Cover Sheet

A REPORT

ON

HYDROTREATING PROCESSES (HDT)

IN IOCL GUWAHATI REFINERY

BY

Name(s) of the Student(s)	ID.No.(s)
Krishna Vamsi	18BPE1015

AT

IOCL Guwahati Refinery,

IOCL Training Centre

CHANDIGARH UNIVERSITY

(Jan, 2021)

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Krishna Vamsi	18BPE1015	B.E Petroleum

Prepared in partial fulfillment
of the Practice School-I Course

IOCL Guwahati Refinery, IOCL Training Centre

A Practice School-I Station of

CHANDIGARH UNIVERSITY

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Abstract Sheet

CHANDIGARH UNIVERSITY

(PUNJAB)

Station: IOCL Guwahati Refinery **Centre**: IOCL Training Centre

Duration: 4 weeks **Date of Start**: 17-12-2020

Date of Submission: 21-01-2021

Title of the Project: Hydrotreating processes (HDT) in IOCL Guwahati Refinery

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Discipline(s)/of the student(s): B.E Petroleum

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Name(s) of the PS Faculty: Dr. Saubhagya Ranjan Mahapatra

Key Words: Hydrotreating, Hydrodesulphurization, Hydrodenitrogenation, Resid, Gasoline, Distillate Upgrading, Desulfurization, Denitrogenation

Project Areas: Hydrotreating Process operations, units and process variables, Industrial exposure to the environment maintaining for unit, Catalyst developments and storage, Plant design information.

Abstract: This report reproduces the basic operating methodology of the Hydrotreater Unit, which is made possible by the original facts and data obtained from the industry. This is simply about the literature work based on the subject, using the resources of IOCL Guwahati Refinery.

Krishna Vamsi

Signature(s) of Student(s)

Signature of PS Faculty

Date:

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1. Introduction

IOCL Guwahati Refinery is the first public sector refinery of the country with Digboi Refinery being first private refinery operated. It is built with Romanian collaboration, was inaugurated by Late Pt. Jawaharlal Nehru, in the year, 1962. It had an initial capacity of 0.75 million metric tonnes per annum (MMTPA) and later increased to 1 MMTPA. The Refinery symbolizes the Nation's march towards indigenisation of the refining technology. Guwahati Refinery processes the crude oil drilled from the Upper Assam Oil Fields and supplies to the demands of the oil and petroleum products of the North Eastern States.

Its major products are LPG, Motor Spirit/Gasoline (Petrol), Aviation Turbine Fuel (ATF), High Speed Diesel, Kerosene, Light Diesel Oil and Raw Petroleum Coke. Guwahati Refinery is making tiring efforts to produce innovative products with respect to the environmental changes happening due to increase in greenhouse effect. It is the only refinery in India to produce green needle coke, a high value import substitute.

In the era of fight against ecological imbalance, Guwahati Refinery has installed three new units: the ISOSIV, the Hydrotreater and the INDMAX in 2002-2003. In 2010, MSQU (Motor Spirit Quality Upgradation unit) and in 2017, INDAdept unit was commissioned to produce motor spirit with high octane number resulting in high ignition quality. The Hydrotreater Unit (HDT) enables the Refinery to produce High Speed Diesel of very less sulphur content and high cetane number applying to BIS specifications. The HDT also produces ATF, Superior Kerosene Oil with high smoke point and low sulphur and low nitrogen.

Normal capacity of the Hydrotreater is 0.6 MMTPA of fresh feed. However, the unit is designed for the running capacity of 0.66 MMTPA of fresh feed (an extension of 10% on design capacity is kept). The unit is being operated only in two blocked out modes so far; Kerosene and Diesel. A new Naphtha Hydrotreater unit has been proposed to put up. Occasionally, the unit will operate in a blocked out mode to produce ATF. Detailing for inviting bids as well as Project Management Consultancy for the unit was performed by Engineers India Limited, New Delhi (EIL).

The HDT unit decreases the Sulphur and Nitrogen Content of Diesel by treating it with Hydrogen at High Temperature and Pressure over Catalyst to convert the bound Sulphur in the diesel to H_2S and Nitrogen to Ammonia. The unit is also able to achieve 49 Cetane number during Diesel operation (EOR) and 21 mm smoke point during Kerosene operation (EOR). The unit also have the flexibility to process Straight Run Kerosene-I alone to produce Aviation Turbine Fuel (ATF) if it is required.

2. Brief description of process

The various processing steps involved in the process are:

a) Pumping of Feed to the desired pressure

b) Mixing Recycle Gas with Feed

c) Heating of Feed and Recycle Gas Mixture to the desired temperature

d) Contacting the Feed and Recycle Gas Mixture with catalyst

e) Cooling the Reactor Effluent

f) Separating Liquid and Vapour from the Reactor Effluent

g) Recycling the Separated Gases to reactors inlet

h) Stripping the Liquid Reactor Effluents to remove lower boiling fractions as wild naphtha

i) Cooling and polishing of product before sending to storage.

3. Objectives

1. To understand the complete process flow of the refining through various units and operations giving different products.
2. To deeply understand the process description of Hydrotreating Unit in IOCL Guwahati refinery.
3. To conceptualize the association of Hydrotreating unit to other units whose product/feed need hydro treatment.
4. To learn the technical idea of the running of the unit.

4. Process principles

Petroleum fractions contain various amounts of naturally occurring contaminants including organic sulfur,nitrogen, and metal compounds. These contaminants may contribute to increased levels of air pollution,equipment corrosion and cause difficulties in the further processing of the material. The Unionfining process is a proprietary, fixed-bed; catalytic process developed by UOP for hydrotreating a wide range of feedstock. The process uses a catalytic hydrogenation method to upgrade the quality of petroleum distillate fractions by decomposing the contaminants with a negligible effect on the boiling range of the feed. Unionfining is designed primarily to remove sulfur and nitrogen. In addition, the process does an excellent job of cetane no improvement (49 min.) and of processing kerosene to get better smoke point (21 min.), by saturating olefinic and aromatic compounds while reducing Conradson carbon and removing other contaminants such as oxygenates and organometallic compounds. Unit is also capable of processing Straight Run Kerosene-I [SRK-I] to produce Aviation Turbine Fuel [ATF].

The desired degree of hydrotreating is obtained by processing the feedstock over a fixed bed of catalyst in the presence of large amounts of hydrogen at temperatures and pressures dependent upon the nature of the feed and the amount of contaminant removal required. Naphtha used as feedstock to catalytic reforming (Platforming) units must be hydrotreated to such an extent that they are essentially free of all contaminants (less than 0.5 ppm Sulfur), whereas, 0.2 wt% Sulfur may be permissible in heavy distillates intended for fuel oil use.

Hydrotreating units are designed for dependable, stable operation. UOP's selective, high-activity catalysts operate for long periods of time between regenerations. Specific process objectives determine which UOP catalyst is best suited for a particular installation. The activity and selectivity of the catalyst is influenced only to a slight extent by the type of feed processed. The same catalyst in varying quantities can be used to hydrotreat straight run naphtha, vacuum gas oil as well as catalytically and thermally cracked distillates. The widespread use of catalytic reforming units has made available large quantities of excess hydrogen, making it feasible to hydrotreat many, or all, of the distillates produced by the refinery.

This manual will discuss all aspects of the start-up, shutdown and operation of Hydro-treating Unit designed to process distillate oil.

Hydro-treating is carried out at elevated temperatures and pressures in a hydrogen atmosphere. Pressures and temperatures may range up to 80-93 kg/cm 2 g and 350-428 0 C respectively. The Hydro-treating catalysts are formulated by compositing varying amounts of nickel or cobalt with molybdenum oxides on an alumina base. The specific catalyst system and unit design parameters are evaluated on an economic basis for each unit. Each design is based on feed quality, desired product properties, ease of operation, desired cycle length, operating flexibility, construction schedule and operating costs.

5. Crude Refining Process at a Glance

Crude Oil is refined to get LPG, Motor Spirit, High Speed Diesel, Petrol/Gasoline, Bitumen, Peat, Petroleum Coke, Coker Oil products and other petroleum product bases and their raw material. There are a series of steps involved in refining crossing many units and operations there.

Desalter Unit:

It removes the salts of various metals and ionic compounds present in the drilled raw crude oil.

Crude Distillation Unit:

It is the primary unit of a refinery. It majorly takes the action to separate the crude into various products based on their difference in points of volatility. It gives various unprocessed products such as naphtha, LPG, Gasoline, Diesel, Kerosene-1, Kerosene-2, Gas oil, Petrol coke, Raw coke oil, etc.

Naphtha Splitter Unit:

It role is to split the Straight run Naphtha coming from CDU into 3 forms of naphtha: Light Naphtha, Reformer Naphtha, Heavy Naphtha.

Delayed Coking Unit:

This unit produces middle distillates from heavy ends. The residual oil feed is heated to its thermal cracking temperature to give Coker Gas oil and pet coke. Thermal cracking and Catalytic cracking are the major processes involved in this unit.

INDMAX Unit:

It increases the LPG production by fluidized catalytic cracking process.

Hydrotreating Unit:

This unit is responsible for removing the Sulphur and Nitrogen content from the oil feed by treating with hydrogen. It also improves the smoke point of Kerosene/Aviation fuel and increases cetane number for the diesel product.

Hydrogen Generation Unit:

It provides the required amount of Hydrogen for the Hydrotreating process based on steam reforming technology.

MS Quality Upgradation Unit:

It improves the Motor Spirit quality by removing sulphur and nitrogen content improving the octane number of the Gas oil feed.

INDAdept[G] Unit:

It has the same function of a Hydrotreater unit by deeply removing sulphur content in Gasoline.

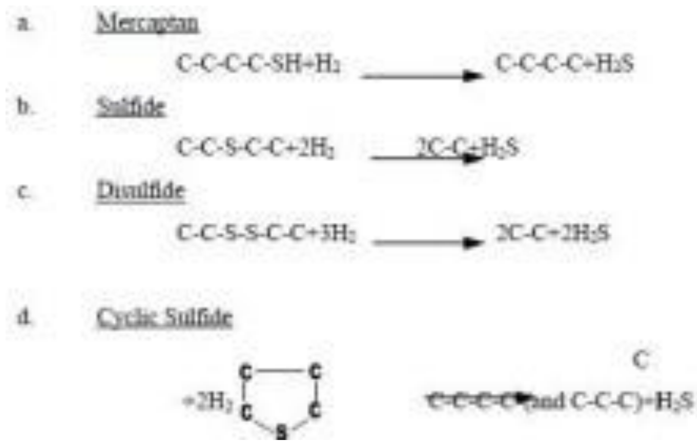
Sulphur Recovery Unit:

This unit removes the sour gases of H_2S released from the Hydrotreating and hydrodesulphurization processes which is further converted into elemental sulphur by Claus process in Amine treatment.

6. Process Chemistry

Sulfur Removal

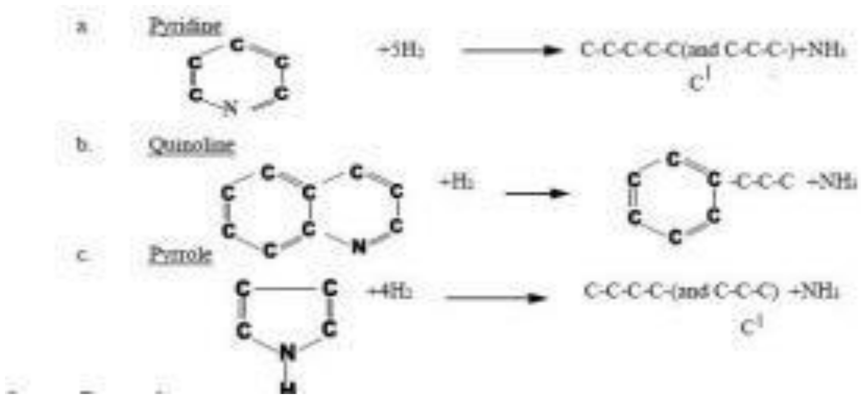
Typical feedstock to the Hydro-treating unit will contain simple mercaptans, sulfides and disulfides. These compounds are easily converted to H_2S. However, feedstock containing heteroatomic aromatic molecules is more difficult to process. Desulfurization of these compounds proceeds by initial ring opening and sulfur removal followed by saturation of the resulting olefin. Thiophene is considered 15 times more difficult to process compared to diethylsulfide.



Nitrogen Removal

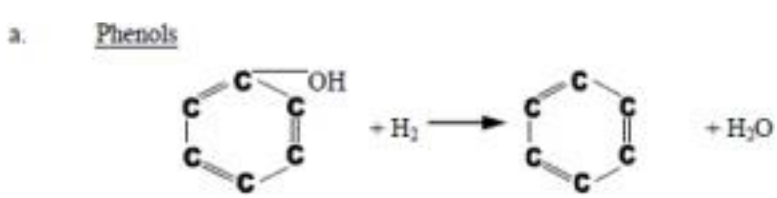
Denitrogenation is generally more difficult than desulfurization. Side reactions may yield nitrogen compounds more difficult to hydrogenate than the original reactant. Saturation of heterocyclic nitrogen containing rings is also hindered by large attached groups.

The reaction mechanism steps are different compared to desulfurization. The denitrogenation of pyridine proceeds by aromatic ring saturation, ring hydrogenolysis and finally denitrogenation.



Oxygen Removal

Organically combined oxygen is removed by hydrogenation of the carbon-hydroxyl bond (C-OH) forming water and the corresponding hydrocarbon.

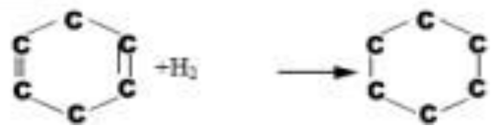


Olefin Saturation

Olefin saturation reactions proceed very rapidly and have a high heat of reaction.

a. C-C=C-C +H_2 ➔ C-C-C-C

b. Cyclic Olefins



Aromatic Saturation

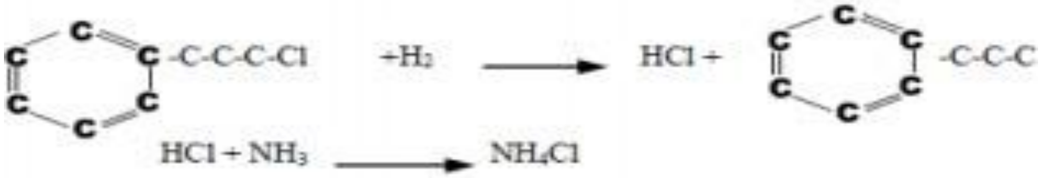
Aromatic saturation reactions are the most difficult. The reactions are influenced by process conditions and are often equilibrium limited. Unit design parameters consider the desired degree of saturation for each specific unit. The saturation reaction is very exothermic.

Metals Removal

The mechanism for this is not completely understood. However we know that metals are retained on the catalyst by a combination of absorption and chemical reactions. For e.g. Iron can be found concentrated at the top of catalyst bed like iron sulfides, which are corrosion products. Na, Ca and Mg are due to contact of the feed with salt water and additives. Pb may also be deposited.

Halides Removal

Organic halides, such as chlorides and bromides, are decomposed in the reactor. The inorganic ammonium halide salts which are produced when the reactants are cooled are then dissolved by injecting water into the reactor effluent or leave with the stripper off-gas. Decomposition of organic halides is considered difficult with a maximum removal of about 90%.



Hydrocracking Reactions

The products of the Hydro-treating reactions are of a lower density than the feedstock. Therefore, the total liquid yield is greater than the feed and may be as high as 102 % (liq. vol).

Some hydrocracking may take place in the Hydro-treating process. This is especially evident towards the end of an operating cycle when reactor temperatures are raised to compensate for lower catalyst activity. Total liquid yield and hydrogen consumption increases as hydrocracking reactions proceed. The Hydro-treating unit is designed for maximum bottoms production. Under normal operation, the net stripper overhead liquid produced in a Hydro-treating unit should not exceed 2% (liq.vol) of the unit feed.

Hydrogen Consumption

The hydrogen consumed by the Hydro-treating reactions is supplied externally and must be boosted to reaction system pressure. If the hydrogen is obtained from a naphtha reforming unit, its purity may vary between 70% to 90% H_2 . Hydro-treating units are not designed to operate at hydrogen purities below 70% due to the adverse effect on the catalyst performance and excessive compressor wattage.

7. Hydrotreating Unit

Hydrotreating/Hydrodesulphurization is a refinery operation accessed to remove the Sulphur, Nitrogen and Metal contents present in the oil products obtained by primary and secondary refining operations by treating them with Hydrogen gas at high temperatures and pressures. It is also responsible for removal of various oxides and halides present in it. It's another appreciable function is that it improves the smoke point of Kerosene & Aviation Turbine Fuel and also increases the cetane number of Diesel fuel.

Types of Hydrotreater Units

There are majorly six kinds of Hydrotreater units used in refineries.

a) Naphtha Hydrotreating:

It is used to pre-treat naphtha for downstream processes like catalytic reforming, paraffin isomerization, etc. It removes majorly Sulphur, Nitrogen content and also other impurities producing pure Gasoline.

b) Kerosene Hydrotreating:

Kerosene is hydrotreated to remove sulphur and nitrogen leading to improve its quality by developing its smoke point. It produces purified Kerosene as well as Aviation Turbine Fuel.

c) Middle Distillate Hydrotreating:

It is hydrotreatment of the middle distillate product of the CDU. It is also termed as Diesel Hydrotreating and operated at high temperatures and moderate pressure. This is responsible for increasing the cetane number of Diesel, which improves its ignition quality.

d) VGO Hydrotreating:

In this process, Vacuum Gas Oil is hydrotreated with Hydrogen to reduce sulphur content before entering Fluidized Catalytic Cracking Unit.

e) FCC Gasoline Hydrotreating:

In this method, Gasoline coming out from FCC is hydrotreated reducing sulphur in it.

f) Residue Hydrotreating:

Here, Atmospheric or Vacuum residue is hydrotreated to reduce sulphur before entering Residue Catalytic Cracking unit.
There are only two kinds of Hydrotreaters being used presently in IOCL Guwahati Refinery: Diesel and Kerosene Hydrotreater units. A Naphtha Hydrotreater Unit is proposed to put up in the refinery soon.

Brief Process description

I. Reactor section

Feed (diesel/Kerosene/ATF) is passed from storage to the pumps where Pressure, Temperature and Flow limits are provided. The pump raises feed pressure, and the feed is directed to the coalesce where water is coalesced from the feed and then separated.
The feed from the coalesce then passes into the surge drum where backwashing and filtering is done. Filtered feed id then directed to the shell side of the feed preheat exchanger where it gets heated. The preheated feed now passes to the feed surge drum, where pressure is controlled to be above a certain specified set point.
Feed from this drum passes to charge pumps, which pump it around to a pressure of 121 kg/cm^2. A spillback line has been provided to maintain minimum throughput and avoid damage to these pumps.

Feed Heating:

Feed discharged from the pump passes through the shell side of cold heat exchangers and then hot feed exchanger, before passing into the charge heater.
Recycle gas from the recycle gas compressor goes upstream of the cold combined feed exchanger and part of recycle gas from compressor is diverted into the reactors 1 and 2 along with the feed. The combined gas-liquid is preheated with reactor effluents. The combined feed flows on the shell side whereas effluents flow within the tubes.
Differently numbered heat exchangers heat the liquid and gas mixtures and effluents coming from different reactors. The feed-gas mixture is then passed for further heating in a charge heater to proper reactor inlet temperature.

Reactors:

Combined feed after heating is passed into reactors for reactions over catalyst beds. The unit currently has 2 reactors with third being installed. Outlet is first introduced to reactor no. 1 which has catalyst divided into two beds, and then the outlet from the bottom bed of reactor 1 is directed into reactor no. 2. Effluents from reactor 1 are quenched with recycle gas and admitted into reactor no. 2. During the course of the process the temperature required is gradually increased to maintain product quality as the catalyst is gradually deactivated.

Final cooling of the reactor effluent stream is then performed in the effluent condenser. Wash water is injected into the stream before it enters the condenser. The sulfur and nitrogen contained in the feed are converted to NH_3 and H_2S in the reactor. These two can combine in vapor phase to form vaporized ammonium salts which may solidify and precipitate. The purpose of washing is to dissolve these salts.

Cooled effluents are then directed into the high-pressure separator. Vapor, liquid and sour water are separated here in a horizontal vessel with mesh blanket and a weld overlay.

Recycle Gas stream:

The overhead recycle gas goes into the recycle gas compressor suction drum for entrained liquid removal before going into the recycle gas compressor.

II. Fractionation Section

This section is for separating sour gas and naphtha form the hydrodesulfurised diesel/ kerosene/ATF product. This is done using a stripper. The hydrocarbon liquid from the separator is sent to stripper. The feed gets preheated by exchanging heat with striipper bottoms and reactor effluents. Vapor liquid mixture is directed into the stripper receiver where separation of vapour, liquid and water takes place. The discharge from stripper is sent to the product coalesce, which is a horizontal vessel provided with a coalescing element (mesh) and water boot to separate water from hydrocarbons.

During the diesel mode of operation product is passed through sand filter and salt drier keeping caustic wash tower bypassed. For the final removal of water the salt drier is a packed vessel filled with rock salt, which is hygroscopic and picks up free moisture from the flowing diesel in which it is dissolved. The salt solution collected is drained regularly.

During the kero/ATF run the product from coalsecer is sent to the caustic wsh tower to remove any residual hydrogen sulfide from the product stream, and then through the sand filter.

Major Equipment:

- Feed coalescer:

Horizontal carbon steel vessel in which feed flows through coalescing media.

- Reactors

High strength corrosion resistant low alloy steel vessel. Fluid enters the top with a very high velocity over the multiple catalyst beds. The reactor effluents and quench gas flows down into the liquid collection tray

- Salt drier

- High Pressure separators

Killed carbon steel vessel whose purpose is to separate recycle gas, water and hydrocarbon in the reactor effluent. It is equipped with a full diameter stainless steel mesh blanket which removes liquid droplets from the gas.

- Recycle gas compression suction drum
- Stripper

Vertical vessel made of killed carbon steel having 38 valve trays. Stripped bottoms are pumped out of the column while liquid reflux is returned to the top. The upper portions thus contain high concentrations of H_2S

- Stripper receiver
- Diesel product coalescer

  It is typically equipped with some means of removing water from the stripper bottoms product. Here it is done by sending the bottom product through a coalescer.

Heat Exchangers:

a.) Shell and tube type: number of parallel tubes inside a shell. One fluid flows inside the tubes (tube side fluid) and one flows outside (shell side fluid).
b.) Air (Fin-Fan) coolers: contains a fan with one or more heat transfer sections mounted horizontally. The fan speed is set and determined by the tip speed.

Compressors:

Typical HDT unit has a recycle gas compressor and a makeup compressor.

Pumps:

Four general types of pumps are found in a hydro treating unit:

a) Proportioning
b) Single stage centrifugal
c) Multi stage centrifugal
d) Sundyne.

Charge Heater:

A natural draft furnace with a radiation and convection section . three burners, each having a pilot burner.

Chemical Description:

- Soda ash and sodium nitrate – for preparing neutralizing solution
- Dimethyl disulfide- catalyst and sulfiding agent required during the start of diesel process.

- Caustic regeneration- 419 m^3 of 10 % by wt caustic is used for one catalyst regeneration
- Caustic wash tower- 10% wt caustic used
- Rock salt- 51900 kg rock salt used for salt drier
- · Sand- required for the sand filter

Waste:

- Spent caustic
- Sour water (from stripper receiver boot and high-pressure separator boot)
- Regenerated waste gas (formed during reactor catalysis)
- Stripper receiver vent gas
- Contaminated rain water

Catalyst system

STARS catalysts have superior activity for sulphur and nitrogen removal and hydrogenation reactions. They are designed with a maximum number of so-called Super Type II Active Reaction Sites (STARS). Type II Active Sites exhibit extraordinarily high intrinsic activity and are therefore preferred over Type I active sites found on conventional catalysts.

Safety: STARS catalyst may emit a little CO (carbon monoxide), especially if stored for a long time or at elevated temperatures. Read the safety instructions before handling.

Details of fresh catalyst system are indicated below:

- Grading catalysts: CatTrap50, CatTrap30 (supplied by M/s UOP / M/s Crystaphase)
- Metal Guard: HYT-8119 (Ni-Mo)
- Silicon Guard: HYT-9119 (Ni-Mo)
- Arsenic Guard: UF-80 (Nickel Oxide)
- Main Active Catalyst in 49-R-01 and 49-R-02: HYT-6219 (Ni-Mo)

The Star catalysts used in HDT consist of oxides of nickel and molybdenum impregnated on an alumina base. A size graded catalyst bed is used to limit pressure drop across the top bed. The specific catalyst selected for a given unit is based on type of feedstock, desired product properties and process design conditions.

Catalyst Deactivation

Catalyst activity is reduced whenever molecules cannot reach active sites. Catalyst deactivation may be caused by one or more of the following mechanisms: Coke Deposition, Metal accumulation and Catalyst Sintering. The following parameters influence catalyst deactivation;

Reactor Temperature:

Reactor temperature should be minimized while maintaining desired product quality. Increasing reactor temperature will greatly accelerate the rate of coke formation and reduce the length of the operating cycle.

Feed Boiling Range:

Sulphur, Nitrogen and Metal content of typical feed increase with relative volatility and endpoint requiring higher reactor temperatures.

Charge Rate:

Liquid distribution in the reactor may become unequal resulting in preferential flow and poor catalyst utilization.

Hydrogen partial pressure:

At a given system pressure, the recycle gas purity will determine the partial pressure of hydrogen in the reactor. At reduced hydrogen purities, the Hydro-treating reactions do not proceed at the same rate. The hydrogen deficient atmosphere also creates a greater tendency to form coke. These conditions cause the catalyst to lose apparent activity.

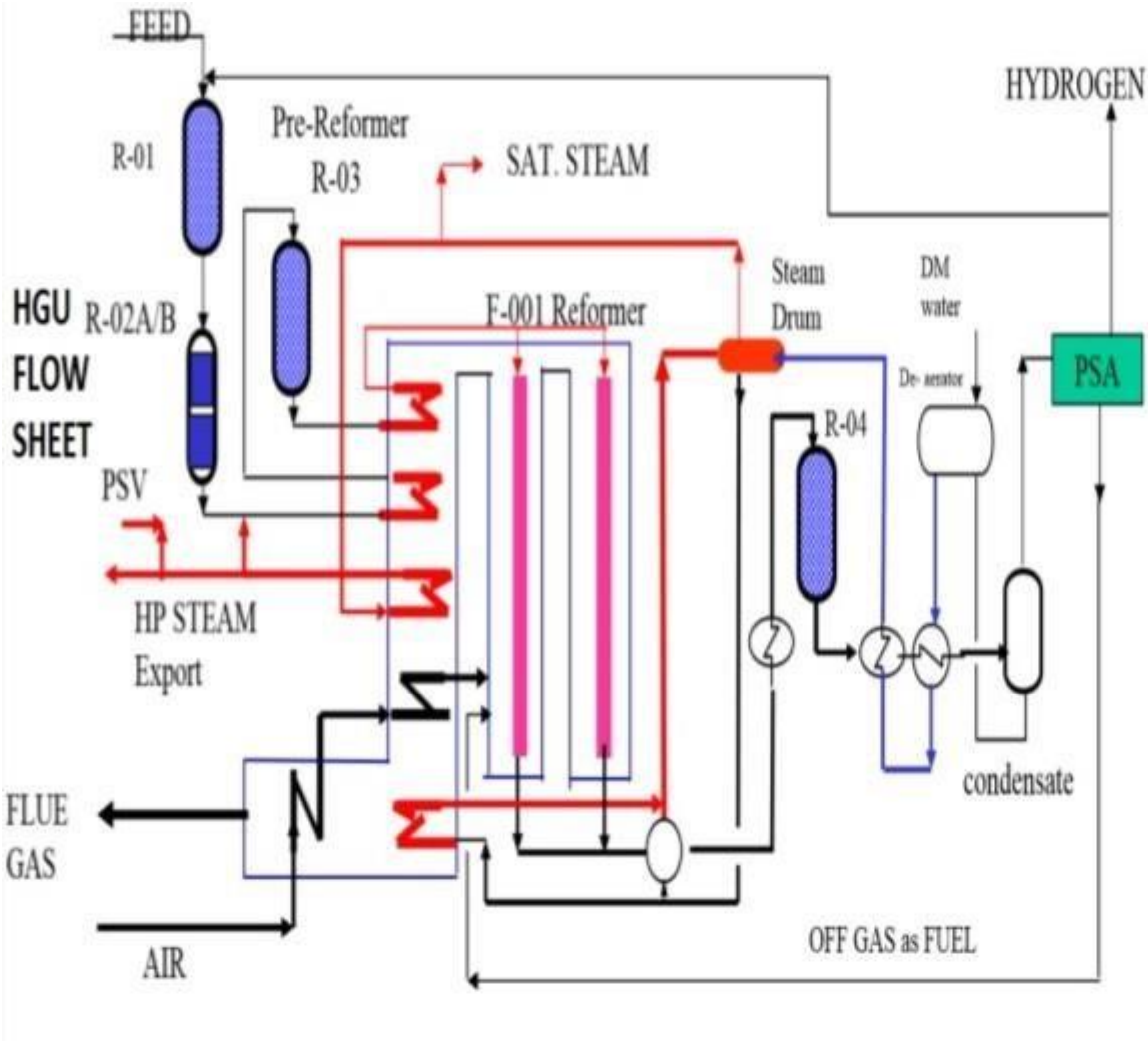
Recycle Gas rate:

The large quantity of gas recycled from the high pressure separator to the reactor serves the following purposes:

- Helps hold down charge heater and combined feed exchanger tube wall temperatures by increasing the flow through the equipment. The excess H_2 prevents the formation of coke as the charge is heated to reaction temperature.

8. Hydrogen Generation Unit

The Hydrogen Generation Unit has a key function in the finalization of the refining process. Hydrotreating is required to produce the product at the desired quality output in order to comply with the required specifications. As we have done before, the hydrotreating process involves a lot of operations such as deulphurisation, denitrification, saturation of olefins and aromatic compounds, etc. Not just the Hydrotreating Unit, However, the Motor Spirit Quality Upgradation Unit, the INDAdeptG Unit and the ISOSIV Unit also deal with similar operations that require a high level of hydrogen for process reactions. This Hydrogen Generation Unit will therefore be responsible for producing the large amount of hydrogen required for these processes.



Process Principles

The Hydrogen Generation Unit comprises 6 main principles of steps to generate our product Hydrogen Gas: Feed Hydrodesulphurization, Pre-Reforming, Reforming, Heat Recovery, High/Low Temperature Changes and Product Recovery in the Pressure Swing Adsorption Unit. Some amount of hydrogen formed is recycled to the feed treatment section so that it can meet the demand for hydrogen and purge gas from the PSA unit is used as fuel in the reforming section.

Light gases from LPG Recovery Unit and Straight Run Light Naphtha composite the feed of HGU.

Process Chemistry

Feed Hydrodesulphurization:

In addition to H2S, the light gasses from LRU contain significant amounts of olefins. Light naphtha contains Mercaptans as well as trace amounts of heavy metals such as arsenic, lead, vanadium and copper, which are catalyst poisons.

Olefin saturation:

R=R + H_2 RH-RH

Hydrogenation of organic sulphur and chlorine compounds to form H2S
and HCL:

RSH + H_2 RH + H_2S
RCl + 1/2 H_2 RH + HCl
$RISR_2$ + $2H_2$ RIH + R_2H + H_2S

$RISSR_2$ + $3H_2$ RIH + R_2H + $2H_2S$

C_2H_5SH + H_2 C_2H_6 + H_2S

C_6+H_5SH + H_2 C_2H_6 + H_2S

CH_3-S-C_2H_5 + $2H_2$ C_2H_6 + H_2S

C2H_5-S-S-C_2H_5 + $3H_2$ $2C_2H_6$ + $2H_2S$

C_4H_8S + $2H_2$ C_4H_{10} + H_2S

C_4H_4S + $4H_2$ C_4H_{10} + H_2S

COS + H_2 CO + H_2S

Dechlorination:

HCl + Na-Aluminate NaCl + H_2O

ZnO + H_2S ZnS + H_2O

Pre-reforming and Reforming:

Steam Reforming of Naphtha takes place in two Reactors, Adiabatic Pre-Reformer & Tubular Reformer. Both Reactors are having Nickel based Catalyst.

The reactions taking place in the Pre-reformer and the Reformer are:

C_nH_m + nH_2O nCO + (½m +n) H_2 (Endothermic)

CO + H_2O CO_2 + H_2 (Exothermic)

Shift Conversion:

Further shift conversion is applied at lower temperatures to convert carbon monoxide to hydrogen. The principal reaction is:

CO + H2O CO2 + H2 (Exothermic)

<u>Adsorbent Activation:</u>

Adsorbent is transformed to its active state by reducing he metal oxides formed during combustion. $NiO + H_2 \; Ni + H_2O$

This reaction is exothermic (~ 34 kcal/mol). Completion of this step is as necessary as the combustion step to maximize the desulfurization activity of the adsorbent.

<u>$DESO_x$ Section:</u>

Basically, scrubbing reactions take place here.

$SO_2 + NaOH \; NaHSO_3$

$SO_2 + 2NaOH \; Na_2SO_3 + H_2O$

$SO_2 + H_2O + 2NaOH \; Na_2SO_3 + 2H_2O$

$SO_2 + H_2O \; H_2SO_3$

$H_2SO_3 + 2NaOH \; Na_2SO_3 + 2H_2O$

$SO_3 + NaOH \; NaHSO_4$

Brief Process Description

Adsorption:

The Reactor section consists of two Reactors in parallel. At any time one of the Reactors will be operating in Adsorption mode and other in Regeneration mode. After a time interval of around 120 hrs there is switch in the mode of operation of Reactors. There will be recycle H_2 flowing in it, which brings adsorption of active sulphur present in it.

<u>Desulphurization:</u>

INDAdept^{G}is a process based on reactive adsorption. When sulphur-bearing hydrocarbon molecule comes into contact with the adsorbent surface in the presence of hydrogen, C-S bond in the hydrocarbon molecule is broken and sulphur gets attached to the adsorbent effecting the desulfurization.

<u>Olefin Saturation:</u>

Cracked feedstock's (thermal as well as catalytic) typically have high olefin content. These unsaturated components present in the feedstock get saturated in the presence of H_2 and catalytic environment (Ni) and form corresponding paraffinic compounds.

Regeneration:

The effluents are cooled with feed mixture where it separates into desulphurized naphtha & H_2 and sent to regeneration section. The mixture is depressurized and purged with N_2 gas and combustion of coke & sulphur, reducing further sulphur content by separating SO_2, SO_3, H_2O and CO_2.

Combustion:

Combustion step is carried out once in every cycle after Adsorption to remove coke deposited on the adsorbent and sulphur attached to the adsorbent (as ZnS and NiS) during desulfurization.

Adsorbent Activation:

Adsorbent is transformed to its active state by reducing he metal oxides formed during combustion. This is achieved by injecting a controlled quantity of H_2 (up to 1 vol% in N_2) in to the Reactor. This reaction is exothermic (~ 34 kcal/mol).

$DESO_x$:

The above gases produced are scrubbed with help of NaOH and water as caustic scrubber. Then pure products of gasoline are obtained.

9. Motor Spirit Quality Upgradation Unit

The MSQU consists of SR Light naphtha splitter, Naphtha hydrotreatment and isomerization unit. Their objectives are:

- To produce light-light naphtha with reduced C7+ contents in naphtha splitter unit from feed of light naphtha from existing splitter of CDU.
- To treat a mixture of the light-light naphtha and heart cut from the 3-cut splitter in NHDT in order to produce Sulphur free stabilized naphtha.
- To increase RON of the hydrotreated light naphtha cut I the isomerization unit.

Operating conditions:

- Temperature range: 126-145degreeC
- System Pressure: 33.5kg/cm^2

The 3 main units are:

Naphtha Splitter Unit

This section consists of feed surge drum, splitter and associated equipment. The SR light naphtha is routed to the surge drum at 40 degree C to the splitter's feed/ heat exchanger, where it is preheated by exchanging heat. Then the splitter operates on it using the reboiler. The splitter column has total 45 trays. The Light naphtha is routed towards the NHDT Feed Tank and heavy LN naphtha at the bottom of the splitter is cooled and sent to existing HGU feed tanks with excess NHDT naphtha from splitter.

Naphtha Hydrotreating Unit

The purpose of the NHDT Unit is to produce a clean desulphurized naphtha cut to be processed in the isomerization unit after removal of all impurities which are poisons for catalysts (sulfur, nitrogen, water, halogens, diolefins, arsenic, Hg and other metals).

Process Chemistry:

a) Hydrorefining:

Desulfurization:

Denitrification

$R\text{-}NH_2 + H_2 \rightarrow R\text{-}H + NH_3$

Brief Process Description:

Two feeds enter the unit – Straight Run Light Naphtha from Light Naphtha splitter and a heart cut stream from a 3-cut splitter.

Fresh feed is mixed with liquid recycle for olefin dilution and then with hydrogen rich recycle gas from HDT compressors. The mixture is then preheated in reactor feed/effluent exchangers before entering the HDT reactor.

Hydrotreating is performed in two steps: first step is hydrogenation of olefins and diolefins in the first reactor bed and second one corresponds to desulfurization and denitrification, taking place in the second reactor bed.

The feed is then directed towards the stripper section of the NHDT unit where the desulphurized naphtha is routed to ISOM part of the MSQU unit.

Isomerization Unit

The purpose of this unit is the conversion of low octane straight chain compounds to their higher octane branched isomers. The light hydrodesulphurised naphtha feed is dried and passed over an activated chloride catalyst in presence of once through (dried) hydrogen. The reactor temperature is kept low in the range of 120-160 degree C taking advantage of higher concentration of isomers at low temp and minimizing backtracking of equilibrium.

A deisohexaniser tower is included in the flow scheme to recycle the low octane C6 n-paraffins and methyl pentanes back to the reactor circuit to obtain high octane product.

The unit Feed is light hydrotreated naphtha from NHDT unit.

10. Conclusion

Hydrotreating or catalytic hydrogen treating removes objectionable materials from petroleum fractions by selectively making react these materials with hydrogen in a reactor at relatively high temperatures and at moderate pressures. These objectionable materials include, but are not solely limited to, sulphur, nitrogen, olefins, and aromatics. The lighter distillates, such as naphtha, are generally treated for subsequent processing in catalytic reforming units, and the heavier distillates, ranging from jet fuels to heavy vacuum gas oils, are treated to meet strict product quality specifications or for use as feed stocks elsewhere in the refinery.

Hydrotreating is also used for upgrading the quality of atmospheric and vacuum resids by reducing their sulphur and organometallic levels. Hydrotreaters are designed for and run at a variety of conditions depending on many factors such as feed type, desired cycle length, and expected quality of the products. Until about 1980, hydrotreating was a licensed technology being offered by a fairly large number of companies. From 1980 until the end of the last century, hydrotreating catalysts were becoming more commoditized as the formulations were less differentiated among the various suppliers.

Many of the product quality specifications are driven by environmental regulations, and these regulations are becoming more stringent every year. With the advent of ultra-low-sulphur fuel regulations ushering in the first decade of the twenty-first century, however, it was required for hydrotreating research and development to deliver quantum improvements in catalyst performance and process technology. This was accomplished in the form of so-called Type II supported transition metal sulphide (TMS) catalysts, unsupported/bulk TMS catalysts, improved bed grading catalysts and stacking strategies, advanced catalyst loading techniques, improved trickle-flow reactor internals designs, and more effective catalyst activation methodologies.

IOCL Guwahati is planning to put up a new Naphtha Hydrotreater plant along with a 90 KTPA Catalytic Reforming Unit in the refinery. Proposed CRU consists of subsections viz. Naphtha Hydro Treating, Fixed Bed Platforming and Benzene Saturation Section (BENSAT). In order to assess the potential environmental impacts due to the proposed Naphtha Hydro Treatment Unit (NHDT) & Catalytic Reforming Unit (CRU), M/s IOCL, GR has engaged Hubert Enviro Care Systems (P) Limited, Chennai to undertake EIA study. The nature of consultancy service rendered covers terrestrial environmental assessment.

Commercial users don’t prefer using branded fuels.

➔HPCL gives IOCL a big competition and people have much more preference towards HP.

➔Income groups of less than 20000 are reluctant towards buying the branded fuels.

11. References

- Operating manuals of Hydrotreating Unit, Hydrogen Generation Unit, MS Quality Upgradation Unit and INDAdept G Unit of IOCL Guwahati (given by mentor).

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