximum light cycle oil production and maximum LPG production.

2.3.1   Maximum Gasoline Production

The maximum gasoline mode is characterized by use of an intermediate cracking temperature, high catalytic activity and high catalyst to oil ratio. The recycle stream is not normally used since the conversion after a single pass through the riser is already high. Maximization of gasoline yield requires the use of an effective feed injection system, a short contact time vertical riser, and an efficient riser effluent separation to maximize the cracking selectivity to gasoline in the riser and to prevent secondary reaction from degrading the gasoline after its exits the riser.

2.3.2   Maximum middle distillation

The maximum middle distillate mode of operation is a low severity operation in which the first pass conversion is held to a low level to restrict recracking of LCO formed during initial cracking. Severity is lowered by reducing riser outlet temperature and catalyst to oil ratio. The lower catalyst to oil ratio is often achieved by the use of a fired feed heater, which significantly increases feed temperature. Additionally, reducing fresh catalyst make-up rate sometimes lowers catalyst activity. Since during lower severity operations a substantial portion of the feed remains unconverted in a single pass through the riser, recycle of heavy cycle oil to the riser is used to reduce the yield of lower value heavy streams such as slurry products.

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When maximizing middle distillate production crude distillation, units operated to minimize middle distillate component in the FCCU feed stock, since these components either degrade the quality or convert to gasoline and lighter products in the FCCU.

2.3.3 Maximum light olefin yield

The yields of propylene and butylenes may be increased above that of the maximum gasoline operation by increasing the riser temperature by increasing the riser temperature above $538^\circ c$ and by use of the catalyst ZSM- 5. At the same time, other operating variables may require adjustment to keep the regenerator temperature in an optimum range.

2.4.0 REACTION CHEMISTRY

Fluid catalytic cracking is fundamentally different from thermal cracking. The catalyst does not simply accelerate the same reactions it uses a different mechanism. Thermal cracking occurs through the formation of free radicals. The primary pathway of catalyst cracking is through the formation of carbonium ions. Both of these are unstable species, which ease the transformation of hydrocarbons (fluid catalytic cracking process technology, UOP).

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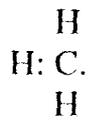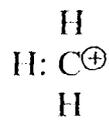
```
      H                              H
 H: C.                          H: C⊕
      H                              H

 Free Radical                   Carbonium ion
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Fig. 1

One theory proposes that the carbonium ion is formed from an olefin, which in turn could be formed by thermal effects upon initial catalyst oil contact or may be present in the feed. The carborium ion could be formed by the action of a Bronsted or Lewis acid site as state in (fluid catalytic process technology UOP). The exact mechanism is not well understood. Either of the above mechanisms for carbonium ion formation would be reversible

$$R_1 - CH = CH_2 - CH_3 + HB \longrightarrow R_1 - CH_2 - \overset{\oplus}{CH} - CH_2 - CH_3 + B^-$$
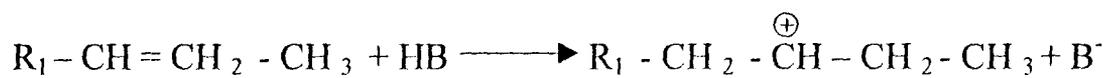
Fig 2

Where HB is a Bronsted acid site, a proton donor.

$$R - CH_2 - CH_2 - CH_3 + L \longrightarrow R - \overset{\oplus}{CH} - CH_2 - CH_3 + LH$$
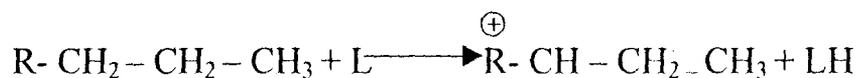
(Fig. 3)

Where L is a Lewis acid site, on electron pair acceptor.

Once the catalyst forms the carbonium ion it may do several things.

1. Crack to smaller molecules

2. React with other molecules

3. Isomerlse to a different form

4. React with the catalyst to stop the chain

The cracking reaction will normally follow the β rule. The C – C bond in the β position relative to the positively charged carbon tends to donate electrons to the charged atoms. This weakens the β bond so that it will split under the influence of high temperature (fig 4). Both of the two smaller molecules are reactive. The olefin may form a new carbonium ion with the catalyst; the R^+ ion is again a relatively unstable species.

Cracking According to β rule (β scission)

$$R_1 = CH_2 - \overset{\oplus}{CH} - CH_3 \longrightarrow R_1 + CH_2 = CH\text{-} CH_2 - CH_3$$

Fig4 β scission

Another reaction, which may occur, is the dealkylation of aromatics. The larger the side chain (alkyl group) the greater the driving force for cracking of the molecules.

Benzene   Carbonium ion
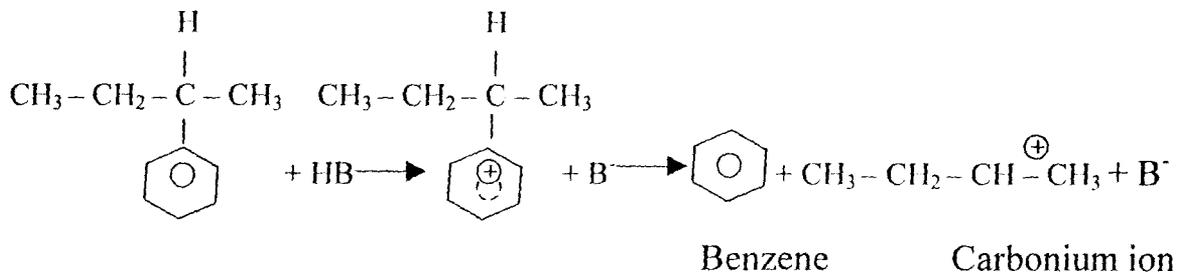
Fig 5. Dealkylation of an aromatic.

(Where HB is a Bronsted acid site, B⁻ is a "Reacted" Bronsted acid site)

25

A second group carborium ion reactions is exchanged with another species.

$$R_1 - CH_2 - \overset{\oplus}{CH} - CH_2 - CH_3 + R_2 - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3 \longrightarrow$$

$$R_1 - CH_2 - CH_2 - CH_2 - CH_3 + R_2 - CH_2 - \underset{\underset{CH_3}{|}}{\overset{\oplus}{C}} - CH_2 - CH_3$$

Fig 6. Carbonium ion exchange – paraffin.

$$R_1 - CH_2 - \overset{\oplus}{CH} - CH_2 - CH_3 + R_2 - CH = \underset{\underset{CH_3}{|}}{C} - CH_2 - CH_3 \longrightarrow$$

$$R_1 - CH = CH - CH_2 - CH_3 + R_2 - CH_2 - \underset{\underset{CH_3}{|}}{\overset{\oplus}{C}} - CH_2 - CH_3$$

Fig. 7. Cambium ion exchange – olefin

The driving force for many of these exchanges would be the stability of the final cambium ion. These ions may be classified in decreasing order of stability as benzyl and tertiary, secondary, primary and methyl.

$$\text{Methyl} \qquad H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \oplus$$

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Primary 1°

$$CH_3 - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{\oplus}$$

Secondary 2°

$$CH_3 - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\oplus}{C}} - CH_3$$

Tertiary 3°

$$CH_3 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\oplus}{C}} - CH_2 - CH_3$$

Benzyl

Benzyl, 3° > 2° > 1° > methyl

Fig. 8 Carbonium ion stability

The higher order ions are more stable because the adjacent carbon atoms can partially donate electrons to lessen the unstabilizing effect of the positive charge. This can be seen by comparison of two dealkylation reactions. Reaction one proceeds easily; cumene is not a common constituent of FCCU product. The cracking of toluene in reaction two will lead to the formation of a methyl carbonium ion. This species has a very high energy of formation; therefore the reaction is less likely to occur. Toluene is usually found in FCCU gasoline.

Cumene → Benzene + 2° ion s

$$CH_3 - \overset{\overset{H}{|}}{\underset{\underset{\bigcirc}{|}}{C}} - CH \xrightarrow{\text{Catalyst heat}} \bigcirc + CH_3 - \overset{\oplus}{C}H - CH_3$$
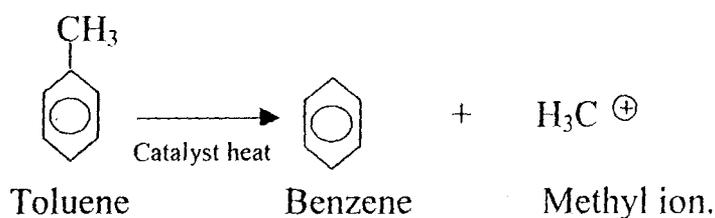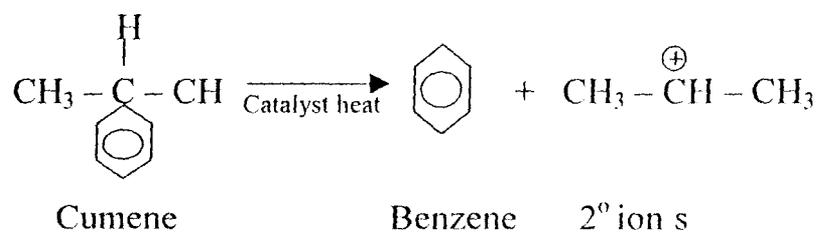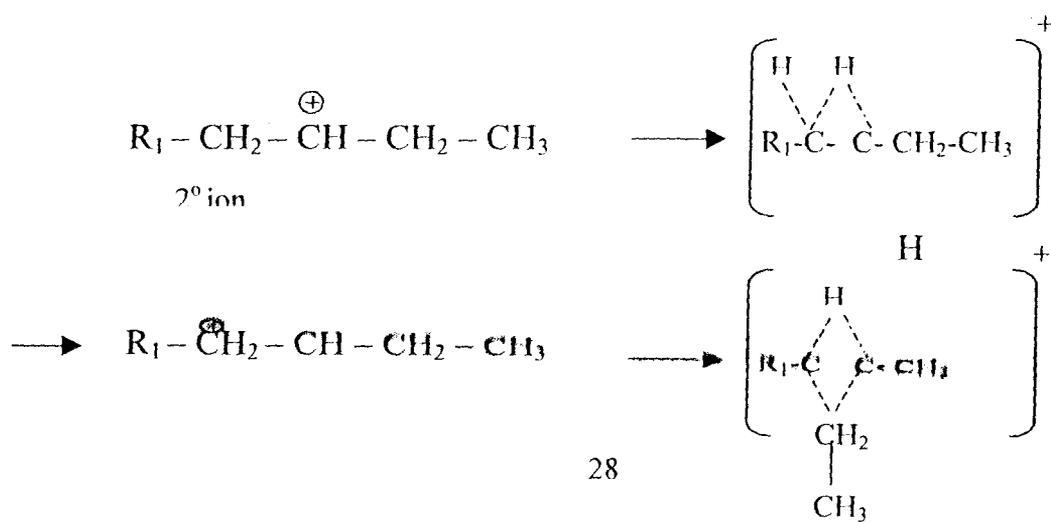

Toluene → Benzene + Methyl ion.

Fig 9 composition of dealkylation reactions

A re-arrangement can occur if it leads to a more stable carbonium ion. This isomerization is usually referred to a an alkyl or hydride shift. This rather complicated shifting is driven by the greater stability of the tertiary carbonium ion. The alkyl shift is probably responsible for much of the iso products found in FCC gasoline. These have high octane numbers and as such are valuable for improving the quality of the gasoline.

$$R_1 - CH_2 - \overset{\oplus}{C}H - CH_2 - CH_3 \longrightarrow \left[R_1 - \overset{\overset{H}{\diagdown}}{C} - \overset{\overset{H}{\diagup}}{C} - CH_2 - CH_3 \right]^{+}$$

2° ion

$$\longrightarrow R_1 - \overset{\oplus}{C}H_2 - CH - CH_2 - CH_3 \longrightarrow \left[R_1 - \overset{H}{C} \overset{\overset{H}{\diamond}}{} C - CH_3 \right]^{+}$$

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$$\longrightarrow \quad R_1 - \overset{\oplus}{\underset{\underset{\underset{CH_3}{|}}{\underset{CH_2}{|}}}{C}} - CH_3$$
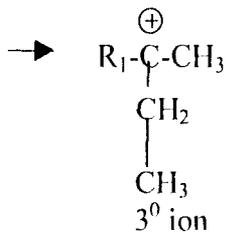
3⁰ ion

Fig 10 Carbonium ion rearrangement

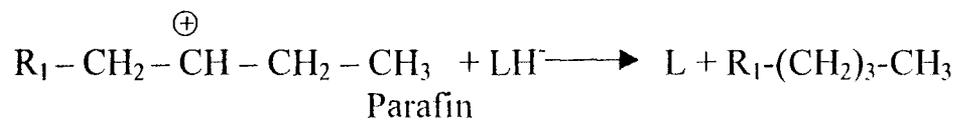The reactions that produce carboium ion are reversible. This fact is considered to be the cause of their destruction.

$$R_1 - CH_2 - \overset{\oplus}{CH} - CH_2 - CH_3 \text{-}\beta^- \longrightarrow HB + R_1\text{-}CH=CH\text{-}CH_2\text{-}CH_3$$
Olefin

$$R_1 - CH_2 - \overset{\oplus}{CH} - CH_2 - CH_3 + LH^- \longrightarrow L + R_1\text{-}(CH_2)_3\text{-}CH_3$$
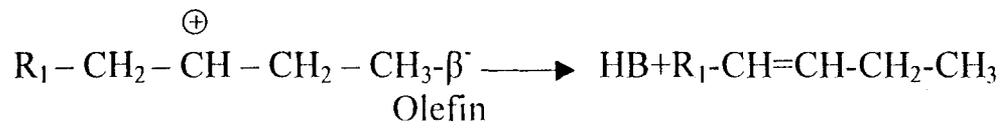Parafin

Fig 11. Destruction of carbonium ions.

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CHAPTER THREE

3.0 PROCESS CALCULATIONS

The FCC unit produces large volumes of high octane gasoline, olefinic LPG, fuel oil (LCO and MCB), fuel gas, steam and electricity (fluid catalytic cracking technology) the yield is mainly determined by process variables. Performance test are recommended periodically to provide accurate yield structures at particular sets of operating conditions and to provide base points for further testing.

The test normally includes heat and material balances. The refiner can use these test to assess the potential of the unit and determine possible bottlenecks. (Fluid catalytic cracking technology).

3.1.0 FCCU MATERIAL BALANCE

A material balance on an FCCU is done by drawing an envelope around the unit in a manner that flow rates are known for all streams. The balance gives the losses, extant of conversion and gasoline yield by accounting for material flow in and out of the unit.

Assumptions

1. Assume volume correction factor of gasoline 0.9784.

Constants (k) for liquids and Gases

1) Raw oil – 0.979

2) Light cycle oil (LCO)   0.9882

3) Main column bottom (MCB)-   1.0582

4) Gasoline   0.8817

5) Liquefied petroleum Gas (LPG) 0.7671

6) Fuel gas -   4.1092

7) Air   11.459

8) Mass flow (Q_w)   1.293

9) Volumetric flow coke (Q_v)   11.459

10) Q_w of coke   1.293

11) Q_w/ k, where k =28.4 for wet air

12) Q_w/k, where k =1.03 for dry air.

3.1.2 FOR LIQUID CALCULATION

$$Q_L = (Q_c) \times (K) \frac{(G_f) \frac{1}{2}}{S_g}$$

Where

Q_L – mass flow (corrected)

Qc - mass flow from computer (average)

K - constant for feed charge

G_f - flow grant

S_g - specific grant at $60^o / 60^oF$

3.3.2.1 Feed (Raw oil)

K = 0.979

Temp = 399.2^{o}F

S_g = 0.914

American Petroleum Institute (API) $= \left[\dfrac{141.5}{S_g}\right]$ - 131.5 = 23.31

Volume correction factor (VCF) = 0.9849

G_f = 0.914 x 0.9849 = 0.900

Q_c = 194,773 Kg / hr $\Rightarrow$ 429, 400 1b/hr

$Q_L = Q_c \times k \times \dfrac{(G_f)^{1/2}}{S_g}$

$= 429,400 \times 0.979 \times \dfrac{(0.9)\ \frac{1}{2}}{0.914}$

Q_L = 436,334 1b/hr

3.1.2.2 Light cycle oil (LCO)

K - 0.9882

Temperature – 88^{o}F

S_a – 0.9416

Flow rate – 38,481 kg/hr $\Rightarrow$ 84, 836 1b/hr

$$API = \left[\frac{(141.5)}{1.00514}\right] - 31.5$$

$$API = 14.046$$

Volume correction factor (VCF) = 0.9895

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

$$Q_L = Q_c \times K \times \frac{(G_f)^{1/2}}{S_g}$$

$$= 84,836 \times 0.9862 \times \frac{(0.9317)^{1/2}}{0.9416}$$

$$Q_L = 85,940 \ \text{lb/hr}$$

3.1.2.3 Main Column Bottom (MCB)

K – 1.0582

Temperature – 174°F

S_g – 1.0514

Flow rate – 16,774 kg/hr. $\Rightarrow$ 36,980 lb/hr

$$API = \left[\frac{141.5}{1.0514}\right] - 131.5$$

$$API = 3.082$$

Volume correction factor (VCF) = 0.9614

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

$$Q_L = Q_c \times K \times \frac{(G_f)^{1/2}}{S_g}$$

$$= 36,980 \times 1.0582 \times \frac{(1.0108)^{1/2}}{1.0514}$$

$Q_c = 37,419$ 1b/hr

3.1.2.4 Gasoline (Petrol)

K- 0.8817

Temperature – 89°F

S_g – 0.7581

Flow rate – 91,414 kg/hr $\Rightarrow$ 201, 533 1b/hr.

$$API = \left(\frac{(141.5)}{0.7581}\right) - 131.5$$

API = 55

VCF= 0.9784

G_f = 0.9784 x 0.7581

G_f = 0.7417

$$Q_L = Q_c \times k \times \frac{(G_f)^{1/2}}{S_g}$$

$$= 201, 533 \times 0.8817 \times \frac{(0.7417)^{1/2}}{0.7581}$$

$Q_L = 201,862$ lb/hr

3.1.2.5 Liquefied Petroleum Gas (LPG)

K = 0.7671

Temperature – 94°F

S_g – 0554

Flow rate – 23,600 kg / hr $\Rightarrow$ 52 029 1b / hr

VCF – 0.956

$G_f = 0.956 \times 0.554$

$\qquad = 0.529$

$Q_L = 52,\,029 \times 0.7671 \times \dfrac{(0.529)^{1/2}}{0.554}$

Qc = 52, 398 1b /hr

3.1.2.6 Fuel Gas

K- 4.1072

Temperature – 44.43 ^{0}c $\Rightarrow$ 317 43k, 111, 974°F

Pressure – 13 .603 kg /cm^2 $\Rightarrow$ 1 .603 + 1.023 = 14. 626 A

Flow rate – 9.0 KNM^3/hr

M_w = (mm x mol %)

= H_2 (2.02 x 0.1569) + N_2 (28 x .0.009) + CH_4 (16.032 x 0.427) + $C_2 H_6$ (30.48 x0 298) + C_3H_8 (44. 064 x 0 .004) + iso $C_5 H_{10}$ (58.08 x 0.0141) + n C_4H_{10} (58. 08 x 0.007)+ C_4H_8 (56.064 . 0.0003) + iso C_5H_{10} (72. 096 x 0.0005) + n (C_5H_{10}) (172 .096 x 0.0001) + $C_6 H_{14}$ (86. 122 x 0.0004)

= 0.3169 + 2 .772 + 6.845 + 8.9212 + 0.1762 + 0.8189 + 0.0406 + 0.0168 + 0.0360 + 0.00072 + 0.0344

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$M_w = 19.9787$

$S_g = M_w \text{ gas} / M_w \text{ air} = 19.9787/ 28.97$

$$= 0.6896$$

3.1.3 For Vapour

$Q_g = Q_c \times K \times (P_f / T \times S_g)^{1/2}$

$Q_{fg} = 9.0 \ 4.1092 \left[\dfrac{(14626)}{317.43 \times 0.6896)} \right]^{1/2}$

$Q_{fg} = 9.5596 \ KNM^3 \ /hr$

Inert Equation

$= (\% N_2) (Q_c) (M_w N_2) (10^3/22.4) (1/0.4536)$

$= (0.099) (9.0) (2.8)(10^3/22.4) (1/0.4536$

$= 2.455. 39 \ 1b / hr$

Mass Flow of Vapour

$Q_w = Q_g \times K \times S_g \times 103$

$= 9.5596 \times 1.293 \times 0.6896 \times 1000 \times (1/0.4536)$

$Q_w = 18789. 99 \ 1b \ /hr.$

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Corrected mass flow = Q_w – Inert

Q_{wc} = 18789.99 1b / hr

Q_{wc} = 18.789.99 – 2, 455. 39 = 16, 334. 60 1b / hr

3.1.4 COKE

Flow rate of regeneration air.

$$Q_v = Q_c \times K \times \left[\frac{(P_f)^{1/2}}{T_r \times S_g} \right]$$

$$= 134 \times 11.459 \times \left[\frac{(3.62)^{1/2}}{449 \times 1} \right] = 137.87 \ KNM^3/hr$$

$$Q_w = (Q_v)(K)(S_g)(10^3)(1/0.4536)$$

$$= 137.87 \times 1.293 \times 1.0 \times 1000 \times (1/0.4536)$$

$$= 393, 020. 67 \ 1b/ hr$$

Mols/ hr (wet air)

$$\frac{Q_w}{K} = \frac{393\ 020.\ 67}{28.4} = 13, 838 \ lbmol \ wet \ air \ / \ hr$$

Dry Air;

$$\frac{Q_w}{1.03} = \frac{393.\ 020.67}{1.03} = 381873.\ 46 \ 1b \ dry \ air \ / \ hr$$

$$\frac{Qdry}{29} = \frac{381573.46}{29} = 13, 15\ 7.70 \ 1b \ males \ dry \ air \ /hr$$

Assuming humidity of 3%

$H_2O = 13,838 - 13,157 = 680.29$ lbmol /hr

Flue gas composition;

$CO_2 - 1380\%$ mol $N_2 = 100 (13.82 \times 3.2) = 83.0\%$ mal.

$O_2 - 3.20\%$ mol

By nitrogen balance;

Nitrogen is inert therefore:

N_2 in air inert = (N_2 fraction in flue gas) (moles of flue gas)

Moles flue gas = $\dfrac{(N_2 \text{ fraction in air}) (\text{mol dry air})}{(N2 \text{ fraction in flue gas})}$

$= \dfrac{0.79 \times 13,157}{0.83}$

$= 12522.92$ lbmol / hr flue gas

Coke production;

$C + O_2 \longrightarrow CO_2$
1   1   1

∴ Moles of CO_2 in flue gas = mole fraction CO_2 x moles flue gas

38

$$= (0.138 \times 12,522.92)$$

$$= 1728.16 \text{ mol of } CO_2$$

From eqn above.

Moles of carbon that reacted = 1728. 16 moles

By O_2 Balance;

O_2 in inlet air $= O_2$ (excess) in flue gas $+ O_2$ reacted to CO_2 reacted to H_2O.

O_2 in inlet air = (air flow rate) (CO_2 fraction)

$$= (13,157)(0.21)$$

$$= 2762.97 \text{ moles}$$

O_2 excess in flue gas = (0. 032) (12, 522. 92) = 400. 73

O_2 in air $\longrightarrow$ | O_2 reacted to CO_2
O_2 reacted to H_2O | $\longrightarrow O_2$ (excess)
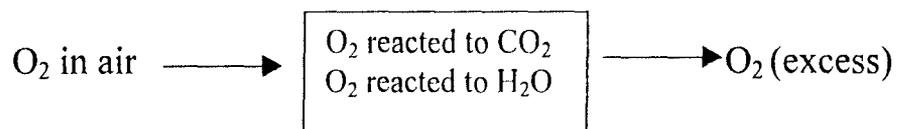
O_2 reacted to CO_2 = (0.138) (12, 522. 92) = 1, 728.16

O_2 reacted to $H_2O = O_2$ in air $- (O_2\text{-} CO_2 + O_2 \text{ excess})$

$$= 2762. 97\text{-} (1, 728. 16 + 400. 73)$$

39

= 634. 07 moles.

$$2H_2 \quad + \quad O_2 \longrightarrow 2H_2O$$

2   1   2
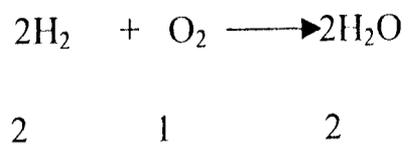
If 1mol of O_2 reacts with 2 moles of H_2

634. 07 of O_2 reacts with x moles H_2

x = 2 x 634. 07 = 1268. 15 1b moles H_2

From carbon 1, 728 x 12. 01= 20753. 28 1b/ hr

From Hydrogen 1,268 x 202 = 2561. 36 1b / hr.

Total = 23. 314. 36 1b /hr

Mass Balance

IN	1b /hr	% Wt	ft^3/ hr	Vol %
Feed	436, 334	100	476.34	100
Out	1b/hr	%wt	ft^3 / hr	Vol %
MCB	37, 419	8.90	35.58	6.95
LCO	85, 940	20.59	91.27	17.83
Gasoline	201, 862	47.27	266. 27	52.06
LPG	52, 398	13. 75	94. 58	18.49
FG	16, 334	3.91	23.68	-
Coke	23,314	5.58	-	-
Total	417,267	100.00	511.38	95.33

Conversion = feed rate – (LCO +MCB) x 100
$$\qquad\qquad\qquad \text{Feed rate}$$
$$= \frac{476. 34 - (91.27 + 35.58)}{476.34} \times 100$$

= 73.36%

Gasoline yield = 52.06 vol %

3.2.0 HEAT BALANCE

Burning of coke in the regenerator provides the heat necessary for the operation of the unit. Yet roughly 40% of heat generated is lost as flue gas. The remainder is absorbed by the regenerated catalyst, which takes the heat to reactor.

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The amount of heat energy associated with the units operation is determined from catalyst section heat balance. The most important value that can be calculated from the energy balance is the catalyst/oil weight ratio, this ratio is important because it is a major factor in hydrocarbon conversion and coke lay down.

The flue gas analysis is obtained by chromatography in the laboratory. The air rate referred to here is the total air sent to the first and second stages of the regenerator.

The balance for a stable operation may be unbitten as: -

Energy in + Energy produced = Energy out + Energy consumed where

Energy in = Energy (air + raw oil + stripping steam)

Energy produced = combustion heat of coke

Energy out = Energy (flue gas + reactor Vapour + radiation losses)

Energy consumed = Heat of reaction

So therefore: -

Energy (air + raw oil + stripping steam) + H coke = energy (flue gas + reactor Vapours + radiation) + H reaction.

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Heat balance calculations

Combined feed	401 °F
Reactor	988 °F
Regenerator	1,261 °F
Dense	1,315 °F
Flue gas	1,304 °F
Air bowler discharge	348 °F
Stripping steam	350 °F

Flow rates:	lb/hr
Raw oil	430,138
Stream stripping	6.023
Regeneration air	380, 264

1. Flue gas composition (mol %)

(By Gas chromatograph method)

CO	0.0
CO_2	13.80
$O_2 + Ar$	3.20
N_2	83.00

2. Preliminary calculations

a) Flue gas composition adjustment

The oxygen content of flue gas not contains argon. Argon is 1.2% of N_2

Therefore

0.012 x 83.0 = 1 mol%

Corrected flue gas composition

CO	0.00
CO_2	13.80
O_2.	2.20
$N_2 + Ar$	84.00

b) Combustion air conversion to dry basis.

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Using a spectrometric chart use to obtain moisture content of regeneration air at atmospheric condition of 101% and relative humidity of 60%. The moisture content is.

Moisture content =

$\dfrac{0.0289 \text{ kg } H_2 0}{\text{kg dry air}}$	2.2046 kg	$\dfrac{1b}{2.20462kg}$

$$= \frac{0.0289 \text{ 1b } H_2 O}{\text{1b dry air}}$$

$$\frac{380,5831b \text{ dry air}}{hr} \quad x \quad \frac{1b \text{ dry air}}{1+0.0289 \text{ 1b H20}} \quad = \frac{369,583 \text{ 1b dry air}}{hr}$$

$$\frac{369,5831bdry \text{ air}}{hr} \quad x \quad \frac{1b \text{ mol}}{29.016} \quad = \frac{12,744 \text{ 1b mol dry air}}{hr}$$

$$\frac{369,5831b \text{ dry air}}{hr} \times \frac{0.0288 \text{ 1b } H_2O}{\text{1b dry air}} \times \frac{\text{1b mol}}{181b} = \frac{593 \text{ 1b mol water Vapours}}{hr}$$

c) Calculate the catalyst coke burn

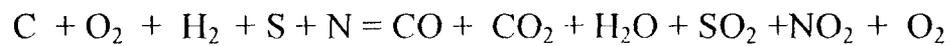$$\frac{Mol (N_2 + Ar) \text{ in regeneration air}}{hr} = \frac{mol (N_2 + Ar) \text{ in flue gas}}{hr}$$

$$\frac{12,744 \text{ 1b mol dry air}}{hr} \times \frac{79 \text{ mol } N_2}{100 \text{ mol air}} = \frac{\text{1b mol flue gas}}{hr} \times \frac{84 \text{ mol (Mol } (N_2 \times Ar)}{100 \text{ mol flue gas}}$$

$$10,067 = \frac{\text{1b mol flue gas}}{hr} \times \frac{84}{100}$$

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$$\underline{11, 985 \text{ 1b mol}} = \text{flue rate.}$$
$$\text{hr}$$

$$\text{Flue gas rate} = \underline{11, 985 \text{ 1b mol}}$$
$$\text{hr}$$

D) Carbon content of coke is calculated from flue gas composition

$$C + O_2 + H_2 + S + N = CO + CO_2 + H_2O + SO_2 + NO_2 + O_2$$

From the chemical equation I male of carbon burned for each male of CO or CO$_2$ produced

$$\underline{11, 985 \text{ 1b mol flue gas}} \quad x \quad \underline{0 \text{ mol CO} + 13. 8 \text{ mol CO}_2} \quad x \quad \underline{1 \text{ mol C}}$$
$$\text{hr} \qquad\qquad 100 \text{ mol flue gas} \qquad \text{mol CO or CO}_2$$

$$= \underline{1, 653 \text{ 1b mol carbon}}$$
$$\text{hr}$$

E) The hydrogen content of coke is calculated from a O$_2$ balance.

O$_2$ in regeneration air = excess O$_2$ in flue gas

+ O$_2$ reacted to CO (0.5 mol O$_2$/ 1 mol CO)

+ O$_2$ reacted to CO$_2$ (1 mol O$_2$/ mol CO$_2$)

+ O$_2$ reacted + H$_2$ (0.5 mol O$_2$ /mol H$_2$O)

+ O$_2$ reacted to SO$_2$ (1 mol O$_2$/ mol SO$_2$)

+ O$_2$ reacted to NO$_2$ (1 mol O$_2$ / mol NO$_2$)

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Where

O_2 in regenerator air = $\dfrac{12,744 \text{ lb mol dry air}}{\text{hr}} \times \dfrac{21 \text{ mol } O_2}{\text{hr}} = \dfrac{2676 \text{ lb mol } O_2}{\text{hr}}$

excess O_2 in FG = $\dfrac{11,985 \text{ lb mol FG}}{\text{hr}} \times \dfrac{2.20 \text{ mol } O_2}{100 \text{ mol FG}} = \dfrac{263 \text{ lb mol } O_2}{\text{hr}}$

O_2 reacted to CO = $\dfrac{11,985 \text{ lb mol FG}}{\text{hr}} \times \dfrac{0 \text{ mol CO}}{100 \text{ mol FG}} \times \dfrac{0.5 \text{ mol } O_2}{\text{mol CO}} = 0$

O_2 reacted to CO_2 = $11.985 \dfrac{\text{lb mol FG}}{\text{hr}} \times \dfrac{13.8 \text{ mol CO2}}{100 \text{ mol FG}} \times \dfrac{1 \text{ mol } O_2}{\text{mol } CO_2}$

= $\dfrac{1,653 \text{ lb mol } O2}{\text{hr}}$

O_2 reacted to SO_2 = $\dfrac{11\,985 \text{ lb mol FG}}{\text{hr}} \times \dfrac{0 \text{ mol } SO_2}{100 \text{ mol FG}} \times \dfrac{1 \text{ mole } O_2}{\text{mol } SO_2}$

O_2 reacted to NO_2 = $\dfrac{11,985 \text{ lb mol FG}}{\text{hr}} \times \dfrac{0 \text{ mol } NO_2}{100 \text{ mol FG}} \times \dfrac{1 \text{mol } O_2}{\text{mol } NO_2}$

O_2 reacted to H_2O By difference is

= 2, 676- (263+ 0+1, 653 + 0 +0)

= $\dfrac{760 \text{ lb mol } O_2}{\text{hr}}$

Hydrogen burned by oxygen in regeneration is

H_2 burned by O_2 = $\dfrac{760 \text{ lb mol } O_2}{\text{hr}} \times \dfrac{2 \text{ mol } H_2}{\text{mol } O_2} = \dfrac{1,520 \text{ lb mol } H_2}{\text{hr}}$

F) Coke from carbon and hydrogen.

The mass of coke combusted to CO+ CO_2 + H_2O is

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from carbon = $\dfrac{1,653 \text{ lb mol C}}{\text{hr}} \times \dfrac{12.01 \text{ lb C}}{\text{lb mol}} = \dfrac{19,886 \text{ lb carbon}}{\text{hr}}$

From hydrogen = $\dfrac{1,520 \text{ lb mol } H_2}{\text{hr}} \times \dfrac{2.01 \text{ lb } H_2}{\text{lb mol}} = \dfrac{3,040 \text{ lb } H_2}{\text{hr}}$

Total = $19,836 \times 3,040 = \dfrac{23,876 \text{ lb coke}}{\text{hr}}$

G) The coke yield from raw oil feed is

Coke yield = $\dfrac{(\text{coke lb/ hr}) (100)}{\text{fresh feed lb /hr}}$

= $\dfrac{22,876 \text{ lb /hr}}{430,138 \text{ lb/hr}} \times 100 = 5.3 \text{ wt \% coke}$

H) Hydrogen content of coke is

H_2 in coke = $\dfrac{H_2 (\text{lb / hr})}{\text{Coke lb/hr}} \times 100$

H_2 in coke = $\dfrac{3,040 \text{ lb/hr } H_2}{22,876 \text{ lb /hr coke}} \times 100$

= $13.2 \text{ wt \% hydrogen}$

Air / coke radio

Air to coke = $\dfrac{(\text{Air lb/ hr}) (100)}{\text{coke lb/hr}}$

Air to coke = $\dfrac{369,583 \text{ lb/hr}}{22,876 \text{ lb /hr}} \times 100 = \dfrac{16.15 \text{ lb of dry air}}{\text{lb at coke}}$

    i)   Heat of combustion of coke

.

At the 1,304 of flue gas temperature

$H_c (CO_2) = \dfrac{1,653 \text{ lb mol}}{\text{Hr}} \times (169,784 + \dfrac{1304-1300}{1350-1300} (169,808 - 169\,789$

$$= 169, 784 \; \underline{x4} \; (24)$$
$$50$$

$$= 169, 885 \times 1653 = 280, 656125 \; \text{BTU/ hr}$$

$$= 280 \times 10^6 \; \text{BTU/ hr}$$

$$H_c \; (H_2O) = \underline{1520 \; lb \, mol} \times [106, 610 + \underline{1304 - 1300} \; (106, 687 - 106,610)]$$
$$hr \qquad\qquad\qquad 1350 - 1300$$

$$= 162, 056, 563 \; \text{BTU /hr}$$

$$280, 656, 125 + 162, 056, 563 = \underline{442, 712, 688 \; \text{BTU}}$$
$$hr$$

Uncorrected heat of combustion

$$\underline{442, 712, \; 688 \; \text{BTU / hr coke}} = \underline{19 \; 352 \; \text{BTU coke}}$$
$$22, 876 \; \text{lb/hr} \qquad\qquad hr$$

The heat of combustion is corrected by the equation

$$\text{correction} = 1, 133 - 134. \, 6 \; (\text{wt} \% \; H_2)$$

$$= 1, 133 - 134. \, 6 \; (13.2)$$

$$= 1, 133 - 1, 776$$

$$= 643 \; \text{BTU /lb coke}$$

Heat of combustion 13

$$19, 352 - 642 = \underline{18, 708 \; \text{BTU coke}}$$
$$lb$$

J) Heat consumed to heat up regenerated air.

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Air is heated from a discharge temperature of 348°F to flue gas temperature of 1,304°F at an average specific heat of 0.26 BTU / lb %

$$\frac{369,583 \text{ lb /hr dry air}}{22,876 \text{ lb / hr coke}} (1,304 - 348\%) \frac{0.26 \text{ BTU}}{\text{lb}°\text{F}}$$

$$= \frac{4,015 \text{ BTU}}{\text{lb coke}}$$

K) Heat consumed to heat up the regenerated air water Vapour. Water Vapour is heated from 348° F to 1,304° F at on average specific heat of 0.485 BTU /lb ° F

$$\frac{593 \text{ lbmol/hr water Vapour}}{22,876 \text{lb /hr coke}} (1,304 - 348) \times 0.485 \frac{\text{BTU}}{\text{lb}°\text{F}} \times \frac{18 \text{lb}}{\text{lbmol}}$$

$$= \frac{216 \text{ BTU}}{\text{lb coke.}}$$

L) Heat consumed to heat up coke.

Coke is heated from reactor temperature of 989° F to flue gas temperature of 1,304°F at specific heat of 0.4 $\frac{\text{BTU}}{°\text{F}}$

$$\frac{0.4 \text{ BTU}}{\text{lb}°\text{F}} (1,304 - 989 \text{ of}) = 126 \frac{\text{BTU}}{\text{lb}} \text{ coke}$$

M) Regeneration heat balance

With regenerator heat lass rate at 250 BTU / lb coke heat consumed to heat up catalyst is:

$$18,108 - (4,015 + 216 + 126 + 250) = \frac{14,101 \text{ BTU}}{\text{lb coke}}$$

N) Catalyst circulation rate.

Catalyst is heated up from a reactor temperature of 989° F to a flue gas temperature of 1,304° F at an average specific heat of 0.275 $\frac{BTU}{lb°F}$

$$\frac{22,876\,lb\,coke}{hr} \times \frac{14,101\,BTU}{lb\,coke} \times \frac{lb°F}{0.275\,BTU} \times \frac{1}{1304-989°F}$$

$$= 3.72 \times 10\,6\,\frac{lb}{hr}$$

$$= \frac{3.72 \times 10\,6\,lb}{hr} \left| \frac{ton\,1}{2204\,lb} \right| \frac{hr}{60mm}$$

$$= 28.1\,ton/min$$

O) Catalyst / oil ratio

$$\frac{3.72 \times 10^6\,lb/hr\,catalyst}{430,138\,lb/hr\ raw\,oil} = 8.6$$

P) Air / coke radio

$$\frac{369,583\,lb/\,hr\,dry\,air}{22,876\,lb/\,hr\,coke} = 16$$

Delta coke wt%

$$\frac{22,876\,lb/hr\,coke}{3.72 \times 10\,6\,lb/\,hr\,catalyst} \times 100 = 0.61\,wt\,\%$$

Regenerator Efficiency

$$Rg\,Eff = \frac{Rg\,Heat \times 100}{\Delta h\,combustion\,of\,coke}$$

$$= \frac{14,101 \times 100}{18,708}$$

$$= 75\%$$

CHAPTER FOUR

4.0   DISCUSSION OF RESULT

In the evaluation of a fluid catalytic cracking unit the most important variables that need to be considered are the conversion, gasoline yield, material loss and catalyst circulation rate, catalyst/oil ratio and coke laydown. The operating values are obtained from material and energy balances performed on the unit with data obtained over a period of 24 hours.

These values are compared with the design values to ascertain the unit performance level.

Performance Variables in the Fluid catalytic cracking unit		
Variables (units)	Operating values	Design values
Conversion (Vol%)	73.36	74.00
Gasoline yield (Vol %)	52.06	56.80
Material loss (%)	3.52	0.00
Catalyst circulation rate (ton/min)	28.10	26.70

Catalyst/oil ratio	8.60	6.50
Coke lay down (wt%)	0.61	0.77
Regenerator Efficiency (%)	75.00	62.00
catalyst cracking Efficiency (%)	70.30	76.75

Conversion is defined as the volume percent of the feed that is converted to gasoline and lighter products. The design value for conversion is 74% while the operating value was 73.36%. The deviation of the operating value from design value is due to the mode of addition of fresh catalyst to the reactor. Due to faulty reactor catalyst control valve (i.e. automatic control valve) the fresh catalyst is added manually by the operators on an 8-hour interval. The manual addition of catalyst results into an excess quantity of catalyst in the system and consequently instability in the cracking operation. The instability reduces the conversion of the system. This problem can be averted by the use of the appropriate automated control valve. An increased conversion can also be obtained by hydrotreatment of the feed. The FCCU feed is not presently hydrotreated before use. Results obtained from a test company hydrotreated and unhydrotreated vacuum gas oil (VGO) shows that the conversion and gasoline yield is higher for hydrotreated feed than that of

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the unhydrotreated feed. The hydrotreated feed had a conversion value of 78.7 while the unhydrotreated had 74.4 vol %.

Gasoline yield is the volume percent of gasoline obtained from the feed. The design value for gasoline yield is 56.8 vol % while the operating value was 52.06 vol %. The variation between the design and operating values is due to the incorrect mode of addition or loading of catalyst to the reactor. Due to the faulty automatic control valve, when fresh catalyst is lined up manually for a period of time an excess amount of fresh catalyst is present in the system, which results in a high cracking temperature of 1000.4°F and an excessively high catalyst to oil ratio. This results in the cracking of the feed to a higher percentage of propylene and butylenes. Then after several runs of the catalyst through the regenerator it losses some of its activity. Consequently the systems operation is at a low severity thereby producing larger percentages of light cycle oil and heavy cycle oil. This problem can be solved by use of appropriate control valve for the catalyst addition to the reacting mixture.

Material loss is the percentage of raw material and product loss in the course of the process. The design value is a zero percent loss while operating value was 3.52% loss. This loss is in form of catalyst and

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products. The losses occur due to the use of faulty cyclones. These cyclones do not properly separate the spent catalyst from the vapour oil, which causes loss of valuable hydrocarbon. The cyclones in the regenerator do not separate the regenerated catalyst from the flue gass properly resulting in loss of catalyst. These problems can be solved by regular screening and required repair work on the cyclones can solve these problems. A regular turn around maintenance is recommended every two years on the entire plant for optimum operation.

Catalyst circulation rate is the rate of circulation of catalyst between the reactor and the regenerator in ton/min. Its design value is 26.70 ton/min while the operating value is 28.10 ton/min. the slight variation between the design value and operating value for catalyst circulation rate is due to an excess amount of catalyst in the system. The excess catalyst in the process was due to the inaccurate manual mode of catalyst addition to the reactor. The solution to this problem is the use of an automatic control valve.

Catalyst to oil ratio is the ratio of the rate of catalyst circulation to rate of raw oil charged into the system. It is the most important determinant for conversion and coke lay down. A high catalyst to oil

ratio favours an increase in conversion, increased fuel gas yield, increase in liquefied petroleum gas (LPG) yield and coke yield. An excessively high catalyst to oil ratio indicates an excess amount of catalyst in the process. This results in a higher conversion but larger percentage of fuel gas (methane, ethane), and liquefied petroleum gas (propane, butane) is produced rather than the desired gasoline (pentane – hexane). The design value for the catalyst to oil ratio is 6.50 while the operating value is 8.60. This is due to the excess amount of catalyst in the system. The consequences of an excessively high catalyst to oil ratio are seen above. This problem should be tackled by proper control of the rate of addition of fresh catalyst to the process.

Coke lay down represents the amount of coke produced during the cracking reaction. Coke is a mixture of carbon, hydrogen with trace amounts of Sulphur, nitrogen and metals which are deposited on the active sites of catalysts. Burning of the coke in the regenerator provides heat required to run the unit. 40% of heat generated in the regenerator is lost as flue gas while the remaining 60% is absorbed by catalyst. Therefore large amounts of coke is required to produce the heat that will compensate the 40% heat loss. Presently the design value for coke lay down is 0.77 wt% while the operating value is 0.61 wt%. The variation

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improper addition of fresh catalyst to the process. Consequently, lower amount of gasoline is realized from the feed. The catalyst cracking efficiency is therefore caused, as it is directly proportional to the gasoline yield and inversely proportional to the conversion.

In conclusion the unit is performing below standard as evident from the results discussed above. Regular and proper maintenance work is recommended for the unit and the entire plant.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMEDATION

From the results of the evaluation it was clearly evident that the fluid catalytic cracking unit of the Port Harcourt refinery was performing below standard at the period of this investigation.

The unsatisfactory performance of the unit was caused by faulty automatic control valve for fresh catalyst and cyclone in both the reactor and regenerator. A material loss of 3.52% was obtained for the operation as against 0.00% loss for the design. This loss was caused by continued use of faulty regenerator and reactor cyclones. The operating value for gasoline yield was 52.06 (vol%) while the design value is 56.80 (vol%) the operating value for catalyst cracking efficiency was 70.30% while the design value is 76.75%. The variation in the above mentioned parameter was due to the mode of addition of fresh catalyst to the reactor which resulted in unstable cracking of the hydrocarbon feed consequently the operating conversion was 73.36 (vol%) while the design value for conversion is 74.00 (vol%).

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In conclusion the performance of the unit can be improved by proper and regular turn around maintenance on the FCCU and the plant as a whole.

5.1 RECOMMEDATION

The Port Harcourt Refining Company is the largest and most important refinery in Nigeria today. It produces the largest amount of gasoline, which is the most desired product of the petroleum refining process in Nigeria. Presently the official selling price of gasoline is N36.00 per litre. Increased production of gasoline would be a welcomed idea.

1. The increment in gasoline yield, conversion capacity, and a reduction of coke formation is achievable by hydrotreatment of the vacuum gas oil feed stock. The crackability of the feed is also increased by hydrotreatment.

Hydrotreatment is therefore recommended as a means of increasing the gasoline yield of the feed.

2. The feed injection in the reactor should be made in such a way that it is sprayed into the reactor to allow for more contact area with the hot catalyst.

These optimizing steps will greatly increase the conversion and gasoline yield if taken.

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APPENDIX I

NOMENCLATURE

K	-	Constant
LCO	-	Light Cycle Oil
MCB	-	Main Column Bottom
LPG	-	Liquefied Petroleum Gas
Q_W	-	Mass flow
Q_V	-	Volumetric flow
Q_L	-	Mass flow (corrected)
G_P	-	Flow Gravity
S_g	-	Specific Gravity at $60^O/60^Of$
API	-	American Petroleum Institute
M_W	-	Molecular weight
VCF	-	Volume Correction factor
P_f	-	Flow pressure
T_k	-	Temperature in kelvin
FG	-	Fuel Gas
lb	-	Pound
lbmol	-	Pound Mal
Kg	-	Kilogram
^Of	-	Degree Fahrenheit
hr	-	Hour
R_g	-	Regenerator
BTU	-	British thermal unit
wt%	-	weight percent

APPENDIX II

Combustion Heat of Coke

(BTU/lb)

TEMPERATURE, °F	77	1,100	1,200	1,300	1,350	1,400
$x = CO$		47,565	47,847	47,980	48,123	48,199	48,274
$y = CO_2$		169,332	169,677	169,735	169,760	169,808	169,835
$z = H_2O$		104,129	106,279	106,448	106,529	106,610	106,744

THE COMBUSTION HEAT IS INTERPOLATED FROM THIS TABLE
USING THE FLUE GAS TEMPERATURE, AND IS CACULATED AS

Laboratory Result Sheet For FCCU product

Sample name	FCC Fuel Gas	FCC C_3	FCC Flue gas	FCC C_4
Unit	17AP003	14AP005	16AP002	14AP009
Hydrogen Mol%	15.69			
Nitrogen Mol%	9.90			
Oxygen Mol%			3.20	
Carbon Dioxide Mol%			13.80	
Methane Mol%	42.70			
Ethane Mol%	29.69			
Propane Mol%	0.40	24.37		0.04

Propylene Mol%		75.24	
Iso Butane Mol%	1.41	0.36	
N-Butane Mol%	0.07		9.52
Butene Trans Mol%	0.03		9.74
Butene Cis Mol%			7.71
Iso Pentane Mol%	0.05		
N-Pentane Mol%	0.01		
C_5 Olefin Mol%			0.12
C_6 + Mol%		0.04	

OPTIMUM TEMPERATURES

Feed temperatures	450^oF
Reactor Temperature	975^oF
Regenerator temperature	1370^oF