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Hydrodesulphurizaton of Heavy Oil

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Abstract—*Hydrotreating processes have been used in the refining industry as pretreating processes to protect catalysts from poisons (e.g. reformer) and as post treatment processes to give color improvement and stability for long time. Due to environmental factors and the goal for fuels with higher hydrogen and lower aromatics, hydroprocessing has come to play a central role in refining industry. Moreover, the imperative for conversion of resids with high amount of heteroatoms (S, N, metals etc.) to cleaner fuels has made hydroprocessing more of a necessity. Hydroprocessing includes hydrotreatment of light and middle distillates, mild hydrocracking, resid hydrocracking, hydrofinishing of lubes and waxes and hydroisomerization. Direct catalytic hydrodesulphurization in presence of hydrogen is presently one of the most preferred methods employed to lower the sulfur content of crude oils as well as to improve the quality of the catalyst feedstock. This paper presents the study on hydrodesulphurization of heavy oil, which is bottom product of fluid catalytic cracking. The heavy oil is treated to lower the sulfur level and asphaltene contents while retaining the aromatics. Experiments were carried out at different operating conditions viz. temperature, pressure and LHSV (Liquid Hourly Space Velocity) to optimize the process and to obtain the desired range of sulfur content.*

Keywords*: Hydrodesulfurization, H_2 to oil ratio, LHSV, DMDS, catalysts.*

1. INTRODUCTION

It is well accepted that the crude oils available to refineries presently are heavier as compared to previously available crude oils [1]. Meanwhile, the demand for high value products such as gasoline and middle distillates is increasing. The trend towards heavy feedstock and urgent demand for high quality products as well as tightening fuel regulations are presenting new challenges for refineries. Several types of commercial processes for upgrading various petroleum feeds involve either hydrogen addition to the feed or carbon rejection [2]. The hydrogen addition processes require the presence of an active catalyst.

The difficulty of upgrading increases with increasing content of contaminants (e.g., metals, resins, asphaltenes, sulfur, and nitrogen) in the feed. Catalysts play a vital important role in the heavy oils upgrading process [3]. The catalysts used in hydroprocessing technology are usually composed of oxides of Mo, Co, Ni, and W on a matrix or carrier of alumina, silica, and silica/alumina.

The catalyst activity, selectivity, particle size and shape, pore size and distribution, as well as the type of the reactor, have to be optimized according to the properties of the heavy oils and to the desired purification and conversion levels [4].

2. OPERATING VARIABLES

There are basically four principal operating variables for the hydrotreating process [5].

a) *Pressure:* The increase in partial pressure of hydrogen increases the hydrotreating rate and diminishes the coke deposits on the catalyst, thereby reducing the catalyst fouling rate and increasing the catalyst life.
b) *Temperature:* The hydrotreating reactions are favoured by an increase in temperature, but at the same time, high temperature causes coking reactions, diminishing the activity of the catalyst. The desulfurization reactions are exothermic and it is necessary to find a compromise between the reaction rate and the overall catalyst life.
c) *Liquid Hourly Space Velocity:* The liquid hourly space velocity (LHSV) is defined as:

$$LHSV = \frac{Per\ hour\ feed\ rate\ of\ the\ charge\ (cc/hr)}{volume\ of\ catalyst\ bed\ (cc)}$$

Hydrotreating reactions are favoured by a reduction in Liquid Hourly Space Velocity.

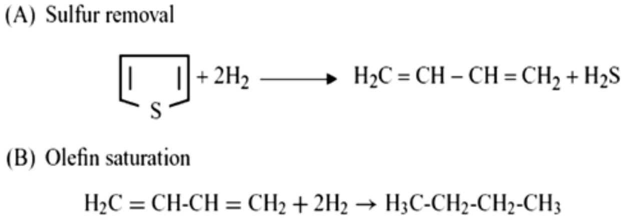
d) *H_2/Oil ratio:* The hydrogen/oil ratio influences the multiphase hydroprocessing reactions. High hydrogen concentration in the reactor helps in lowering the partial pressure of hydrogen sulphide generated during the process in the reactor.

Hydrotreating is a class of high temperature catalytic reactions which are carried out in the presence of hydrogen. Of these Hydrodesulfurization (HDS), i.e. removal of sulfur compounds is the major reaction [6].

Hydrotreating catalysts are mixed sulfides of mostly CoMo or NiMo supported on high–surface–area carriers such as γ–alumina. While CoMo sulfide is the preferred combination for Hydrodesulfurization (HDS) operations [7]. The main reason for their wide application lies in the high tolerance towards H_2S, an inevitable poison produced during HDS operation. The oxide catalysts are less active therefore sulfiding is done for these catalysts. In sulfiding process, the oxide form is converted into more active sulfide form. Sulfiding is generally done with a sulfiding agent like DMDS (Dimethyl disulfide).

The purpose of removing the sulfur is to reduce the sulfur dioxide (SO_2) emissions that result from using those fuels in automotive vehicles, aircraft, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion [8]. Another important reason for removing sulfur from the feed streams within a petroleum refinery is that sulfur, even in extremely low concentration, poisons the metal catalysts [9].

Desulfurization mechanism [10]:



3. EXPERIMENTAL SETUP

For all the experiments, feedstock was taken from the bottom of the fractionator in FCC (Fluid Catalytic Cracking) also known as slurry oil [11]. Asphaltenes are the most hydrogen deficient constituents of slurry oil. They become more active and react with one another at higher temperatures and especially in the presence of metal surfaces, to form coke [12].

The experimental unit was operated in down-flow liquid once-through mode [13]. The catalyst sulfiding was done with the straight run gas oil with a sulfiding agent DMDS (Dimethyl disulfide) based on the given sulfiding procedures. After the catalyst sulfiding, the unit was operated at start of run conditions with the given test feed. The operating parameters e.g. pressure, temperature, hydrogen to hydrocarbon ratio, LHSV was maintained at the given conditions.

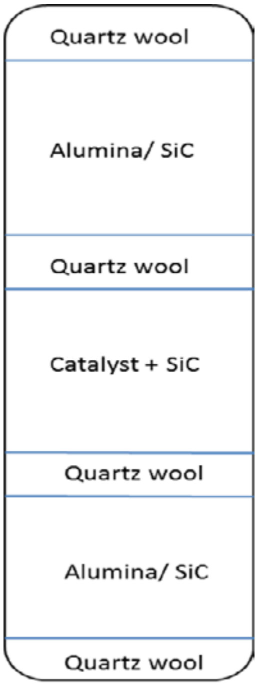
Reactor **W**eighted **A**verage **B**ed **T**emperature (WABT) was in the range of 320-380°C, LHSV in the range of 0.5-2 h^{-1}, H_2 partial pressure in the range of 20-80 kg/cm^2g and H_2/oil ratio in the range of 300-800 Nm^3/m^3.

4. EXPERIMENTAL PROCESS

The steps involved in the process are as follows:

1. MFC Calibration: Mass flow controller (MFC) is a device used to measure and control a specific type of gas at a particular range of flow rates. Calibration of a MFC was done to have the best possible accuracy and reliability in the instrument. It ensured the accurate measurement of hydrogen (H_2) flow and hence the requirement input of hydrogen was considered reliable.

2. Catalyst Loading: The catalyst loading is done as shown in the figure below.



The catalyst must be loaded carefully, as rough handling may cause breakage and produce fines which can result in variable pressure drop [14]. Diluent is added to catalyst bed to fill the voidage to minimize the wall effects. Glasswool is required to be provided between two consecutive beds.

Initially, glass wool plug is used so as to assure that the alumina balls above the bed do not move out and plug the lines. Then alumina balls are added as inert support to the catalyst bed. The alumina balls bed height is adjusted to maintain the catalyst bed height at the required zone in furnace.

The catalysts are added in stages with intermediate addition of inert and then the reactor is vibrated mildly to ensure filling of voidage to remove channelling. Alumina balls are then introduced at the top of the catalyst bed to ensure the proper distribution of feed over the catalyst bed and also to act as a preheat zone [15].

3. Pressure Testing: After the catalyst is loaded in a reactor, the entire high pressure gas loop was checked for leakage by pressurizing the loop with nitrogen gas (N_2) up to a pressure slightly in excess to the operating pressure for 24 hrs.

4. Catalyst Activation/Sulfiding: The catalyst is converted to an active form by activation process. Non-noble metal catalysts are activated by transforming the inactive metal oxides into active metal sulfides (sulfiding). The sulfiding operation is critical as it has a direct impact on the activity and run length and performance of the catalyst [16]. Sulfiding is generally done with the straight run gas oil/Light gas oil with a sulfiding agent like DMDS (Dimethyl disulfide) usually at the intermediate temperature (200 - 250°C).

After the catalyst sulfiding, the unit was operated at start of run conditions with the given test feed. The operating parameters e.g. pressure, temperature, hydrogen to hydrocarbon ratio, Liquid hourly space velocity (LHSV) was maintained at the given conditions.

Operating parameters	
WABT	320 – 380 (°C)
H_2 partial pressure	20 – 80 (kg/cm^{2}g)
LHSV	0.5 – 2 (h^{-1})
H_2/oil	300 – 800 (Nm^3/m^3)

5. Sampling: After the final operating conditions are set, the unit takes more than 24hrs for stabilization. Once the unit gets stabilized, material balance is conducted and finally stable samples are collected for sampling for simulated true boiling point (SIMTBP), S, N, aromatics and density tests.

6. Shut Down: Shut down procedure was split up into two sections: normal and emergency. In all cases, the catalyst was kept fully sulfided to prevent excessive coke formation which occurs when oil is in contact with hot catalyst without H_2 circulation. The general rule for a successful shut down (be it either planned or emergency) was that after the oil flow has been stopped, oil was stripped from the catalyst by applying maximum H_2 flow rates.

The unit was shut down and maintained at low pressure under either a H_2 or N_2 environment depending on the duration of the shut down and its purpose. Under no circumstances was the catalyst allowed to come into contact with oxygen if it has not been regenerated.

5. RESULTS AND DISCUSSION

The unit was operated at the typical hydrodesulfurizing conditions with the heavy oil. The operating parameters e.g. pressure, temperature, hydrogen to hydrocarbon ratio, Liquid hourly space velocity (LHSV), etc. was maintained at typical hydrodesulfurizing conditions as given in table below.

Description		
Catalyst sample	**Hydrotreating Catalyst**	
Attributes	**Feed (Heavy oil)**	**Hydrodesulfurized Product**
Sulphur (wt.%)	1-2.5	< 0.5

The material balance was conducted and it was observed that the material balance was within the considerable limit (less than 2 % error) [17]. The characteristics of the heavy oil feed and hydrodesulfurized product are given in table below:

The experiments were carried out for the hydrotreatment of the gas oil and the hydrodesulfurized product obtained has < 0.5 wt. % S. It was observed that the standard values taken for the design parameters were able to successfully achieve the significant S removal that was the aim of the project.

6. CONCLUSION

High aromatic content, low sulfur levels, and low asphaltene content are the preferred characteristics oil should have in order to obtain the valuable products such as Needle Coke.

In the present study, hydrodesulphurization has been carried out with commercial hydrotreating catalyst. Experiments have been conducted at the given operating conditions and it has been found that desulfurized product obtained has S < 0.5wt.%.

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