

# **Hydrocracking of Vacuum Residue into Middle Distillates using Slurry Phase Technology**

*Project semester report submitted in partial fulfilment of the  
requirement for the degree of BE (Chemical Engineering)*

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# **CERTIFICATE FROM INDUSTRY**

# DECLARATION

I, **Abhinav Mishra** hereby declare that the project work entitled “**Hydrocracking of Vacuum Residue into Middle Distillates using Slurry Phase Technology**”, submitted to **Thapar Institute of Engineering & Technology, (Deemed to be University), Patiala (INDIA)**, for the partial fulfilment of the requirement for the degree of **Bachelor of Engineering in Chemical Engineering** is an authentic record of my work carried out at **CSIR – Indian Institute of Petroleum, Dehradun** during the period **10<sup>th</sup> June – 10<sup>th</sup> December 2019**, under the supervision and guidance of **Dr. S.K.Maity, Senior Principal Scientist, CSIR – Indian Institute of Petroleum, Dehradun**.

I declare that this written submission represents my own ideas and wherever the ideas of other's are included, it has been adequately cited with the original source of reference. I also declare that this work has not been submitted elsewhere for a degree or diploma at this or any higher education institute.

Signature of the Student with Date

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Certified that the above statement made by the student is correct to the best of my knowledge and belief. I have checked all the requirements, formatting and other essential components of this report and it is as per the guidelines and standards.

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# ABSTRACT

Petroleum Products (fossil fuels) like petrol, diesel and kerosene are the major requirements in any industry but today they are rapidly depleting. The stockpile, true to form is diminishing step by step and actually the interest has quickly expanded.

To meet the current and future demands of humanity the petrochemical industry is working continuously on different fields and is coming up with a number of technologies to make alternate forms of fuels. One of these technologies is the up-gradation of vacuum residue (VR) obtained from the vacuum distillation unit at temperature greater than 565°C. VR is the waste obtained after the crude oil at different temperatures and extracting every possible useful middle distillate (for e.g. petrol, diesel, kerosene, jet fuel). There are various different techniques to upgrade this VR namely, **Delayed Coking, Vis-breaking, Fluidized Catalytic Cracking and Hydrocracking.**

This project is based on the hydrocracking method wherein, the VR is thermally cracked at very high temperature and pressure in presence of Hydrogen gas. Hydrocracking is used for:

- Prevention of arrangement of polycyclic aromatic compounds if feedstock has a high paraffinic content.
- Reducing tar arrangement and pollutions
- Preventing the development of coke on the catalyst
- Achieving high cetane number fuel
- Converting Sulphur and Nitrogen present in the feedstock to  $H_2S$  and  $NH_3$  (Sulphur being one of the major constituents of the VR,  $H_2S$  formation is a very important part)

In hydrocracking, the technology used in the project is called slurry hydrocracking as the project title suggests, slurry phase technology. This means that the feed to be processed in the reaction is not a regular fluid but slurry which constitutes the vacuum residue mixed with the catalyst and this blend is called slurry.

The VR is of not much use currently, but if it gets converted into useful fuel while also being economically feasible, it can reduce the high dependency on fossil fuels and can make them last for longer time.

The project consists of reactions performed on a slurry hydrocracker pilot plant and a high batch reactor where different conditions i.e. temperatures and pressures are set and reactions are performed accordingly. The feed used in the project is vacuum residue

provided by Bharat Petroleum Corporation Limited and so it is called BPCL-VR. The catalyst used in the reactions is developed in the residue up-gradation laboratory itself (called IIP Catalyst informally) and is called NiMo catalyst (because it contains nickel and molybdenum). The major goal of the project is to check the quality of the product achieved at every condition and also deduce the best condition to perform the cracking at a larger (industrial) scale.

Apart from this project work other reactions have also been performed in this time period which were very different from the highly viscous BPCL-VR and different catalysts developed by BPCL and HPCL have also been used as per the requirements. Another side work was a reaction using delayed coking technology for which the set-up was also made. These tasks were a training on how different types of feeds should be handled for residue upgradation purpose.

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# Chapter 1

## INTRODUCTION

### 1.1 Brief Information about IIP



**Figure 1.1.1** CSIR – Indian Institute of Petroleum

CSIR – Indian Institute of Petroleum is one of the main constituent labs of the Council of Scientific and Industrial Research (CSIR). Set up in 1960, the establishment is committed to multidisciplinary territories of innovative work in the downstream area of hydrocarbon and related industry. It has dedicated, experienced and quality staff and is equipped with comprehensive state of the art R&D facilities including pilot plants.

The institute undertakes R&D work in areas of petroleum refining, natural gases, alternative fuels, and petrochemical utilization of petroleum products in IC engines and mechanical and household ignition. The establishment likewise offers specialized and investigative types of assistance to oil refining and related industry including innovation move for creating novel, state of art technologies and products.

The foundation keeps up its driving situation in conduction preparing programs for specialized work force from refining industry, petrochemical plants, car segment, power plants and other related client businesses.

CSIR-IIP is committed to provide globally competitive technologies and services for hydrocarbon and related industries. This is accomplished through all out quality administration and by

foreseeing and surpassing the desires for clients through development, collaboration and responsibility. The securing of ISO-9001 confirmation by the foundation in 1998 and its accreditation to ISO: 9001-2008 demonstrates responsibility towards quality administrations and the executives.

## **1.2 Quality Policy of IIP**

Indian Institute of Petroleum is committed to develop into an internationally reputed R&D centre of excellence for providing globally competitive technologies and services for hydrocarbon and related industries.

In its quest for scientific and technological innovations, marketing and managerial competence, and continual improvement, it has set the following quality objectives.

- Development of innovative technologies and petroleum products
- Providing science based technical support to industry
- Customer satisfaction through committed quality, cost and deliveries
- Emphasis on Knowledge Management (KM)

## **1.3 Major Achievements of IIP**

Institute has developed a larger number of processes and technologies. Thirty eight advancements having authorized limit around 25 million tons for each annum moved to the business.

- Almost each processing plant in the nation has innovations authorized by the foundation
- Test systems created for assessment of oil based goods remembered for BIS details
- Established worldwide tie-ups for contract research and specialized administrations.
- The intellectual property rights protected with the patents filed and sealed in India and abroad.
- Based on the research work conducted in the institute PhD degrees awarded to the fifty research fellows and Scientists of the institute by various universities.
- A large number of research papers published in reputed International and National Journals.

## **1.4 Various Divisions at IIP**

IIP has three major divisions:

### **1.4.1 R&D Division**

- Analytical Sciences
- Automotive Fuels and Lubricants Application
- Bio Fuels
- Chemical and Material Sciences
- Distillate and Heavy Oil Processing
- Light Stock Processing
- Material Resource Efficiency
- Separation Processes
- Tribology and Combustion
- Upstream and Wax Rheology

### **1.4.2 Support Division**

- Engineering Service Division

### **1.4.3 Administration**

- Administration
- Finance and Accounts
- Store and Purchase

## **1.5 Major Future Programs**

The future programs of IIP will be delivered towards the development of petroleum refining process, catalysis, speciality chemicals, fuel quality and emission studies, alternate sources of hydrocarbons, development of fuel-efficient industrial and domestic appliances and microbial enhanced recovery of oil.

## **1.6 Background and Objectives of the Project**

### **1.6.1 Distillate and Heavy Oil Processing Division (DHOPD)**

Distillate and Heavy Oil Processing is one of the significant procedures in refining to get greatest net revenue. CSIR – IIP is working right now its commencement. This division mainly is working in several different sub areas such as,

- Coking
- Vis-breaking
- Fluid Catalytic Cracking (FCC)
- Residue Hydroprocessing

Recently an indigenous technology called “Soaker internal vis-breaking” has been commercialized in three Indian refineries, HPCL (Vizag), IOCL (Mathura) and IOCL (Haldia). This is an example of outcome from the research work in this division. The division’s focus is not limited to industrial research work but also the implementation commercially.

Slurry hydrocracking is the most upcoming process and the division is working with Bharat Petroleum Corporation Limited, Hindustan Petroleum Corporation Limited and Engineers’ India Limited for the development of a technology to convert the most contaminant feed to the valuable products.

### **1.6.2 Hydrocracking**

Hydrocracking is a procedure utilized in oil processing plants for changing over the high-bubbling constituent hydrocarbons in oil rough oils to progressively important lower-bubbling items, for example, gas, lamp oil, and fly fuel and diesel oil. The process takes place in a hydrogen-rich atmosphere at elevated temperature and pressure. The procedure fundamentally, breaks high-bubbling, high sub-atomic weight hydrocarbons into lower-bubbling, lower weight olefinic and sweet-smelling hydrocarbons and afterward hydrogenates them. Any sulfur and nitrogen present in the hydrocracking feedstock are to an enormous degree, additionally hydrogenated and structure vaporous hydrogen sulfide ( $\text{H}_2\text{S}$ ) and smelling salts ( $\text{NH}_3$ ) which are along these lines expelled. The outcome is that the hydrocracking items are basically liberated from sulfur and nitrogen debasements and comprise for the most part of paraffinic hydrocarbon <sup>[1]</sup>.

### **1.6.3 Project Objectives**

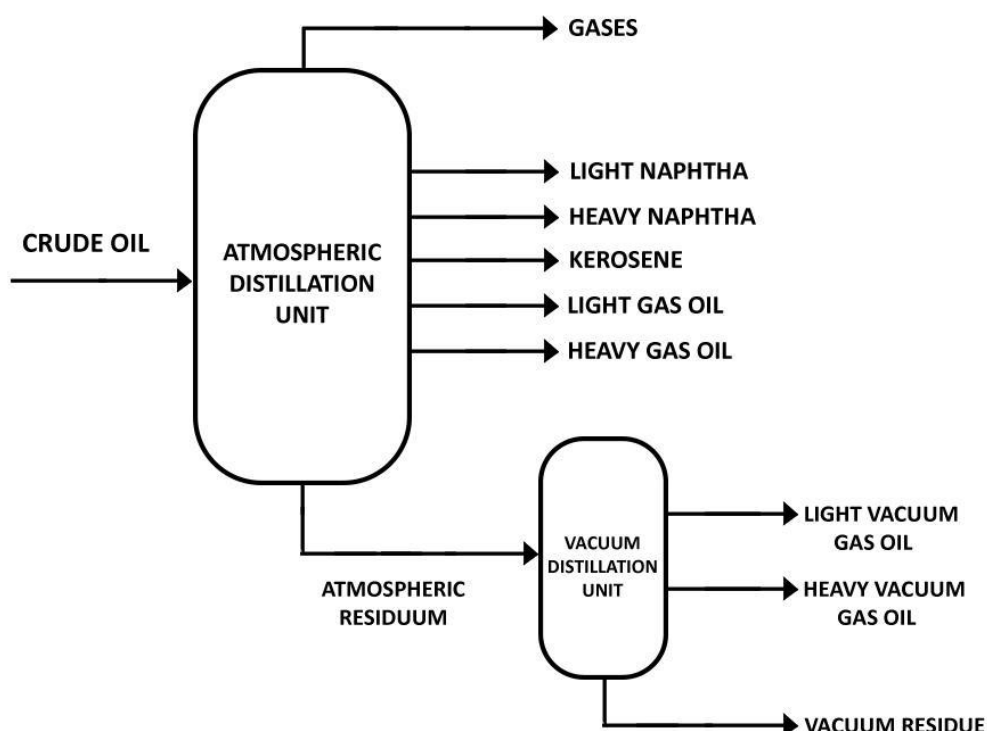
The objectives during the project semester was to get the optimal conditions for carrying out the hydrocracking of vacuum residue into useful middle distillates using the slurry phase technology by comparing the products generated for different parameters. This included working on both, a batch reactor and a slurry hydrocracker pilot plant. After performing reactions and getting the products as the output, the next task was to conduct different analyses on the products and understand the need of these analyses since these results were used for the comparison of the products in different respects. While doing all this, minimizing the coke formation after the reaction was one of the most important aspects.

## Chapter 2

# LITERATURE REVIEW

### 2.1 Vacuum Residue

Each refinery has two important distillation units-crude distillation and vacuum distillation unit. Vacuum residue is the end product from the vacuum distillation unit.



**Figure 2.3.1** Atmospheric Distillation Unit, Vacuum Distillation Unit and Different Type of Products

Distillation of crude oil is first done in the atmospheric distillation unit where it is heated up to 370°C as shown in figure 2.3.1. Vaporized liquid is condensed on different alternate plates based on their boiling points and sent for further refining whereas the heaviest fraction that remains at the bottom of the distillation column is collected as atmospheric bottoms which can be further used as feed in the vacuum distillation column. A similar process is carried out in the other fractionator but under reduced pressure (1-20<sup>th</sup> of the atmospheric pressure also called vacuum pressure). Under this low pressure, the atmospheric residue vaporises at a certain temperature below its cracking point (the actual temperature range is 370°C - 565°C which the atmospheric pressure equivalent of the



cracking point under vacuum conditions) and sent for further processing. End products that get collected are refinery gas, higher naphtha, heavier naphtha, kerosene and the bottom end product as the vacuum residue [2].

Vacuum residue is a dense black highly viscous liquid which is semi-solid at room temperature having a pour point of 60 °C - 70 °C. It is the heaviest of distillation cuts also known as the bottom of the barrel. It has a high content of sulphur, asphaltene, and metals like vanadium and nickel as compared to other feedstock. The ash content of VR feedstock is totally dependent on mineral matter originating from crude oil and the efficacy of upstream desalination. Due to the presence of high percentage of contaminants, the processing of this vacuum residue is very challenging task for the refinery.

## **2.2 Slurry Hydrocracking**

The hydro-conversion process of heavy oil and residue is one of the main processes for converting a heavy carbonaceous feedstock to lower-boiling products. In general, the heterogeneous catalysts like sulphides of cobalt, molybdenum, or nickel supported by alumina or silica-alumina are used in the process. The constituents with higher molecular weight in heavy oil and residue deposit on the surface of the catalyst and they block the pores of the catalyst which results in the rapid decline of the hydrogenation activity [3]. Eventually, the coke and metal impurities which get removed from the heavy oil and residue deposit on the surface of the catalyst and result in deactivation of the catalyst. The rapid increase in the pressure drop of the bed layer makes it difficult to maintain normal operations, which becomes more serious when the feedstock contains higher metal and carbon residue. Thereby, the catalysts display short service life and bad operation stability leading to frequent shut-downs.

To solve these problems, slurry-phase hydrocracking processes which adopt unsupported dispersed catalyst have been developed. The technology has the same processing as thermal cracking, with the difference being that, the feed, hydrogen gas and the dispersed unsupported catalysts together go through the reaction. The reaction is mainly about thermal cracking while the purpose of the catalyst and hydrogen was inhibition of coke formation by hydrogenating the coke precursor and removing heteroatoms. The catalyst acts as a supporter of coke and therefore, reduces coking of the reactor wall [4]. Accordingly, slurry-phase hydrocracking has adopted single use catalyst without taking

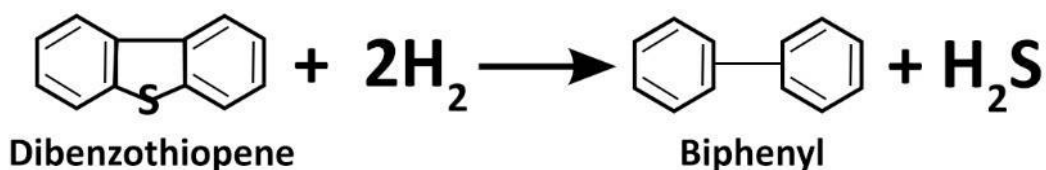
care of the deactivation, thus being able to process inferior residues containing sulphurous compounds in exceedingly large quantities, nitrogenous compounds, and high molecular weight organometallic complexes.

## 2.3 Chemical Reactions

Chemical reactions in a hydrotreater reactor takes place in liquid phase. The residual feed is saturated with hydrogen gas, which makes the molecules absorb on the catalyst surface where the reaction takes place. This exothermic reaction allows the breakdown of molecules in the feed that contains sulphur, nitrogen, and heavy metals (Nickel and Vanadium) <sup>[5]</sup>.

### 2.3.1 Hydrodesulphurization

It is the most common of hydrotreating reactions. Hydrocarbon molecules containing sulphur comes in a multitude of forms, and varies in levels of difficulty when attempting to separate sulphur from the base molecule. Dibenzothiophene (DBT) molecules are very difficult to separate due to the ring structure, attached on both sides.



**Figure 2.4.1** Hydrodesulphurization Reaction of Dibenzothiophene

The figure above is a pictorial representation of the reaction that occurs in the hydrotreating process to desulfurize the dibenzothiophene molecule. The reaction produces the by-product of hydrogen sulphide, which must be removed in a downstream separation process to complete the reaction <sup>[6]</sup>.

### 2.3.2 Hydrodenitrogenation

It starts with the aromatic ring being saturated to naphthalene. The saturation step places the particle in equilibrium and sets the rate at which the reaction happens. Hydrocarbon atoms containing nitrogen are arranged into two primary categories; basic nitrogen and neutral nitrogen. Since nitrogen compounds are much more complex than sulphur compounds, denitrification is more difficult than hydrodesulphurization.

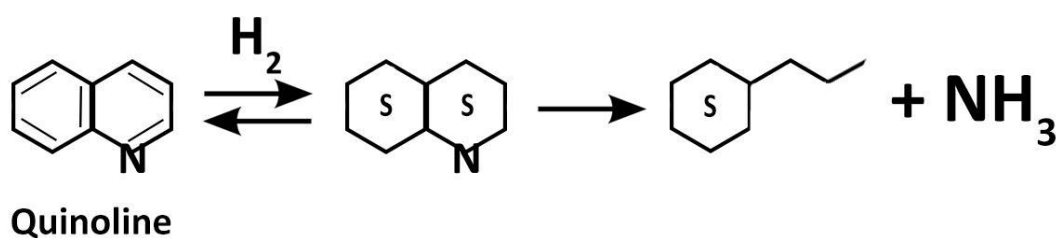


Figure 2.4.2 Hydrodenitrogenation of Quinoline

The figure depicts the reaction occurring in the hydrotreating process to remove nitrogen from quinoline molecule. This reaction gives the by-product of ammonia which should be removed in a downstream separation process to complete the reaction.

### 2.3.3 Hydrodemetallization

It is the removal of metals which include nickel and vanadium. In the event that these metals aren't removed, they can be noxious to downstream reactant units and posture ecological issues. Vanadium is a lot simpler to expel when contrasted with nickel, be that as it may, both require a permeable impetus to permit section of the enormous atoms that contain the metals. Previously, a purifier would work a hydrotreater until the impetus has spent its ability to retain overwhelming metals. The cutting edge hydrotreater has an exceptional impetus or swing reactors to process crudes with high metal substance, creating longer unit run times since the reactor can be exchanged.

## 2.4 Removal of Asphaltene

Asphaltene constituents are a solvency class that is accelerated from oil, substantial oil and bitumen and in this way don't have a solitary, interesting structure or explicit atom weight. At the point when scattered in oil, asphaltene constituents apparently increment

oil consistency and antagonistically influence the profitability of oil wells and additionally the methods for refining. Inferable from the adjustments in the piece of oil just as varieties of temperature, pressure, oil might be upset and asphaltene constituents are probably going to be hastened. The partition of asphaltene constituents, or coke is a typical issue in oil refining <sup>[7]</sup>. This problem has increased due to the need to use heavy crude oil as refinery feedstocks for processes such as slurry hydrocracking. While most of procedures are intended to split asphaltene constituents to fluid and coke, preheating feedstocks preceding infusion into the reactor can well change the character of the responded asphaltene item and postpone the beginning of coking. Any procedure that changes the dissolvability or dispersability of asphaltene constituents in oil can instigate asphaltene partition. This is unmistakably apparent while changing the working weight which can replace the unrefined petroleum thickness adequately enough to cause asphaltene constituents to flocculate and isolate from the feedstock. This is because of transforming from an oversaturated condition to beneath the air pocket purpose of the feedstock <sup>[8]</sup>.

## **2.5 Effects of Reaction Conditions**

Reaction conditions (i.e. temperature and pressure) play a vital role in determining the quality of product formed after hydrocracking.

### **2.5.1 Effect of Temperature**

The most important parameter for the hydrocracking process is the temperature. It is a known fact that conversion of heavy distillates into middle distillates requires treatment at high temperature. In more technical language, it can be said that the yield of gas, light oil (naphtha and diesel) and coke increases with increase in the reaction temperature, while the yield of liquid  $C_{5+}$  decreases.

However the yields of gas, naphtha and coke in slurry phase hydrocracking are higher than that in thermal cracking. The small hydrocarbon molecules are produced through the cracking of bigger hydrocarbon, which gets promoted by the increase in the temperature of reaction which results in the increase of gas and light oil yields. Also, the high reaction temperature facilitates the condensation of hydrocarbon free radical resulting in increased coke yield. Hydrogen gets easily split into hydrogen free radicals on the active site of a

dispersed Mo catalyst, thus the high concentration of a hydrogen free radical could inhibit condensation of a hydrocarbon free radical. Therefore, the yields of gas, naphtha, in slurry phase hydrocracking [16] are higher than that in thermal cracking at the same temperature [9].

### **2.5.2 Effect of Pressure**

As compared to the significance of temperature in hydrotreating, the effect of pressure does not play a very major role. All the major aspects for hydrocracking gets fulfilled at the higher temperature itself. But, as the temperature of the reaction keeps on increasing, the coke formation in the reaction keeps on increasing. That's why hydrocracking requires processing at high temperature as well high pressure.

The yields of coke decreased gradually with the increase of hydrogen pressure. In the slurry phase hydrocracking process, the large carbon chains break to form smaller molecules by hydrogenolysis and side-chain breaking. Under a high hydrogen pressure, more hydrogen molecules participate in slurry-phase hydrocracking of the Vacuum Residue. Thus, during the thermal cracking and condensation if hydrocarbon would be further suppressed by high hydrogen pressure, it results in the decreasing yields of coke. Both, hydrodesulphurization and hydrodenitrogenation rates increase with the increase of hydrogen pressure. Furthermore, the hydrodesulphurization rate increases rapidly in the beginning and then decreases with the increase of hydrogen pressure unlike hydrodenitrogenation rate which increased continuously.

## **2.6 Process Description**

The procedure starts with the feed being preheated in the bottoms/feed exchanger. The feed at that point enters a feed flood drum and is then directed into the charge pumps, the charge pumps pressurize the feed dependent on the response pressure. The feed is then combined with preheated hydrogen gas which are further sent for preheating purposes. Once the final heating is done, i.e. the reaction temperature is achieved, the mixture is charged into the reactor. Once into the reactor, the catalytic reaction takes place where the catalyst's contribution comes into picture which is thoroughly discussed in section 2.2. After the reaction, the reacted mixture is sent into the hot separator (high temperature high pressure separator).

The hot separator cuts the overwhelming and light response items and recuperates the hydrogen flashed off during the let-down from the reactor. The overwhelming item fluid is let-down in pressure and is gathered in the substantial item tank. The light item fluid is cooled and wash water is added to retain smelling salts and hydrogen sulfide. The mixture is further cooled before entering the low temperature high pressure separator using HHP Separator Cooler (Chiller). The cold separator isolates the vapour, sour water and light hydrocarbons <sup>[10]</sup>.

## Chapter 3

# EXPERIMENTATION

### 3.1 Instrumentation

A number of instruments and methods were used for the product analysis after the reaction to get results like the sulphur amount, micro carbon residue amount, kinematic and dynamic viscosity etc. of the products which were used for comparing the products formed in both, the reactor and the hydrocracker plant.

#### 3.1.1 Viscometer

Viscometer is used to measure the kinematic and dynamic viscosity of the fluid. The viscometer setup in the lab is Anton Paar Stabinger Viscometer which can measure viscosity for a wide range i.e. 1 to 5000 cP [24]. This viscometer measures kinematic and dynamic viscosity along with the density of the fluid sample. It takes a shot at the guideline dependent on Couette (stream of a thick liquid in the space between two surfaces, one of which is moving digressively comparative with the other) and has an incorporated thickness estimating cell. The little thickness estimating cell contains a cylinder which pivots at a consistent speed and is loaded up with test liquid. The sample's shear forces drive the rotor while magnetic effects retard its rotation.



**Figure 3.1.1** Anton Paar Stabinger Viscometer

Shortly after the measurement starts, the rotor reaches equilibrium speed. This speed is a measure of the fluid's viscosity [25]. Kinematic viscosity is automatically calculated from the dynamic viscosity and density of the sample. The method of finding the viscosity in this instrument is also simple because we need to inject the sample, set the temperature in which we need to measure the viscosity and enable it. The sample is heated and cooled to the desired temperature and the results are displayed on the screen. The results shown in the machine are dynamic viscosity, kinetic viscosity and density mPa.sec, mm<sup>2</sup>/sec and g/cc respectively. The analyses were done at 15.6 °C, 30 °C and 40 °C for the batch reactor but in the case of the hydrocracker it was only done at 15.6 °C and that's why the comparison table has values mentioned at 15.6 °C only.

### 3.1.2 XRF Sulphur Analyser

Sulphur plays an important part in the coke composition and coke formation after the reactions. The more the amount of H<sub>2</sub>S formed during reaction, the more is the cracking. High concentration of sulphur could lead to extreme puffing and increase the CTE of the coke. Sulphur concentration needs to be optimized by mixing feeds. For the evaluation of sulphur concentration in feed and liquid products of the hydrocracking reactions, Oxford Lab-x3500 sulphur analyser is used. It is a very easy to operate device and can be used by non-technical staffs also.



**Figure 3.1.2** XRF Sulfur Analyser

As the name suggests, the principle used in the instrument is spectroscopy which means that, x-rays are used to excite the electrons in the sample, spectrum is formed when electrons return to the initial stage and this spectrum is used to determine the sulphur concentration of the sample. To install the samples, a special cup made of polyfilm (Poly-

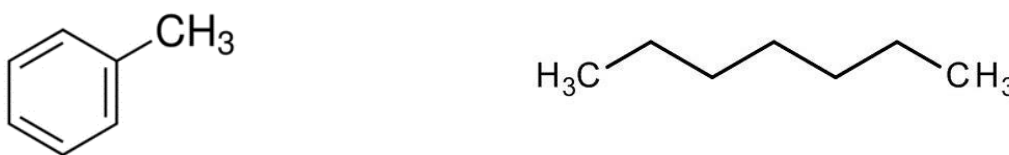


M) is used, which is the only tedious task in the analysis. The films are very thin so the cups need to be made gently. Then the cup with the sample is placed inside the instrument. The instrument has calibration done for different ranges to measure sulphur accordingly. The different ranges are 0-5%, 0-1%, 0-1000ppm and etc. The sample used for the analysis can be recovered and the instrument can be easily calibrated using standard sulphur solution.

### 3.1.3 Measurement of Asphaltene and Coke

Asphalt is one of the main constituents of the Vacuum Residue and other bottom of barrel products. Meanwhile, after treating the feed with hydrogen, coke formation in the product happens. To estimate the concentration of asphaltene and coke, the methods are almost the same, the only difference being the solvent used in both cases are different.

Asphaltene and coke analysis is done together for the detection of asphalt and coke in any product sample. The compounds used in the analysis are n-heptane and toluene <sup>[29]</sup>.



**Figure 3.1.3** Structural Formula of Toluene and n-heptane

For doing the analysis, first 2gm sample of the liquid product in a beaker. Then 80ml of n-heptane is measured in a measuring cylinder and it is mixed with the 2gm sample. Then the solution is placed on a heating plate which is placed inside the fuming hood. The temperature of the plate is set to 110°C and the RPM is set to 200. After 1-2 hours of heating the solution is taken out for filtration. A filter paper is taken and setup on a conical flask which is attached to the vacuum pump. The using a dropper, the solution is poured on the filter paper. The filter paper is left for drying and then weighed. This value is the amount of heptane insoluble compounds which here are asphalt and coke. The same analysis is done using toluene instead of n-heptane and this gives the amount of toluene insoluble compound which is coke. This gives the amount of coke in the sample. Subtracting this value from the heptane insoluble content gives the amount of asphalt in the sample. The calculated amount is the concentration in 2gm of product. Further using unitary method the concentration of asphalt and coke is calculated in the total liquid product <sup>[30]</sup>.

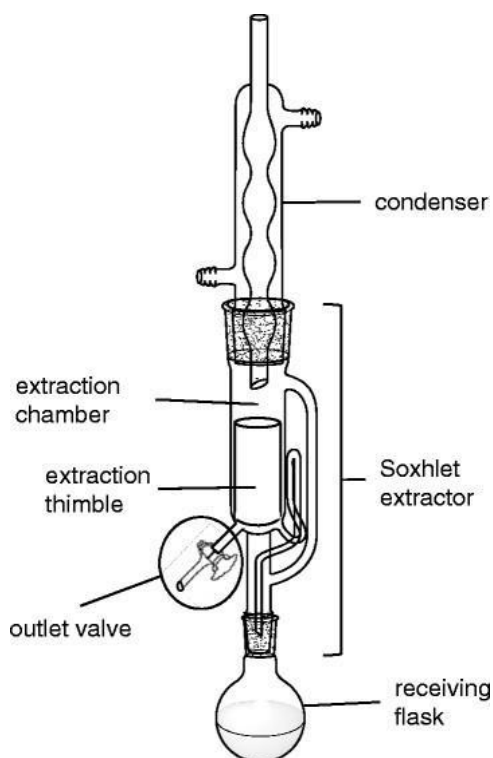
### 3.1.4 Soxhlet Extraction

Soxhlet extraction is a continuous solid/liquid extraction. This process in the lab is done to calculate the amount the coke obtained from solids. A solid which contains the material to be extracted is placed in what is called a thimble.



**Figure 3.1.4** Thimbles inside a soxhlet extractor

A thimble is made out of a material which will contain the solid but allow liquids to pass through which is very similar to a filter paper. It contains the material and is placed in the soxhlet extractor. An organic solvent is then heated at reflux (n-heptane was the organic solvent used here). As boiling happens, the vapour rises up and gets condensed by the condenser. The condensed solvent then fills up the thimble and when it we filled with enough solvent, it goes back down into the container of n-heptane.



**Figure 3.1.5** Soxhlet Extraction Schematic Setup

The process happens over and over until all the material to be extracted from the solid in the sample is extracted into n-heptane. After the extraction is complete, the non-soluble of the extracted solid remains in the thimble and is usually discarded [26].

### 3.1.5 Gas Chromatography

A gas chromatograph (GC) is an analytical tool for measuring the content of different parts of a sample. Gas chromatography is the analysis performed by a gas chromatograph.

The rule of gas chromatography is that the sample arrangement infused into the gadget enters the gas stream, which move the sample to a different cylinder called the "segment". (Helium or nitrogen, known as the transporter gas, is utilized.) Different parts are isolated inside the section. The finder gauges the quantity of parts leaving the section. To gauge an example with an obscure fixation, a standard model with a realized focus is brought into the gadget. For concentration calculation, the standard sample maximum retention time (display time) and area were compared with the test sample [27].



**Figure 3.1.6** Scion 456-GC

In practice, the current is on and the gas flow opens with helium, nitrogen, and hydrogen. We must wait until the setpoint temperature device is reached. The gas model is introduced into the device and a fast RGA method is applied to analyse the gas samples. Different gases can be detected at different retention times already calibrated according to the gases commonly formed in the samples. The run is usually 6 minutes and the next month requires some time to re-balance the device. This process is followed by successive runs of the same gas sample to accurately identify the gases in the sample. When it is first closed, the temperature should be cooled by the ColdDown method. The obtained data are represented in a mole percentage, where we need the mass percentage. The next one

requires a proper conversion. It is necessary to consider temperature and pressure conditions when converting. The mass percentage is the required data to determine the mass balance of the entire process.

Therefore, all equipment must be careful because it is an expensive device and needs to be used carefully. Proper gas supply at the right flow rate is essential for accurate identification of gases. Some gases are not detected by the low volume of the gas sample. Protection of the device against pests is also recommended, as it opens the back of the device.

### 3.1.6 Micro Carbon Residue (MCR) Analysis

Micro Carbon Residue is the carbonaceous residue remaining after the oil's evaporation and pyrolysis. MCR is an important parameter for the determination of the coke forming tendency of the product obtained from the reaction using some of its amount as the sample. The device used in the lab to measure the carbon residue is the Micro Carbon Residue Tester ACR-M3.



**Figure 3.1.7** Micro Carbon Residue Analyser

ACR-M3 is a tester to be used for the determination of the amount of carbon residue formed after evaporation and pyrolysis of petroleum material under certain conditions and is intended to provide some indication of the relative coke forming tendency of such materials. A weighed quantity of sample is placed in a glass vial and heated to 500°C under an inert atmosphere (nitrogen gas) in a controlled manner for a specific time. Small vials are installed with sample in them and machine is started under controlled flow of

nitrogen gas to meet inert conditions. After the analysis, the vials are weighed and calculations are done for MCR. The formula to calculate MCR is simple:

$$\left( \frac{\text{weight loss}}{\text{initial weight of sample}} \times 100 \right)$$

There is a chance for error to occur because of the inaccuracy in the device so as a precaution, 2-3 samples are installed for each product and the average value is considered for the final result. Since the analysis happens at a higher temperature, after the analysis is done the instrument is left to cool down. After this, the vials are stored into a desiccator to avoid error due to humidity. The nitrogen flow to maintain the inert condition is controlled at 0.6L/min.

### 3.1.7 Simulated Distillation

Simulated distillation (SIMDIS) by gas chromatography (GC) is often used in the petrochemical industry to analyse the composition of an oil or gas sample by measuring the boiling point range distribution of the sample components. By understanding the boiling point range distribution of petrochemical products one can be able to select the proper methods to process the feed stocks, for process control, for contaminant identification and for development of new test methods. SIMDIS methods are analytical methods, developed through consensus and prescribed by the American Society of Testing and Materials International (ASTM) to provide standardizations.

As per the project requirements, the SIMDIS analysis was done for all the products formed after the reaction as well as the feed. The feed's SIMDIS was done for determination of residue conversion in the product above 565°C. The product were sent for the evaluation for the characterisation of the fuel i.e. what all fractions are present in the product oil. The temperatures at which the products were analysed are <150°C where naphtha is found, 150°C-350°C where AGO (atmospheric gas oil) is found, 350°C-565°C where VGO (vacuum gas oil) is found and finally >565°C which is the vacuum residue. After the analysis, a formula was applied for the calculation of the residue conversion (in percentage) in the product.

$$\left( \frac{\text{g of 565°C + hydrocarbon in Feed} - \text{Vg of 565°C + hydrocarbon in Product}}{\text{g of 565°C + hydrocarbon in Feed}} \times 100 \right)$$

## 3.2 Reactions Performed in the Slurry Hydrocracker Pilot Plant

The first part of the project was performing reactions on a pilot plant which is the slurry hydrocracker. The setup consists of a feed tank where the VR is fed and a feed pump is attached after the tank which is used to control the flow of feed. External pipelines to feed gases into the plant are attached. There are preheaters on for the feed and the other for the gas. A mass flow controller (MFC) is attached to the gas lines to control the gas flow. The reactor in which the feed is treated is called bubble slurry reactor. There are separators and tanks to collect the products. There are vents to release the gases and a gas flow meter to measure the flow of the gas and to calculate the pressure gradient. There is a cooling system (chiller) to condense the gas and collect it in liquid form.

Most of the plant is controlled using a computer. The plant is configured using a PLC (programmable logic control) while the PLC is controlled on the computer using SCADA (Supervisory Control and Data Acquisition). This system is developed by Honeywell.

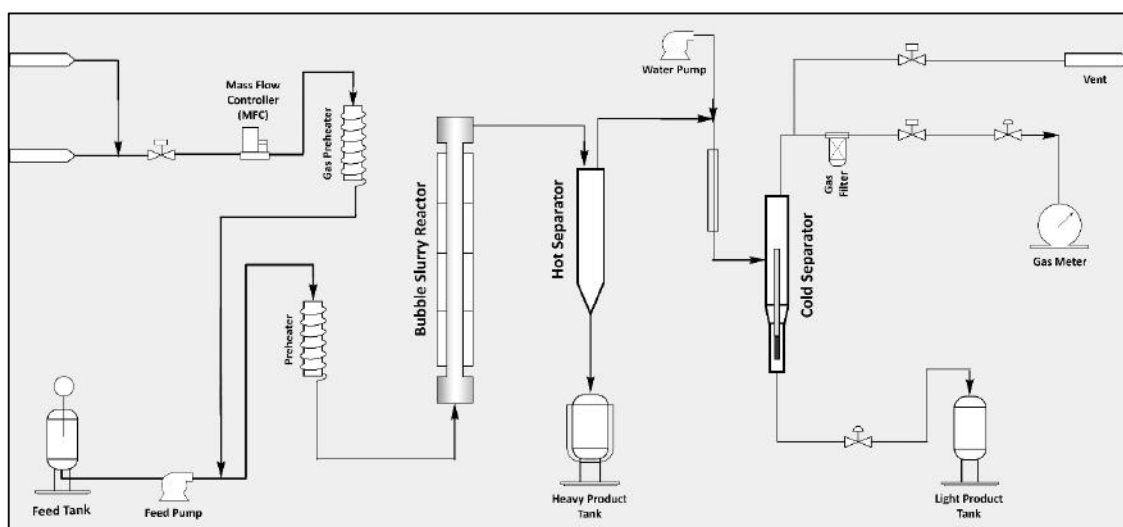


Figure 3.2.1 PFD of the Slurry Hydrocracker Pilot Plant

The reaction conditions for the plant runs were 150 bar pressure and 410°C temperature, 150 bar pressure and 420°C temperature, 150 bar pressure and 430°C temperature and 175 bar pressure and 430°C temperature. The feed used was BPCL-VR and catalyst was Nickel Molybdenum (NiMo) catalyst. The amount of feed was approximately 2500 grams (because of high viscosity and high temperature the amount of feed couldn't be kept constant every time). Therefore the catalyst was added accordingly using the formula **'0.75 grams of catalyst for every 100 grams of feed'**. Prior to the reaction the vessels (tanks) and pipelines in the plant are to be completely cleaned and there should be no

leakage in the lines to avoid any mishaps. The packing of feed into the feed tank is done one day prior to the reaction. The feed is heated at 150°C in a high range oven and then fed into the feed tank along with the calculated amount of catalyst. Stirrer is then attached with the feed tank and is locked. The reaction on the next day is started early morning. The heating of feed is started and once the temperature is achieved to make the feed movable, the feed is moved forward using the feed pump. The gas flowing through the pipe is sent in at the desired flow rate and before mixing it with the slurry feed it is heated in the preheater.

The gas mixed with the feed is sent to the second preheater where the reaction temperature is achieved and the feed is further sent to the reactor where the hydrocracking of the VR takes place. The duration of the reaction is 8 hours. There are two different products achieved in the process, a heavy product containing the heavy fraction of the distillate and the light product consisting of the lighter oil fractions. The heavy product is separated using the hot separator (high pressure high temperature separator) in the heavy product tank. This consists of the fraction having high boiling point. The remaining reacted part forms into gas which is also needed to be collected. For this purpose a cold separator (high pressure low temperature separator) is used where the gas is sent. Using an additional cold water supply (from chiller using a water pump.) the temperature of the gas is reduced to bring it in liquid form and then it is collected in the light product tank.

Once the 8 hour reaction time is complete the product from the different tanks and the lines are collected along with the unprocessed feed, the reactor drain and feed drain. The total gas in and out is also noted. 3 hours into the reaction, 5-10 bar of gas sample is collected in a gas sampler and the GC analysis of the sample is done. Similarly 2 and 4 hours after the first analysis, the GC analysis is again done. After the products gets collected the plant is cooled down. Next day, the light product which is mixed with water because of the effect of the chiller is filtered manually. Then a sample of the product is needed for further analysis, for this heavy and light product are mixed and after that different analyses like, simulated distillation, asphalt analysis, and MCR etc. is done. Finally after all the different analyses on the product, the data is compiled together and mass balances are done. The mass balances in the case of reactions in the plant were done in two different types. One included the reactor and feed drain while the other excluded them. The data used for comparison will be the one excluding these products.

After the reaction is performed and products are collected from the tanks, cleaning of the plant is needed to be done for further reactions. First of all, clean diesel is run throughout

the reactor to clear the leftover reacted and unreacted feed to clean-up the lines. After this nitrogen gas is run through the lines and heat is provided. This process clears up the leftovers by burning up the residue and venting them out from vents. Then a leak test is performed at joints and then the reactor is ready for the next reaction.

There are a number of components in the plant which are required to make it run. The pressure gauge is important for maintaining the pressure likewise the MFC is needed to control the flow of the gas supplied. There are different valves to control the flow between lines. Essentially, a valve manages, controls or coordinates the progression of a liquid by opening, shutting, or halfway deterring liquid stream. In basic words, a valve is a mechanical gadget that controls the stream and weight of a liquid inside a framework or procedure for example it controls stream and pressure. Selection of valves depends upon the requirements which can be related to the economics or the operation of the process plants <sup>[17]</sup>. Some commonly used valves are, gate valves, check valve and butterfly valve.

The following significant substance, a mass stream controller (MFC) is a gadget used to quantify and control the progression of fluids and gases. A mass stream controller is structured and aligned to control a particular sort of fluid or gas at a specific scope of stream rates. The MFC can be given a set-point from 0 to 100% of its full scale go however is regularly worked in the 10 to 90% of full scale where the best exactness is accomplished. The gadget will control the pace of stream to the given set-point. MFCs can be either simple or advanced. An advanced stream controller is normally ready to control more than one sort of liquid while a simple controller is restricted to the liquid for which it was adjusted.

All mass stream controllers have a delta port, an outlet port, a mass stream sensor and a corresponding control valve. The MFC is fitted with a shut circle control framework which is given an info signal by the administrator (or an outside circuit/PC) that looks at to the incentive from the mass stream sensor and alters the corresponding valve in like manner to accomplish the necessary stream. The stream rate is determined as a level of its aligned full scale stream and is provided to the MFC as a voltage signal. Mass stream controllers require the stockpile gas or fluid to be inside a particular weight territory <sup>[18]</sup>. Low weight will keep the MFC from liquid and cause it to neglect to accomplish its set-point. High weight may cause sporadic stream rates.

Critical creation techniques and alignment empower an estimating precision of  $\pm 0.2\%$  at standard stream rate and approx.  $\pm 0.5\%$  over the whole estimating range.



The significant favorable position and the prevalence of volumetric gas meters over other estimation standards, which decide gas volume utilizing auxiliary quantifiable factors, for example, speed, heat limit, hot-wire opposition or comparative, is the immediate estimation of volume. That implies that the condition and the piece of the gas have no impact on the estimation precision.

Correcting factors which consider gas type, temperature, dampness and so forth are in this way a bit much. It ought to be noticed that with other, non-volumetric estimations the precision given for the estimation must be accomplished if the adjusting factors for the genuine gas condition or gas blend are actually known.

As prior referenced, the feed and gas are warmed in preheaters. A preheater is a gadget that is utilized to expand the temperature of oil fluids just as gaseous petrol before taking care of them into further procedure. For instance, fuel oil or heater oil is warmed to a specific temperature before it is utilized as a feedstock in the reactor <sup>[20]</sup>. Keeping up a specific measure of fuel temperature guarantees its total burning in this manner lessening contaminations. Essentially, flammable gas is warmed to a specific temperature to long separations in pipelines. A basic case of a preheater is the warmth exchanger utilized in the ignition office of an evaporator or a heater to warm up the feedstock fuel to a specific temperature before taking care of it into a kettle or a heater. The essential target of utilizing a preheater for preheating the fuel is to expand the warm proficiency of the procedure and diminish the carbon discharges when a preheated fuel is copied. Aside from preheating the fuel for burning purposes, there are numerous occasions where pipelines that transport overwhelming unrefined petroleum are preheated <sup>[21]</sup>. This is done with the goal that the thick and exceptionally gooey substantial unrefined petroleum can stream effectively in a pipeline starting with one area then onto the next.

At the point when the light item is conveyed forward, a chiller is expected to condensate it, and to store in the item tank. Chillers are utilized in an assortment of utilizations where chilled water is flowed through procedure gear. The capacity of a chiller is to move heat starting with one area then onto the next spot. In many procedure cooling applications, a siphoning framework flowed cool water or a water/glycol arrangement from the chiller to the procedure. The cool liquid evacuates heat structure the procedure and warm liquid comes back to the chiller. The procedure water is the methods by which warmth move from the procedure to the chiller. Chillers contain a substance compound, called a refrigerant. There are numerous kinds of refrigerants relying upon the applications yet they all work on the essential rule of pressure and stage change of the refrigerant from a

fluid to a gas and back to a fluid. This procedure of warming and cooling the refrigerant and transforming it from a gas to a fluid and back again is known as the refrigeration cycle <sup>[23]</sup>.

### **3.3 Reactions Performed in the Batch Reactor**

The aim of the experiment was to conduct the reactions in the reactor at the same conditions and to understand the differences between the products formed in the batch reactor and the slurry hydrocracker. Also, the aim was to find the optimum condition to perform the reaction. Successive runs in the batch reactor were executed keeping the feed constant i.e. 200gm BPCL-VR mixed with 1.5gm NiMo catalyst. The different reaction conditions at which the feeds were processed are 150 bar pressure and 410°C temperature, 150 bar pressure and 420°C temperature, 150 bar pressure and 430°C temperature and 175 bar pressure and 430°C temperature. Respective products from the reactions were then collected in airtight bottles of 250ml capacity. Their different properties and yield quality were then studied. Analysis for viscosity, density, asphaltene content, coke content, micro carbon residue, product distribution, and residue conversion were then done for these products.

The figures 3.3.1 shows the front and side angles of the batch reactor in which the reactions were performed. This is a high pressure high temperature reactor which has a gauge reading of 344 bar pressure on it. The pressure gauge is a very important component of this reactor. In general definition, pressure gauge is a fluid intensity measurement device. Pressure Gauges are required for the set-up and tuning of liquid power machines, and are crucial in investigating them. Without pressure checks, liquid force frameworks would be both flighty and temperamental. Checks help to guarantee there are no breaks or weight changes that could influence the working state of the water driven framework.

The hydraulic system is designed to work in a set pressure range so the gauge must be rated for that range. Hydraulic pressure gauges can be used to measure up to 10,000 psi, but the maximum hydraulic pressure is mostly in the 3,000 to 5,000 psi range <sup>[22]</sup>. Hydraulic gauges are often installed at or near the pump's pressure port for indication of system pressure, but can be installed anywhere on the machine where pressure needs to be monitored—especially if sub-circuits operate at a pressure rate different from pump pressure, such as after a reducing valve.

The pressure gauge contains an important part within in which is the rupture disc which is a non-reclosing pressure relief safety device that protects a pressure vessel from overpressurization or potentially damaging vacuum conditions. It is a type of sacrificial part because it has one-time use membrane that fails at predetermined differential pressure. The material used to make it is usually metal but nearly any material can be used to suit a particular application. Rupture discs provide instant response to an increase or decrease in system pressure, but once the disc has ruptured it will not reseal.



**Figure 3.3.1** Parr Batch Reactor with 1.8L capacity

The reaction setup consists of this single unit only. The capacity of the reaction vessel for the reactor is 1.8L. The controller attached with the reactor is a 4848B controller manufactured by Parr Instruments itself. Its features are PID programming with auto-tuning capability for precise temperature and minimum overshoot. It has the capacity of motor speed control, a high or low force radiator switch, lockout hand-off and reset for over temperature insurance and a discretionary extension modules for weight and high temperature alert controller.

The motor speed during the reactions was set in the range of 700-800 RPM and the reaction time was 3 hours. The vacuum residue feed is highly viscous therefore to pour it into the reactor vessel, the viscosity needs to be reduced and hence it needs to be heated. Using a high range oven at 150°C -170°C the feed is first heated for 4-5 hours. Meanwhile the reactor vessel is cleaned and 1.5gm of the catalyst is measured separately. Once the feed gets heated it is taken out of the oven and 200 grams of the feed is poured

into the vessel. Then the catalyst is added into it which forms the slurry. The vessel is then joined with the reactor and then fixed by tightening the screws. The tightening of the screws were needed to be done properly in order to avoid leakage. Therefore the tightening was first done using a simple wrench and again done using a torque wrench.

Once the reactor is ready, the nitrogen connection to the reactor is turned on and 150 bar of nitrogen gas is added into the reactor. Then it is left overnight and if there's only a minute change in the pressure reading next day, this denoted there is no leakage and the reaction is set to be done. The nitrogen gas is then released and the reactor is flushed twice using hydrogen gas. After this, using the ideal gas equation of  $P_1/T_1 = P_2/T_2$  hydrogen is added into the reactor according to the desired pressure and temperature. The heater is then attached to the reactor vessel and heating is turned on. There is a high range and a low range heater integrated into it and first the low range heater is turned on using the PID controller and the set point is kept at 200°C. When the temperature nears 200°C the high range heater is turned on and the set point is kept according to the reaction condition (i.e. 410°C, 420°C or 430°C). Once the desired temperature is reached, the stirrer is turned on and the timing is noted. This marks the beginning of the reaction and henceforth 3 hours later the reaction is turned on.

Starting from addition of hydrogen to the completion of the reaction at intervals of 15-20 minutes the temperature and pressure of the reaction is noted. Once the reaction is complete the reactor is left isolated for the temperature to decrease. Once the temperature falls below 250°C, the setup and the chiller are turned off and overnight the temperature comes at the room temperature. The next day the final temperature and pressure are noted and using a gas sampler, around 5-10 bar of gas sample is taken for the GC analysis. Rest of the pressure is then released and the reactor is flushed using nitrogen. The screws are then loosened and the vessel is opened. An external exhaust pipe is kept near the reactor to suck the harmful gases and to avoid foul smell. After some time the liquid product from the vessel is collected in an airtight bottle and is measured. Along with the liquid and gas there is some amount of coke formation too in the reaction and it is also collected separately and measured. Then various analyses for the product is done which are namely gas chromatography (GC), density and viscosity analysis, MCR analysis etc. The results are then compiled and the mass balances are done for the reaction in order to observe the weight losses which are a result of escaping of gases, formation of coke, leftover residue in pipes and sometimes improper handling of the instruments. The data is then compiled with the plant data and an overall analysis is done.

## Chapter 4

### RESULTS AND DISCUSSIONS

A total of 8 runs, 4 in the batch reactor and 4 in the pilot plant were conducted in the project duration. The conditions in the batch reactor and the hydrocracker plant were kept the same. The temperature range was kept between 410°C - 430°C while three of the 4 reactions were conducted at 150 bar and one at 175 bar. The reaction processes for both the setups are explained in the experimentation section while the instruments and methods used for the various analysis and results are also explained there. The results from the reactions and the analyses are mentioned hereby along with different comparisons wherever required.

#### 4.1 Feed Characterization

The feed used for the reactions was the Vacuum Residue from BPCL. Various analyses were done to study the characteristics of the feed, for example, sulphur content, MCR and asphaltene content. The table below shows the results:

**Table 4.1** Feed Characterization of BPCL-VR

<b>BPCL – Vacuum Residue</b>			
Sulphur (Weight %)	MCR (Weight %)	Asphaltene (Weight %)	Material at and above 565°C (Weight %)
6.15	26.19	15.03	61.2

#### 4.2 Reactions in Batch Reactor

The process of performing the reactions in the batch reactor is explained thoroughly in the experimentation section. The reactions were performed at 4 different conditions, which had a total of 3 different temperatures and 2 different pressures. Study of effect of temperature is more important therefore, more emphasis has been given on the

temperature conditions. The reaction time as earlier mentioned was kept three hours for each of the reaction. For the analysis of the product, first the gas sample is taken from the reactor which is then analysed in the gas chromatographer. The liquid product is then decanted from the solid-liquid mixture to obtain the maximum liquid free of other particulates. At last the bottom product which is the solid product is collected. All of the products are then analysed and measured and the table 4.2 shows the results.

**Table 4.2** Product Yield at Different Conditions

<b>Batch Reactor</b>				
<b>Reaction Conditions</b>	<b>150 bar and 410°C</b>	<b>150 bar and 420°C</b>	<b>150 bar and 430°C</b>	<b>175 bar and 430°C</b>
<b>Gas wt %</b>	7.09	13.28	14.93	19.52
<b>Liquid wt %</b>	88.76	82.36	76.00	72.70
<b>Coke wt %</b>	4.15	4.36	9.06	7.78
<b>Residue Conversion</b>	76.72	83.52	91.44	90.20

From the table it can be said that the cracking of the feed is increasing with increasing pressure since the residue conversion can be seen increasing. The residue conversion is calculated by a simple formula as mentioned in experimental section.

There are two variable conditions applied in this study. One is temperature and other is pressure. It is clearly noted from the table 4.2 that with increasing temperature, the yield of gases increase. Even if we look, the residue conversion, similar trend is also observed. It means that with the temperature, large hydrocarbon molecules are effectively broken into the smaller molecules which are ultimately give high percentage of gas products. It also leads more coke formation. Since more gas is formed, the overall liquid yield decreases with the increasing of temperature. In the last two runs, where the reaction temperature is fixed at 430OC, but pressure is varied from 150 to 175 bar. It is noted that with the increased pressure, the coke yield increases. Therefore, hydrogen partial pressure plays an important role to control the coke formation during hydroprocessing reaction. And hence all hydrocracking reactions are carried out at high hydrogen pressure.

### 4.3 Reaction in Slurry Hydrocracker

The process of performing the run in the slurry hydrocracker pilot plant can be found in chapter 3, the experimentation section. Like the batch reactor, the reactions in the hydrocracker were performed at the exact same conditions with the change being the reaction time which was, in this case, 8 hours. The steps for the product analysis in this case are different from the batch reactor. First of all for the gas analysis, samples are taken while the reactions are going on. Three different samples are taken at an interval of two hours each. The reason is that in the first analysis, there might be gas present in the pipelines from before which would not give the accurate result. After the completion of reaction, the liquid products are collected from the product tanks as well as the separators. The heavy and light products are collected and weighed separately. Then mass balances are applied using the data and error (losses) are calculated. Table 4.3 shows the data obtained after performing the reactions.

**Table 4.3** Product Yield at Different Conditions

<b>Slurry Hydrocracker</b>				
<b>Reaction Conditions</b>	<b>150 bar and 410°C</b>	<b>150 bar and 420°C</b>	<b>150 bar and 430°C</b>	<b>175 bar and 430°C</b>
<b>Gas wt %</b>	21.86	18.53	17.31	21.58
<b>Liquid wt %</b>	66.82	74.42	72.65	70.01
<b>Error %</b>	11.32	7.04	10.04	8.41
<b>Residue Conversion</b>	61.60	73.24	76.41	81.41

Again, as in the case of batch reactor it can be seen that the residue conversion in the product keeps on increasing with increase in temperature, and the coke formation at high pressure is less.

The main focus behind these reactions is always to minimize the coke formation and maximize the amount of the lower fractions of hydrocarbons which can be useful. It can also be observed that when the temperature and pressure are being increased, the coke formation does decrease but so does the liquid and the amount of gas product increases.

To make the results clearer, cumulative graphs for both batch reactor and hydrocracker have been made and given in the following section.

## 4.4 Gas Chromatography

The gas samples from the reactions were taken for GC analysis and this section will discuss the results obtained from the analysis which were later used to calculate the gas yield which was mentioned in table 4.2 and 4.3 respectively for the batch reactor and slurry hydrocracker.

Gas chromatography of all the eight experiments were performed. This analysis is used to calculate the gas yield which is shown in the tables 4.4 and 4.5 as well as figure 4.5.1. The process is explained in the experimentation section. Each sample is done three times to ensure better accuracy of results. The results are observed and the best analysis is considered. Normally, errors can occur in the first run due to the already present gases in lines or due to atmospheric gases while injection. Therefore, usually the 2nd and 3rd run are taken into consideration. The data for all the 8 runs are shown in the tables below with the samples from batch reactor and hydrocracker mentioned separately in different tables. The data depicts the molecular weight of different components at different conditions.

**Table 4.4** GC analysis for Batch Recator

<b>Batch Reactor</b>				
<b>Component</b>	<b>150 bar and 410°C</b>	<b>150 bar and 420°C</b>	<b>150 bar and 430°C</b>	<b>175 bar and 430°C</b>
H <sub>2</sub>	1.8624	1.2485	1.2323	1.2839
CO <sub>2</sub>	0.3742	1.8082	1.9914	1.9259
O <sub>2</sub>	0.0504	0.1811	0.2723	0.0963
N <sub>2</sub>	0.0000	0.0000	0.0000	0.0000
CO	0.0000	0.0000	0.0000	0.0000
H <sub>2</sub> S	0.9201	5.5341	4.7670	4.6246
CH <sub>4</sub>	0.1999	0.8674	0.9339	0.9287
C <sub>2</sub> H <sub>6</sub>	0.2676	1.2231	1.2253	1.1872
C <sub>2</sub> H <sub>4</sub>	0.0000	0.0074	1.4032	1.2919



C <sub>3</sub> H <sub>8</sub>	0.0021	0.0084	0.0000	0.0000
C <sub>3</sub> H <sub>6</sub>	0.0975	1.4416	0.8879	0.7906
C <sub>4</sub> H <sub>10</sub>	0.0073	0.2969	0.0317	0.0432
C <sub>4</sub> H <sub>8</sub>	0.2743	0.9911	0.6376	0.3006
C <sub>4</sub> H <sub>6</sub> -butadiene	0.0130	0.2080	0.1325	0.1233
C <sub>5</sub> H <sub>12</sub>	0.0088	0.1239	0.1389	0.0610
C <sub>5</sub> H <sub>10</sub>	0.1743	0.5647	0.2164	0.2386

**Table 4.5** GC analysis for Slurry Hydrocracker

<b>Slurry Hydrocracker</b>				
<b>Component</b>	<b>150 bar and 410°C</b>	<b>150 bar and 420°C</b>	<b>150 bar and 430°C</b>	<b>175 bar and 430°C</b>
H <sub>2</sub>	1.9452	1.9483	1.9535	1.9345
CO <sub>2</sub>	0.0439	0.0011	0.0504	0.1450
O <sub>2</sub>	0.4379	0.0957	0.4480	0.0228
N <sub>2</sub>	0.0000	0.0000	0.0000	0.0000
CO	0.0000	0.0000	0.0000	0.0000
H <sub>2</sub> S	0.0285	0.3476	0.1016	0.4572
CH <sub>4</sub>	0.0238	0.0451	0.0239	0.0658
C <sub>2</sub> H <sub>6</sub>	0.0440	0.0633	0.0439	0.1180
C <sub>2</sub> H <sub>4</sub>	0.0286	0.0000	0.0024	0.0000
C <sub>3</sub> H <sub>8</sub>	0.0000	0.0791	0.0000	0.1223
C <sub>3</sub> H <sub>6</sub>	0.0756	0.0202	0.0505	0.0270
C <sub>4</sub> H <sub>10</sub>	0.0000	0.0909	0.0000	0.0047
C <sub>4</sub> H <sub>8</sub>	0.0741	0.0704	0.0367	0.0409
C <sub>4</sub> H <sub>6</sub> -butadiene	0.0000	0.0157	0.0044	0.0069
C <sub>5</sub> H <sub>12</sub>	0.0549	0.0058	0.0041	0.0147
C <sub>5</sub> H <sub>10</sub>	0.2816	0.1551	0.0044	0.1876

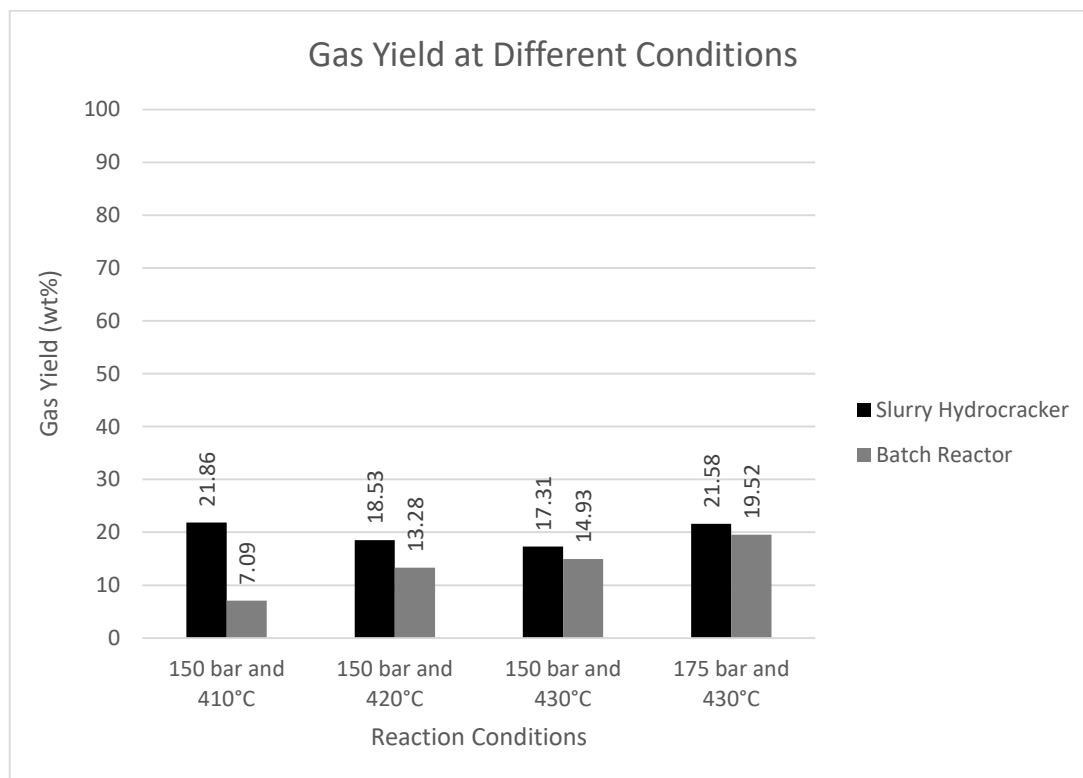
In the above tables, the data is in terms of molecular weight but the results obtained from the chromatographer are mole percentages. Therefore, to convert them, two formulas can be applied.

$$\left( \frac{\text{Percentage Volume}}{100} \times \text{Total Volume} \right) \times \text{Density}(25^{\circ}\text{C})$$

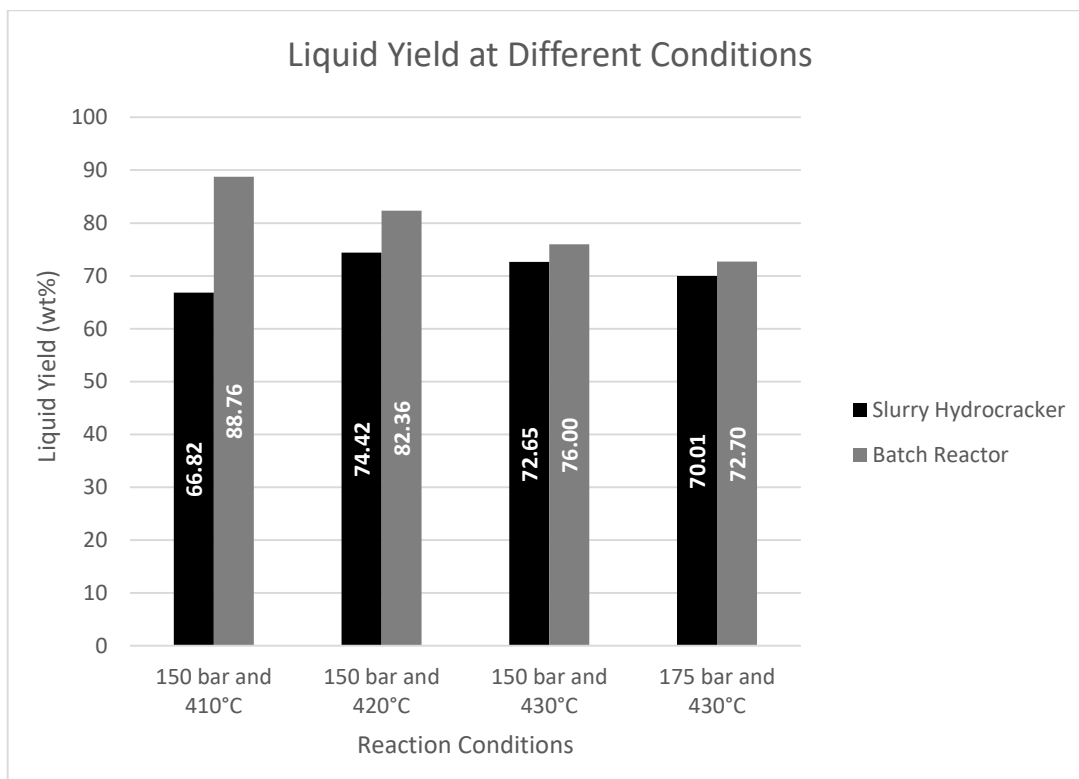
$$\frac{\text{Total Volume} \times \text{Mole Percentage} \times \text{Molecular Weight}}{22.4 \times 100}$$

## 4.5 Comparison of results from Batch Reactor and Slurry Hydrocracker

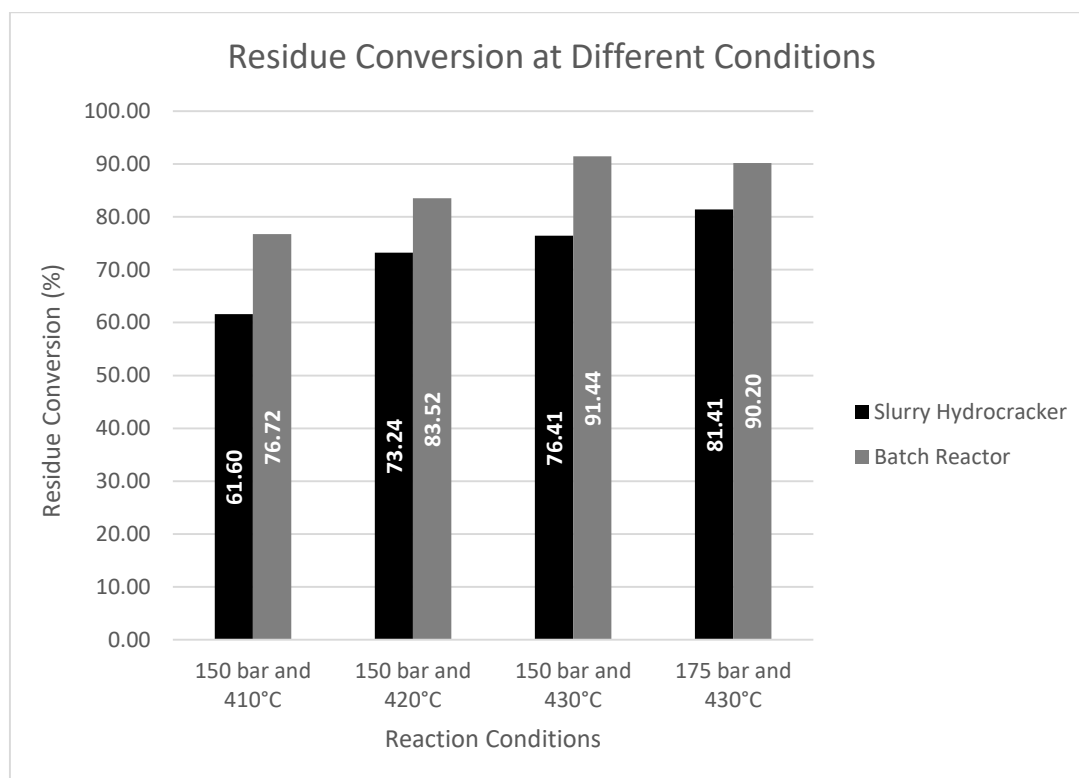
The four graphs below are the comparison of the different results for the products from section 4.2 and section 4.3. The graphs show, at different conditions, the comparison of gas yield, liquid yield, and coke formed/error after mass balance and the residue conversion in the product formed for the slurry hydrocracker and the batch reactor.



**Figure 4.5.1** Comparison of Gas Yield in Batch Reactor and Slurry Hydrocracker

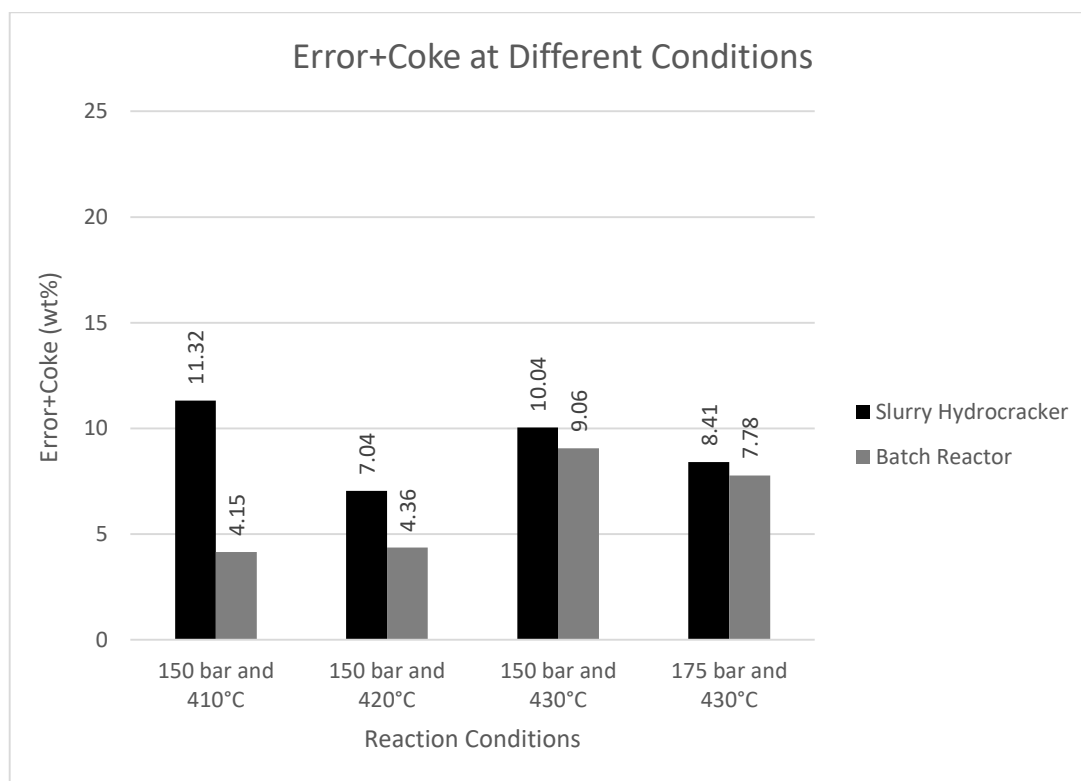


**Figure 4.5.2** Comparison of Liquid Yield in Batch Reactor and Slurry Hydrocracker



**Figure 4.5.3** Comparison of Residue Conversion Yield in Batch Reactor and Slurry Hydrocracker

In figure 4.5.3, it is seen that as the temperature of the reaction is increased, the residue conversion increases which means more cracking. The same observation can be made in both the cases, i.e. batch reactor and the slurry hydrocracker.



**Figure 4.5.4** Comparison of Error/Coke formation in Batch Reactor and Slurry Hydrocracker

In the above figure, when the third and fourth case i.e. conditions 150 bar and 175 bar at 430°C are compared for both the reactors, there is decrease in the amount of coke formation when the temperature is kept constant while the pressure is increased. The drop in the coke weight percentage is quite significant.

## 4.6 Physico-Chemical Characterization

Four different methods were used to calculate 5 characteristics for each of the product. Starting with the first analysis, Density and Viscosity at 15.6°C were calculated in the viscometer. Then the sulphur content was measured using the XRF analyser. Even in the GC analysis and previous sections, we can see that when there is maximum formation of H<sub>2</sub>S, the cracking turns out to be the best. This means that the sulphur content in the best product should be the least. Same goes with the asphaltene analysis. The low amount of insoluble hydrocarbon in n-heptane justifies a better product. Heavy oil contains large amounts of like the ones discussed till now. Another one of them is MCR (Micro Carbon Residue). Since our aim till now has been making the product light, the low amount of MCR is also necessary for this.

Following are two tables, one for the batch reactor and the other for the slurry hydrocracker.

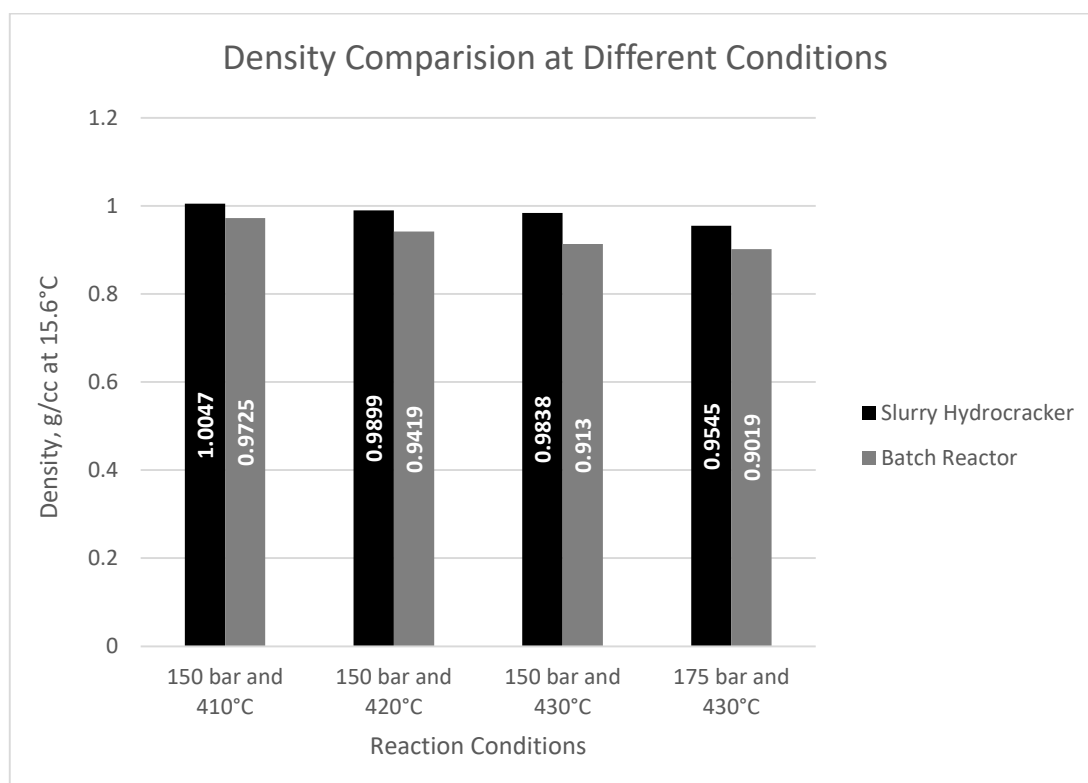
**Table 4.6** Physico-Chemical Characterization of Products from Batch Reactor

<b>Batch Reactor</b>				
<b>Reaction Conditions</b>	<b>150 bar and 410°C</b>	<b>150 bar and 420°C</b>	<b>150 bar and 430°C</b>	<b>175 bar and 430°C</b>
<b>Density, g/cc at 15.6°C</b>	0.9725	0.9419	0.913	0.9019
<b>Viscosity, cSt at 15.6°C</b>	630.75	90.11	16.214	13.453
<b>Sulphur, wt%</b>	3.53	2.71	2.77	2.00
<b>Asphaltene, wt%</b>	17.88	4.59	4.15	8.50
<b>MCR, wt%</b>	12.13	12.02	11.83	9.42

**Table 4.7** Physico-Chemical Characterization of Products from Slurry Hydrocracker

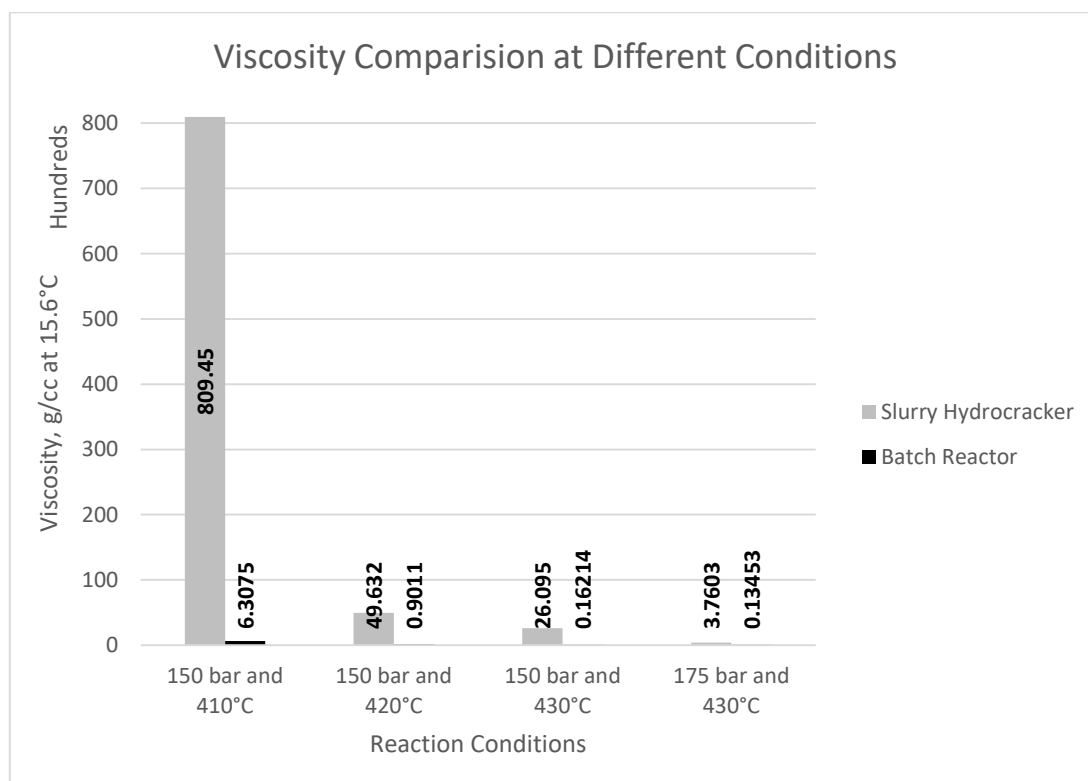
<b>Slurry Hydrocracker</b>				
<b>Reaction Conditions</b>	<b>150 bar and 410°C</b>	<b>150 bar and 420°C</b>	<b>150 bar and 430°C</b>	<b>175 bar and 430°C</b>
<b>Density, g/cc at 15.6°C</b>	1.0047	0.9899	0.9838	0.9545
<b>Viscosity, cSt at 15.6°C</b>	80945	4963.20	2609.50	376.03
<b>Sulphur, wt%</b>	3.77	3.21	3.59	3.12
<b>Asphaltene, wt%</b>	9.93	9.56	9.31	8.84
<b>MCR, wt%</b>	16.78	16.17	14.61	13.79

Following are graphs from the tables to make the analysis and trends the analyses follow, more understandable.



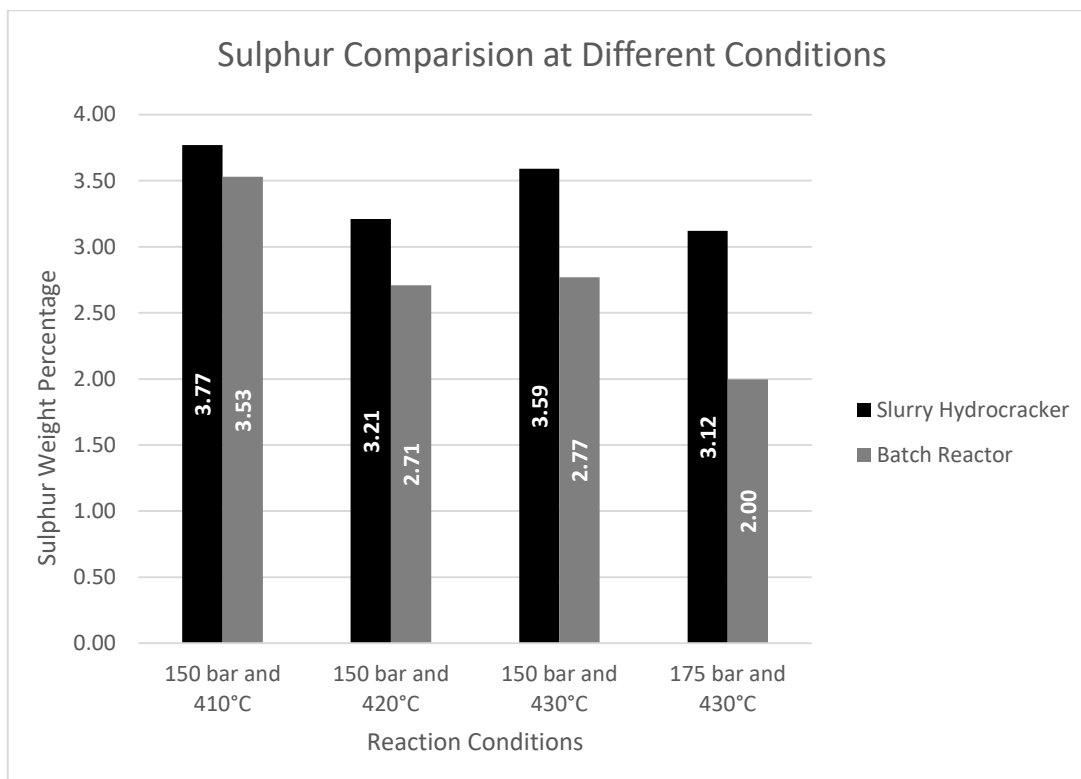
**Figure 4.6.1** Cumulative Density Comparison

It can be seen in both cases (batch reactor and slurry hydrocracker) that the density keeps on decreasing with increasing temperature and pressure. This justifies that the product becomes lighter with the changes made in the conditions.

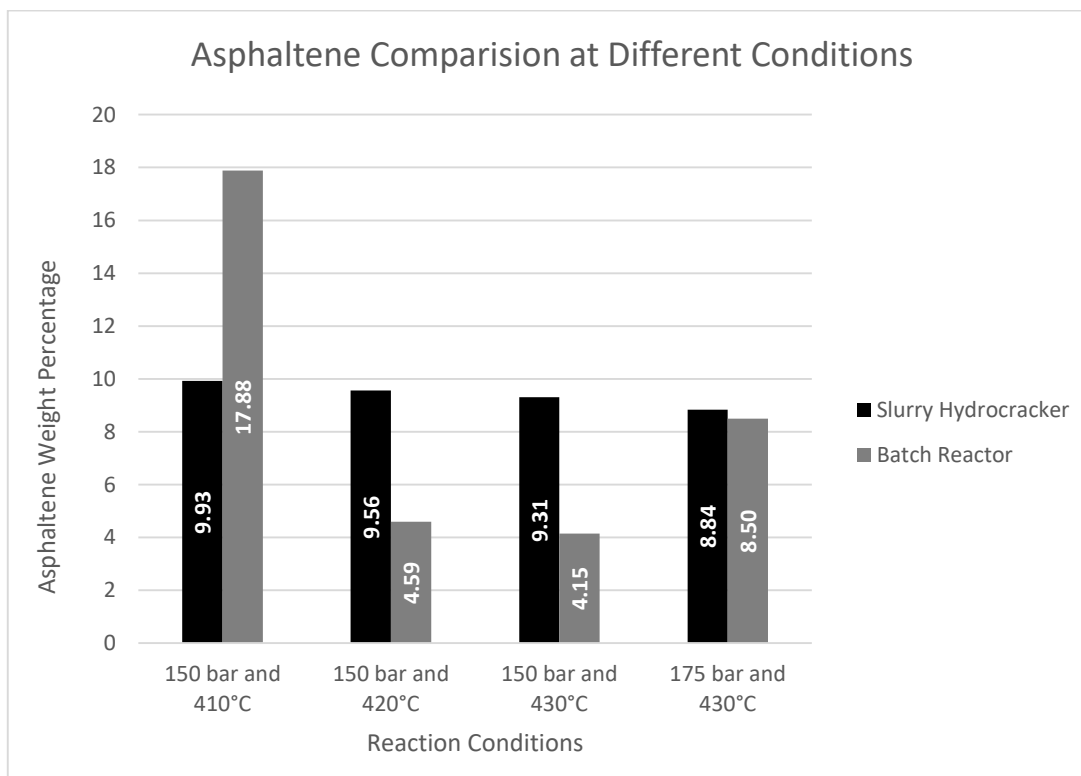


**Figure 3.6.2** Cumulative Viscosity Comparison

The viscosity change in the batch reactor is there and the product is becoming lighter with increase in temperature and pressure similar to that in the case of density. In case of 410 °C temperature, the viscosity is very high as compared to the rest of cases. The same observation can be made for the hydrocracker. A statement can be made that although the liquid yield at this condition is the best and the coke formation is the least this does not mean that the product obtained will be the best. The density and viscosity are very high meaning that the desired amount of cracking is not achieved.

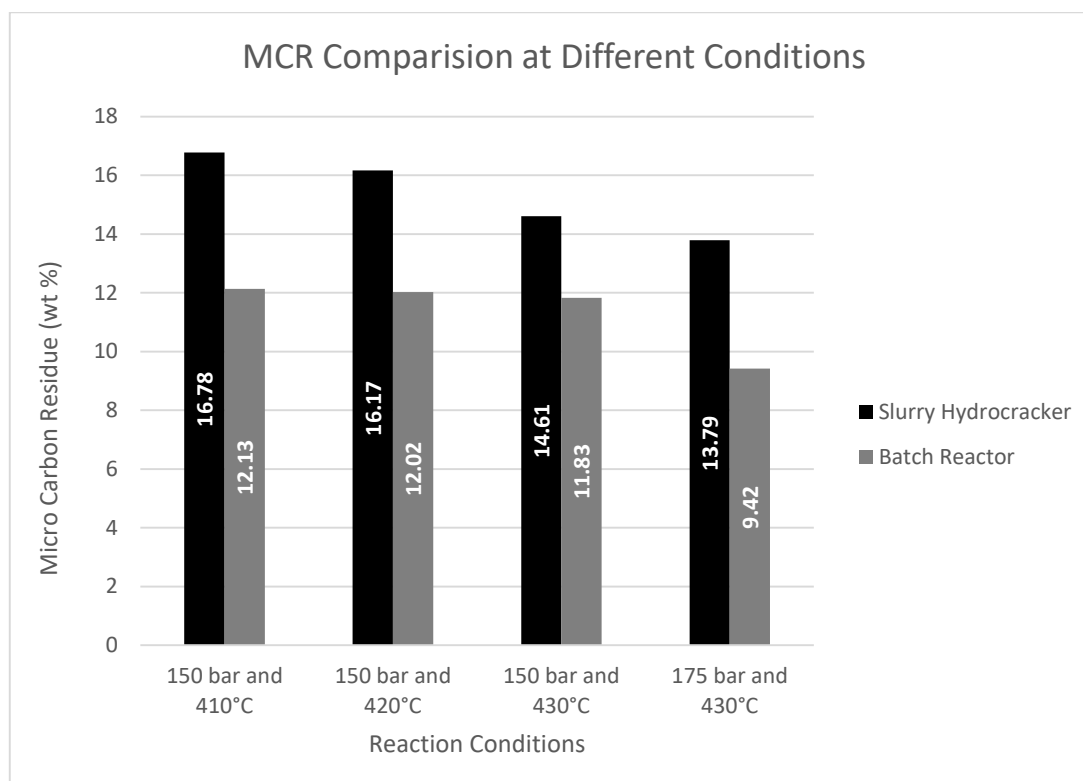


**Figure 4.6.3** Cumulative Sulphur Comparison



**Figure 4.6.4** Cumulative Asphaltene Comparison





**Figure 4.6.5** Cummulative MCR Comparision

From figures 4.3.3 and 4.3.5, an observation can be made that with increase in the temperature conditions, the sulphur and MCR content continuously decreases which prove the sulphur removal as well as the removal of carbonaceous residue. This results in a better conversion of residue in the product as compared to feed.

## 4.7 Product Distribution

After all the different analyses, simulated distillation for all the products were done. This is used to determine the different fractions of AGO and VGO present in the product formed after the reactions. Following two tables show the product distributions of the products respectively for the batch reactor as well as the slurry hydrocracker. This analysis was used in determining the residue conversion in the product when compared to the feed. Also, more the residue conversion, the better is the product can be said. This will help in determining the best condition to perform the hydrocracking of vacuum residue.

**Table 4.8** Product Distribution in Batch Reactor

<b>Product Distribution</b>				
<b>Reaction Conditions</b>	<b>150 bar and 410°C</b>	<b>150 bar and 420°C</b>	<b>150 bar and 430°C</b>	<b>175 bar and 430°C</b>
<b>&lt;150°C (Naphtha)</b>	6.65	8.59	10.76	12.26
<b>150°C - 350°C (AGO)</b>	26.53	31.41	41.12	38.74
<b>350°C - 565°C (VGO)</b>	52.57	49.95	42.89	43.00
<b>&gt;565°C</b>	14.25	10.05	5.24	6.00

**Table 4.9** Product Distribution in Slurry Hydrocracker

<b>Product Distribution</b>				
<b>Reaction Conditions</b>	<b>150 bar and 410°C</b>	<b>150 bar and 420°C</b>	<b>150 bar and 430°C</b>	<b>175 bar and 430°C</b>
<b>&lt;150°C (Naphtha)</b>	5.98	7.36	3.28	4.11
<b>150°C - 350°C (AGO)</b>	32.80	34.82	25.31	42.55
<b>350°C - 565°C (VGO)</b>	44.82	43.39	47.91	41.95
<b>&gt;565°C</b>	16.40	14.44	23.5	11.38

It is very clear from the table that below 150 °C the fractions are categorized as naphtha which are the lightest among the different fractions. Similarly the fractions above 565°C are categorized as the Vacuum Residue (VR). Overall (except a few cases), it is seen that the amount of residue keeps on decreasing with increasing reaction conditions. The same is shown in section 4.1 also.

## CONCLUSION

All Indian refineries produce a substantial amount of vacuum residue. It's conversion into a valuable products is very much essential for making the profit. In this study, different reaction conditions are used to convert the vacuum residue to the more valuable lighter products. Even two reactor systems-batch reactor and slurry phase continuous reactor were used. A very simple conclusion can be made that reaction conditions (temperature and pressure) play a very important part in this method. Reaction temperature has very crucial part for the conversion of large hydrocarbon molecules into the lighter valuable products. Residue conversion increases with the increasing reaction temperature. On the other hand, high hydrogen pressure decreases coke formation. Apart from this, several different properties also determine the quality of the product which has been depicted throughout the report. For instance, the splitting and hydrogenation immersion of asphaltene gets advanced by high hydrogen pressure. The products till now have had acceptable efficiencies (yield and other properties) at lab scale but need to be tested at commercial scale, for which the work is being done.

After the experimentation, following conclusions are drawn:

- Temperature is the most important parameter for hydrocracking of heavy distillates because, more the temperature, better the cracking.
- As the temperature of the reaction are increased, the coke formation tendency also increases which is not beneficial.
- To decrease the coke formation, the role of pressure comes into play. By increasing the pressure, the amount of coke formed decreases because more hydrogen molecules participate in slurry phase hydrocracking of the vacuum residue.
- The liquid, coke and gas yield is not the only important factor in determination of the product quality as it is seen in the cases in the result section.
- As the temperature and pressure are increased, the density and viscosity, both decrease for the product meaning that lighter products are formed at higher values of conditions.
- Sulphur and MCR content are the real major factors to determine the cracking that has happened during the reaction.
- This is because, the lesser the amount of sulphur in the product, more H<sub>2</sub>S formation has happened and more hydrogenation has taken place.

- After product characterisation using simulated distillation, it was learnt that there a number of fractions present in the product which are needed to be separated using distillation for further usage.
- The residue conversion is another important factor during analysis. The product when compared with the feed tells us the conversion occurred which tells the conditions at which the best reaction happens.

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