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ANALYSIS OF ALTERNATIVES FOR UPGRADING VENEZUELAN HEAVY CRUDE OILS

by

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ABSTRACT

Three different Venezuelan heavy crude oils were analyzed. They were identified as CT-1, CT-2, and CT-3. The three types of heavy oil showed low API gravity, high sulfur content, high metals content, high nitrogen content, low H/C atomic ratio, and high percent of asphaltenes.

A brief description of different available upgrading processes was also included. Analysis of advantages and disadvantages showed demetallization-desulfurization process, FCC + Demet III, and Gulf HDS process among the more attractive alternatives for upgrading Venezuelan heavy crude oils.

The major processing cost was estimated for four upgrading alternatives: direct desulfurization, demetallization-desulfurization, Gulf HDS process, and H-oil process. The demetallization-desulfurization process can be considered as one of the cheapest ways for upgrading Venezuelan heavy crude oils. Heavy crude oil (8.4°API, 520 ppm V + Ni) can be upgraded at a Venezuela location using this process at a cost of $2.25 per barrel of feed. This cost only includes major operating costs and depreciation of the major investments.

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INTRODUCTION

The shortage of crude oil supply has placed an increased emphasis on methods of upgrading petroleum residua and heavy oils. The economics of production and recovery of heavy oils are becoming increasingly attractive, influenced by the increases of light oil price.

How can heavy crude-oil- a resource that is two to three times more abundant worlwide than light crude- be developed beyond its present, limited production and upgrading status?. Today, those countries with high reserves of heavy oil, including Venezuela, are looking for a profitable and appropriate technology to make heavy crudes more marketable by reducing viscosity, increasing API gravity and removing contaminants.

The high metals content of many heavy crude oils puts a limitation on the variety of processes that could be used to upgrade heavy feed stocks. Metals in relatively high concentration will result in poisoning of the catalysts used in processes such as catalytic cracking, hydrocracking or hydrotreating.

The primary objective of this work was to analyze three different types of Venezuelan heavy crude oils; with the final idea of obtaining a good characterization of each one.

The secondary objective was to present a brief description of different alternatives availables today, to upgrade heavy feed stocks. Advantages and disadvantages of upgrading processes that could be considered for Venezuelan heavy oils, were also included.

The third objective was to calculate, using available data, the major processing costs of four different alternatives for upgrading Venezuelan heavy crude oils. These included: direct desulfurization, demetallization-desulfurization, Gulf HDS process, and H-oil process. Then by using these results, an economic comparison was made to select the least expensive process.

I. LITERATURE SURVEY

1. Heavy Crude Oils in the World. Reserves and Importance

Heavy oil: what it is, and where it can be found: " Heavy Oil " does not have a precise accepted definition. For example, some authors consider that the term heavy oil extends to a wide variety of crudes with a 400 - 100,000 cp viscosity range, and API gravities of 20 - 25 or less.

Driesen (1) considers in his analysis, that a heavy oil is one with an API gravity of 16 or less. Ondish and Suchanek (8) define as characteristics of heavy crudes, the following: low API gravity (10 - 15), high sulfur (3 - 4 %), high viscosity (500 - 2500 SUV), relatively high metals content (100 - 500 ppm), low naphtha yield (1 - 6 %), and high concentration of residual material (35 - 50 %).

Because of low gravity and high viscosity, heavy crudes are very difficult to produce and to transport via pipeline.

About the origin of the heavy oils, several hypotheses have been advanced. One theory postulates that they are not far removed from the hypothetical proto-petroleum, the light crude oils being derived from them by physical and chemical changes induced by deep burial and tectonic forces. Another hypothesis postulates that they are the most mobile hydrocarbons which have been polymerized and immobilized by low temperature chemical changes, aided by mineral catalysts or by biochemical activities, as they migrated laterally towards the margins of the sedimentary basins (2).

" Heavy oil is everywhere ", says Dr. J. Barnea, an energy specialist and former director of natural resources at the United Nations. There are indications that large quantities of heavy oil can be found in over 60 countries-including, of course, the OPEC nations.

The United States, Canada, Venezuela, and the Soviet Union are amoung the countries having the largest deposits of heavy oil; worldwide reserves are estimated at over 4,000 billion bbl, whereas recoverable light-crude reserves are pegged at about 2,000 billion bbl-according to a paper presented by British Petroleum Co.

U.S. heavy oil reserves are estimated to be over 100 billion barrels (1). Most heavy oil is located in California, but some is found in Texas, Louisiana, Oklahoma, Mississippi and Wyoming.

Canadian reserves are generally classified by region and are loosely spoken of as " Lloydminster, " " Cold Lake, " " Athabasca, " " Peace River, " " Wabasca, " and " Buffalo Head " types. Total reserves are nearly 800 billion barrels of tar sands and 200 billion barrels of heavy crudes. Tar sands is an expression commonly used in the petroleum industry to describe sandstone reservoirs impregnated with a very heavy viscous crude oil which can not be produced through a well by conventional production. The oil of the tar sands probably has the same origin as the crude oil produced from wells (2). The largest and best known deposit of tar sands in the world is the Athabasca deposit. For purposes of comparison Table 1 shows the average properties of Athabasca bitumen and a conventional crude oil.

Venezuela heavy crudes are estimated to be from 700 billion to 3 trillion barrels. The official figure is given as 700 billion barrels. Using the present state of production technology it is calculated that there is a 10 percent recovery factor, thus giving some 70,000 million barrels (3). Much of the Venezuela heavy oil is located in the region of the Orinoco oil belt, band about 400 mile long and 40 miles wide north of the Orinoco River. The gravity of this crude oil goes from 9°API to 14°API and the viscosity from 1500 to

TABLE 1

Crude Oil Properties

Property	Athabasca bitumen (1)	Conventional Crude Oil (1)
API gravity, 60°F	8.7	36.8 - 25.7
Sulfur, wt %	4.48	0.1 - 2.0
Carbon, wt %	83.36	86
Hydrogen, wt %	10.52	13.5
Nitrogen, wt %	0.43	0.2
Oxygen, wt %	1.21	0.2 - nil
H/C atomic ratio	1.50	1.87
Vanadium, ppm	213	2 - 10
Nickel, ppm	67	(total metals)
Asphaltenes, wt % (Pentane Ins.)	15.5	X

Notes: (1) Data from reference 19

4500 cp, the sulfur content varies from 2 to 5 percent by weight, and nickel plus vanadium contents vary from 200 to 500 parts per million (1). Recently cost estimation shows that the production cost of the Venezuela heavy crudes is about twice the cost of conventional crude.

Three factors point toward the need to start developing the Orinoco oil belt by Venezuela: at the present production rate , " Conventional " reserves (medium and light crudes) will last only 20 years; Venezuela's dependence on the oil industry; and the massive effort required to find new conventional sources.

Experts have surmised that, as reserves of conventional crude continue to decline while the world price of light oil rises, and with newer finds (such as those from offshore wells) requiring more-expensive recovery methods, synthetic crudes obtained from heavy oil will become more competitive.

2. Chemistry of Heavy-Oil Contaminants

Heavy oils are characterized by the presence of many different contaminants, which cause increasing problems in upgrading processes.

Petroleum contains the following contaminants:

a) Non-hydrocarbons, which are heterocyclics containing sulfur, nitrogen, and oxygen.

b) Minerals such as silica and metals. Vanadium and nickel are the metals with higher concentrations.

c) High molecular weight, large asphaltic molecules.

They are the source of environmental pollutants and the cause of corrosion of equipment and poisoning of processing catalysts (4).

The nitrogen compounds are highly concentrated in the asphaltenes. These are partially converted into ammonia. The nitrogen compounds in petroleum are classified as basic and nonbasic and the amount of nitrogen present increases markedly with increased boiling range of the fraction (5).

Trace metals in petroleum represent the link between formation of petroleum from basins and refinement into the final products. Understanding the true nature of the role of trace metals in petroleum processing will help the progress of petroleum industries. The more abundant metals are vanadium and nickel. The removal of metals is a more complex problem due to the following:

1. Metals are chelated or complexed in ligands that are completely compatible in petroleum and make separation difficult.
2. Metals are generally associated with the heterogoles

and the asphaltic fraction.

3. Refining and upgrading must involve the use of catalysts, which can be poisoned by metals.

As a rule of thumb, both vanadium and nickel increase with the asphaltic content of the crude oil (API gravity is an indicator). Currently, the metallic components in petroleum can be classified into the following categories (4) :

a) Metalloporphyrin chelates.

  aa) Vanadyl and nickel porphyrins

  ab) Chlorophyll and other hydroporphins

  ac) Highly aromatic porphin chelates

  ad) Porphyrin descomposition ligands

b) Transition metal complexes of tetradentate mixed ligands such as V, Ni, Fe, Cu, Co and Cr.

c) Organometallic compounds such as Hg, Sb and As.

d) Carboxylic acid salts.

e) Colloidal minerals.

There are only two major classes of metals of primary importance in the above list, the porphyrin metals and the nonporphyrin metals. The metalloporphyrins are volatile. Thus these species are potentially more deleterious than the nonporphyrins. Heterocyclic atoms at the vanadium sites are essential in keeping the homogeneity of petroleum oil.

Many physical properties of heavy fractions of crude oil, such as flow and viscosity, depend on the geometrical arrangement of the vanadium sites (4).

II. ANALYSIS OF THREE TYPES OF VENEZUELAN HEAVY CRUDE-OIL

1. Characterization of Heavy Crude-Oil

In processing heavy crude oils it is important to know their characteristics, to have an idea of how heavy the oil is and to help the selection of the best upgrading process.

For example, metals in petroleum are important especially in heavy feedstocks, because they are the main cause of catalyst deactivation. Significant characterization of crude oil can be made by inspection of properties and elemental composition.

To help in classification the following properties and composition were considered very important : API gravity, sulfur content (wt %), Conradson carbon, metals content (vanadium and nickel), carbon (wt %), hydrogen (wt %), nitrogen (wt %), oxygen (wt %), and asphaltenes (wt %). From the carbon and hydrogen composition data, H/C atomic ratio can be calculated. This relation is an indication of degree of unsaturation in hydrocarbons.

Three different samples of Venezuelan heavy crude oil were provided by Lagoven, a Venezuelan oil organization, to be used as base of this analysis. These samples came from the eastern part of the country.

To ease the identification of the three types of heavy crude oil, the following nomenclature was used:

CT-1 : Venezuela heavy crude oil type 1

CT-2 : Venezuela heavy crude oil type 2

CT-3 : Venezuela heavy crude oil type 3

These three types of crude were analyzed in this work, and this information was used in the analysis and selection of upgrading processes.

2. Analytical Methods

This section describes the various analysis procedures for the characterization of the three samples of Venezuelan heavy crude -oil. The following analyses were performed:

1. API gravity
2. Total sulfur analysis
3. Total Carbon-Hydrogen-Nitrogen analysis
4. Metals content (vanadium and nickel)
5. Pentane insolubles (asphaltenes)

2.1. API gravity

The American Petroleum Institute (API) has adopted a standard method of expressing the gravity, or unit weight, of petroleum products. API gravity is reported at 60°F.

API gravity is measured by means of hydrometers (ASTM, D287). To determine the API gravity of a sample at a reference temperature of 60°F, the API gravity and the temperature of the sample are measured. Then, this value is corrected to 60°F by means of standard tables of volume corrections (ASTM-IP Petroleum Measurement Tables).

2.2. Total sulfur analysis

Total sulfur in liquid or solid was determined by a Leco Induction Furnace technique. This is an empirical method for the rapid analysis of total sulfur in oil, oil additives, oil sludges, tar, asphalt, and other hydrocarbon materials. The method is applicable to samples:

a) Boiling above 350°F

b) Containing more than 0.06 % sulfur

c) Chlorine content less than 1 %

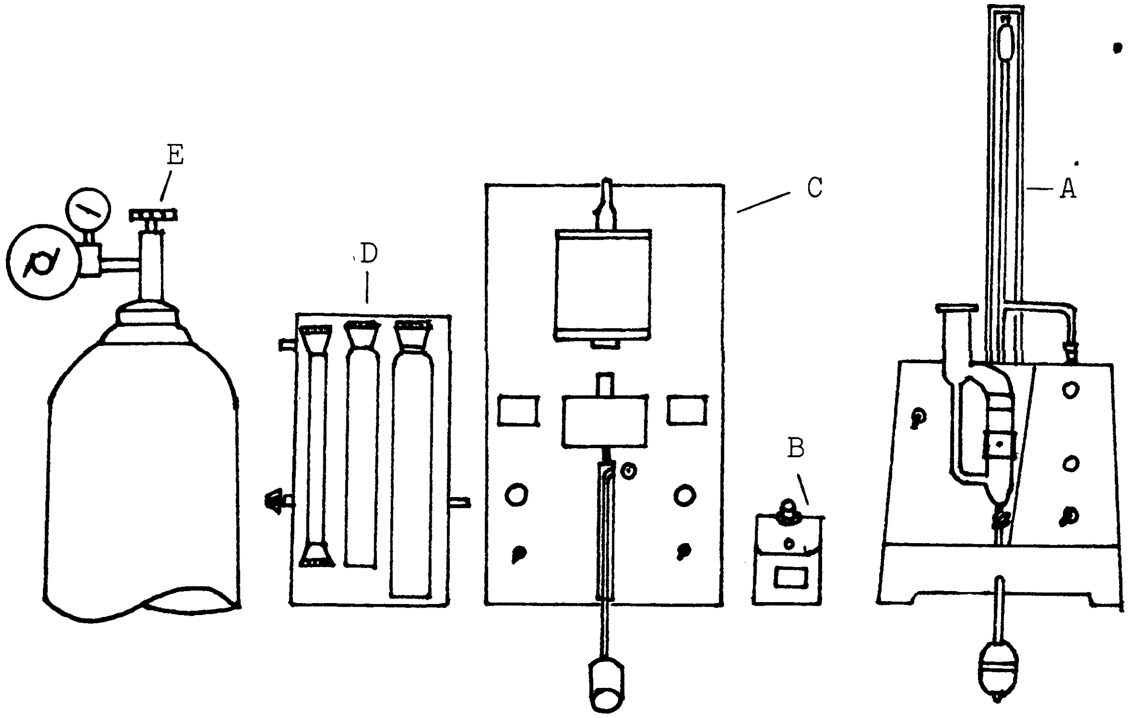
d) Nitrogen content less than 0.1 %

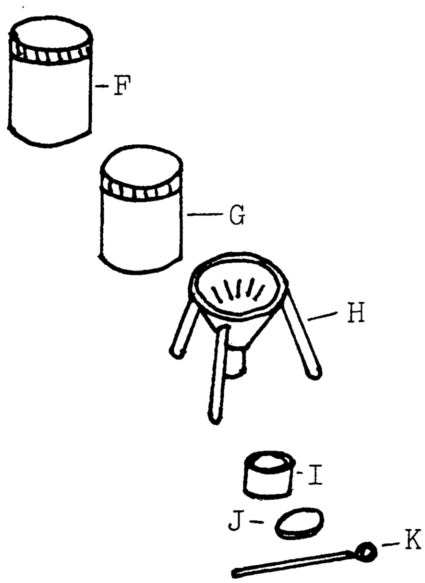
Limits set for items (a) through (d) are not absolute but serve as guides. In previous hydrocarbon determinations using the same equipment have been found no interference of nitrogen for content higher than 0.1 % .

This method generally compares quite favorably with the regular ASTM method D129 (bomb). The reproducibility of the two methods is about the same, while the repeatability of the high temperature combustion method is equal or better than D129 in most cases.

In the Leco technique, the sample is heated in an induction field where it is burned in a stream of oxygen. The major portion of the sulfur is converted to SO_2 which is titrated by the Iodometric method. An empirical factor F , called furnace constant, is determined by the use of an oil sample well standardized by means of another analysis method.

The system is illustrated in Figure 1, consisting of an induction furnace, a purification train, and a semi-automatic titrator. The gas purifying train contained an acid tower, a dry reagent tower, and a rotameter, and was used to measure and scrub any residual sulfur from the entering oxygen. The exhaust gases from the induction furnace combustion chamber were sent through a glass delivery tube into the Leco semi-automatic titrator. This titrator uses an idiometric reaction with a color change end point





A. Semi-Automatic Sulfur Titrator
B. Automatic Timer
C. Leco Induction Furnace
D. Purifying Train
E. Tank Oxygen with 2-Stage Regulator
F. Tin Metal Accelerator
G. Low Sulfur Iron Powder
H. Loading Funnel
I. Crucible
J. Porous Cover
K. Accelerator Scoop

FIGURE 1 - LECO RAPID SULFUR DETERMINATOR INSTALLATION

to analyze the combustion gases . The result is reported as weight percent sulfur in the sample with an accuracy of ± 0.05 weight percent sulfur.

2.3. Total Carbon-Hydrogen-Nitrogen analysis

To determine carbon, hydrogen, and nitrogen a Carlo-Erba CHN was used. The organic material, of which the CHN percent composition must be determined, is weighed into a small tin container. The container is loaded in an automatic sampler by means of which it is introduced into the combustion tube filled with Cr_2O_3 plus Co_3O_4, where the organic substance is pyrolized in an oxygen enriched atmosphere and the decomposition products are converted to the desired state of oxidation (CO_2, H_2O, and nitrogen oxides).

The mixture of these products passes through a reduction tube filled with reduced copper for the conversion of nitrogen oxides to nitrogen and is then carried by the constant helium flow into a chromatographic column where the N_2, CO_2 and H_2O are separated. As each component emerges from the column, it enters a thermal conductivity detector which develops an electrical signal proportional to the concentration of the components. The technique was proved to be rapid and reliable.

The analyzer was equipped with an HP 3380 A recording integrator, which provides weight percent of carbon, hydrogen, and nitrogen of the sample.

2.4. Metals content (vanadium and nickel)

Proceedure for vanadium and nickel analysis in petroleum samples: the petroleum samples were transferred to tared porcelain crucibles, weighed and ashed at 500°C for 30 minutes. The residue was then digested in a nitric-perchloric acid mixture and diluted to 100 ml with deionized water. The resultant solution was then analyzed by atomic absorption with nickel being atomized by a conventional air-acetylene flame system and the vanadium by carbon rod to eliminate certain interferences that are commonly encountered in flame systems and to achieve greater sensitivity. The final results were reported as parts per million (ppm) of vanadium and nickel. These analyses were run at Colorado School of Mines Research Institute.

2.5. Pentane insolubles (asphaltenes)

To determine the weight percent of pentane insolubles (asphaltenes) of the samples, a modified PERC (Pittsburgh Energy Research Center) method was used. Detail of the procedure is as follows:

1. Weight out a 5 gm liquid sample in centrifuge tube.
2. Add 150 ml. pentane to the tube.
3. Sonicate for 5 min.
4. Centrifugate at 50 rpm for 10 min.
5. Decant pentane solubles.
6. Add 100 ml. pentane into the tube. Repeat steps 3, 4, and 5. Perform another such 100 ml. pentane extraction.
7. Decant pentane solubles.
8. Allow pentane insolubles to dry overnight at room temperature, then weigh.

3. Results of the Analyses

This section includes the results of the various analyses procedure for the characterization of the Venezuelan crude-oil samples.

For the three types of Venezuelan heavy crude oil, API gravity, total sulfur, total carbon-hydrogen-nitrogen, vanadium and nickel, and pentane insolubles were determined. The values that are shown in table 2 represent the final results or averages of several measurements. Details of the different measurements were included in Appendix B.

TABLE 2

Results of the Analysis
(crude oil samples)

Property	CT-1	CT-2	CT-3
API gravity (60°F), ±0.5	14.5	13.6	8.4
Sulfur, wt % ± 0.05	2.83	3.10	3.84
Carbon, wt % ± 1.53	83.42	82.78	83.97
Hydrogen, wt % ± 0.45	11.00	12.02	10.34
Nitrogen, wt % ± 0.09	0.77	0.79	0.90
Oxygen, wt %$^{(1)}$	1.94	1.31	0.95
H/C atomic ratio$^{(2)}$	1.57	1.73	1.47
Vanadium, ppm	260	260	420
Nickel, ppm	80	87	100
Asphaltenes, wt % ±0.70 (Pentane Ins.)	15.93	19.72	23.03

Notes: (1) Calculated by difference

(2) Calculated

The portion of pentane insolubles was also characterized. Total sulfur, total carbon-hydrogen-nitrogen, vanadium and nickel were determined for this portion. The final results are shown in Table 3.

In addition, the average 50 % distilled for each type of crude oil was provided by a Venezuelan source. These values were as follows:

Sample	50 % dist., °F
CT-1	880
CT-2	930
CT-3	870

This information was used to calculate "Watson characterization factor" (K_W) and "correlation index" (CI), making the approximation that the mean average boiling point equals the temperature of 50 % distilled. These factors were defined by the following equations:

$$K_W = (T_B)^{1/3}/G \qquad (1)$$

$$CI = (87{,}552/T_B) + 473.7G - 456.8 \qquad (2)$$

TABLE 3

Results of the Analysis
(Asphaltenes samples)

Property	CT-1	CT-2	CT-3
Sulfur, wt % ± 0.05	4.80	4.56	5.13
Carbon, wt % ± 0.26	84.12	84.09	84.27
Hydrogen, wt % ± 0.14	8.46	9.02	8.94
Nitrogen, wt % ± 0.09	1.86	1.76	1.81
Oxygen, wt %(1)	0.76	0.57	-
H/C atomic ratio(2)	1.20	1.26	1.26
Vanadium, ppm	1200	1100	1200
Nickel, ppm	398	300	276

Notes: (1) Calculated by difference

(2) Calculated

where:

T_B = mean average boiling point, °R

G = specific gravity at 60 °F

The final values are shown in Table 4.

The results of the different analyses, that were produced for the three types of Venezuelan heavy crude-oil (see Table 2), show that the crude oils CT-1, CT-2, and CT-3 can be considered as good representatives of heavy oils. These results show low API gravity, high sulfur content, high metals content, high nitrogen content, low H/C atomic ratio, and high percent of asphaltenes.

The crude CT-1 shows results which indicate that it is the lightest of three samples. This fact could indicate that CT-1 is the type of crude oil with less problems for the upgrading process. On the other hand, CT-3 results show that this crude is the heaviest of the three samples, thus major processing problems could be expected.

Table 1 indicated the different properties for conventional crude-oil. the API gravity for conventional crudes ranges from 36.8 to 25.7 . The samples CT-1, CT-2, and CT-3 show an API gravity of 14.5 , 13.6, and 8.4 respectively. This comparison shows the heaviness of three samples.

TABLE 4

Characterization Factors

Sample	K_W	CI
CT-1	11.4	67.6
CT-2	11.4	68.1
CT-3	10.8	88.1

Another source of comparison is provided by the data given for Athabasca bitumen in Table 1. The three samples of Venezuelan heavy-oil show similarities with the Athabasca bitumen in API gravity, sulfur content, H/C atomic ratio, metals content, and asphaltenes. For all these reasons, any processing experience coming from Athabasca bitumen could be very helpful in the development of alternatives for upgrading Venezuela heavy crude oils. The low H/C atomic ratio indicates a high degree of unsaturation, which would require a high amount of hydrogen to saturate.

The determination of the Watson characterization factor and the correlation index provide another source of characterization (see Table 4). These two factors are considered two of the most widely used correlations between the aromaticity and parafinicity of crude oils. The watson characterization factor ranges from less than 10 for highly aromatic materials to almost 15 for highly paraffinic compounds. Crude oils show a characterization factor varying from 10.5 for highly naphthenic crude to 12.9 for a paraffinic base crude (6).

Samples CT-1 and CT-2 show similar characterization factor , 11.4, thus these two crude oils can be considered as an intermediate crude, neither highly naphthenic nor highly paraffinic. Nelson (30) classifies crudes according to the characterization factor as follows: Paraffin(P), Paraffin-inter. (PI), Intermediate-paraffin(IP), Intermediate(I), Intermediate-naphthene(IN), Naphthene-inter.(NI), and Naphthene(N). Using the Nelson classification, CT-1 and CT-2 could be considered IP or I.

The characterization factor of the CT-3 sample was 10.8. This crude can be classified as highly naphthenic according to the two classifications given before. Most naphthene-base oils are of low API gravity and contain superior solvents and naphthas, but yields are usually lower than from paraffin-base oils (17).

The correlation index (more useful for fractions) is based upon straight-chain paraffins having a CI value of 0 and benzene having a CI value of 100. The lower the correlation index the greater the concentration of paraffin hydrocarbons in the fraction, and the higher the CI value the greater the concentration of naphthenes and aromatics (10). Using this classification and the correlation factors of the three samples shown in Table 4, the characterization results obtained from the Watson characterization factor were verified.

The asphaltene fraction from each type of crude oil was also analyzed. The results in Table 3 show how the contaminants (metals, nitrogen, sulfur) were concentrated in the asphaltenes, which agreed with the expected results. Also, these fractions show lower H/C atomic ratio than the crude oil samples.

III. PROCESSES FOR UPGRADING RESIDUA AND HEAVY CRUDE-OIL

The shortage of crude oil supply has placed an increased emphasis on methods of upgrading petroleum residua and heavy oils. However, the high metal content of many of these stocks will result in poisoning of the catalysts used in processes such as catalytic cracking, hydrocracking or hydrotreating. Also, most refineries have not been designed for a heavy-oil feed, and a dilemma hinges on heavy oil's high carbon-to-hydrogen ratio.

The simplest method of utilizing heavy oil as a refinery feedstock is to blend it with lighter oils. But this procedure, which has been practiced for many years, is limited in scope (a blend might consist of only 20 % heavy crude or less).

The processes to upgrade heavy oils can be considered in two categories, via coking or hydrotreating.Coking,"the carbon out" route today appears to provide a better return on investment. Hydrotreating, "hydrogen-in" processes provide an acceptable option only if the cost of hydrogen can be reduced.

Commercial coking processes, however, yield byproduct coke, which may not be marketable if the sulfur levels are too high.

In this section, a brief description of different available upgrading alternatives were included.

1. Catalytic Hydrorefining

1.1. Direct Desulfurization

Hydrotreating is a process to catalytically stabilize petroleum products and/or remove elements as sulfur from products or feedstocks by reacting them with hydrogen. When the process is employed specifically for sulfur removal it is usually called hydrodesulfurization or HDS (6). Figure 2 illustrates a typical desulfurization unit.

The oil feed is mixed with hydrogen-rich gas either before or after it is preheated to the proper reactor temperature. Most hydrotreating reactions for medium feedstocks are carried out below 800°F to minimize cracking and the feed is usually heated to between 500 and 800°F. 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 catalyst (surface) and the

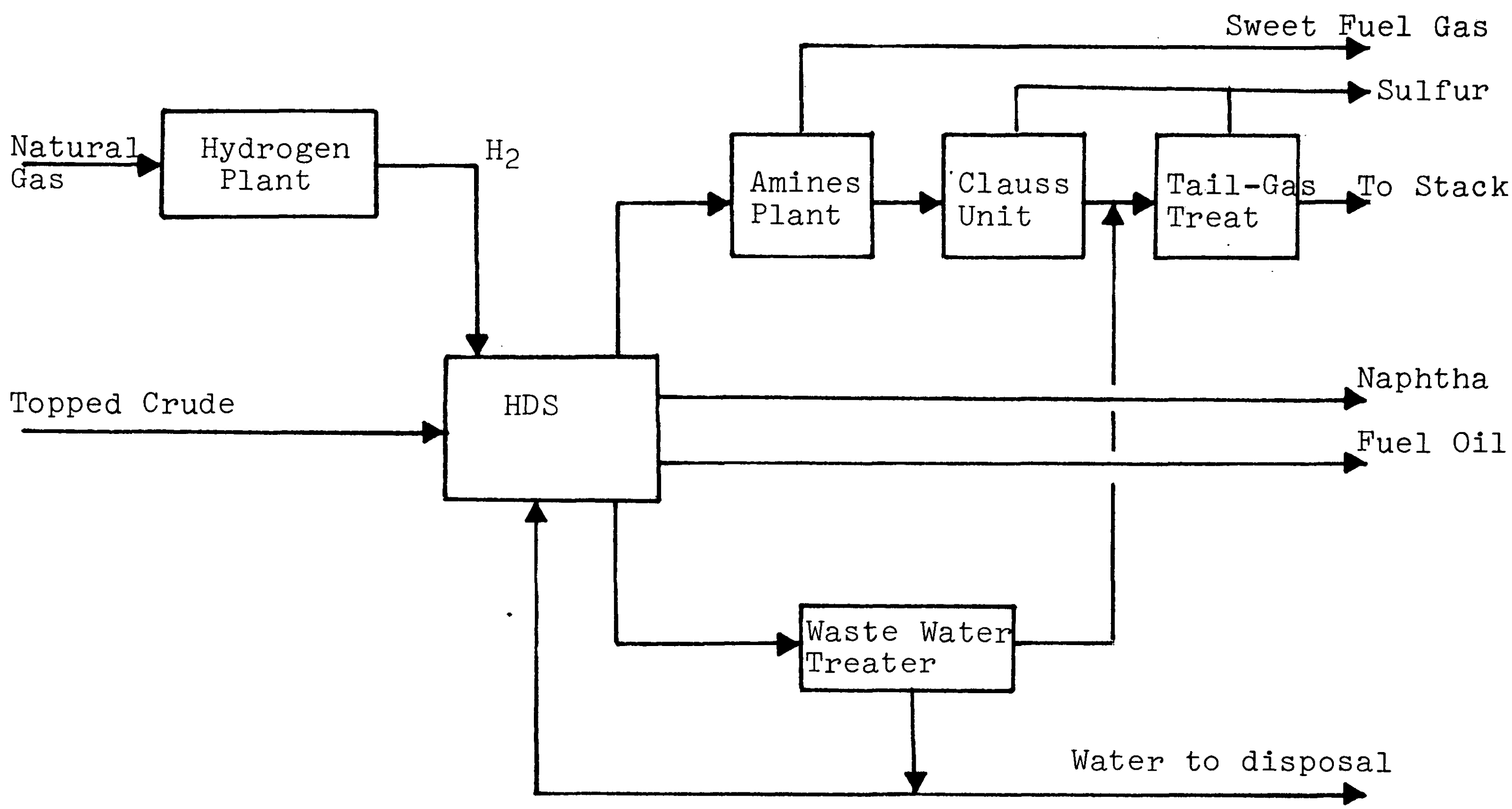


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FIGURE 2 - DIRECT DESULFURIZATION FLOW DIAGRAM

other products leave the reactor with the oil-hydrogen stream. The reactor effluent is cooled before entering a separator to separate the oil from the hydrogen-rich gas. The oil is stripped of any remaining H_2S and light ends, and the gas is treated to remove hydrogen sulfide and recycled to the reactor (6).

For heavy feed stocks several considerations have to be taken into account. The ability of catalytic hydroprocessing to upgrade high sulfur, high metals (vanadium and nickel) feed stocks depends on the ability of the catalyst to treat the high molecular weight asphaltene fraction which contains the highest concentration of contaminants.

The metal complexes probably do not directly consume a significant amount of hydrogen. Rather, deposition of metals on the catalyst must induce cracking- or decomposition-type of reactions that consume hydrogen. Removal of sulfur requires only a relatively small amount of the total hydrogen consumption. Nitrogen removal requires even less.

Nitrogen is usually not removed as completely as sulfur which may be due to the fact that nitrogen is contained in the highest-boiling parts of the feed. Of course, the carbon/hydrogen ratio, density, API gravity,etc. greatly affect hydrogen consumption. There is no clear indication that differences in chemical structure, other than as reflected in gravity, affects hydrogen consumption (8).

Most of the chemical hydrogen (about 70 % for low-metal feeds) is consumed by the cracking reactions. When removing the same number of pounds of sulfur per barrel, the average percentage of total chemical hydrogen required for cracking increases as API gravity declines (8,9).

A variety of catalysts have been developed for hydrotreating processes. The cobalt and molybdenum oxides on alumina catalysts are in most general use (6). During catalytic hydroprocessing of heavy feeds it has been recognized that when contaminant removal levels are pushed to high values, the unique refractoriness of asphaltenes becomes the dominant factor in determining catalyst activity (10).

Deactivated catalysts require larger volumes and/or higher catalyst replacement rates. This has the direct result of increasing reactor investment and increasing Co/Mo catalyst consumption rate. The Co/Mo type of catalysts used in residual hydrodesulfurization removes metals along with sulfur. The relationships between vanadium and nickel removal vs. sulfur removal are shown in Figures 3 and 4. As a result of the direct relationship between metals and sulfur removal, an increase in temperature and/or residence time to increase sulfur removal will also increase the vanadium-nickel-deposition rate and increase the catalyst-deactivation rate. The two lines shown in both Figures 3 and 4 represent catalysts with different pore structures.

Three design changes can be made in residual hydrodesulfurization units to compensate for metals poisoning:

1. Higher temperature-initially increases the rate of desulfurization but the conversion and hydrogen consumption will also increase, which may not be desirable. Higher temperature will cause higher levels of carbon deposition on the catalyst. Therefore, raising temperature is not very effective in compensating for metals poisoning.
2. Larger reactors- a higher vanadium-deposition rate can be compensated for by using increased reactor residence time and a lower average catalyst activity. Larger reactors increase the cost of desulfurizing.
3. Higher catalyst usage - a higher vanadium-deposition rate can be compensated for by increasing the

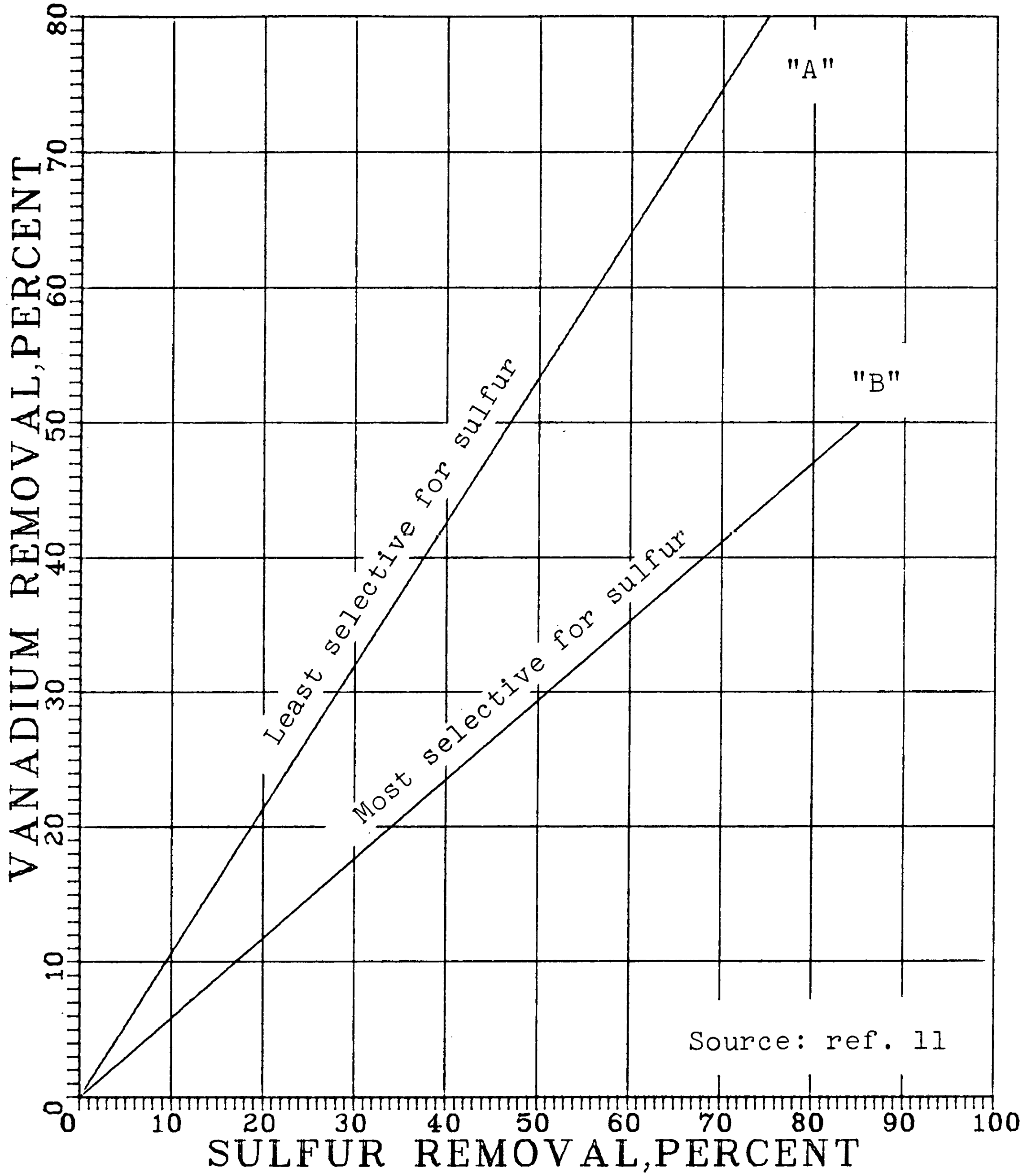


FIGURE 3

V VS. S REMOVAL,CO/MO CATALYST

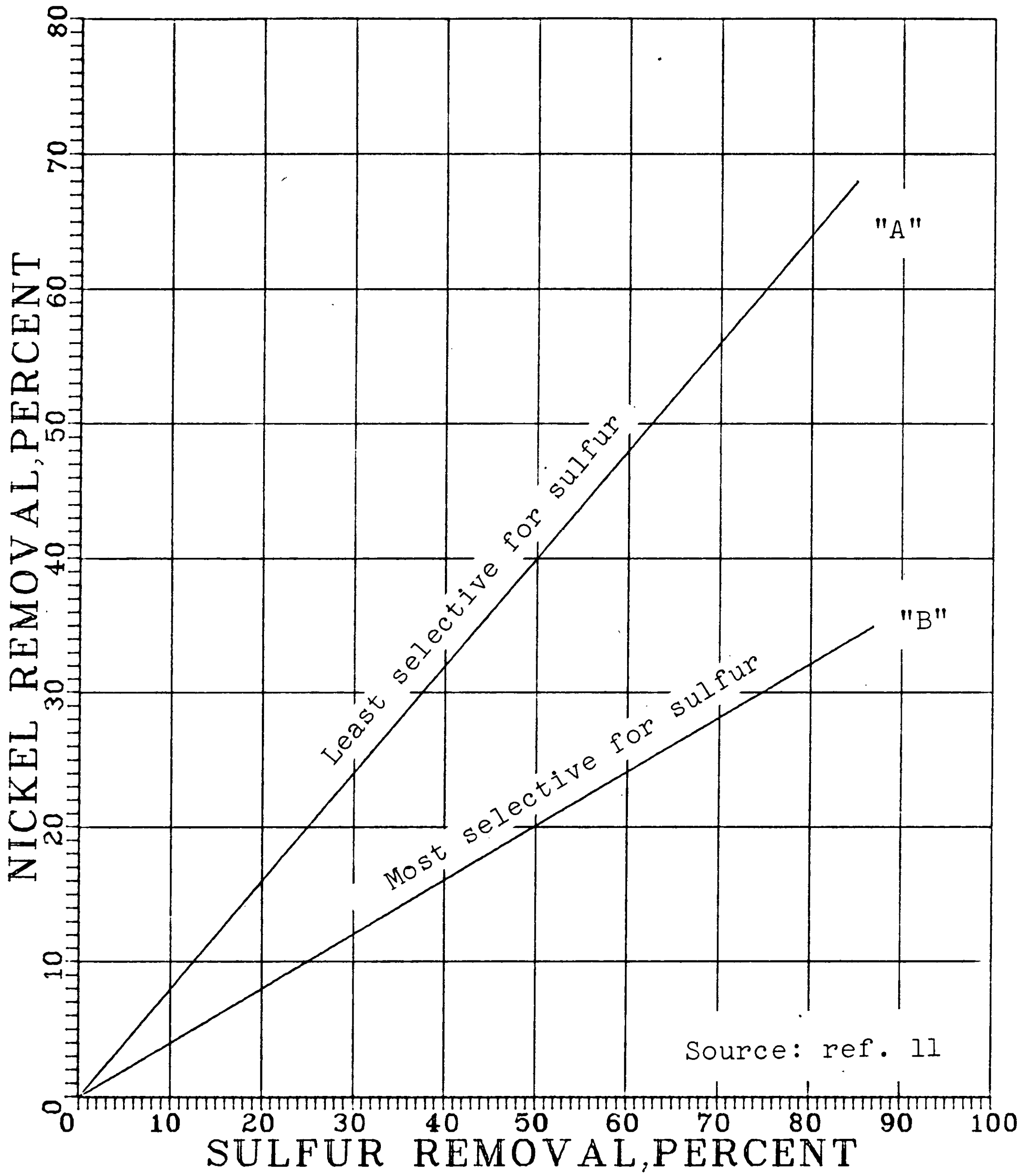


FIGURE 4

NI VS. S REMOVAL,CO/MO CATALYST

catalyst addition rate and spreading the vanadium deposited over more pounds of catalyst.

Direct desulfurization of residua is possible (technically) but requires (7):

- High pressure (1,500-3,000 psi)
- Low space velocities (between 0.25 and 1.0 LHSV)
- High hydrogen recycle rates (around 5,000-6,000 scf/bbl)

1.2. Demetallization-Desulfurization

The metals, mainly vanadium and nickel, deactivate Co/Mo catalyst by covering the catalytic sites with metal sulfides. Residual oils usually contain more vanadium than nickel on a mass or molar basis. Vanadium is considered the major deactivating agent with time. For this reason the vanadium content of residual oils is used in correlations as a measure of the influence of metals on hydrodesulfurization.

In processing residual oils with vanadium contents above 200-300 ppm, the economics sometimes favor an alternate scheme of demetallization-desulfurization in the same process unit. This method uses a demetallization ebullating or fixed bed reactor of inexpensive natural catalyst followed by one or more desulfurization ebullating or fixed bed reactors of Co/Mo catalyst (see Figure

5). The reactor design is basically the same for both the demetallization and desulfurization reactors (11).

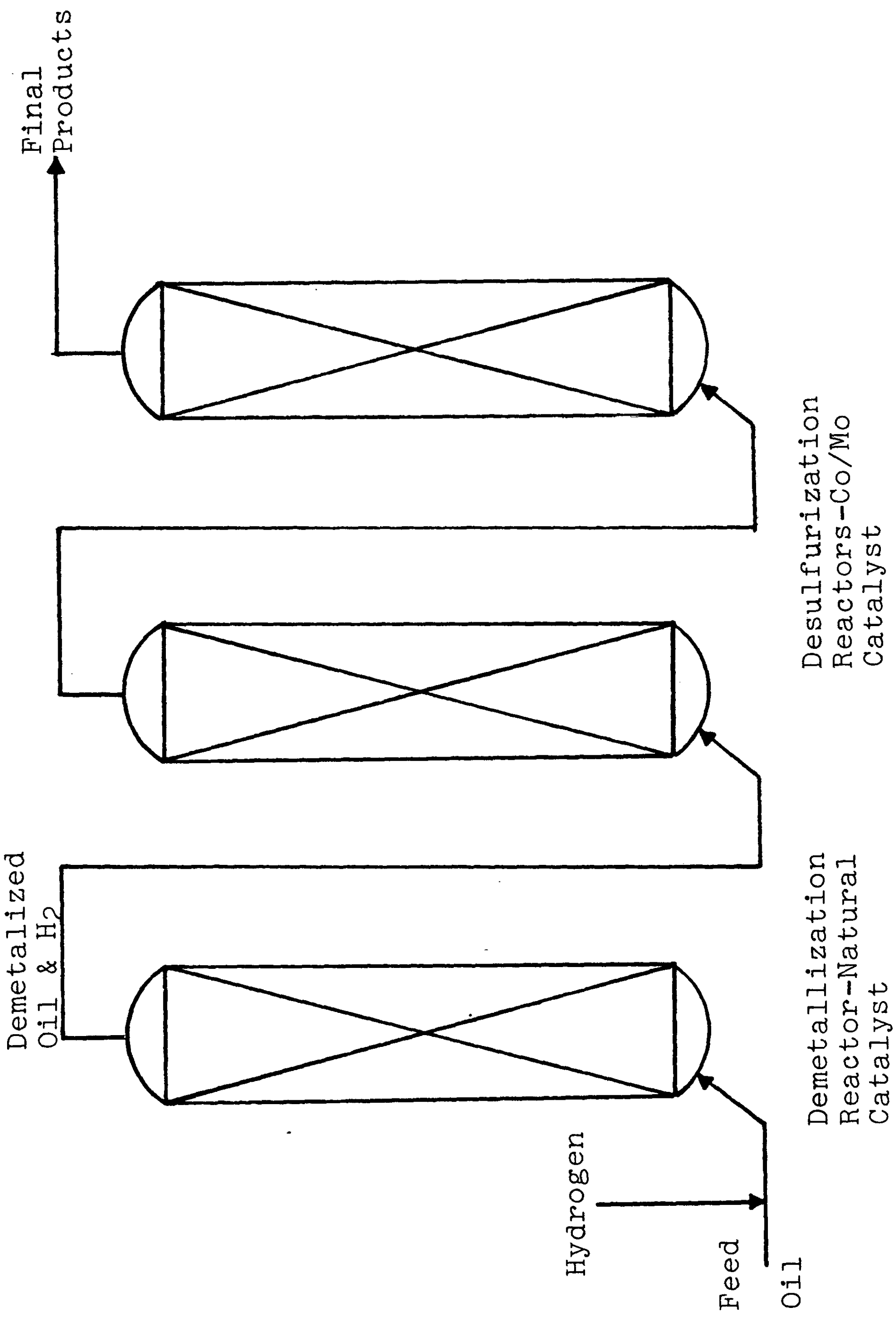
A demetallization catalyst consisting of naturally occuring alumina impregnated with a few tenths of one percent molybdenum has been used. The main advantage of the natural catalyst is its selective catalytic activity for demetallization and its low cost which is about 5-10 % of Co/Mo catalyst(11).

The advantages of an ebullated bed reactor are: first, the catalyst can be continually replenished, thus maintaining a constant quality product and second, the plugging problems due to ash in the feed or heavy carbon deposit at "hot spots" are minimized. However, fixed bed reactors can offer simplicity in design and in some cases are more economical for residua processing (12).

1.3. Gulf HDS Process

Gulf HDS upgrades in a simple processing step; produces no unsaleable product, such as coke; produces a pipeline quality crude refinable in existing refineries; without addition of extensive desulfurization facilities; is economically attractive, perhaps more so than existing upgrading facilities (8).

Very briefly, Gulf HDS is a fixed-bed catalytic hydro-



Source: ref. 11

FIGURE 5 - DEMETALLIZATION-DESULFURIZATION REACTORS CONFIGURATION

genation process, which is operated at moderately elevated temperatures and pressures for periods of 6-12 months.

Gulf's Type I and Type II residue HDS processes are commercially proven processes for the removal of sulfur from petroleum residues to produce low sulfur fuel oil by direct desulfurization. Gulf has developed a family of coke resistant catalysts. Use of one of these catalysts in the Gulf Type III HDS process leads to decreased catalyst loading and longer catalyst life in the second section(13). Figure 6 illustrates a typical Gulf HDS Type II unit.

The primary reactions are desulfurization, demetallization, denitrogenation, and upgrading of asphaltenes. The latter is related to contaminant removal, since contaminants are bound to a large extent in asphaltene molecules and their removal causes fragmentation of the asphaltenes. This fragmentation, followed by hydrogen saturation, produces marked upgrading of API gravity, viscosity, and carbon residue. As an HDS run progresses, however, the contaminants (coke, metals) laid down on the catalyst causes catalyst deactivation, which must be compensated for by increases in reaction temperature.

Because residua vary substantially in their tendencies to desulfurize, demetallize, and form coke for the

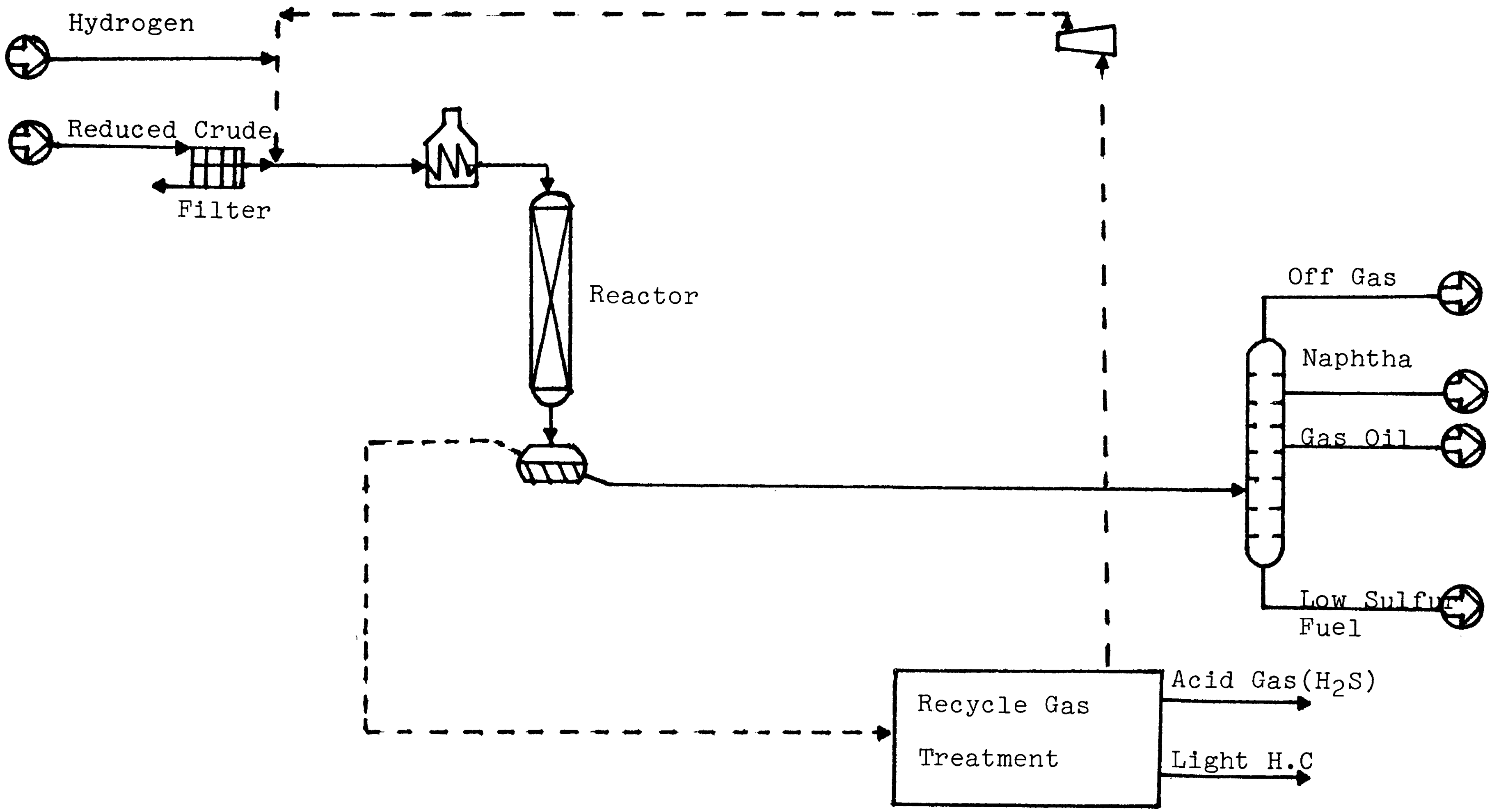


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FIGURE 6 - GULF HDS, TYPE II PROCESS

utilization of the Gulf HDS process it is recommended that: first, pilot plant studies, using different catalysts, are required on each heavy crude and second, conditions must be optimized to achieve proper, optimun balance and practical catalyst life. Certain heavy crudes which are very high in metals probably could not be economically processed directly via HDS.

Crudes as Lloydminster (203 ppm, V + Ni), Cold Lake (236 ppm,V + Ni), and Morichal (468 ppm, V + Ni) are considered good candidates for Gulf HDS upgrading process. Ondish and Suchanek (8) believe that metals contents of about 500-600 ppm may be the limit of practical, economical HDS upgrading, although higher metals-containing residua have not been tested.

1.4. Residfining

The residfining process is a fixed bed catalytic desulfurization process that produces low sulfur fuel oils from atmospheric or vacuum residuum. This process has been developed by Exxon Engineering.

Typical operating conditions are as follows:

- Temperature, 750°F
- Pressure, 1000 psig

. Hydrogen treat rate, 3000 scf/bbl

. Hydrogen consumption, up to 1000 scf/bbl

A new RT-621 catalyst, developed by Exxon, extends the capabilities of the residfining process to contaminant removal from asphaltenes as required in processing residua and other non-conventional heavy oils. Contaminant removal results in significant conversion of the vacuum residuum to lighter products. Excellent activity maintenance of the RT-621 catalyst was demostrated in long-term pilot plant studies on several heavy feeds (14). A heavy venezuelan crude (8.8°API, 549 ppm V + Ni) and a heavy canadian crude (11.1°API, 246 ppm V + Ni) were among the heavy crudes tested. These samples were processed without prior fractionation, and the results showed a good catalyst activity maintenance.

The RT-621 catalyst is designed with a unique pore structure by which the catalytic surface is made accesible to the very heavy, asphaltenic material contained in vacuum residua and heavy oils.A very high degree of desulfurization and demetallization of residua is thus made possible (14).

Application of the residfining process includes upgrading of coker stocks, visbreaker bottoms, deasphalted oils, and heavy oils from non-conventional crudes.

1.5. Shell Hydrodesulfurization Process

Hydrodesulfurization of feed-stocks with a high metals content has been developed by Shell. Results of extensive long-duration pilot-plant testing and operation of a commercial-scale unit have proved that high-metals feedstocks can be desulfurized to an accepted level (15).

Shell's major efforts were focused on development of a suitable catalyst, including these considerations: reduced life spans from metal poisoning of catalyst, near impossible coke burn-off regeneration methods, reduced susceptibility of oil to desulfurization because of high viscosity and high asphaltene content, high coke-forming tendency and presence of particulate matter which could cause plugging of a fixed catalyst bed.

Metals in feedstock shorten useful life of a hydrodesulfurization catalyst. The problem can be tackled in three ways (15):

- Suppressing deposition of metals on catalyst.
- Developing a catalyst with accepts the metals and has the capacity to store a considerable quantity of them without substantial reduction of its activity.
- Removing metals before hydrodesulfurization.

The first two methods are alternative approaches. The third method is indicated for feedstocks with a high metals content. It calls for a separate demetallization step, ahead of the hydrodesulfurization reactors, applying a special catalyst.

A simplified process-flow scheme of the Shell HDS is shown in Figure 7. For high-metal feed-stocks, to achieve an acceptable unit-running time, an excessively large inventory of catalyst would be required. To avoid the disadvantages of a swing-reactor system, a special reactor has been developed from which spent catalyst can be withdrawn and to which fresh catalyst can be added during operation of the unit. This reactor, applicable for trickle operation, is called a "bunker-flow reactor" (15).

The metals content of the catalyst withdrawn from this reactor depends on the catalyst replacement rate applied and can thus be controlled up to its maximum value. An additional advantage is that the product from this reactor, which is the feedstock to the downstream hydrodesulfurization reactors, will have a constant metals content during the entire operating time of the unit. The system is particularly useful for processing feedstocks with vanadium content above 100 ppm. The reactor system serves to

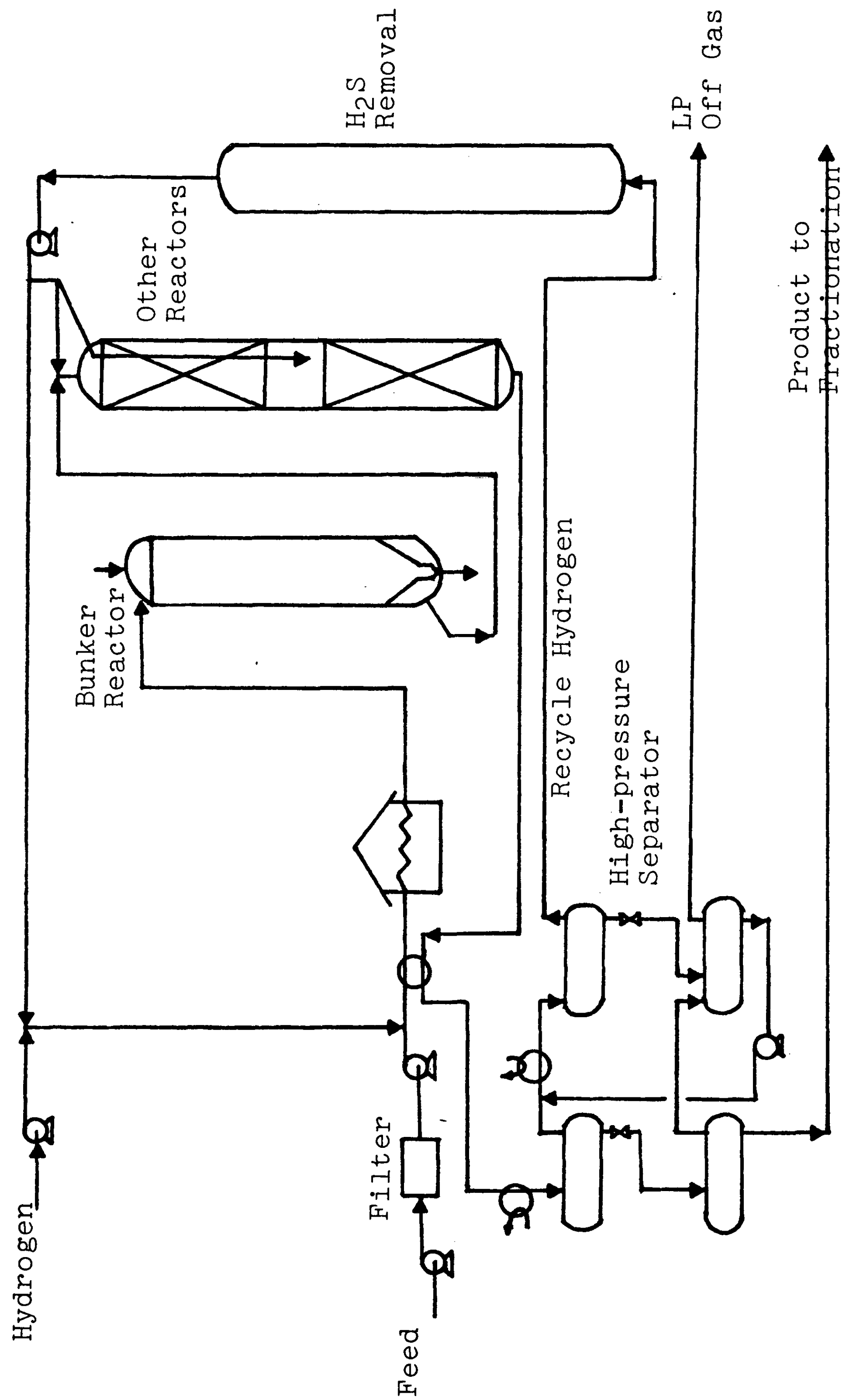

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FIGURE 7 - SHELL HDS FLOW SCHEME

establish an intimate contact of the three phases, catalyst, oil, and hydrogen so a high conversion can be obtained.

2. Catalytic Hydrocracking

2.1. H-Oil Process

Fixed-bed processes can be used for up to 150-200 ppm metals content. But at higher contents, cost of catalyst replacement makes fixed-bed process too expensive. For these cases, the H-oil process is recommended.

The H-oil process is a hydrogenation process capable of desulfurizing, demetallizing and hydrogen upgrading a wide spectrum of heavy hydrocarbons.

A typical H-oil process flow is shown in Figure 8. Feed oil passes through a multistage centrifugal pump to the heater and mixes with hydrogen before entering the first reactor. Hydrogen is generally heated in a separate furnace. Oil and hydrogen feed passes through the reactors and into a hot high-pressure separator.

The reactor is an expanded bed reactor (see Figure 9). Expanded bed design allows very heavy feedstocks to be processed while never shutting the unit down for

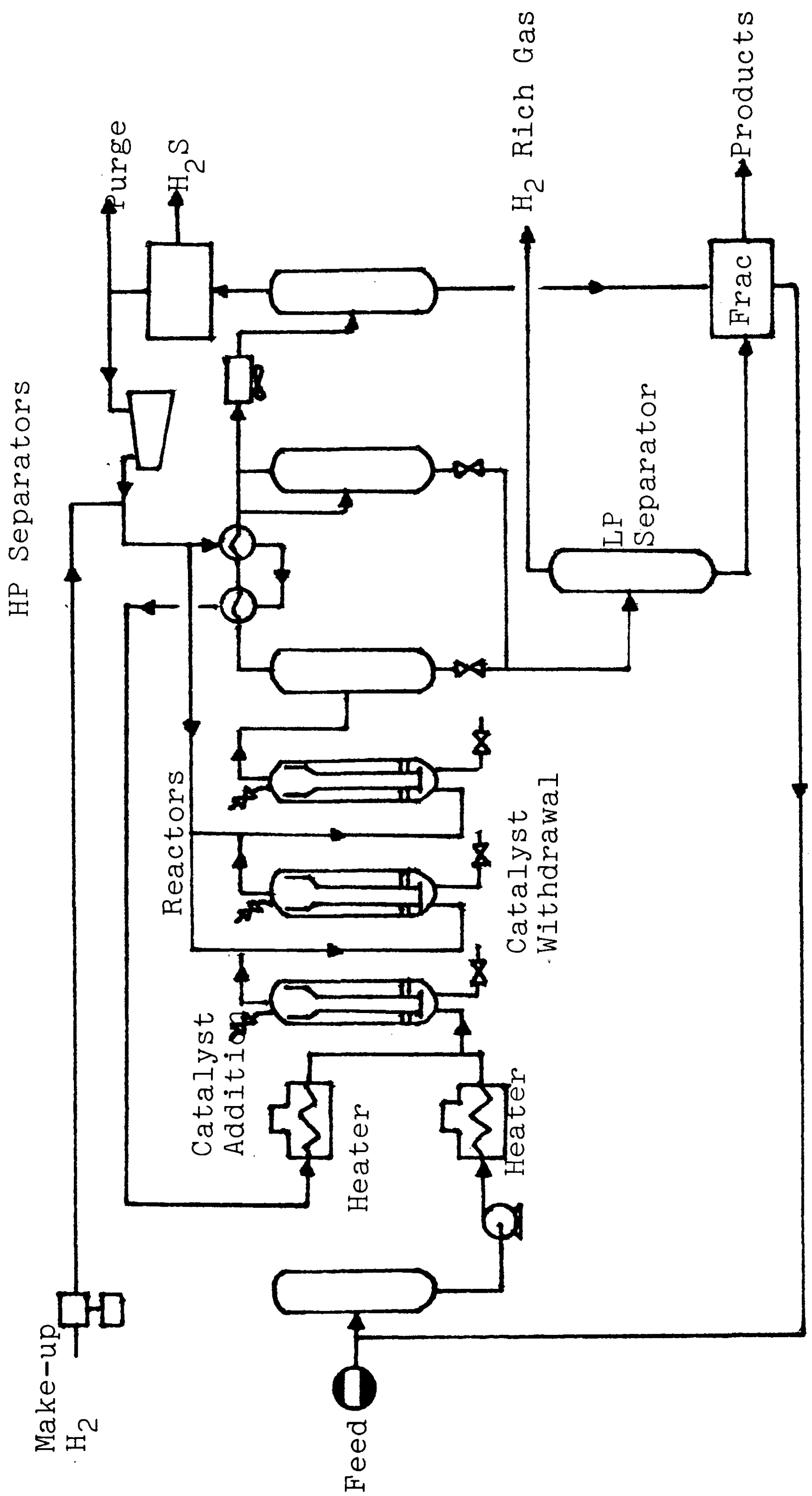

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FIGURE 8 - TYPICAL H-OIL PROCESS FLOW

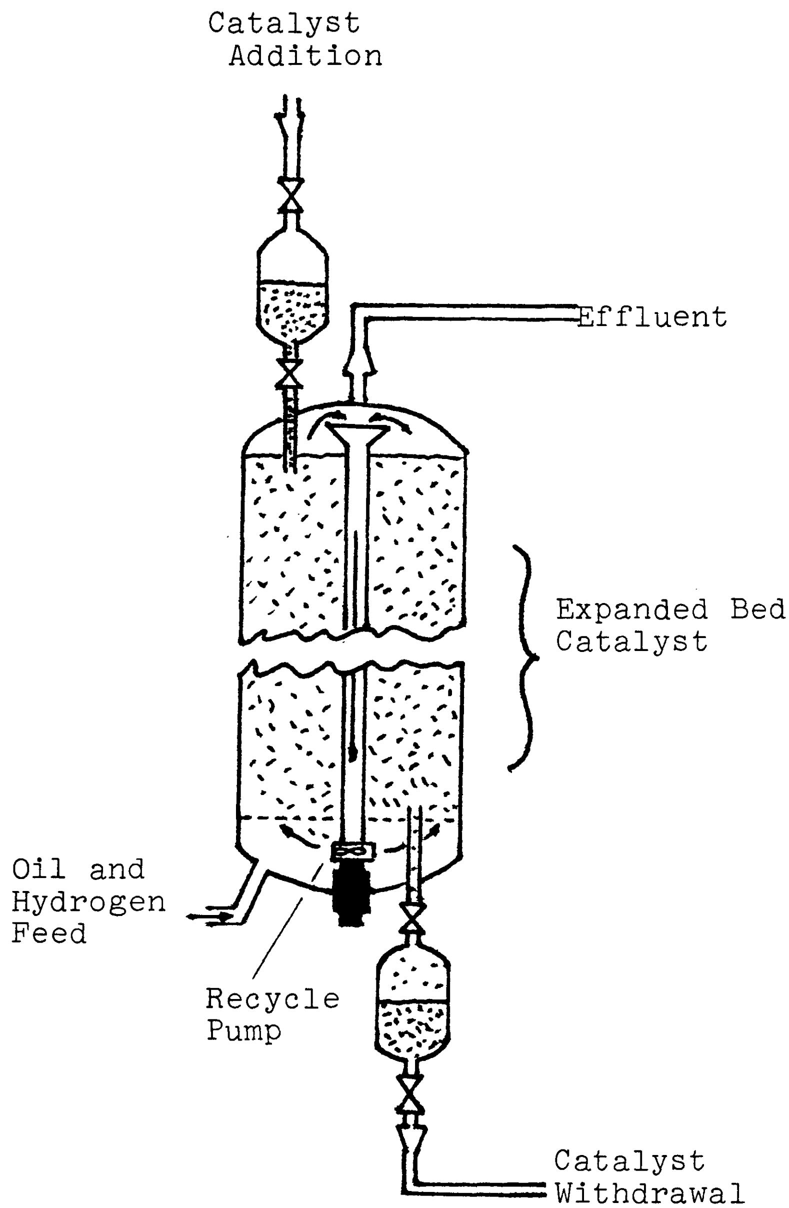

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FIGURE 9 - H-OIL REACTOR

catalyst replacement. There is ample free space between particles for entrained solids to pass through the catalyst bed without accumulation, plugging, or increased pressure drop (1).

The H-oil process has been tested on over 50 feedstocks from various parts of the world (16). Hydrocarbon Research, Inc. has accumulated a lot of hours of experience in H-oil bench-scale and pilot plant operations specifically on Athabasca bitumen and Lloydminster residuum (13).

In processing feedstocks having high metals content, it is usually more economic to employ a demetallization step ahead of the reactor containing catalyst.

2.2. Unicracking/HDS

This method is a new way to process sour crudes. Light hydrocarbons are made from reduced crude containing high amounts of metals and asphaltenes. This method combine hydrodesulfurization (HDS) and a special version of a fixed-bed catalytic process.

Unicracking/HDS is a fixed-bed catalytic process developed for hydrodesulfurization of residua by Union Oil Co. of California (17).

Figure 10 illustrates the basic Union process flow for a typical single reactor train. Briefly, the resid feed is filtered to remove 25 micron and larger solids, pumped to unit pressure, heated, combined with hot recycled gas, and charged to a catalytic guard chamber. The guard chamber removes the fine entrained materials in a filter bed and begins desulfurization. It is bypassed after pressure drop through the catalyst bed reaches a predetermined level.

Guard chamber effluent then passes through the reactors. The first reactor contains a filter bed, similar to the guard chamber, to accept fine solids in the oil with minimal pressure drop increase after the guard chamber is bypassed. Typically, there are three or four reactors.

The cobalt-molybdenum-alumina catalyst (RF-series) used by Union, have a microstructure that is controlled to maintain maximum desulfurization activity while tolerating the presence of metals in the feed. This is accomplished by setting pore size distribution to inhibit asphaltenes and metals from reaching active desulfurization sites . Eventually, however, metals and coke do succeed in reaching the active sites and masking them (17).

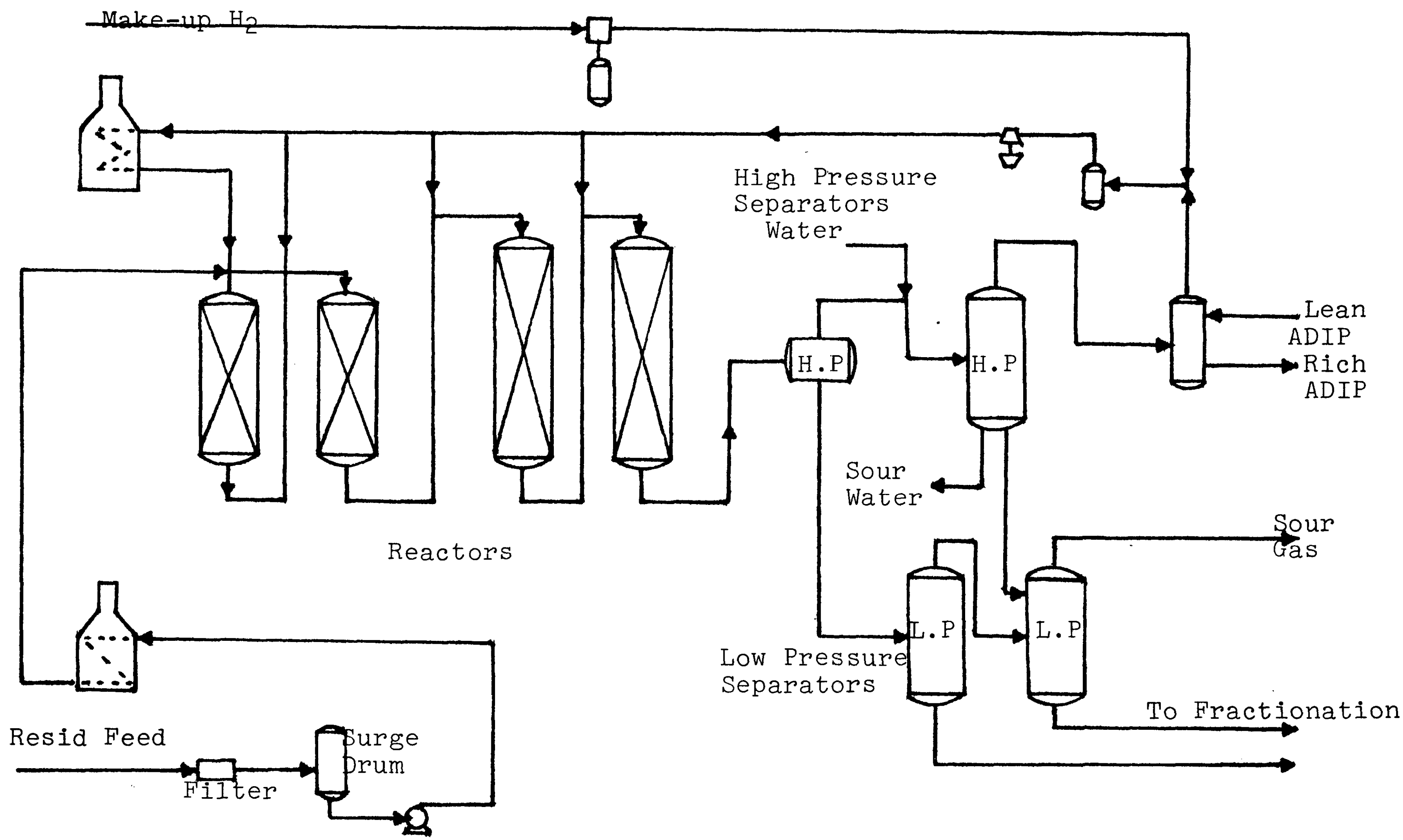

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FIGURE 10 - FLOW SCHEME OF UNICRACKING/HDS PROCESS

An RF-series catalyst normally is used once and is not regenerated due to the deposition of metals. The metals, primarily nickel and vanadium, can be reclaimed with existing technology, but the catalyst structure is destroyed during the reclamation.

In general, to get better results, a Unicracking/HDS unit is used as a pretreater for an Heavy Oil Cracking (HOC) unit, where better products can be obtained.

3. Catalytic Cracking

3.1. Heavy Oil Cracking (HOC)

The heavy oil cracking process converts residual fraction to gas, light hydrocarbons and to gas oils. The HOC process requires considerable flexibility to be able to efficiently convert reduced crudes with the broad range of qualities, specifically metals and carbon residue. This process has been developed by Kellogg.

The Kellogg HOC process is a special version of the familiar fluid catalytic cracking (FCC) process adapted to conversion of reduced crudes containing high amounts of metals and asphaltenes. In the HOC process, the oil and resin fractions are cracked in a manner similar to that of the oils in a FCC unit to give light hydrocarbons (17).

The asphaltene fraction is deposited quantitatively on the catalyst and goes through the reactor and stripper sections and eventually to the regenerator. The heat liberated by burning the asphaltenes is used to produce high-pressure steam by direct heat transfer to coils located in the bed of the regenerator. The number of coils used depends on the excess coke and the amount of steam to be made. Usually a single layer is preferred, but Pullman-Kellogg has designed units with multiple layers of steam coils at the wall area.

Because of the adverse effect of vanadium on catalyst activity, the basis for effective cracking of reduced crudes has been to maintain the vanadium content of the equilibrium catalyst to 0.5 % or less (17). The catalyst makeup rate to achieve this limiting vanadium content is simply a function of feedstock density and the metal content. With a reduced crude containing 10 ppm of vanadium, a catalyst makeup rate of 0.67 lb/bbl would be required to maintain an equilibrium catalyst metals content of 0.5 %. With a feedstock containing 50 ppm of vanadium the required makeup rate increases to 3.35 lb/bbl.

3.2. Fluid Catalytic Cracking (FCC) + Demet III

FCC is a highly effective means for processing crude oil or reduced crudes to useful products. Its volume yield of distillate products exceeds that of many other processing sequences for handling residuum-containing feedstocks (18).

A key feature in the high-yield cracking operation is maintaining the proper activity-selectivity rating of the unit's catalyst inventory. This requires that the level of metals on the catalyst, deposited from the residuum, be kept under control. The addition of fresh catalyst can accomplish such control for low-metal-content feedstock operations, but catalyst cost becomes exorbitant for high-metal-content stocks. Conventional gas-oil FCC is generally conducted with catalysts having less than 0.1 % metal content for feed with very low metals content. For high metal level feeds, catalyst discard becomes prohibitive.

For example, for a 50,000 b/d cat cracker with 50 ppm V + Ni in the feedstock, about 40 tons/d of fresh catalyst must be added to prevent the metal level from exceeding 1 %.

Recognition of this factor has led to Atlantic Richfield's development of a catalyst demetallization process which will extend application of FCC to high-metal-content feedstocks. The process, known as Demet III, is a low-cost chemical and physical treatment which removes metals from either zeolitic or amorphous cracking catalysts (18).

Figure 11 shows how Demet III can be combined with standard FCC process. Metal content of the catalyst inventory is controlled by the Demet III process. A slipstream of catalyst is withdrawn continuously from the FCC regenerator, processed in the demetallization unit, and then returned to the FCC unit. The only fresh catalyst addition required is that necessary to make up for the loss of catalyst fines.

Coke produced in the reactor is burned in the regenerator to provide process heat. Normally in reduced crude cracking there will be excess heat over that required to heat balance the FCC unit. The excess heat is removed by generation of high-pressure steam in steam coils located in the regenerator.

The Demet III treating system is shown in Figure 12. The process consists of the following sections:

. Chemical-treatment steps to remove metals.

. Pretreatment steps to activate metal for removal.

. Washing steps for physical separation of contaminants from catalyst.

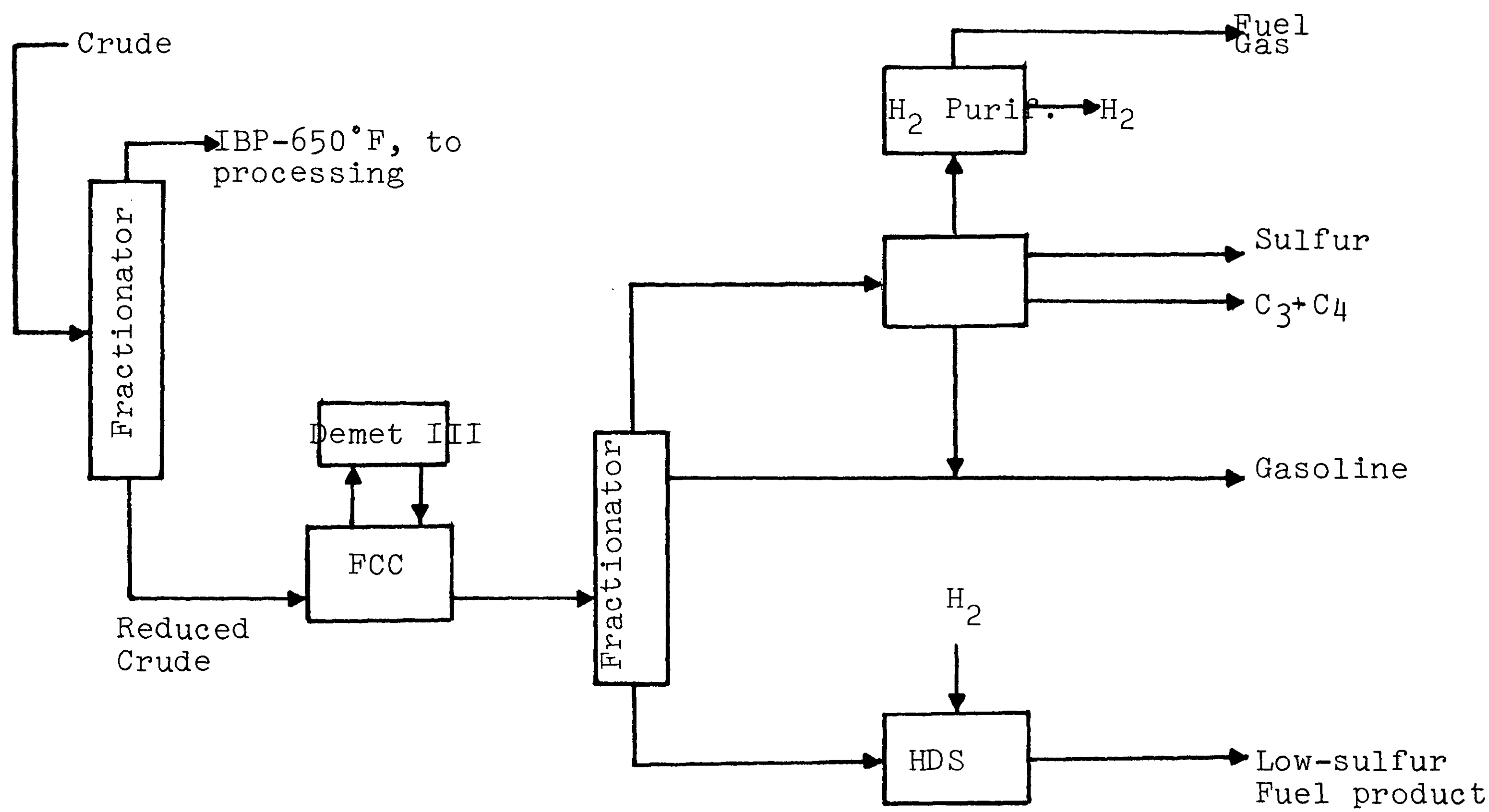

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FIGURE 11 - COMBINATION OF FCC AND DEMET III

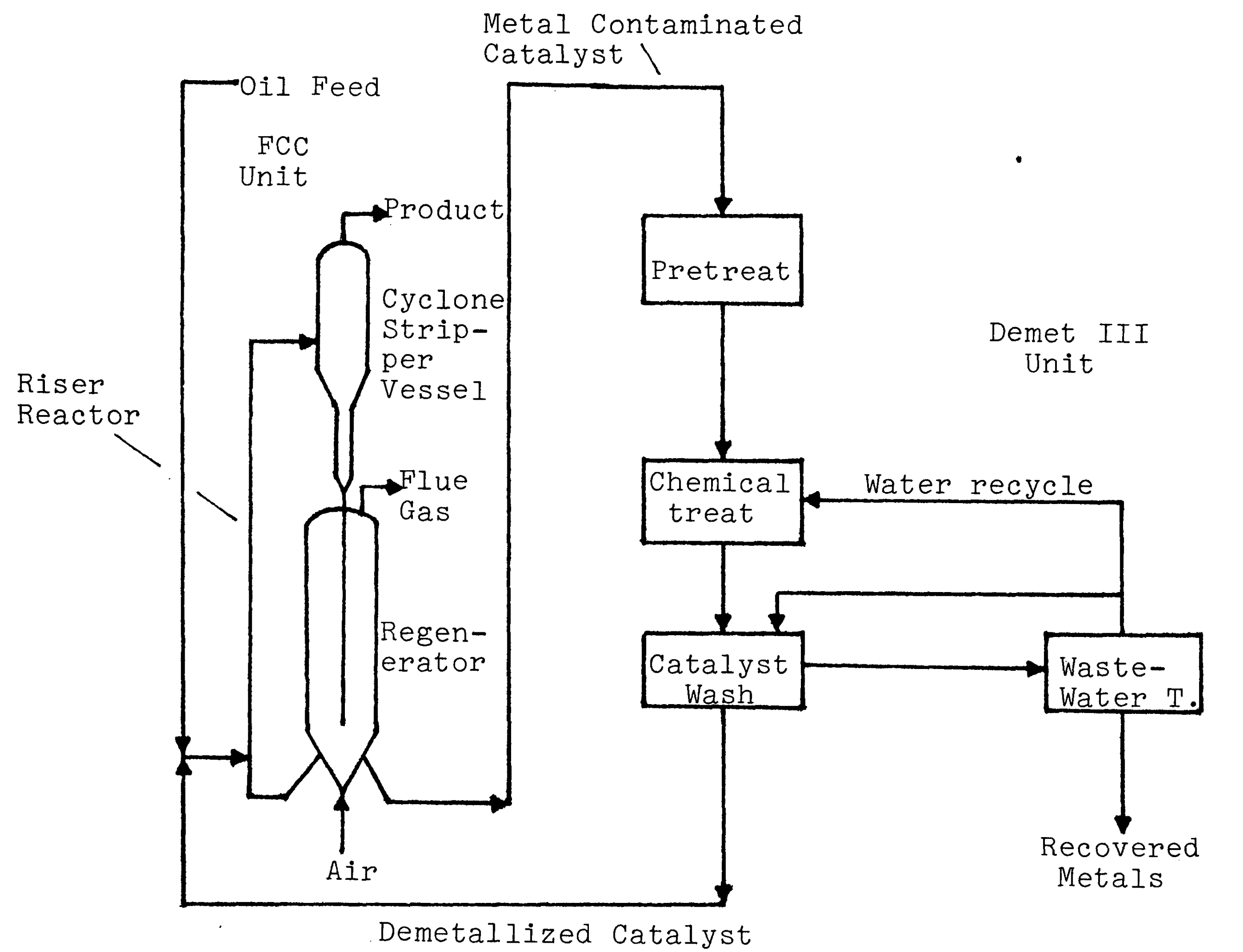

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FIGURE 12 - OPERATING STEPS OF DEMET III

. Waste treatment for recovery of metals from wash effluent with recycle of water to system.

Several extensive pilot-plant programs have been conducted for the Demet III process. The programs demonstrated removing metals contaminants from equilibrium zeolite catalysts while operating with high metals level in the FCC unit feed(18). Also, it demonstrated that properties of the zeolite catalysts are maintained by the Demet III process. This includes activity, yield-selectivity, surface area, and attrition resistance.

4. Others

4.1. Heavy Solvent Deasphalting (SDA)

Billon and Peries (7) consider heavy solvent deasphalting (SDA) the key to upgrading heavy crudes. Since the presence of numerous poisons prohibits the direct conversion of heavy residues we must find processes that can selectively eliminate these impurities either partially or completely. The SDA is considered one of these processes, for the desulfurization and conversion of petroleum residues.

The main objective of deasphalting is to produce deasphalted oil (DAO) containing a minimum amount of asphaltenes and metals compatible with downstream process. Figure 13 shows a flow scheme for solvent deasphalting process.

A wide range of crudes has been studied ranging from very light crudes to very heavy crudes such as Boscan which contains more than 1000 ppm of metals and more than 15 % of asphaltenes (7). The amount of asphaltenes precipitated from petroleum by heptane, pentane, and propane are different because the average molecular weight of the petroleum is different when these solvents are added to the petroleum. The use of a C_5 fraction as solvent, rather than propane is very advantageous because the yield in DAO is multiplied by a factor of 2 to 3. The use of pentane solvent coupled with a high yield in DAO leads to a degree of demetallization in a range of 70 % to 90 % (7).

The nitrogen compounds are highly concentrated in the asphaltenes, for this reason high degree of denitrification is achieved. The main drawback of the deasphalting process is that it also yields a byproduct of relatively low value-the asphalt.

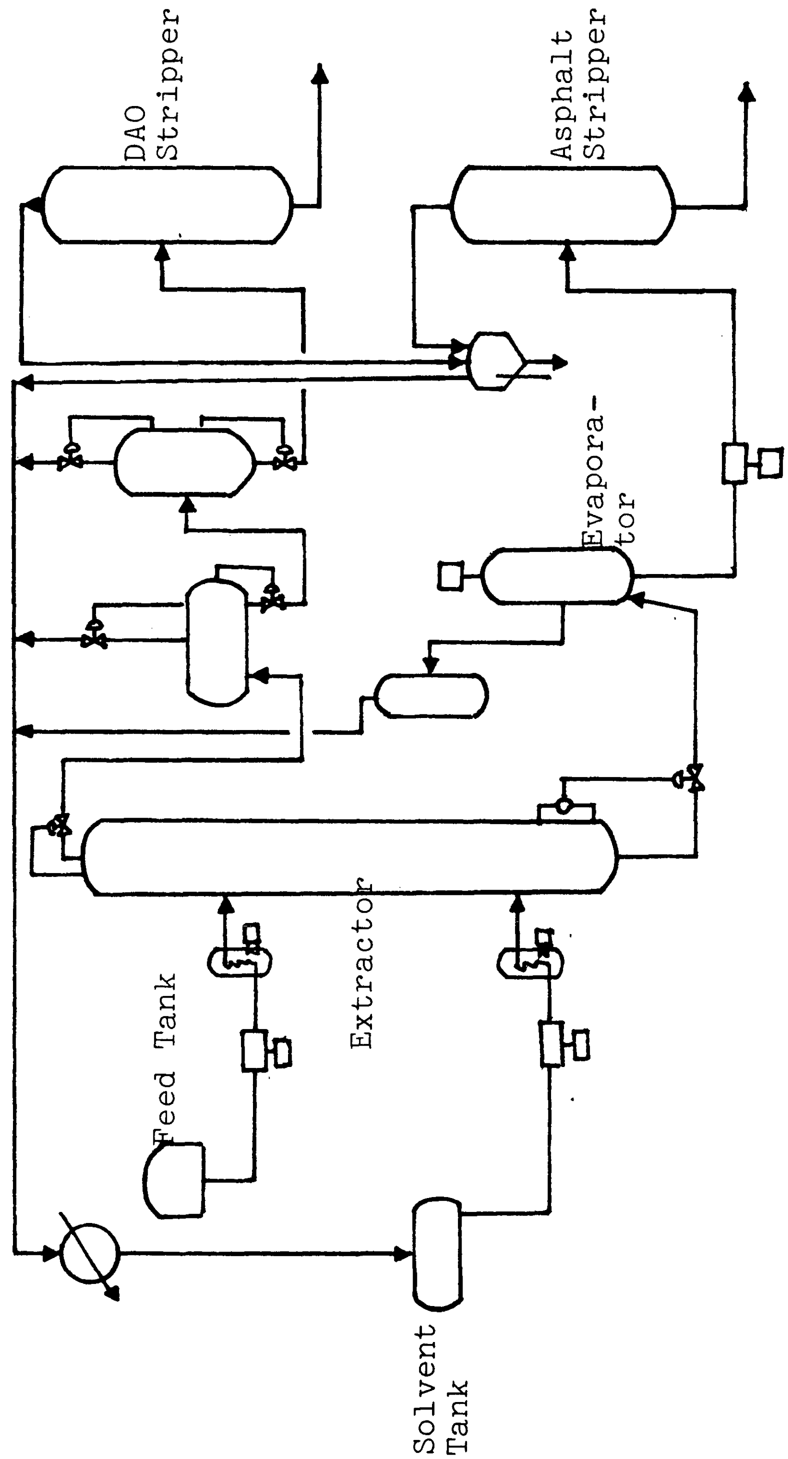

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FIGURE 13 - SOLVENT DEASPHALTING(SDA) PROCESS

4.2. Thermal and Catalytic Hydrocracking Process

The thermal hydrocracking process has been found, on the basis of pilot-plant-scale runs, to give a high distillate yield and eliminate the production of waste coke in the processing of Athabasca bitumen (19). The schematic of the proposed two-stage thermal and catalytic hydrocracking process (CDH) is shown in Figure 14.

The bitumen and hydrogen are mixed and they flow up through a tubular reactor. The mixture of gas and liquid from the top of the tubular reactor enters the hot separator which is maintained at the same temperature as the reactor. The gases from the hot separator are sent to an up-flow fixed bed catalytic hydrocracker which is the second stage of the CDH process.

The results presented by Ranganathan, Pruden, Ternan and Denis (19) showed that the two-stage thermal and catalytic hydrocracking process could be used for upgrading Athabasca bitumen and for producing reformer naphtha feedstock, fuel oils and catalytic cracking gas-oil feedstock. Studies of different catalysts and operating conditions should be carried out for different feedstocks to get the optimum results.

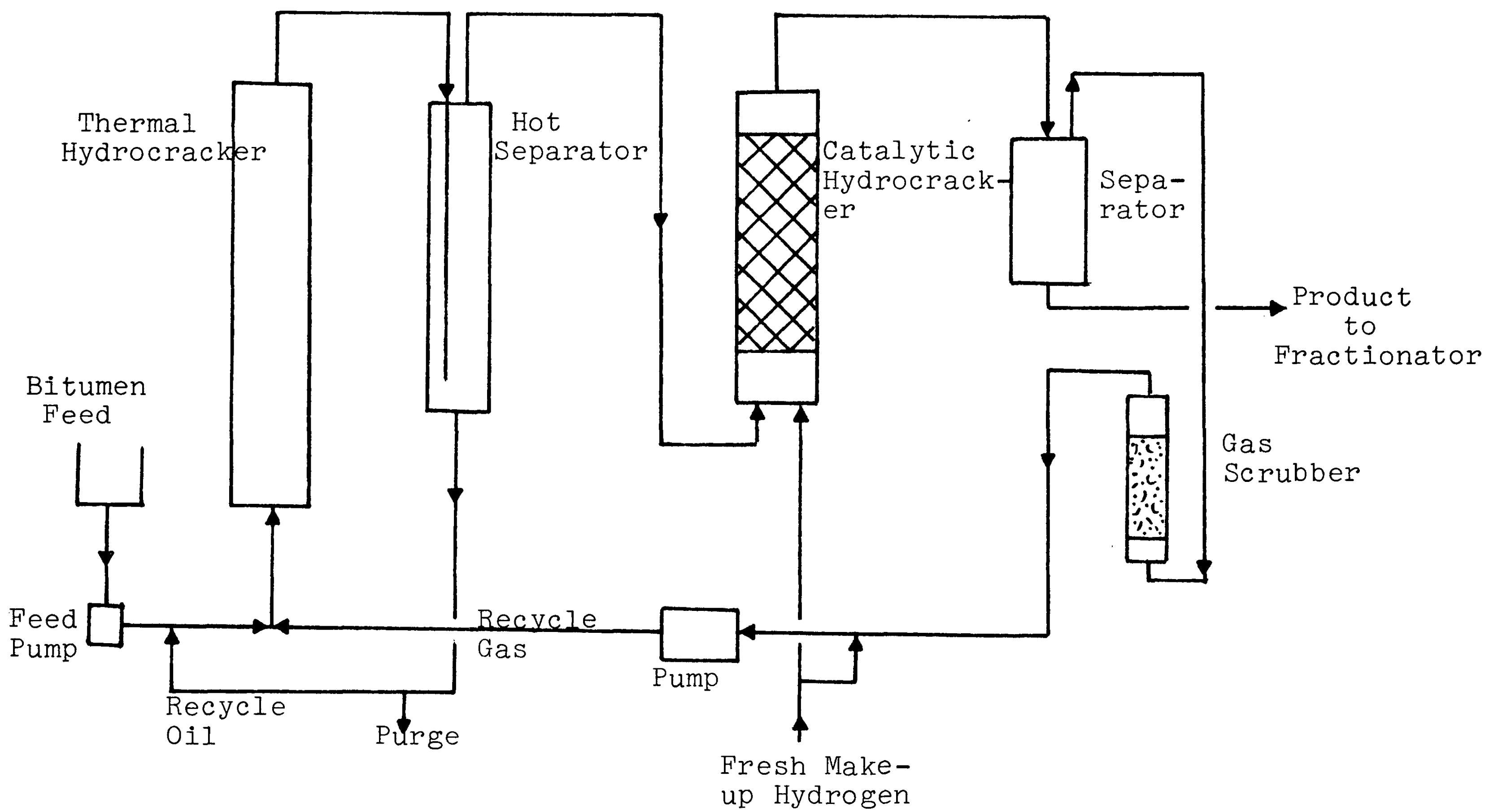

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FIGURE 14 - THERMAL AND CATALYTIC HYDROCRACKING

4.3. Catalytic Demetallization Using Manganese Nodules

Naturally occurring manganese nodules have been found to possess catalytic activity for demetallization of topped petroleum crude in the presence of hydrogen(20). Their relative high surface areas and transition metal oxide content (CoO, MoO_3) has aroused interest in their catalytic properties.

The nodule catalysts are only moderately active for desulfurization and essentially inactive for denitrogenation under the test conditions used by Chang and Silvestri(20). The removal of metals from the organometallic complexes presumably occurs via reduction and deposition of the metals with concurrent hydrogenation of the organic moiety.

Manganese nodules have been found both on ocean floors and in fresh water. It is interesting to note that the ocean nodule catalysts which contain substantial amounts of Ni, Co, and Mo, metals normally associated with hydrogenation and hydrodesulfurization activity are less active than the fresh water nodules which contain only very low levels of these metals.

4.4. Non-hydrogenative Demetallization

Fischer and Garwood(21) report the use of manganese nodules as a potentially inexpensive porous "seeding" surface for the thermal non-catalytic decomposition of the metal components of residua.

Studies using different feedstocks, with moderate metal content, have shown that high demetallization can be obtained with relatively low coke formation. Also, it has been found that the higher the asphaltene content of the stock, the more difficult it is to demetalize.

This type of operation may be valuable in processing high metal, asphaltic heavy oils such as those found in Canada and Venezuela (21).

IV. ALTERNATIVES FOR UPGRADING VENEZUELAN HEAVY CRUDE-OIL

1. Advantages and Disadvantages of Different Upgrading Process

This section includes advantages and disadvantages of upgrading processes that could be considered for Venezuelan heavy crude oils.

Process	Advantages	Disadvantages
. Direct Desulfurization	. Removal of contaminants in one step	. High catalyst consumption (10 bbl feed/lb catalyst)
	. Final products with low level of contaminants	. High hydrogen consumption (800-2000 scf/bbl)
	. No coke is produced	. Operates at high pressure (1500-3000 psi) and temperature (above 800°F)
		. Requires large reactors
		. Limitations for very high metals feed stocks

Process	Advantages	Disadvantages
. Demetallization-desulfurization	. Inexpensive demetallization catalyst . Final products with low level of contaminants . No coke is produced . No too high desulfurization catalyst consumption	. Possible limitation for very high metals feed stocks
. Gulf HDS process	. Upgrades in a simple step . No unsaleable product, coke, is produced . Final products with low level of contaminants	. Operates at moderately elevated temperature and pressure . Maximum level of metals content on feed: 500-600 ppm
. Residfining	. Heavy feed (low gravity) can be processed directly . High degree of desulfurization and demetallization	. Operates at high pressure (1000 psi) . High hydrogen treat rate (3000 scf/bbl) . High hydrogen consumption (1000 scf/bbl)

Process	Advantages	Disadvantages
. Shell hydro-desulfurization process	. Use of a special reactor make easy adding or removing catalyst . Product with constant metals content . High conversion	. Requires more tests for very high metals content feedstocks . High catalyst consumption
. H-oil process	. Demetallization, desulfurization, and upgrading is achieved in one step . Products with low levels of contaminants . The reactor design avoid plugging and accumulation when very heavy feed is processed	. Operating difficulties of the expanded bed reactor . High hydrogen consumption (1500 scf/bbl) . For high metals content feed is recommended a previous demetallization step
. Unicracking/HDS	. Good solid removal system allows high variety of heavy feed stocks . Light hydrocarbons as products . Special catalyst allows to keep high desulfurization activity	. Normally requires three or four reactors . The catalyst is not regenerated . It is not recommended for very high metals content. This process could be used with the HOC process

Process	Advantages	Disadvantages
. Heavy Oil Cracking (HOC)	. Cracked products are obtained: gas, light hydrocarbons, and gas-oil . Similarities with the FCC process . Heat balance unit allows steam production	. For very high asphaltic feed, heat balance problems could appear . High catalyst make-up rate (3.35 lb/bbl, for a feed containing 50 ppm V) . Requires special regenerator design
. FCC + Demet III	. Cracked products are obtained . FCC is a well known process . Avoid excessive fresh catalyst addition . Removal of metals from catalyst without affecting catalyst properties . Source of vanadium and nickel production . High catalyst activity is maintained . Generation of high-pressure steam	. Requires special regenerator design . For very heavy feed, heat balance problems could appear

Process	Advantages	Disadvantages
. Heavy Solvent Deasphalting	. Production of a deasphalted oil, with low content of contaminants . Solvent deasphalting is a very well known process	. High production of asphalt (15-25 wt%) with high content of contaminants
. Thermal and Catalytic Hydrocracking	. High distillate yield	. The production of coke in the thermal unit can be excessive
. Catalytic Demetallization using Manganese Nodules	. Good as a pretreatment process . Use of a natural catalyst . Product with low metals content	

2. Major Processing Cost of Four Different Alternatives

This section covers details of how the major processing cost, of four different alternatives for upgrading Venezuelan heavy crude oils, was estimated. The three types of Venezuelan feedstocks (CT-1, CT-2, and CT-3) were considered in this analysis. Direct desulfurization, demetallization-desulfurization, Gulf HDS process, and H-oil process were the four considered alternatives.

These four alternatives were selected because enough data were found in the literature which could be used for estimation of the major processing cost of the three types of Venezuelan heavy crude oils.

To establish the bases of the calculations, two different grades of fuel oil as final product were defined. One grade was defined with a sulfur content of 0.5 wt% and other with 1.0 wt%. Also, a process capacity of 100,000 bbl/sd was assumed.

The major processing cost was defined as the cost of hydrogen, catalyst, and depreciation of investment. To come out with this cost for different alternatives, data available from the literature were used. Details about these reference data are presented in Appendix C.

Because the reference data were in some cases out of date, and for different capacities, a method to correct and put them up to date was defined. Factors such as , Nelson (Inflation) refinery construction index, productivity, capacity relation, and location factor were used to convert the data. Details about these factors and equations are included in Appendix A. This appendix also includes others economic parameters such as cost of manufacturing hydrogen and catalyst cost.

The major processing cost at a Venezuela location was calculated for the following processes: direct desulfurization, demetallization-desulfurization, Gulf HDS process, and H-oil process.

2.1. Direct Desulfurization

. Hydrogen requirement:

Hydrogen constitutes the largest element of operating cost in hydrodesulfurization processes. But, if the feed contains large amounts of metals, cost of catalyst may exceed that of hydrogen.

The reference data are shown in Figure 15. This correlation was developed by Nelson (22). Details about these reference data are included in Appendix C.

The chemical hydrogen for desulfurization of 6 and 16°API feed and for the two different grades of fuel oil (0.5 and 1.0 wt% S) were determined from Figure 15. These values were determined for 2, 3, and 4 % sulfur in feed. These data were used to develop Figure 16, where a straight line correlation was assumed.

Figure 17 was developed from Figure 16. The chemical hydrogen for desulfurization of 8, 13, 14, and 15°API and for the two grades of fuel oil were determinated from Figure 16. These values were determinated for 2, 3, and 4 % sulfur in feed. Then, these data were used to develop Figure 17.

Figure 17 was used to estimate the hydrogen requirement for hydrodesulfurization of the three types of Venezuelan heavy crude oil (CT-1, CT-2, and CT-3). The value obtained from Figure 17 was corrected for high metals feeds using correction factors from Figure 18. These corrections factors were developed by Nelson (22). The final results are shown in Table 5.

. Catalyst consumption:

In direct desulfurization of residua and heavy feed, large amount of metals cause rapid deteriora-

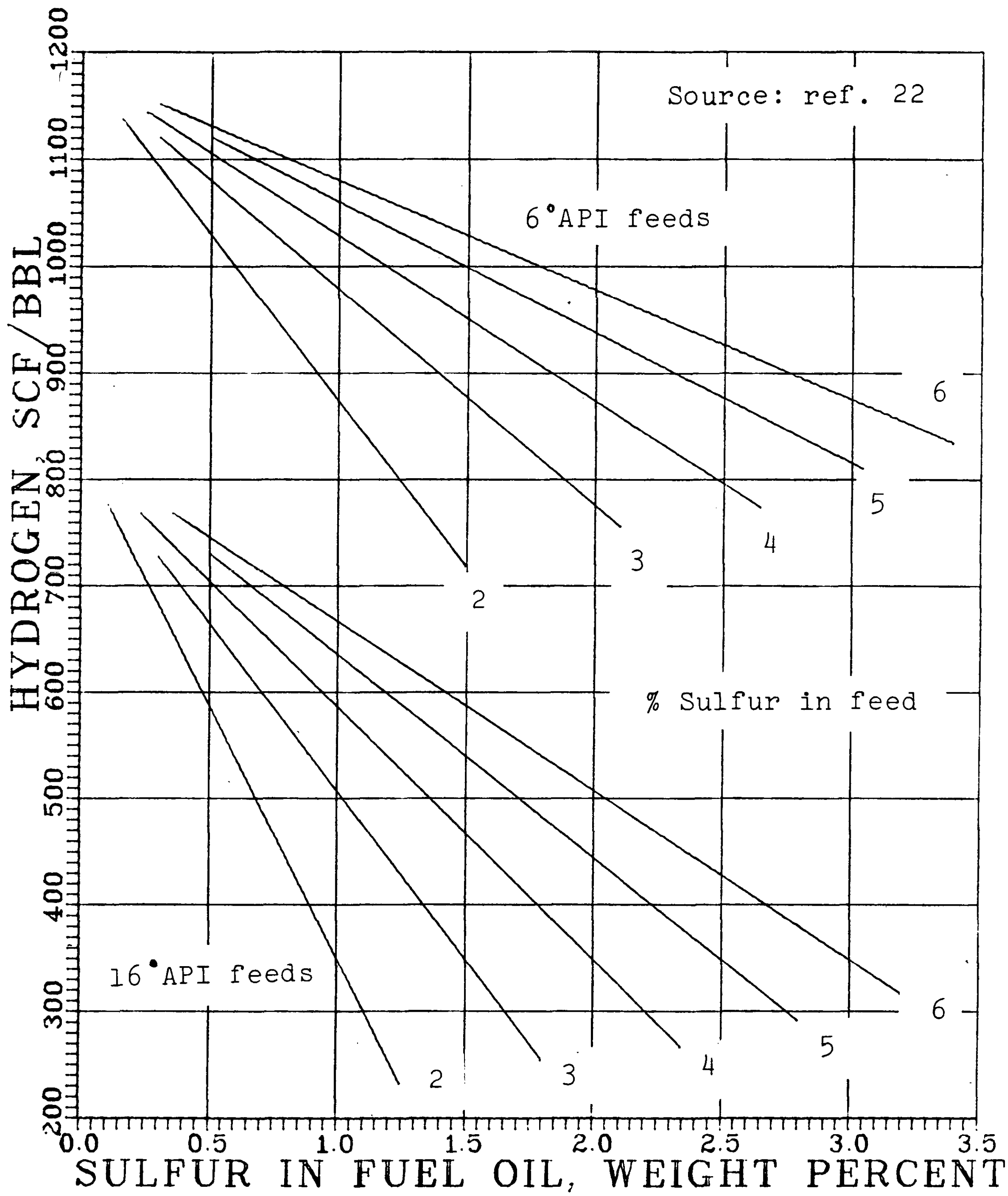

FIGURE 15

HYDROGEN FOR ATMOSPHERIC AND VACUUM RESIDUA

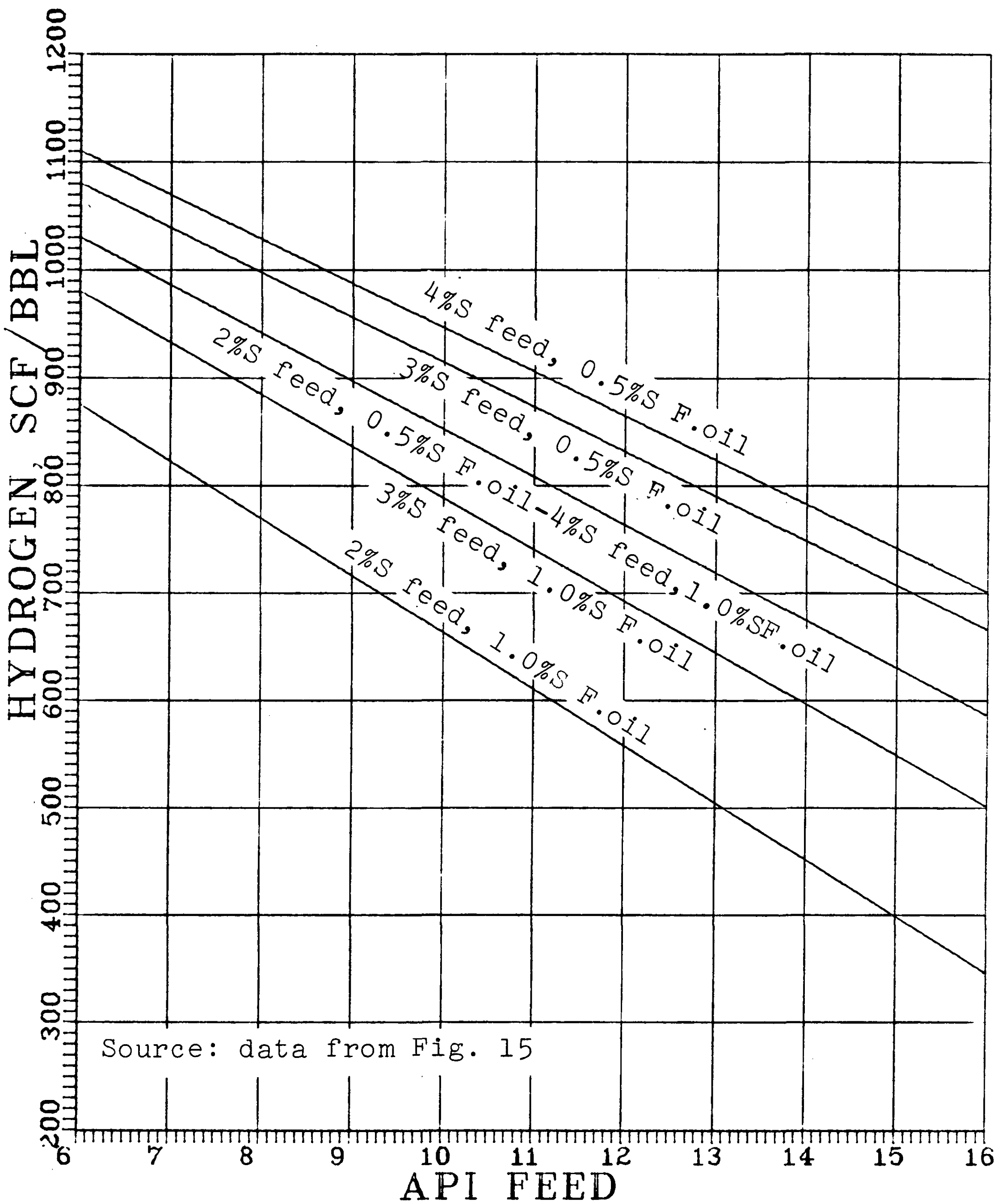

FIGURE 16

HYDROGEN VS. API FEED

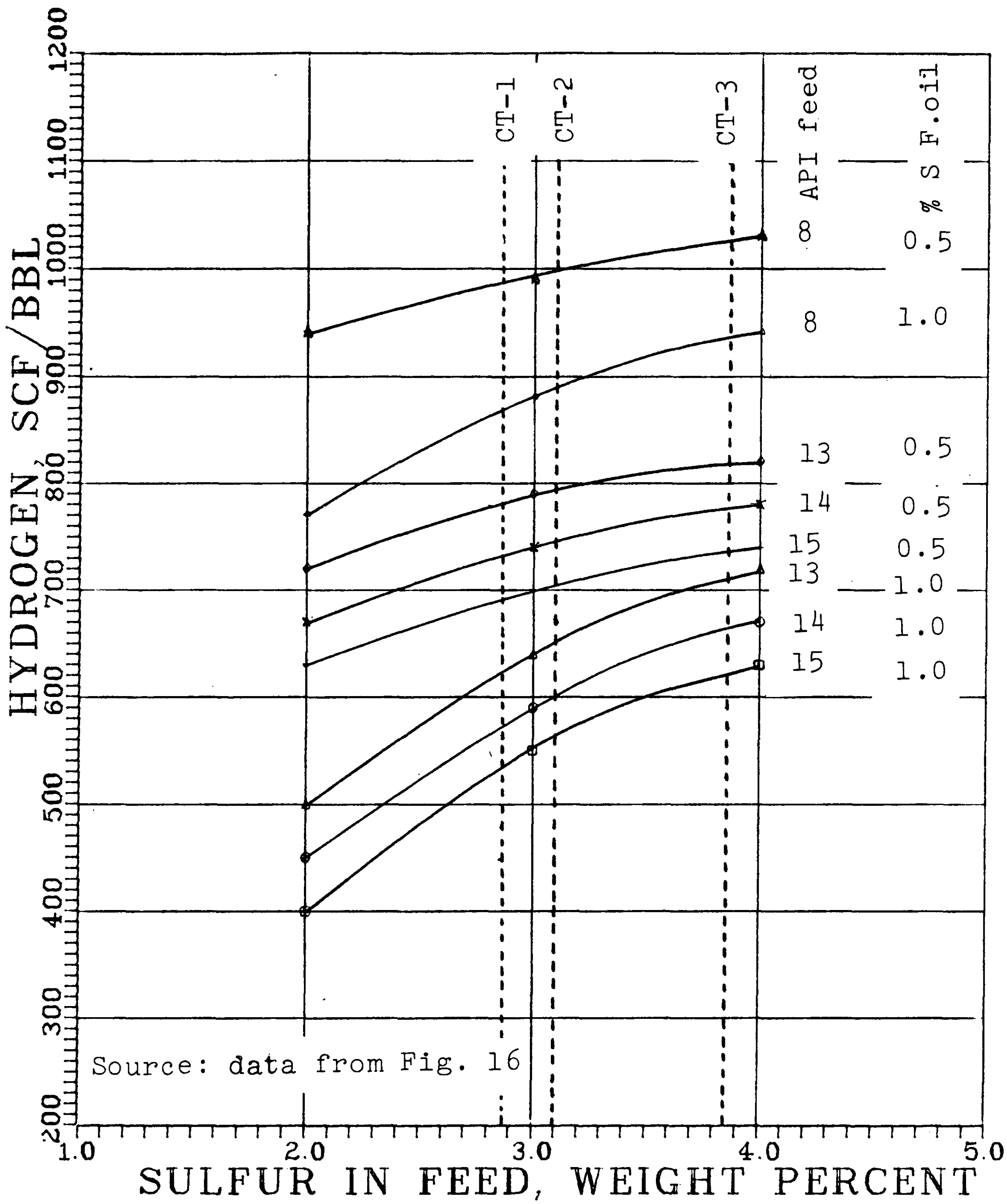

FIGURE 17

HYDROGEN VS. SULFUR IN FEED

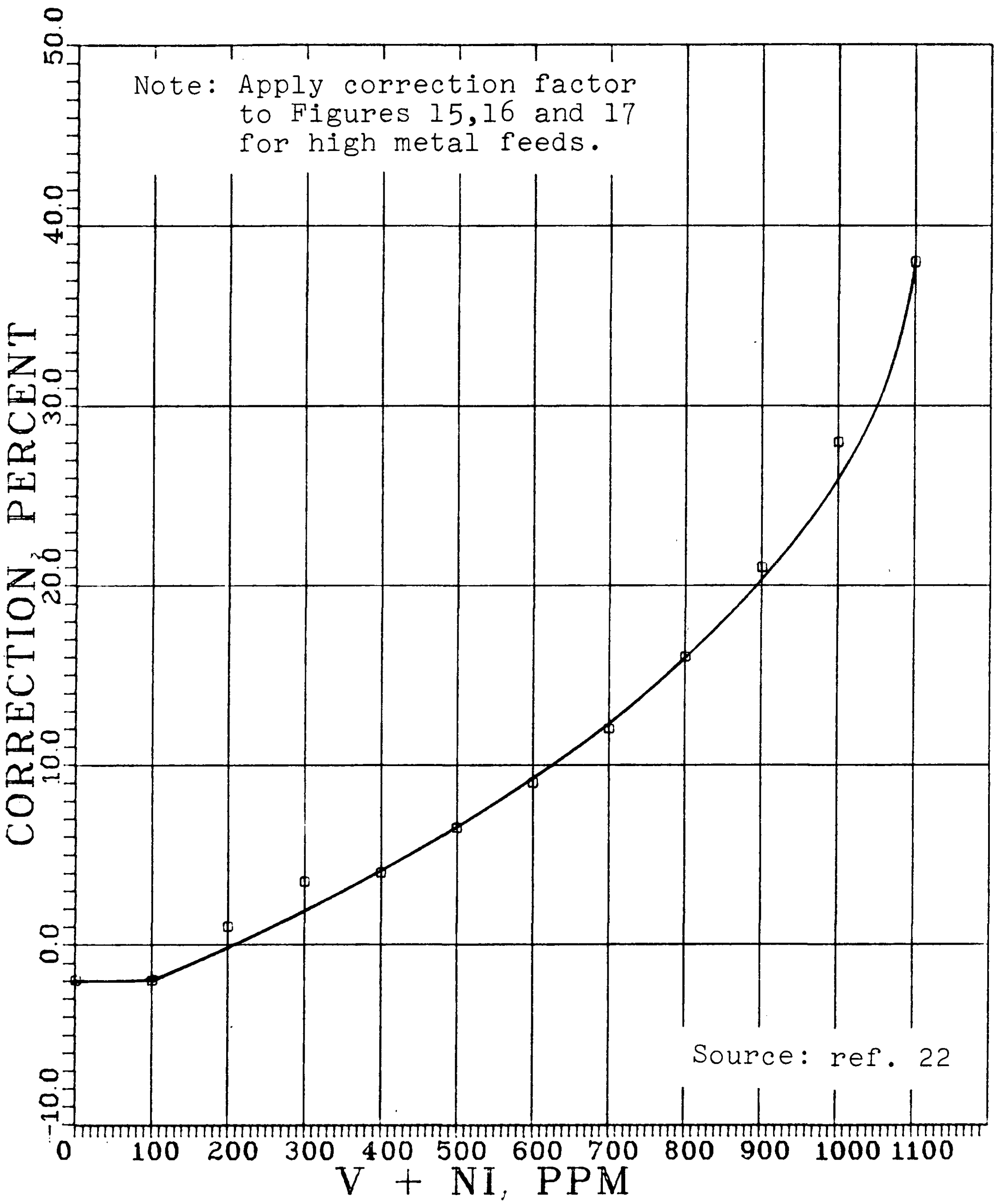

FIGURE 18

CORRECTION FACTOR FOR HIGH METALS

tion of the common Co/Mo catalyst. Thus, catalyst consumption is rapidly increased.

Nelson (9) has put together a much experimental data about catalyst consumption for desulfurizing residua. He presents a figure entitled "Pattern of Catalyst Consumption" that could be used for estimation of catalyst consumption. This reference data is shown in Figure 19.

The final results (bbl feed/lb catalyst) are shown in Table 5.

. Cost of hydrogen plant:

Ondish and Suchanek (8) report hydrogen plant cost that was used as a basis in this work. They report a cost (1979, U.S. Gulf Coast) of $ 45.5 Million for a steam reforming unit required for a 100,000 bbl/sd desulfurization unit (769 scf H_2/bbl).

This information was used to calculated the investment necessary at a Venezuela location for different size plants, by using capacity relation and location factor(see Appendix A). Table 5 shows the final results.

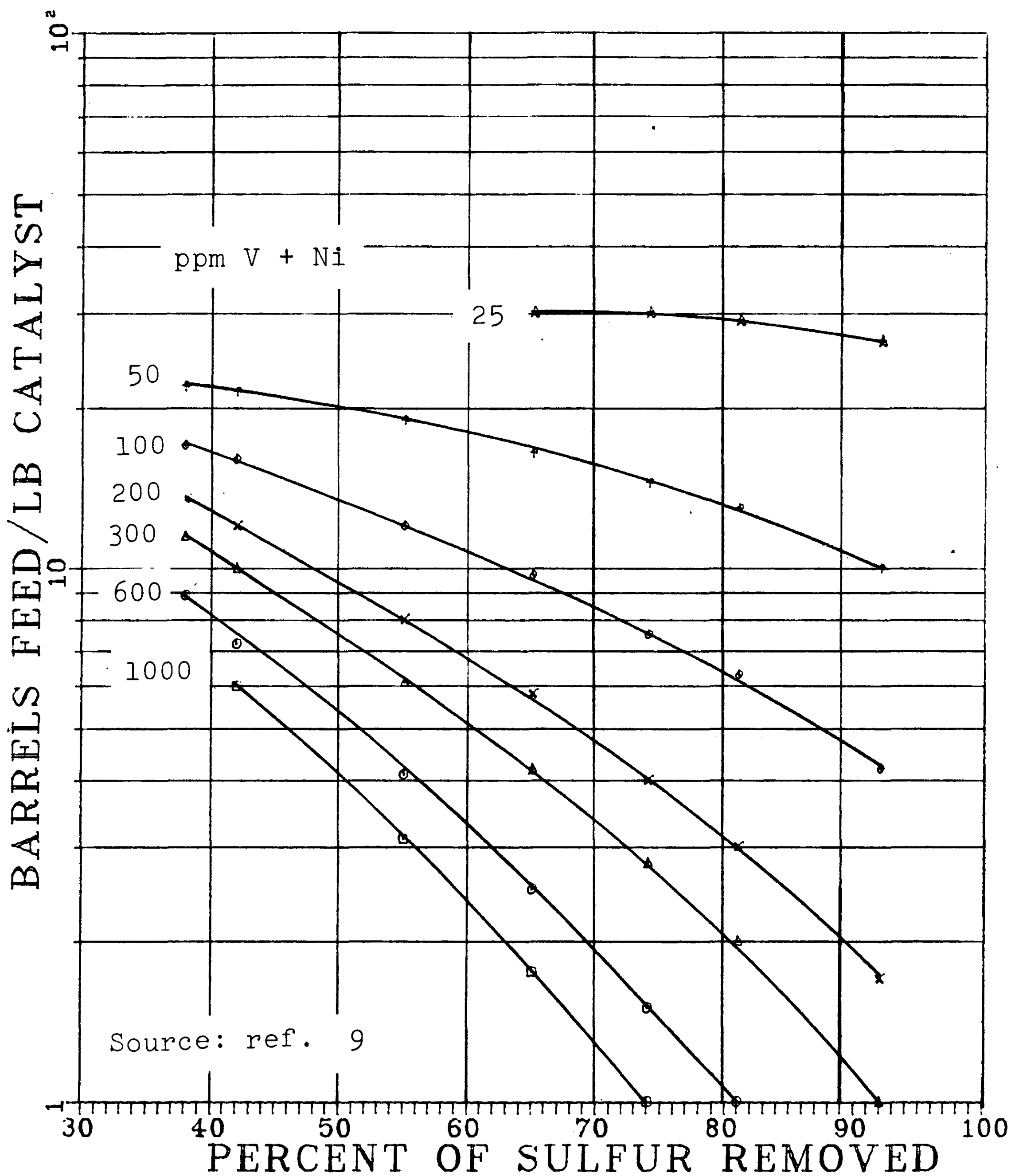

FIGURE 19

PATTERN OF CATALYST CONSUMPTION (IN DESULFURIZING RESIDUA)

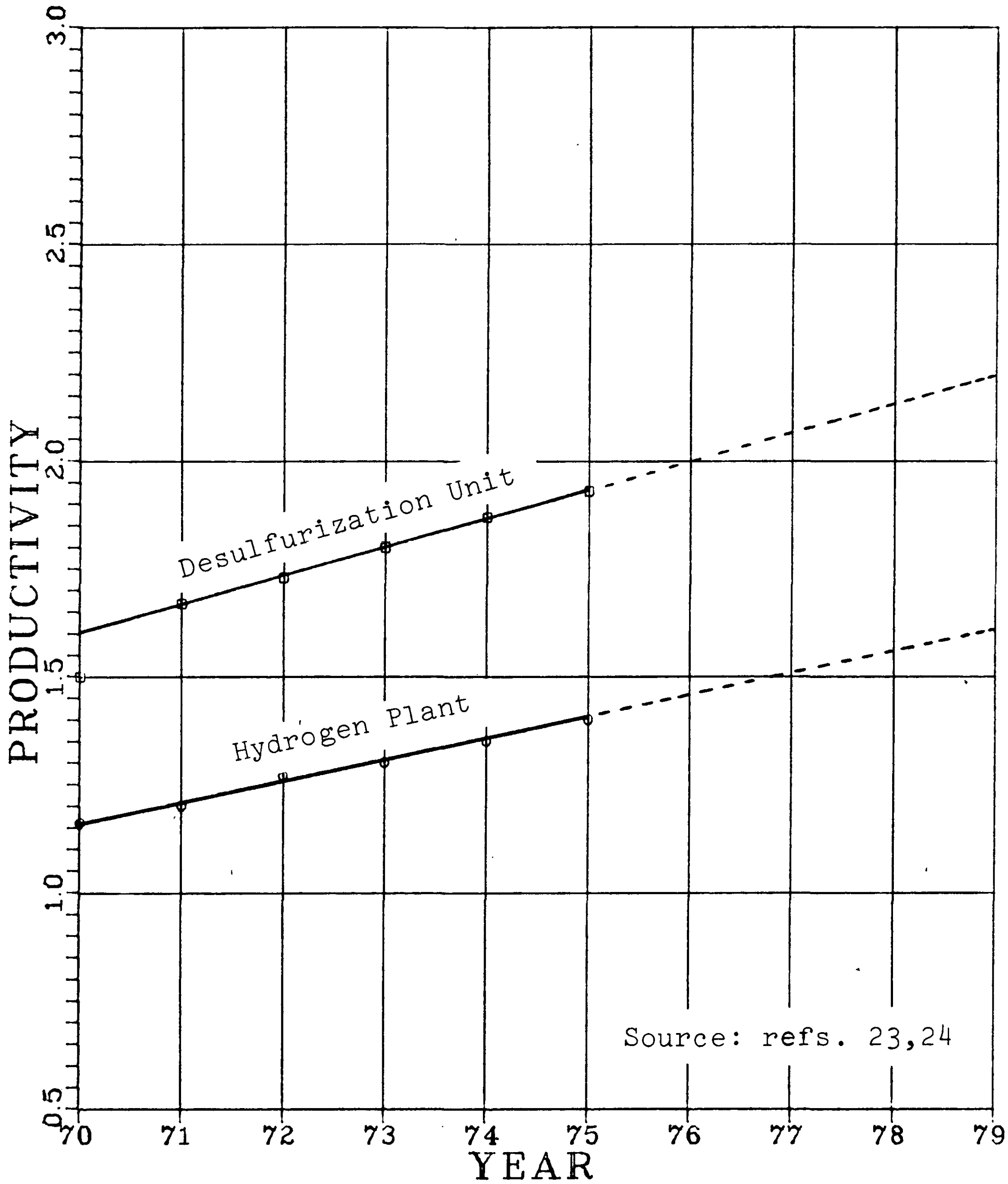

FIGURE 20

PRODUCTIVITY (PROCESS)

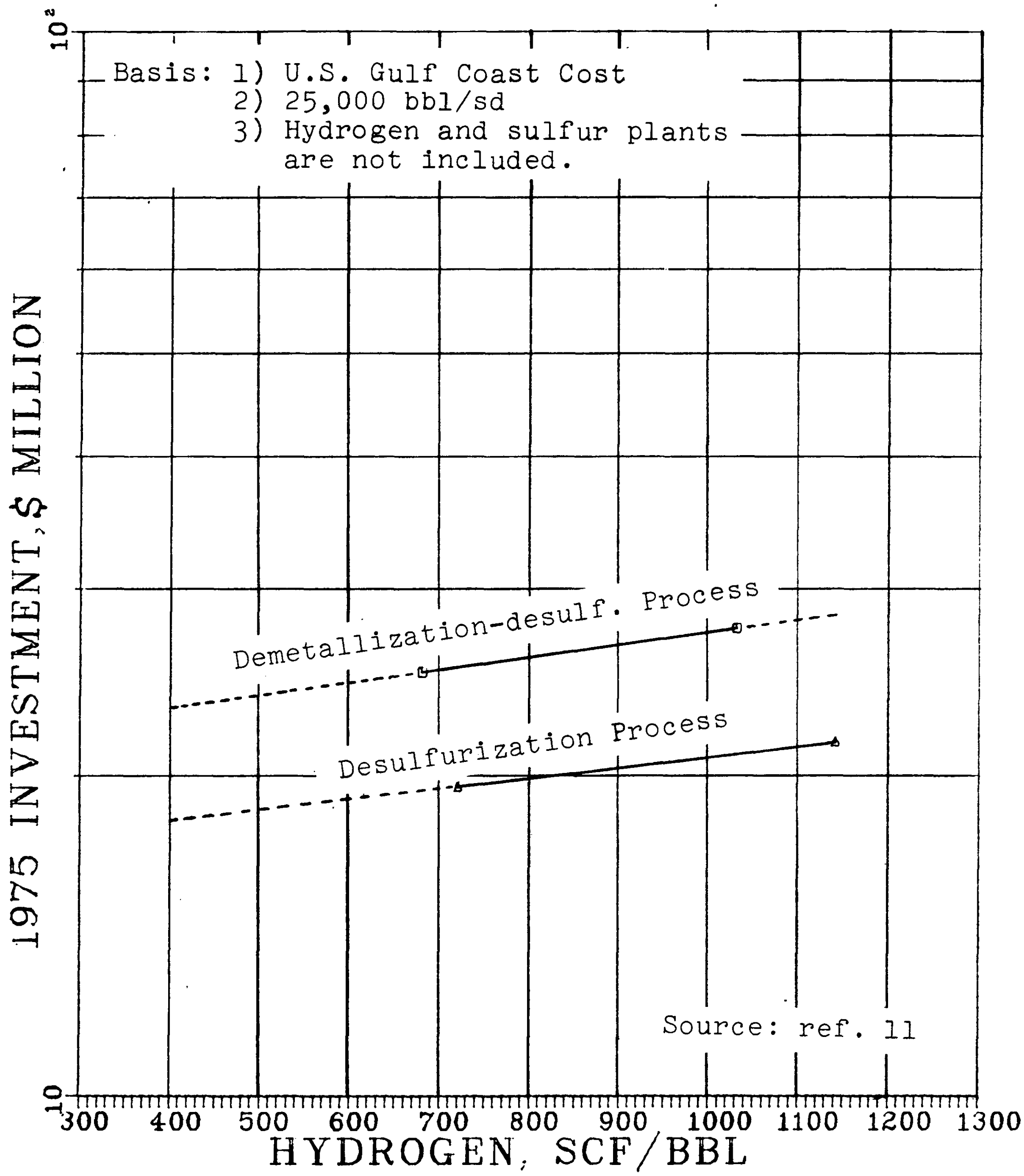

FIGURE 21

COST OF DESULFURIZATION AND DEMETALLIZATION-DESULF. PLANTS

TABLE 5

Direct Desulfurization. Major Processing Cost
(100,000 bbl/sd, 1979 Venezuela cost)

Sample	CT-1		CT-2		CT-3	
API gravity	14.5		13.6		8.4	
V + Ni, ppm	340		347		520	
% S feed	2.83		3.10		3.84	
% S Fuel oil	0.5	1.0	0.5	1.0	0.5	1.0
% S removed	83	65	84	68	87	74
H_2 (scf/bbl)	675	516	724	583	998	900
Cat.Co/Mo (bbl/lb)	1.65	3.90	1.55	3.40	<1	1.85
Desulfurization unit invest.($MM)	56.0	54.0	56.8	54.6	91.4	89.3
Hydrogen unit invest.($MM)	57.7	49.1	60.1	52.8	72.9	68.5
Major processing cost						
Catalyst cost(¢/bbl)	152	64	161	74	>250	135
Hydrogen cost*(¢/bbl)	104	81	111	91	150	136
Invest.** (¢/bbl)	17	16	17	17	28	27
Total cost(¢/bbl)	273	161	289	182	>428	298

Catalyst cost = $ 2.50/lb   Hydrogen manufac. cost = $ 1.28/Mscf
Investment payout over 10 years in ¢/bbl, based on 0.90 on-stream factor

* Including hydrogen manufac. cost and hydrogen plant investment
** Investment including desulfurization unit only

. Cost of desulfurization unit:

In the desulfurization process, the greater the hydrogen consumption, the larger the cost of the reactors and the hydrogen-recirculation system, but the increase in cost is not proportional to consumption because large high-pressure chambers, etc., are much more expensive than small ones (23). Details about these reference data are shown in Appendix C (see Table C1).

The available data are shown in Figure 21. Nelson construction index, productivity(from Figure 20), capacity relation, and location factor were used to convert and put up to date the available data. Table 5 shows the final results. These values do not include sulfur and hydrogen units.

2.2. Demetallization-Desulfurization

The following assumptions were made:

- Very low sulfur removing in the demetallization reactor.
- 80 % demetallization is achieved in the metal removal step. This means that only 20 % of the metal content of the feed-stock goes to the desulfurization step.

- Cost of catalyst consumption in the demetallization step is very low with respect to the desulfurization catalyst consumption cost.
- The hydrogen consumption for the demetallization-desulfurization process is reduced by 6-10% with respect to direct desulfurization process hydrogen consumption(from the reference 11). An average of 8% reduction was assumed.

. Hydrogen requirement:

The hydrogen requirements were calculated in the same manner as was made for the direct desulfurization process, and then they were reduced by 8%. Final results are shown in Table 6.

. Catalyst consumption:

The catalyst consumption was determined in the same manner as was made for the direct desulfurization process. Table 6 shows the final results.

. Cost of hydrogen plant:

Cost of hydrogen plants were calculated in the same manner as was made for the direct desulfurization

TABLE 6

Demetallization-Desulfurization. Major Processing Cost
(100,000 bbl/sd, 1979 Venezuela cost)

Sample	CT-1		CT-2		CT-3	
API gravity	14.5		13.6		8.4	
V + Ni, ppm	340		347		520	
% S feed	2.83		3.10		3.84	
% S Fuel oil	0.5	1.0	0.5	1.0	0.5	1.0
% Demetallization	80	80	80	80	80	80
% Desulfurization	83	65	84	68	87	74
H_2 (scf/bbl)	621	475	666	536	918	828
Cat.Co/Mo (bbl/lb)	10.5	14.5	10.0	14.0	5.0	7.5
Demet.-desul. unit invest. ($MM)	71.6	69.0	71.9	69.0	117.6	113.1
Hydrogen unit invest. ($MM)	54.8	46.7	57.2	50.2	69.3	65.2
Major processing cost						
Catalyst cost (¢/bbl)	24	17	25	18	50	33
Hydrogen cost* (¢/bbl)	96	75	103	84	139	126
Invest.** (¢/bbl)	22	21	22	21	36	34
Total cost (¢/bbl)	142	113	150	123	225	193

Catalyst cost = $ 2.50/lb   Hydrogen manufac. cost = $ 1.28/Mscf
Investment payout over 10 years in ¢/bbl, based on 0.90 on-stream factor

* Including hydrogen manufac. cost and hydrogen plant investment
** Investment for demet.-desul. unit only

process. The final results are shown in Table 6.

. Cost of demetallization-desulfurization unit:

The cost of these units were estimated from available data. These data are shown in Figure 21. Details about these reference data are included in Appendix C (see Table C2).

Nelson refinery construction index, productivity (assumed the same as direct desulfurization), capacity relation, and location factor were used to convert and put up to date the available data. Table 6 shows the final results.

2.3. Gulf HDS process

. Hydrogen requirement:

Figure 22 was used to estimate the amount of hydrogen required for each case. This figure shows reference data for different grades of feed-stock depending on the API gravity. Details about these reference data are presented in Appendix C (see Table C3).

To estimate the hydrogen requirement for the considered cases, extrapolations and interpolations were used. The final results are shown in Table 7.

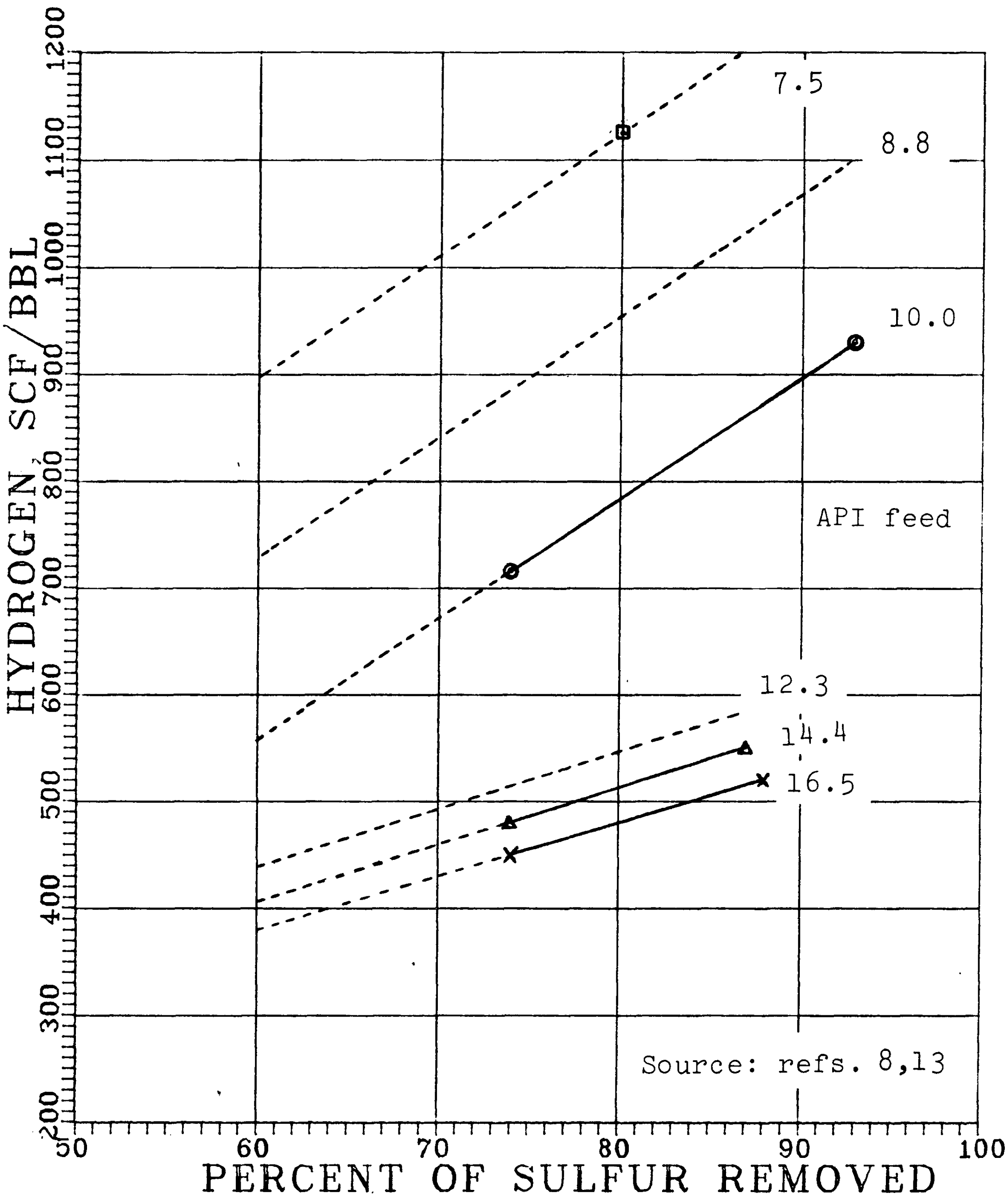

FIGURE 22

GULF HDS DESULFURIZATION PROCESS. HYDROGEN CONSUMPTION

. Catalyst consumption:

A catalyst cost data for processing 100,000 bbl/sd of Morichal heavy crude oil is given by Ondish and Suchanek (8). From this data, an average cost of catalyst consumption was calculated as follows:

Plant capacity: 100,000 bbl/sd

Feed: heavy crude oil (Morichal)

API feed = 9.6

V + Ni,ppm = 468

% Sulfur removed = 83

On-stream factor = 0.9

Catalyst cost ($M/yr) = 17,800 (1979)

Then,by using this data

Average catalyst cost =($ 17,800x10^3/yr)

(1/100,000x0.9 bbl/dx365 d/yr)(100 ¢/1 $)

(1/83% S) = 0.65 ¢/bbl/1% S removed (1979)

If the total percent sulfur removed is known, the catalyst cost (¢/bbl) for each case can be determined using the average catalyst cost. The final results are shown in Table 7.

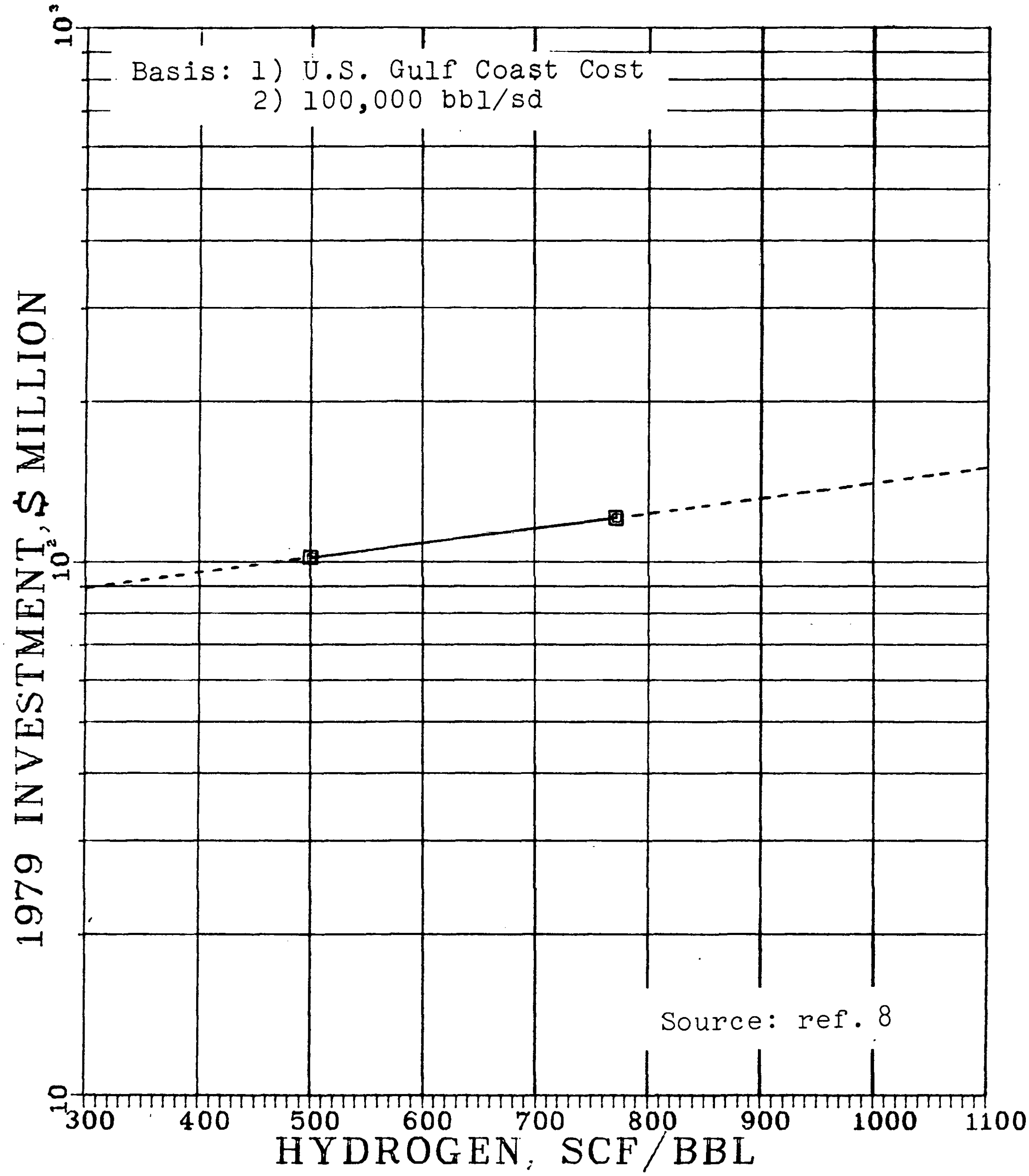

FIGURE 23

COST OF GULF HDS TYPE II PROCESS

TABLE 7.

Gulf HDS Type II Process. Major Processing Cost
(100,000 bbl/sd, 1979 Venezuela cost)

Sample	CT-1		CT-2		CT-3	
API gravity	14.5		13.6		8.4	
V + Ni, ppm	340		347		520	
% S feed	2.83		3.10		3.84	
% S Fuel oil	0.5	1.0	0.5	1.0	0.5	1.0
% S removed	83	65	84	68	87	74
H_2 (scf/bbl)	530	430	550	465	1030	880
Gulf HDS unit invest. ($MM)	143.9	134.3	143.9	137.0	199.0	181.0
Hydrogen unit invest. ($MM)	49.9	44.0	51.0	46.1	74.3	67.6
Major processing cost						
Catalyst cost(¢/bbl	54	42	55	44	57	48
Hydrogen cost*(¢/bbl	83	68	86	74	155	133
Invest.** (¢/bbl)	44	41	44	42	61	55
Total cost(¢/bbl)	181	151	185	160	273	236

Catalyst cost = 0.65¢/bbl/1%S removed   Hydrogen manufac. cost = $ 1.28/Mscf
Investment payout over 10 years in ¢/bbl, based on 0.90 On-stream factor

* Including hydrogen manufac. cost and hydrogen plant investment
** Investment for Gulf HDS type II unit only

. Cost of hydrogen plant:

Hydrogen unit investment for each case was calculated in the same manner as was made for the direct desulfurization process. Table 7 shows the final results.

. Cost of Gulf HDS unit:

Available data for Gulf HDS type II process are shown in Figure 23. Appendix C includes details about these data. Straight line correlation was assumed, and by extrapolation the investment for each case was determined.

These values, 1979 U.S. Gulf Coast cost, were converted to a Venezuelan location by using location factor of 1.37. The final results are shown in Table 7.

2.4. H-oil process

. Hydrogen requirement:

Using available data (14,16,25), Figure 24 (Chemical hydrogen vs. percent of sulfur removed) was developed. Details about these reference data are presented in Appendix C (see Table C4). Straight line correlation was assumed.

Table 8 shows the hydrogen requirement for each case which were determined from Figure 24.

. Catalyst consumption:

Cost of catalyst consumption for the H-oil process is available for some heavy feed stocks in the literature (14,16,25). Appendix C includes details about these reference data (see Table C5). These values were used to develop Figure 25.

The catalyst consumption (cost) for each case was determined from Figure 25. In some cases, an approximation by interpolation was necessary. The final results are shown in Table 8.

. Cost of hydrogen plant:

The required investment for the hydrogen unit in each case was estimated in the same manner as was made for the direct desulfurization process. Table 8 shows the final results.

. Cost of H-oil unit:

Cost data from the literature (14), was converted and put up to date for a Venezuela location.

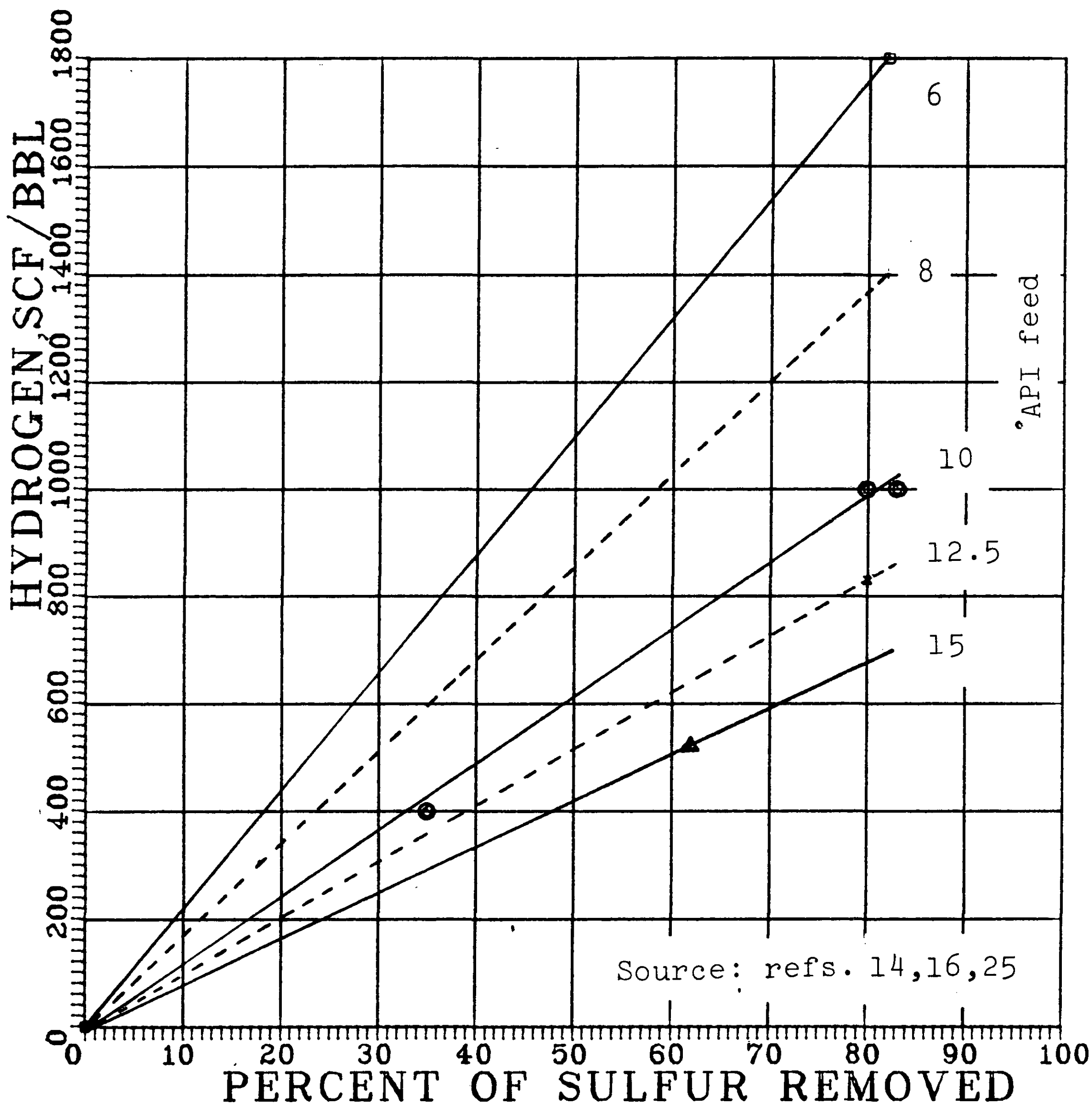

FIGURE 24

H-OIL PROCESS. HYDROGEN VS. PERCENT OF SULFUR REMOVED

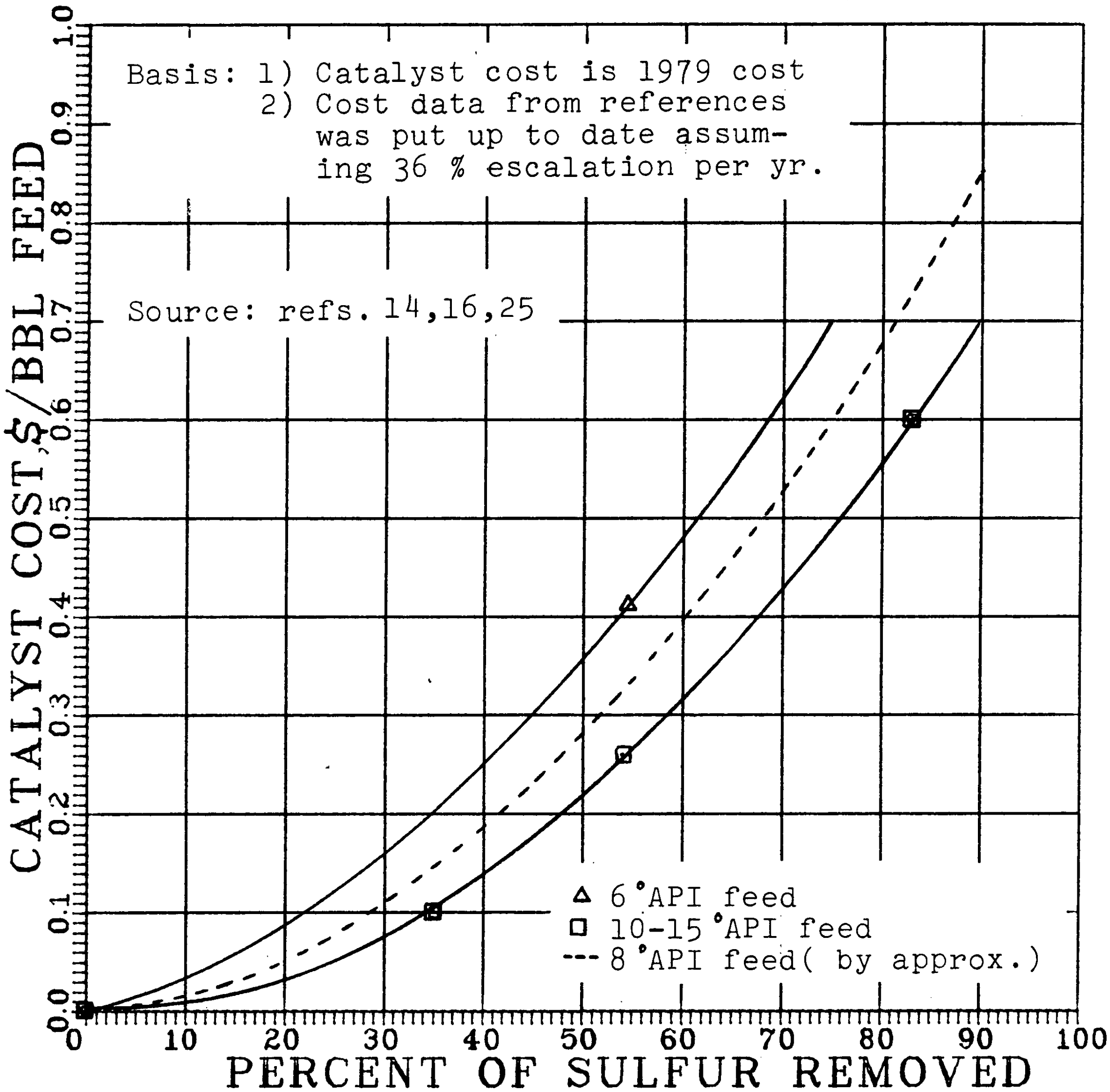

FIGURE 25

H–OIL PROCESS. CATALYST CONSUMPTION VS. PERCENT OF SULFUR REMOVED

These data were used to develop Figure 26. Details about the reference data are given in Appendix C (see Table C6).

Table 8 shows the required investment for each case. These values do not include sulfur plant, and hydrogen production unit.

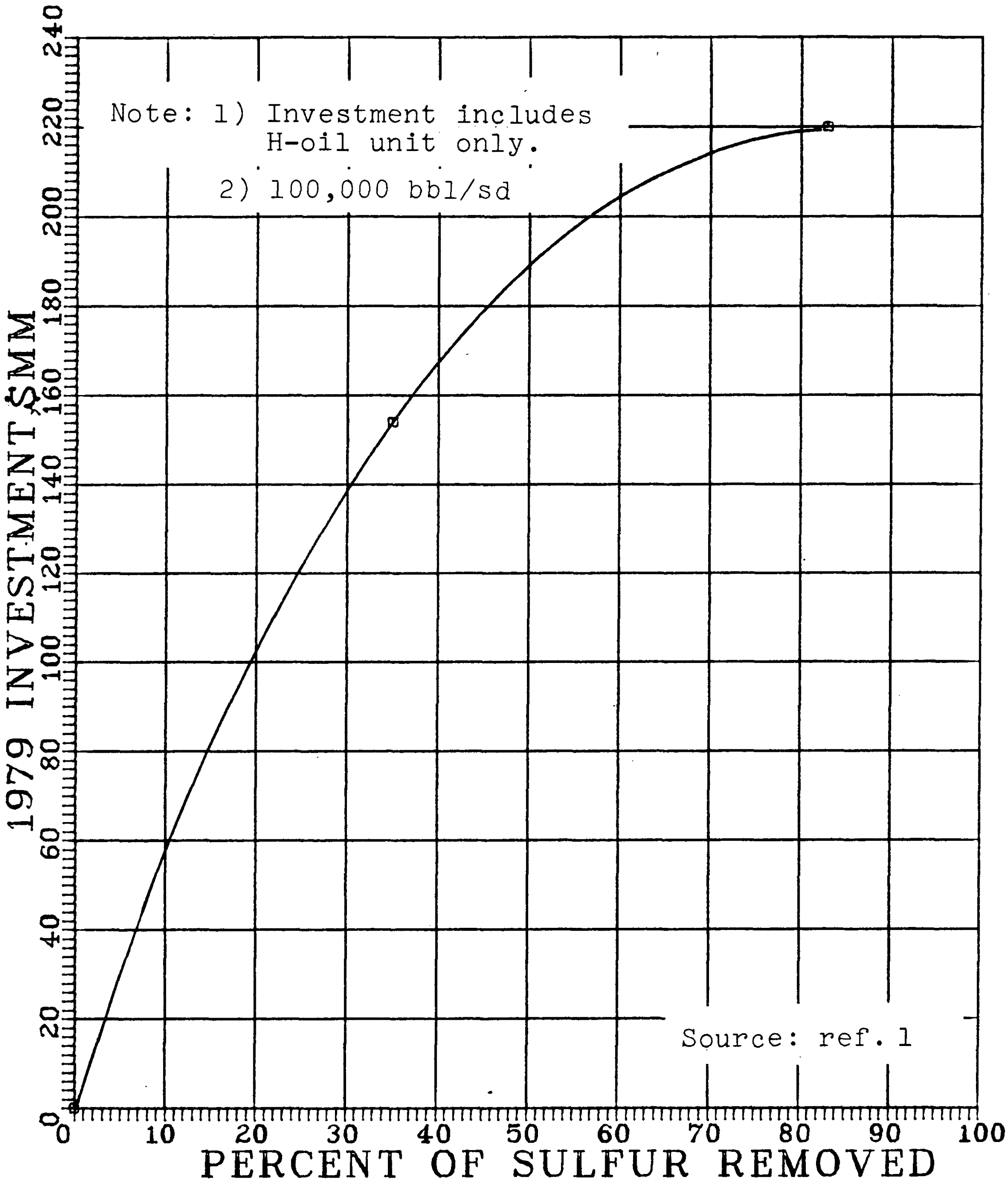

FIGURE 26

H–OIL PROCESS. 1979 VENEZUELA INVESTMENT

TABLE 8

H-Oil Process. Major Processing Cost
(100,000 bbl/sd, 1979 Venezuela cost)

Sample	CT-1		CT-2		CT-3	
API gravity	14.5		13.6		8.4	
V + Ni, ppm	340		347		520	
% S feed	2.83		3.10		3.84	
% S Fuel oil	0.5	1.0	0.5	1.0	0.5	1.0
% S removed	83	65	84	68	87	74
H_2 (scf/bbl)	750	595	840	660	1480	1260
H-oil unit invest. ($MM)	220.0	204.0	220.0	210.0	225.0	214.0
Hydrogen unit invest. ($MM)	61.4	53.4	65.7	56.9	92.3	83.8
Major processing cost						
Catalyst cost(¢/bbl)	60	37	60	40	80	60
Hydrogen cost*(¢/bbl)	115	92	128	102	218	187
Invest.** (¢/bbl)	67	62	67	64	68	65
Total cost(¢/bbl)	242	191	255	206	366	312

Hydrogen manufacturing cost = $ 1.28/Mscf
Investment payout over 10 years in ¢/bbl, based on 0.90 on-stream factor

* Including hydrogen manufac. cost and hydrogen plant investment
** Investment for H-oil unit only

V. DISCUSSION

As a secondary objective of this work, a brief description of different available alternatives for upgrading heavy feed stocks were included. Most of them are hydrogenative and/or catalytic processes. The major difficulty that these upgrading processes face is the poisoning of the catalyst caused by metals and coke formation. These contaminants decrease catalyst activity because they cover active sites.

Advantages and disadvantages of these upgrading processes were also included, which can be helpful in the selection of a final upgrading process for Venezuelan heavy crude oils. In addition to treating feeds such as high metals heavy crudes, and vacuum residua, there has also been a change in process objective. Hydrodesulfurization is no longer the only key reaction; other reactions such as nickel, vanadium and nitrogen removal, along with conradson carbon residue conversion, are now also important. Most of the cited literature mention the inclusion of a demetallization step previous to any additional process, as the best and more economical manner for upgrading heavy feeds.

The demetallization-desulfurization process looks like a very good alternative because the demetallization step considers the use of a natural and inexpensive catalyst and because the feed to the desulfurization reactor becomes a feed with low or moderate metals content. Another advantage is that no coke is produced in this process.

A very different process, FCC + Demet III, also looks like a good upgrading alternative. This process uses the technique of the well known FCC process with some modifications in the regenerator design. Metals from the catalyst are removed by the Demet III process, then the demetalized catalyst is returned to the FCC unit. According to test results this metal removal step does not affect catalyst characteristics, and vanadium and nickel are recovered as byproducts.

How economical is recovering vanadium and nickel as byproducts? Consumption of vanadium has increased steadily since the early 1960's. Furthermore, it is expected that the construction of thousands of miles of large diameter vanadium steel pipelines, along with increasing use of high strength-structural steels, will continue to improve the demand for vanadium. The estimated 1980 world production of vanadium (from standard sources) was set at 71.9 million pounds and the projected demand at 51.7 million pounds, thus the estimated production represents 139 % of projected demand. For this reason the relative economics of recovery of vanadium from petroleum should be carefully evaluated before capital investments are seriously considered (4).

Another good possibility is the Gulf HDS process. It is a commercially proven process for the removal of sulfur from petroleum residue to produce low sulfur fuel oil by direct desulfurization using a coke resistant catalyst. This process achieves desulfurization, demetallization, denitrogenation, and upgrading of asphaltenes in one step.

Lastly, to come out with a final recommendation, an economic analysis was taken into account. The major processing cost was determined for the following processes: direct desulfurization, demetallization-desulfurization, Gulf HDS process, and H-oil process. Tables 5, 6, 7, and 8 show details of the major processing cost for the four considered alternatives (100,000 bbl/sd installation).

In direct desulfurization when high degree of desulfurization is required, the cost of the catalyst becomes increasingly higher than the cost of hydrogen. In demetallization-desulfurization process low desulfurization catalyst cost is achieved because of the previous demetallization step, which helps reduce the major processing cost. For the Gulf HDS process, and H-oil the required investment for the main units becomes increasingly high affecting the total cost.

Although some assumptions were made to estimate the major processing costs, these can be useful in making process decisions. Table 9 shows the final results. From this table it is concluded, that demetallization-desulfurization process can be considered as one of the cheapest ways for upgrading Venezuelan heavy crude oils. CT-3, the heaviest, can be upgraded by this process for $ 2.25 per barrel of feed with 87 % sulfur removed and capacity installation of 100,000 bbl/sd. This cost only includes major operating costs and depreciation of the major investments.

Figure 27 shows how major processing cost of demetallization-desulfurization process varies with the amount of sulfur removed from the three types of samples: CT-1, CT-2, and CT-3. A decrease in API gravity of the feed stock and/or increase in required degree of desulfurization will also increase the major processing cost.

TABLE 9

Comparison of Major Processing Costs
(100,000 bbl/sd, 1979 Venezuela cost)

Sample	API gravity	% S F.oil	% S removed	($/bbl) Desul.	Demet.-desul.	Gulf HDS	H-oil
CT-1	14.5	0.5	83	2.73	1.42	1.81	2.42
		1.0	65	1.61	1.13	1.51	1.91
CT-2	13.6	0.5	84	2.89	1.50	1.85	2.55
		1.0	68	1.82	1.23	1.60	2.06
CT-3	8.4	0.5	87	>4.28	2.25	2.73	3.66
		1.0	74	2.98	1.93	2.36	3.12

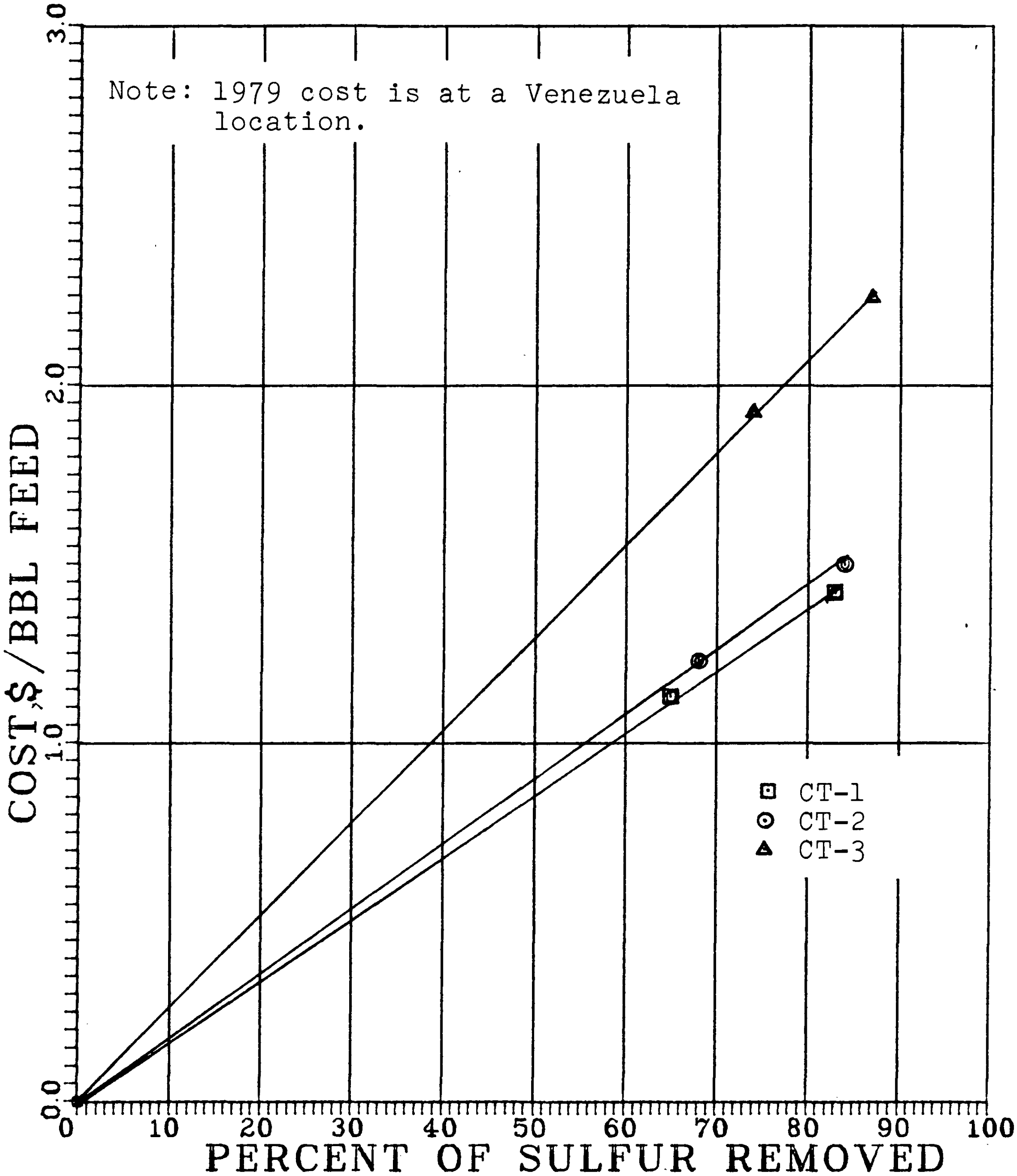

FIGURE 27

MAJOR PROCESSING COST FOR DEMETALLIZATION -DESULFURIZATION PROCESS

VI. CONCLUSIONS

1. Three different Venezuela heavy crude oils have been analyzed in this work. They were identified as CT-1, CT-2, and CT-3.
2. The three heavy crude oil samples can be considered as good representatives of heavy oils. They showed low API gravity, high sulfur content, high metals content, and high percent of asphaltenes.
3. The three Venezuela heavy crude oil samples showed similarities with the Athabasca bitumen in their properties.
4. Demetallization-desulfurization process, FCC + Demet III, and Gulf HDS process were considered among the more attractive ways for upgrading Venezuela heavy crude oils.
5. Comparison of the major processing cost for four different alternatives was made. It showed that demetallization-desulfurization process can be considered as one of the cheapest ways for upgrading Venezuelan heavy crude oils.

6. A barrel of heavy crude oil (8.4°API, 520 ppm V + Ni) can be upgraded at a cost of \$ 2.25 (Venezuela location) by using the demetallization-desulfurization process. This cost only includes major operating costs and depreciation of the major investments.

VII. RECOMMENDATIONS

1. It is recommended that a laboratory-scale apparatus be developed to simulate a demetallization-desulfurization process using samples of Venezuela heavy crude oils and/ or Athabasca bitumen.
2. It is recommended that manganese nodules be used as demetallization catalyst in testing demetallization-desulfurization process.
3. It is recommended that different catalysts (from different manufacturers) be used to check catalyst deactivation and kinetics in the desulfurization step when processing heavy feed stocks.
4. It is recommended that estimation of major processing cost for other processes be achieved to get a better economic comparison.
5. It is recommended that a more extensive economic analysis be made considering a cheaper way of producing hydrogen, and considering the credits that can be obtained from different final products.

VIII. APPENDICES

APPENDIX A

Economic Parameters and Definitions

. Nelson Refinery Construction Index

The Nelson Refinery(Inflation) Construction Index (NRC) measures the inflation that has been and is ocurring. This index measures the relative cost of constructing a barrel of refining or process capacity at various dates, incorporating all the changes that have occurred in productivity of construction, process design, and installation, all in the United States. Values of this index are published in the first issue of The Oil and Gas Journal each month.

The cost of an installation at a desired date is obtained using the following equation:

$$C = C_k(N/N_k) \qquad \text{(A-1)}$$

where: C = Cost at desired date

C_k = Known cost at some date

N = Nelson(inflation) index at desired date

N_k = Nelson(inflation) index for date of known cost

Sample calculation:

Process: Hydrodesulfurization

Capacity: 25,000 bbl/sd

Hydrogen requirement: 675 scf/bbl

C_k = \$ 19.5 Million (1975 U.S. Gulf Coast Cost, Desulfurization unit only)

C = 1979 cost

N_k = 575.5 (1975)

N = 737.2 (1979)

C = 19.5(737.2/575.5)

C = \$ 25.0 Million (1979 U.S. Gulf Coast Cost)

. Productivity

To get a better result of the estimated cost, Nelson (26) considers productivity as a correction factor.

All (Nelson) productivities are divisors to be used with the Nelson refinery cost index. These productivities are estimated for each kind of process.

Productivities values have been publishing for different refinery processes. However, such information is historical, and therefore current values must be estimated by extrapolation. Productivities for hydrodesulfurization process and hydrogen plants have been listed by Nelson (23,24).

The cost of an installation at a desired date, by using productivity, is obtained using the following equation:

$$C = C_k(N/N_k)(P_k/P) \qquad \text{(A-2)}$$

where: C, C_k, N, and N_k have been already defined

P = Productivity at desired date

P_k = Productivity for date of known cost

Sample calculation: (using the same sample case)

$P = 2.20$ (1979)

$P_k = 1.93$ (1975)

These values have been estimated by extrapolation (see Figure 20)

$$C = 19.5(737.2/575.5)(1.93/2.20)$$

$$C = \$\ 21.9 \text{ Million} \quad \text{(1979 U.S. Gulf Coast Cost)}$$

. Capacity Relation

A method for making rapid capital-cost estimates uses capacity ratio exponents and is based on existing cost data. This procedure has the advantage of not requiring any design work or the establishment of heat and mass balances.

Let the cost of a piece of equipment or plant of size or capacity, Q_1, be C_1. The cost, C_2, of a similar piece of equipment or plant of size or capacity, Q_2, can be calculated from:

$$C_2 = C_1(Q_2/Q_1)^x \qquad \text{(A-3)}$$

where: x = Capacity ratio exponent

The value of the exponent x depends on the type of equipment or plant. Some typical values of x for various items of equipment and for complete process plants have been listed in reference 29. However, for complete process plants, the exponent x is usually taken to be 0.6.

From available data (23,24), the exponent x was estimated for the following processes:

Process	Exponent, x
Hydrogen Plant(steam reforming)	0.6
Resid-hydrodesulfurization unit	0.45 for hydrogen <800 scf/bbl
	0.75 for hydrogen >800 scf/bbl

Sample calculation: (using the same sample case)

C_1 = \$ 21.9 Million

Q_1 = 25,000 bbl/sd

C_2 = Cost for capacity Q_2

Q_2 = 100,000 bbl/sd

Hydrogen consumption : 675 scf/bbl

Thus, $x = 0.45$ (hydrodesulfurization unit)

$$C_2 = 21.9(100{,}000/25{,}000)^{0.45}$$

C_2 = \$ 40.9 Million (1979 U.S. Gulf Coast Cost, for 100,000 bbl/sd unit)

. Location Factor(LF)

The common method of comparing costs of refineries or process units at various locations is by what are called "location factors" relative to costs at the Gulf Coast U. S.A. (Basis= 1.0). In fact, location factors involve all costs that compose the construction cost of a refinery (27).

Bridgwater (28) derived empirically a list of 1979 international construction cost location factors for estimating the overall cost of building a process plant in any part of the world. Geographical variations in capital costs are usually quantified by means of a location factor that is the ratio of capital costs between two locations.

The factors that primarily cause the capital costs of new facilities to vary in different locations are the following (28):

- Labor
- Material and equipment
- Transportation, handling and construction
- Local effects
- Legislation

Bridgwater (28) reports a location factor of 1.35 (Based on U.S. Gulf Coast) for South America (North). Fluor Corp. (California) provided a location factor for Venezuela of 1.37 (Based on U.S. Gulf Coast, 1979 Cost). A factor of 1.37 was used in this work.

Sample calculation: (using the same sample case)

Cost for a hydrodesulfurization unit of 100,000 bbl/sd capacity, at a Venezuela location.

C = $ 40.9 Million (1979 U.S. Gulf Coast Cost)

$$C = 40.9 \times 1.37$$

$$C = \$\ 56.0 \text{ Million (1979 Venezuela Cost)}$$

A final equation, which shows all the factors affecting capital costs, can be written:

$$C_2 = C_1(N/N_k)(P_k/P)(LF)(Q_2/Q_1)^x \qquad \text{(A-4)}$$

. Catalyst Cost

The price of catalyst depends on the type of catalyst. Nickel-cobalt-molybdenum catalyst is one of the most common type of catalyst used in residual hydrodesulfurization.

Venezuela has to import all of the catalysts that are used in catalytic process. Most of them import from the United States. For this reason was assumed in this work that the catalyst price at a Venezuela location is the U.S. price.

An estimated 1979 price for nickel-cobalt-molybdenum catalyst was provided by Gulf Research & Development Company (Pittsburgh). $ 2.25-2.75/lb of catalyst.

For calculation purposes, an average value of $ 2.50/lb was assumed.

. Hydrogen Cost

The price of producing hydrogen varies depending on the process. Hydrogen can be produced by steam-reforming of naphtha or methane(natural gas), or by partial-oxidation of heavy feed(asphalt).

Steam-reforming of natural gas was considered as the supplier of hydrogen in this work. To come out with an average cost of manufacturing hydrogen at a Venezuela location, the following data was available:

- 1979 Venezuela cost = \$ 2.06/MMBtu (Natural gas)
- Net Heating Value = 1,100 Btu/scf (Natural gas)
- 100 scf of natural gas can produce 315 scf of hydrogen (steam-reforming process)

Using this data, the average raw material cost is given by:

$$1{,}100 \text{ Btu/scf} \times \$\ 2.06/10^6\text{Btu} \times 100 \text{ scf}/315 \text{ scf} = \$\ 0.72/\text{Mscf } H_2$$

The average operating cost for a steam-reforming unit was also available. \$ 0.56/Mscf H_2 (direct + indirect costs).

Average manufacturing cost = \$ 1.28/Mscf (at a Venezuela location)

APPENDIX B

Properties and Composition Determinations

. API gravity

Standard hydrometers were used to determine the API gravity of the samples. Table B1 shows the results that were obtained for the API gravity determination of each type of Venezuelan heavy crude oil. Also, the average values are reported.

. Total sulfur analysis

Total sulfur was determined by a Leco induction furnace technique. Table B2 shows the results that were obtained for the three types of crude oil.

The asphaltene fractions were also analyzed. Table B3 shows the results obtained from these fractions. The average values are also included for each case.

. Total Carbon-Hydrogen-Nitrogen analysis

A Carlo-Erba CHN was used to determine carbon, hydrogen, and nitrogen. Table B4 shows the results that were obtained for the total carbon-hydrogen-nitrogen analysis of each sample of crude oil. Table B5 shows the results obtained for the asphaltenes fractions. Also, the average compositions are reported.

. Metals content (vanadium and nickel)

Tables 2 and 3 show the final results. These were obtained by the Colorado School of Mines Research Institute.

. Pentane insolubles (asphaltenes)

A modified PERC method was used to determine the weight percent of pentane insolubles of the samples. Table B6 shows the result of each run. The average values are also included.

TABLE B1

API Gravity
(crude oil samples)

Sample	Run	API gravity, 60°F*	Average API
	1	14.3	
CT-1	2	14.5	14.5
	3	14.6	
	1	13.6	
CT-2	2	13.5	13.6
	3	13.6	
	1	8.4	
CT-3	2	8.5	8.4
	3	8.3	

* Corrected at 60°F

TABLE B2

Total Sulfur Analysis
(crude oil samples)

Sample	Run	Wt % Sulfur	Average, wt % S
	1	2.78	
CT-1	2	2.85	2.83
	3	2.85	
	1	(2.85)	
CT-2	2	3.10	3.10
	3	3.10	
	1	3.81	
CT-3	2	3.85	3.84
	3	3.83	

TABLE B3

Total Sulfur Analysis
(asphaltenes samples)

Sample	Run	Wt % Sulfur	Average, wt % S
CT-1	1	4.71	4.80
	2	4.88	
CT-2	1	4.56	4.56
	2	4.56	
CT-3	1	4.98	5.13
	2	5.27	

TABLE B4

Total Carbon-Hydrogen-Nitrogen Analysis
(crude oil samples)

Sample	Run	C, wt %	H, wt %	N, wt %
	1	81.95	10.96	0.85
CT-1	2	84.89	11.04	0.68
	Average	83.42	11.00	0.77
	1	79.67	11.57	0.71
CT-2	2	85.89	12.46	0.86
	Average	82.78	12.02	0.79
	1	83.01	10.42	0.94
	2	87.14	11.17	0.95
CT-3	3	83.06	9.99	0.88
	4	82.65	9.79	0.86
	Average	83.97	10.34	0.90

TABLE B5

Total Carbon-Hydrogen-Nitrogen Analysis
(asphaltenes samples)

Sample	Run	C, wt %	H, wt %	N, wt %
	1	84.04	8.23	1.87
	2	83.14	8.38	1.79
CT-1	3	84.80	8.77	1.78
	4	84.48	8.44	2.01
	Average	84.12	8.46	1.86
	1	83.95	8.79	1.75
	2	83.72	9.02	1.74
CT-2	3	84.32	9.22	1.75
	4	84.38	9.04	1.78
	Average	84.09	9.02	1.76
	1	84.22	8.97	1.78
	2	84.42	8.80	1.87
CT-3	3	84.61	9.40	1.66
	4	83.82	8.58	1.91
	Average	84.27	8.94	1.81

TABLE B6

Pentane Insolubles

Sample	Run	Pentane insolubles, wt %	Average, wt %
CT-1	1	14.9	15.93
	2	15.7	
	3	17.5	
	4	15.6	
CT-2	1	19.9	19.72
	2	20.8	
	3	18.7	
	4	19.5	
CT-3	1	23.9	23.03
	2	21.7	
	3	26.5	
	4	20.0	

APPENDIX C

Reference Data

. Direct desulfurization

. hydrogen requirement:

Nelson (22) presents a figure entitled "Hydrogen for Atmospheric and Vacuum Residua" that could be used to estimate hydrogen requirements. Nelson used over 100 sets of data available from 32 references or sources giving the hydrogen consumed in desulfurizing residua. Part of the effect of metals in increasing hydrogen consumption in the 4-12°API range is already reflected in Nelson's figure.

Nelson developed correction factors for high metals feed-stock (22).

. Cost of desulfurization unit:

Hastings, James, and Mounce (11) developed data for Venezuelan high metals feeds. Table C1 shows these reference data.

. Demetallization-desulfurization

. Cost of demetallization-desulfurization unit:

Hastings, James, and Mounce (11) present cost data for Venezuelan high metals feeds. These reference data are shown in Table C2.

. Gulf HDS process

. Hydrogen requirement:

The reference data used to estimate hydrogen requirements are shown in Table C3. These data are presented by Ondish, and Suchanek (8) and by Brunn, Montagna, and Paraskos (13).

. Cost of Gulf HDS unit:

Ondish and Suchanek (8) present a cost data for Gulf HDS unit. They report a cost (1979 U.S. Gulf Coast) of $ 122 million for a Gulf HDS type II unit (100,000 bbl/sd and 769 scf H_2/bbl). This investment does not include the hydrogen unit.

. H-oil process

. Hydrogen requirement:

References 14, 16, and 25 present hydrogen requirement data for the H-oil process. These reference data are shown in Table C4.

. Catalyst consumption:

References 14, 16, and 25 present catalyst consumption data for the H-oil process. Table C5 shows these reference data.

. Cost of H-oil unit:

Driesen, Carspers, and Campbell (1) present a cost data for H-oil units. These reference data are shown in Table C6.

TABLE C1

Cost of Desulfurization Unit
(reference data)

	Case 1	Case 2
Feed, bbl/sd	25,000	25,000
API gravity, feed	11.8	10.4
V + Ni, ppm	430	1,185
Space velocity (V_o/hr/V_r)	0.49	0.53
H_2, scf/bbl	720	1,140
1975 investment* $ MM	19.8	21.8

* U.S. Gulf Coast cost

TABLE C2

Cost of Demetallization-Desulfurization Unit
(reference data)

	Case 1	Case 2
Feed, bbl/sd	25,000	25,000
API gravity, feed	12.7	10.4
V + Ni, ppm	455	1,185
Space velocity (V_o/hr/V_r)	0.31	0.49
H_2, scf/bbl	680	1,030
1975 investment* $ MM	25.2	27.7**

* U.S. Gulf Coast cost

** Corrected value

TABLE C3

Gulf HDS Process Hydrogen Consumption
(reference data)

Feed	API gravity	V + Ni (ppm)	% S removed	H_2, scf/bbl
Cold Lake (ATB)	10	236	94	930
			74	715
East Vene. (ATB)	14.4	274	74	480
			87	550
Mixed Iranian (ATB)	16.5	183	74	450
			88	520
Agha Jari (VAB)	7.5	274	80	1,125

ATB = Atmospheric bottom

VAB = Vacuum bottom

TABLE C4

H-Oil Process Hydrogen Consumption
(reference data)

Feed	API gravity	V + Ni (ppm)	Wt % Sulfur	% S removed	H_2 scf/bbl
Jobo	9.2	499	4.1	35	400
				83	1,000
Lloydmins. (ATB)	10.1	195	4.2	80	1,000
Athabasca bitumen	6.3	209	4.6	82	1,800
Vene., atm.	15.0	x	2.1	62	525

TABLE C5

H-Oil Process Catalyst Consumption
(reference data)

Feed	API gravity	V + Ni (ppm)	% S removed	Catalyst cost ($/bbl)
Jobo	9.2	499	35	0.10 (1979)
			83	0.60 (1979)
Lloydmins. (VAB)	6.4	259	54	0.24 (1977)
Vene., atm.	15.3	x	55	0.15 (1977)

TABLE C6

Cost of H-Oil Unit
(reference data)

Feed	API gravity	Capacity (bbl/sd)	% S removed	Investment* ($ MM)
Jobo	9.2	50,000	35	74
Jobo	9.2	50,000	83	106

* 1979 U.S. Gulf Coast Cost. This cost only includes H-oil major units.

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