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Design Parameters for a Hydro desulfurization (HDS) Unit for Petroleum Naphtha at 3500 Barrels per Day

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ABSTRACT

The present work reviews the setting up of a hydrodesulphurization unit for petroleum naphtha. Estimating all the properties of the given petroleum fraction including its density, viscosity and other parameters. The process flow sheet which gives the idea of necessary equipment to be installed, then performing all material and energy balance calculations along with chemical and mechanical design for the entire setup taking into account every instrument considered. The purpose of this review paper takes involves an industrial process, a catalytic chemical process widely used to remove sulfur (S) from naphtha.

Keywords: hydro desulfurization; naphtha; petroleum; sulfur

Relevance to Design Practice - The purpose of removing the sulfur is to reduce the sulfur dioxide emissions that result from using those fuels in automotive vehicles, aircraft, railroad locomotives, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion.

1. INTRODUCTION

Hydrodesulphurization (HDS) is a catalytic chemical process widely used to remove sulfur (S) from natural gas and from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils. The purpose of removing the sulfur is to reduce the sulfur dioxide (SO₂) emissions that result from various combustion practices. Another important reason for removing sulfur from the naphtha streams within a petroleum refinery is that sulfur, even in extremely low concentrations, poisons the noble metal catalysts (platinum and rhenium) in the catalytic reforming units that are subsequently used to upgrade the octane rating of the naphtha streams.

The industrial hydrodesulphurization processes include facilities for the capture and removal of the resulting hydrogen sulfide (H₂S) gas. In petroleum refineries, the hydrogen sulfide gas is then subsequently converted into byproduct elemental sulfur or sulfuric acid (H₂SO₄). In fact, the vast majority of the 64,000,000 metric tons of sulfur produced worldwide in 2005 was byproduct sulfur from refineries and other hydrocarbon processing plants.

The terms hydrotreating, hydroprocessing, hydrocracking, and hydrodesulphurization are used rather loosely in the industry because in the hydrodesulphurization and hydrocracking processes, cracking and desulfurization operations occur simultaneously, and it is relative as to which predominates. In this text, hydrotreating refers to a relatively mild operation whose primary purpose is to reduce the sulfur content (and not to change the boiling range) of the feed.

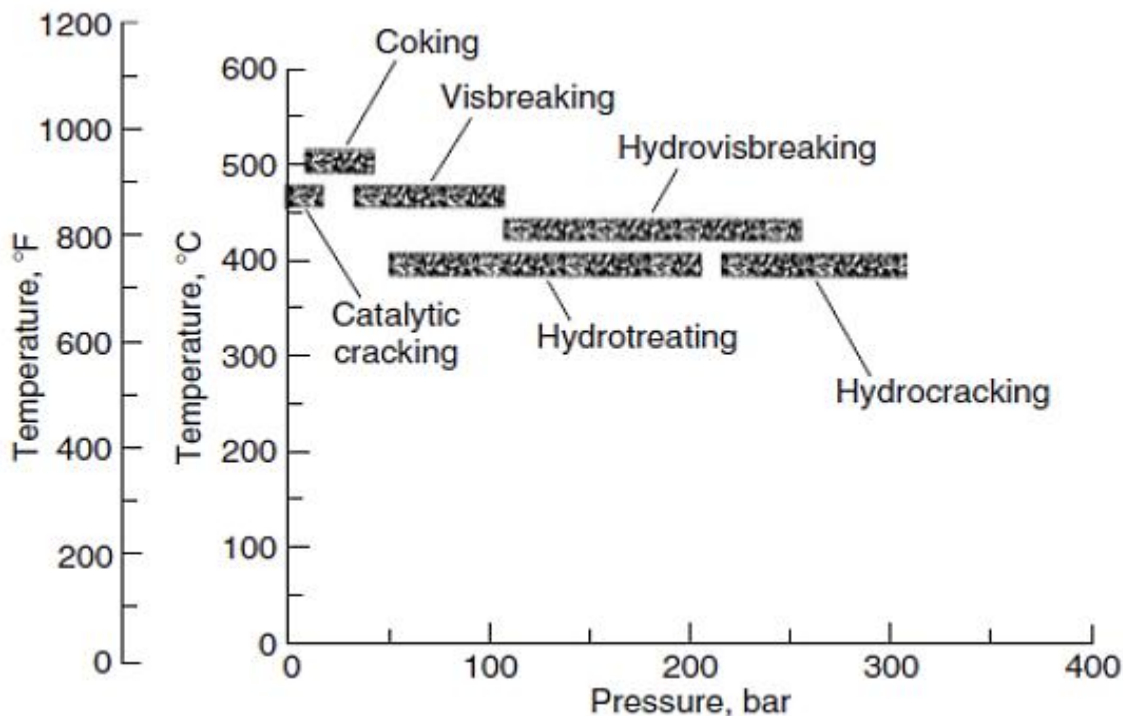


Figure 1. Process conditions (temperature and pressure ranges) for refinery processes.

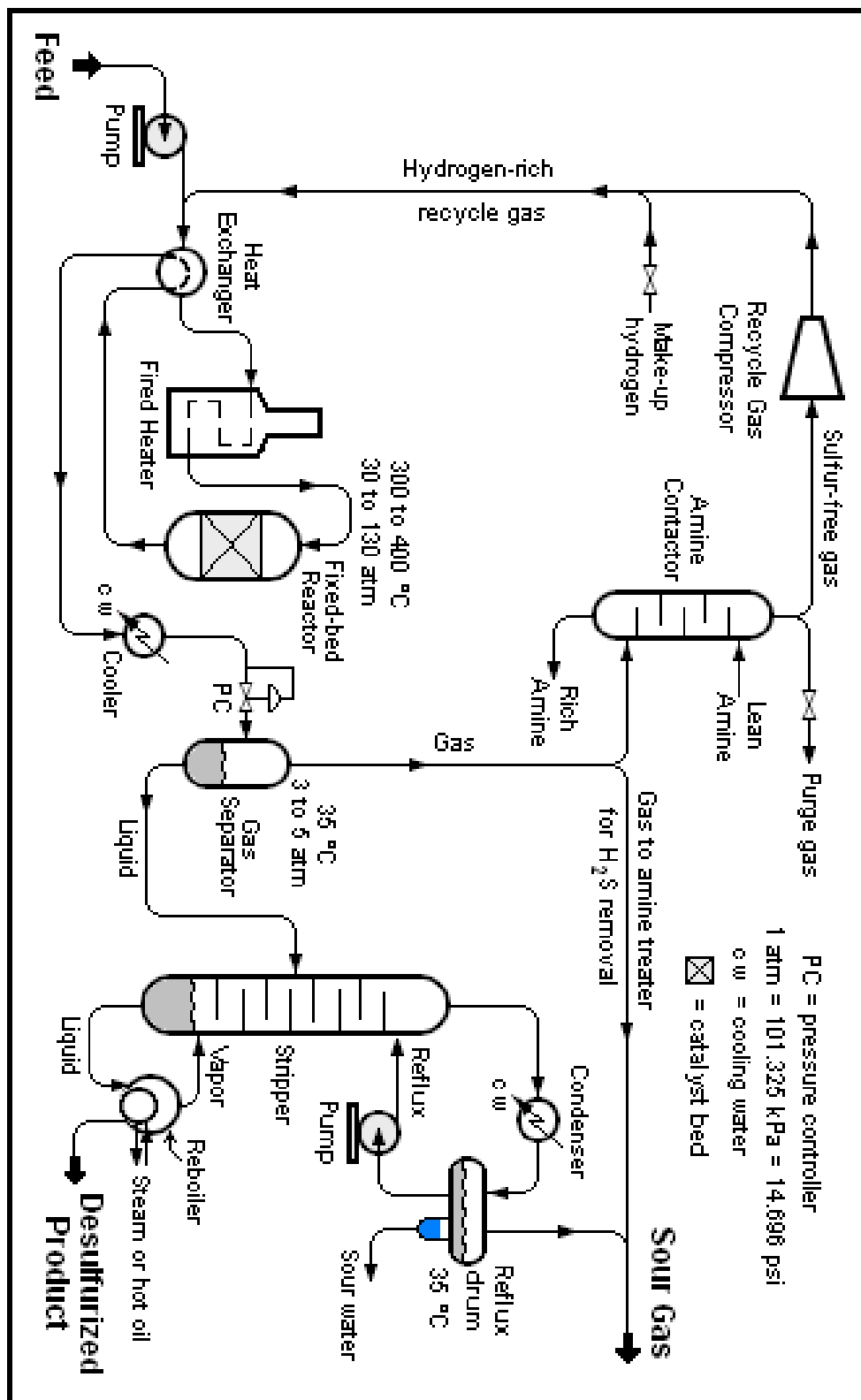


Figure 2. A typical hydrodesulphurization unit.

Hydrocracking refers to processes whose primary purpose is to reduce the boiling range and in which most of the feed is converted to products with boiling ranges lower than that of the feed. Hydrotreating and hydrocracking set the two ends to the spectrum, and those processes with a substantial amount of sulfur or nitrogen removal and a significant change in boiling range of the products versus the feed are called hydro-processing in this text.

Hydrotreating is a process to catalytically stabilize petroleum products by converting olefins to paraffins or remove objectionable elements from products or feedstock by reacting them with hydrogen. Stabilization usually involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable di-olefins to paraffins. Objectionable elements removed by hydro treating include sulfur, nitrogen, oxygen, halides, and trace metals.

Hydrotreating is applied to a wide range of feedstock, from naphtha to reduced crude. When the process is employed specifically for sulfur removal, it is usually called hydrodesulphurization.

To meet environmental objectives, it also may be necessary to hydrogenate aromatic rings to reduce aromatic content by converting aromatics to paraffins.

Although there are about 30 hydro-treating processes available for licensing, most of them have essentially the same process flow for a given application.

The oil feed is mixed with hydrogen-rich gas either before or after it is preheated to the proper reactor inlet temperature. Most hydro-treating reactions are carried out below 800 °F (427 °C) to minimize cracking, and the feed is usually heated to between 500 and 800 °F (260 and 427 °C). The oil feed combined with the hydrogen-rich gas enters the top of the fixed-bed reactor. In the presence of the metal-oxide catalyst, the hydrogen reacts with the oil to produce hydrogen sulfide, ammonia, saturated hydrocarbons, and free metals.

The metals remain on the surface of the catalyst, and the other products leave the reactor with the oil–hydrogen stream. The reactor effluent is cooled before separating the oil from the hydrogen-rich gas. The oil is stripped of any remaining hydrogen sulfide and light ends in a stripper. The gas may be treated to remove hydrogen sulfide and ammonia, and then recycled to the reactor.

2. HYDROTREATING CATALYSTS

Catalysts developed for hydro-treating include tungsten and molybdenum sulfides on alumina. These metals are considered the hydrogenating catalysts but their properties are modified by adding either cobalt or nickel sulfides. Nickel sulfide, nickel thio-molybdate, tungsten and nickel sulfides, and vanadium oxide are also hydrogenation catalysts. Cobalt and molybdenum sulfide on alumina catalysts are in most general use today because they have proven to be highly selective, easy to regenerate, and resistant to poisons. Usually, when purchased the metals are in the oxide state, and they must be activated by converting the hydrogenation metals from the oxide to the sulfide form.

The most economic catalysts for sulfur removal contain cobalt and molybdenum sulfides (CoMo) on alumina supports. If, however, the removal of nitrogen is a significant consideration, catalysts composed of nickel-cobalt-molybdenum or nickel-molybdenum (NiMo) compounds supported on alumina are more efficient.

Nitrogen is usually more difficult to remove from hydrocarbon streams than sulfur, and any treatment that reduces excess nitrogen concentration to a satisfactory level usually will effectively remove excess sulfur.

Nickel-containing catalysts generally require activation by presulfiding with carbon disulfide, mercaptans, or dimethyl sulfide before bringing up to reaction temperature. However, some refiners activate cobalt-molybdenum catalysts by injecting the sulfiding chemical into the oil feed during start-up. The sulphiding reaction is highly exothermic, and care must be taken to prevent excessive temperatures during activation to prevent permanent catalyst deactivation.

Table 1. Typical ranges of Hydrotreating Catalyst Properties.

| | |
|---|-------------|
| Nominal Catalyst Dia | 1/8 to 1/20 |
| Average length of extrudates, in. | ~ 1/4 |
| Packed catalyst density, lb/ft ³ | 30 to 50 |
| Surface area, m ² /g | 200 to 300 |
| Nickel content, wt% | 0 to 6 |
| Cobalt content, wt% | 0 to 6 |
| Molybdenum content, wt% | 5 to 15 |

Cobalt-molybdenum catalysts are selective for sulfur removal, and nickel-molybdenum catalysts are selective for nitrogen removal, although both catalysts will remove both sulfur and nitrogen. Nickel-molybdenum catalysts have a higher hydrogenation activity than cobalt-molybdenum, which results, at the same operating conditions, in a greater saturation of aromatic rings.

Simply stated, if sulfur reduction is the primary objective, then a cobalt-molybdenum catalyst will reduce the sulfur a given amount at less severe operating conditions with a lower hydrogen consumption than a nickel-molybdenum catalyst. If nitrogen reduction or aromatic ring saturation is desired, nickel-molybdenum catalyst is the preferred catalyst.

Actually, nickel-tungsten is most effective for nitrogen removal and saturation of aromatic rings to reduce aromatic content but is much more expensive than nickel-molybdenum and is, therefore, seldom used in fuels refineries.

The ability to adjust pore size to concentrate pores around a particular diameter has a great impact on the hydrotreating activity both at start-of-run (SOR) and as the catalyst ages. Reactions taking place in the hydrotreating of gas oils [400 to 1050°F (200 to 566°C)] generally require a minimum pore size to overcome most diffusional restrictions.

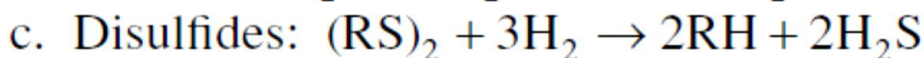
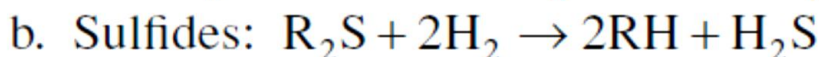
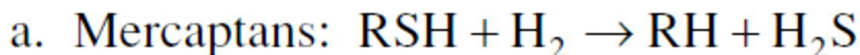
Pores that are larger than necessary lend little to improving diffusional characteristics, and as the pore diameters of the catalyst increase, the surface area decreases (at constant pore volume). Activity generally decreases with surface area, and loss in pore volume occurs in the smallest diameter pores first.

Highest activity retention is maintained if the pore volume is concentrated in a very narrow range of pore diameters. At the hydrotreating severity to reduce sulfur in LCO to 0.05 wt%, the performance of high-activity NiMo and CoMo catalysts appears to be equivalent. Catalyst consumption varies from 0.001 to 0.007 lb/bbl (0.003 to 0.02 kg/m³) feed depending upon the severity of operation and the gravity and metals content of the feed.

3. REACTIONS

The main hydrotreating reaction is that of desulfurization, but many others take place to a degree proportional to the severity of the operation. Typical reactions for this project are:

Desulfurization



d. Thiophenes:

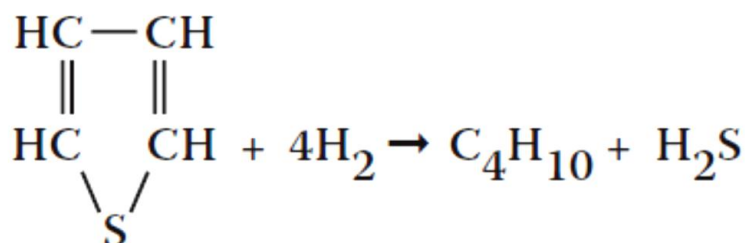


Figure 3. Sulfur forms present in petroleum fractions.

The ease of desulfurization is dependent upon the type of compound. Lower-boiling compounds are desulfurized more easily than higher-boiling ones. The difficulty of sulfur removal increases in this order: paraffins, naphthenes, aromatics.

Nitrogen removal requires more severe operating conditions than does desulfurization. For middle distillate fractions from crude oils containing high concentrations of nitrogen compounds, more efficient nitrogen reduction is achieved by using a catalyst charge of 90% nickel-molybdenum and 10% nickel-tungsten.

Hydrogen consumption is about 70 scf/bbl (12.5 Nm³/m³) of feed per percentage sulfur about 320 scf/bbl (57 Nm³/m³) oil feed per percentage nitrogen, and 180 scf/bbl (32 Nm³/m³) per percentage oxygen removed.

Hydrogen consumption for olefin and aromatics reduction can be estimated from the stoichiometric amounts required.

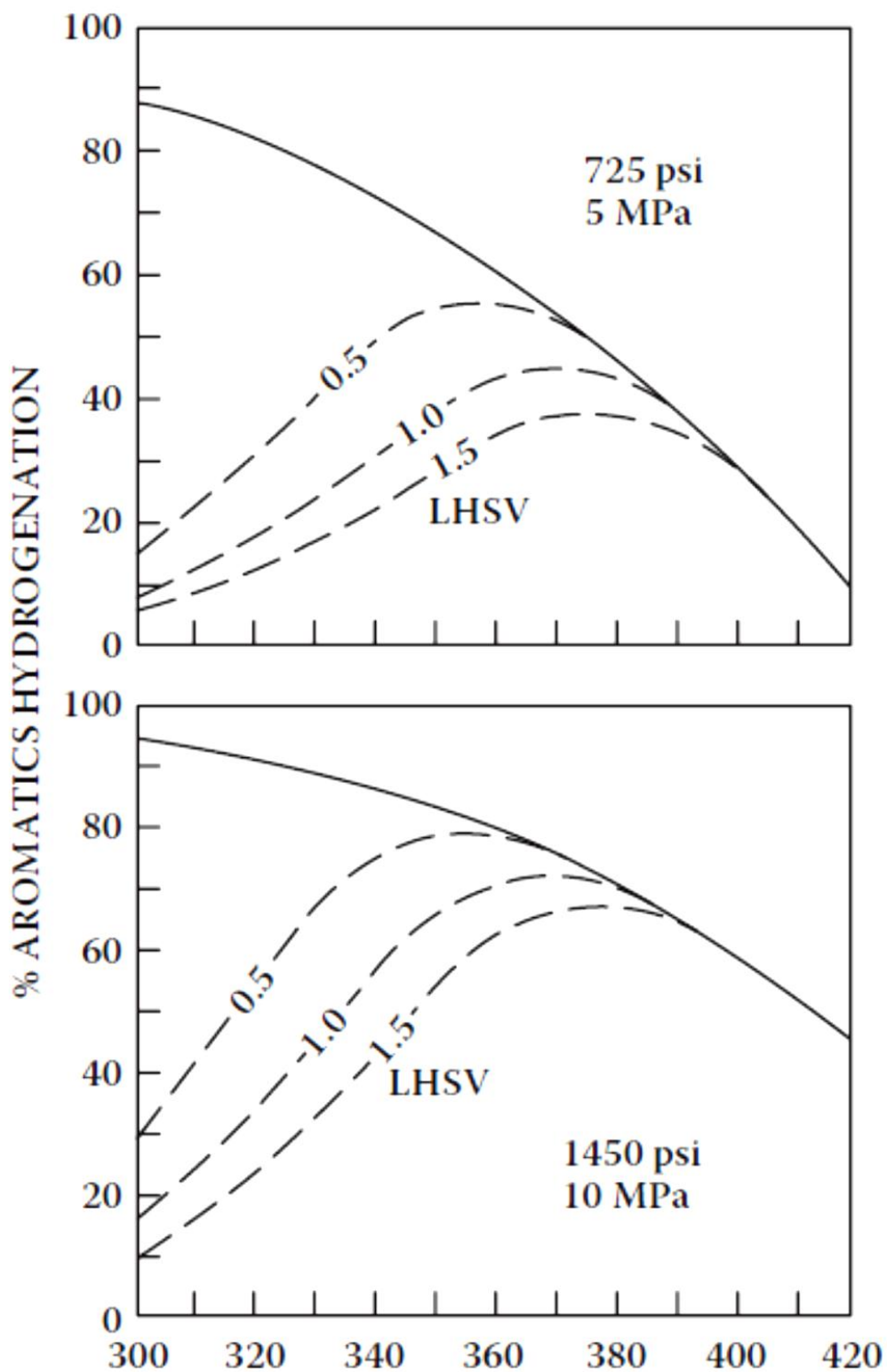


Figure 4. Kinetics and Thermodynamic Equilibrium effects on Aromatic reduction.

If operating conditions are severe enough that an appreciable amount of cracking occurs, hydrogen consumption increases rapidly.

It is important to note that actual hydrogen makeup requirements are from two to ten times the amount of stoichiometric hydrogen required. This is due to the solubility loss in the oil leaving the reactor effluent separator and the saturation of olefins produced by cracking reactions.

All reactions are exothermic, and depending on the specific conditions, a temperature rise through the reactor of 5 to 20 °F (3 to 11 °C) is usually observed.

4. PROCESS VARIABLE

The principal operating variables are temperature, hydrogen partial pressure, and space velocity.

Increasing temperature and hydrogen partial pressure increases sulfur and nitrogen removal and hydrogen consumption. Increasing pressure also increases hydrogen saturation and reduces coke formation. Increasing space velocity reduces conversion, hydrogen consumption, and coke formation.

Although increasing temperature improves sulfur and nitrogen removal, excessive temperatures must be avoided because of the increased coke formation. Typical ranges of process variables in hydrotreating operations are:

| Parameter | Naphtha | Residuum |
|--|----------------|-----------------|
| Temperature (°C) | 300 to 400 | 340 to 425 |
| Pressure (atm.) | 35 to 70 | 55 to 170 |
| LHSV | 4.0 to 10.0 | 0.2 to 1.0 |
| ¹ H ₂ recycle rate (scf/bbl) | 400 to 1000 | 3000 to 5000 |
| Catalyst life (years) | 3.0 to 10.0 | 0.5 to 1.0 |
| Sulfur removal (%) | 99.9 | 85.0 |
| Nitrogen removal (%) | 99.5 | 40.0 |

Figure 5. Process parameters for Hydrodesulfurization

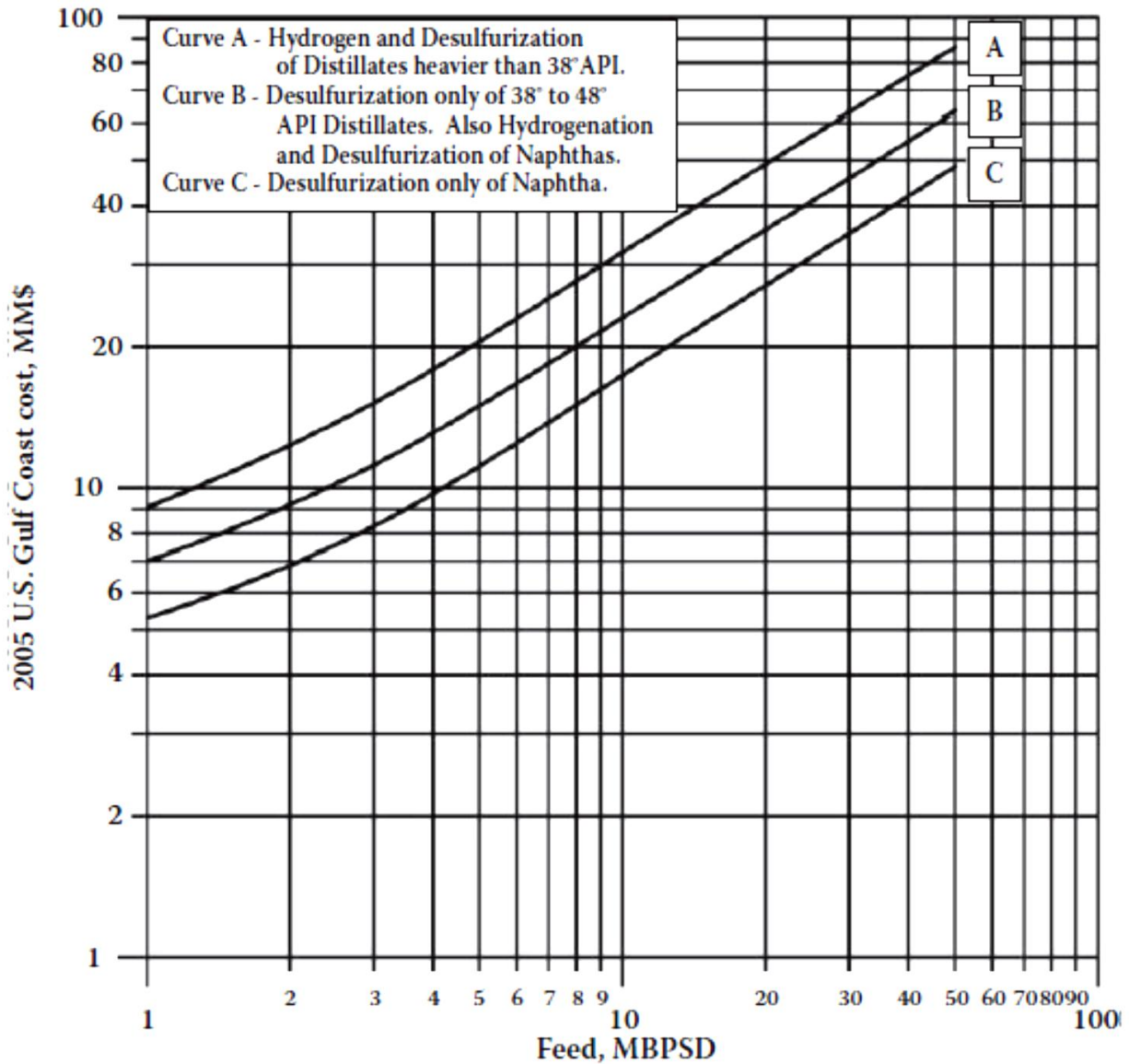


Figure 6. Catalytic Desulphurization and hydrogenation unit investment cost, 2005, US Gulf Coast

5. PETROLEUM NAPHTHA

Naphtha is a complex mixture of liquid hydrocarbons, with boiling ranges of about 40 to 140 °C and with vapor pressures of about 0.69 bar. Crude distillation, catalytic cracking, delayed coking and visbreaking units produce naphtha with low octane number and contain different types of contaminants at the same time. As more demand for high Gasoline Octane number continues; to match with modern motor such is done. Chemical structure modification is achieved on an expensive Platinum catalyst at Catalytic reforming and Isomerization unit. Sulfur, Nitrogen, Oxygen and other impurities in Naphtha work as a poisonous for Pt catalyst activity.

Hydro-treating is used to prepare a clean feedstock to protect catalyst used in naphtha reforming. A catalytic reforming unit uses platinum as the catalyst to convert naphtha into high octane gasoline or aromatics. As a platinum catalyst is easily poisoned by the presence of sulfur, oxygen, nitrogen, and metallic components, it is essential to pre-treat naphtha before reforming. This, in fact, is done simultaneously in a catalytic hydrogen pretreatment reactor. Naphtha stream, i.e., 90° C – 140 °C fraction, from the naphtha re-distillation column is usually desulphurized in a catalytic hydrogenation unit and is then sent to a platinum reforming unit where high octane gasoline or aromatics (BTX) are produced. In this unit, naphtha is preheated by a train of heat exchangers and further heated in a pipe-still heater to a temperature of 350 °C in the presence of hydrogen under a pressure of 20 – 25 kg/cm² over a catalyst (Co-Mo sulfides supported on alumina) packed bed reactor.

6. HISTORY OF NAPHTHA HYDRO-TREATING

1897: Paul Sabatier, “French chemist” discovered the fixation of hydrogen on hydrocarbon (ethylene, benzene) double bonds using nickel containing catalyst.

1903: Wilhelm Normann, “German chemist” applied catalytic hydrogenation to Saturate Organic acids.

1950's: First catalytic reforming process was commercialized. At the same time, the catalytic Hydrodesulphurization of the naphtha feed to such reformers was also commercialized.

Currently, all petroleum refineries world-wide have one or more HDS units.

7. METHOD

To proceed with the calculations some of the initial parameters were given, which are:

For Naphtha:\

Feed rate (Given) = 3500 BPD (Barrels Per Day)

Aromatics = 30 %

Olefins = 1.3 %

Sulfur = 4 %

Also,

| | |
|----------------------------|--------|
| Initial Boiling Point | 40 °C |
| Final Boiling Point | 140 °C |
| Mean Average Boiling Point | 90 °C |

Given is considered a heavy petroleum fraction and for calculating molecular weight of a heavy petroleum fraction the following equation is used:

$$M = 223.56 \nu_{100}^{(-1.2435 + 1.1228S)} \nu_{210}^{(3.4758 - 3.038S)} S^{-0.6665}$$

Where:

M = Molecular weight of the petroleum fraction

ν_{100} = Kinematic viscosity of petroleum fraction at 100 F, in centistokes

ν_{210} = Kinematic viscosity of petroleum fraction at 210 F, in centistokes

S = Specific gravity, 60 F/60 F

For above calculation of molecular weight, viscosity is estimated at 100 °F and 210 °F along with specific gravity.

At 100°F,

$$\nu_{100} = \nu_{ref} + \nu_{cor}$$

$$\log \nu_{ref} = -1.35579 + 8.16059 \times 10^{-4} T_b + 8.38505 \times 10^{-7} T_b^2$$

$$\log \nu_{cor} = A_1 + A_2 K$$

Where:

$$\begin{aligned} A_1 &= c_1 + c_2 T_b + c_3 T_b^2 + c_4 T_b^3 \\ A_2 &= d_1 + d_2 T_b + d_3 T_b^2 + d_4 T_b^3 \\ c_1 &= 3.49310 \times 10^1 \\ c_2 &= -8.84387 \times 10^{-2} \\ c_3 &= 6.73513 \times 10^{-5} \\ c_4 &= -1.01394 \times 10^{-8} \\ d_1 &= -2.92649 \\ d_2 &= 6.98405 \times 10^{-3} \\ d_3 &= -5.09947 \times 10^{-6} \\ d_4 &= 7.49378 \times 10^{-10} \end{aligned}$$

And for 210 °F we use the following:

At 210 F,

$$\log v_{210} = B_1 + B_2 T_b + B_3 \log (T_b v_{100})$$

$$B_1 = -1.92353$$

$$B_2 = 2.41071 \times 10^{-4}$$

$$B_3 = 0.511300$$

v_{100} = kinematic viscosity at 100 F, in centistokes.

v_{210} = kinematic viscosity at 210 F, in centistokes.

T_b = mean average boiling point, in degrees Rankine.

SG = specific gravity, 60F/60F.

$$\text{Watson K factor} = \frac{T_b^{1.3}}{\text{SG}}$$

note: API gravity may be converted to specific gravity using the equation,

$$\text{specific gravity} = \frac{141.5}{(\text{API} + 131.5)}$$

Heat of Formation calculation for hydro desulfurization reaction

$$H_L = A_1 [T - 259.7] + A_2 [T^2 - (259.7)^2] + A_3 [T^3 - (259.7)^3]$$

Where:

H_L = enthalpy of liquid petroleum fraction with $T_r \leq 0.8$ and $P_r \leq 1.0$, in British thermal units per pound.

$$A_1 = 10^{-3} \left[-1171.26 + (23.722 + 24.907 \text{ sp gr}) K + \frac{(1149.82 - 46.535 K)}{\text{sp gr}} \right].$$

$$A_2 = 10^{-6} \left[(1.0 + 0.82463 K) \left(56.086 - \frac{13.817}{\text{sp gr}} \right) \right].$$

$$A_3 = -10^{-9} \left[(1.0 + 0.82463 K) \left(9.6757 - \frac{2.3653}{\text{sp gr}} \right) \right].$$

p_r = reduced pressure = p/p_{pc} .

p = pressure, psia.

p_{pc} = pseudocritical pressure, psia.

T_r = reduced temperature = T/T_{pc} .

T = temperature, degrees Rankine.

T_{pc} = pseudocritical temperature, degrees Rankine.

K = Watson characterization factor.

sp gr = specific gravity, 60 F/60 F.

8. RESULTS

The following were obtained for the given naphtha feed:

| Parameters | Values |
|---|-------------------|
| Average Molecular weight | 100.133 |
| Specific Gravity | 0.69 |
| API Gravity | 73.572 |
| Heat of formation for Hydrodesulphurization | -251000 KJ/K-mole |
| Watson Characterization Factor | 6.494 |

9. DISCUSSIONS AND CONCLUSIONS

This paper attempts to explain few physical properties determination which can potentially harbor the hydrodesulphurization (HDS) operation for an oil refinery which uses petroleum naphtha as feed. Every attempt has been made to do justice with this industrial research problem, which despite technological advances still faces challenge because as days go by, environmental laws are being more rigid about pollution and its control, essentially this projects attempts to speculate what kind of setup with related material can be used, which can be the next step in the Hydrodesulphurization Unit of an Oil Refinery.

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