DESULFURIZATION OF RESIDS

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INTRODUCTION

For the past several years there has been an increasing incentive to develop suitable technology for removing sulfur from petroleum residua(1,2,3,4,5). New York City now specifies a 1.0% maximum allowable sulfur concentration for its fuels(6), and similar restrictions have been, or soon will be, adopted in other metropolitan areas. However, typical sulfur concentrations in the resids from several important crude sources are:

	Characteristics of Resids		
Crude Source	Type	Vol% on Crude	Wt% Sulfur
Domestic	Vacuum	0 - 20	1.0 - 4.0
Caribbean	Atmospheric	56	2.6
Middle East	Atmospheric	50	2.5 - 5.0

Consequently, the need for desulfurized fuels is expected to increase rapidly in the near future.

Anticipating this need, American Oil Company has developed a fixed-bed catalytic hydrodesulfurization process that is now ready for commercialization. Among its unique features is a stable catalyst that resists poisoning by sulfur, nitrogen, metals, coke-forming materials, and other troublesome constituents of resids.

The process was developed in various bench-scale units, and then commercial feasibility was demonstrated in a fully integrated pilot plant having a maximum feed rate of 2 B/SD. Whenever possible, experimental runs were designed to simulate all operations required in a full-scale unit. As a result, the evaluations cover the effects of anticipated variations in catalyst performance and life, types of feedstocks, and desired desulfurization levels. Work has also been started on a process model for the prediction of plant size and process conditions for the most economical desulfurization of any given feed.

EXPERIMENTAL

Equipment

Figure 1 typifies the bench-scale units. The smaller ones have reactors varying in capacity from 20 to 250 cc of catalyst with allowable pressures up to 3500 psig. Operations were based on once-through gas and oil flow, batch-type product accumulation, and continuous gas release. Larger units capable of containing 1000 cc of catalyst and having gas scrubbing and recycle systems were also used.

The 2-B/SD pilot plant is shown schematically in Figure 2. The reactor section, which is 30 feet long and has an internal diameter of 2 inches, allows mass velocities about 50% as high as those anticipated for commercial design. Operation is adiabatic. Several separately controlled gas quenches are located along the reactor wall for the automatic injection of cooling gas to compensate

for the temperature rise in individual catalyst beds. A traveling thermocouple passes axially through the reactor to measure the complete temperature profile within the beds. A typical profile is shown in Figure 3.

The pilot plant also includes separators and fractionating towers. The only inputs are raw residual oil, hydrogen, and water for cooling and gas-scrubbing. Outputs are a desulfurized and stabilized residual oil, a naphtha fraction, and a gas stream which is continuously monitored by gas chromatography. In addition, the plant contains its own gas recycle and scrubbing facilities and is typically operated on pressure control. Only enough fresh hydrogen is added to compensate for hydrogen consumption and solubility losses.

Feedstocks

Table I lists the properties of typical resids and crudes used in the process evaluations. They cover a wide range of processing difficulty. The atmospheric resids from the Middle East are examples. Those designated B (Kuwait) and C are comparatively high-gravity, low-viscosity materials that are relatively easy to process. At the other extreme, Resid A is highly viscous, contains 5.2 wt% sulfur and 18-20 wt% asphaltenes (heptane insolubles), and has a 9.5°API gravity.

CATALYST EVALUATIONS

Over 140 possible catalysts were evaluated for the process. Criteria included:

1. low cost
2. high initial activity for removing sulfur
3. good activity maintenance
4. ability to resist poisoning by sulfur, nitrogen, metals, and other harmful constituents of petroleum resids.

The catalyst selected appears to have an optimum combination of the above attributes.

The deposition of metallic contaminants, especially vanadium and nickel, within the catalyst structure can be an especially severe problem in desulfurization processes. Hence, particle size is important; the most satisfactory catalysts have a high ratio of external surface area to total volume within the limitations of pressure drop considerations.

During some evaluation runs, the accumulation of vanadium and nickel in used catalyst particles was great enough to almost double the original weight of the fresh catalyst. However, the higher concentration of metals was always found near the outer surface, and considerable internal volume of the catalyst particle still had only a small concentration of metals. The distribution of metals longitudinally through the catalyst bed also showed a distinct pattern. Catalyst particles removed from the lower zone always contained considerably less vanadium and nickel than those taken from the top zone adjacent to the feed entrance.

Coke formation was never a problem when proper temperature profiles and hydrogen partial pressure were maintained in the reactor system. In

contrast to the deposition pattern of metals, carbon was fairly evenly distributed throughout the catalyst particle.

PROCESS PARAMETERS

Production of a material containing only 1 wt% sulfur from any given feedstock was the criterion for success in the application of the process. However, the feedstock itself strongly influences the process severity required to reach a given level of desulfurization.

With suitable variations in process conditions, all the feedstocks in Table I were desulfurized to the desired level. Table II shows typical data for Resids A and C, where the yields correspond to the production of a 1 wt% sulfur, 350+°F resid. There is very little conversion to materials that must be removed to permit the product to meet flash specifications for a residual fuel. As a result, hydrogen consumption is also low (shown as a negative yield in the table). For both resids, gravity increased, viscosity decreased, and sulfur, nitrogen, and metals contents were all reduced. In addition, carbon residue decreased by about 50%.

Effect of Reactor Volume on Desulfurization Level

Figure 4 shows the effect of reactor volume on the sulfur content of resids A and B at constant pressure, temperature, and catalyst activity. The relative reactor volume is, of course, proportional to the reciprocal of space velocity in volumes of oil per hour per volume of catalyst. Sulfur content of the product is intentionally plotted on a logarithmic scale to show that resid desulfurization deviates sharply from first-order kinetics, which would result in a straight line on such a plot.

A comparison of the points at which the curves pass through the 1 wt% sulfur level (dashed line) indicates that Resid A requires a reactor almost three times as large as the one required by Resid B to reach the 1 wt% sulfur level. Similar curves for various feedstocks can be developed and related qualitatively to the physical and chemical properties of individual resids.

Although such curves can be fitted by pseudo second-order kinetics, this approach is not considered appropriate because desulfurization of lighter individual molecules has been shown to be first order(7). Therefore, Figure 4 probably reflects a series of first-order desulfurization reactions with rate constants that depend on the chemical structure in which the sulfur atoms reside. This, in effect, explains the bending over or flattening of the curve as the sulfur level is reduced and more-difficult-to-remove sulfur atoms are encountered.

Effect of Desulfurization on Product Properties

As shown in Table II, hydrodesulfurization profoundly affects the viscosity of a residual fuel. Although only a small amount of atmospheric resid is converted to lower-boiling materials during desulfurization, the viscosity of the desulfurized resid is more readily correlated with the conversion to a particular boiling-range material than with the sulfur level of the product. This effect is illustrated in Figure 5 which shows the product viscosities of several typical desulfurized resids as functions of the amount of 650+°F resid converted to material boiling below 650°F. In some cases, such as Resids B, C, and D, it was possible to produce a low-sulfur material meeting No. 6 oil viscosity specifications. In other cases, such as Resids A and G, over-conversion of the resids would be required to meet specifications. This, of course, would

TABLE II

DESULFURIZATION DATA FOR RESIDS A AND C

	Properties of Feed and Product			
	Resid C		Resid A	
	Feed	Total Liquid Product	Feed	Total Liquid Product
Gravity, °API	17.2	23.7	9.5	19.5
Sulfur, Wt%	4.3	1.0	5.2	1.0
Nitrogen, ppm	1600	1300	4100	2600
Ramsbottom Carbon, Wt%	8	4	17	8
Pour Point, °F	65	55	85	20
Viscosity, SSF at 122°F	101	60	14000	90
Metals, ppm				
Nickel	9	4	58	22
Vanadium	32	9	167	50

	Desulfurization Yields					
	Resid C			Resid A		
	Wt%	Vol%	Sulfur, Wt%	Wt%	Vol%	Sulfur, Wt%
H_2	-0.8	--	--	-1.2	--	--
$H_2S + NH_3$	3.6	--	--	4.8	--	--
C_1-C_4	0.8	--	--	1.2	--	--
C_5-350°F	1.7	2.1	0.05	1.0	1.3	0.01
350+°F	94.7	98.5	1.0	94.2	101.3	1.0
	100.0	100.6		100.0	102.6	

Hydrogen Consumption = 480 SCFB

Hydrogen Consumption = 760 SCFB

result in too high a hydrogen consumption and thus a higher processing cost. In these cases, dilution with cutter stock is usually a better way to meet viscosity specifications.

Metals removal is not particularly significant in the production of a residual fuel. However, it is important with respect to overall economics because deposited metals ultimately limit the useful life of the catalyst. Figure 6 shows the relationship between demetalation and desulfurization for several feedstocks. Although there is a distinct relationship for each feed, the overall pattern suggests that a generalized correlation is possible.

SUSTAINED OPERATION

The commercial feasibility of the resid desulfurization process depends principally on how well the catalyst performs in sustained operations over significant periods of time. Figure 7 shows the 350+°F product sulfur content plotted as a function of time-on-oil for the desulfurization of Resid C in a continuous operation in bench-scale equipment. Conditions were selected to yield a 350+°F product containing less that 1 wt% sulfur. Over a 60-day period, no problems were encountered in maintaining this sulfur level.

Figure 8 shows the results of a considerably more difficult continuous operation in which Resid A was desulfurized in the 2 B/SD integrated pilot plant. Over a period of about three months, the 350+°F product showed a level of no more than 1 to 1.2 wt% sulfur. Following this operation, samples of catalyst were removed from the reactor and used in subsequent bench-scale studies of catalyst life with a variety of resid feedstocks. Thus, total on-oil time for this catalyst was extended to over seven months.

Ultimately, sustained operation depends on how catalyst activity is affected by both the metals content of the feedstock and the severity of operation required to reach a particular sulfur level. As a result, general numbers for catalyst life cannot be quoted. However, the results in Figures 7 and 8 indicate that catalyst life will be in excess of one year for the desulfurization of a material like Resid C to the 1 wt% sulfur level, and at least six to eight months for a material like Resid A.

PROCESS MODEL

Work is now under way to develop a process model for predicting process requirements for the desulfurization of any given feed. The approach centers in first separating petroleum resids into oils, resins, and asphaltenes--the three fractions common to all resids. Next, reaction rates are determined for each fraction from various resids. Finally, a generalized process model is constructed on the basis of these rates.

Reaction rates for the same fractions from a variety of resids are proving to be remarkably similar. Typical curves of product composition versus overall conversion of the resid are given in Figure 9. These curves illustrate the behavior of the three fractions as well as the 650-1000°F gas oil during the hydroprocessing of Resid C. The resins, which are highly aromatic and contain significant quantities of sulfur, readily disappear; however, the oils, which are more paraffinic and contain less sulfur, disappear at a significantly lower rate. The curve for asphaltenes is similar to that for resins but has a flatter slope, indicating that asphaltenes are significantly less reactive. The curves being developed for other feedstocks will be incorporated in the process model for resid desulfurization.

ECONOMICS

The hydrodesulfurization process is still relatively expensive by petroleum processing standards. The capital investment for large reactors which operate at high pressures and high temperatures, the consumption of hydrogen during the processing, and the use of large volumes of a catalyst with a relatively short life all contribute to the costs. Moreover, processing costs also depend on the feedstock. As an example, Table III shows the difference in costs for desulfurizing Resid B and the more difficult-to-process Resid A to the same 1 wt% sulfur level. The comparison is based on Gulf Coast installation costs and fuel at 4¢ per FOE gallon, power at $0.004 per KWH, and steam at $0.45 per 1000 lb. These data show conclusively that even with feeds of similar sulfur contents which are desulfurized to similar levels, significant differences in processing costs exist. Capital charges and catalyst costs vary with the reactor size required. Utilities costs depend on hydrogen consumption and would be subject to further variability if a different fuel value were used. Consequently, specific cost estimates must be based on a specific feed, a specific desulfurization level, a specific place of investment, and a specific fuel value.

CONCLUSION

A process for the removal of sulfur from a wide variety of resid-containing materials has been developed. Sustained operation has been successfully demonstrated in pilot scale equipment using a proprietary catalyst. A process model which will allow the prediction of process performance for any feedstock under any set of processing conditions is now being developed. Where direct resid desulfurization is attractive for sulfur emissions control, use of this process and attendant model will allow design and operation of commercial units.

TABLE III

COMPARISON OF DESULFURIZATION COSTS
FOR 50,000 B/SD OF RESIDS A AND B

Basis: 1 Wt% sulfur in the 350+°F product

	Economics Costs for Resid A minus B
Costs, ¢/B of resid	
Utilities	3.7
Catalyst and Chemicals	4.3
All other direct and overhead	4.5
Capital charge	12.4
Total	24.9
Sulfur Credit	-3.2
Vanadium Credit	-1.4
Difference in upgrading costs, ¢/B of resid	20.3

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FIGURE 1

BENCH-SCALE UNITS FOR RESID DESULFURIZATION

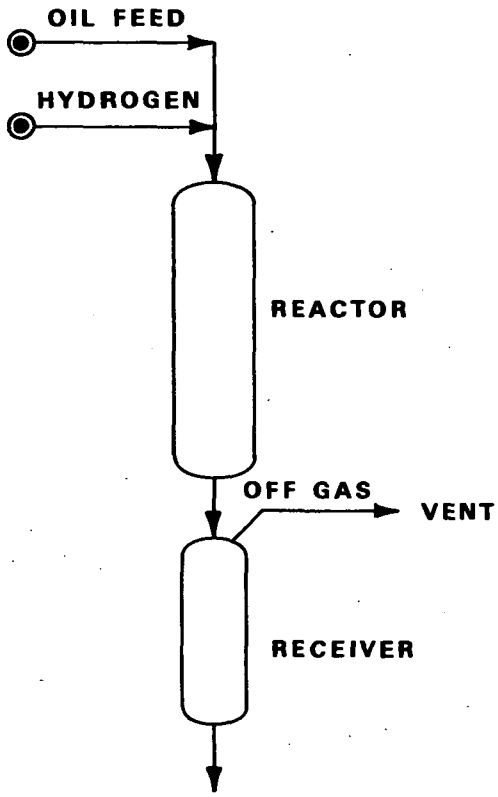


FIGURE 2

2 B/SD PILOT PLANT FOR RESID DESULFURIZATION

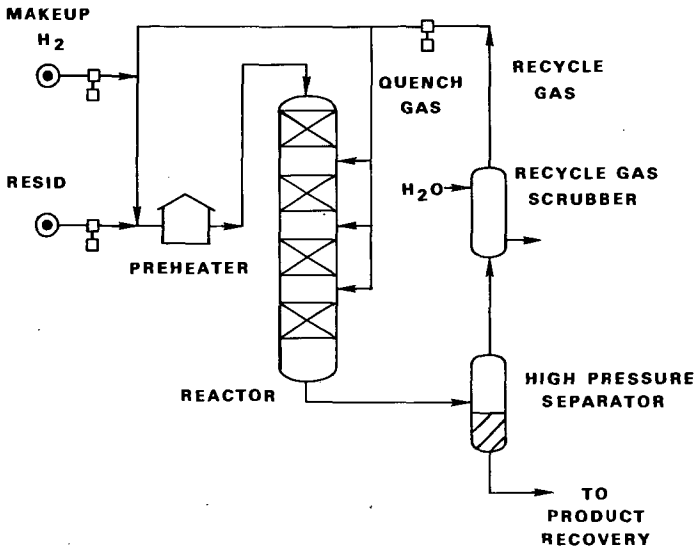


FIGURE 3

TYPICAL TEMPERATURE PROFILE IN 2 B/SD PILOT PLANT

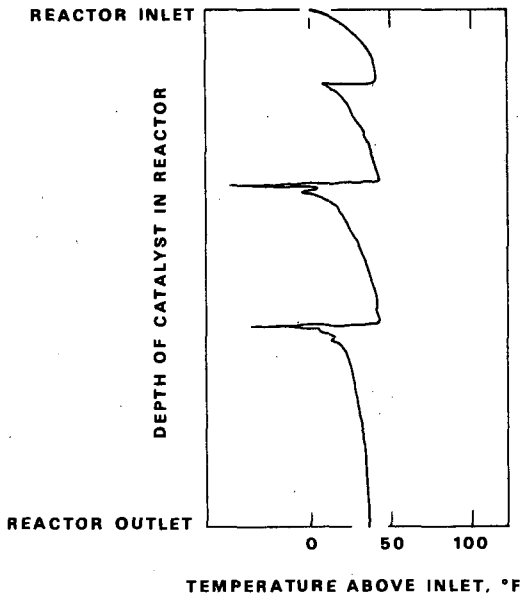


FIGURE 4

EFFECT OF REACTOR SIZE ON DESULFURIZATION LEVEL OF RESIDS A AND B

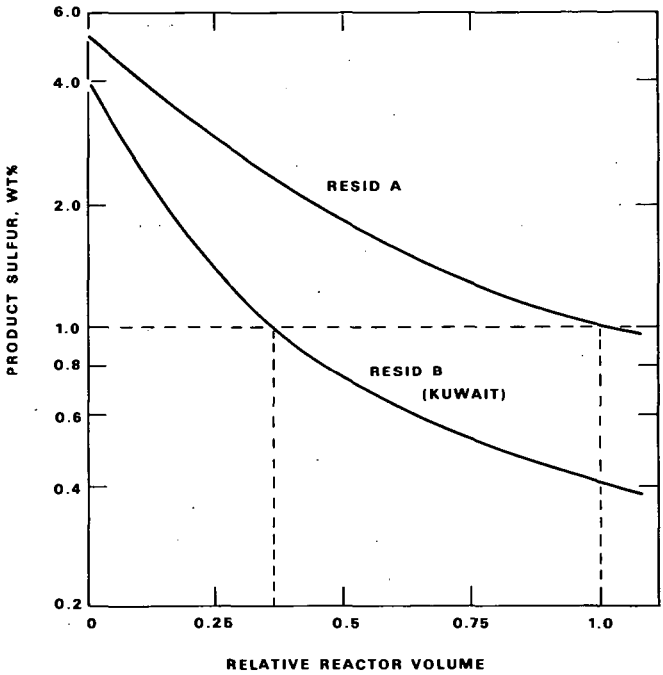


FIGURE 5

EFFECT OF PROCESS SEVERITY ON 350+°F PRODUCT VISCOSITY OF VARIOUS RESIDS

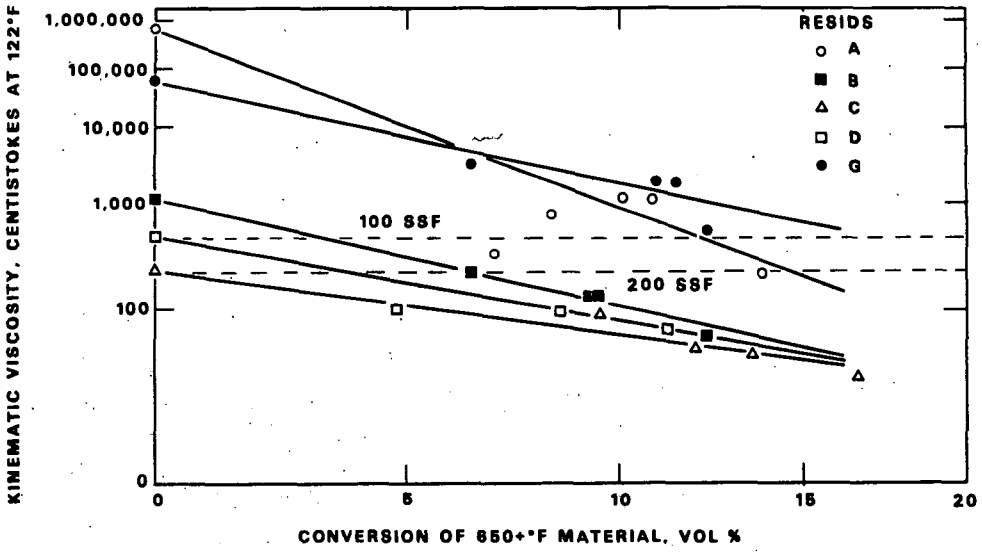


FIGURE 6

RELATIONSHIP BETWEEN DEMETALATION AND DESULFURIZATION OF VARIOUS RESIDS

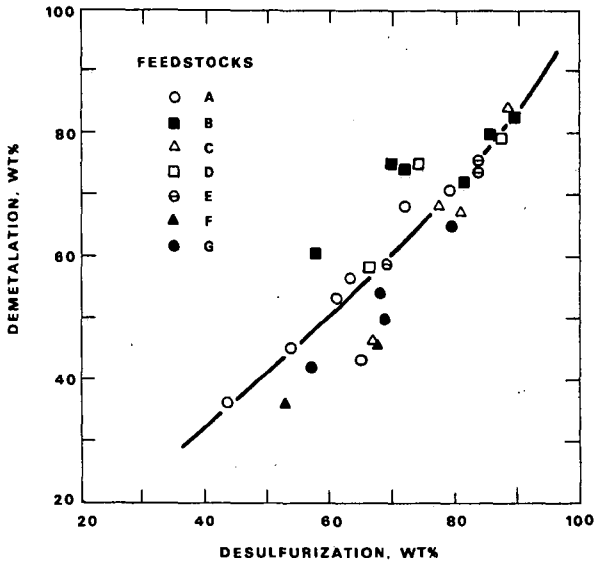


FIGURE 7

CONTINUOUS DESULFURIZATION OF RESID C IN A BENCH-SCALE UNIT

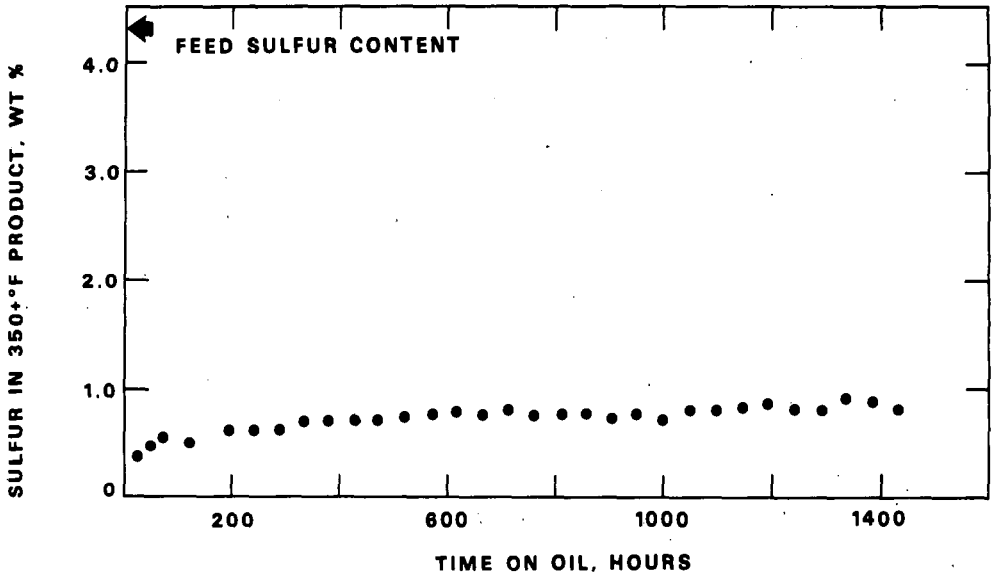


FIGURE 8

CONTINUOUS DESULFURIZATION OF RESID A IN THE 2 B/SD PILOT PLANT

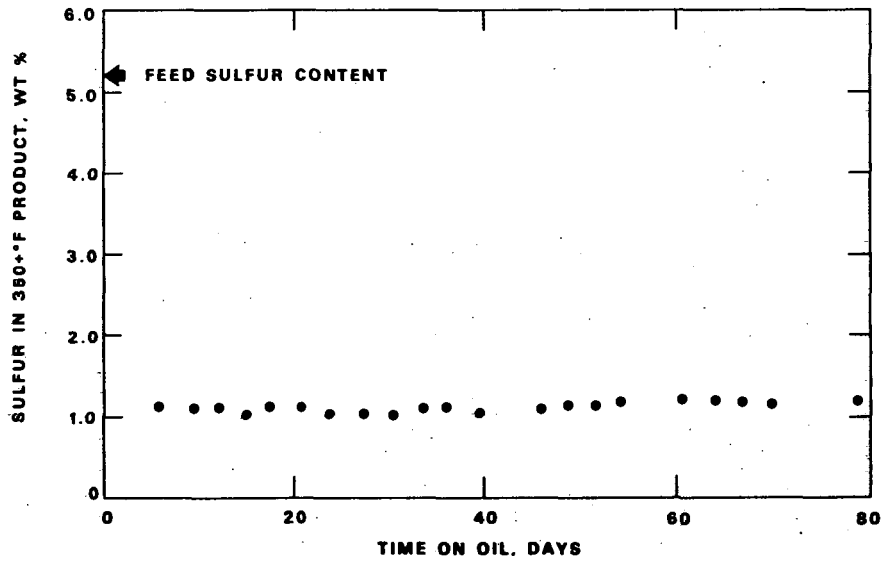
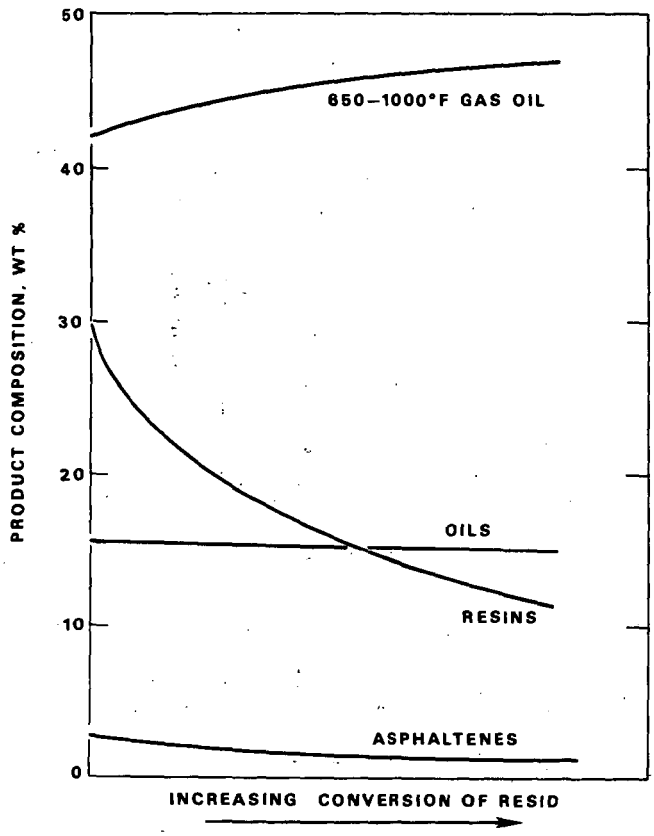


FIGURE 9

HYDROPROCESSING OF RESID C