A Study on Role of Catalyst used in Catalytic Cracking process in Petroleum Refining

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Abstract : Catalytic cracking has emerged as the most widely used petroleum refining process in the world. This paper highlights the importance of Catalytic Cracking and its main process called as FCC, and the different types of catalyst used in Fluid Catalytic Cracking. A typical barrel of crude is approximately 30% straight run gasoline, but demand is nearly 60% per barrel. This goes to show the need for an efficient catalytic cracking unit to increase gasoline production. Catalytic cracking reactions produce coke as a by-product through hydrogen disproportionation. One major problem associated with this process includes coking on the catalyst surface. This regeneration process is exothermic, whereas the cracking reactions are endothermic which allows for the unique opportunity of a heat-balanced reaction if the catalyst can be regenerated continuously. This also creates a problem of how to create a reactor that can continuously regenerate catalyst while capturing the heat generated to run cracking reactions. Therefore, the FCC unit was then developed to solve this problem in refining industries.

Keywords : *Crude, Cracking, FCC, catalyst, gasoline, exothermic.*

Introduction

Catalytic cracking process was developed in1920 by Eugene Houdry for upgradation of residue was commercialized latter in 1930[1]. Houdry process was based on cyclic fixed bed configuration. There has been continuous upgradation in catalytic in catalytic cracking process from its incept of fixed bed technology to latter fluidized bed catalytic cracking (FCC).The feed stock for catalytic cracking is normally light gas oil from vacuum distillation column. Catalytic cracking cracks low value high molecular weight hydrocarbons to more value added products (low molecular weight) like gasoline, LPG Diesel along with very important petrochemical feedstock like propylene, C_4 gases like isobutylene, iso-butane, butane and butane [2].

The principal catalytic processes used in crude oil refining include hydrocracking, Hydrotreating, and fluid catalytic cracking (FCC). Hydrocracking processes help convert residual oil into lower boiling point. These processes are particularly suited for feedstocks high in coke precursors (aromatics and polyaromatics and asphaltenes) sulfur, nitrogen, and metals.

The principal purpose of a cracking unit is to break high molecular weight hydrocarbons into smaller pieces of lower boiling point fractions, especially gasoline. Originally, thermal operations were used to crack heavy oil, but the discovery of a catalyst that gives a higher yield of gasoline with a higher octane number quickly brought on the use of catalytic cracking units. Today, the most commonly used catalytic cracking unit is the Fluid Catalytic Cracker or FCC.

The idea of cracking large hydrocarbon molecules into smaller ones began in the late 1800's when it was found that the large molecules broke into smaller molecules at high temperatures[3]. Development of cracking units revolutionized the refinery industry, which led to a rapid change in thinking about petroleum processing. An important discovery was that an aluminum chloride catalyst made the process easier by operating at lower temperatures and pressures. The McAfee Process, a unit that utilized the aluminum chloride catalyst, came on line in 1915, just two years later after the Burton thermal process. A major drawback to the McAfee Process was the loss of the expensive catalyst due to coking on the catalyst surface [4]. Thus, a catalyst regeneration system was the next step in developing a better cracking unit.

Catalytic cracking was pursued as a desirable process over thermal cracking for two major reasons. The first reason being that catalytic cracking gives more control over the products by breaking large hydrocarbons more towards the middle minimizing the yield of light hydrocarbons and maximizing the yield of gasoline [5]. Also, the gasoline produced in catalytic cracking is of much higher quality, namely a higher octane number. This is due to the skeletal isomerization, dealkylation of aromatics, and dehydrogenation reactions that take place in a reactor. Thus, the reason for the development of the catalytic cracker over thermal units is because of the higher yield and quality of gasoline.

Modern cracking uses zeolites as the catalyst. These are complex aluminosilicates, and are large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions. The alkane is brought into contact with the catalyst at a temperature of about 500°C and moderately low pressures.The zeolites used in catalytic cracking are chosen to give high percentages of hydrocarbons with between 5 and 10 carbon atoms - particularly useful for petrol (gasoline). It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.

Fluid catalytic cracking uses a free-flowing catalyst to help break apart molecules of heavy gas oil. The catalyst is actually a fine, slick powder that causes bonds within the hydrocarbon chain to snap [6]. Once the process is complete, the contents of the reaction chamber are spun into a cyclone that separates the heavier catalyst from the lighter hydrocarbons so that the catalyst can be reused.

Crude Oil Refining and Zeolites Catalyst

Crude oil consists of hydrocarbons with a range of molecule lengths and boiling points. This includes short chain, low boiling point / volatile gas such as propane through to long chain, heavy / high boiling point fractions such as bitumen [7]. The most valuable components of crude oil are the mid-range hydrocarbons which are used for gasoline and diesel. The term cracking refers to the breaking of the long chain hydrocarbon molecule into shorter fractions. The selectivity of the catalyst to produce molecules in the gasoline range is an important characteristic. Catalytic cracking was first employed in the 1940s to increase aviation fuel production and utilized natural clay minerals that contained aluminosilicate minerals that promoted the cracking of crude oil. Zeolites are alumina silicates with specific structures and it was the development of Synthetic (man-made) zeolites with unique structures and high selectivity for gasoline that revolutionized oil refining in the 1960s [8]. The active constituent of an FCC catalyst is the zeolite which is an alumino silicate consisting of Aluminium, Silicon and Oxygen atoms arranged in regular structures that form a porous framework of "cages" and "super cages". The caged structures vary according to the ratio of silica to alumina and the presence of other elements [9]. A number of structures are depicted below of which two are particularly relevant to FCC for crude oil refining; type Y and ZSM-5.

Catalytic cracking:

Catalytic cracking breaks up complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. Heavy hydrocarbons are exposed at high temperature and low pressure to catalysts which promote chemical reactions. This process rearranges the molecular structure; converting heavy hydrocarbon feed stocks into lighter fractions such as kerosene, gasoline, LPG, heating oil and petrochemical feed stocks.
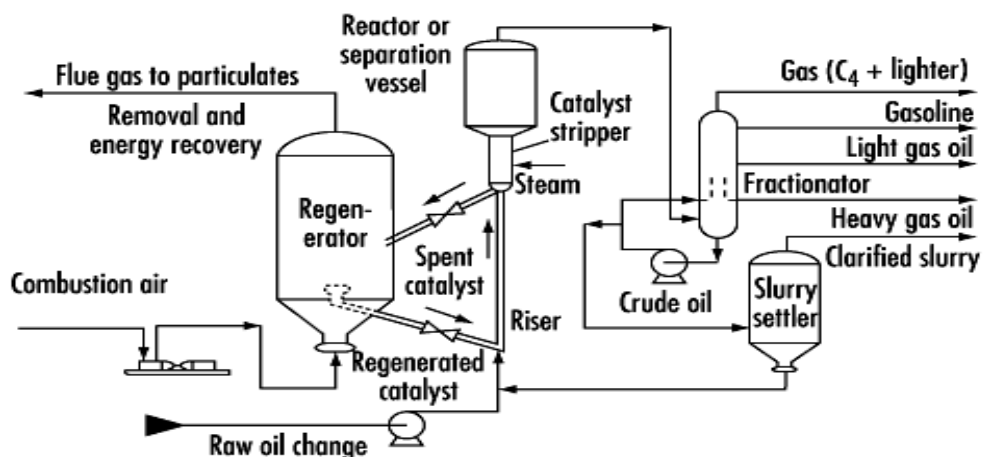
Source: OSHA 1996.

Figure.1. Schematic representation of Catalytic Cracking process

Catalytic methods

The catalytic cracking process involves the presence of acid catalysts (usually solid acids such as silica-alumina and zeolites) which promote a heterolytic (asymmetric) breakage of bonds yielding pairs of ions of opposite charges, usually a carbocation and the very unstable hydride anion. Carbon-localized free radicals and cations are both highly unstable and undergo processes of chain rearrangement, C-C scission in position beta as in cracking, and intra- and intermolecular hydrogen transfer. In both types of processes, the corresponding reactive intermediates (radicals, ions) are permanently regenerated, and thus they proceed by a self-propagating chain mechanism. The chain of reactions is eventually terminated by radical or ion recombination

Fluid Catalytic Cracking

Fluid catalytic cracking is now major secondary conversion process in Petroleum refinery since 1942[10]. There are more than 500 FCC units in world. The process provides around 50 percent of all transportation fuel and 35percent of total gasoline [11]. FCC is a multicomponent catalyst system with circulating fluid bed reactor system with reactor regenerator configuration.

The major reactions involved in catalytic cracking are:

- Isomerization
- Dehydrogenenation
- Hydrogen transfer
- Cyclization
- Condensation

Fluid catalytic cracking is used to increase the yield of gasoline light and heavy gas oils, naphtha, and some residual oil. Compared to the older thermal cracking processes, FCC produces hydrocarbons with high anti-knock properties, reduces the formation of olefinic hydrocarbons (which form gum deposits in gasoline), and reduces the formation of methane and C_2 hydrocarbon gases in favor $C_3$and C_4 hydrocarbons used in liquefied petroleum gas (LPG)[12]. The main limitation of the FCC process is it produces coke deposits that quickly deactivate the catalyst, thus requiring it to be regenerated. It is also poisoned by metals in the feed to the extent that it must be replaced on a daily basis. The FCC catalyst generally requires pretreatment of the oil by the other catalytic processes in order to minimize its exposure to metals [13]. FCC catalysts do not operate in a hydrogen environment and work by promoting cracking to produce branched hydrocarbons that are good in gasoline blends. However, even small quantities of metal deposits (on the order of hundreds of ppm) catalyze coke production, thereby reducing yield, and change the composition of the oil to one that is less favorable for gasoline blending.

Feed Stock

1. Vacuum gas oil (VGO), Hydro-treated VGO, Hydro-cracker bottom, Coker gas oil (CGO), Deasphaltedoil (DAO), Reduced crude oil (RCO), Vacuum residue (VR)
2. Typical feedstock consists of Vacuum and Atmosphere gas oil but may include other heavy stream.
3. Major contaminant in the feed includes carbon residue and metals.
4. While FCC process feed containing up to 4% Conradson carbon MSCC can process all kinds of feed**.**

Process steps in FCC Unit

Three basic functions in the catalytic cracking process are:

Reaction - Feedstock reacts with catalyst and cracks into different hydrocarbons;

Regeneration - Catalyst is reactivated by burning off coke; and recirculated to reactor

Fractionation - Cracked hydrocarbon stream is separated into various products like LPG and Gasoline, like light cycle oil and heavy cycle oil are withdrawn as side stream

**Cracking of Oil in Refineries**

The cracking process produces carbon (coke) which remains attached to the catalyst particle and rapidly lowers its activity. To maintain the catalyst activity at a usable level, it is necessary to regenerate the catalyst by burning off the coke with air. As a result, the catalyst is continuously moved from the reactor to the regenerator and back to the reactor. The fresh feed and recycle gas oil streams are preheated and enter the reactor at the base of the feed riser, where they are mixed with the hot, regenerated catalyst. The heat from the catalyst vaporizes the feed and brings it up to the desired temperature. The mixture of catalyst and hydrocarbon vapor travels up the riser into the reactor. The catalyst is a very fine particle; therefore the mixture of catalyst and vapor behaves like a fluid. The cracking reactions start when the feed contacts the hot catalyst in the riser and continues until the hot oil vapors are separated from the catalyst in the reactor. The catalyst leaving the reactor is called spent catalyst and contains hydrocarbons absorbed on the surface. These are removed by steam stripping before the catalyst leaves the reactor. The spent catalyst is separated from the hydrocarbons by a cyclone stripper with the hydrocarbons leaving the top of the reactor and the catalyst traveling down a pipe to the regenerator. The hydrocarbon vapors leaving the top of the reactor are sent to the main fractionator.

FCC Units in Oil Refineries

The catalysts are used in the FCC unit which consists of a mixing chamber where hot catalyst is contacted with a hydrocarbon stream at approximately 550 degree C and the mixture rises through a vertical pipe in which the cracking reaction occurs over a matter of seconds. The catalyst promotes several chemical reactions:

• Cracking – breaking of long chain hydrocarbons
• Isomerization – e.g. recombining light fractions into gasoline

The solid catalyst material is separated from the hydrocarbon gases in a chamber employing cyclones. The "spent" catalyst is directed to a regeneration unit where coke is burnt from the surface and the catalyst is pre-heated ready for return to the mixing chamber. It is in the regeneration step that Aluminium can be removed from the zeolite structure by contact with steam, which reduces the catalyst activity and weakens the physical structure of the zeolite. Lanthanum works to prevent this degradation of the catalyst. The future of Crude Oil refining faces a number of challenges which call for new and improved catalysts that operate under different conditions and promote different reactions [15].
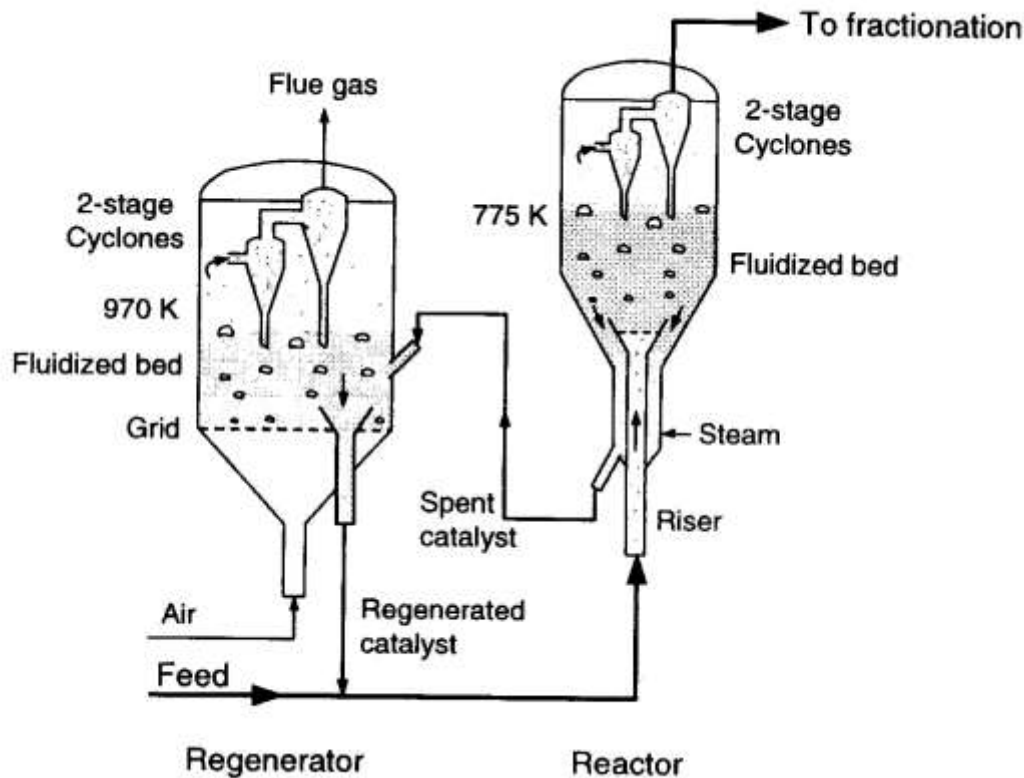
Figure: 2. Fluid bed catalytic Cracker along with Regenerator

Refineries vary by complexity; more complex refineries have more secondary conversion capability, meaning they can produce different types of petroleum products [16]. Fluid catalytic cracking (FCC), a type of secondary unit operation, is primarily used in producing additional gasoline in the refining process. Unlike Atmospheric distillation and Vacuum distillation, which are physical separation processes, fluid catalytic cracking is a chemical process that uses a catalyst to create new, smaller molecules from larger molecules to make gasoline and distillate fuels.

The catalyst is a solid sand-like material that is made fluid by the hot vapor and liquid fed into the FCC (much as water makes sand into quicksand)[17]. Because the catalyst is fluid, it can circulate around the FCC, moving between reactor and regenerator vessels. The FCC uses the catalyst and heat to break apart the large molecules of gas oil into the smaller molecules that make up gasoline, distillate, and other higher-value products like butane and propane. After the gas oil is cracked through contact with the catalyst, the resulting effluent is processed in fractionators, which separate the effluent based on various boiling points into several intermediate products, including butane and lighter hydrocarbons, gasoline, light gas oil, heavy gas oil, and clarified slurry oil.

The butane and lighter hydrocarbons are processed further to separate them into fuel gas (mostly methane and ethane), propane, propylene, butane, and butene for sale, or for further processing or use. The FCC gasoline must be desulfurized and reformed before it can be blended into finished gasoline; the light gas oil is desulfurized before blending into finished heating oil or diesel; and the heavy gas oil is further cracked in either a hydrocracker (using hydrogen and a catalyst) or a coker. The slurry oil can be blended with residual fuel oil or further processed in the coker. Carbon is deposited on the catalyst during the cracking process. This carbon, known as catalyst coke, adheres to the catalyst, reducing its ability to crack the oil. The coke on the spent catalyst is burned off, which reheats the catalyst to add heat to the FCC process. Regeneration produces a flue gas that passes through environmental control equipment and then is discharged into the atmosphere.

Typical operating parameter of FCC

Raw oil feed at heater inlet: 114 cubic meter /h

Furnace outlet temperature: 291°C
Reactor feed temperature: 371°C
Reactor Vapour temperature: 549°C

Major Products Obtained from FCC

- Light gas -H2, C1, and C2s
- LPG C3s and C4s – includes light olefins
- Gasoline C5+ high octane component for gasoline or light fuel
- Light cycle oil (LCO) blend component for diesel or light fuel
- Heavy cycle oil (HCO) Optional heavy cycle oil product for fuel oil or cutter stock
- Clarified oil (CLO) or decant oil: slurry for fuel oil
- Coke by-product consumed in the regenerator to provide the reactor heat demand

Fluidized-Bed Catalytic Cracking (FCC) is the most important and widely used refinery process for converting low value, heavy oils into more valuable gasoline and lighter products. The typical FCC process will convert 75% or more of the heavy oils into gasoline and lighter products. Originally, chemical cracking was accomplished by thermally heating the oil to extremely high temperatures, but the catalytic process has almost completely replaced thermal cracking. The catalytic process produces more gasoline with a higher octane value, and with less unsaturated compounds. The light gases produced by the catalytic process are sent to a Vapor Recovery Unit (VRU), where the olefins are recovered. The olefins will then be used as feed to an alkylation unit for conversion to high octane products.

FCC Catalysts

The development of active and stable FCC catalysts went parallel with the FCC design development. It was known, that for cracking of C-C bonds, the acid catalysts are needed. The first acid catalyst, tested for cracking of heavy petroleum fraction, was aluminium chloride. Silica-alumina catalysts were created and greatly improved over the natural clay catalysts. It was Houdry, who were the first used acid-activated bentonite as active acid catalyst for catalytic cracking. But the most significant advance came to light when zeolite catalysts were incorporated into the silica-alumina structures. Advances in catalysts have produced the greatest overall performance of FCC units over the last fifty years. After natural alumosilicates, also synthetic alumosilicates were prepared with outstanding cracking properties. Both natural and synthetic aluminosilicates (silica-alumina catalysts) were known for their Lewis acid sites. The early synthetic amorphous aluminosilicate catalysts contained about 13 % wt. of Al_2O_3 (low alumina), but when the zeolites were put into their structure, strong Bronsted acid sites resulted, with very easily accessible Lewis acid sites also present. The FCC-catalyst contains the active macro porous matrix, mesoporous synthetic silica-alumina, and zeolite[18]. The activated clay after calcinations also plays role as a binder and gives to FCC spheres strong resistance against attrition.

Modern FCC catalysts are fine powders with a bulk density of 0.80 to 0.96 g/cm^3 and having a particle size distribution ranging from 10 to 150 μm and an average particle size of 60 to 100 μm. The design and operation of an FCC unit is largely dependent upon the chemical and physical properties of the catalyst. The desirable properties of an FCC catalyst are:

- Good stability to high temperature and to steam
- High activity
- Large pore sizes
- Good resistance to attrition
- Low coke production

The matrix component of an FCC catalyst contains amorphous alumina which also provides catalytic activity sites and in larger pores that allows entry for larger molecules than does the zeolite. That enables the cracking of higher-boiling, larger feedstock molecules than are cracked by the zeolite. The binder and filler components provide the physical strength and integrity of the catalyst. The binder is usually silica sol and the filler is usually a clay (kaolin).Nickel, vanadium, iron, copper and other metal contaminants, present in FCC feed stocks in the parts per million range, all have detrimental effects on the catalyst activity and performance. Nickel and vanadium are particularly troublesome [19]. There are a number of methods for mitigating the effects of the contaminant metals

Regenerator Flue gas

The combustion in the regenerator of the coke on the spent catalyst may or may not be complete combustion to carbon dioxide CO_2. The combustion air flow is controlled so as to provide the desired ratio of carbon monoxide (CO) to carbon dioxide for each specific FCC design.

The combustion flue gas (containing CO and CO_2) at 715 °C and at a pressure of 2.41 bar is routed through a secondary catalyst separator containing swirl tubes designed to remove 70 to 90 percent of the particulates in the flue gas leaving the regenerator.

The expanded flue gas is then routed through a steam-generating boiler (referred to as a CO boiler) where the carbon monoxide in the flue gas is burned as fuel to provide steam for use in the refinery as well as to comply with any applicable environmental regulatory limits on carbon monoxide emissions. The flue gas is finally processed through an electrostatic precipitator (ESP) to remove residual particulate matter to comply with any applicable environmental regulations regarding particulate emissions. The ESP removes particulates in the size range of 2 to 20 µm from the flue gas. Particulate filter systems, known as Fourth Stage Separators (FSS) are sometimes required to meet particulate emission limits. These can replace the ESP when particulate emissions are the only concern.

Conclusion

Fluid Catalytic Cracking is one of the most important processes in Cracking of gaseous and liquid feedstock. It has become a new technology in the refineries with a wide range of catalyst used in FCC process. FCC feed crack 2% outside the catalyst pores and remaining inside the catalyst pores. FCCs and the riser crackers extensively use catalysts of variable pore size and active sites. One of the recommended catalyst and widely sued catalyst is Zeolite which prevents excessive coke deposition. The use of zeolite catalysts in today's petroleum refineries, and emphasizes some of the newer refining applications including gasoline sulfur removal and dewaxing via isomerization. Zeolite catalysts are also finding new applications at the refinery–petrochemical complex interface.

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