HYDRODESULFURIZATION OF RESIDUALS

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INTRODUCTION

Since the first commercial H-Oil Unit came on-stream at Lake Charles in 1963, a variety of feedstocks have been processed -- including heavy cycle oils, atmospheric bottoms, vacuum bottoms and cutback propane deasphalter bottoms.

The Unit has operated successfully with both microspheroidal and extrudate catalysts and is being expanded to 6,000 BPD.

Besides the Lake Charles H-Oil Unit, three other commercial units were designed for hydrocracking. The units, though designed for hydrocracking, can be utilized for desulfurization. That is now the primary objective for the Cities Service Lake Charles Unit.

LAKE CHARLES H-OIL EXPERIENCE

The H-Oil Unit was designed to convert 2,500 BPD of West Texas Sour Vacuum Bottoms into lighter products.[1] Later it was found possible to process a heavier lower value feedstock, cutback propane deasphalter bottoms.[2] In late 1966 and early 1967 a commercial demonstration of residual desulfurization was made, feeding West Texas Atmospheric Residuum. The demonstration run was quite successful. Sulfur was reduced from 2.5 to 3.0 weight percent in the feed to 0.3 to 0.5 weight percent in the product. Catalyst usage was approximately 0.05 lbs/bbl.

From 1963 to 1967 a 1/32-inch extrudate catalyst was used. In 1967 relatively minor modifications were made to accommodate a microspheroidal fine catalyst. This eliminated the need for the internal recycle pump previously required to supply the liquid velocity necessary for bed expansion. Operating and performance data have been described previously.[3,4]

From 1967 through 1971 the unit operated with the fine catalyst. During this period the feed was West Texas Sour Vacuum Bottoms cutback with 20% heavy cycle oil. In the last few months of operation with the fine catalyst, conversion of vacuum bottoms to distillate ranged from 55% to 75%, with 75% to 80% sulfur removal. The performance of the microspheroidal or fine catalyst has been demonstrated to be equivalent to the performance of the 1/32-inch extrudate. The unit was expanded from 2,500 BPD capacity to 6,000 BPD. It was necessary to return to the extrudate catalyst at the higher feed rate to avoid excessive expansion of the catalyst bed.

FACTORS AFFECTING DESIGN

A number of design factors must be considered when desulfurizing resids. These are caused by: (1) the complex feedstock characteristics, (2) the tendency to deposite metallic impurities and coke on the catalyst, (3) the required operating severity, (4) the extent and desirability of concurrent reactions, such as hydrocracking, and the relatively high hydrogen consumption and design considerations given to the heat released.

FEEDSTOCK CHARACTERISTICS

Several important feed characteristics considered in H-Oil desulfurization are:

1. The character of the residuum, i.e., whether vacuum, atmospheric, deasphalter bottoms, cracked tars, blends, etc.

2. The asphaltene and metal content.

3. The sulfur level and degree of desulfurization required.

These feed characteristics ultimately influence the selection of operating temperature, hydrogen partial pressure, space velocity, and catalyst type and usage.

CATALYST

Microspheroidal and extrudate catalysts have been used commercially. These catalysts consist of a combination of metals such as cobalt and molybdenum or nickel and molybdenum on an alumina support. An earlier publication reported that a 1/32-inch extrudate performs[3] better than a 1/16-inch extrudate.[5] The most active catalyst is the one with the greatest surface area.[6,7]

Organometallic compounds in the feed are the primary cause of catalyst deactivation. The deactivation rate is influenced by feedstock characteristics, catalyst characteristics and operating severity.

OPERATING CONDITIONS FOR RESIDUUM DESULFURIZATION

Temperature, space velocity, hydrogen partial pressure and catalyst consumption are the essential operating conditions considered in residual desulfurization. These normally range from 700 to 800°F,[6] 0.3 to 3.0 V/Hr/V,[8] and 0.02 to 1.0 lbs/bbl respectively. The ranges do not necessarily represent technical limits but are based on judgment and economic considerations.

DESIGN CONSIDERATIONS

The reaction in residuum desulfurization is exothermic. In the ebullated bed the reactor is isothermal. The temperature is controlled by charging the feed below the reactor temperature.

Solids entering with the feed pass through the expanded catalyst bed without causing a pressure buildup. Catalyst activity and product quality are maintained by adding and withdrawing catalyst while on-stream. Constant catalyst replacement gives the refiner flexibility when changing feedstock.

With the fine catalyst, the velocity required to expand the catalyst is achieved by the flow of the liquid-gas feed mixture passing upward through the reactor.[4] Catalyst inventory and bed expansion are essentially a function of the catalyst particle size and density, liquid viscosity, and liquid and gas velocities. Catalyst is added with the feed and leaves with the product.

The extrudate catalyst requires higher liquid velocities than the fine catalyst to maintain the desired bed expansion. The liquid velocity is provided by recycling a portion of the effluent back to the inlet. The recycle or ebullating pump can be located internal or external to the reactor.

H-OIL DESULFURIZATION COSTS

A wide variety of atmospheric and vacuum residuals can be desulfurized using the H-Oil Process.

Costs for desulfurizing Kuwait Atmospheric, Kuwait Vacuum, Khafji Atmospheric, Khafji Vacuum, Venezuelan Atmospheric and Venezuelan Vacuum Residuals are presented. These feedstocks were selected because they are representative of different types of crudes. The Kuwait Atmospheric and Vacuum Residuals are representative of a high sulfur and low metals crude with moderate gravity and asphaltene content. The Khafji Atmospheric and Vacuum Residuals reflect a high sulfur and moderate metals crude with moderate gravity and high asphaltene content. The Venezuelan Atmospheric and Vacuum Residuals are representative of a low sulfur and high metals crude with moderate gravity and high asphaltene content.

Figure 1 shows 975°F+ conversion and chemical hydrogen consumption varying with sulfur in the 400°F+ fuel oil product. It is apparent from Figure 1 that hydrogen consumption and 975°F+ conversion vary inversely with product sulfur content. In addition, the high metals (or Venezuelan feedstocks) experience the highest increase in conversion and hydrogen consumption when going to lower sulfur levels - followed by Khafji and then Kuwait, respectively. As expected the vacuum residual feeds consume the most hydrogen and represent the highest conversion operations.

Figure 2 is a graphical presentation of the processing costs for the feedstocks considered. The costs represent 1971 dollars and include fuel, power, labor, supervision, overhead, water, catalyst and hydrogen. Figure 2 is intended to show the relative costs for desulfurizing the residual feedstocks considered. The economics, though accurate for this purpose, may not be specific enough for a given company, because the costs do not reflect a return on investment. As is well known an acceptable rate of return on investment differs between companies.

As would be expected, the Kuwait Atmospheric Residual is the least expensive to process of the six stocks. The Venezuelan Vacuum Bottoms are the most expensive followed by Khafji Vacuum, Kuwait Vacuum, Khafji Atmospheric and Venezuelan Atmospheric, respectively. In addition, the Venezuelan stocks show the highest rate of increase in operating costs when going to lower sulfur levels.

SUMMARY

Commercial H-Oil experience using 1/32-inch extrudate and fine catalysts were shown to be equally successful. Important design parameters considered in residual desulfurization include the feed characteristics, catalyst characteristics and operating severity. The range of operating conditions employed for residual desulfurization was presented. Process design considerations using the fine or extrudate catalyst were reviewed. The most attractive system will depend on each application. The cost of desulfurizing Middle East and Venezuelan feedstocks were presented.

The H-Oil Process was developed by Cities Service Research Incorporated. Units have been licensed to the Kuwait National Petroleum Company, Humble Oil and Refining Company, Petroleos Mexicanos and Cities Service Oil Company.

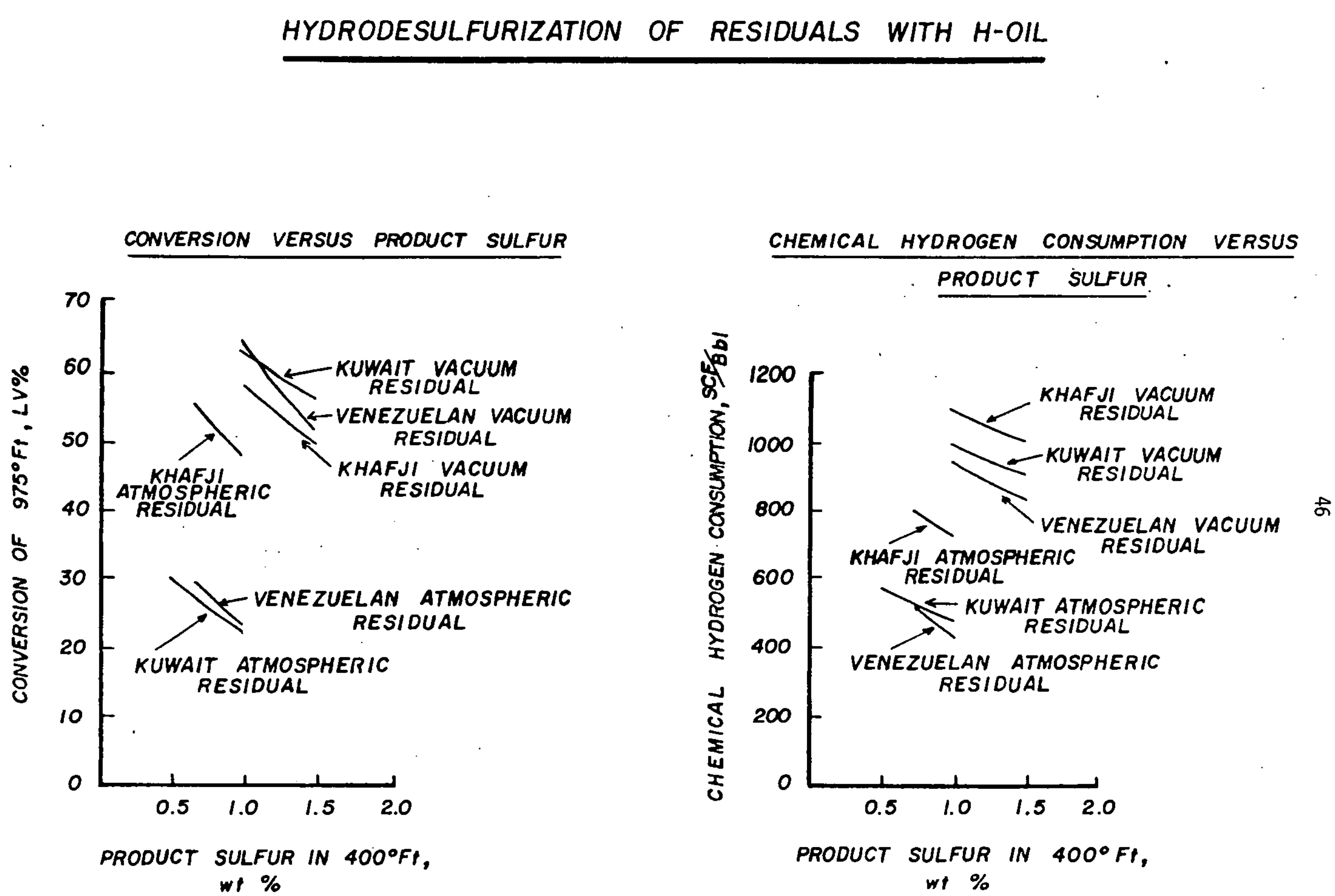
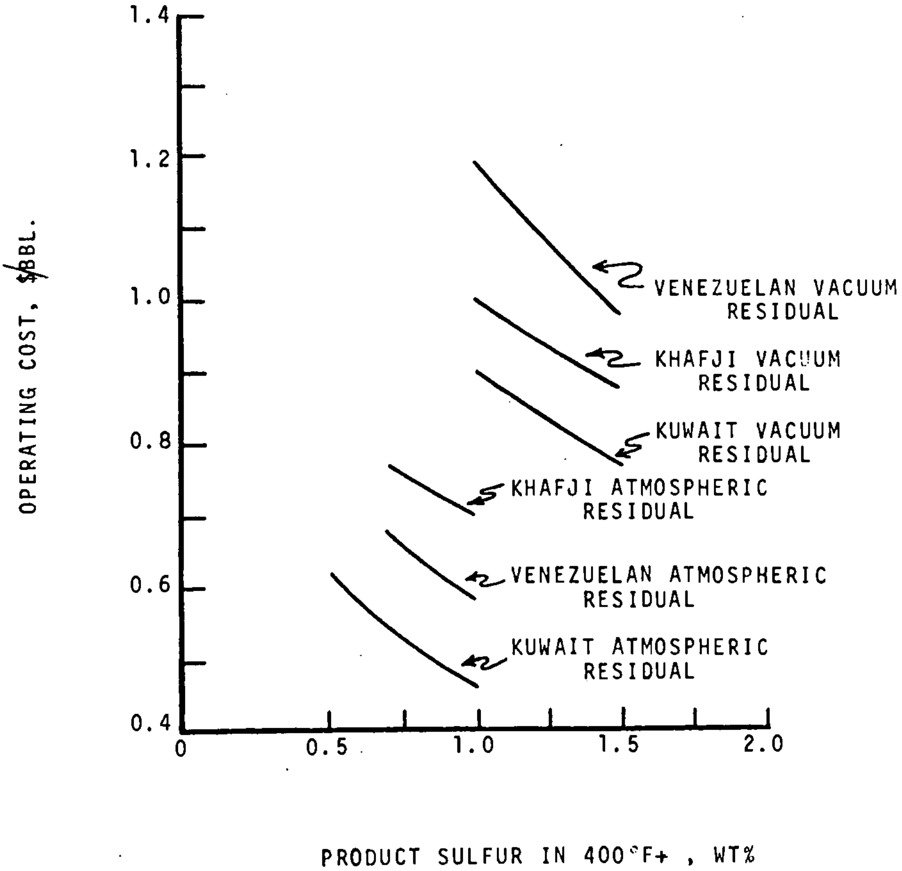

HYDRODESULFURIZATION OF RESIDUALS WITH H-OIL
CONVERSION VERSUS PRODUCT SULFUR
CONVERSION OF 975°F+, LV%
70
60
50
40
30
20
10
0
0.5
1.0
1.5
2.0
PRODUCT SULFUR IN 400°F+, wt %
KUWAIT VACUUM RESIDUAL
VENEZUELAN VACUUM RESIDUAL
KHAFJI VACUUM RESIDUAL
KHAFJI ATMOSPHERIC RESIDUAL
VENEZUELAN ATMOSPHERIC RESIDUAL
KUWAIT ATMOSPHERIC RESIDUAL
CHEMICAL HYDROGEN CONSUMPTION VERSUS PRODUCT SULFUR
CHEMICAL HYDROGEN CONSUMPTION, SCF/Bbl
1200
1000
800
600
400
200
0
0.5
1.0
1.5
2.0
PRODUCT SULFUR IN 400°F+, wt %
KHAFJI VACUUM RESIDUAL
KUWAIT VACUUM RESIDUAL
VENEZUELAN VACUUM RESIDUAL
KHAFJI ATMOSPHERIC RESIDUAL
KUWAIT ATMOSPHERIC RESIDUAL
VENEZUELAN ATMOSPHERIC RESIDUAL

Figure 1

FIGURE 2

HYDRODESULFURIZATION OF RESIDUALS WITH H-OIL

NOTE: THE COSTS REPRESENT 1971 DOLLARS AND ARE FOR GULF COAST CONSTRUCTION. FUEL @ 25¢/MM BTU, POWER @ 1¢/KWH, WATER @ 1¢/M GAL., LABOR @ $5.00/HR., SUPERVISION AND OVERHEAD @ 50% OF LABOR, CATALYST @ 95¢/LB., HYDROGEN @ 35¢/MSCF, AND DEPRECIATION @ 10% OF INVESTMENT. THE ON-STREAM FACTOR IS 0.9.



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