

**Lecture 5**

**Catalytic Cracking: Fluid  
Catalytic Cracking And  
Hydrocracking**

# LECTURE 5

## CATALYTIC CRACKING

Catalytic cracking process was developed in 1920 by Eugene Houdry for upgradation of residue was commercialized latter in 1930. 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, C4 gases like isobutylene, Isobutane, butane and butane. Main Catalytic Cracking Reaction is given in [Table M-VI 5.1](#).

### Main reactions involved in catalytic cracking are

- Cracking
- Isomerisation
- Dehydrogenation
- Hydrogen transfer
- Cyclization
- Condensation
- Alkylation and dealkylation

Major primary reactions taking place in catalytic cracking is given in Table

Paraffins                       $\longrightarrow$  Smaller paraffins + olefins  
 Alkyl naphthene             $\longrightarrow$  naphthene + olefin  
 Alkyl aromatic               $\longrightarrow$  aromatic + olefin  
 Multiring naphthene       $\longrightarrow$  alkylated naphthene with fewer rings

**Table M-VI 5.1 Main Catalytic Cracking Reaction**

<b>Paraffins</b>	<b>Cracking <math>\longrightarrow</math> Paraffins + Olefins</b>
<b>Olefins</b>	<b>Cracking <math>\longrightarrow</math> LPG Olefins</b>
	<b>Cyclization <math>\longrightarrow</math> Naphthenes</b>

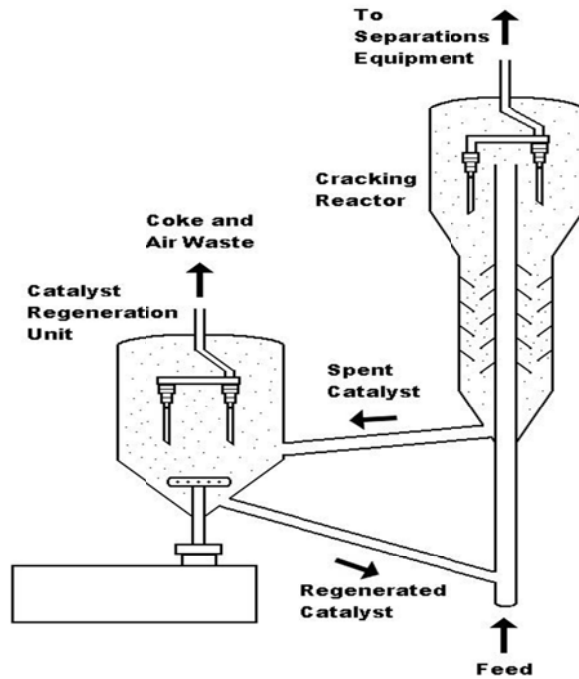
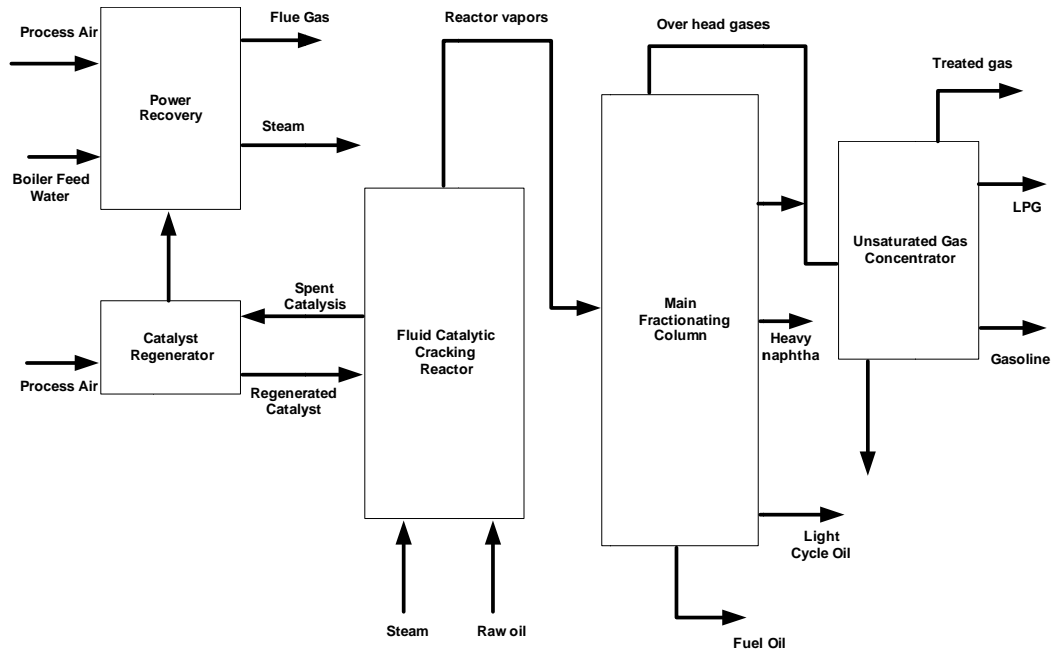
	<b>Isomerization</b> → <b>Branched Olefins</b> → <b>H Transfer</b> → <b>Branched Paraffins</b> <b>H Transfer</b> → <b>Paraffins</b> <b>Cyclization</b> → <b>Coke</b> <b>Condensation</b> → <b>Coke</b> <b>Dehydrogenation</b> → <b>Coke</b>
<b>Naphthenes</b>	<b>Cracking</b> → <b>Olefins</b> <b>Dehydrogenation</b> → <b>Cyclo- Olefins</b> → <b>Dehydrogenation</b> → <b>Aromatics</b> <b>Isomerization</b> → <b>Naphthenes with different rings</b>
<b>Aromatics</b>	<b>Side chain cracking</b> → <b>Unsubstituted aromatics + Olefins</b> <b>Trans alkylation</b> → <b>Different alkyl aromatics</b> <b>Dehydrogenation</b> → <b>Polyaromatics</b> → <b>Alkylation</b> → <b>Dehydrogenation</b> → <b>Coke</b> <span style="margin-left: 150px;"><b>Condensation</b></span>
<b>Hydrogen Transfer</b> → <b>Naphthene + Olefin</b> → <b>Aromatic + Paraffin</b>	

## FLUID CATALYTIC CRACKING

Fluid catalytic cracking is now major secondary conversion process in Petroleum refinery since 1942. there are more than 400 FCC units in world. The process provides around 50 percent of all transportation fuel and 35percent of total gasoline pool. Major land marks in the history of FCC has been:[Ghosh,2002]

- Introduction of zeolite catalyst during 1960 which has resulted in lower residence time
- Introduction of ultra stable Y-zeolite in mid 60's
- Switch over from bed cracking to riser cracking
- Introduction of large number of additives for boosting of gasoline octane/yield of light naphtha
- SOx control
- Nickel and vanadium passivation

FCC is a multi-component catalyst system with circulating fluid bed reactor system with reactor Regenerator system configuration. Figure M-VI 5.1 shows details of FCC process and FCC reactor.



**Figure M-VI 5.1: Fluid Catalytic Cracking Process and FCC Reactor**

## FEED STOCK

Vacuum gas oil (VGO), Hydro-treated VGO, Hydro-cracker bottom, Coker gas oil (CGO), De-asphalted oil (DAO), Reduced crude oil (RCO), Vacuum residue (VR)

- Typical feedstock consists of Vacuum and Atmosphere gas oil but may include other heavy stream.
- Major contaminant in the feed includes carbon residue and metals.
- While FCC process feed containing up to 4% Conradson carbon MSCC can process all kinds of feed.

## Process Steps

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

**Reactor and Regenerator Section:** Catalyst section consists mainly of the reactor and regenerator

- The feed to unit along with recycle streams is preheated to temperature of 365°C-370°C and enters the riser where it comes in contact with hot regenerated catalyst ( at a temperature of about 640-660°C. Finely divided catalyst is maintained in an aerated or fluidized state by the oil vapors.
- The catalyst section contains the reactor and regenerator & catalyst re circulates between the two.
- Spent catalyst is regenerated to get rid of coke that collects on the catalyst during the process. Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed. Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process

**Fractionation** - Cracked hydrocarbon stream is separated into various products. LPG and gasile are removed overhead as vapour. Unconverted product like light cycle oil and heavy cycle oil are

withdrawn as side stream. Overhead product is sent to stabilisation section where stabilised gasoline is separated from light products from which LPG is recovered.

### 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

### Product Obtained

- Light gas -H<sub>2</sub>, C<sub>1</sub>, and C<sub>2s</sub>
- LPG C<sub>3s</sub> and C<sub>4s</sub> – includes light olefins
- Gasoline C<sub>5+</sub> high octane component for gasoline pool or light fuel
- Light cycle oil (LCO) blend component for diesel pool 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

### FCC Catalysts

Major breakthrough in the catalytic cracking process was development zeolite catalysts which demonstrated vastly superior activity, gasoline selectivity, and stability characteristics compared to original amorphous silica alumina catalyst [Hemler & Smith, 2004].

Year	1950	1970	1990
Zeolite content, wt%	0	10	Upto 40
Particle density, g/cc	0.9	1	1.4
Relative Attrition Index	20	5	1

Today's FCC catalysts Porous spray dried micro-spherical powder

- Particle size distribution of 20 -120 micron & particle density ~ 1400 kg/m<sup>3</sup>

- Comprising Y zeolite in many derivatives of varying properties
- Supplied under various grades of particle sizes & attrition resistance
- Continuing improvement metal tolerance, coke selectivity

New breed of catalyst are high metal tolerance with high matrix catalyst having better accessibility, regenerability and strippability [[Ghosh, 2006](#)]

### **Options for Clean Fuel:**

For upgrading FCC products into acceptable blending components following three steps are being used [[Letzsch, 2005](#)];

- Severe hydro processing of feed to FCC
- Treating each of the products in hydrotreater
- Combination of both upstream and downstream processing

## **MODIFIED CATALYTIC CRACKING PROCESSES**

### **Resid FCC (RFCC) Process:**

The RFCC process uses similar reactor technology as the FCC process and is targeted for residual feeds greater than 4 wt-% Conradson carbon. A two stage regenerator with catalyst cooling is typically used to control the higher coke production and resulting heat.

### **Deep Catalytic Cracking (DCC):**

### **Milli Second Catalytic cracking (MSCC) Process:**

Improvements in riser termination devices have led to significant decreases in post-riser residence time and post-riser cracking. The benefits of shorter catalyst-and oil contact time have been lower dry gas yields, lower delta coke on catalyst and more selective cracking to gasoline and light olefins.

- Due to improvement in reactor design there is lower regenerator temperature and higher catalyst recovery.

## **Petro FCC Process**

The Petro FCC process targets the production of petrochemical feedstock rather than fuel products. This new process, which utilizes a uniquely designed FCC unit, can produce very high yields of light olefins and aromatics when coupled with aromatics complex. The catalyst section of the Petro FCC process uses a high-conversion, short-contact time reaction zone that operates at elevated reactor riser outlet temperatures

**Indmax Technology-** Residue to Olefin was developed by IOC R&D center and has been successfully commissioned in IOC Guwahati Unit [[Bhattacharya, 2001](#)]

Some of the special features of the technology are:

Operational features of Indmax technology

- Very high cat/oil ratio(15-25)
- Higher riser temperature (>550<sup>0</sup> C)
- Higher riser steam rate
- Relatively lower regeneration temperature.

### **Benefits**

- LPG 35-65 wt%
- Propylene 17-25 wt% feed
- High octane gasoline (95+)

### **Multifunctional proprietary catalyst**

- Higher propylene selectivity
- Superior metal tolerance
- Lower coke mate

## **Maximizing Propylene Output in FCC**

New FCC processes are being operated to maximize the yield of propylene due to growing demand of propylene. Significant scope exists in the refinery in Asia region to enhance the production of propylene in Asia region [[Ghosh, 2006](#)]. Maximizing propylene yield from FCC is typically accomplished by combining a low rare earth catalyst system with severe reaction condition [[Amano,T.,Wilcox,J. and Pouwels,C. “ Process and catalysis factors to maximize](#)



propylene output” [Petroleum Technology Quarterly 3, 2012,p.17](#)]. some of the olefin maximizing technology are deep catalytic cracking (DCC) based on riser bed catalytic cracking, Propylene –Max technology by ABBS Lummus global, Maxofin Process by Mobil-M.W. Kellogg

## HYDROCRACKING

The development of upgrading technology for heavier stocks having high sulfur, nitrogen and heavy metal (Ni, V) are becoming important. Hydrocracking is one of the most versatile processes for the conversion of low quality feed stocks into high quality products like gasoline, naphtha, kerosene, diesel, and hydrowax which can be used as petrochemical feed stock. Its importance is growing more as a refiners search for low investment option for producing clean fuel. New environmental legislations require increasing and expensive efforts to meet stringent product quality demands.

Hydrocracking processes uses a wide variety of feed stocks like naphtha, atmospheric gas oil, vacuum gas oils, coke oils, catalytically cracked light and heavy cycle oil, cracked residue, deasphalted oils and produces high quality product with excellent product quality with low sulfur contents. Comparison of catalytic cracking and hydrocracking is given in [Table M-VI 5.1](#).

The history of the hydrocracking process goes back to late 1920 when hydrocracking technology for coal conversion was developed in Germany. During World War II, two stage hydrocracking were applied in Germany, USA and Britain. However, real breakthrough in hydrocracking process was with the development of improved catalyst due to which processing at lower pressure. Hydrocracking can process wide variety of feedstocks producing wide range of products.

**Feed:** Straight run gas oil, Vacuum gas oils, Cycle oils, Coker Gas oils, thermally cracked stocks, Solvent deasphalted residual oils, straight run naphtha, cracked naphtha.

**Product:** Liquefied petroleum gas (LPG), Motor gasoline, Reformer feeds, Aviation turbine fuel, Diesel fuels, heating oils, Solvent and thinners, Lube oil, FCC feed

**Table M-VI 5.1: Comparison of Catalytic Cracking and Hydrocracking**

<b>Catalytic Cracking</b>	<b>Hydro-cracking</b>
Carbon rejection	Hydrogen addition
Riser-regenerator-configuration	Downflow packed bed
LPG/gasoline	Kerosene/diesel
Product rich in unsaturated components	Few aromatics, low S- and N-content in product

### **Recent Development Hydrocracking:**

There has been continuous development in the hydrocracking technology both in process and catalyst. Some of the important development in hydrocracking has been mild hydrocracking and resid hydrocracking. Mild hydrocracking (MHC) is characterized by relatively low conversion (20-40%) as compared to convention hydrocracking which give 70-100% conversion of heavy distillate at high pressure. MHC route produces low sulphur (10 ppm sulphur as desired by future diesel specification) diesel. New mild hydrocracking route produces 10 ppm sulphur diesel which is produced by hydro-cracking under mild pressure. MHC allows increasing diesel production through VGO hydro-conversion.

The yield of middle distillates obtained from hydro cracker is much more than that obtained from other processes also, hydro cracker does not yield coke or pitches as by product. The increased demand for environmentally acceptable products forced the refiners to accept stringent specifications for gasoline & diesel necessitating the use of hydrocracking technology to limit sulphur & aromatic in petroleum products. No post treatment is required for the hydro cracker products.

### **Hydro-treatment & Hydrocracking Catalyst**

Hydrocracking processes involved two types of catalyst:

- Hydro pretreatment catalyst
- Hydrocracking catalyst

## **Hydrotreating (Pretreat) Catalyst**

The main objective of pretreat catalyst is to remove organic nitrogen from the hydro cracker feed allowing

- (i) Better performance of second stage hydrocracking catalyst, and
- (ii) The initiation of the sequence of hydrocracking reactions by saturation of aromatic compounds

Pretreat catalyst must have adequate activity to achieve above objectives within the operating limits of the hydrogen partial pressure, temperature and LHSV.

## **Hydrocracking Catalyst**

Hydrocracking catalyst is a bi-functional catalyst and has a cracking function and hydrogenation-dehydrogenation function. The former is provided by an acidic support whereas the latter is imparted by metals. Acid sites (Crystalline zeolite, amorphous silica alumina, mixture of crystalline zeolite and amorphous oxides) provide cracking activity. Metals [Noble metal (Pd, Pt) or non noble metal sulphides (Mo, Wo or Co, Ni)] provide hydrogenation dehydrogenation activity. These metals catalyze the hydrogenation of feedstocks making them more reactive for cracking and hetero-atom removal as well reducing the coke rate

Zeolite based hydrocracking catalysts have following advantages of greater acidity resulting in greater cracking activity; better thermal/hydrothermal stability; better naphtha selectivity; better resistance to nitrogen and sulphur compounds; low coke forming tendency, and easy regenerability.

## **Once through Hydrocracking Process**

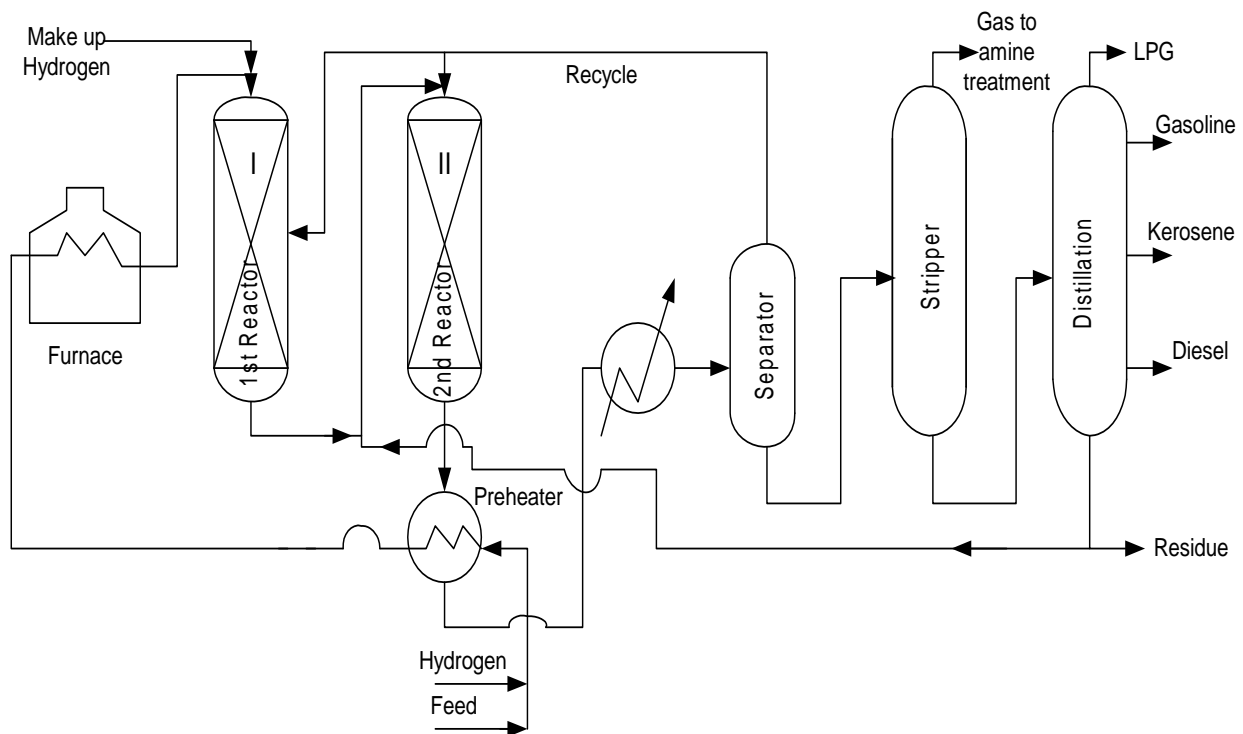
The unit consists of the following sections:

- Furnace
- First stage Reactor section
- Second stage Reactor section
- High pressure separator
- Fractionation Section
- Light Ends Recovery section

In single stage process both treating and cracking steps are combined in a single reactor. Single stage hydrocracking flow diagram is show in [Figure M-VI 5.3\[ Mall,2007\]](#).

In this process the feed along with recycle unconverted residue from the fractionator is first hydro-treated in a reactor and then the combined stream gases are fed to second reactor where cracking takes place in the presence of hydro-cracking catalyst.

In the single stage process the catalysts work under high  $H_2S$  and  $NH_3$  partial pressure.



**Figure M-VI 5.3: Once Through Hydrocracking**

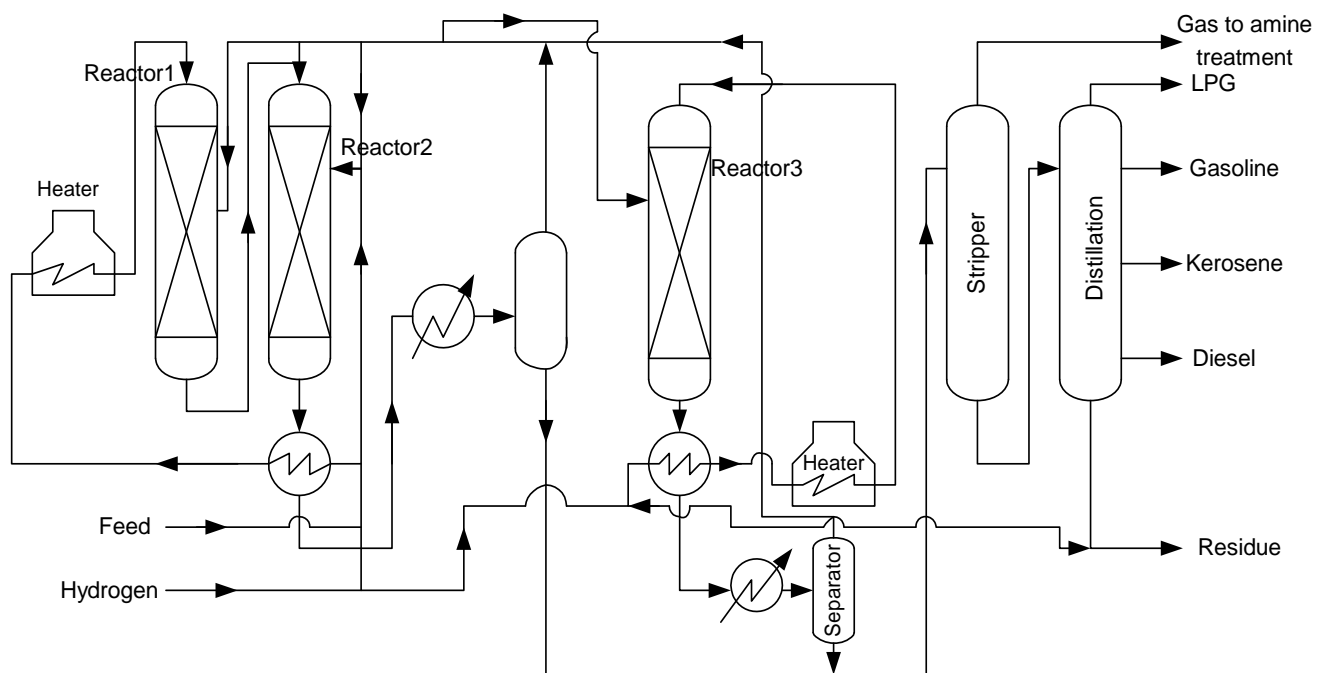
## Two Stage Hydrocracking Process

The unit consists of the following sections:

- Furnace
- First stage Reactor section.
- Second stage Reactor section
- Third stage reactor
- Fractionation Section

- Light Ends Recovery section

Preheated feed is first hydro treated in a reactor for desulphurization and denitrogenation in presence of pretreat catalyst followed by hydrocracking in second reactor in presence of strongly acidic catalyst with a relatively low hydrogenation activity. In the first stage reactor the sulphur and nitrogen compounds are converted to hydrogen sulphide and ammonia with limited hydrocracking. The two stages process employs interstage product separation that removes  $H_2S$  and  $NH_3$ . In case of two stage process, hydrocracking catalyst works under low  $H_2S$  and  $NH_3$ . Process flow diagram for two stage hydrocracking process is shown in [Figure M-VI 5.4 \[ mall 2007\]](#).

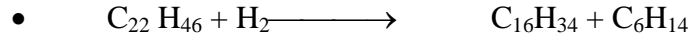


**Figure M-VI 5.4: Two Stage Hydrocracking Process**

## HYDROCRACKING CHEMISTRY

Hydrocracking process is a catalytic cracking process which takes place in the presence of an elevated partial pressure of hydrogen and is facilitated by bio-functional catalyst having acidic sites and metallic sites. During hydrocracking process hydrotreating reactions and hydrocracking reactions are two major reactions which take place.

A typical hydrocracking reaction is as follows.



Various hydrotreating reactions are hydrodesulphurization, denitrogenation, hydrodeoxygenation, hydro metallization, olefin hydrogenation partial aromatics saturation.

Various hydrocracking reactions are splitting of C-C bond and or C-C rearrangement reaction (hydroisomerisation process) Hydrogenation and dehydrogenation catalyst.

### **Effect of Operating Parameters**

#### **Various operating parameters affecting hydrocracking are**

- Reaction temperature
- Hydrogen partial pressure
- Hourly feed velocity of the feed
- Hydrogen recycle ratio

Temperature increase in temperature accelerates cracking reaction on acid sites and displaces the equilibrium of hydrogenation reactions towards dehydrogenation. Too high temperature limits the hydrocracking of aromatic structure [Raseev, 2003].

The pressure influences significantly the equilibrium of dehydrogenation-hydrogenation reactions that takes place on the metallic sites. The increase in pressure for a given molar ratio  $H_2$ /feed corresponds to increase in the partial pressure of hydrogen, will produce an increase the conversion of the aromatic structures to saturated products which will improve the quality of jet fuel, diesel fuel and oil with very high viscosity index.

***Effect of Feedstock:*** a higher content of aromatic hydrocarbons requires higher pressure and higher hydrogen/feed ratio, the lowest possible temperature and a higher hydrogen consumption of hydrogen and the severity of the process

***Effects of Feed Impurities:*** Hydrogen sulphide, nitrogen compounds and aromatic molecules present in the feed affect the hydrocracking reactions. Increase in nitrogen result in lower conversion.

Ammonia inhibits the hydrocracking catalyst activity, requiring higher operating temperatures. Polymeric compounds have substantial inhibiting and poisoning effects. Polynuclear aromatics present in small amount in the residue deactivate the catalyst.

### **Effect of various parameters on catalyst life:**

<b>Variable</b>	<b>Change Effect on catalyst life</b>
Feed rate	Increase-Decrease
Conversion	Increase-Decrease
Hydrogen partial pressure	Increase-Increase
Reactor pressure	Increase-Increase
Recycle gas rate	Increase -Increase
Recycle gas purity	Increase -Increase

## **HYDRO-CRACKING TECHNOLOGY PROVIDER**

- Chevron: Isocracking
- UOP: Uni-cracking
- IFP: Hydrocracking
- B.P. U.K: Hydrocracking
- Shell: Hydrocracking
- Standard Oil: Ultracracking
- Linde: Hydrocracking
- Union Oil Co.: Uni-cracking

## **CATALYST DEACTIVATION**

Catalyst activation may occur due to coke deposition and metal accumulation.

Coke Depositions may be due to condensation of poly-nuclear and olefinic compounds into high molecular weight which cover active sites. Metal Accumulation occurs at the pore entrances or near the outer surface of the catalyst

## **CATALYST REGENERATION**

Catalyst regeneration is done by burning off the carbon, and sulphur and circulation of circulate nitrogen with the recycle compressor, injecting a small quantity of air and maintaining catalyst temperature above the coke ignition temperature.

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