Fluid catalytic cracking

by

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A REPORT

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Abstract

Catalytic cracking is a process in which hot, powdered catalyst is intimately mixed with a hot petroleum-derived feedstock, then transported through a turbulent reaction zone with a reactant residence time of 1-5 seconds. It has enabled refineries to produce a tremendous amount of high-octane number gasoline from high-boiling stocks using catalysts. It progresses through a carbocation to produce active species on acidic catalytic sites.

This process involves acidic catalysts like zeolite in the breaking up of long carbon chains of n-alkanes into shorter chains alkanes like iso-alkanes, cycloalkanes, and aromatics. Other products like Liquefied Petroleum Gas (LNG), cycle oils, and olefin-rich light hydrocarbons (C3, C4) are also produced. The olefin-rich light hydrocarbons are used as petrochemical feedstock, and as reactants in alkylation and polymerization reactions.

Refining shale crude oil presents a very difficult challenge because of its very low hydrogen to carbon ratios. The production of good quality gasoline, kerosene, and diesel are very poor due to high levels of heavier components such as asphaltene and Sulphur-containing species. Many petroleum refineries combine two methods in order to convert and refine this heavy crude oil: conventional fluidized catalytic cracking followed by residue fluidized catalytic cracking, allowing heavy oils with high viscosity to be processed and refined.

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Chapter 1 - Introduction

1.1 Qualitative Overview.

Fluid catalytic cracking (FCC) is a conversion process in petroleum refining which involves the breakdown of heavy gas oil fractions of crude oil into gasoline, olefins and by products by bringing this heated gas oil into contact with powdered catalyst [5]. It is one of a host of processes carried out in a refinery which include distillation, catalytic reforming, hydrocracking, coking, and alkylation. FCC is ubiquitous in most refineries around the world due to the high octane rating in the gasoline it produces, with studies showing that nearly half of the world's refineries have FCC units incorporated in them, producing 44 million barrels per day as of 2014 [19]. As a result, the process has been and still continues to be the subject of research and development by industrialists and academics alike. In this report, a background of the FCC process is discussed, and we show by highlighting recent research activity that the field is still one that leaves room for improvement.

As long as there has been crude oil, there has been a process of refining it into more useful products. The exact origin of crude oil is yet unknown – first thought to have been discovered and used by the Chinese in I Ching writings 2000 years ago [1] – however, the first oil fields were exploited for their "hundreds of shiploads" in the late 9th century as described by Marco Polo four centuries later [2]. The process of refining usually involves heating up the crude oil to separate the mixture into components phase separable at distinct temperatures (volatilities). In modern times, James Young is lauded for his work separating crude into light thin oil, machine oil and paraffin wax which eventually led to his patent in October 1850, [3]. A detailed account on the history of petroleum refining can be seen in [4].

In a nutshell, the refining process involves several processes which depend on the composition of the crude oil fraction. Raw crude is initially distilled in the distillation unit which separates the mixture into fractions with components having similar boiling points. The components are: residue oil, gas oil, diesel oil, kerosene/jet fuel, heavy naphtha, light naphtha, and sour gas. Light and heavy naphtha produce gasoline after hydrotreatment; isomerization is used for the former and catalytic reforming for the later. Diesel oil produces diesel after hydrotreatment, the middle distillates undergo mercaptan oxidation treatment to produce jet fuel or kerosene, residue oil undergoes vacuum distillation to produce light and heavy vacuum oil which together with gas oil make up the feed to the FCC unit. Finally, sour gas is sweetened by amine treatment and then passed to the mercaptan oxidation treater to produce liquefied petroleum gas (LPG) and butanes [5]. Figure 1.1 shows a detailed schematic of the refining processes.

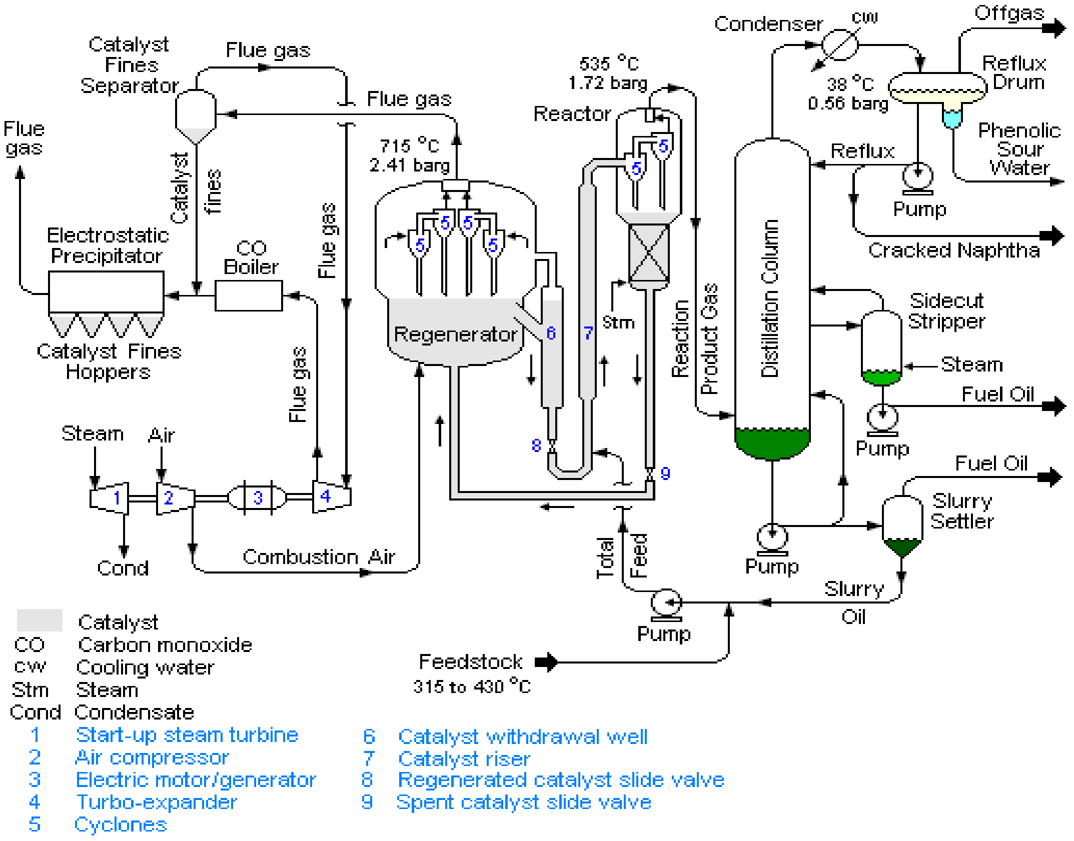

Figure 1.1: A schematic flow diagram of a Fluid Catalytic Cracking unit as used in petroleum refineries [25]

Petroleum refining produced more heavy distillate fractions (gas oil, residue oil) than the more desirable lighter fraction before the incorporation of the FCC and thus it was introduced to optimize the refining process [7]. Popa & Patrascioiu [8] describe FCC as involving four stages: the interfusion stage, which occurs at the bottom reactor where the feedstock is quickly vaporized by direct contact with regenerated catalyst; the rising stage where chemical reactions take place in adiabatic plug flow, the stripping stage where a cyclone system strips the catalyst particles of unreacted feedstock and reaction products in the gas phase at the top reactor; and the regeneration stage in which the catalyst is regenerated by burning off coke deposition from the catalyst surface. Depending on market demand and the variety of petroleum products, some crude oil refineries utilize simple conversion processes (atmospheric distillation, vacuum distillation), yet others operate complex configurations including multiple fluid catalytic cracking units. The more complex refineries are equipped with secondary transformation capability, wherewith production of different petroleum products are possible.

FCC differs from atmospheric and vacuum distillation in the sense that it is a chemical process which uses a catalyst to create new, smaller molecules from larger molecules to make gasoline and distillate fuels. Other products include olefins (propylene, butylene) and raw materials in the production of more petrochemicals, e.g., naphtha and FCC gas oil, which give fuel oil and gasoline [5]. The FCC catalyst is a solid, sand-like material with pore size on the order of 100 μm [9]. In the manufacture of FCC catalysts, there are four generic methods identifiable mainly by how the ingredients (e.g. zeolite, alumina) are bound together into a microsphere. They are silica sol, alumina sol, alumina gel and clay-based microspheres [10]. O’Connor et al. [11] outline these methods in their review.

Although FCC has been practiced for nearly a century, and the field has been researched extensively, it is still the subject of many academic and industrial inquiries. This is because new developments and challenges continually arise. The goal of these seemingly perpetual investigations (as is with most industrial processes) is the optimization of the process. Thus, avenues to maximize feed rate and conversion while constrained by feed quality, surrounding conditions and market demand are sought. Some approaches to this challenge include the computational approach. For example, Reyes et al. [14] described how a dynamic neural network was trained with data from an existing FCC unit in order to create a virtual plant, which can explore optimization routes too complex/expensive to implement, Cuadros et. al. [12] work used a hybrid of the deterministic sequential quadratic programming (SQP) and stochastic genetic algorithms (GA) to establish a sweet spot between local and global optimization to determine process conversion and regenerator emissions.

Another approach focuses on catalyst regeneration. For example, Wallace et al. [15] used 13C-(labelled compounds) to probe catalytic coke formation and reveal that a part of catalytic products is derived from benzene and toluene. Kuehler et. al. [9], highlighted mass transfer barriers resulting from the cracking process that ultimately deteriorate the performance of the FCC catalyst. Other approaches focus on the dynamics of flow in the regeneration unit,[16].

The modern FCC units have many different units with better configuration which includes a riser reactor, a stripper, a disengager, a regenerator, a fractionator, and catalyst transport lines. Also, it includes several other supporting units such as: cyclones, air blower, expander, wet gas compressor, feed pre-heater, air heater, catalyst cooler, The new FCC designs and technologies that have been developed by the major FCC designers and licensors are explained in the next chapter. It is the aim of this report to highlight such approaches with the objective of encouraging other researchers to explore this field of study.

1.2. Report Outline

The main sections of the present work are:

Chapter 1. The FCC unit and its operation

Chapter 2. History and the processing methodology involve in modern refinery.

Chapter 3. The variables of FCC unit and process suitable for chemical reaction.

Chapter 4. The FCC operation unit and catalyst material such as zeolite.

Chapter 5. Conclusions.

Chapter 2. Fluid catalytic cracking

2.1. History and Background

FCC has passed through a remarkable innovation period, which has resulted in its common place utilization in most modern refineries. Over the past century, a number of discovery events including zeolitic catalysis, residue cracking, and, most recently, as an avenue for producing chemical feedstock such as propylene have made FCC the juggernaut that it is today [17]. A few occurrences and researchers cannot be overlooked when an account of history of FCC is to be discussed; this section highlights just this.

In 1928, France-born mechanical engineer, Eugene Houdry, discovered a porous clay that acted as a catalyst for cracking gas oil to produce higher octane number gasoline than from thermal cracking. In his work, he found that burning coke from the by-product from cracking made it possible to regenerate the catalyst and thus make it useful for several reuses. As with many novel discoveries, it was difficult to get big oil companies of the time to scale up his lab scale unit; thus, Eugene Houdry’s first scaled up plant was not built-commissioned until mid 1936 when he was funded by Vacuum Oil Company and Sun Oil Company. The unit was called the Houdry unit. This was the first catalytic cracking unit, producing 15,000 barrels per day, and it was built in Paulsboro, New Jersey [92]. The first full-scale commercial plant went on-stream in 1937 at Sun Oil's refinery in Marcus Hook PA, USA [17]. Three years later, fourteen Houdry units were in operation in the United States. In 1936, Jersey Standard launched research into developing a new processing method using powdered and pelleted catalyst instead. This proved very lucrative as yield was much better.

By January 1938, Warren Lewis and Edwin Gilliland of Massachusetts Institute of Technology, (MIT) who had consulted for Jersey Standard in their catalytic cracking research, proposed that downward flow of powdered catalyst over alternately pitched baffles in counter flow with steam would strip off hydrocarbons from the catalyst. In 1940, J.W. Moorman, a student of Lewis and Gilliland found in his experiments that pressure drop challenges from counter flow could be overcome by a “Catalyst Head-Injector (Catastatic) System” which injected catalyst with air from the bottom of that column. He later developed a theory for predicting what velocity of this gas would sufficiently maintain this catastatic system. Moorman termed it “blow out” velocity: the gas velocity sufficient to blow all or almost all the solid material out of the reactor in a very short time [18].

After powdered clay catalyst was replaced by a synthetic silica-alumina in the late 1940's, the process enabled the production of high-quality aviation fuel for the Allies during World War II. The history of this process began in one man's laboratory and was catapulted by the emergence of World War II into one of the primary means of producing aviation jet fuel. Although the fluid catalytic cracking process is quite old, the research scope is still enormous due to changing fluid catalytic cracking feedstock, gradual shifts in market demands, and evolved unit operations. This fluid catalytic cracking technology can be applied fully in grassroots units or partially, as applicable, in the revamp of existing units. A more thorough account of how the first FCC unit came about can be found in Squires et al. [65].

2.2. Process Description

Petroleum refineries are very large industrial complexes that involve many different processing units and auxiliary facilities.

Basically, each refinery has its own unique arrangement and combination of refining processes largely determined by the refinery location, desired products, and economic considerations. The number of individual products produced varies from month to month and year to year as refineries adjust production to meet market demand and to maximize profitability. According to Termeer, [66] for refineries to meet the business objectives, the process designer selects from an array of basic processing units.

These units perform a lot of different functions which are itemized as follows:

1. At high temperature and pressure, crude oil is separated into hydrocarbon fractions based on their chemical properties within the reactor.
2. Further chemical reactions convert hydrocarbon fractions into more desirable raw products for petrol chemical industries.
3. The last process is the purification of petroleum products into wanted and unwanted compounds based on the market demand including compounds for continuous processing.

In FCC, although there are various designs each requiring a license for use or reference, some general principles apply. Figure 2.1 shows a schematic of the most general design.

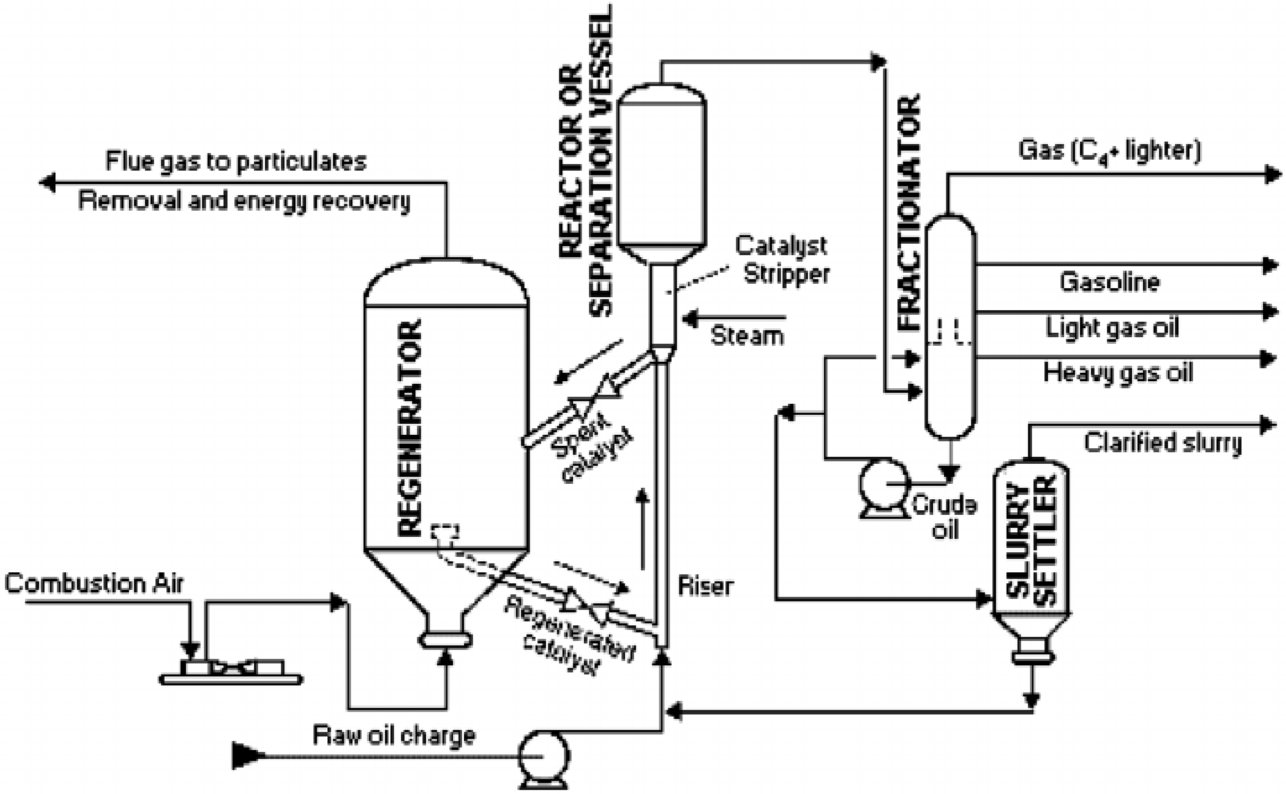

Figure 2.1: Schematic of a generic FCC design [64].

The feedstock (heavy gas oil typically with boiling point $340°C$ and average molecular weight between 200 and 610g/mol) is heated and then brought into intimate contact with a fluidized bed of powdered catalyst and injected steam at the riser entrance as they rise towards the reactor.

The hot catalyst particles coming from the regenerator unit vaporize the feed gas oil on contact in the riser, and cracking starts as the gas oil vapors and the catalyst particles move upward into the reactor. Besides coke, there are other petroleum products produced as a result of cracking reactions including dry gas (C1-C2),liquefied petroleum gas (LPG) (C3-C4),gasoline (C5-C11),light cycle oil (LCO) ,heavy cycle oil (HCO), and slurry/decant oil.

The gasoline produced from FCC usually amounts to about 60% of the gasoline pool of a refinery. Because cracking is endothermic, the temperature of the catalyst particles drop as they encounter hydrocarbon and reactions proceed as the mixture rises. Because most of the reactions are occurring on the catalyst pellet, a significant amount of coke deposits on the catalysts surface, which leads to the deactivation of the catalyst. The mixture is then stripped of the adsorbed hydrocarbons, and the coked catalyst is sent to the regeneration unit to burn off the coke with hot air [64].

Figure 2.2 below depicts the flow chart of petroleum refining operations. This is aimed to outline the complexity of petroleum refining including the numerous processing pathways and various end products. Understanding these intricacies or complexities of petroleum processing is vital to building a fundamental knowledge of the refining industry

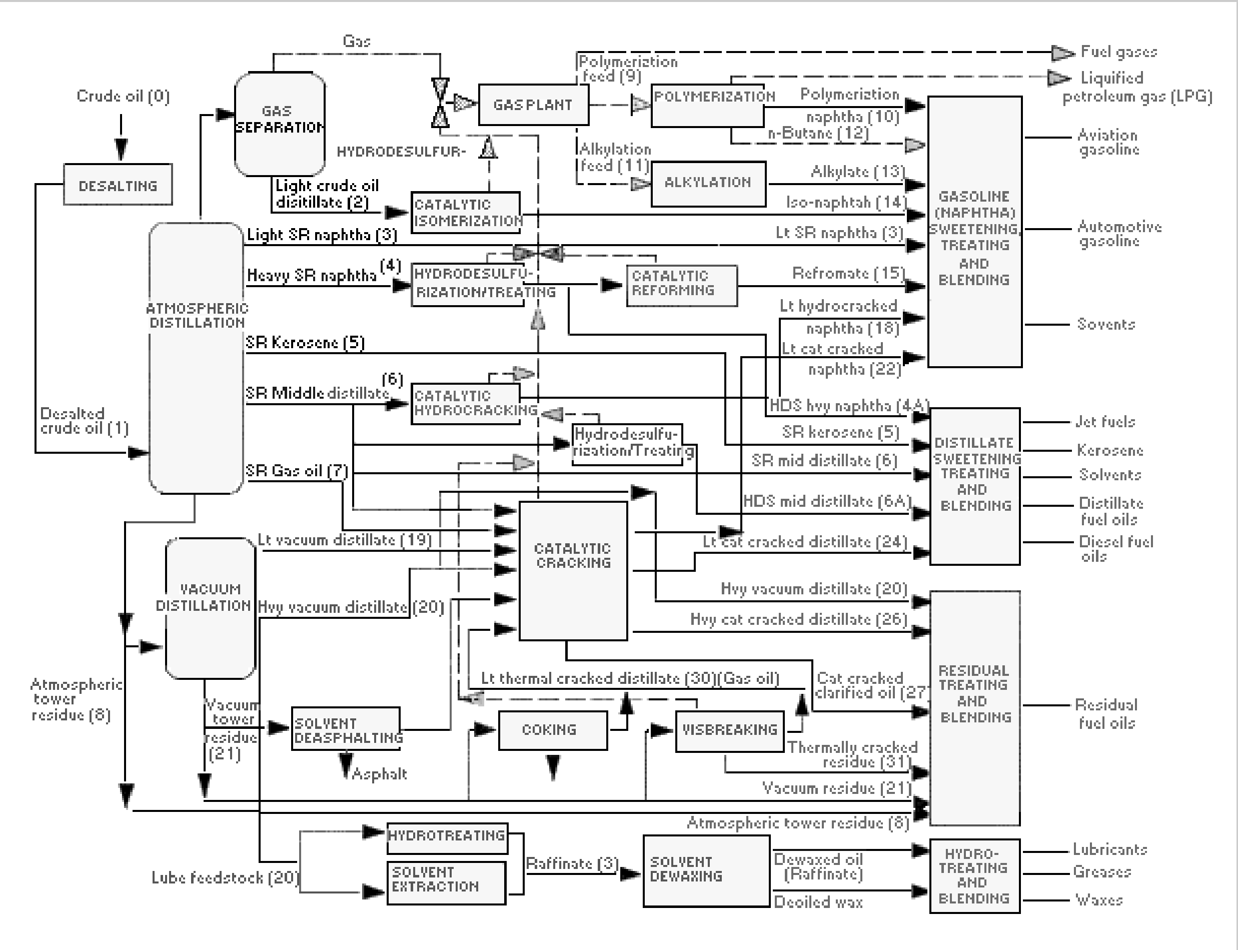

Figure 2.2: Overview of Petroleum Refining Processes,[64].

Heat released from burning the coke deposit increases the temperature of the catalyst particles that are returned to the riser to complete the cycle. The burning in the regenerator provides the energy necessary for cracking without much loss, thus increasing the thermal efficiency of the process. The products are then sent to the fractionator for recovery after they are separated from the catalyst particles in the upper section of the reactor [65].

At the higher-octane levels, product yields are smaller, and more frequent catalyst regenerations are required. During the course of the reforming process, minute amounts of carbon are deposited on the catalyst, causing a gradual deterioration of the product yield pattern.

According to findings from Vogt & Weckhuysen, [19], some units are semi-regenerative facilities which means they must be removed from service periodically to burn off the carbon and rejuvenate the catalyst system. However increased demand for high-octane fuels has also led to the development of continuous regeneration systems, which help to avoid the periodic unit shutdowns and maximize the yield of high-octane reformate. Researchers continue to study ways in which these processes could be changed to eliminate downtime. For example, another unit can be introduced to keep catalyst and the process in a continuous regeneration. The continuous regeneration method employs a moving bed of catalyst particles that is gradually withdrawn from the reactor system and passed through a regenerator vessel, where the carbon is removed, and the catalyst rejuvenated for reintroduction to the reactor system.

In the reactor, the cracking reactions are initiated on the active sites of the catalysts with the formation of carbocations and the ensuing ionic chain reactions produce branched alkanes and aromatic compounds to constitute the cracked gasoline with high octane number, light olefins, cycle oils, and slurry oil that are sent to the fractionator as can be seen in figure 2.3. Hot catalyst material is combined with pre-heated feedstock at the bottom of the riser reactor and a catalyst-to-oil ratio is larger than one sometimes a ratio of 5.5:1. The temperature at the bottom of the riser is typically in the range of 400 to 550 °C. The reactants mixture expands due to the cracking reaction as gases are formed, and catalyst feedstock mixture is rapidly transported up the riser reactor, at speeds approaching 40 m s^{-1}. The normal contact time in a riser between catalyst and feedstock is on the order of seconds. At the top of the riser reactor, the temperature has dropped to about 500°C because catalytic cracking is an endothermic reaction process.

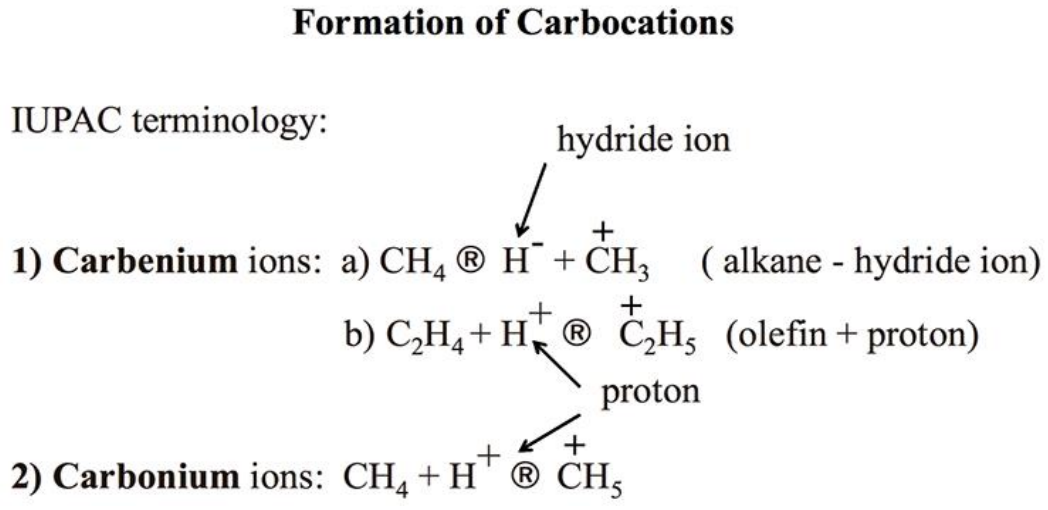

Figure 2.3: Chemistry of FCC reaction [68]

The catalyst is separated from the product mixture and stripped of remaining useful product by steam treatment as the products are further refined downstream. Depending on the exact conditions such as the oxygen availability, the regenerator temperature can reach up to 760 °C. The catalyst temperature cycles are between 500 °C and 760 °C, while it is moving at great speed. It is clear that this means the catalyst is exposed to harsh reaction conditions.

The current refining process makes it difficult to selectively detach deactivated catalyst, hence, refiners remove a small portion of the finished inventory of the regenerator at fixed intervals, usually daily; the removed catalysts are then replaced with fresh ones. Vogt & Weckhuysen, [19], state that when this process is conducted for a longer period, roughly, a steady state is reached in the catalyst life-time dissemination, known as equilibrium catalyst. Subject to the magnitude of the FCC unit as well as the operational parameters, catalyst removal rates can range from 1 to 30 tons per day.

2.3. The FCC Configuration

From the first FCC designed until now, the configuration and setup has been changing as the process has evolved. The primary purpose of the Fluid Catalytic Cracking (FCC) unit is to crack the crude oil into more desirable hydrocarbon fraction and produce additional petroleum products. Today, Fluid Catalytic Cracking units are all designed to function in a continuous process, which operate twenty-four hours a day for as much as two to three years before shutdowns for turn-around maintenance. Different configurations of the fluid catalytic cracking unit exist with the reactor and the regenerator positioned differently. Two basic Fluid Catalytic Cracking unit configurations in use today are the side by side and stacked-up, as seen in Figure 2.4.

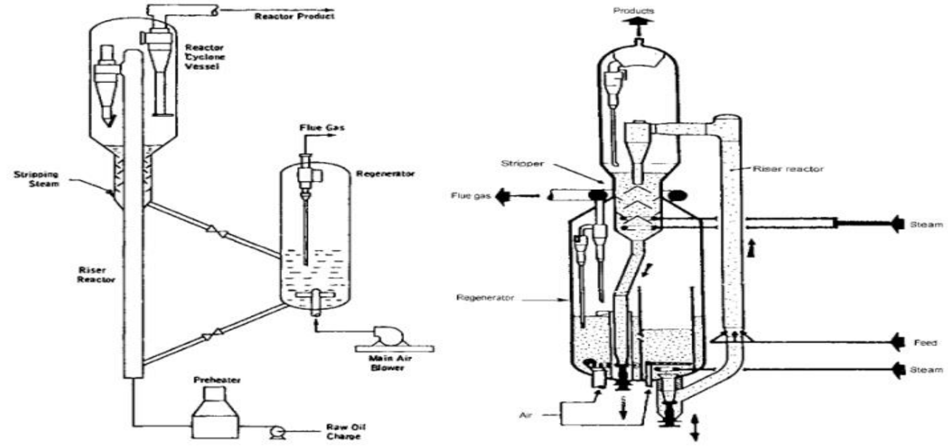

Figure 2.4: Examples of the two possible FCCU configurations. Left: side-by-side Right: stacked up *[78].*

There are two types of FCC configurations that have been approved for modern Fluid Catalytic Cracking units. Each design is licensed and can only be purchased through the licensor for any petroleum refining company who desires to construct and operate FCC units. Major licensor companies that use the Fluid Catalytic Cracking unit with side by side configurations are:

Chicago Bridge &Iron/ Lummus
ExxonMobil Research and Engineering

Shell Global Solutions International
Stone & Webster Engineering Corporation/Institut Francais du Petrole (IFP),
Universal Oil Products (UOP).

The only major licensor company that uses the FCC processes with stacked-up configurations is
Kellogg Brown & Root (KBR)

All fluidized catalytic cracking units have three major sections—the reactor-riser, the regenerator, and the fractionators. In the side-by-side design, as depicted in figure 2.4, the reactor vessel is located next to the regenerator vessel and in some cases relates to the riser. In other designs, the catalyst standpipe and the regenerated catalyst standpipe connect these two vessels. Mostly, the side-by-side configuration of the reactor and regenerator is applicable to large scale refineries which can process more than 20,000 barrels per stream day (BPSD) of fresh feed with feed rate set at 62,000 barrels per stream day(BPSD).

In such configuration, the riser is inside the steam stripper with the operating pressure of 8-30 psig, which is generally limited to 15 to 20 psig corresponding to the design and pressure balance of the reactor and regenerator [79].Because the reactor and regenerator stand close in this type of configuration, the processing time of crude oil from the feedstock is very short.

The stacked-up configuration as illustrated in Figure 2.4, the reactor and regenerator is applicable to small scale refineries which can process less than 20,000 barrels per stream day (BPSD) of fresh feed with feed rate set at 2,500 barrels per stream day(BPSD).

Innovations in the stacked-up configuration have improved the refining processes. For example, Shende & Wasewar, [72], found that these advancements and improvements have enabled accommodation of higher temperatures sustaining reactors within the stacked-up configuration. In this regard, it is commonly found that the metallurgy of old reactor units is incompatible, and new reactors with high temperature compatibilities are now preferred. Before this advancement, reactor temperature placed a limitation and constraint on stacked-up unit configuration in the refinery. This conversion and reactor replacement allows the owner of an existing stacked-up configuration to greatly increase the processing capacity of the unit and to process heavier feedstock. Common approaches to upgrade stacked-up configurations include the replacement of internal equipment with more heat resistant equipment and the use of internal insulation or external convection devices to reduce the skin temperature of metal components such as conduits and vessel shells[79].

Over time, the capacity of FCC units has steadily increased. New FCC units process between 40,000 to 60,000 BPSD. At the present time, any FCC unit processing anything less than 20,000 BPSD will not be profitable to the refinery. Because FCC unit is the heart of every refinery, constant innovation and research are being studied every day.

Chapter 3. Variables of FCC Unit

3.1. FCC Unit Feedstock and Products

FCC has passed through a remarkable innovation period, which has resulted in its common place utilization in most modern refineries. Modern FCC units can process different types of feedstocks and as well accommodate the operational conditions in maximizing production of gasoline, middle distillate (LCO), or light olefins to meet different market demands [57]. The FCC unit serves as an important foundation in the production of butene, pentene and olefins used in refinery processes such as in the alkylation unit.

3.1.1 Feedstock

The FCC feedstock is heated to the range of 150°C and 350°C to lower the viscosity and surface tension for separation and mixing of the water. This temperature is restricted by the vapor pressure of the crude oil feedstock. The main feedstock used in FCC unit is the Gas Oil, which has a boiling temperature ranging from 316°C to 566°C. Below is a list of some gas oil feedstock which FCC units will accommodate:

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

These gas oils in some case are regarded as a mixture of aromatic, naphthanic, and paraffinic molecules. Some have unpredictable contaminants such as sulphur, nitrogen, and metals, particularly in the higher boiling fractions.

These distinctions in feed composition and contaminants will affect the operating conditions needed to acquire the desired yields. To preserve the catalyst, the feedstocks are pretreated using hydrotreating to remove contaminants and improve the feedstock cracking characteristics. The principal limitation on charge stocks are the Conradson Carbon Residue (CCR) and metal contaminants. Conradson Carbon Residue provides an indication of coke-forming tendencies on oil or the amount of carbonaceous residue remaining after crude oil evaporates. This effect of Conradson carbon is to form a deposit on the catalyst and reduce catalyst activity, promote coke and hydrogen formation [58].

Paraffinic atmospheric and vacuum gas oils are used as feedstocks because they are very easy to crack when put into the catalytic cracker. Feedstocks are grouped according their crackability or how quickly it is converted in an FCC unit. Crackability is based on the of the relative magnitudes of the paraffinic, naphthenic, and aromatic sample within the feedstock as shown in Table 3.1.

Range of characteristic factor Kuop	Relative Crackability	Feedstock type
> 12	High	Paraffinic
11.5 – 11.6	Intermediate	Naphthenic
< 11.3	Low refractory	Aromatic

Table 3.1 Feedstock Crackability [24].

FCC gasoline yield largely depends on changes in feed. According to Sadeghbeigi, [74], he states that FCC gasoline yield largely depends on changes in feed quality, catalyst properties, and operating variables, for feedstock quality: paraffinic feedstocks can produce the best gasoline yield, but with the lowest octane. There are common indicators of any increase in feedstock paraffinicity which are:

- increase in the Kuop factor
- increase in the nickel-to-vanadium ratio
- increase in the aniline point, and
- decrease in the fraction of Coker gas oil material

3.1.2 Products

Table 3.2 shows the percentage yields and the product characteristics obtained by the catalytic of vacuum distillate (VGO) and the required treatments valorizations.

Products	*Yield wt%*	*Product characteristics – Complementary Treatments - Valorizations*
GAS C_2^- & H_2S	3 – 5	• Large amount of H_2S produced with high sulfur feeds • Requiring purification treatments (amine washing – Claus plant)
C_3 CUT - Propane - Propylene	5 – 9	• 70% propylene in the C_3 fraction • Propylene recovery by distillation for further use in petrochemicals
C_4 CUT - Butanes - Butenes	6 – 12	• 50 – 60% butenes in the C_4 fraction • Possible valorization of butenes in ALKYLATION plant to increase gasoline production • Selective valorization of isobutene in MTBE plant

GASOLINE $C_5 – C_{11}$	45 – 55	• Most desirable product • Medium octane rating for unleaded gasoline RON 92 – 93, MON 79 – 80 • Relatively good stability • Corrosive and bad odor mercaptans require sweetening by MEROX type process • Possibility to improve octane numbers by separating a gasoline heart cut and then processing it.
GAS OIL (LCO)	15 – 20	• Very aromatic • Low cetane number • S% generally high • Good diluents for heavy fuel oil
HEAVY streams (HCO + SLURRY)	6 – 10	• Very aromatic products • Diluents for heavy fuel oil
COKE	4 – 6	▪ Self – consumed as fuel in the regenerator

Table 3.2 Typical FCC unit products [87].

3.2 Catalytic Cracking Reactions

The core chemical reaction within the FCC unit is the catalytic cracking of the light crude oil. These crude oil branches are paraffin, olefins, naphthenes and aromatics. A network of reactions happens in the FCC unit as illustrated in Figure 3.1. The VGO undergoes a primary cracking into gasoline and LCO. A secondary reaction also occurs, which must be limited, such as a hydrogen transfer reaction which lowers the gasoline yield and causes the cycloaddition reaction. The latter could lead to coke formation needed to provide heat for catalyst regeneration [24].

Carbon atoms bond with one another in various ways namely single bonds, double bonds, and triple bonds to form several categories of hydrocarbons. The physical and chemical properties of hydrocarbon species, or molecules, depend not only on the number of carbon atoms in the molecule but also the nature of the chemical bonds between them. Paraffins, aromatics, naphthenes and olefins as shown in Figure 3.1 illustrate the carbon-to-hydrogen(C/H) ratios.

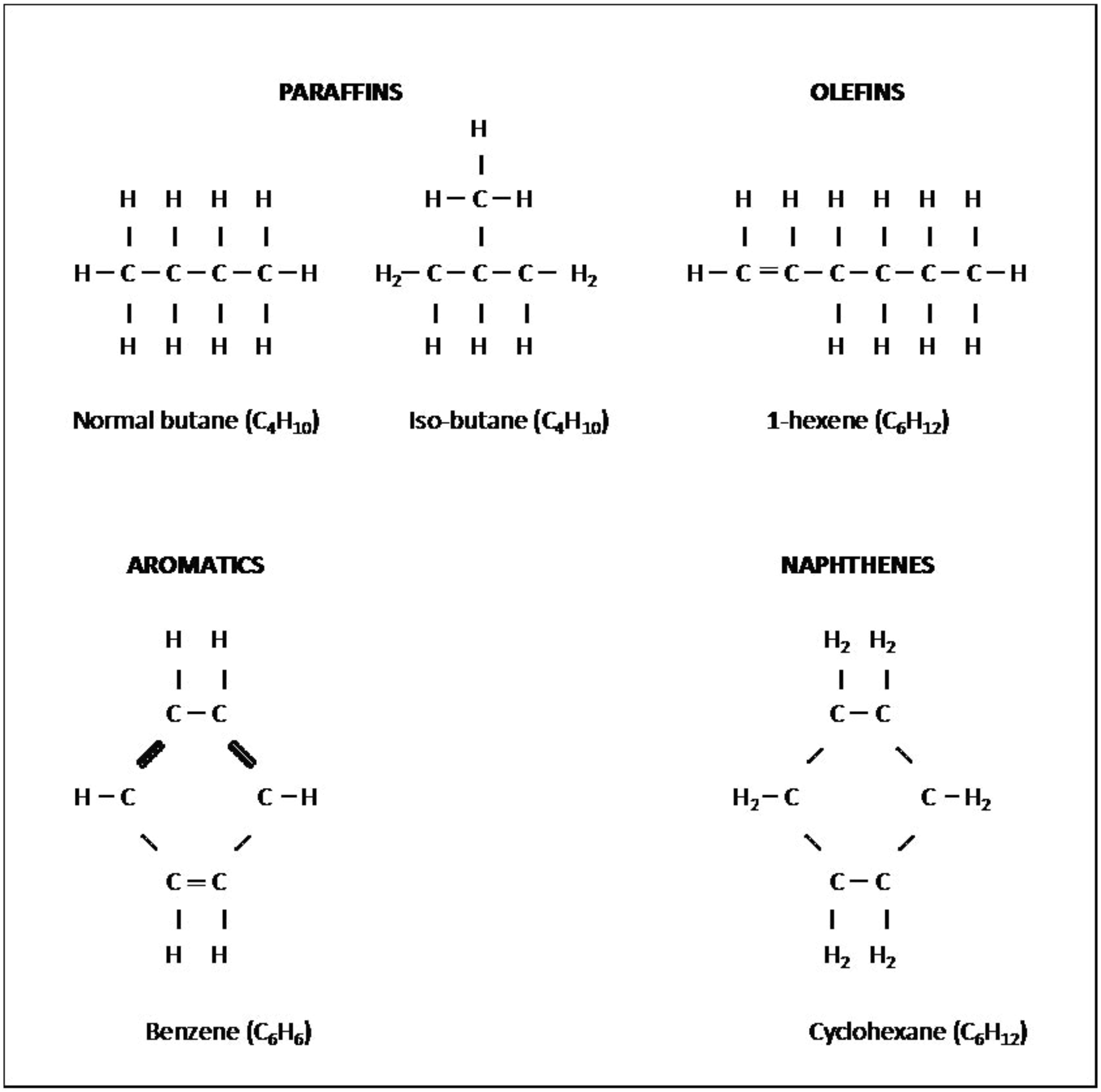

Figure 3.1. Molecular structure of hydrocarbons [89].

Figure 3.2 shows the reaction network of a conventional fluidized catalytic cracking followed by residue fluidized catalytic cracking, allowing heavy oils with high viscosity to be processed and refined.

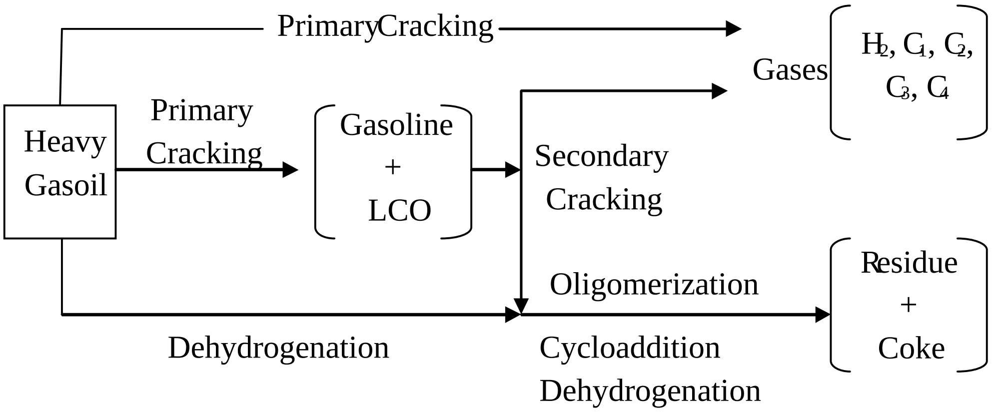

Figure 3.2 FCC reaction network [88].

3.3 Riser

One of the most important units in the FCC process is the riser. The first reaction in the catalytic cracking process takes place in the riser. The high temperature and pressure in the riser provide perfect reaction conditions for hydrocarbons to break down into short carbon chains. Some FCC units today, have multiple riser-reactors to enable the increase in production and reduce the residence time. Here, the mixture of catalyst and hydrocarbon are transported by the lift media through the riser prior to their separation via the cyclone. The only heat inlet for the riser is the hot catalyst that mixes with the feed to provides all the heat required for the vaporization and the cracking reactions. The principal functions of the riser terminate once they reach the disengager [31].

3.3.1 Riser chemistry

According to Ali et al. [26], the chemical reactions that occur inside the riser are very complex and difficult to define; these reactions breakdown the C-C and C-H chain bonds. Outside of the riser unit, the cracking reactions of C-C and C-H bonds are rare and cannot be observed under laboratory setting. The reactions that occur in the riser are globally endothermic, leading to a reduction of the temperature along the riser. It should be noted that natural petroleum has very little or no olefins; as such, the olefins that react in the riser originate from the cracking reactions themselves. The chemical reactions that occurs in the FCC riser reactor are summarized in Figure 3.3

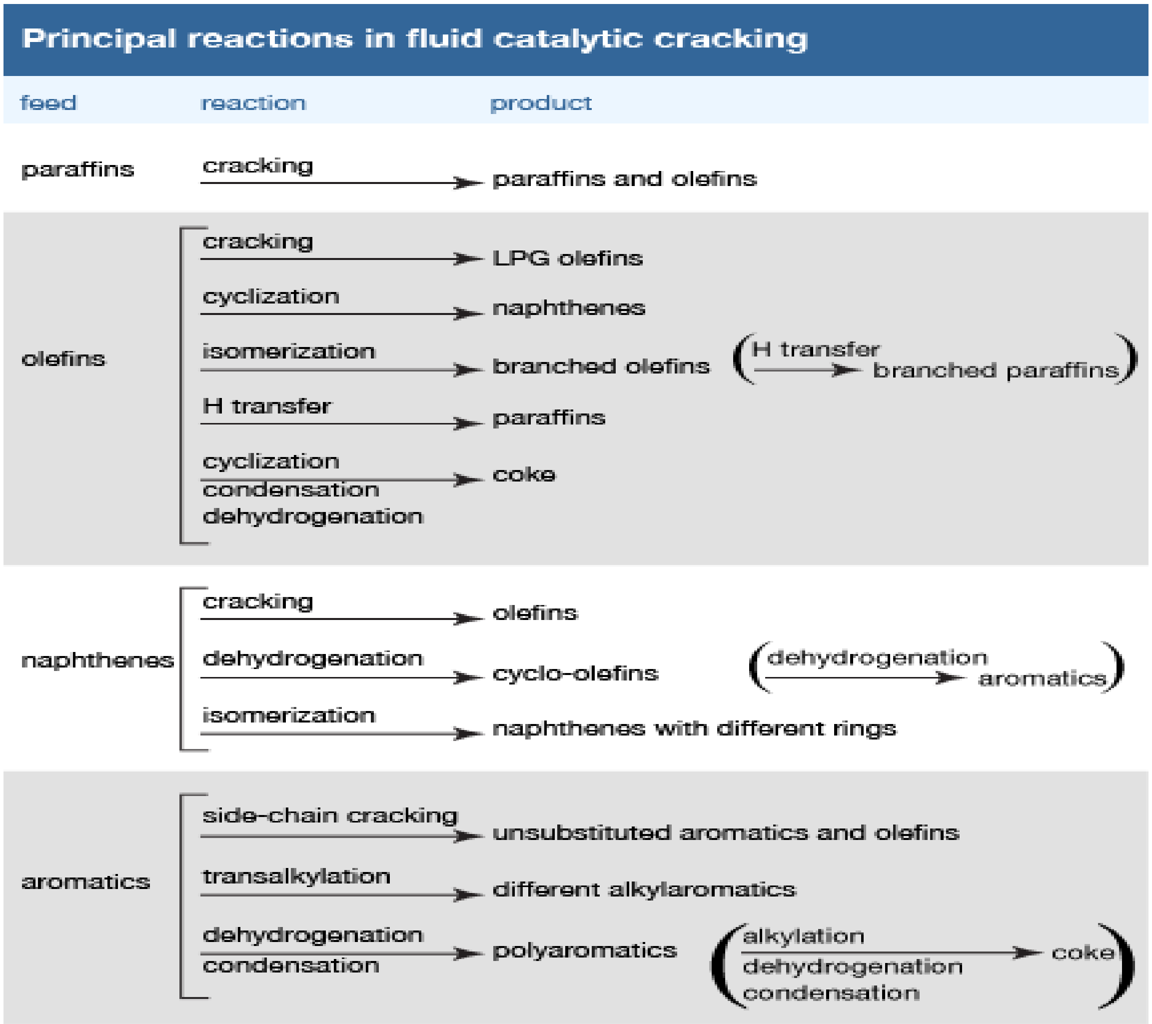

Figure.3.3.Reactions in fluid catalytic cracking [99].

3.3.2 Hydrodynamics in the Riser

Basically, the hydrodynamics that take place within the riser are considered plug flow because of the radial dispersion of hydrocarbon and the catalyst particles. Several catalyst particles are transported by the vapors of the cracked hydrocarbons through the riser because the hydrocarbons vapor velocity is higher than that of the catalyst particles. This phenomenon known as slip velocity is the difference between the velocity of the hydrocarbons and that of the catalyst particles. This slip velocity is greater than the terminal velocity for a single particle due to the formation of catalyst clusters, which behave like a big particle and, as such, have a higher terminal velocity.

Fernandes et al. [31], explained the physics in the riser in his core-annulus model, where free catalyst particles were conveyed by the air within the core of the riser and near the wall region has almost no flow of hydrocarbons and catalyst particles. As the reaction progresses there's an increase in the number of moles in the vapor phase, which causes the vapor to expand. This expansion is the greatest driver for the transport of the catalyst.

3.3.3 Catalyst Deactivation

Catalysts undergo several deactivations within their lifetime due to coke formation. One of the most known reactions that take place in the riser is coke formation. Coke is a generic name given to this hydrocarbon species that is formed and deposited in the catalyst's active surface. In order to deactivate it, catalyst particles are subjected to high burning temperature. Coke is usually considered to be composed of polyaromatic compounds with a high molecular weight and low H/C ratio.

According to refiners, this type of coke produced in these types of chemical reactions are known as catalytic coke. There are other types of coke such as Conradson Carbon Residue coke, which is present in the feed of the FCC unit, and soft coke, which are hydrocarbons that remained adsorbed on the catalyst when it reaches the regenerator, among other types [31].

The formation of coke on hydrocarbon processing catalysts is of considerable technological and economic importance and a great deal of work has been carried out in its study. There are several methods of modifying the catalyst to inhibit deactivation but none of them have proven to be economical effective. Another method to address catalyst deactivation is the burning of catalyst under high temperature, which is reversible with the catalytic activity regenerated in the regenerator. The existence of permanent deactivation necessitates that catalyst that circulates inside the FCC unit be constantly removed with a make-up of fresh catalyst while new ones are being added simultaneously. This constant removal and addition leads to a distribution of residence time of the catalyst particles inside the FCC unit. This mixture of catalyst particles with changing residence times that circulates in the FCC unit is called equilibrium catalyst [31].

3.4 Strippers/Disengagers

The riser terminates in the disengager. The primary purpose of the disengager is to separate the hydrocarbons that were cracked in the riser from the catalyst particles, which are now deactivated and have lost most of their catalytic activity. To prevent further cracking, the separation is done as fast as possible; a slower processing time leads to undesirable fraction, such as production of dry gas. The disengager includes a two-stage cyclone which separates the catalyst particles from the hydrocarbons. The hydrocarbons are then transported downstream for fractioning process, while the catalyst particles drop to the stripper via the disengager.

Furthermore, in the stripper, the catalyst accumulates and then is washed with the stripping stream. The stripper may have baffles or packing to improve the catalyst/steam contact. The steam displaces the entrained hydrocarbons in the catalyst, sending them to the downstream fractioning processes, but most of the adsorbed hydrocarbons on the catalyst remain with the catalyst particle when these are sent to the regenerator. These remaining hydrocarbons in the catalyst may react further to give lighter fractions [31].

3.5 Regenerators

In the regenerator, the catalyst is burned with hot air to remove the deposited coke on the catalyst and restore the catalyst activity. The regenerator generally contains two phases: a dilute phase and a dense phase. The dense phase is where most of the combustion takes place including catalyst burn off. The catalyst then may circulate either in the same or opposite direction of the air flow. This can function in either partial or full combustion. In partial combustion, a substantial amount of CO is found in the flue gases; in this case, CO boiler is required in the downstream regenerator. In complete or full combustion, all CO had been converted to CO2. Lawler et al.[83], states that some FCC units with the multi-stage may operate in two categories: the first regenerator vessel runs in partial combustion, to prevent the higher temperatures of complete combustion; the second one operates in complete combustion, to lessen the amount of coke residual in regenerated catalyst, thus maximizing its activity at the riser inlet.

In some units, particularly RFCC an external heat exchanger may be required to maintain the heat integration of the entire FCCU. As a residue feed forms more coke than other feeds, some of the heat generated from the burning of the coke must be removed to keep the FCC in steady state. Such an external heat exchanger produces steam that may be used elsewhere in the refinery [83].

3.5.1 Regenerator chemistry

As previously mentioned, the regenerator may operate in either partial or full combustion. According to Lawler et al. [83], the main reactions that take place are as follows:

$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \tag{1.1}$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{1.2}$$

$$CO_{(a)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \tag{1.3}$$

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \tag{1.4}$$

$$2H_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \tag{1.5}$$

Figure 3.4 FCC reaction network [24]

These types of reactions occur mainly in the dense phase, which is the gas phase region. Because of this type of reaction, an increase in the regenerator temperature are required until the flue gases leave the dense phase, as most of these reactions are exothermic in nature. At the regenerator, coke is burned off, to restore activity of the catalyst, just as the high temperatures steam also permanently deactivates the catalyst. This challenge inspired the invention of the multi-stage regenerator design. The combustion of hydrogen is very important because its steam have faster kinetics than the carbon combustion. As such, much of the steam formed during the first regenerator are removed from the combustion. In the second regenerator, as most of the steam has already been formed and removed from the reacting environment, the operation can be in full combustion, to completely remove the remaining coke still on the catalyst [83].

The presence of such combustion promoters, like Pt metals, catalyzes the oxidation of CO to CO2. This may not be desirable in a regenerator designed to operate in partial combustion, since there would be competition for the limited supply of oxygen: combustion of C to CO (to restore activity) and combustion of CO to CO2.

3.5.2 Hydrodynamics in the Regenerator

Inside the regenerator there are two different regions: the dense bed and the freeboard. The dense bed is where most of the combustion to regenerate the catalytic activity takes place. Air, or an air and oxygen mixture, is injected at the bottom of the dense bed, fluidizing the catalyst particles and burning off deposited coke.

In the freeboard, the catalyst particles are ejected from the surface of the dense phase and transported by the combustion gases. Most particles fall back down to the dense bed, but others are pneumatically transported. At the height where no more particles will return to the dense bed on their own there is a cyclone system that separates the remaining catalyst particles.

Chapter 4. FCC Unit Operation Variables

The main goal for any FCC unit operator is to maximizing unit conversion and achieve the desired product selectivity. Any FCC operation has to create ways to manage the feedstock quality which can be divided into two groups: catalytic and process.

4.1. Catalytic Activity and Catalyst Design

According the history of FCC, the first catalysts used were natural occurring clays, but these had low cracking activity and poor fluidization characteristics. In 1940's, synthetic silica/alumina catalysts were developed and used to process hydrocarbon. As technology evolved, zeolite catalysts were developed to replace the synthetic silica/alumina catalysts. Zeolite catalysts performed very well and were able to greatly increase the activity, stability, and improved the hydrocarbon selectivity. It has been realized for some time that better FCC unit yield could be achieved with shorter contact time between the feedstock and the catalyst by using zeolite catalysts. With the earlier catalysts of low activity and long residence time, some of the gasoline formed cracked further in the catalyst bed to LPG resulting in lower gasoline yield [90].

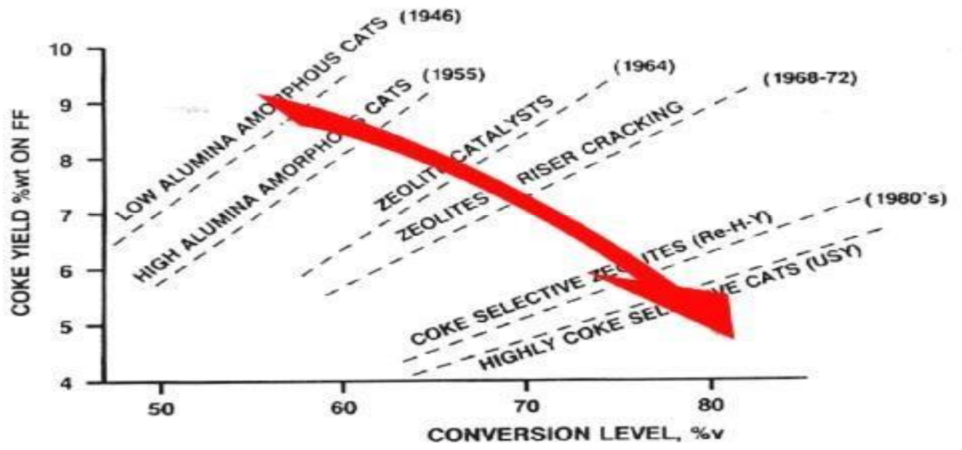

Figure. 4.1 Evolution in structure of FCC catalysts before 1990 [91]

The figure above shows the continuous improvements in the performance of FCC catalysts 1990. Modern FCC catalysts are comprised of silica and alumina, which provide the acid sites necessary to crack petroleum. They are typically applied as fine powders with a particle size distribution ranging from 10 to 150 µm and an average particle size of 60 to 100 µm. Bulk density is usually between 0.8 and 0.96g/cc [90].

Physically, the catalyst must have the following characteristics: satisfactory fluidization characteristics and sufficient resistance to attrition so that excessive loss of fine particles is not encountered. Chemically, the catalyst must have these characteristics: It must have adequate activity and maintenance of activity with age. It must also promote the formation of the desired reaction products without forming extensive amounts of undesired by-products such as gas and coke [92].

Amorphous catalysts have higher attrition resistance and are less costly than zeolitic catalysts. Most commercial catalysts contain approximately 15% zeolites providing both the higher activity and gasoline selectivity of the zeolites and the lower costs and make-up rates of the amorphous catalysts [76]. During cracking catalyst deactivation occurs by deposition of trace metals in the feed such as Nickel and Vanadium, where vanadium can destroy the zeolite activity, and coke deposition which temporarily block some of the catalytic sites; The spent catalyst entering the regenerator contains between 0.4 to 2.5 wt% coke, this coke is burned off in the regenerator.

Based on Gary& Handwerk [76], regenerated catalyst contains between 0.01 and 0.4%wt residual coke. This is an important parameter that the unit operator to monitor closely. The CRC is an indicator of regenerator performance (Figure4.2).

Catalyst loss also occurs due to the attrition. For this reason, a daily makeup rate of fresh catalyst is added, typically 0.045 to 0.14 Kg per barrel of fresh feed.

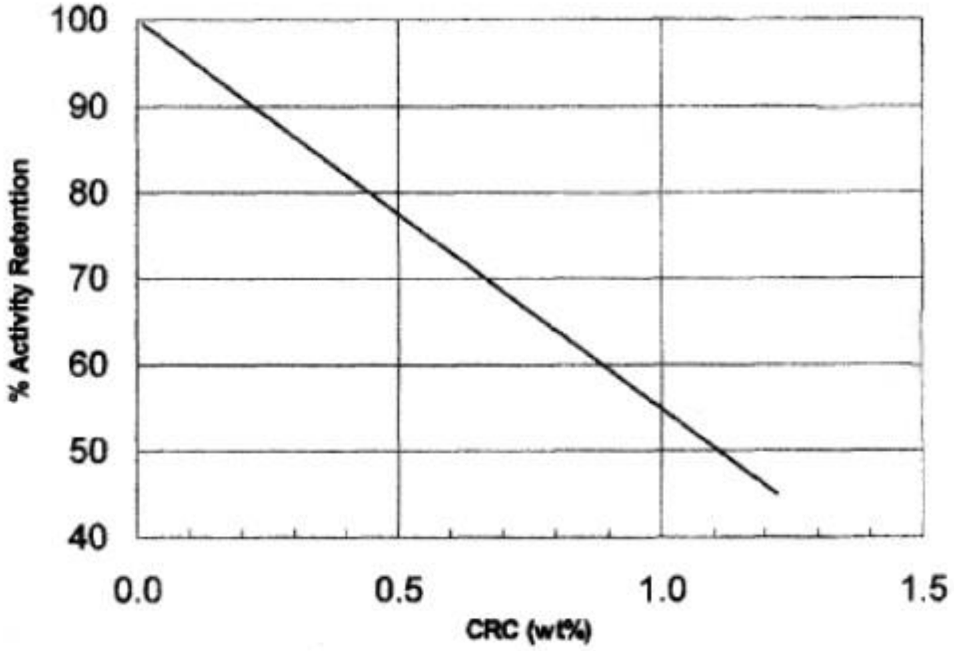

Figure 4.2. Catalyst activity retention vs. Coke on regenerated catalyst [74].

In general, the deactivation in a given unit is largely a function of the unit's mechanical configuration, its operating condition, the type of fresh catalyst used, and the feed quality. The primary criterion for adding fresh catalyst is to arrive at an optimum steady state catalyst activity level. A too-high equilibrium catalyst (E-cat) activity will increase delta coke on the catalyst, resulting in a higher regenerator temperature. The higher regenerator temperature reduces the catalyst circulation rate, which tends to offset the activity increase. The amount of fresh catalyst added is usually a balance between catalyst cost and desired activity [34].

4.2. Process Variables

4.2.1 Independent Variables

These variables are directly regulated and can be controlled using controlling devices.

4.2.1.1 Feed Rate

As the flow rate of the feed decreases, the space velocity decreases and the contact time increase, causing an increase in the conversion rate. Conversion has been observed in some units to increase 1% absolute for a 3-5% relative decrease in fresh feed rate. Charge rate is set as desired by the refinery based on the existing economics [55].

4.2.1.2 Feed Preheat Temperature

When the feed preheat temperature decreases, there following will happen at the riser outlet temperature:

- Increase the catalyst circulation rate
- Slightly increase conversion
- Increase the coke production rate 0.1 – 0.15 %wt on feed for every 10oC reduction in preheat temperature
- Decrease the delta Coke (kg coke/kg catalyst) Decrease the Regenerator temperature

4.2.1.3 Reactor Pressure

According to UOP Operating Manual and Wolschlag and Couch [55], the pressure in the reactor is normally varied very little. There is a tradeoff here as a higher reactor pressure would reduce the Gas Concentration Unit gas compressor horsepower requirements, but it would also increase the main air blower horsepower. Higher pressure would also reduce the required size of the vessels. Increasing the hydrocarbon partial pressure lowers the olefin content of the products while increasing conversion slightly. Coke laydown will increase slightly, but this can have an effect that may be offset by adding steam or inert gas to reduce the hydrocarbon partial pressure. This may, however, defeat the original purpose of raising the reactor pressure. Reactor pressure normally varies slightly with changes in feed rate and loading of the main column. The operator must control pressure within narrow limits around the design value to avoid problems with riser and cyclone velocities. Normal first stage cyclone inlet velocities are in the (20 m/s) range. Higher velocities are better for cyclone efficiency but lead to a greater amount of catalyst being carried up. Higher velocity also increases cyclone erosion problems.

4.2.1.4 Reactor Temperature

Reactor temperature is the key controller of the reactor severity. Changing or increasing the reactor temperature will communicate to the regenerator about the new temperature. This will force the regenerator catalyst valve to increase the temperature of the hot catalyst flow to achieve the desired riser outlet temperature. Once there is an increase in the catalyst circulation rate, this will result in an increase on the conversion.

Basically, higher temperature will accelerate intermolecular motions thereby helping the transformation of the rate of chemical process. The dependence of rate constant of chemical reaction and absolute temperature were described by the Arrhenius equation. The cracking rate constant is improved by the temperature of the riser as a result, the conversion of the feed into light products increases [94].

An increase on cracking temperature also increases gasoline octane, and LPG olefinicity with their potential for alkylation feed. Cracked gasoline from high temperature operation are mostly beneficial in blending components for leadfree gasoline. The higher the conversion and temperature, the higher the octane rating. The higher octane is a result of primary cracking reactions relative to secondary hydrogen transfer reactions which saturate olefins in the gasoline boiling range and lowers gasoline octane. An increase in the unit conversion does not automatically mean gasoline yield will increase, because beyond a certain temperature, gasoline yield will begin to be reduced [76].

Aver. Reactor temperature, °C		510	538	558
Feed conversion, vol. %		85	87	89
yields	Gasoline, vol. %	71	68	64
	Propylene, vol. %	7.8	10.6	11.5
	Butenes, vol. %	7.4	8.5	10.6
	Coke, wt %	3.6	3.4	3.5
Research octane rating of gasoline, clear		87	90	93

Table 4.1 : Effect of operating Temperature of the reactor on the performance of a fluidized bed cracking; Feed: Mid – continent gasoil [94].

While increasing reaction temperature provides a number of benefits, cracking at higher temperatures also produces more gas and coke which are less desirable products. The optimum temperature is when just enough coke is formed on the catalyst so that the heat of combustion in the regenerator can provide all the heat required for reaction when the catalyst returns to the riser-reactor.

4.2.2 Dependent Variables

These dependent variables depend on the independent variables

4.2.2.1 Catalyst-To-Oil Ratio

Catalyst to oil ratio (C/O) is the ratio of kilogram per hour of catalyst circulated to kilogram per hour of fresh feed. It is a dependent variable, where it increases with an increase in reactor temperatures, and decreases with higher regenerator or feed preheat temperatures.

With UOP RxCat Technology, the riser Catalyst/Oil ratio is defined as the ratio of kilogram per hour of both regenerated and recirculated spent carbonized catalyst to kilogram per hour of fresh feed. This ratio can be directly manipulated by the amount of spent catalyst that is recirculated to the UOP MxR chamber without affecting the heat balance of the reactor/regenerator system. Based on Wolschlag and Couch[55], analysis, an increase in spent catalyst recirculation to riser at a constant reactor temperature will:

- Increase conversion.
- Decrease light gas yield.
- Increase C3 and C4 yields.
- Increase gasoline aromatic content.
- Increase gasoline yield.
- Decrease LCO.
- Increase regenerator temperature.
- Decrease C/O rate.

4.2.2.2 Regeneration Temperature

The coke yield of a given cat cracker is essentially constant. However, a more important consideration is delta coke. Delta coke controls the regenerator temperature. Reducing delta coke will lower the regenerator temperature. Many benefits are associated with a lower regenerator temperature. The resulting higher cat/oil ratio improves product selectivity and/or provides the flexibility to process heavier feeds. According to Sadeghbeigi, [74], there are many factors influencing delta coke. These are:

- Feedstock quality: The quality of the feedstock impacts the yield output. When the feedstock is filled with standard quality, the concentration of coke on the catalyst entering the regenerator will reduced. A feedstock containing heavy oil with higher concentration of coker gas oil will increase the delta coke as compared with a lighter residue free feedstock.

- Feed/catalyst injection: A well-designed catalyst injection system delivers a rapid and uniform vaporization of the liquid feed. It will lower the delta coke by minimizing non-catalytic coke deposition and reduce the deposits of heavy material on the catalyst. It will also reduce the catalyst injection time.
- Riser design. A well-designed riser will help decrease delta coke formation by reducing the back-mixing of already coked-up catalyst with fresh feed. The back-mixing causes unwanted secondary reactions which causes a lot of coke formation.
- Cat/oil ratio. An increase in the cat/oil ratio reduces the formation of delta coke by circulating out some coke-producing feed components over more catalyst particles thereby, lowering the intensity of coke on each particle.
- Reactor temperature. A change in the reactor temperature will also affect delta coke formation by encouraging cracking reactions over hydrogen transfer reactions. Hydrogen transfer reactions produce more coke than cracking reactions.
- Catalyst activity. An upsurge in catalyst activity will cause an increase in delta coke formation. As catalyst activity rises, the number of adjacent sites increases, which result to the increase of hydrogen transfer reactions to occur.

Chapter 5. Conclusion

5.1 Conclusion

The qualitative review presented here suggests that FCC catalysts and processes are very much flourishing. Although FCC has been practiced for nearly a century, and the field has been researched extensively, it is still the subject of academic and industrial inquiry. This is because new developments continually arise and ergo new challenges. The goal of these seemingly perpetual investigations (as is with most industrial processes) is the optimization of the process. Thus, avenues to maximize feed rate and conversion while constrained by feed quality, surrounding conditions and market demand are sought. As a result, the process has been and still continues to be the subject of research and development by industrialists and academics alike. In this report, a background of the FCC process is discussed, and we show by highlighting recent research activity that the field is still one that leaves room for improvement.

Despite the age, the research scope is still enormous due to changing fluid catalytic cracking feedstock, gradual shifts in market demands and evolved unit operations. This fluid catalytic cracking technology can be applied fully in grassroots units or partially, as applicable, in the revamp of existing units. Recent changes in the availability of feedstocks, including renewables and shale oils, and the trending demand for propylene, gasoline, and middle distillates require further developments in both catalyst and process.

Because Fluid Catalytic Cracking is among the largest catalytic refineries in the world, any improvement either in the process efficiency or product selectivity will be measured with exceedingly large factors. For example, burning coke from FCC amounts to at least 100 million tons of CO2 per year.
Researching into FCC catalysts and processes, as well as analytical methods, is highly relevant, as new way of combating today challenges will be welcomed.

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