

H-OIL DESULFURIZATION OF HEAVY FUELS

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INTRODUCTION

In many areas of the world residual fuel oil has become the principal source of industrial, commercial and utility fuel. In these services it has historically been the marginal energy source with locally produced coal or natural gas being the fuel of choice on economic grounds. At present, however, air pollution control regulations relating to fuel sulfur content have limited the use of many sources of coal, and in many important areas low cost natural gas is becoming critically short in supply. Because of these factors, fuel oil consumption is growing rapidly - and in many instances at a rate substantially above the normal growth in energy demand. This growth in demand - coupled with increasingly stringent sulfur content specifications, is leading in the direction of a shortage in residual fuels - particularly those of lower sulfur contents.

These factors have already led to a substantial investment in fuel oil desulfurization facilities in several parts of the world - notably in Japan, the Middle East and the Caribbean area. With some few exceptions these facilities have been based on indirect desulfurization - i.e. vacuum distillation, desulfurization of the vacuum gas oil and reblending. This technique has a real limitation in a market for fuels below the 1% sulfur level since none of the heavy high sulfur vacuum residue is processed. To some extent this can be mitigated by preferentially blending this material to bunkers and by the use of naturally occurring low sulfur residues as blending stocks.

In many supply and consumption areas we are now nearing - or have passed - the limits of these approaches, and the industry is giving serious consideration to the installation of facilities which will process the entire residue to achieve the desired end product. It is the purpose of this paper to consider some of the problems associated with processing residual oils and to present some major new developments in the H-Oil process which relate to the solution of these problems. Because of these new developments it is now possible to design a processing facility which can economically produce fuel oils of 0.3% sulfur content, interchangeably from a broad range of feedstocks encompassing most of the commercially important residues. One of the most significant aspects of these new developments involves the ability to economically desulfurize the high metals content residues from Venezuela.

FACTORS AFFECTING A FUELS PROCESSING FACILITY

In this paper we will concentrate on the problems associated with a market-related fuels process facility - specifically one which would serve the East Coast of the United States. Planning such a facility involves the several fundamental questions considered below.

Source of Supply

The traditional source of fuel oil supply for the U.S. East Coast has been Venezuelan imports. Under the impact of the newer sulfur content specifications, an increasing portion of this fuel is being obtained from African crudes, and it is possible that the Middle East may also become an important factor in this market. For these reasons, as well as from a national security standpoint - particularly as we become more dependent on fuel oil for basic energy - the refiner will be faced with the problem of providing the capability to handle a broad range of feedstocks.

Market Requirements

The requirements for low sulfur fuel oil have become increasingly stringent, and the market requirements for this product is subject to the vagaries of local and national regulations. Consequently, market requirements cannot be forecast with a high degree of accuracy. For this reason the facility must be flexible in terms of the quality of product produced.

Adaptability

At a future date the market for low sulfur fuel oil may become less attractive due to several factors. Among these are: increasing use of nuclear energy, the installation of stack gas desulfurization processes or increased availability of low sulfur fuels. Should this occur it would be desirable to make alternate use of any facility installed today to desulfurize fuel oil. At such a time the market could revert to the traditional U.S. pattern in which high sulfur residual oil is a low value material, and there would be a consequent economic incentive to convert it into lighter products.

Considering these factors an optimum fuels processing facility should possess the following basic characteristics:-

1. The ability to process fuel oil at low unit cost
2. Be able to handle a broad range of residual fuels as feedstock
3. Have the capability of meeting changing fuel oil specification requirement
4. Have an economical alternate use in the event of a decreased demand for low sulfur fuel oils.

In a later section of this paper we describe a facility which meets these requirements. First, however, we would like to consider some of the technical problems associated with residual oil processing - and how the solutions to these problems are approached in the H-Oil process.

TECHNICAL ASPECTS OF RESIDUE DESULFURIZATIONReaction Mechanism

Various investigators have shown that a first order kinetic model adequately describes the desulfurization of the individual sulfur compounds contained in petroleum fractions. In the case of residual oils, however, we are not dealing with individual compounds or with a few similar species, but rather with a complex mixture of compounds having widely differing reaction rates. Since the compounds which are easier to react will tend to disappear first, while those having a lower reaction rate constant will desulfurize last, desulfurization of these materials, viewed on an overall basis, does not follow a first order kinetic model. Beuther and Schmid<sup>(1)</sup> found that desulfurization of residues can be represented adequately by use of a second order model. These authors recognized that the individual reactions were probably first order, but that a second order model would best represent the overall data. By using a psuedo second order approach, the fact of increasing difficulty of desulfurization is reflected in the concentration term of the rate equation, enabling one to use a fixed reaction rate constant.

Our work in this area has confirmed the observations of Beuther and Schmid and in Figure 1 we show, for the desulfurization of Kuwait atmospheric residue, a comparison of the fit of the data to first and second order models. In developing this plot, average first and second order K-values were calculated from data obtained under various operating conditions over fresh catalyst. The curves shown were then prepared and compared with the data. It is apparent that the second order relationship more accurately represents the situation. In use of these relationships, however, it should be borne in mind, that this is an empiricism and data extrapolations must be treated with caution.

A practical consequence of the psuedo second order model is, that as market requirements dictate a lower sulfur content product, the reaction rate in the final stages of a process will be quite low. With a second order model the reaction rate in the final incremental portion of a reactor system will be only one tenth at the 0.3% sulfur level what it would be at the 1% sulfur level.

Catalyst Aging

In hydroprocessing of residual oils, catalysts lose activity at a much higher rate than is the case in gas oil processing. This is due to the presence of organometallic compounds, asphaltenes and the general higher molecular weight of the material being processed. Further, since there is a considerable range in the metals contents of the various stocks available for processing, residues from different crudes will deactivate catalysts at different rates. Figure 2 illustrates this point by comparing the aging characteristics of Kuwait and Venezuelan atmospheric residues. Psuedo second order reaction rate constant is plotted versus catalyst age for these two stocks processed under the same conditions. While both stocks exhibit a rate of activity decline considerably above that which would be experienced in processing of gas oils, the effect of the higher metals content in the Venezuelan oil is rapidly apparent from the higher rate of activity decline.

### Effect of H<sub>2</sub>S on Reaction Rate

As the desulfurization reaction proceeds, H<sub>2</sub>S is produced. This material, while mainly in the vapor phase, is in equilibrium with a concentration of dissolved H<sub>2</sub>S in the liquid. Under certain conditions the mass action effect of this material can have a strong effect on the overall rate of the desulfurization reaction. Figure 3 shows the effect, for one set of circumstances, of H<sub>2</sub>S partial pressure on the pseudo second order reaction rate constant. Again, it should be emphasized that the constant shown is not a true reaction rate constant - which would be independent of such parameters - but is rather an overall representation of several simultaneously occurring forward and reverse desulfurization reactions.

When operations are directed to achieving very low levels of sulfur in the product, this effect-coupled with the other difficulties of such an operation - can have important design consequences.

### THE H-OIL APPROACH TO THE PRODUCTION OF LOW SULFUR FUEL OILS

Several previous papers by HRI and Cities Service Research and Development Company 2,3,4,5 have reviewed the H-Oil process with respect to its principal characteristics and commercial performance. The major difference between H-Oil and the other processes for production of low sulfur fuels is a novel reactor system in which the oil and hydrogen are passed upflow through the reactor at a velocity sufficient to maintain the catalyst in a suspended or ebullated state. This reactor system offers several advantages:-

1. It is isothermal,
2. It is not susceptible to pressure drop build up due to suspended materials contained in the feed,
3. Catalyst can be added and withdrawn during operation to maintain a constant level of catalyst activity.

### Reactor Staging

For practical purposes, the H-Oil reactor can be considered as a completely back mixed system. In such a reactor, the character of the reacting mixture is essentially identical to the material leaving the reactor. From the point of view of the desulfurization reaction then, as a consequence of the second order rate equation,

$$r = kc^2$$

the reaction rate will be proportional to the square of the concentration of the effluent. As the process is required to produce a lower sulfur content product then, the reaction rate will decrease rapidly. As noted earlier the rate at 0.3% sulfur will be only one tenth that at 1% sulfur. In theory then a single reactor to produce a 0.3% sulfur product would be well over ten times as large as one producing a 1% sulfur product - all other factors being equal.

In the H-Oil process this problem is solved by staging the reactor system by using two or more reactors in series. In this way the reaction is carried out at several decreasing sulfur contents. This provides for higher reaction rates in those reactors in which the bulk of the desulfurization is occurring.

Figure 4 illustrates this effect for the processing of Kuwait atmospheric bottoms at various sulfur contents. Relationships are shown for the desulfurization efficiency of one, two and three stages in series versus a theoretical plug flow reactor.

#### Catalyst Counterflow

A further area of design optimization relates to the catalyst aging effects discussed earlier. If we use three H-Oil stages in series in order to achieve a very high degree of desulfurization, then there is a distinct advantage in charging all of the makeup catalyst to the third reactor stage. This material would then be withdrawn, charged to the second stage and in like fashion the second stage catalyst would be then charged to the first reactor. We thereby achieve a counter-current flow of oil and catalyst, in which the freshest catalyst is exposed to the cleanest oil in the reactor which requires a high degree of catalyst activity in view of the low sulfur concentration present. At the same time, the faster reactions take place in a reactor in which the catalyst has reached its final equilibrium level prior to being discarded. The line for the back staging of catalyst in a three stage system, shown in Figure 4, indicates that by this approach virtual equivalence is attained between the H-Oil system and a theoretical plus flow reactor.

#### Split H<sub>2</sub> Recycle

A process flow scheme using the backflow catalyst/three stage system is shown in Figure 5. This is basically the reactor scheme which would be utilized within an H-Oil unit designed to achieve very low sulfur contents. A further aspect of this system, shown in Figure 5, is the use of a split recycle system. In this way H<sub>2</sub>S free hydrogen would be sent to the third reactor thereby maintaining an extremely low H<sub>2</sub>S partial pressure at this critical point in the reactor system.

#### Residue Demetallization

One of the most difficult problems associated with design of a facility to process a broad range of feedstocks has been the problem of handling those residues having a high concentration of organo-metallic compounds. Figure 2, shown earlier, illustrates the rate at which H-Oil catalyst deactivates while processing a medium Venezuelan residual oil. Operation with this feed to produce a low sulfur fuel would require a very high rate of catalyst addition.

A joint HRI/CSRD research program has been underway for more than three years at the HRI laboratories to develop a demetallization procedure which would reduce the nickel and vanadium contents of fuel oils in order to produce an oil for further processing by H-Oil at low catalyst addition rates. These research efforts have resulted in the development of solid adsorbent materials which are low in cost, and effectively remove the bulk of the organo-metallic compounds present in such oils. These solids are used in an H-Oil reactor with the conventional ebullated bed principle, which is then followed by one or more H-Oil stages using conventional catalysts.

Figure 6 shows the effect of using this newly developed procedure in the processing of Venezuelan oil. The upper curve in Figure 6 shows the desulfurization of a medium Venezuelan residual oil as a function of catalyst age. The lower curve represents the performance of the same oil, over the same catalyst, after it has been processed through the newly developed demetallization procedure. The advantage of such operation are obvious, and this procedure makes practical the processing of these oils at low rates of catalyst usage. This procedure removes the limits previously placed on residue processing by metals content and all of the presently produced crudes can be considered for the production of low sulfur fuels.

#### New Catalyst Developments

In addition to the processing approaches discussed above, HRI and CSRD, together with several catalyst suppliers have engaged in continuing development activities relating to the development of improved H-Oil catalysts. These studies have covered catalyst composition, pore size distribution, catalyst size, etc. Figure 7 illustrates one of the more promising newer catalysts compared with the H-Oil catalyst which has been used in most commercial operations to date.

#### CHARACTERISTICS OF A MULTI-PURPOSE DESULFURIZATION PLANT

We have noted earlier that a refiner or fuel processor must live in an uncertain environment. He is subject to the vagaries of the supply of crude, the requirements of the market, and the perpetual question of the future markets for residual fuel. We have developed a processing approach - using the H-Oil process which provides the degree of flexibility necessary to cope with this uncertain environment. A schematic flow diagram of such a multi-purpose plant is shown in Figure 8. The basic features of this plant, which has been designed for the production of 0.3% sulfur fuel oil from various atmospheric residues, are its flexibility with respect to feedstock, product specifications and future alternate uses of the plant.

The data developed in this illustration have been based on the use of conventional H-Oil catalyst. If one of the newer catalysts, referred to earlier, were used, the same results would be achieved at somewhat lower investment and at substantially reduced rates of catalyst usage.

#### Base Operation

The feedstock flexibility of the plant is illustrated by the data in Table 1. Using the identical plant, we show the ability of this facility to process Venezuelan, Kuwait and West Texas atmospheric residues as well as West Texas vacuum residue to produce 0.3% sulfur fuel oil product. The capacity of the plant varies with each of these stocks because of the varying sulfur contents and difficulty of processing of the various raw materials. The refiner with such a unit should be able to change his source of supply amongst most of the commercially important crude sources, thereby optimizing his operation with respect to raw material supply.

When changing crude type certain operational changes would be required. For example, the optimum catalyst will vary with different crudes, and in the case of high metals stocks such as Venezuelan, the first reactor would be used for the demetallization procedure. These changes, however, would not require extensive shut down and apart from the change of catalyst type, the rest of the processing facility is completely adequate for all of the services.

### Flexibility with Respect to Product Specifications

Again, considering the same processing facility, if it were desired for market reasons to produce a product of higher sulfur content or a variety of grades of products this could be readily accomplished. In such a case plant throughput would increase since hydrogen consumption per barrel of feed would be less.

Should it be necessary at some future date to produce fuel oils having sulfur contents lower than 0.3%, in the same facility, this can be achieved either by reducing flow rate through the plant or by separating some of the desulfurized vacuum residue for sales as bunkers, thereby decreasing the sulfur content of the lighter product.

### Future Applications

If, in the course of time, nuclear power becomes more prevalent, or if stack gas desulfurization processes are brought to a point of economic application, the market for low sulfur fuel oil may contract and the price decrease. Under either of these circumstances we would revert to the classic U.S. position in which high sulfur vacuum residue is a marginal product and a candidate for conversion to lighter materials.

The type of unit described here can, if desired with this future use in mind, be used to convert vacuum residues to lighter materials or to prepare feedstock for low sulfur coke production. These applications of the process have been discussed in several previous papers. A good commercial example of this flexibility is shown in Table 2. These data, taken from a previous Cities Service publication, show operations of the Lake Charles H-Oil unit when processing for conversion and for desulfurization.

### Fuel Oil Processing Costs

Figure 8 is a block flow diagram of the plant under consideration. Included are a hydrogen plant and a sulfur plant, as well as the H-Oil processing facility. The hydrogen plant is supplied with its fuel and raw material from the light products produced within the H-Oil system and therefore the entire complex requires no hydrocarbon raw material other than the fuel oil feed. This is therefore a completely self-contained facility - not dependent on the availability of natural gas or other hydrogen raw material.

Investment and operating requirements for the complex are presented in Table 3, and in Table 4 these factors have been converted into a daily processing cost exclusive of H-Oil catalyst. This latter item is specific to the feed in question.

Unit processing costs are summarized for the various feedstocks in Table 5 which then shows the relationship between feed type and processing costs as well as the effect of product sulfur content on processing cost.

### FUELS REFINERY

The processing scheme just discussed uses atmospheric and vacuum residues as its raw material. Recently, consideration has been given to a fuels refinery concept in which whole crude oil is processed to yield only utility fuels. The processing sequence discussed in this paper would fit quite well into such a processing sequence. A block flow diagram of fuels refinery is shown in Figure 9.

Such a complex would produce low sulfur content fuel oil, turbine fuel, and naphtha. The naphtha product could be a raw material for the production of either SNG or petrochemicals.

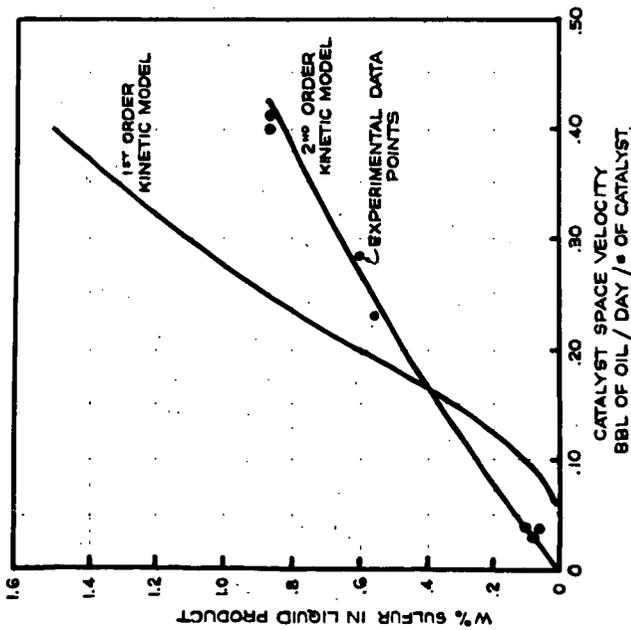
In summary, new developments in the H-Oil process have made it possible and practical to design a fuel processing plant which would have the degree of flexibility necessary to handle raw crudes from various sources and to enable the processor to meet the varying requirements of the markets which may be imposed on him with changing product specifications and product requirement.

#### ACKNOWLEDGMENT

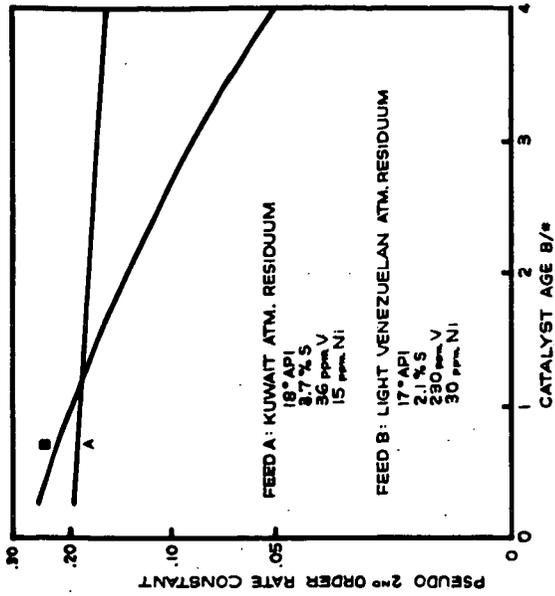
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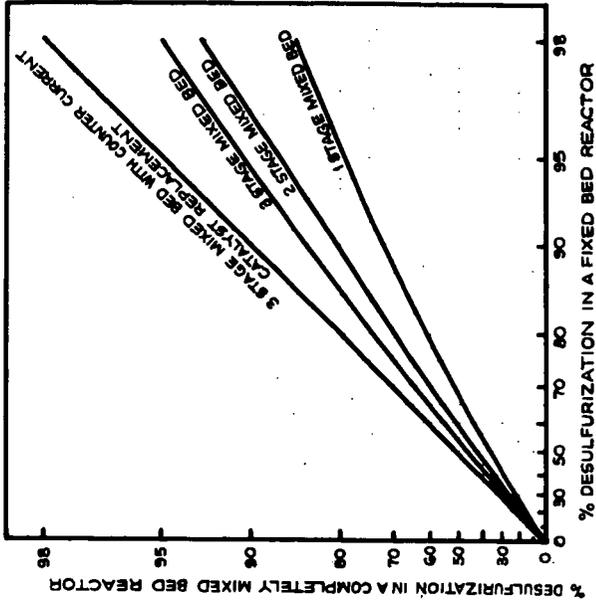
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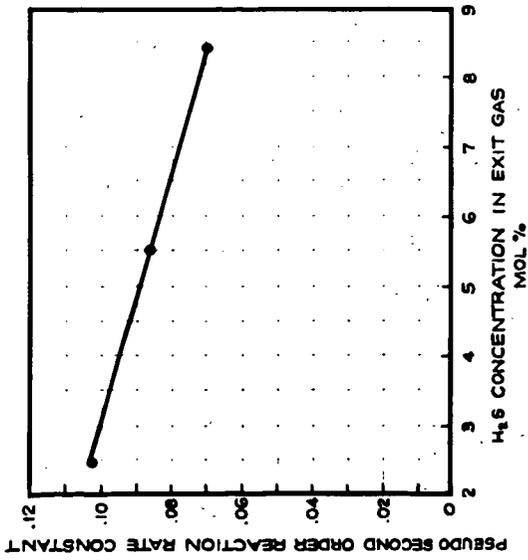
**FIGURE 1**  
**COMPARISON OF KINETIC MODELS**  
**WITH EXPERIMENTAL DATA**  
**KUWAIT ATMOSPHERIC RESIDUE**



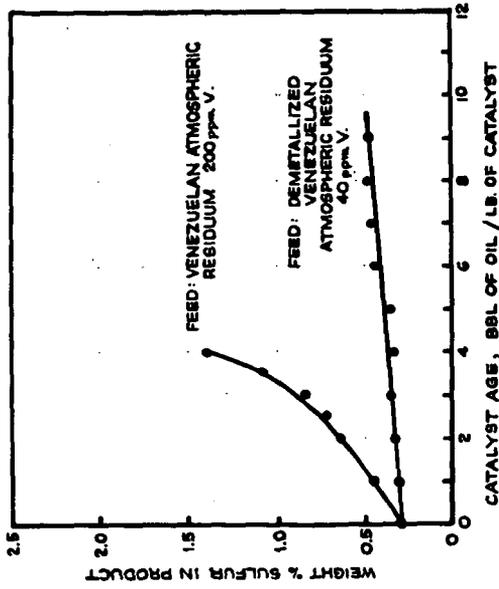
**FIGURE 2**  
**VARIATION OF RATE CONSTANT**  
**WITH CATALYST AGE**



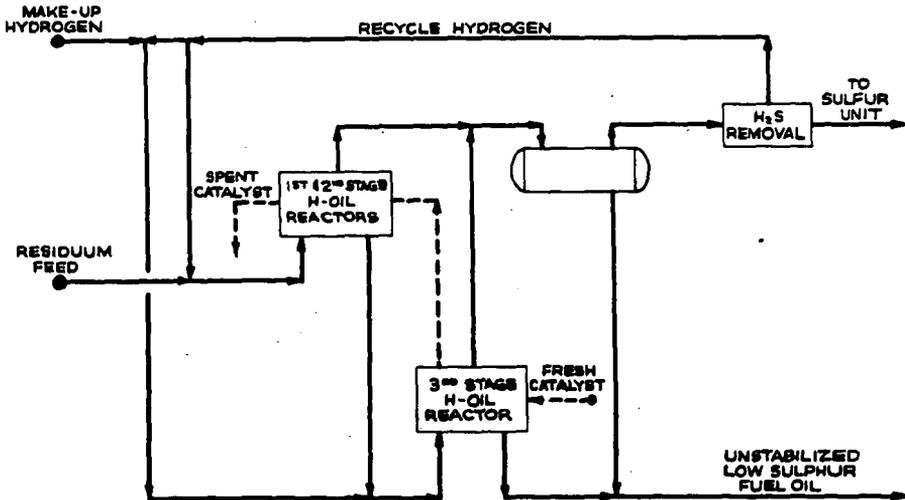
**FIGURE 4**  
**EFFECT OF STAGING ON REACTION**  
**EFFICIENCY OF A COMPLETELY**  
**MIXED BED VERSUS FIXED BED REACTORS**



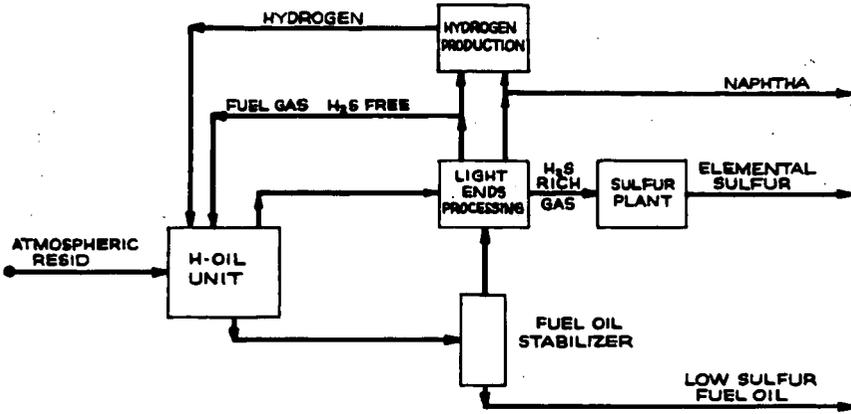
**FIGURE 3**  
**EFFECT OF H<sub>2</sub>S ON**  
**REACTION RATE CONSTANT**  
**KUWAIT FEED**



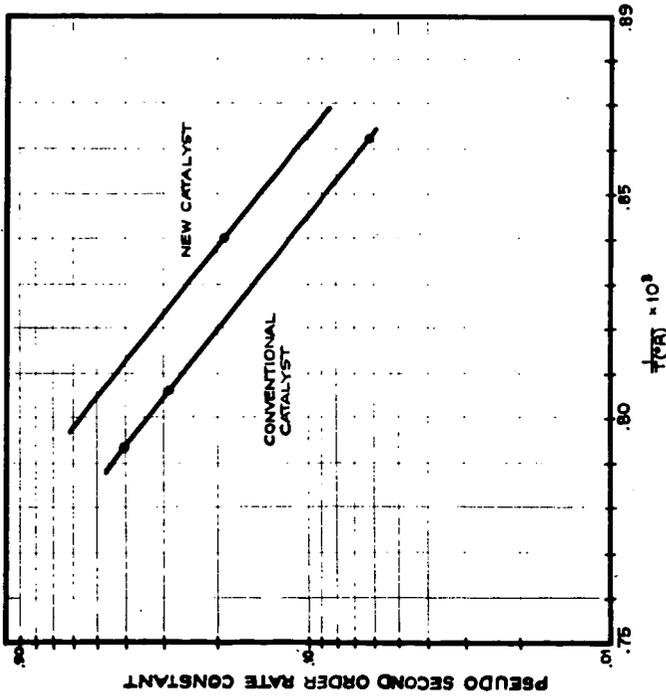
**FIGURE 6**  
**COMPARISON OF CATALYST DEACTIVATION**  
**WHEN DESULFURIZING VIRGIN AND**  
**DEMETHYLIZED VENEZUELAN**  
**ATMOSPHERIC RESIDUA**



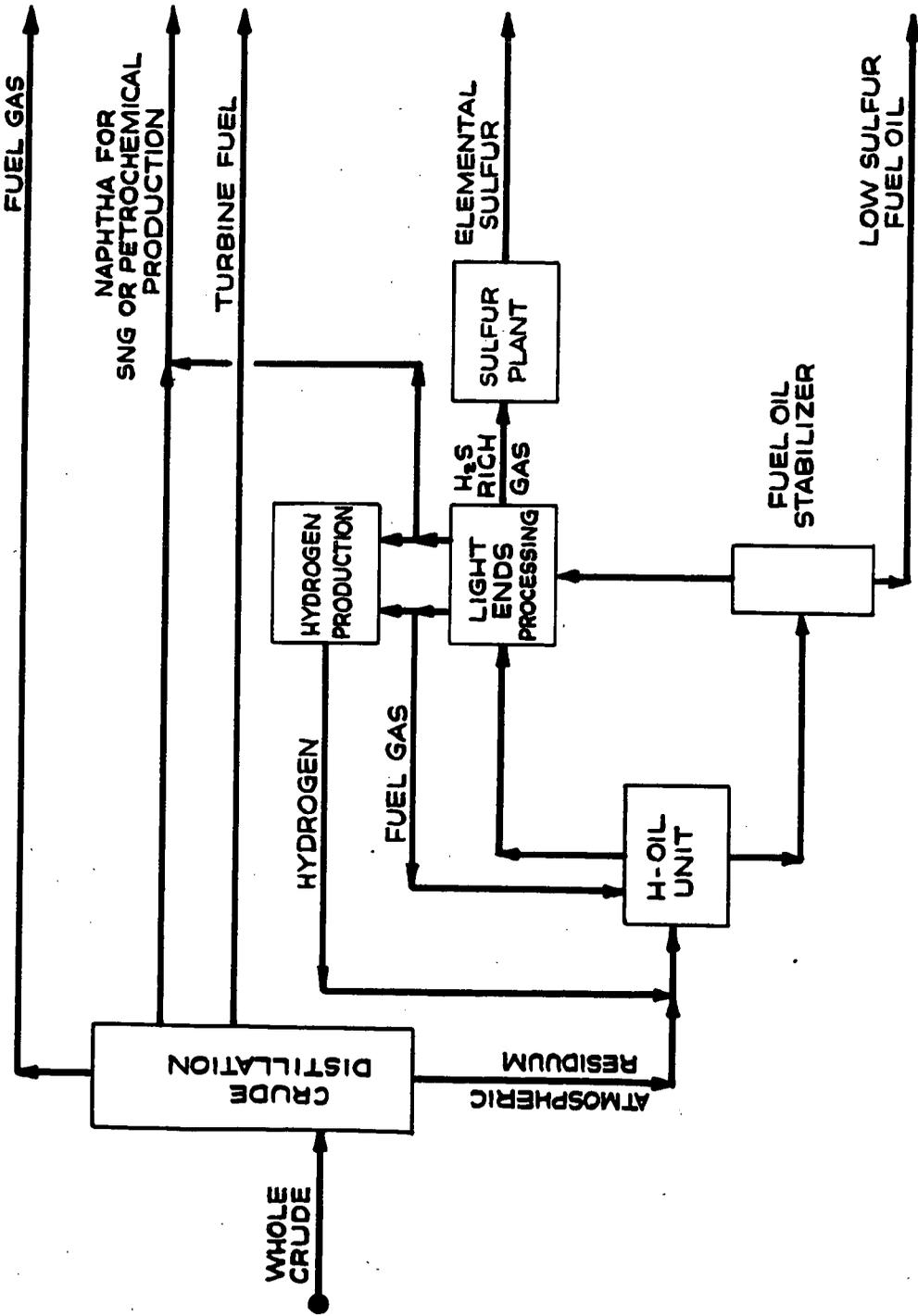
**FIGURE 5**  
**THREE STAGE H-OIL SYSTEM**  
**WITH CATALYST BACKFLOW**



**FIGURE 8**  
**BLOCK FLOW DIAGRAM**  
**MULTI-PURPOSE DESULFURIZATION PLANT**



**FIGURE 7**  
**COMPARISON OF NEW AND**  
**CONVENTIONAL**  
**H-OIL CATALYSTS**  
**KUWAIT FEED**



**FIGURE 9  
FUELS REFINERY**

TABLE 1

## H-OIL PLANT PERFORMANCE

## MANUFACTURE OF 0.3% S FUEL OIL FROM VARIOUS FEEDS

Feedstock	Kuwait Atm.	Medium Venezuelan	West Texas	West Texas
	Resid.	Atm. Resid.	Atm. Resid.	Vac. Resid.
Gravity, °API	17.0	17.2	17.7	10.5
Feed Sulfur, Wt. %	3.8	2.2	2.2	3.2
Vol. % 9750F. +	40.0	45.0	41	80.0
Plant Throughput, BPSD	30,000	30,000	42,100	18,250
Total H <sub>2</sub> Consumption, MM SCFD	21.9	21.9	21.9	21.9
H-Oil Unit Yields				
H <sub>2</sub> S (Wt. %)	3.7	2.3	2.1	3.4
C <sub>1</sub> -C <sub>3</sub> (Wt. %)	1.6	2.3	0.8	2.8
C <sub>4</sub> -350°F. (Vol. %)	7.8	9.6	3.9	11.5
350°F. + Fuel Oil (Vol. %)	95.0	94.0	98.7	94.9
Fuel Oil Sulfur, Wt. %	0.3	0.3	0.3	0.3
Catalyst Replacement Cost, \$/B.	0.15	0.16	0.04	0.18

TABLE 2

COMMERCIAL H-OIL OPERATIONS  
Lake Charles, Louisiana

VARIOUS WEST TEXAS FRACTIONS

Feedstock	Sour Atm. Resid.	Vac. Resid.
°API	17.1	10.9
% S	2.80	1.95
% 975°F.+	47.0	82.0
Operation	Desulfurization	Conversion
Goal Achieved	100 Vol.% yield of stabilized 300°F.+ fuel oil of 0.28% S	49% conversion of 975°F.+ total product at 0.62% S

TABLE 3

## FUELS PROCESSING COMPLEX

## INVESTMENT AND OPERATING REQUIREMENTS

BASIS: Operations Described in Table 1

## Investments

H-Oil Unit	\$ 13,400,000
Light Ends & Gas Processing	1,300,000
Hydrogen & Sulfur Plants	7,100,000
Offsites	5,500,000
Total Investment	\$ 27,300,000

## Operating Requirements

Fuel, MM BTU/Hr.	(1)
Power, KW	12,700
Steam, Lb/Hr. (2)	65,000
Cooling Water, GPM	4,750
Boiler Feed Water, GPM	135

Catalyst &amp; Chemicals (other than H-Oil), \$/D 225

Labor, Men/Shift 6

(1) Supplied from H-Oil Gases and Light Ends

(2) Net External Steam Requirement

TABLE 4

## FUELS PROCESSING COMPLEX

DAILY PROCESSING COSTS  
(Basis: 330 Days)

	<u>\$/SD</u>
Investment Related Costs @ 20% of Total Capital	16,600
Labor Related Items	1,440
Utilities <sup>(1)</sup>	3,550
Catalyst & Chemicals (Ex H-Oil)	<u>225</u>
Total Processing Cost	21,815

## (1) Utility Unit Costs:

Power	0.8¢/kwh
Steam	70¢/1000 lbs.
Cooling Water	0.3¢/1000 gal.
BFW	3.0¢/1000 gal.

Hydrogen Plant Feed and Fuel for the complex supplied from H-Oil gases, light ends and 150 BPSD of product fuel oil.

TABLE 5

## FEEDSTOCK PROCESSING COST

Feedstock	Charge (BPSD)	Fuel Oil* Product (BPSD)	Operating Cost (Ex. H-Oil-Cat) ¢/B feed	H-Oil Catalyst Replacement Cost ¢/B feed	Total Processing Cost ¢/B feed
Kuwait Atm Resid.	30,000	28,350	73	15	88
Lt. Venezuelan Atm. Resid.	30,000	28,050	73	16	89
West Texas Atm. Resid.	42,100	41,400	52	4	56
West Texas Vac. Resid.	18,250	17,165	\$ 1.20	18	\$ 1.38

\*after plant fuel consumption