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UPGRADING OF COAL LIQUIDS

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UPGRADING DISTILLATES FROM COAL LIQUEFACTION

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ABSTRACT

Distillates from DOE sponsored coal liquefaction products have been examined as potential feedstocks for commercial petroleum refining processes. The ultimate objective is to provide a new source of transportation fuels and environmentally acceptable fuel oils.

Coal-derived naphthas from the H-Coal and Exxon Donor Solvent (EDS) and SRC-II processes have been hydrotreated and reformed in research pilot plants to 100 Research Octane Number (RON) gasoline. Conditions for hydrotreating were relatively severe compared to those required to treat a Middle East naphtha. Reforming proceeded at relatively mild conditions. Hydrogen yield was greatly in excess of the amount required for hydrotreating.

The $400°F^+$ distillates from the H-Coal and EDS processes have been converted in research pilot plants by hydrotreating, hydrocracking and fluid catalytic cracking (FCC). In general, hydrotreatment is required prior to either hydrocracking or FCC to reduce excessive amounts of nitrogen and to enhance processability.

Hydrotreating alone gave high yields of environmentally acceptable No. 2 fuel oil. Hydrocracking to gasoline proceeded at operating conditions somewhat more severe than required for a Middle East gas oil. Hydrogen consumption was high. However, a portion of the hydrogen can be recovered by reforming the hydrocracked naphtha to 100 RON gasoline. Additional hydrogen can potentially be recouped by steam reforming light gases.

The hydrotreated distillates, including SRC-II distillates, responded to fluid catalytic cracking as well as petroleum derived stocks of comparable hydrogen content. FCC gasoline product octane numbers ranged from 92 to 99 RON.

1.0. INTRODUCTION

"Coal is the dirtiest of all fuels commercially burned," observes a boilermaker, who must design to contend with ash that slags in the furnace and fouls heat exchanger tubes. Coal is also chemically "dirty". Chemically combined sulfur, oxygen, nitrogen, and metals can wind up as air pollutants, catalyst poisons, and valve deposits.

Coal liquefaction, as a first step in coal clean-up, provides a route to separate the coal ash, either by filtration, solvent extraction, or distillation of the primary coal liquefaction product. However, it does an indifferent job on the chemical "dirt". The object of this contract is to upgrade the deashed coal liquids so that they will resemble the high quality petroleum derived fuels to which the U. S. public is accustomed.

The difficulty of the upgrading process depends on the route followed to separate the coal ash. If filtration or solvent extraction are used, the deashed coal liquid is a heavy, non-distillable residuum which can be difficult to process. A number of DOE sponsored products of this type were upgraded by UOP, Inc. on a research scale under a previous contract. If the coal ash is separated with the bottoms fraction of a vacuum distillation, the distillate taken overhead can be processed directly in conversion facilities found in many present day petroleum refineries. The current contract addresses the upgrading of these coal derived distillates.

The program, as originally drawn up in February of 1977, comprised four tasks: Task 1, two stage hydrocracking of coal derived distillates boiling in the gas oil range to maximum fuel oil and to maximum naphtha; Task 2, hydrotreating the distillates, followed by fluid catalytic cracking to gasoline and cycle oil; Task 3, hydrotreating and reforming coal derived naphthas, either primary naphthas, or hydrocrackates generated in Task 1, to make high octane gasoline; and Task 4, correlation of results with feedstock properties and process conditions. The distillates to be processed originally included naphthas and distillates from the H-Coal and Exxon Donor Solvent (EDS) processes. In October, 1978, naphtha and distillate from the SRC-II process were added as feedstocks for Tasks 2 and 3, but not Task 1.

In February, 1979, Task 4 was expanded to include economic studies on coal oils and petroleum blends. This topic is not covered in this Annual Report, which is the second published under the contract.

The first Annual Report (FE-2566-26, May, 1979) discussed principally results attained with H-Coal distillates. This report emphasizes comparison of results obtained with distillates from all three sources, H-Coal, EDS, and SRC-II. Tasks 1, 2 and 3 are each covered in a separate section. In addition, correlations of results with feedstock properties or process conditions have been developed, as required under Task 4, and are included as Appendix A. Detailed process data will be included only by reference to Intermediate Reports, of which eight have been published. Sample numbers and plant run numbers have been retained in this report to assist in referencing.

2.0. HYDROCRACKING COAL DERIVED DISTILLATES

Hydrocracking of petroleum stocks is characterized by flexibility to produce varying ratios of motor fuels and middle distillates from high boiling vacuum gas oil (VGO). Its companion process, hydrotreating, is mandatory for coal distillates to make acceptable fuels, or feedstocks for downstream processing. Addition of more hydrogen to hydrocrack the hydrotreated stock gives high volumetric yields of clean fuels. The cost of this incremental hydrogen, as well as that of additional high pressure reactors, is an important consideration in choosing this route from coal derived distillates to transportation fuels.

2.1. Conditions

Hydrocracking is commercially carried out at 343-482°C (650-900°F), 700-3000 psig, and 0.2-5.0 hr^{-1} liquid hourly space velocity (LHSV). In this report, as in the preceding interim reports, the conditions used are expressed relative to base conditions:

Temperature	T-T(base), °C
Pressure	P-P(base), psi
Space Velocity	LHSV/LHSV(base)
Combined Feed Ratio	CFR/CFR(base)

The base conditions selected for reference represent those employed commercially for hydrocracking a typical Arabian gas oil.

2.2. Catalysts

Hydrocracking catalysts comprise pelletized silica/alumina promoted with Group VI and Group VIII metals. Commercial UOP catalysts employed in this study include first stage hydrocracking catalysts (DCA, DCB), black oil conversion catalysts, and second stage hydrocracking catalysts (HCA).

2.3. Equipment and Procedures

UOP Research pilot plants with trickle bed reactors holding 50-800 ml of catalyst were employed. For hydrocracking coal distillates to produce maximum gasoline, the most successful arrangement was a three reactor, two stage system. The two stages were not integrated. The single first stage reactor (Figure 1) served for hydrotreating. Little or no naphtha was made under the relatively mild conditions used in this operation. The entire stripper bottoms was available as second stage feed.

Two reactors in series containing UOP-DCB and UOP-HCA catalysts were used for the second stage (Figure 2). The second reactor effluent was continuously fractionated and the 375°F+ bottoms were recycled to the first reactor. Temperature of the second reactor was adjusted to obtain complete conversion to gasoline at the combined feed ratio specified.

For hydrocracking coal distillates to produce maximum fuel oil, a single reactor second stage was employed and the cut point of the fractionator was raised to 600°F (Figure 3). Under the conditions used, 60-85 wt-% of the first stage product boiled below 600°F, in the fuel oil and gasoline ranges. Hence, the incremental yield of fuel oil from second stage hydrocracking of the 600°F+ first stage bottoms was not great.

2.4. Charge Stocks

Inspections of coal derived distillates received at UOP Inc. for this study are listed in Table 1. They include samples from the H-Coal, EDS and SRC-II processes. It may be debated whether these samples represent typical operations of the pilot plants from which they were generated; or how exactly they forecast the quality of products from commercial processes. However, these inspections amply define the chamistry of the distillates, and the scope of the upgrading problem.

The three distillates all have low end points compared to a petroleum vacuum gas oil (VGO). The H-Coal and EDS distillates boil 60 vol-% in the fuel oil range (e.g., 375-600°F), while the SRC-II sample contains 80% naphtha and fuel oil. This implies that for fuel oil production, relatively little cracking is needed.

The three distillates are all low in hydrogen compared to VGO, and high in aromatics and polar compounds. Heteroatoms, particularly nitrogen and oxygen, are very high. The H-Coal distillate has benefited from some catalytic hydrodesulfurization in the H-Coal liquefaction reactor. The distillates will require severe hydrotreatment to obtain clean fuels. This hydrotreatment will inevitably saturate some of the aromatic rings to naphthenes, and hydrogen consumption will be high.

Other contaminants, which affect the hydrotreating catalyst life, are the heptane insolubles and ash. The heptane insoluble content of the H-Coal distillate was an order of magnitude beyond the tolerance of a first stage hydrocracking catalyst. Rerunning the feedstock to 95% overhead reduced the heptane insolubles from 1.6% to 0.06%.

In the case of the EDS product, the heptane insolubles were almost two orders of magnitude too high. Rerunning to 87 vol-% overhead failed to reduce these heptane insolubles below 1.75%. Rather than distorting the nature of the feedstock by removing more bottoms, it was decided to process the EDS distillate as received, using UOP black oil conversion catalyst in the first stage. This catalyst is designed for conversion of heptane insolubles in petroleum, commonly called asphaltenes. It should be noted, however, that the heptane insolubles found in EDS distillate are not asphaltenes in the conventional sense, but comprise distillable polycyclic aromatic structures with up to four oxygen atoms per molecule. They may derive from weathering of coker distillate included in the sample furnished UOP Inc.

The SRC-II distillate was not scheduled for processing under Task 1, but is listed in Table 1 for comparison. The levels of ash and heptane insoluble are both marginal for a hydrocracking feed. The high ash is remarkable for an overhead product of such a low end point. Most likely, this stock would be rerun prior to catalytic processing.

2.5. Hydrocracking to Fuel Oil

2.5.1. Product Distribution and Hydrogen Consumption

Tables 2 and 3 summarize the product distribution obtained by hydrocracking H-Coal and EDS distillates to make fuel oil. Three runs are listed for each feedstock: a mild single stage hydrocracking, which amounted to little more than a hydrotreatment; a severe single stage hydrocracking, run at higher pressure and/or temperature; and two stage hydrocracking, in which the 600°F$^+$ bottoms from the preceding operation were hydrocracked to extinction. The product distribution in the last case is that calculated for the overall two stage process. Yields of over 100% include hydrogen consumed.

In Figure 4, the yield of 375-600°F fuel oil is plotted vs. wt-% hydrogen consumed. The initial part of the sigmoid curve represents hydrogen consumed in heteroatom removal, without scission of carbon-carbon bonds. The sharply rising center section represents hydrocracking of the 600°F$^+$ distillate. The curves finally flatten and will fall when the 600°F$^+$ distillate is exhausted, and hydrocracking of fuel oil to 375°F$^-$ naphtha takes place.

The H-Coal distillate consumed less hydrogen to make fuel oil than did the EDS distillate. This probably reflects a difference in selectivity between the UOP-HCA catalyst used for processing the H-Coal distillate, and the black oil conversion catalyst used for processing the EDS distillate. The latter catalyst possesses a lower ratio of hydrocracking activity to hydrogenation activity. This effect may have been accentuated by the higher pressure used in the EDS case.

From 40 to 60% of the hydrogen consumed can be recovered by steam reforming the 375°F$^-$ light ends. In the case of two stage hydrocracking, it is probably preferable to reform the naphtha to 100 RON:

Plant 638, Run No.	9B	9A	9A/14A[a]	20	19	19/23A[a]
H_2 Consumption, Wt-% of feed	1.4	2.0	2.6	1.9	3.7	4.3
H_2 Available, Wt-% of feed						
From steam reforming light ends	0.2	1.2	1.1	0.8	1.7	1.4
From reforming naphtha	-	-	0.2	-	-	0.3
Total	0.2	1.2	1.3	0.8	1.7	1.7
Percentage of H_2 requirement available from 375°F$^-$ product	14	60	50	42	46	40

[a] Two stage. See footnote a, Table 3.

In the case of mild hydrotreating of the H-Coal distillate (Run 9B), the yield of light ends, and hence recoverable hydrogen, was unusually low. However, this point was consistent with the general trend of the data, as illustrated in Figure 5.

2.5.2. Product Quality

The fuel oils should be environmentally acceptable, in view of the low residual nitrogen and sulfur levels. No tests were made with respect to storage stability or biological activity. The API gravities are all below the minimum specified for No. 2 fuel oil. These gravities could be raised by addition of heavy naphtha, to the limit set by flash point specifications.

A correlation of residual sulfur, nitrogen, and oxygen with process conditions is given in Appendix A of this report.

2.5.3. Used Catalysts

First stage catalysts operated at 500 psi above base pressure--the DCA catalyst in Run 9A, and the black oil conversion catalyst in Runs 19 and 20--showed no measurable catalyst deactivation. Run lengths were 648, 542, and 232 hours, corresponding to 1.4, 0.8, and 1.3 barrels/lb. catalyst service. It is believed that these catalysts would give commercially acceptable service at base pressure.

Stability of the second stage catalyst is illustrated in Figure 6 for Run 14A, and Figure 7 for Run 23A. (The "A" designates the initial part of each run, carried out at 500 psi above base pressure.) The data indicate commercially acceptable service.

Accumulation of inorganic elements in the first stage catalyst of Run 7 and Run 19 was measured, and compared with the amount of corresponding elements charged with the feedstock. (Run 7 was a severe first stage hydrocracking operation on H-Coal distillate, similar to Run 9A.) Results are summarized below.

Plant 638, Run No.	7				9			
Metal	Ca	Ti	Fe	B	Ca	Ti	Fe	B
Charged, µg/g cat.	0	0	310	1270	15	210	5300	250
Recovered, µg/g cat.	130	<30	210	360	260	180	320	3240

In general, the balances are poor. Previous experience has indicated that titanium deposits on the catalyst at high recovery, while Fe and Ca do not. This indicates that titanium is present as a relatively stable organic complex, which is decomposed only on the catalyst. Iron and calcium may be present as less stable naphthenates, or as particulates, which decompose or are filtered out in the upstream portion of the equipment. Trace boron in coal liquids has not been measured previously at UOP, and analyses are considered to be approximate.

2.5.4. Conclusions

To meet a fuel oil market, coal oil distillates should be hydrotreated to a point where the products have adequate storage stability and are environmentally and biologically acceptable. For H-Coal distillate, operating conditions are substantially equivalent to those required to hydrocrack an Arabian VGO into the fuel oil range. The EDS distillate, due to a high percentage of heptane insolubles, may require higher pressures.

In either case, the hydrotreated products should be routed to a market where the minimum API gravity specification of 30° API can be waived. It is believed that more detailed engineering and economic analyses will disclose that it is not profitable to use more hydrogen to raise the API gravity, nor to add valuable heavy naphtha for this purpose. Hydrogen should not be used to hydrocrack the minor amount of heavy ends into the fuel oil range. It can probably be better used elsewhere.

2.6. Hydrocracking to Gasoline

Both H-Coal and EDS derived distillates were hydrocracked to gasoline in a series flow second stage operation. Feedstock in each case was material which had been processed in a first stage reactor. As indicated in the previous section, yield of gasoline in this first stage operation was minimal.

2.6.1. Charge Stocks

Properties of charge stocks to the series flow second stage are given in Table 4. The properties of a typical Arabian VGO charge stock to series flow hydrocracking are listed for comparison.

The two first stage hydrocrackates were generated over different catalysts. However, operating conditions were selected to give similar nitrogen contents (600-1000 wt-ppm). Compared to the H-Coal product, the EDS product contained considerably more sulfur and oxygen, fewer aromatics, and retained a low level of heptane insolubles.

The corresponding petroleum VGO charge stock for series flow hydrocracking is totally different. Its initial boiling point is not far below the end point of the coal derived charge stocks. Nitrogen is comparable, but sulfur is very high. Hydrogen content is higher, corresponding to a lower aromatic content.

2.6.2. Product Distribution and Hydrogen Consumption

Table 5 compares overall product distribution and hydrogen consumption in hydrocracking coal derived distillates and Arabian VGO to gasoline. The data for the VGO are taken from a UOP estimate based on a two reactor series flow operation.

For purposes of comparison, series flow runs were selected which were made at 500 psi below base pressure. This was the only pressure tried for series flow second stage hydrocracking of the H-Coal distillate.

Overall, the EDS distillate yielded fewer light hydrocarbons and consumed less hydrogen than the H-Coal distillate. This reflects the 16°C higher temperature in Run 678 as compared to Run 779. This yield advantage was partially offset by the higher water yield, and by the lower research octane number (82.8) of the EDS gasoline produced. Still, if the EDS naphtha were reformed to match the 93.4 RON of the H-Coal naphtha, the EDS feedstock would retain a 3.4 vol-% yield advantage.

Part of this advantage may arise from a slight difference in procedure between the H-Coal and EDS series flow operation. In the H-Coal case (Run 678), Reactor No. 1 was maintained at constant temperature, and the temperature of Reactor No. 2 was increased to maintain conversion. In the EDS case (Run 779), the temperature of Reactor No. 1 was raised to maintain approximately 10 ppm nitrogen in the feed to Reactor No. 2. This decreased severity of operation in Reactor No. 2, and may have contributed to the slightly higher yield. Catalyst temperature histories in Runs 678 and 779 are given in Figures 8-10.

The yield estimate for the Arabian VGO shows a different picture. Hydrogen consumption is much lower, and gasoline yield is substantially higher. However, the poor octane number (68.7 RON) results in a larger volumetric loss on reforming to, say, 93 RON. This illustrates the superior quality of coal derived naphthas as reformer feedstocks.

In contrast to the fuel oil case previously discussed, hydrogen required for hydrocracking to gasoline can be entirely supplied by steam reforming light ends (in this case, C_4 minus) and by reforming the naphtha hydrocrackate:

Run No.	9B/678	20,21A/779
	H-Coal	EDS
H_2 consumed, Wt-% of feed	6.32	5.78
H_2 available, Wt-% of feed		
From steam reforming C_3^-	3.33	1.87
From steam foforming C_4	4.18	3.51
From reforming naphtha to 100 RON	0.71	1.53
	8.22	6.91

2.6.3. Product Quality

The octane number of hydrocracked naphtha will depend on the pressure and temperature of the operation. These determine the hydrogenation-dehydrogenation equilibrium, and hence the aromatic/naphthene ratio in the product.

Sulfur and nitrogen level in the hydrocrackates are of the order of 1 ppm or less. These levels may make them appropriate as reformer feedstocks (Table 10). High values of sulfur have been reported (e.g., for Run 678, Table 64, Report FE-2566-33). These probably are the result of incomplete stripping of hydrogen sulfide.

Residual oxygen in the coal derived hydrocrackates is generally high, compared to levels in petroleum derived products. Mass spectroscopy suggests oxygen is present as furans, benzofurans, and substituted phenols.

2.6.4. Conclusions and Discussion

Both H-Coal and EDS distillates may be completely converted in a three reactor, two stage hydrocracking system, to make naphtha and light gases. Hydrogen required may be generated by reforming the naphtha and steam reforming the light ends. The hydrocrackates may be suitable reformer feeds. Some uncertainty remains as to the long term effects of residual oxygen on naphtha reforming catalysts.

Alternate process flow schemes may be used. Withdrawal of a dragstream from the recycle loop will provide concurrent fuel oil production. This can also extend catalyst life by removing refractory polynuclear coke precursors. Alternate conditions may be arrived at by trade-offs such as residence time for temperature, and operating pressure for catalyst stability. Alternate catalysts may be used as they develop from ongoing research in the petroleum industry.

Optimization of the hydrocracking system would require a detailed economic study which is beyond the scope of this project.

3.0. FLUID CATALYTIC CRACKING OF COAL DERIVED DISTILLATES

For almost forty years, the Fluid Catalytic Cracking (FCC) process has been the major conversion tool for upgrading heavier petroleum fractions. At the beginning of 1980, additional FCC capacity planned or under construction in the United States was over a half million barrels per day, almost ten times the corresponding figure for hydrocracking processes. Modern fluid catalytic cracking is characterized by a combination of a relatively inexpensive investment cost with reliability and high on stream efficiency. Its potential role in upgrading coal liquids must be seriously appraised.

3.1. Conditions

Fluid catalytic cracking is commercially carried out at 454-538°C (850-1000°F), 0-60 psig, and at 4-15 catalyst/oil weight ratio. In this report, as in the preceding interim reports, the conditions used are expressed relative to base conditions:

Temperature	T-T(base), °C
Pressure	P-P(base), psi
Catalyst/Oil Weight Ratio	$\frac{\text{Catalyst/Oil}}{\text{Catalyst/Oil(base)}}$

The base conditions selected for reference represent those employed commercially for cracking a typical Arabian gas oil.

3.2. Catalysts

Equilibrium zeolitic FCC catalysts withdrawn from commercial FCC units were employed in these studies.

3.3. Equipment and Procedures

The UOP Research scale FCC plant used in these studies is diagrammed in Figure 11. It is a once-through Quick Quench (all riser) unit. It comprises a riser reactor, a catalyst regenerator-hopper system, a catalyst stripper-separator system, and a fractionator. The preheated fresh feed enters the unit at the mixing "Y" where it is mixed with the hot regenerated catalyst which flows down from the regenerator-hopper system through the catalyst transfer line. The catalyst and the vaporized feed travel rapidly through the riser reactor. The cracked oil vapors and the spent catalyst enter the stripper-separator system where the adsorbed hydrocarbons are stripped from the catalyst surface, and the oil vapors are separated from the catalyst. The stripped spent catalyst is charged to a catalyst receiver, and samples are taken to determine carbon content. The hydrocarbon vapors from the separator are sent to the fractionator for separation into gas, gasoline, and cycle oil. The spent catalyst is manually reloaded into the regenerator-hopper system, and is batch regenerated prior to the start of the next test.

In these studies, two sets of conditions were employed:

	Operation A	Operation B
T-T(base), °C	+3	+32
P-P(base), psi	-10	-10
$\frac{\text{Catalyst/Oil}}{\text{Catalyst/Oil(base)}}$	1	1.43

3.4. Charge Stock Analyses

From experience in cracking a wide variety of petroleum stocks, it is almost axiomatic that a high conversion level and high gasoline yield can be produced only from a stock with a sufficiently high hydrogen content. Feed hydrogen has much more impact on yield structure and product properties than do operating conditions. This variable was studied in some detail by prehydrotreating the three distillates, H-Coal, EDS, and SRC-II to various hydrogen contents. Procedures were essentially the same as described in Section 2.0 for first stage hydrocracking.

Conradson carbon is a measure of the tendency of a feedstock to lay down carbon on the FCC catalyst. It was substantially reduced or eliminated from the coal derived feedstocks simply by rerunning. In a number of cases the feedstocks were also topped to remove 400°F minus material originally present or made during hydrotreating.

Tables 6, 7 and 8 summarize properties of FCC feedstocks derived from the H-Coal, EDS, and SRC-II distillates respectively. (More detailed analyses can be found in Tables 1 and 4.) These stocks are listed in order of increasing hydrogen content. Also shown are yields of FCC charge, based on original distillate. Yields decrease with increasing hydrogen content, in the case of hydrotreated stocks, because with increased severity of hydrotreatment more distillate is converted into the naphtha boiling range or to C_4 minus light ends.

3.4.1. Sulfur Content vs. Hydrogen Content

Figure 12 is a composite plot for all feedstocks of their sulfur content as a function of hydrogen content. Above 10 wt-% hydrogen, the residual sulfur drops below 100 wt-ppm for all stocks.

3.4.2. Nitrogen Content vs. Hydrogen Content

Figure 13 is a composite plot for all feedstocks of their nitrogen content as a function of hydrogen content. Except for the sample of mildly hydrotreated SRC-II distillate, all values fall on a single curve. Above 11 wt-% hydrogen, residual nitrogen drops below 1000 wt-ppm for the H-Coal and EDS distillates, and probably would for the SRC-II distillate. This nitrogen level is acceptable for petroleum FCC feedstocks.

3.4.3. Aromatic Content vs. Hydrogen Content

Figure 14 is a composite plot for all feedstocks of aromatics, by Fluorescent Indicator Analysis (FIA) as a function of hydrogen content. These values include, in some cases, polar material such as phenols as well as hydrocarbons. There is a less precipitous drop in aromatic content with addition of hydrogen, compared to sulfur and nitrogen. This follows from the highly polycyclic nature of aromatics in coal distillates. These compounds will report as aromatics in the Fluorescent Indicator Analysis as long as one ring remains unsaturated. It is well known that this single remaining ring of such a system is relatively stable towards hydrogenation.

3.4.4. Comparison of Charge Stocks

The analytical data offer no distinctions between the various coal liquefaction processes and coal sources other than those which can be accounted for by hydrogen content. At this point in the conversion of coal to liquid fuels, distinction in minerology or process history have been obliterated.

3.5. Fluid Catalytic Cracking Results

Tables 6-8 summarize conversions and product distributions obtained by cracking the feedstocks under the conditions of Operation A in the Research scale FCC pilot plant. Also shown are the properties of the gasoline produced.

3.5.1. Conversion

Figure 15 shows for all feedstocks the trend in volumetric conversion with hydrogen content. While there is some scatter at lower hydrogen contents, the data show no great differences between the various stocks due to coal source or process history. Conversions enter a practical range at around 10.5 wt-% hydrogen.

A corresponding correlation for a West Coast refinery vacuum gas oil feed is shown as a dashed line. At 13 wt-% hydrogen, the conversions are equivalent. At 12% hydrogen, the petroleum stock is inferior. This may reflect the high nitrogen content of the unhydrotreated VGO, as compared to the low nitrogen content of the hydrotreated coal distillates.

3.5.2. Gasoline Yield

Figure 16 shows for all feedstocks the trend in C_5^+ gasoline volumetric yield with hydrogen content. The data are fit reasonably well by a single line, and overlap the corresponding correlation for petroleum VGO at 12-13 wt-% hydrogen.

3.5.3. Light Ends (C_4-) Yield

Figure 17 shows for all feedstocks the trend in yield of light ends with hydrogen content. As in the case of gasoline yield, a single curve accommodates all the data, and is in reasonable accord with petroleum VGO data at the higher hydrogen levels.

3.5.4. Carbon Yield

Figure 18 shows for all feedstocks the trend in weight percent yield of catalyst carbon with hydrogen content. In this case, there is more scatter. The higher values obtained with the unhydrotreated EDS stocks are probably associated with their high Conradson carbon content. This in turn may have resulted from inclusion of coker distillate in the sample furnished. At a hydrogen content of 11-13 wt-%, the data from EDS and H-Coal correlates with those from petroleum VGO. The hydrotreated SRC-II distillates appear to form somewhat less carbon.

3.5.5. Comparison of Charge Stocks

The research pilot plant FCC data, like the analytical data, offer little or no distinction between the various coal liquefaction processes and coal sources which cannot be accounted for by hydrogen content. Exceptions arise in the case of distillates with high Conradson carbon content. Such distillates can give catalyst carbon yields higher than can be accounted for by hydrogen content.

3.6. Combined FCC and HF Alkylation

The C_3/C_4 stream produced in FCC operations can be used as feedstock to a UOP HF alkylation unit to make high octane motor fuel. This process combines light olefins (primarily mixtures of propylene and butylenes) with isobutane, producing branched chain paraffins. Estimates of alkylation yield are based on analyses of the C_3/C_4 stream including a detailed breakdown of the C_4 olefin portion.

Such an estimate was made only for the severely hydrotreated and topped SRC-II distillate, processed in FCC Operations A and B. This estimate may be found in Report FE-2566-39. It was concluded that for a given quantity of C_3/C_4 FCC product originating from either a $400°F^+$ severely hydrotreated SRC-II gas oil or a petroleum derived vacuum gas oil, the quantity and quality of C_6^+ alkylate will be comparable. The petroleum derived C_6^+ alkylate will exhibit slightly better quality due to a higher C_4/C_3 ratio. This can, however, be overcome in the coal liquid case by increasing the isobutane/olefin ratio. The basic question of the viability of using an FCC/HF Alkylation complex on a given coal liquid feed will depend on selection of the appropriate feed pretreatment level and feed boiling range (which significantly affect alkylate yield). Optimization of the system, including pretreatment and FCC conditions would require a detailed economic study, which is beyond the scope of this evaluation.

3.7. Conclusions

Distillates derived from the three coal liquefaction processes fail to meet the basic requirement of an FCC feed, a sufficiently high hydrogen content. When processed as received, they form excessive catalyst coke at rather low conversions and gasoline yields.

This may be corrected by prehydrotreating the distillates to a hydrogen content of at least 10.5 wt-%. Hydrotreatment improves the cracking characteristics of the distillates by reducing nitrogenous poisons and coke precursors. Partial saturation of condensed aromatic structures provides points of catalytic attack on carbon-carbon bonds and facilitates ring opening. The remaining aromatic rings are responsible for the high octane number of the cracked gasoline.

In order to add sufficient hydrogen to these coal derived distillates, the hydrotreating conditions required will be severe. Yield of FCC charge stock (Tables 6-8) ranged from 45-70 wt-%. The concomitant production of a considerable amount of hydrocracked naphtha is unavoidable. A choice of fluid catalytic cracking as a route to gasoline from coal liquefaction distillates, therefore, implies simultaneous installation of hydrocracking facilities.

A new refinery designed to process coal liquefaction products into gasoline, demands inclusion of hydrotreating facilities. In spite of the attractive features of fluid catalytic cracking, it may be preferable to rely entirely on a flexible hydrocracking system. For existing refineries possessing hydrocracking and/or fluid catalytic cracking units, an economic evaluation would have to be made in each individual case.

4.0. HYDROTREATING AND REFORMING COAL DERIVED NAPHTHA

Catalytic reforming of naphthas over noble metal catalysts has grown into a major route to high octane gasoline since its commercialization by UOP, Inc. in 1949. The two principal chemical reactions in the process are dehydrogenation of naphthenes (cycloparaffins) to aromatics; and dehydrocyclization of paraffins, through naphthenic intermediates, to aromatics. The aromatic structures produced in both cases are responsible for the high octane numbers of the product.

These reforming reactions are promoted by cooperation of metallic and acidic sites on the catalyst, which are therefore often called "bi-functional". These sites are characteristically poisoned by sulfur, nitrogen, and oxygen compounds. Therefore, naphtha charge stocks to a catalytic reformer are usually hydrotreated to reduce the level of these heteroatoms to a tolerable level. More than enough hydrogen is available from the reformer for this purpose.

Primary naphthas produced in the H-Coal, EDS, and SRC-II processes are highly aromatic, but also highly contaminated with phenols, pyridine and thiophenes. These must be removed by relatively severe hydrotreatment to obtain a clean, stable naphtha. Octane number is lowered by saturation of aromatics during hydrotreatment. However, this loss is readily recoverable by reforming the clean naphtha.

Secondary naphthas derived from coal are those produced in hydrocracking or hydrotreating 375°F$^+$ distillates. These may or may not require additional hydrotreatment and/or reforming, depending on the severity of conditions used and the octane number required.

4.1. Conditions

Reforming is commercially carried out at 343-482°C (850-1000°F), 150-500 psig, and 0.2-6.0 hr^{-1} liquid hourly space velocity (LHSV). Hydrotreatment is normally carried out within the range of conditions cited in Paragraph 2.1. Conditions must be chosen which will produce an acceptable reformer feedstock.

In this report, as in the preceding Interim Reports, the conditions used are expressed relative to base conditions:

Temperature	T-T(base), °C
Pressure	P-P(base), °C
Space Velocity	LHSV/LHSV(base)

4.2. Catalysts

Reforming catalysts comprise platinum on acidified alumina. Hydrotreating catalyst used comprised Group VI and Group VIII metals on a high surface area refractory support.

4.3. Equipment and Procedures

Figures 19 and 20 diagram UOP Research scale plants for hydrotreating and reforming naphthas. No attempt was made to optimize conditions for hydrotreating the primary coal naphthas. In the case of the first charge stock hydrotreated, H-Coal naphtha, the plant was operated at a constant pressure and space velocity. The temperature was raised until the effluent contained less than 1 ppm nitrogen and sulfur. These conditions also served to bring the EDS and SRC-II naphthas within the same heteroatom limits.

Reforming tests were made at constant pressure and space velocity, but over a range of temperatures. This program generated yield-octane curves. With increasing temperature, the product research octane number and hydrogen yield increased, while yield of C_5^+ gasoline decreased. The reformates were characterized by mass spectrographic analyses. These give hydrocarbon types (aromatics, naphthenes, and paraffins) as well as isopentane/normal pentane ratio.

4.4. Charge Stocks

Two types of naphthas were investigated, primary coal naphthas, and the hydrocrackates made from H-Coal and EDS distillate as described in Paragraph 2.6. The former were hydrotreated prior to reforming, the latter were not.

4.4.1. Primary Coal Naphthas

Table 9 gives inspections of primary naphthas from the H-Coal, EDS, and SRC-II coal liquefaction processes. All three are extremely high in nitrogen, sulfur, and oxygen, and contain substantial amounts of chloride. Aromatics and naphthenes are the major hydrocarbon constituents. Phenols are the major non-hydrocarbon constituent. These naphthas are very unstable towards oxidation. The as-received H-Coal naphtha was rerun to remove storage impurities and color bodies. However, the color redeveloped almost immediately.

Of these three stocks, H-Coal naphtha was relatively the cleanest, having been derived directly from a catalytic process. EDS naphtha was the dirtiest, especially with respect to oxygen content. This oxygen may well have been picked up during storage and shipment by diolefins added as coker distillate. The SRC-II naphtha contained the most paraffins, i.e., the fewest ring structures. This property was reflected in the yield-octane curves obtained with SRC-II naphtha in comparison with the other two.

4.4.2. Naphtha Hydrocrackates

Table 10 gives the properties of naphtha hydrocrackates obtained from coal derived distillates at 500 psi above and below base hydrocracking pressure. In both cases, the distillates were completely converted by recycling $375°F^{+}$ product. The H-Coal hydrocrackate was generated in a single reactor second stage operation, while the EDS hydrocrackate was generated in a two reactor, series flow, second stage.

These hydrocrackates containing less than 1 ppm sulfur and nitrogen may meet requirements for reformer feedstocks. The residual oxygens are high, particularly in the case of the EDS product. As mentioned before, oxygen is believed to be present as phenols, furans, and benzofurans. Naphtha hydrocrackates generated as coproduct in fuel oil operations did not always meet sulfur and nitrogen requirements. The hydrocrackates generated at the lower pressure contain more aromatics and have a higher octane number. This is consistent with the effect of pressure on the aromatic/naphthene equilibrium.

4.5. Hydrotreating Primary Naphthas

The primary naphthas were all hydrotreated at one eighth of base space velocity, 450 psi above base pressure, and 33°C above base temperature. In absolute terms, these hydrotreating conditions resemble those applicable to a petroleum gas oil. For a naphtha, they are relatively severe. Table 11 summarizes the product properties and hydrogen consumptions.

Hydrotreatment reduced sulfur and nitrogen levels to below 1 ppm. As in the case of the hydrocrackates, oxygen content remained relatively high. Polars and olefins disappeared from the mass spectroscopic types analysis. Research octanes dropped 10-15 numbers. Hydrogen consumption ranged from 480-850 SCFB. This hydrogen is recoverable in subsequent reforming operations.

4.6. Reforming Coal Derived Naphthas

Reforming yield/octane relationships were generated for seven coal derived naphthas--three hydrotreated primary naphthas, and four naphtha hydrocrackates. All tests were run at base pressure, one and one half times base space velocity. The temperature used to generate the yield octane curve ranged from 10° to 120°C below base temperature. Results are given in Tables 12-14. These tables include selected data for three levels of reforming severity.

4.6.1. Yield-Octane Relationships

Yield-octane curves are given in Figures 21-23. They are virtually identical for the H-Coal and EDS process derived naphthas. Yields from SRC-II hydrotreated naphtha are somewhat lower, probably because of its slightly lower cyclic (higher paraffinic) content. Yields are far greater from these highly cyclic stocks than from a typical Middle East naphtha. Yields at 100 RON (Clear) were as follows:

Reformer Charge Stock	C_5+ Yield @ 100 RON (Clear) Vol-%
H-Coal Hydrotreated Primary Naphtha	90.0
H-Coal Naphtha Hydrocrackate (High Pressure)	89.8
H-Coal Naphtha Hydrocrackate (Low Pressure)	92.5
EDS Hydrotreated Primary Naphtha	90.3
EDS Naphtha Hydrocrackate (High Pressure)	∿89
EDS Naphtha Hydrocrackate (Low Pressure)	92.5
SRC-II Hydrotreated Primary Naphtha	88.0
Middle East Naphtha	76.0

4.6.2. Relative Roles of Dehydrogenation and Dehydrocyclization

Except at the most severe reforming conditions used, octane number increase can be attributed exclusively to dehydrogenation of naphthenes. A review of the reformate paraffin analyses in Tables 12-14 shows no change of paraffin content from feed levels in the large majority of cases. Under the relatively mild conditions used, the paraffins have passed through the reaction substantially unchanged, without undergoing dehydrocyclization.

4.6.3. Contribution of Paraffins to Octane Number

The contribution of the paraffins in the various feedstocks and reformates to octane number depend on their degree of branching. An index to paraffin branching is the isopentane/normal pentane mole ratio listed in Tables 12-14. This ratio is high for the hydrocrackates, and low for the hydrotreated primary naphthas.

The acid catalyst used in second stage hydrocracking will tend to produce fragment molecules in the naphtha boiling range which are highly branched. The reactions involve a carbonium ion mechanism. The primary coal naphthas, on the other hand, are formed mainly via a radical mechanism which does not tend to make branched chains.

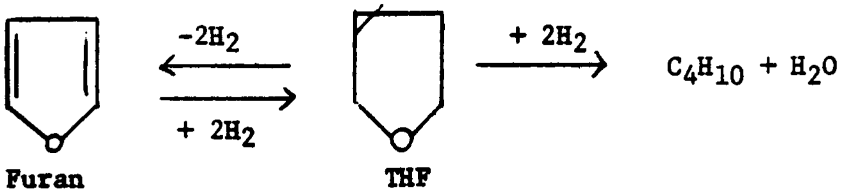
This distinction leads to a different correlation of octane number with aromatic content for the two types of feedstocks and their reformates. Figure 24 illustrates this for the EDS Process derived naphthas. The hydrocrackates have a higher octane number at a given aromatic content due to the superior quality of the paraffins. The difference disappears at high aromatic levels.

4.6.4. Oxygenated Compounds

All the coal derived naphthas contained much higher levels of oxygen than are encountered in petroleum naphthas. This is of some concern, since water formed by deoxygenation can affect reforming catalyst activity and stability.

A limited amount of data obtained with the SRC-II primary naphtha and the EDS hydrocrackates (Tables 13 and 14) show that a surprising percentage of the feed oxygenates survived the reforming operation. Also surprising was that oxygen conversion consistently dropped with increasing reforming temperature.

This can be rationalized by the following reactions of tetrahydrofuran (THF), believed to be an important oxygenate in the reformer feedstocks.

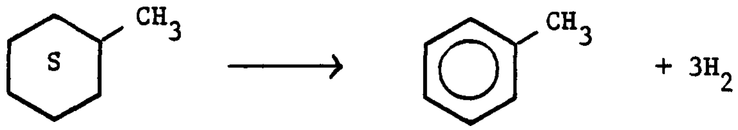


Under dehydrogenation conditions (high temperature) a stable furan is formed. Hydrogenating conditions (low temperature) favor the tetrahydrofuran, which is susceptible to hydrogenolysis to butane and water.

4.6.5. Hydrogen Production

Catalytic reforming of naphthas is an important source of hydrogen in a petroleum refinery. It will be equally important in a coal liquefaction-upgrading complex. In this case, hydrogen management may be simpler, since hydrogen can be reversibly added to or removed from the highly aromatic/naphthenic liquids. Irreversible hydrocracking reactions can be minimized, and the aromatic/naphthene hydrogenation/dehydrogenation equilibrium can be shifted as desired by adjustment of temperature and pressure.

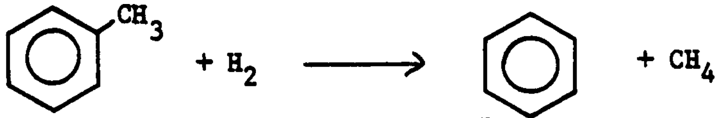
Figure 25 is a plot of hydrogen yield taken from Tables 12-14, as a function of increase in aromatic content (ΔA). The dotted line is the calculated yield obtained by reforming a model feedstock comprising 20 vol-% toluene, and 80 vol-% methylcyclohexane. Hydrogen is generated by aromatization. The experimental



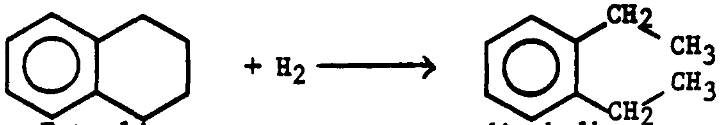
Methylcyclohexane Toluene

curve parallels the model curve but is offset by about 0.7 wt.% hydrogen. This offset represents hydrogen consumed without a corresponding decrease in aromatics; or hydrogen produced without a corresponding increase in aromatics. The reactions involved may be reversible or irreversible.

Irreversible reactions are hydrocracking reactions, such as hydrodealkylation, and ring opening:



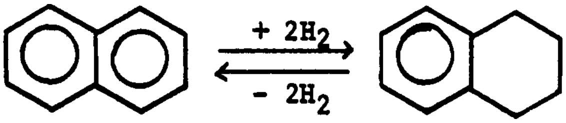
Toluene Benzene



Tetralin o-diethylbenzene

In dealkylation, a portion of the product will appear as C_4 minus light ends. This accounts for about 0.15 wt-% of the 0.7 wt-% offset. In simple ring opening of tetralin, for example, the hydrogen consumed remains in the naphtha.

Reversible reactions in which hydrogen is produced or consumed with no change in aromatic content (at least on a molar basis) comprise, typically, the tetralin/naphthalene equilibrium:



Naphthalene Tetralin

4.6.6. Summary

Coal derived naphthas have a very high cyclic content and make superior reformer feeds. Operating conditions required to reach 100 RON are relatively mild. In general, the results conform to UOP correlations of reformer performance with feedstock quality.

The primary coal naphthas contain excessive amounts of sulfur, oxygen, and nitrogen, and require relatively severe hydrotreatment, under conditions more usually associated with hydroprocessing a distillate. Oxygen is particularly difficult to remove. Its long term effect on catalyst life in a fixed bed, semi-regenerative reformer is uncertain. A UOP Continuous Platforming unit provides for continuous reconditioning of the catalyst, and will minimize the potentially detrimental effect of feedstock oxygenates on reformer performance. However, further investigation is needed to quantify the effect of oxygenates and alternative approaches to their removal may be warranted (i.e., guard bed system).

Octane number increase derives principally from dehydrogenation of naphthenes to aromatics. In only a few instances of severe operation did the disappearance of paraffins indicate that dehydrocyclization is participating. The paraffinic portion of naphtha hydrocrackates contributes more to octane number than the paraffins in hydrotreated primary naphthas. This is because acid hydrocracking catalysts yield more branched chain paraffins than are generated in coal liquefaction processes.

Hydrogen yields amount to as much as 1700 SCFB in some high octane operations. This reformer hydrogen will make an important contribution to hydrogen balance in a coal liquefaction-upgrading complex.

5.0. CONCLUSIONS

Conclusions to be drawn from this work remain unchanged as stated in the first Annual Report. Present day commercial petroleum refinery processes and catalysts are applicable to coal derived distillates. In general, the liquids will require extensive hydrotreatment prior to cracking or reforming to reduce excessive nitrogen, to enhance processability, and to make the ultimate products environmentally and biologically acceptable. Hydrogen consumption is relatively high. Insofar as it is used to saturate aromatics to naphthenes, it can be recovered during reforming by reversing this reaction, i.e., dehydrogenating naphthenes. Steam reforming of light ends will provide additional hydrogen.

Current and future work under this contract comprises economic studies on the impact of substituting coal oil for a portion of imported petroleum as refinery feedstock.

6.0. REFERENCES

The following DOE Interim Reports published under this contract are appended by title:

FE-2566-12 "Hydrotreating and Reforming H-Coal Process Derived Naphthas", March, 1978

FE-2566-20 "Hydrotreating and Fluid Catalytic Cracking of H-Coal Process Derived Gas Oils", August, 1978

FE-2566-23	"Hydrocracking of H-Coal Process Derived Gas Oils", November, 1978
FE-2566-25	"Hydrotreating and Reforming Exxon Donor Solvent (EDS) Process Derived Naphthas", January, 1979
FE-2566-27	"Hydrotreating and Reforming SRC-II Process Derived Naphtha", June, 1979
FE-2566-30	"Hydrotreating and Fluid Catalytic Cracking of EDS Process Derived Gas Oil", August, 1979
FE-2566-33	"Hydrocracking of EDS Process Derived Gas Oils", November, 1979
FE-2566-39	"Hydrotreating and Fluid Catalytic Cracking of SRC-II Process Derived Gas Oils", July, 1980

Table 1

Inspections of Coal Derived Distillates

	H-Coal	EDS	SRC-II[c]
Sample No.	96-3334	3532-2,3	3777-7
°API @ 60°F	9.4	7.8	10.1
Sp. Gr. @ 60°F	1.0043	1.0158	0.9993
Distillation, ASTM D-1160			
IBP, °F	445	404	335
5%	485	430	395
10%	500	440	410
20%	519	460	425
30%	538	490	444
40%	558	526	458
50%	580	570	472
60%	600	630	492
70%	628	730	512
80%	670	832	571
90%	720	910	656
95%	780	-	705
EP	860	-	810
% Over	99.0	90.0	99.0
% Bottoms	1.0	10.0	1.0
Hydrogen, Wt-%	9.36	8.93	8.72
Carbon, Wt-%	89.32	86.5	86.13
Sulfur, Wt-%	0.07	0.66	0.38
Nitrogen, Wt-%	0.39	0.50	0.90
Oxygen, Wt-%	0.51	2.0-2.8	1.73
Ash, Wt-ppm	--	48	277
Conradson Carbon, Wt-%	--	3.6-3.8	0.37
Heptane Insoluble, Wt-%	1.6	8.2-8.8	0.22
Aromatics and Polars (FIA), Wt-%	85.0	--	94.6

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[a] Derived from Illinois No. 6 coal. Elemental (ultimate) and FIA analyses refer to 95% overhead rerun feedstock, 96-3330A.

[b] Derived from Illinois No. 6 coal (believed to contain coker distillate); analyses are average of two drums.

[c] Derived from Powhatan No. 5 mine coal; contains up to 3% Dowtherm (diphenyl/diphenyl oxide) contaminant.

Table 2

Hydrocracking Rerun H-Coal Distillate to Fuel Oil

UOP Research Plant 638, Run No.		9B	9A	9A/14A[a]
Conditions:				
P-P(base), psi		-500	500	500/500
T-T(base), °C		-22	-3	-3/-4
LHSV/LHSV(base)		0.9	0.8	0.8/0.25
Product Distribution, Wt-%	(Feed)			
C_4		0.6	1.6	4.0
C_5-375°F naphtha		0.2	3.3	12.0
375-600°F fuel oil	59.8	64.9	80.6	85.5
600°F+		34.8	15.4	0.0
H_2S, H_2O, NH_3		0.9	1.1	1.1
		101.4	102.0	102.6
Hydrogen Consumption, SCFB		860	1240	1580
Fuel Oil Yield, Vol-%	61.9	69.2	86.0	91.2
Fuel Oil Properties:				
°API @ 60°F	--	20.2	20.3	20.3
Sp. Gr. @ 60°F	--	.9326	.9321	.9323
Sulfur, Wt-ppm	700	<7	2	--
Nitrogen, Wt-ppm	3900	<619	12	--
Oxygen, Wt-%	0.51	<0.14	0.057	--

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[a] Two stage

Table 3

Hydrocracking EDS Distillates to Fuel Oil[a]

UOP Research Plant 638, Run No.		20	19	19/23A[b]
Conditions:				
P-P(base), psi		800	800	800/500
T-T(base), °C		-12	13	13/-27
LHSV/LHSV(base)		1.6	0.5	0.5/0.25
Product Distribution, Wt-%	(Feed)			
C_4-		0.8	2.1	5.1
C_5-375°F naphtha		2.3	5.0	18.2
375-600°F fuel oil	50.3	53.7	71.4	77.3
600°F+		40.7	21.6	0
H_2O, H_2S, NH_3		4.4	3.6	3.7
		101.9	103.7	104.3
Hydrogen Consumption, SCFB		1210	2350	2700
Fuel Oil Yield, Vol-%	54.9	58.9	80.5	87.1
Fuel Oil Properties				
°API @ 60°F	--	26.3	25.0	25.2
Sp. Gr. @ 60°F	--	.9255	.9042	.9032
Sulfur, Wt-ppm	6600	<270	2	--
Nitrogen, Wt-ppm	5000	<850	<1	--
Oxygen, Wt-%	1.9-2.8	<0.3	0.072	--

[a] Errata - Due to transposition of data from Runs 19 and 20 in Interim Report FE-2566-33, Tables 20, 21, 26, 27 and 29 of that report are incorrect. Revised tables, on which the data in this table are based, are included in Appendix B to this report.

[b] Two stage operation

Table 4

Comparison of Feedstocks for Series Flow Hydrocracking to Gasoline

Sample No.	H-Coal 3531-14 ex. Run 9B	EDS 3532-9 ex. Runs 20,21A	VGO ex. Arabian Crude
°API @ 60°F	15.0	17.1	22.2
Sp. Gr. @ 60°F	0.9659	0.9522	0.9206
Distillation, ASTM D-1160			
IBP, °F	377	356	700
5%	463	410	790
10%	484	431	820
20%	502	457	850
30%	519	480	864
40%	540	509	872
50%	560	548	881
60%	580	586	893
70%	607	635	943
80%	641	700	949
90%	685	749	970
95%	729	849	949
EP	790	925	1028
% Over	99.0	99.0	--
% Bottoms	1.0	1.0	--
Hydrogen, Wt-%	10.49	10.85	12.03
Carbon, Wt-%	89.43	88.58	85.77
Sulfur, Wt-ppm	7.6	267	21,100
Nitrogen, Wt-ppm	619	844	600
Oxygen, Wt-ppm	14.3	2982	500
Heptane Insolubles, Wt-%	0	0.14	<0.01
FIA, Vol-%			
A	81.5	71.2	50.8
P&N	18.5	28.8	42.9

Table 5

Comparison of Product Distributions in Two Stage Hydrocracking to Gasoline (Series Flow in Second Stage)

	H-Coal	EDS	V(ex. Arabian Crude
First Stage Hydrocracking	Run 9B	Runs 20, 21A	
Catalyst	DCB	BOC	
P-P(base), psi	-500	800	
T-T(base), °C	-20	-12	
LHSV/LHSV(base)	0.9	1.6	
Second Stage Series Flow Hydrocracking	Run 678	Run 779	UOP Estimate
P-P(base), psi	-500	-500	-400
T-T(base), °C (Rx #2)	27	11	0
LHSV/LHSV(base) (Rx #1/Rx #2)	1.0/1.0	1.0/1.0	1.25/2.80
CFR/CRF(base)	1.2	1.2	1.0
Overall Product Distribution Wt-% of feed			
C_1	0.47	1.67	0.29
C_2	2.07		0.41
C_3	9.93	5.30	2.92
C_4	16.09	13.49	12.15
C_5+	76.86	80.84	85.67
H_2O	0.40	3.15	--
NH_3	0.40	0.81	0.09
H_2S	0.10	0.52	2.13
Total	106.32	105.78	103.66
Overall H_2 Consumption, Wt-% of feed	6.32	5.78	3.66
Overall H_2 Consumption SCFB	3880	3640	2215
Overall C_5+ Yield, Vol-% of feed	97.9	105.0	107.9
C_5+ RON Clear	93.4	82.8	68.7
Yield @ 93 RON, Vol-% of feed	97.9	101.3	75.5

Table 6

FCC Feedstocks from H-Coal Distillate

	As Rec'd.	Rerun	Mild Hydro-treatment	Severe Hydro-treatment and Topping
Sample No.	37-1118	3531-11	3531-25	3531-27
Hydrotreating Plant/Run No.	-	-	601/760	638/17
Yield, Wt-%	100.0	94.7	95.3	45.1
Inspections				
Sp. Gr. @ 60°F	1.0187	1.0078	0.9541	0.8805
Boiling range, °F (IBP/EP)	412/857	415/769	373/685	395/670
Hydrogen, Wt-%	-	9.14	10.68	12.88
Sulfur, Wt-%	0.095	0.080	0.0007	<1 ppm
Nitrogen, Wt-%	0.35	0.41	0.0856	2 ppm
Heptane insolubles, Wt-%	0.37	0.05	<0.01	-
Aromatics (FIA), Vol-%	90.9	90.2	73.0	12.3
Conradson Carbon, Wt-%	0.41	<0.01	<0.01	-
Fluid Catalytic Cracking, Operation A				
Conversion, Vol-%	-	30.6	62.9	82.9
C_5+, Gasoline, Vol-%	-	15.5	45.7	62.2
C_4-, Wt-%	-	4.3	11.8	20.6
Carbon, Wt-%	-	11.1	8.9	6.3
Gasoline Properties				
Sp. Gr. @ 60°F		0.8289	0.8058	0.7661
RON, clear		99.4	95.2	92.1
FIA, Vol-%				
A		54.1	45.2	30.3
O		25.8	6.2	5.8
P&N		20.1	48.6	63.9

Table 7

FCC Feedstocks from EDS Distillate

	As Rec'd.	Rerun	Mild Hydro-treatment	Severe Hydr treatment and Topping
Sample No.	3532-5	3532-10	3532-12	3532-15
Hydrotreating Plant/Run No.	-	-	638/21B	638/22
Yield, Wt-%	100.0	81.3	95.5	71.6
Inspections				
Sp. Gr. @ 60°F	1.0481	1.0143	0.9639	0.9279
Boiling range, °F (IBP/EP)	403/930+	422/940	380/950+	414/801
Hydrogen, Wt-%	8.66	8.97	10.66	11.95
Sulfur, Wt-%	0.49	0.20	0.005	0.0011
Nitrogen, Wt-%	0.71	0.49	0.14	3 ppm
Heptane insolubles, Wt-%	6.45	4.14	0.06	<0.01
Aromatics (FIA), Vol-%	-	85.6	86.6	52.5
Conradson Carbon, Wt-%	6.66	0.95	0.18	<0.01
Fluid Catalytic Cracking, Operation A				
Conversion, Vol-%	43.9	49.7	66.8	77.5
C_5+ Gasoline, Vol-%	18.0	24.6	43.0	54.7
C_4-, Wt-%	7.0	8.0	14.8	17.7
Carbon, Wt-%	19.6	15.4	9.0	6.8
Gasoline Properties				
Sp. Gr. @ 60°F	0.8756	0.8623	0.8294	0.8008
RON, clear	-	96.8	96.8	94.6
FIA, Vol-%				
A	76.7[a]	85.5[a]	56.3	45.4
O	12.2	7.1	4.4	5.6
P&N	11.1	17.4	39.3	49.0

[a] Includes highly polar non-hydrocarbons

Table 8

FCC Feedstocks from SRC-II Distillate

	As Rec'd.	Topped	Rerun Topped	Moderate Hydro-treatment and Topping	Severe Hydro-treatment and Topping
Sample No.	3777-7	3777-36	3777-38	3777-34	3777-41
Hydrotreating Plant/Run No.	-	-	-	638/37	638/38
Yield, Wt-%	100.0	87.3	81.9	78.1	69.4
Inspections					
Sp. Gr. @ 60°F	0.9993	1.0173	1.0093	0.9752	0.9484
Boiling range, °F (IBP/EP)	386/799	400/820	421/738	418/790	408/748
Hydrogen, Wt-%	8.72	8.66	8.89	9.98	10.59
Sulfur, Wt-%	-	0.32	0.29	0.011	0.011
Nitrogen, Wt-%	0.90	1.02	1.00	0.60	0.173
Heptane insolubles, Wt-%	.22	0.48	0.03	0.01	0.01
Aromatics (FIA), Wt-%	90.6	93.3	92.5	89.3	73.9
Conradson Carbon, Wt-%	0.38	0.54	0.11	0.01	0.02
Fluid Catalytic Cracking, Operation A					
Conversion, Vol-%	-	44.8	45.3	49.2	61.9
C_5+ Gasoline, Vol-%	-	25.9	25.1	35.3	46.9
C_4-, Wt-%	-	5.3	5.0	8.4	13.5
Carbon, Wt-%	-	11.6	12.2	7.3	3.9
Gasoline Properties					
Sp. Gr. @ 60°F		0.9309	1.0151	0.8612	0.8109
RON, clear		-	106.7	101.8	97.5
FIA, Vol-%					
A		-	-	-	55.8
O		-	-	-	4.8
P&N		-	-	-	39.4

Table 9

Inspections of Primary Coal Naphthas

	H-Coal	EDS	SRC-II
Sample No.	3531-4[a]	3531-7	3777-1
°API @ 60°F	43.7	38.4	49.7
IBP, °F	132	142	107
EP, °F	396	380	367
S, Wt-ppm	1,289	9,978	4,400
N, Wt-ppm	1,930	2,097	5,140
O, Wt-ppm	5,944	13,700	7,814
Cl, Wt-ppm	23	18	195
MS Types, Vol-%			
Polars	4.2	8.7	6.8
Aromatics	18.6	25.3	16.2
Olefins	5.5	9.9	8.4
Naphthenes	55.5	42.9	37.1
Paraffins	16.2	13.2	31.5
RON, Clear	80.3	83.2	80.8

[a] Rerun

Table 10

Inspections of Naphtha Hydrocrackates from Coal Derived Distillates

	H-Coal		EDS	
Sample No.	3531-18	3531-15	3532-23	3532-26
Hydrocracking Plant/Run No.	601/756,7	601/749,51	601/777	601/779
Pressure, P-P(base), psi	500	-500	500	-500
°API @ 60°F	49.4	49.7	52.3	50.0
IBP, °F	127	120	148	138
EP, °F	518	400	372	392
S, Wt-ppm	-	0.1	0.3	1.3
N, Wt-ppm	0.13	0.1	0.3	0.3
O, Wt-ppm	41.0	41.0	378	237
Aromatics (FIA), Vol-%	23.3	33.6	14.2	27.3
RON, Clear	80.2	84.2	75.2	83.2

Table 11

Inspection of Hydrotreated Primary Coal Naphthas

	H-Coal	EDS	SRC-II
Sample No.	3531-4	3531-12	3777-2
Hydrotreating Plant/Run No.	629/215,6	629/218	505/874
°API @ 60°F	46.8	44.1	52.0
IBP, °F	153	202	136
EP, °F	393	374	388
S, Wt-ppm	-	0.1	0.2
N, Wt-ppm	0.63	0.2	0.8
O, Wt-ppm	34	98	359
Cl, Wt-ppm	4	1	4
MS Types, Vol-%			
Polars	-	-	-
Aromatics	19.4	21.6	22.0
Olefins	-	-	-
Naphthenes	64.6	65.5	52.8
Paraffins	16.0	12.9	25.2
RON, Clear	66.8	64.5	70.9
H_2 Consumption SCFB	480	850	560

Table 12

Reforming H-Coal Process Derived Naphthas

		C_5+	H_2	Product Properties				
Period No.	T-T(base), °C	Yield Vol-%	Yield Wt-%	RON (Clear)	Aromatics Vol-%	C_6+ Paraffins Vol-%	$\underline{i}$-C_5/$\underline{n}$-C_5 Ratio	ΔA^a Vol-%
Hydrotreated Primary Naphtha (3531-4) - Plant 636, Run 220								
	(feed)	100.0	0	66.8	19.4	16.0	-	0
10	-88	92.5	2.5	94.2	65.8	17.8	0.3	46.4
5	-66	91.1	3.0	97.7	71.7	18.9	0.3	52.3
14	-18	88.1	3.4	102.6	83.3	11.7	0.5	63.9
Naphtha Hydrocrackate - High Pressure (3531-18) - Plant 508, Run 1458								
	(feed)	100.0	0	80.2	23.3	14.7	7.4	0
1	-118	96.5	0.9	90.6	46.8	15.0	4.3	23.5
3	-78	94.1	1.5	95.6	59.9	15.3	4.1	36.6
5	-13	89.8	2.2	99.8	81.3	10.6	1.2	48.0
Naphtha Hydrocrackate - Low Pressure (3513-15) - Plant 508, Run 1457								
	(feed)	100.0	0	84.2	32.3	13.2	16.0	0
4	-133	97.0	0.6	91.6	59.4	9.6	4.7	27.1
1	-78	93.4	1.7	98.9	70.5	15.7	4.6	38.2
7	-38	91.5	2.1	101.2	80.2	13.1	2.8	47.9

[a] Increase in aromatics content over feedstock

Table 13

Reforming EDS Process Derived Naphthas

		C_5+	H_2	Product Properties					
Period No.	T-T(base), °C	Yield, Vol-%	Yield, Wt-%	RON (Clear)	Aromatics, Vol-%	C_6+ Paraffins, Vol-%	i-C_5/n-C_5 Ratio	Oxygen, Wt-ppm	ΔA^a Vol-%
Hydrotreated Primary Naphtha (3531-12) - Plant 508, Run 1456									
	(feed)	100.0	0	64.5	21.6	12.9	0.3	98	0
4	-97	92.5	2.7	95.1	66.9	16.6	0.2	-	45.3
2	-73	91.4	3.0	97.9	75.6	15.4	0	-	54.0
9	-39	89.6	3.4	101.5	79.4	15.0	0.3	-	57.8
Naphtha Hydrocrackate - High Pressure (3532-23) - Plant 636, Run 321									
	(feed)	100.0	0	75.2	16.5	18.3	3.1	378	0
1	-118	95.6	1.6	91.2	51.6	19.7	1.0	245	35.1
3	-85	93.1	2.2	96.0	60.7	18.8	2.6	327	44.2
6	-58	91.0	2.7	98.4	69.0	19.4	1.5	326	52.5
Naphtha Hydrocrackate - Low Pressure (3532-26) - Plant 636, Run 334									
	(feed)	100.0	0	83.2	31.6	16.2	4.5	237	0
2	-147	97.4	0.8	91.3	49.7	16.6	3.3	83	18.1
4	-108	95.5	1.5	96.0	64.6	15.4	2.3	219	33.0
6	-67	92.8	2.1	99.7	73.7	16.5	3.1	-	42.1

[a] Increase in aromatics content over feedstock

Table 14

Reforming SRC-II Process Derived Naphtha

Period No.	T-T(base), °C	C_5+ Yield, Vol-%	H_2 Yield, Wt-%	RON (Clear)	Aromatics, Vol-%	C_6+ Paraffins, Vol-%	$\underline{i}C_5/\underline{n}C_5$ Ratio	Oxygen Wt-ppm	ΔA[a] Vol-%
Hydrotreated Primary Naphtha (3777-2) - Plant 636, Run 335									
	(feed)	100.0	0	70.9	22.0	25.2	0.4	359	0
1	-121	91.7	2.4	88.5	58.4	26.4	0.3	160	36.4
2	-87	90.2	2.6	94.5	67.0	23.9	0.2	183	45.0
5	-29	88.0	3.1	99.9	83.8	16.2	0.4	311	61.8

[a] Increase in aromatics content over feedstock

FIGURE 1

BENCH-SCALE UNIT FOR FIRST-STAGE HYDROCRACKING

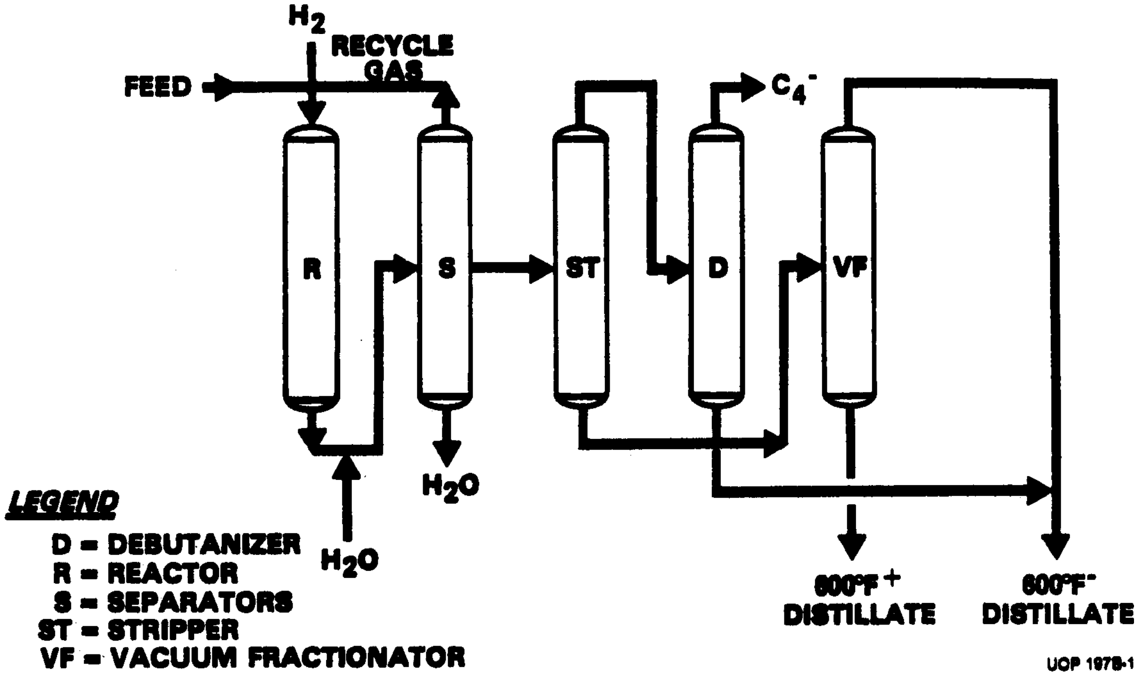


FIGURE 2

BENCH-SCALE UNIT FOR SERIES FLOW SECOND-STAGE HYDROCRACKING

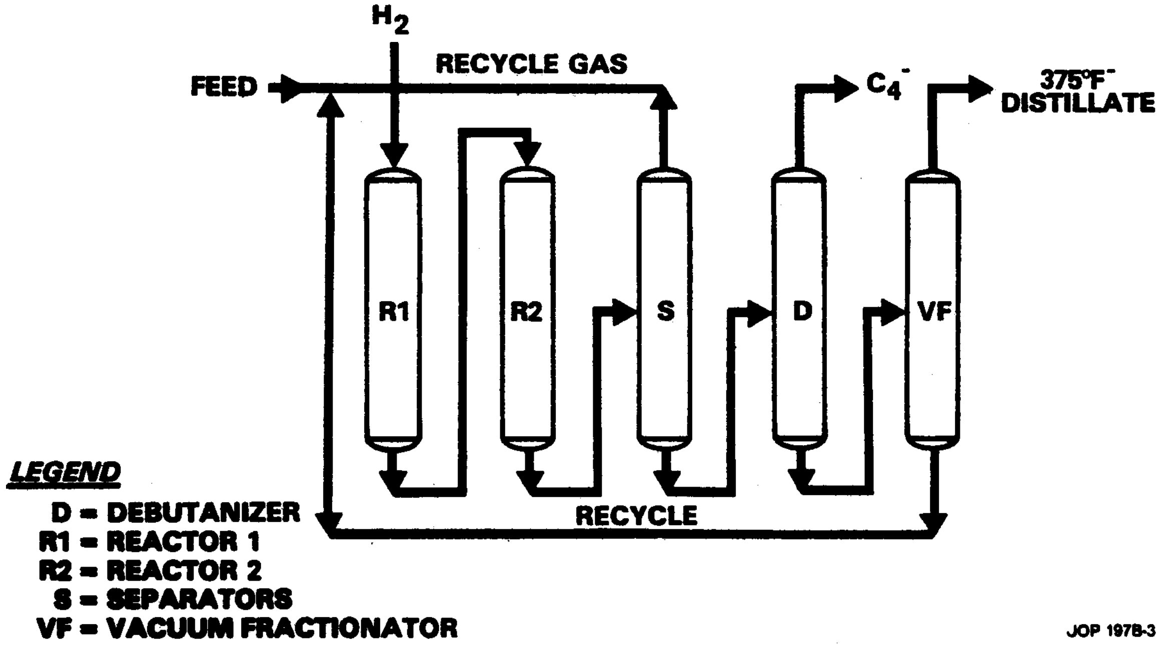
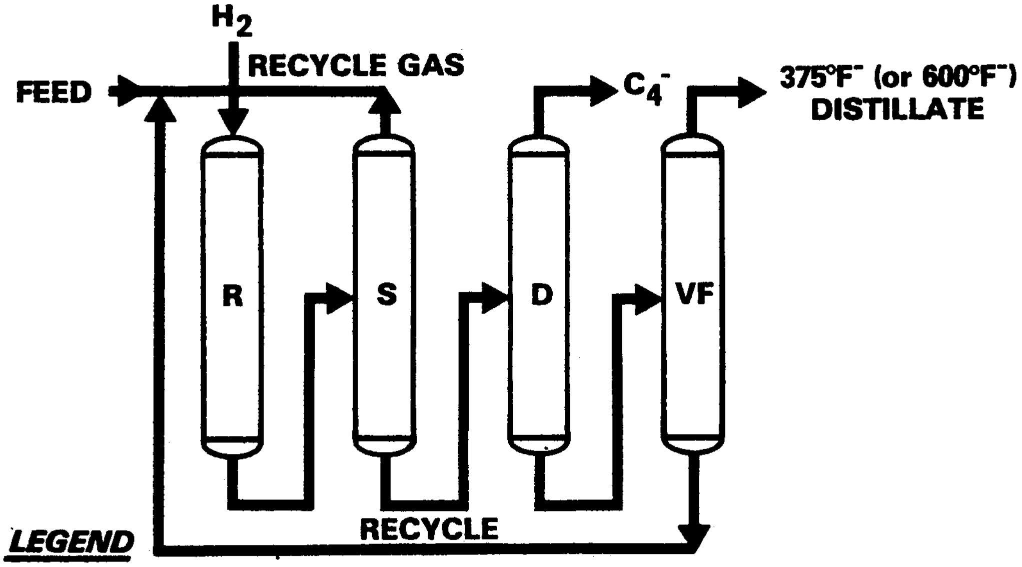


FIGURE 3

BENCH-SCALE UNIT FOR SECOND-STAGE HYDROCRACKING



LEGEND

D = DEBUTANIZER
R = REACTOR
S = SEPARATORS
VF = VACUUM FRACTIONATOR

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FIGURE 4

HYDROCRACKING TO FUEL OIL

VOL-% YIELD vs. H_2 CONSUMPTION

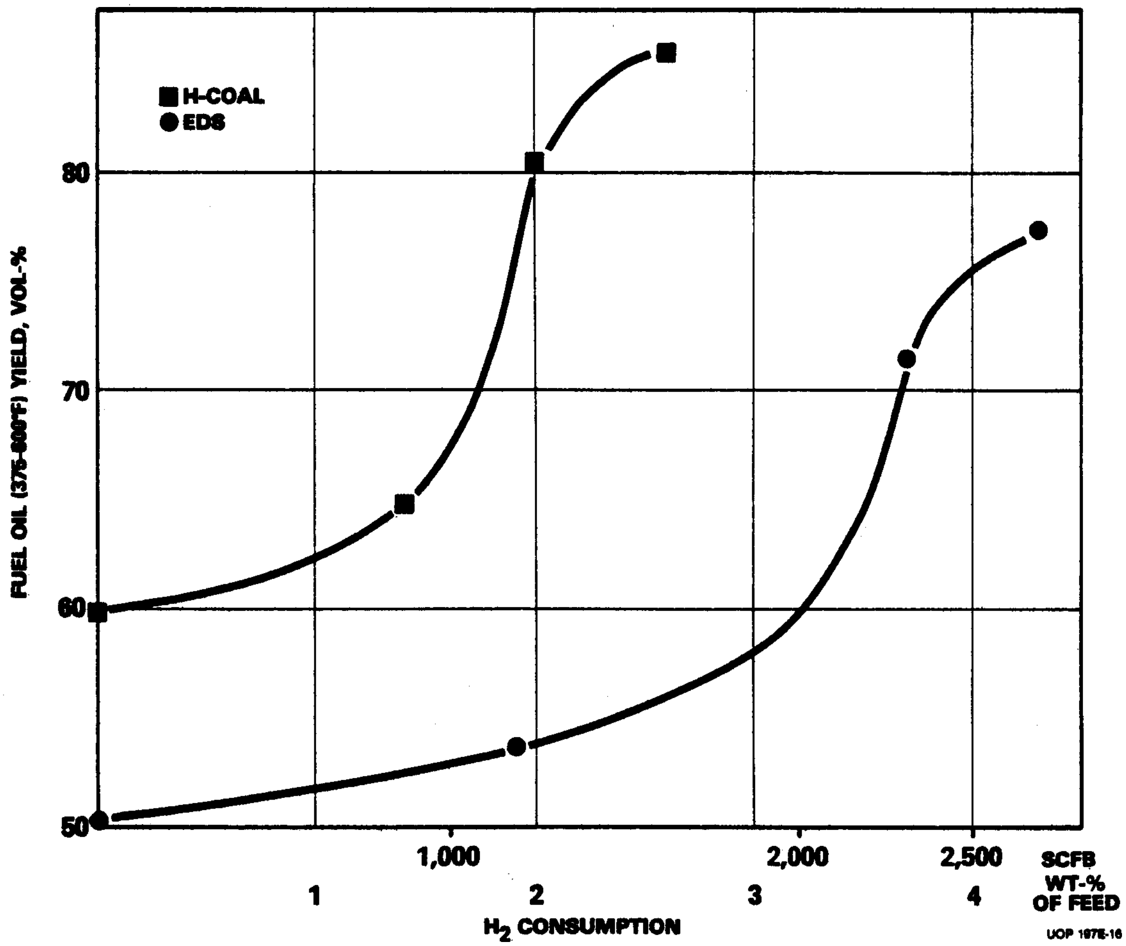


FIGURE 5

HYDROCRACKING TO FUEL OIL

RECOVERABLE H_2 vs. H_2 CONSUMPTION

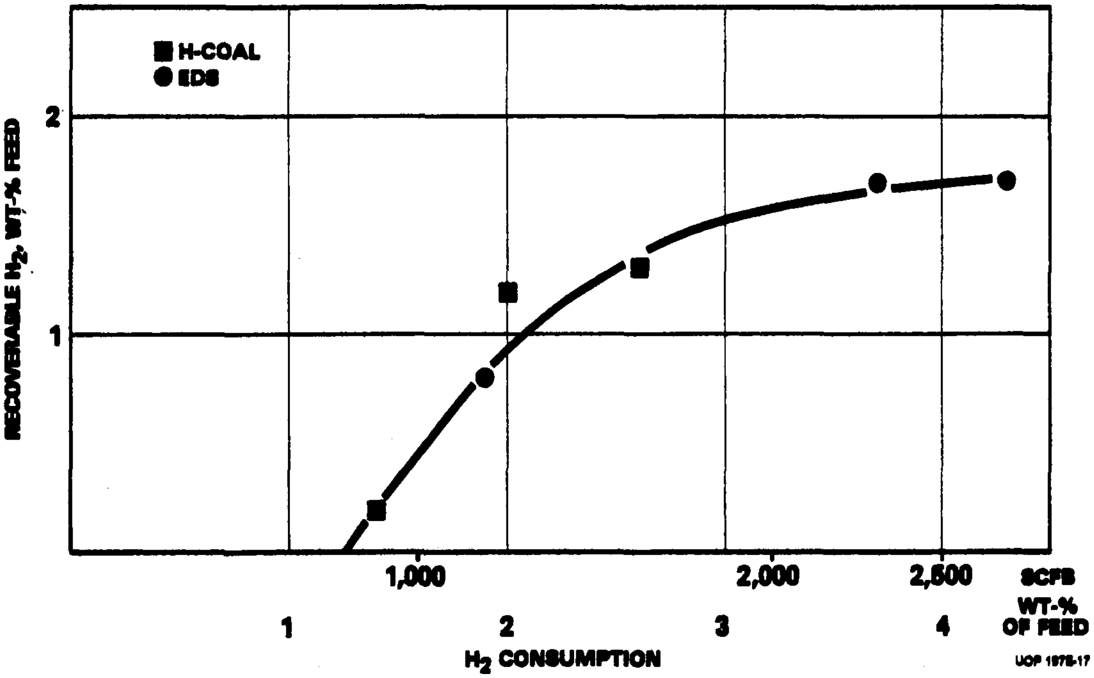
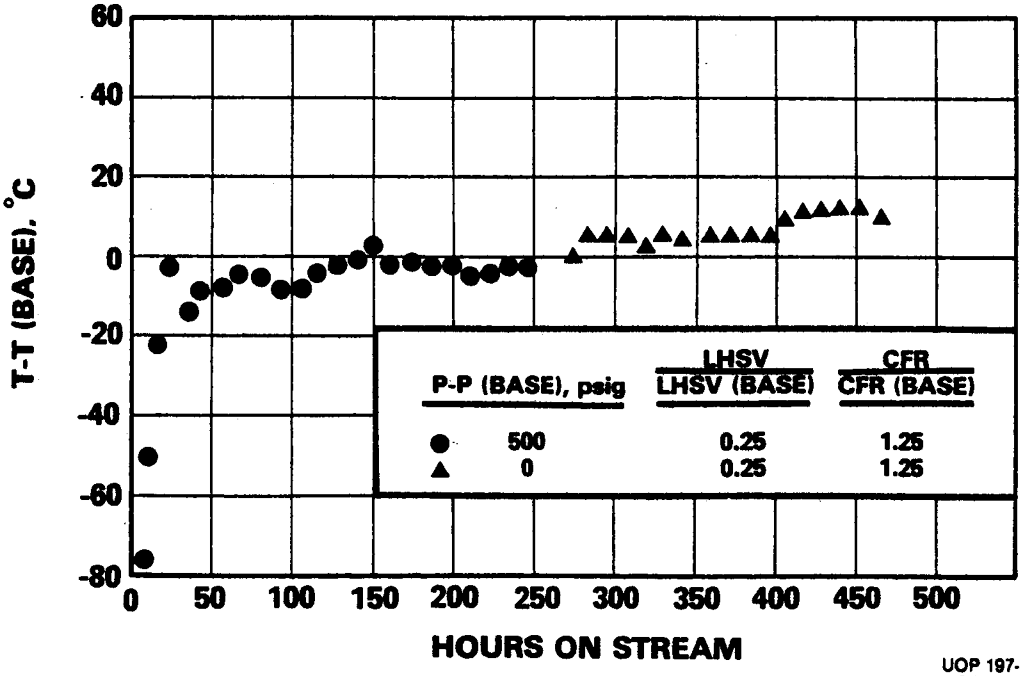


FIGURE 6

TEMPERATURE vs. TIME

SECOND-STAGE HYDROCRACKING OF H-COAL GAS OIL TO FUEL OIL

PLANT 638H, RUN 14



UOP 197-13
UOP 197B-16

FIGURE 7

TEMPERATURE vs. TIME

HYDROCRACKING HYDROTREATED EDS LIQUID PRODUCT 3532-8 TO FUEL OIL-PLANT 638, RUN 23

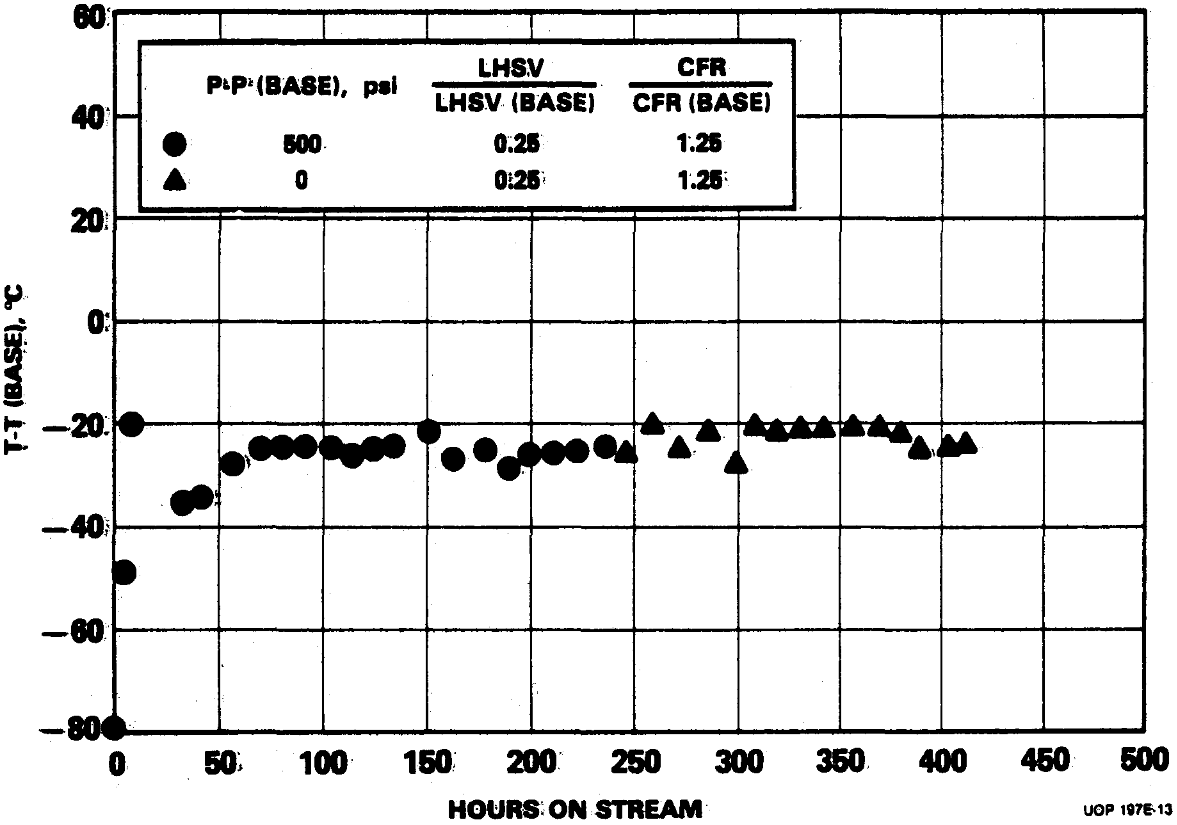
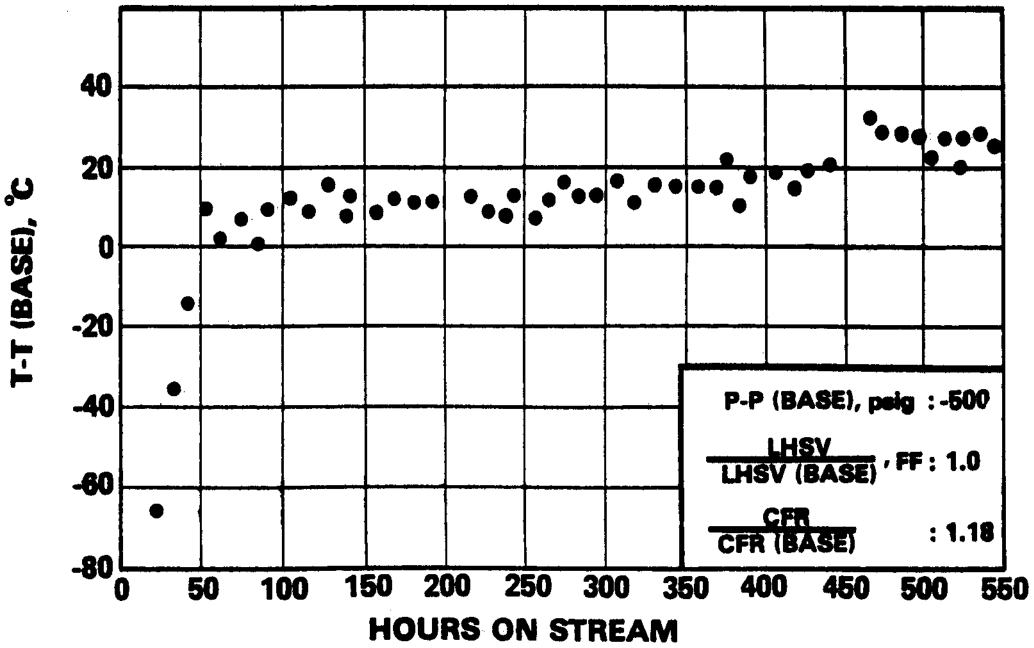


FIGURE 8

TEMPERATURE vs. TIME

SERIES FLOW SECOND-STAGE HYDROCRACKING OF H-COAL GAS OIL TO GASOLINE

PLANT 536, RUN 678 (SECOND REACTOR)



UOP 197-15
UOP 197B-12

FIGURE 9

TEMPERATURE vs. TIME

SERIES FLOW HYDROCRACKING OF EDS LIQUID PRODUCT 3532-9 TO GASOLINE-PLANT 601, RUN 779, FIRST REACTOR

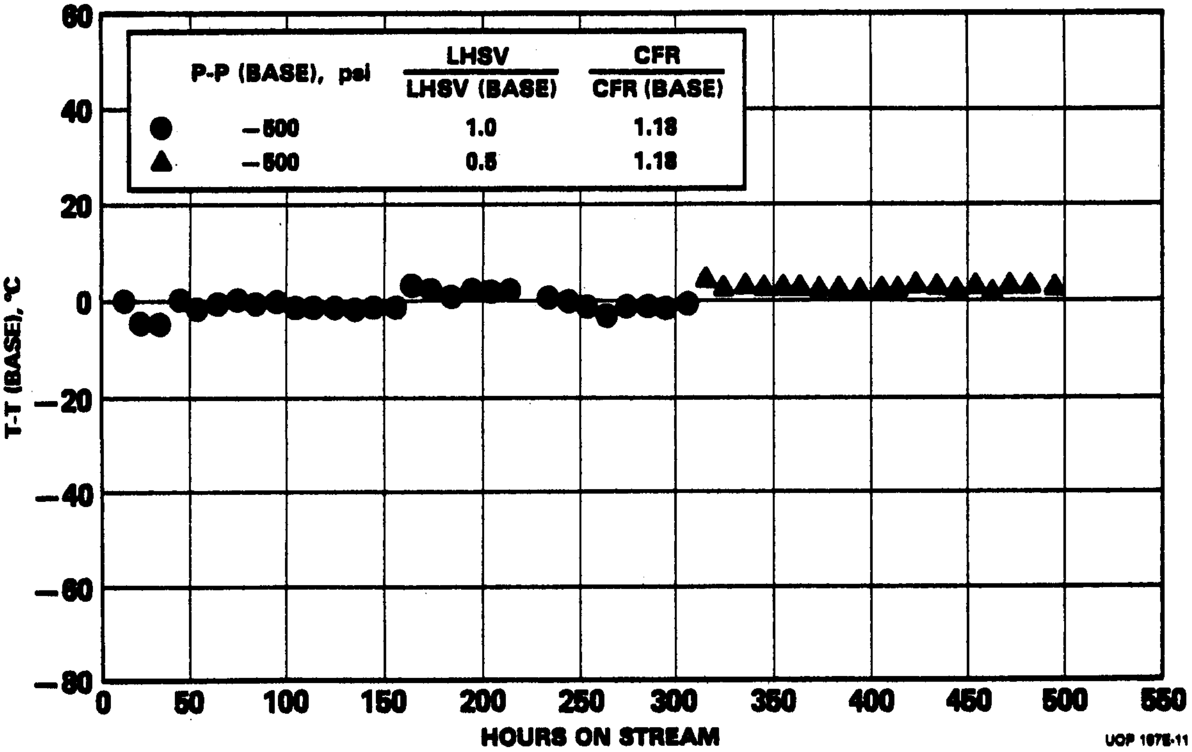


FIGURE 10

TEMPERATURE vs. TIME

SERIES FLOW HYDROCRACKING OF EDS LIQUID PRODUCT 3532-9 TO GASOLINE-PLANT 601, RUN 779, SECOND REACTOR

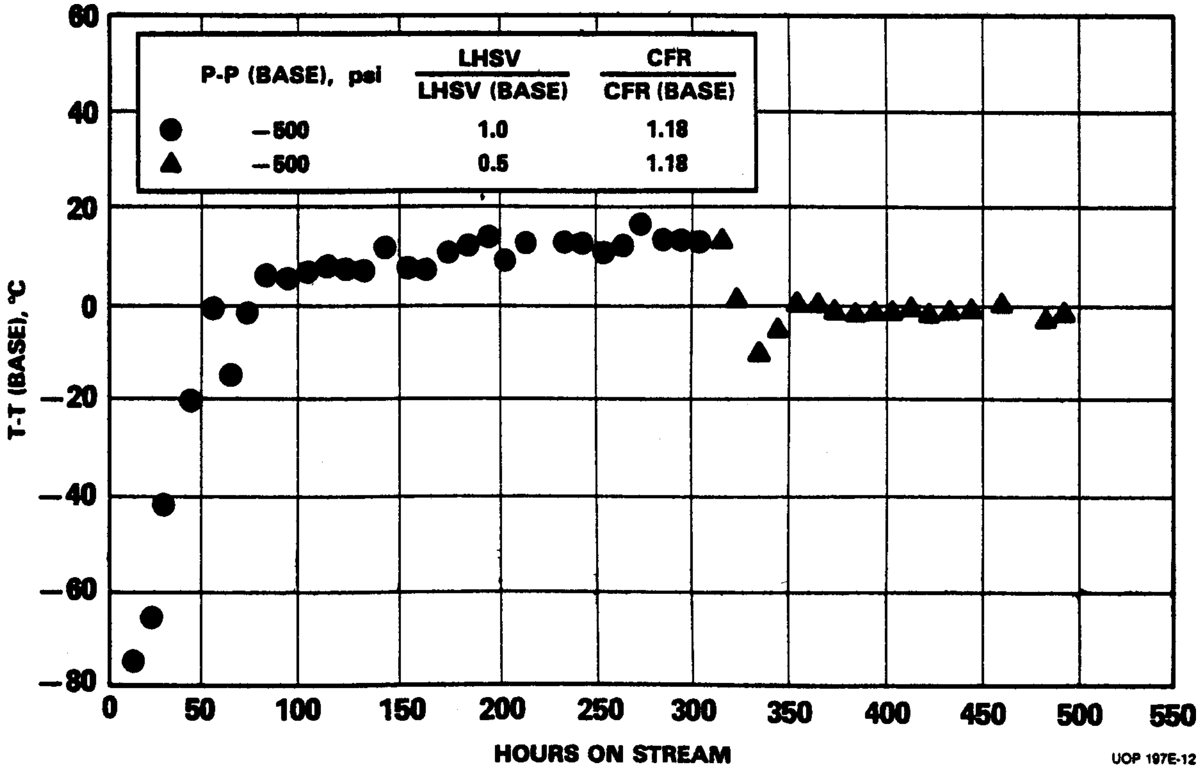


FIGURE 11

SMALL SCALE FLUID CATALYTIC CRACKER

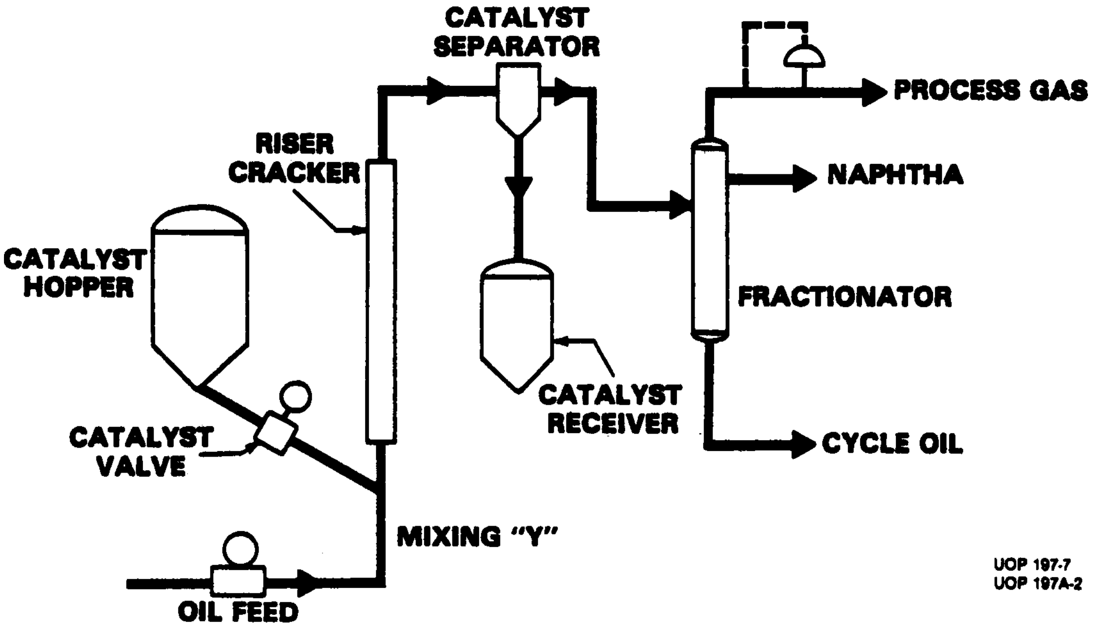


FIGURE 12

COAL DERIVED FCC FEEDSTOCKS

SULFUR CONTENT vs. HYDROGEN CONTENT

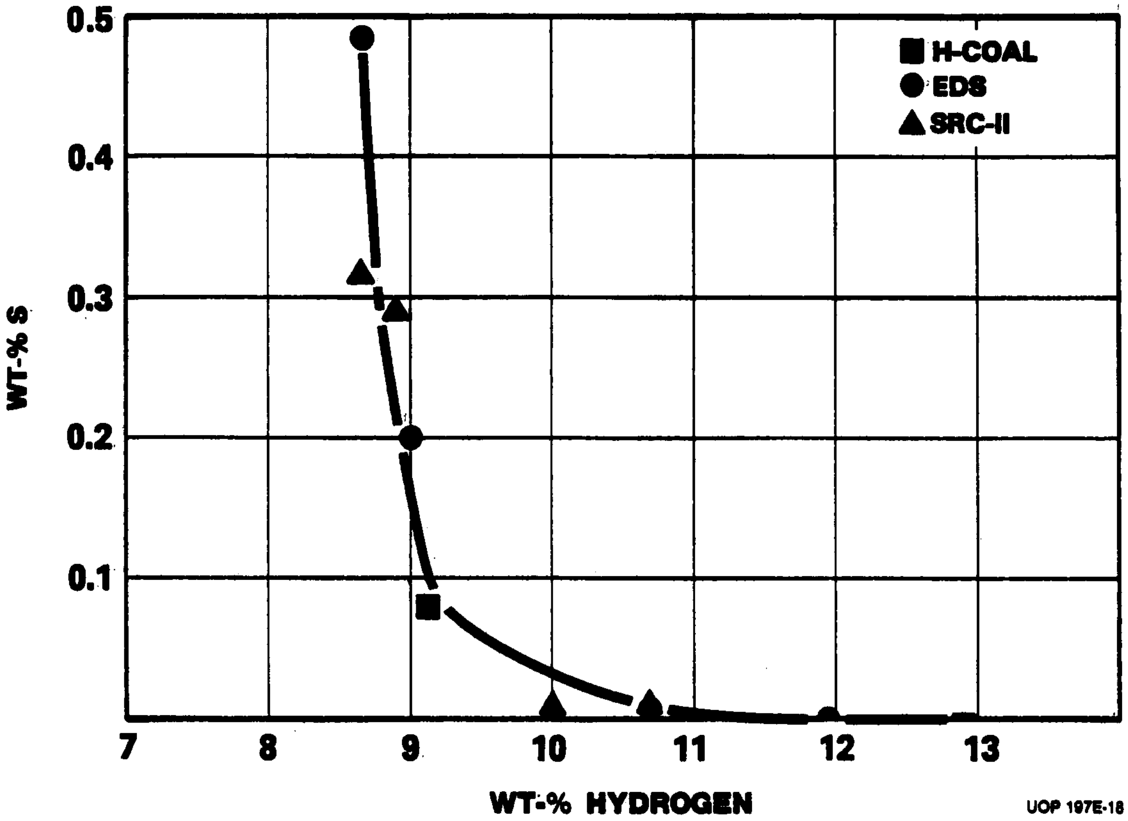


FIGURE 13

COAL DERIVED FCC FEEDSTOCKS

NITROGEN CONTENT vs. HYDROGEN CONTENT

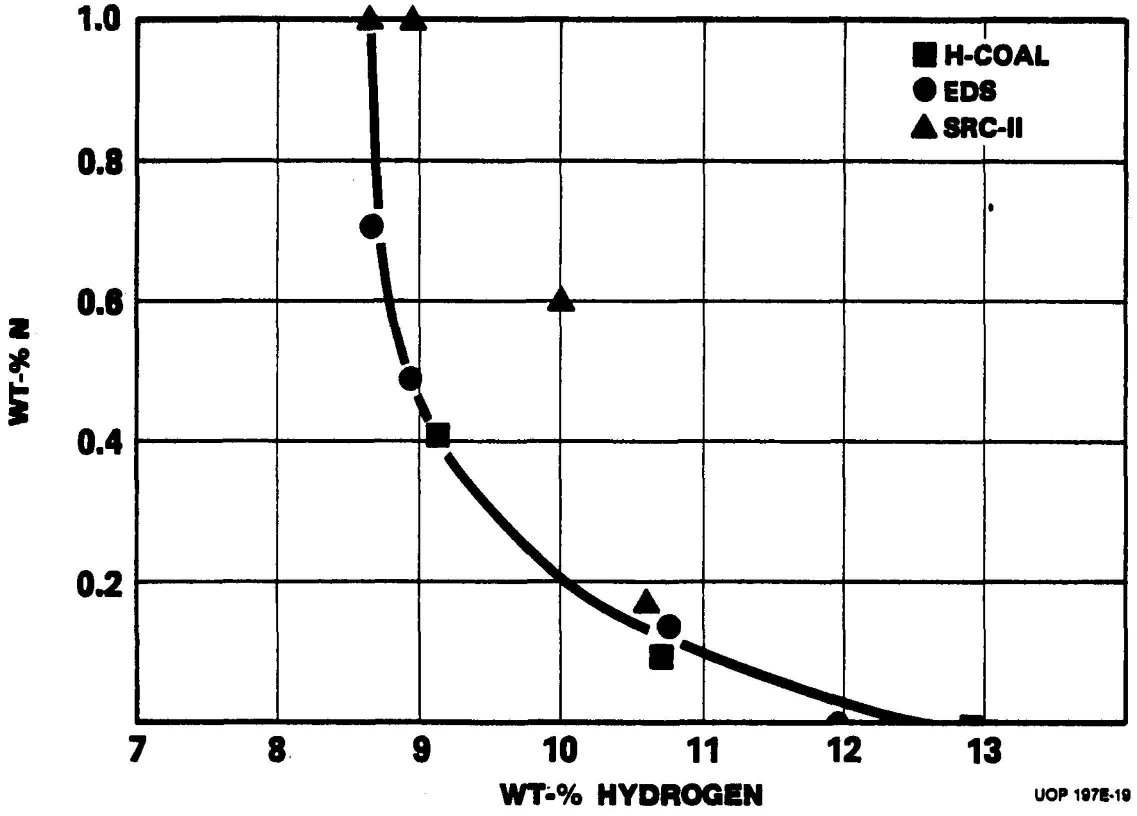


FIGURE 14

COAL DERIVED FCC FEEDSTOCKS

AROMATIC CONTENT vs. HYDROGEN CONTENT

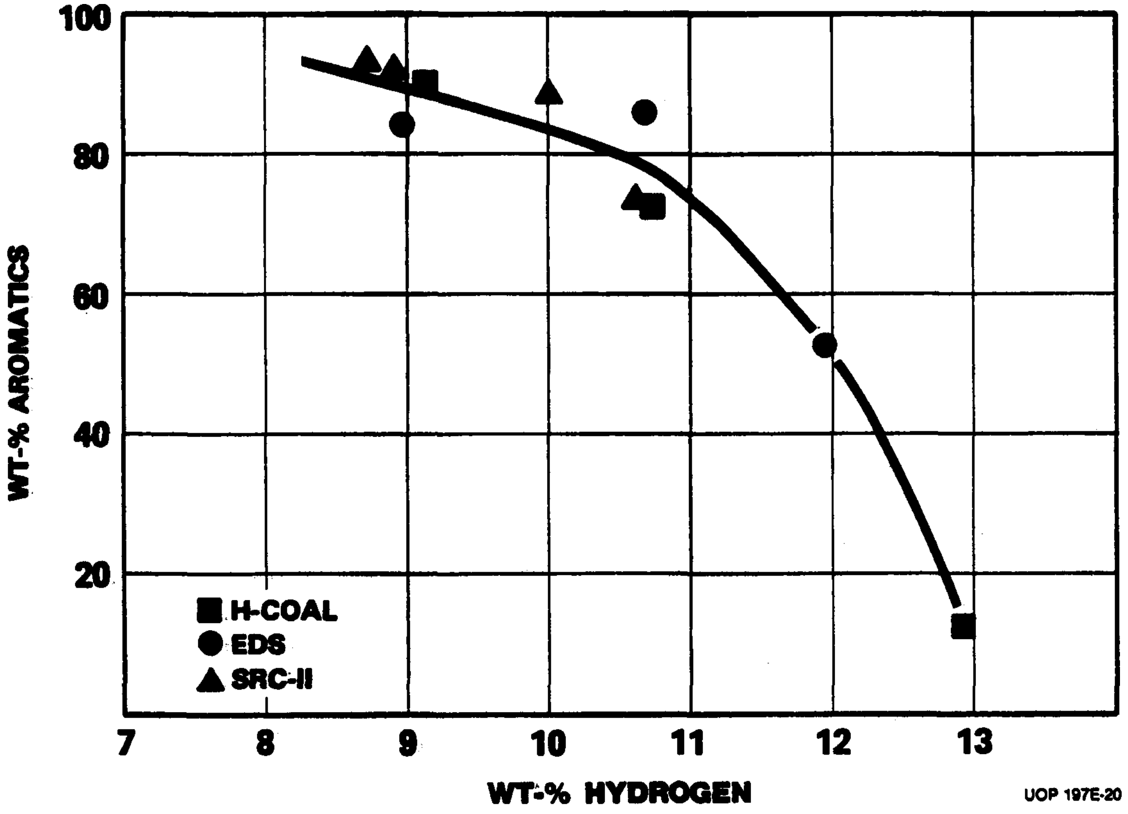


FIGURE 15

FCC CONVERSION OF COAL DERIVED FEEDSTOCKS

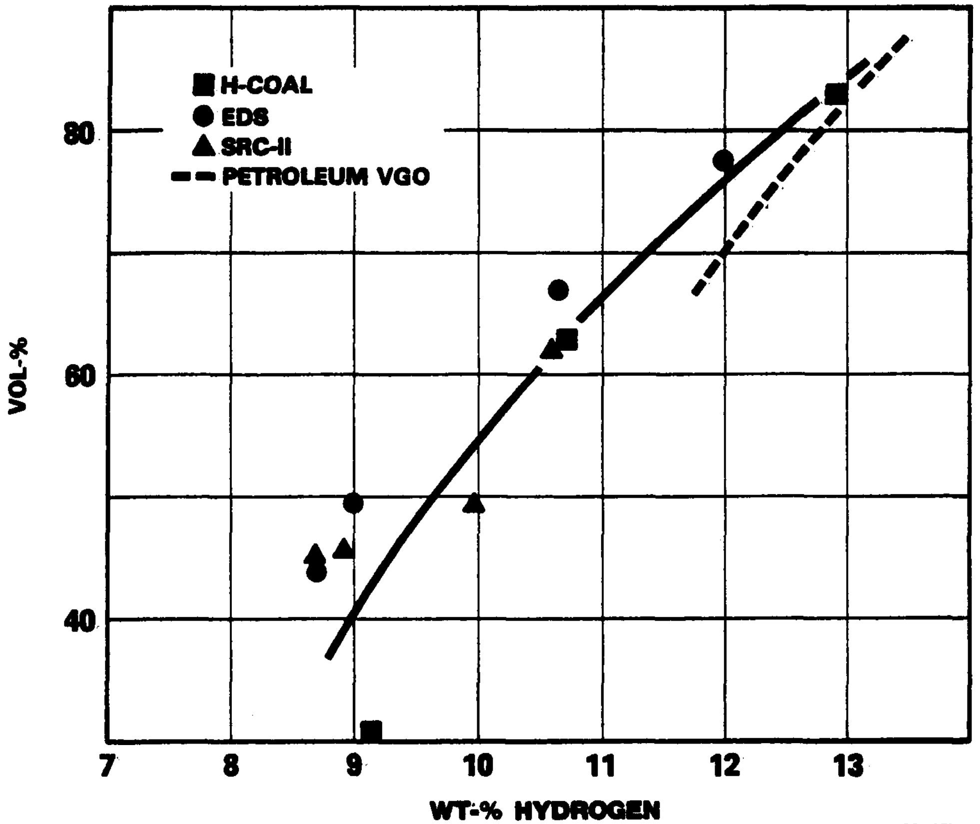


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FIGURE 16

FCC C_5+ GASOLINE YIELD FROM COAL DERIVED FEEDSTOCKS

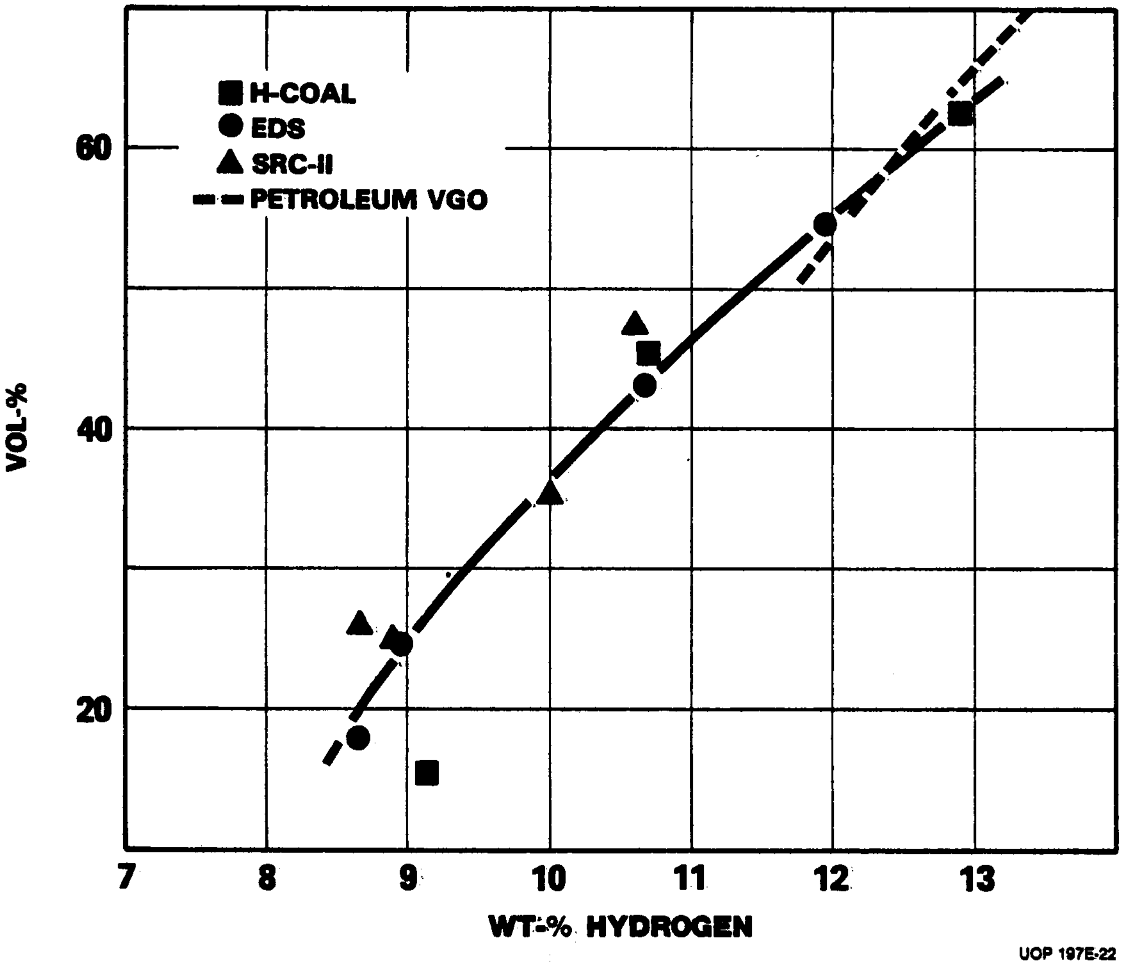

FIGURE 17

FCC C_4^- YIELD FROM COAL DERIVED FEEDSTOCKS

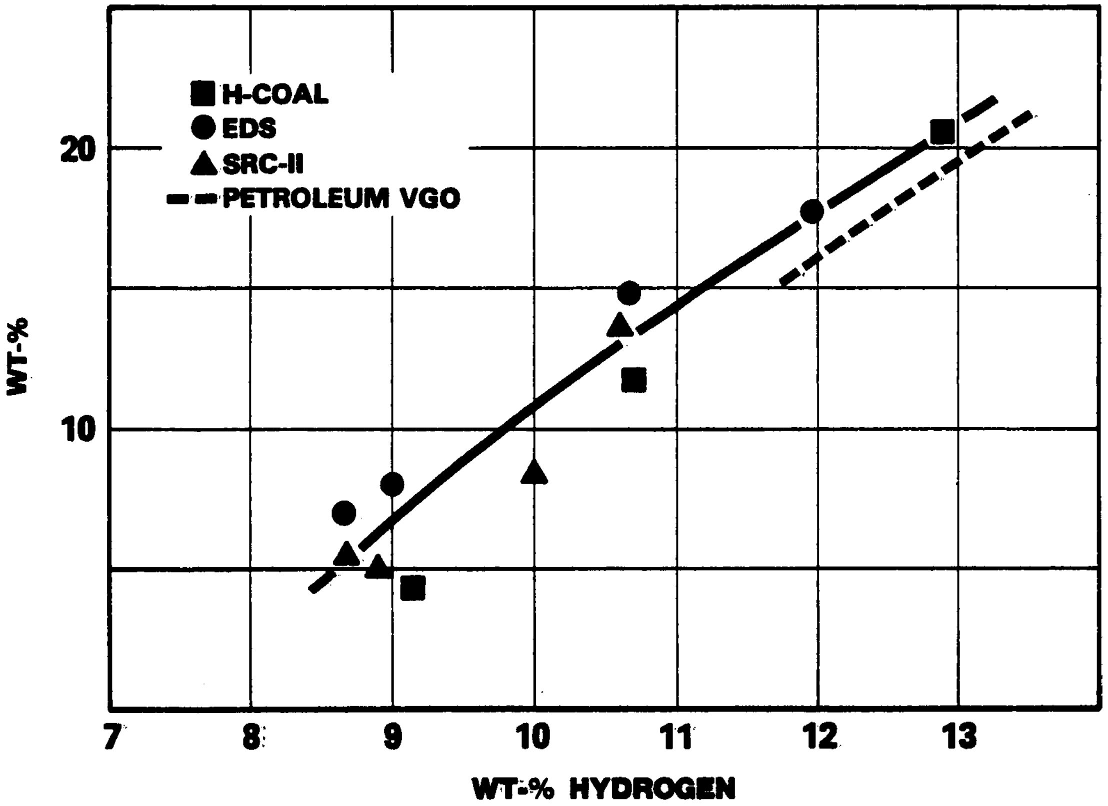

FIGURE 18

FCC CARBON YIELD FROM COAL DERIVED FEEDSTOCKS

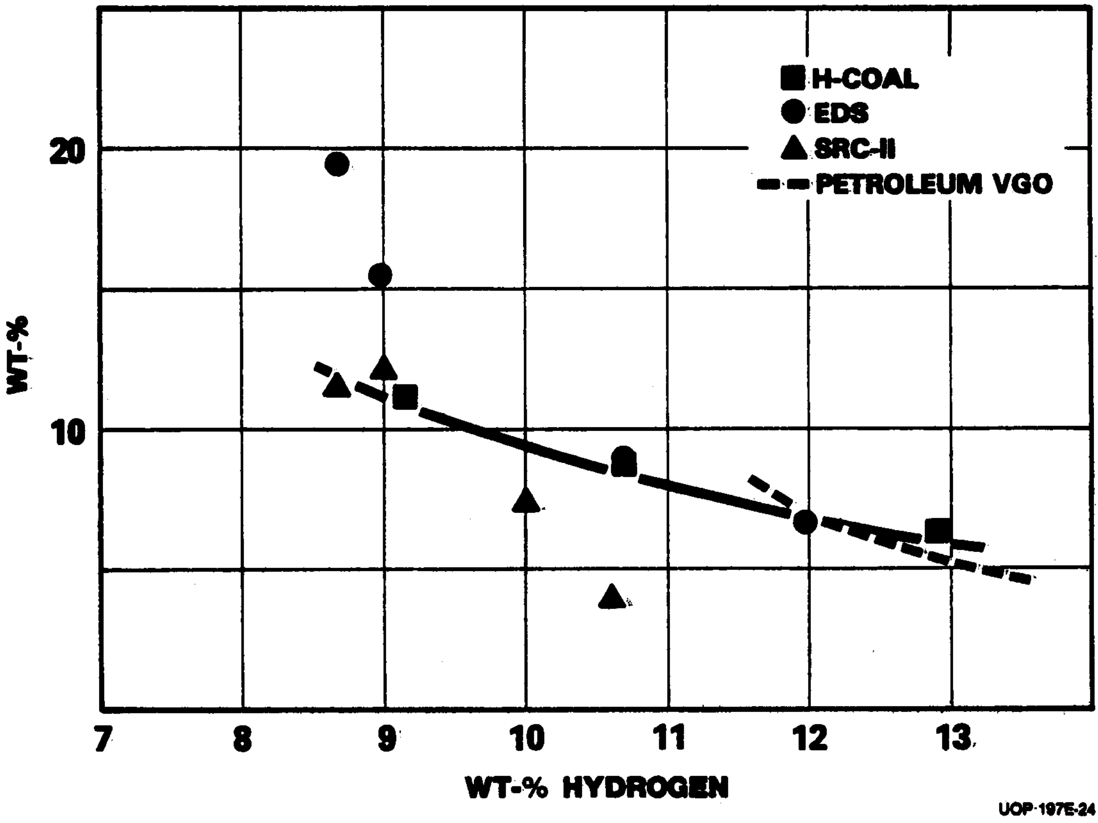

FIGURE 19

NAPHTHA HYDROTREATING PLANT

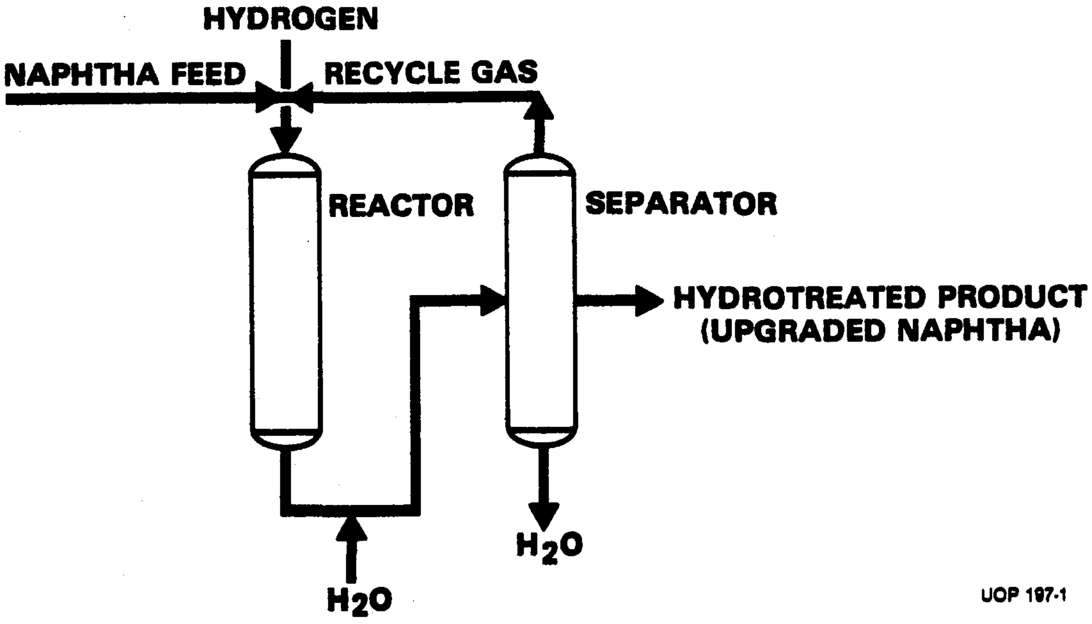

FIGURE 20

NAPHTHA REFORMING PLANT

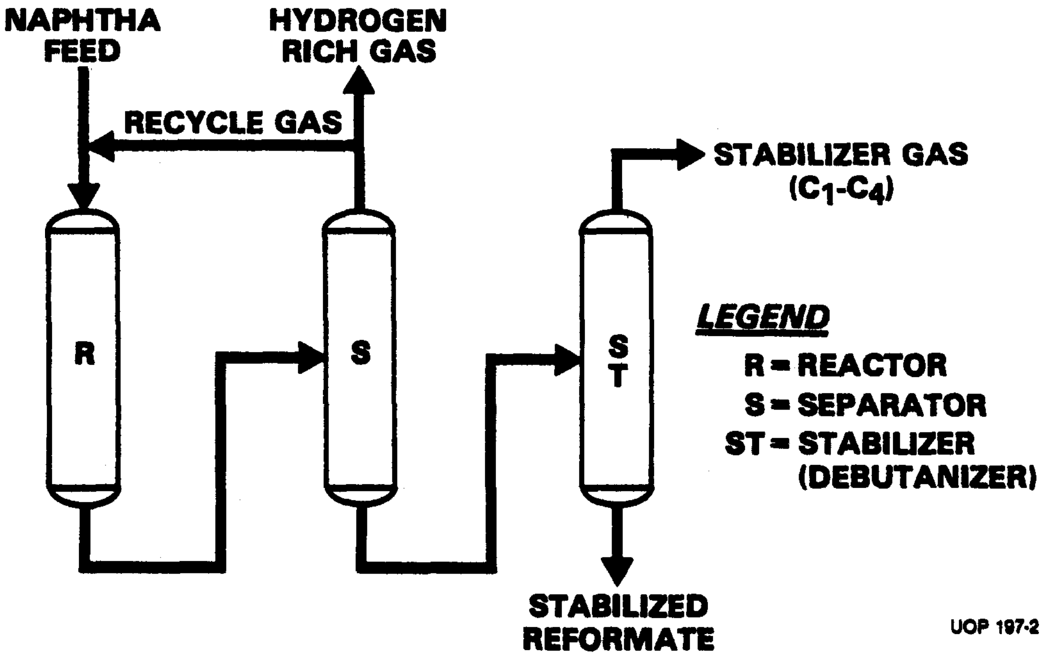

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FIGURE 21

YIELD-OCTANE CURVES FOR H-COAL PROCESS DERIVED NAPHTHAS

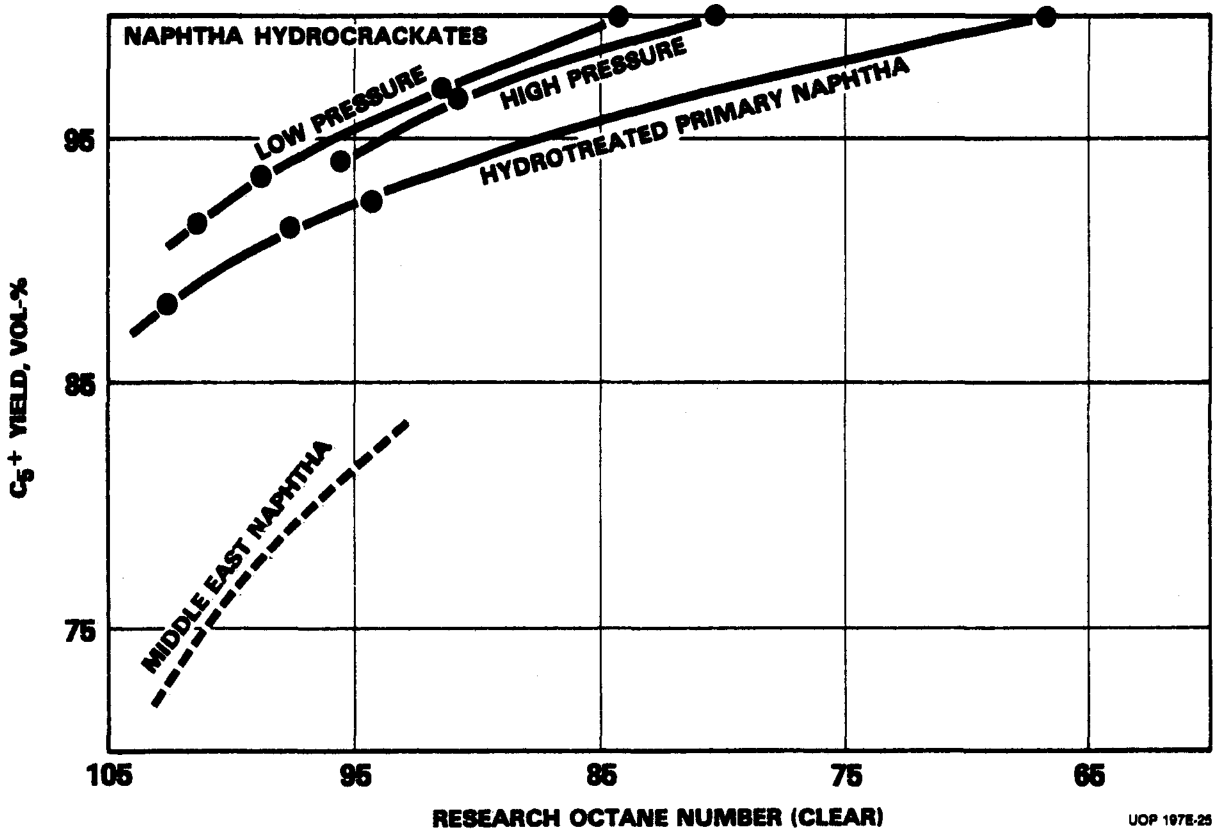


FIGURE 22

YIELD-OCTANE FOR EDS PROCESS DERIVED NAPHTHAS

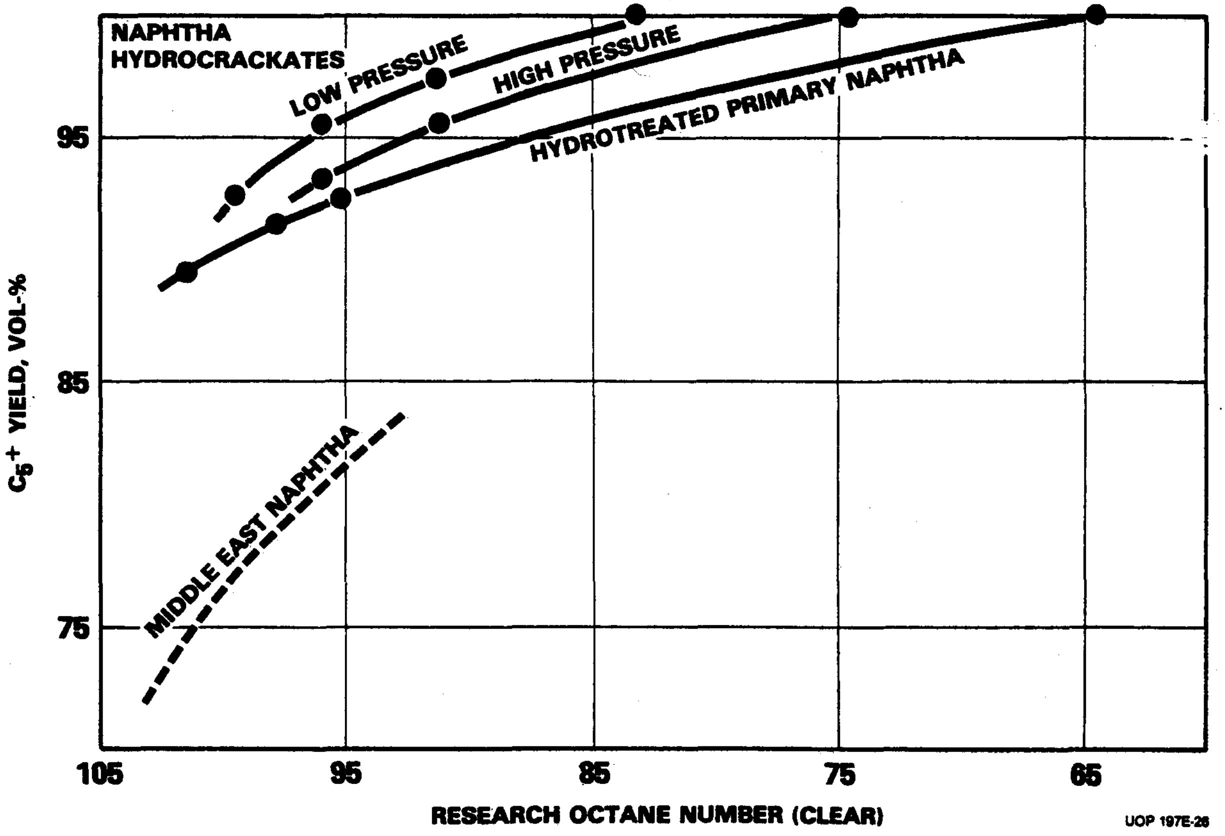


FIGURE 23

YIELD-OCTANE CURVE FOR SRC-II DERIVED NAPHTHA

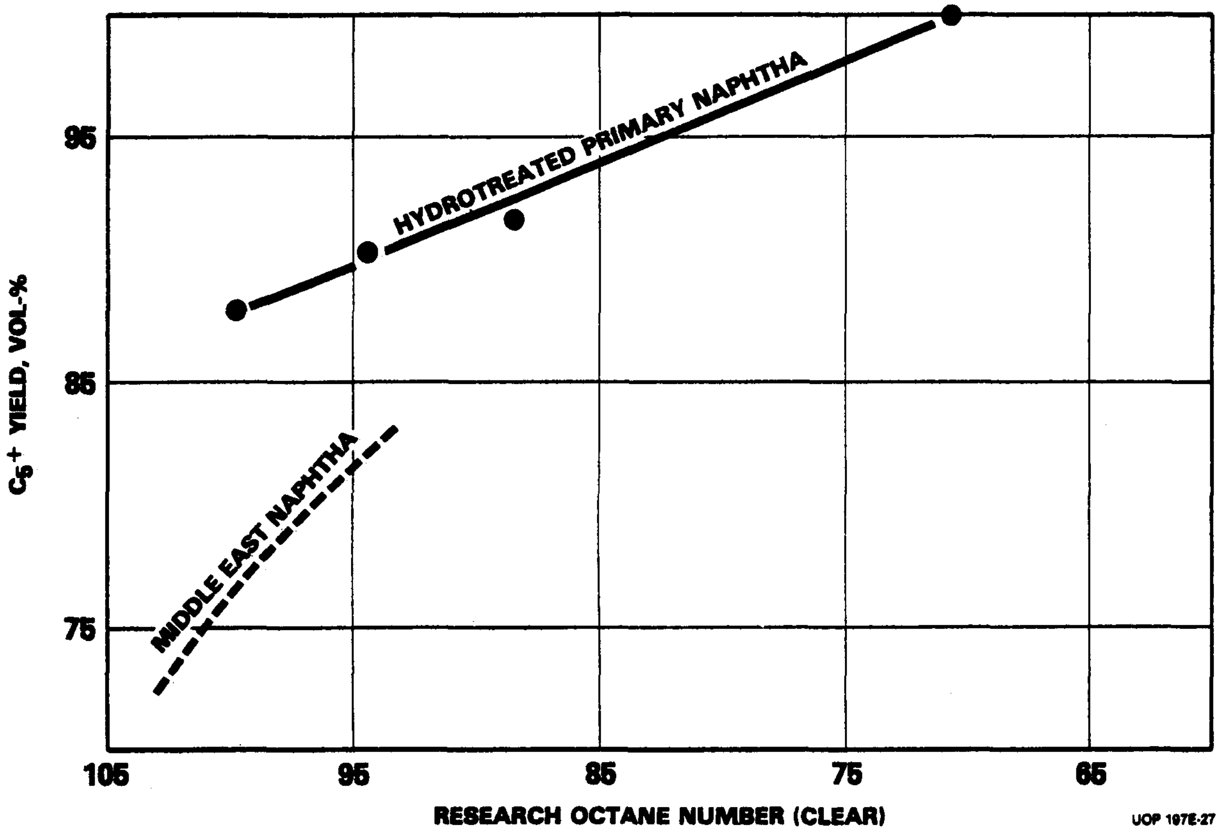


FIGURE 24

RESEARCH OCTANE NO. vs. AROMATIC CONTENT EDS PROCESS NAPHTHAS

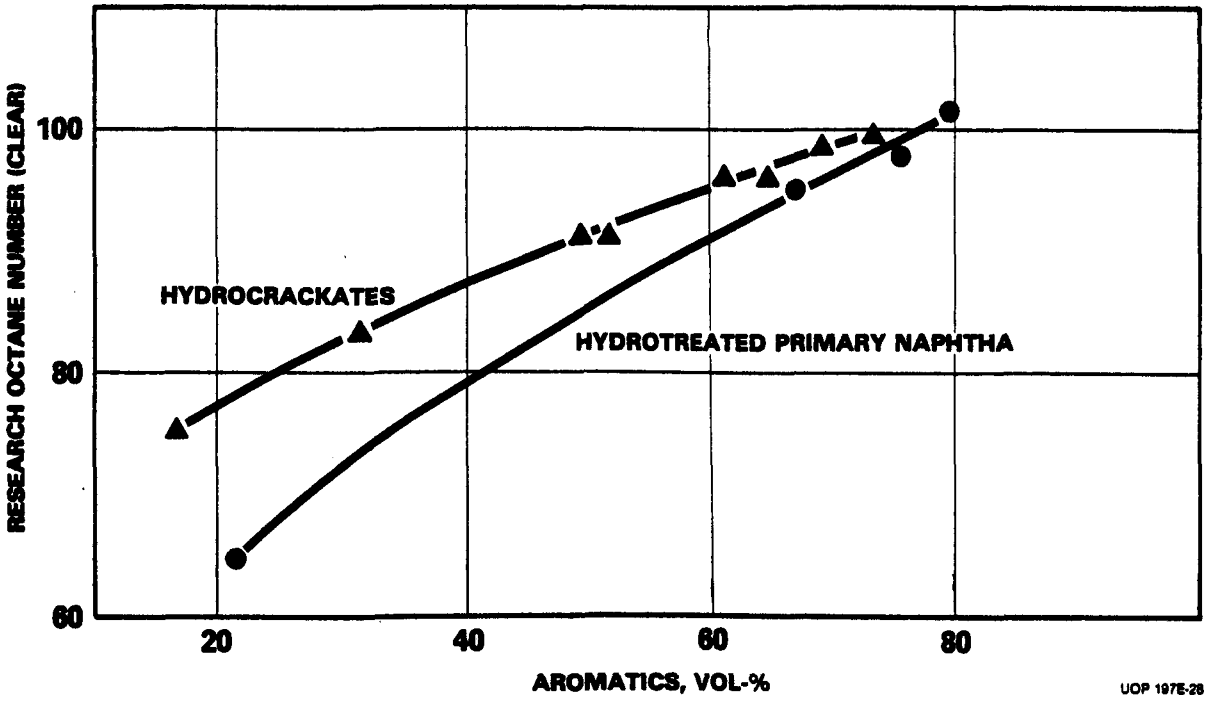
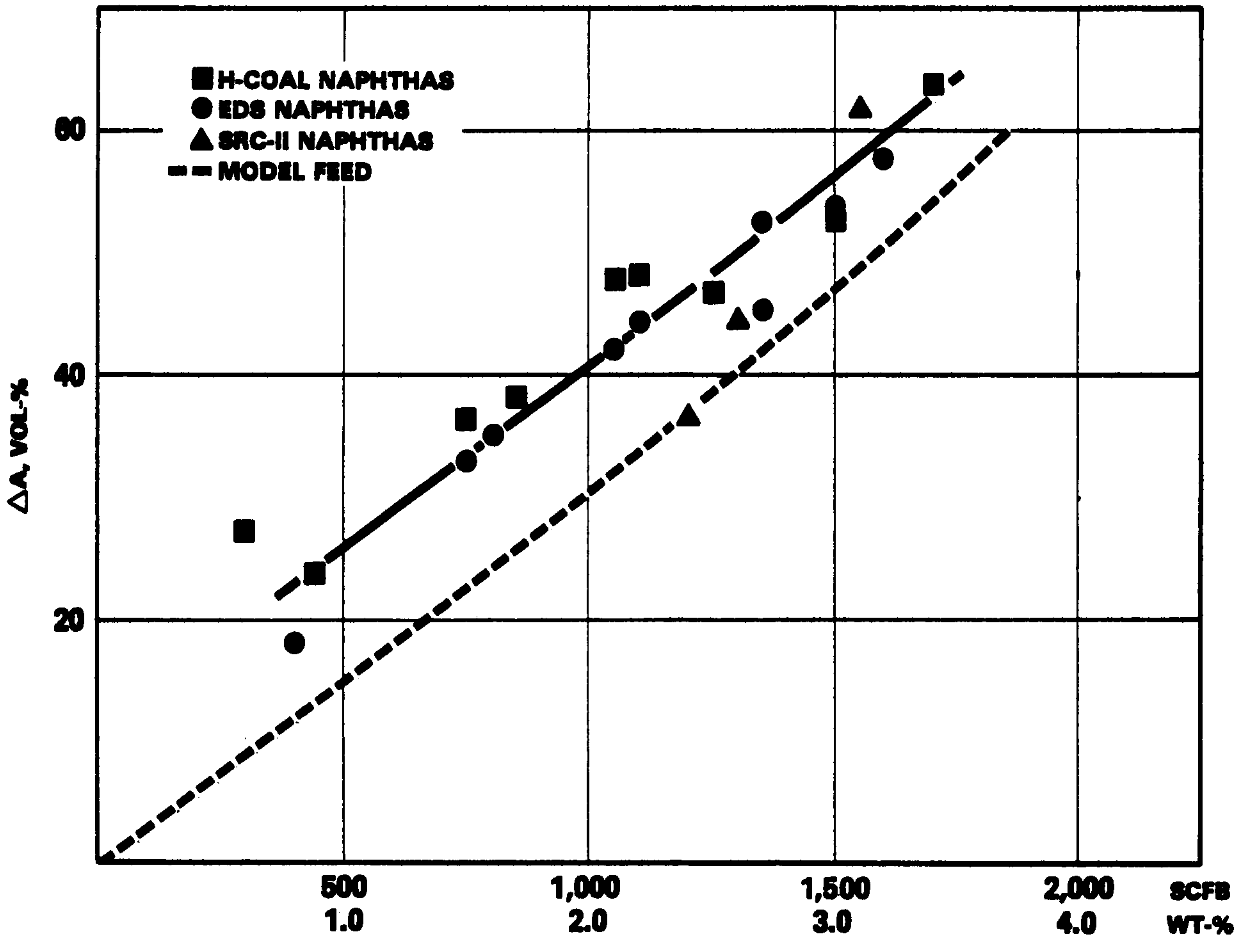


FIGURE 25

INCREASE IN AROMATICS CONTENT BY REFORMING vs. H_2 YIELD



UOP 1978-29

APPENDIX A

KINETICS OF COAL DISTILLATE HYDROTREATING

by

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KINETICS OF COAL DISTILLATE HYDROTREATING

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ABSTRACT

Samples of gas oils derived from the Exxon Donor Solvent (EDS), Solvent Refined Coal (SRC-II) and H-Coal coal liquefaction processes were processed over hydrotreating catalysts to determine their processability relative to conventional petroleum derived charge stocks. Conversions of sulfur, nitrogen and oxygen were examined as a function of relative reactor temperature, pressure and space velocity for each charge stock. A kinetic model was devised to express and compare processability over a wide range of process conditions.

INTRODUCTION

The abundance of the world's coal resources makes coal an attractive candidate for supplying additional energy needs. In addition to the traditional use in electrical power generation, one area of active research and development in the United States is production of liquid fuels from coal. The liquefaction process can be effected by conversion of the coal to synthesis gas (carbon monoxide and hydrogen) and, subsequently, to light and medium boiling range hydrocarbon products using processes such as the Fischer-Tropsch reaction. Alternatively, the coal can be liquefied directly without conversion to a gaseous intermediate. The heavy oil (or syncrude) derived from direct liquefaction can then be converted into high value liquid products.

An attractive method for removing heteroatoms such as nitrogen, sulfur and oxygen from the syncrude is the HC Unibon® process. This process involves catalytic reaction of the charge stock with hydrogen at elevated temperature and pressure. Since the HC Unibon process has been used successfully with a large number of petroleum derived charge stocks, extension to coal-derived liquids is an attractive route, particularly if maximum product slate flexibility is desired. The purpose of this paper is to compare the processability of three coal-derived heavy oils with each other and a typical Middle East petroleum vacuum gas oil (VGO).

EXPERIMENTAL

Charge Stocks

The following coal-derived charge stocks were studied (listed as process name, supplier and coal source): Solvent Refined Coal (SRC-II), Tacoma Pilot Plant, Powhatan No. 5; Exxon Donor Solvent (EDS), Exxon CLPP, Illinois No. 6; and H-Coal, Hydrocarbon Research Trenton PDU, Illinois No. 6. Analyses of these coal distillates and a Middle East petroleum derived reference vacuum gas oil are given in Table 1. All of the coal liquids show lower hydrogen, sulfur and nitrogen concentrations than the petroleum vacuum gas oil. The oxygen, Conradson carbon and heptane insoluble concentrations were found to be higher for the coal-derived liquids. The H-Coal product was found to have the lowest concentration of nitrogen, oxygen, sulfur, Conradson carbon and heptane insoluble concentrations and the highest hydrogen concentration of the three coal-derived liquids. This may be a result of the direct catalyst interaction during the liquefaction process.

Pilot Plant Processing

Each charge stock was processed using the apparatus shown in Figure 1. The liquid feed was charged to the reactor with recycle gas (mostly hydrogen) and enough fresh hydrogen to maintain pressure. The reactor effluent liquid was separated from the recycle gas using a dual temperature gas-liquid separator system. The separator underflow was collected in a product vessel after degassing with nitrogen to remove residual hydrogen sulfide. Conversions of nitrogen, sulfur and oxygen compounds in the charge stocks to ammonia, hydrogen sulfide and water were determined as functions of reactor pressure, temperature and space velocity. A comparison to the typical Middle East vacuum gas oil charge stock operation was then made.

RESULTS

A consideration of downstream processing requirements is necessary to maximize the benefit of the HC Unibon process. The effect of several charge stock component types is known. For example, inhibition of hydrocracking over a platinum on silica-alumina catalyst by heteroatom components has been reported (1). Some of the data from that study, in which the temperature required to obtain a constant liquid product API gravity keeping all other conditions constant, are given in Table 2. These data show the highly deleterious effect that nitrogen compounds can impart to down stream catalyst systems. For this reason, experimental conditions were adjusted to maximize information regarding denitrification.

Table 3 shows that the rate of heteroatom compound conversion varies with charge stock. The conversion rate for heteroatom types was found to increase in the order:

$$O < N < S$$

for the coal derived charge stocks investigated in this study. As a result of the higher desulfurization rates, the organic sulfur compounds in the charge stocks were almost completely converted to hydrogen sulfide.

Nitrogen Conversion

Nitrogen conversion was found to proceed according to apparent pseudo-first order kinetics over a wide range of conversion values:

$$\frac{dC}{dt} = -kC,$$

where C is the concentration of organic nitrogen, t represents the residence time, and k is a pseudo-first order rate constant which increases with increasing temperature and pressure. The residence time is assumed to be inversely proportional to the liquid feed charge rate. The temperature dependence of the reaction rate can be approximated using the Arrhenius equation:

$$k = Ae^{-Ea/RT}$$

where A is a constant, Ea is the activation energy, R is the gas constant and T is temperature (K). Deviation from this equation was slight over the forty degree temperature range studied. A combination of the two equations to describe time and temperature yields the following relationship:

$$-\frac{dC}{dt} = Ae^{-Ea/RT}C$$

$$\ln \frac{C_o}{C} = Ate^{-Ea/RT}$$

Examples of the first order fit of data are shown in Figure 2. Although data for mechanism evaluation are normally obtained at low to moderate conversion values, processability correlations compatible with down stream processes require a much higher conversion. The first order fit described above fits the data remarkably well through about 99.9% conversion and probably indicates the constancy of the carbon-nitrogen bond reactivity.

The values of k were corrected to a constant temperature basis and normalized to a value of 100 for the Middle East reference charge stock. Since the overall reaction is exothermic, some deviation from an isothermal reactor profile is observed. By fitting the data obtained at various temperatures and feed rates to the model equation, it is possible to make a comparison at any conditions within the experiment range. This conversion model of temperature and charge rate is shown graphically in Figures 3-5. The reaction rate was found to increase approximately with the square of the pressure. The data in Table 4 show that the nitrogen conversion rates are 0.3-0.7 times the values derived for the Middle East vacuum gas oil.

Sulfur

The concentration of sulfur in the coal-derived charge stocks was relatively low. The lowest sulfur concentration was found for the catalytically derived H-Coal liquid. As shown in Table 3, the desulfurization rate was found to be much higher than the comparable rates for nitrogen and oxygen removal for the coal derived charge stocks tested.

The kinetic behavior of desulfurization has been widely examined. For example, Satterfield and Roberts (2) demonstrated first order kinetics for the desulfurization of thiophene and several other pure components. Deviation from first order kinetics in the complex charge stocks derived from petroleum has been observed (3). Although desulfurization kinetics are often fit to a second order model, this relationship does not hold at very high conversions. At very high conversions, the rate is usually lower than predicted by the second order fit (4). A proposal for an explanation of this behavior has been made by Wei and Hung (5). In that explanation, a kinetic equation using two first order systems having different rate constants was developed.

As a result of the very high conversion values, lack of fit to a simple processability kinetic equation and extremely low product sulfur concentrations, a model for sulfur conversion was not pursued.

Oxygen

Oxygen was found to be more difficult to remove from the charge stocks than either nitrogen or sulfur. Although the conversion of oxygen approximates first order, the fit is not good enough to quantify with the equations used for nitrogen conversion. An estimate of processability can be made, however, using the data in Table 5. The relative residence times have been indicated using the assumption that residence time is proportional to the inverse of the charge rate. These data show that the oxygen conversion rate for the H-Coal liquid is higher than for EDS and SRC-II derived liquids at conversions below about 80%. Above 80% conversion, the three charge stocks show almost the same processability for oxygen conversion. The oxygen conversion rates of these coal-derived liquids is roughly the same as that observed for the petroleum VGO.

Deviation from a first order fit is probably caused by different reactivity of the oxygen compound types. For example, 53% of the oxygen in the H-Coal derived kerosine is extractable into aqueous sodium hydroxide. However, only 17% of the hydrotreated product oxygen is extractable into aqueous sodium hydroxide. Mass spectroscopic analysis of chromatographically separated samples shows that the extractable components are phenolic and the non-extractable compounds contain a high concentration of cyclic ethers. A comparable analysis of the 300°C + boiling point fraction of the H-Coal charge stock shows oxygenated components having multiple oxygen atoms per molecule and approximately equal division between phenolic-less polar (probably cyclic ether) types. The product 300°C + fraction shows predominently non-polar types having only one oxygen atom per molecule. These data, which indicate a higher reactivity of the phenolic compounds relative to neutral oxygenates, are analogous to results obtained with sulfur analogues (6).

CONCLUSION

Conversion of the heteroatomic compound types present in distillate liquids derived from the Exxon Donor Solvent (EDS), solvent refined coal (SRC-II) and H-Coal processes was found to proceed similarly to a typical Middle East petroleum vacuum gas oil. Nitrogen conversion was found to fit pseudo-first order kinetics over a very large conversion range for all of the charge stocks studied. Despite the lower concentration of nitrogen in the coal derived charge stocks, the lower reaction rate requires a modest increase in reaction severity to produce nitrogen concentrations equal to values obtained for the petroleum derived charge stocks.

In all cases conversion of oxygen containing compounds proceeded at a lower rate than conversion of sulfur and nitrogen. However, concentrations in the range studied are not expected to interfere with down stream processing options.

The rate of sulfur conversion was found to be very high at the process conditions used in this study. Coupled with the low sulfur concentrations in the coal derived charge stocks the high reaction rates result in very low product sulfur concentrations.

ACKNOWLEDGMENT

The data presented are partially based on results from the U.S. Department of Energy Contract EF-77-C-01-2566, "Upgrading of Coal Liquids."

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TABLE 1

PROPERTIES OF COAL-DERIVED LIQUID CHARGE STOCKS

CHARGE STOCK SOURCE	H-COAL	SRC-II	EDS	MIDDLE EAST PETROLEUM
GRAVITY, °API	10.8	9.7	7.6	24.7
DISTILLATION, ASTM D-1160, VOL-%				
IBP,°C (°F)	224(435)	197(386)	208(406)	233(451)
30%	279	229	243	400
50%	299(571)	252(486)	294(561)	426(798)
70%	331	279	382	444
90%	379(715)	341(645)	487(908)	483(901)
EP	454(850)	426(799)	526(978)	538(1001)
% OVER	99	99	96	99
HYDROGEN, WT-%	9.39	8.89	9.02	12.16
CARBON, WT-%	89.6	87.9	88.9	85.00
SULFUR, WT-%	0.070	0.34	0.671	1.79
NITROGEN, WT-%	0.39	0.83	0.473	0.94
OXYGEN, WT-%	0.51	2.07	0.941	0.11
CONRADSON CARBON, WT-%	0.08	0.38	4.0	<0.01
HEPTANE INSOLUBLES, WT-%	0.06	0.17	8.1	<0.01

UOP 880-1

TABLE 2

THE EFFECT OF HETEROATOMS ON HYDROCRACKING ACTIVITY*

	CONC., %	*TEMP. FOR CONST. API PROD., °F*
BLANK	—	691
INDOLE	0.4	789
QUINOLINE	0.4	782
CARBON DISULFIDE	5.0	702
CRESOL	2.0	695
THIOPHENE	3.8	787
QUINOLINE	0.38	

*DATA FROM COONRADT, H.L., W.K. LEAMAN, AND J.N. MIALE, PREPRINTS — DIVISION OF PETROLEUM CHEMISTRY AMERICAN CHEMICAL SOCIETY, PHILADELPHIA (1964).

UOP 550-3

TABLE 3

CONVERSION OF HETEROATOM COMPOUNDS AT CONSTANT CONDITIONS

	OXYGEN	*NITROGEN*	*SULFUR*
PETROLEUM	82.4	>99.9	99.5
H-COAL	81	94	98
EDS	80	96	99.7
SRC—II	90	93	99

UOP 550-4

TABLE 4

NITROGEN CONVERSION PARAMETERS

CHARGE STOCK SOURCE	RELATIVE RATE AT STANDARD CONDITIONS*	Ea (KCAL/MOLE)
PETROLEUM	100	21
H-COAL	30	37
SRC—II	71	32
EDS	35	25

*NORMALIZED TO 100 FOR PETROLEUM.

UOP 560-5

TABLE 5

CONVERSION OF OXYGEN-CONTAINING COMPOUNDS

(VALUES GIVEN AS 1/FEED RATE; NORMALIZED TO 100 FOR 80% PETROLEUM DEOXYGENATION.)

CHARGE	CHARGE STOCK	% DEOXYGENATION			
STOCK ORIGIN	OXYGEN (ppm)	50	70	80	90
PETROLEUM	1,093	38	62	100	—
H-COAL	5,100	8	31	69	105
EDS	9,100	33	58	58	77
SRC-II	17,600	24	39	62	77

UOP 560-10

FIGURE 1

PILOT PLANT SCHEMATIC FLOW DIAGRAM

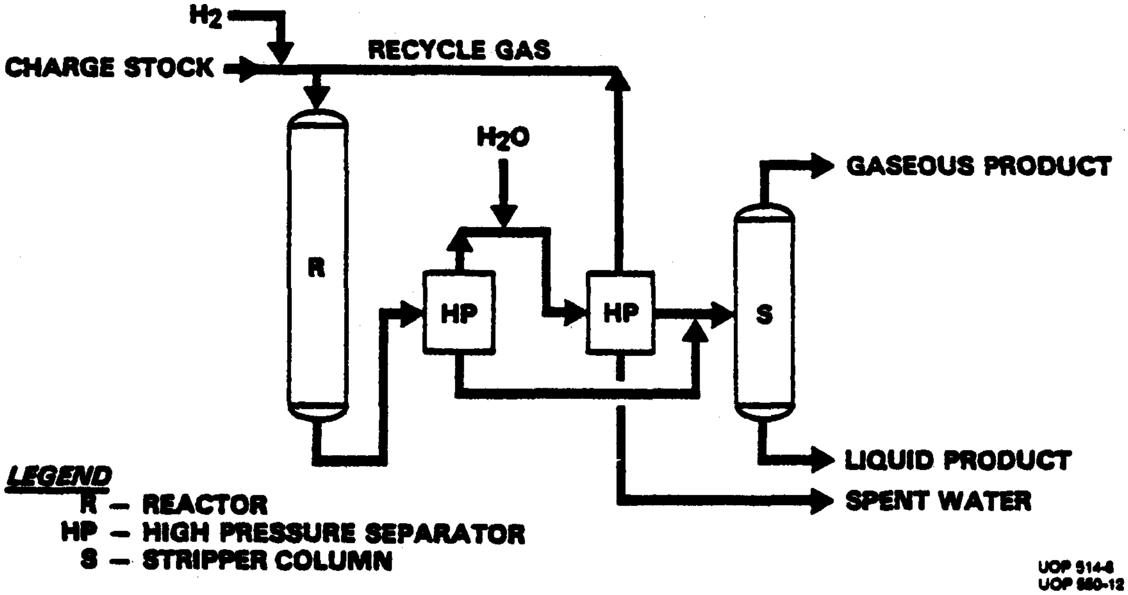


FIGURE 2

TYPICAL PETROLEUM AND COAL DERIVED LIQUID KINETIC CORRELATION

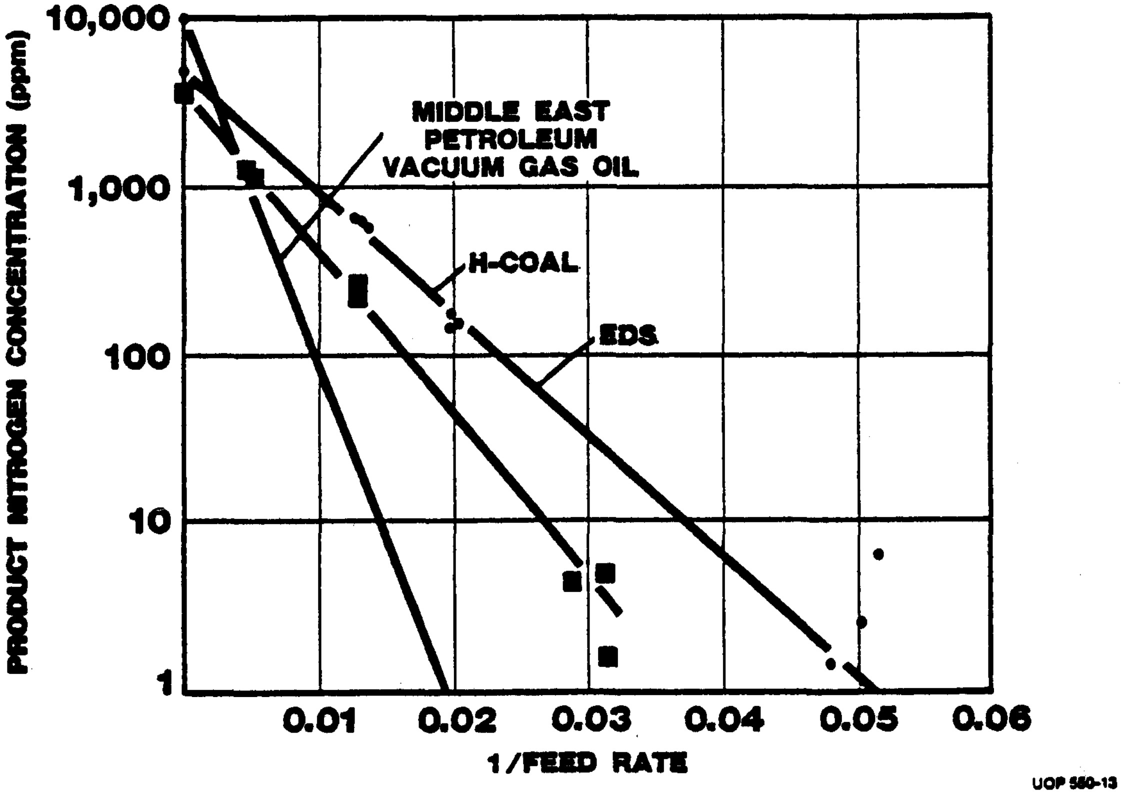
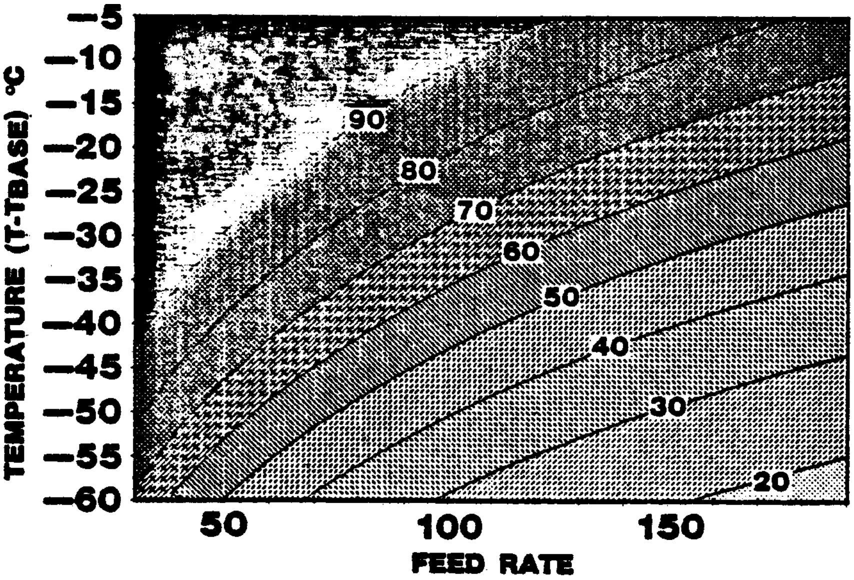


FIGURE 3

NITROGEN CONVERSION vs. TEMPERATURE AND FEED RATE – SRC-II

SHOWN AS CONSTANT CONVERSION CONTOURS – NITROGEN CONVERSION PERCENTAGES INDICATED

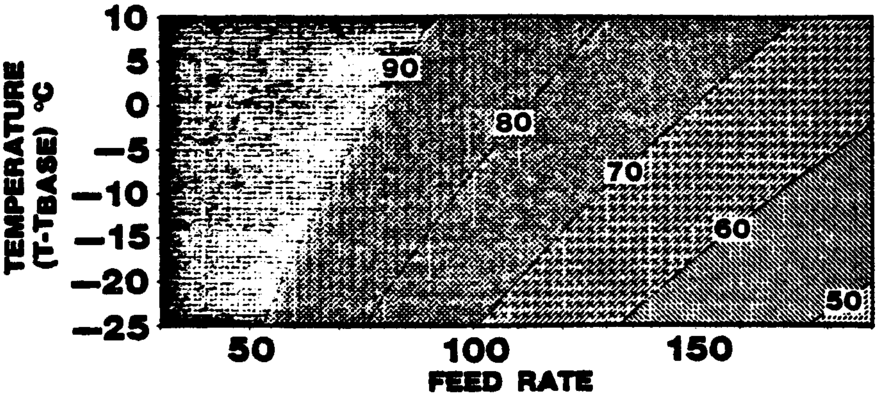


UOP 550-2

FIGURE 4

NITROGEN CONVERSION vs. TEMPERATURE AND FEED RATE – EDS

SHOWN AS CONSTANT CONVERSION CONTOURS – NITROGEN CONVERSION PERCENTAGES INDICATED

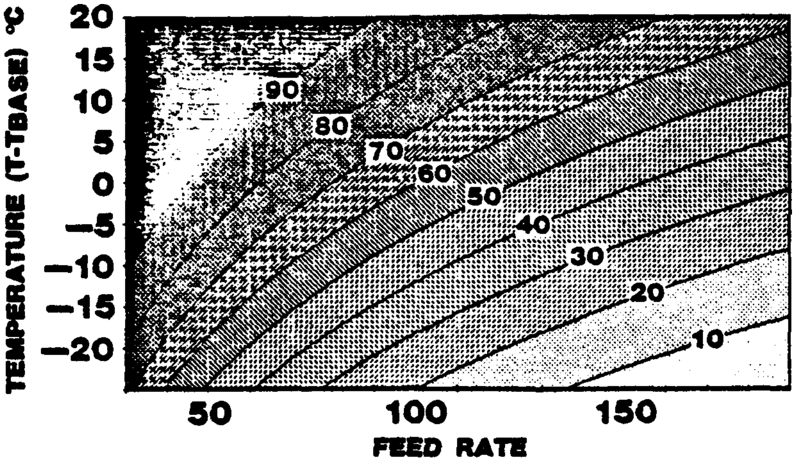


UOP 550-7

FIGURE 5

NITROGEN CONVERSION vs. TEMPERATURE AND FEED RATE – H-COAL

SHOWN AS CONSTANT CONVERSION CONTOURS – NITROGEN CONVERSION PERCENTAGES INDICATED



UOP 560-6

APPENDIX B

Errata

Report FE-2566-27

Report FE-2566-33

Addendum

Report FE-2566-30

Errata, Report 2566-27, p. 6

Table 2

MS Analysis of SRC II Naphtha 3777-1

Series	Hydrocarbon Types	Wt-%	Vol-%
C_nH_{2n+2}	Paraffins	27.8	31.5
	Naphthenes		
C_nH_{2n}	Monocycloparaffins	28.4	28.9
	Cyclopentanes	-	-
	Cyclohexanes	-	-
C_nH_{2n-2}	Bi, Dicycloparaffins	7.1	7.2
C_nH_{2n-4}	Tricycloparaffins	1.0	1.0
	Aromatics		
C_nH_{2n-6}	Alkylbenzenes	17.4	15.6
C_nH_{2n-8}	Indanes/Tetralins	0.7	0.6
C_nH_{2n-10}	Dinaphthenebenzenes	<0.1	Trace
C_nH_{2n-12}	Napthalenes	<0.05	Trace
	Polars		
$C_nH_{2n-5}N$	Pyridines	3.0	2.3
$C_nH_{2n-4}O$	Furans	-	-
$C_nH_{2n-6}O$	Phenols	4.5	3.2
$C_nH_{2n-7}N$	Naphthenopyridines	Trace	Trace
$C_nH_{2n-4}S$	Thiophenes	1.6	1.3
	Olefins*		
C_nH_{2n}	Monoolefins	1.9	2.1
C_nH_{2n-2}	Diolefins and/or Monocycloolefins	5.1	5.0
C_nH_{2n-4}	Triolefins and/or Dicycloolefins	1.4	1.3
	Total	100.0	100.0

Carbon Number Distribution, Vol-%

Carbon No.	Aromatics				Polars
	J = 6	J = 8	J = 10	J = 12	$J = 6^{O}$
5					
6	0.9				2.8
7	3.8				0.4
8	7.3				
9	3.3	0.4	Trace		
10	0.3	0.2	Trace		
11	Trace	Trace			
Total	15.6	0.6	Trace		3.2

*The total olefin number was obtained by SiO_2 separation, but the mono-, di-, tri-olefin split is estimated since no calibration coefficients are available.

Errata, Report 2566-33

Page 1

Paragraph three, line 2 should read "about 87%. . ."

line 5 should read ". . . about 2700 SCF/bbl."

Page 6

Last paragraph, line 10 should read ". . . Some 19%"

line 11 should read ". . 2350 SCF/bbl . . "

Page 11

Second paragraph, line 1 should read ". . between 5.1 - 6.2 wt-%. . "

The table following paragraph two should read:

Second Stage Reactor Press P-P(base), psi	500	0
Overall Yield, Vol-% of Feed		
C_5 - 375°F (gasoline)	24.10	24.82
375 - 600°F (fuel oil)	87.10	85.43
Total	111.10	110.25

Paragraph Three, line 2 should read " . . yield (1.7%), . . "

Page 12

Last paragraph, line 1 should read ". . yielded 71.4% of . . "

line 2 should read ". . and 21.6% of . . "

line 3 should read ". . of 77.3 wt-% fuel oil"

line 4 should read "and 18.2 wt-% naphtha."

Table 20

Hydrotreating Raw EDS Liquid Product 3532-3

Overall Product Distribution

Plant 638, Run 19

Product Distribution, Wt-% of Feed	
C_1	0.37
C_2	0.53
C_3	0.60
C_4	0.57
C_5 (in Plant Gas)	0.25
C_6 (in Plant Gas)	0.91
Stripper Overhead[a]	3.86
Stripper Bottoms[b]	92.97
H_2O	2.28
NH_3	0.63
H_2S	0.71
Total	103.68
H_2 Consumption, Wt-% of Feed	3.68
Consumption SCFB	2350

---

[a] Assumed to be C_5 - 375°F.

[b] Designated as Hydrotreated EDS Liquid Product 3532-4.

Table 21

Hydrotreating Raw EDS Liquid Product 3532-3
Distribution of Hydrogen Consumption
Plant 638, Run 19

	Wt-%
$C_1 - C_4$	10.0
C_5 and C_6 (in Plant Gas)	4.3
Stripper Overhead	2.7
Stripper Bottoms[a]	63.9
H_2O	11.9
NH_3	5.2
H_2S	2.0
Total	100.0
Total Hydrogen Consumption SCFB	2350

[a] Designated as Hydrotreated EDS Liquid Product 3532-4.

Errata, Report 2566-33, p. 40

Table 26

Hydrotreating Raw EDS Liquid Product 3532-2

Overall Product Distribution

Plant 638, Run 20

Product Distribution, Wt-% of Feed	
C_1	0.16
C_2	0.21
C_3	0.22
C_4	0.24
C_5 (in Plant Gas)	0.06
C_6 (in Plant Gas)	0.61
Stripper Overhead[a]	1.58
Stripper Bottoms[b]	94.42
H_2O	3.13
NH_3	0.55
H_2S	0.71
Total	101.89
H_2 Consumption, Wt-% of Feed	1.89
H_2 Consumption, SCFB	1212

[a] Assumed to be C_5 - 375°F.

[b] Included in First Stage Hydrotreated EDS Hydrocrackate 3532-9. Also see Table 30.

Errata, Report 2566-33, p. 41

Table 27

Hydrotreating Raw EDS Liquid Product 3532-2
Distribution of Hydrogen Consumption
Plant 638, Run 20

	Wt-%
C_1 - C_4	3.1
C_5 and C_6 (in Plant Gas)	1.7
Stripper Overhead	1.3
Stripper Bottoms[a]	76.7
H_2O	12.3
NH_3	3.4
H_2S	1.5
Total	100.0
Total Hydrogen Consumption SCFB	1212

[a] Included in First Stage Hydrotreated EDS Hydrocrackate 3532-9.

Table 79

Overall Product Distribution and Hydrogen Consumption

Two Stage Hydrocracking of EDS Liquid Product to Fuel Oil

Feedstock: EDS Liquid Product

First Stage Hydrocracking: Plant 638, Run 19

Second Stage Hydrocracking: Plant 638, Run 23

First Stage Hydrocracking Conditions		
P-P(base), psi	550/800	
T-T(base), °C	0/13	
LHSV/LHSV (base)	0.47	
Second Stage Hydrocracking Conditions		
P-P(base), psi	500	0
T-T(base), °C	-27	-24
LHSV/LHSV(base)	0.25	0.25
CFR/CFR(base)	1.25	1.25
Overall Product Distribution, Wt-% of Feed		
C_1	0.37	0.37
C_2	0.59	0.63
C_3	1.31	1.59
C_4	2.83	3.62
C_5-375°F Fraction	18.18	18.60
375-600°F Fraction	77.34	75.85
H_2O	2.30	2.30
NH_3	0.67	0.67
H_2S	0.71	0.71
Total	104.30	104.34
Overall H_2 Consumption, Wt-% of Feed	4.30	4.34
Overall H_2 Consumption, SCFB	2752	2778
Overall Yield, Vol-% of Feed		
C_5-375°F Fraction	24.10	24.82
375-600°F Fraction	87.10	85.43
Total	111.10	110.25

Errata, Report 2566-33, p. 94

FIGURE 1

BENCH-SCALE UNIT FOR FIRST-STAGE HYDROCRACKING

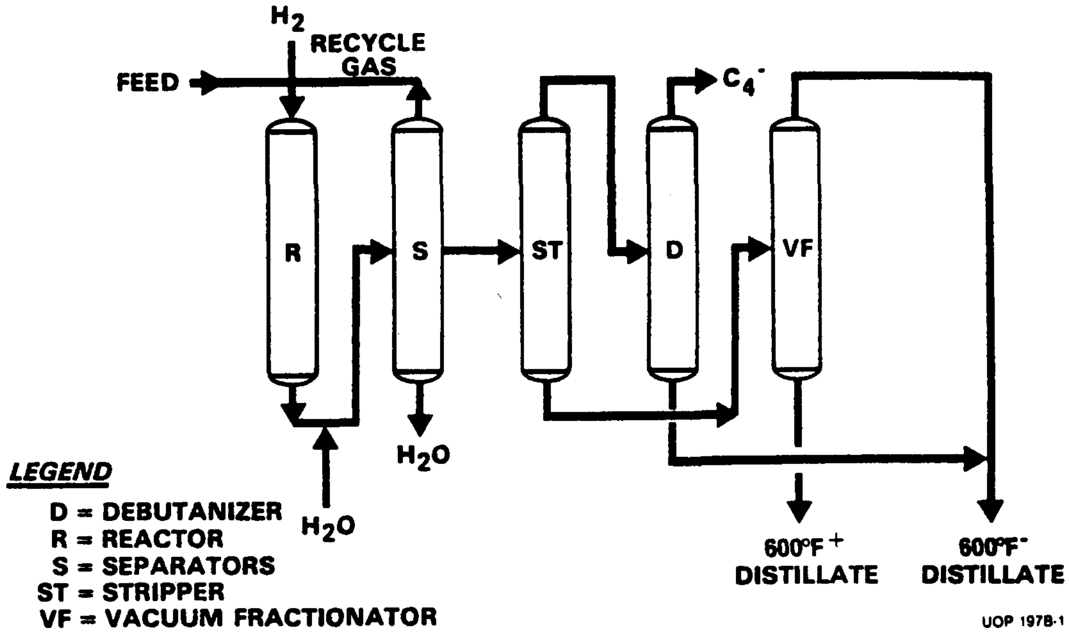
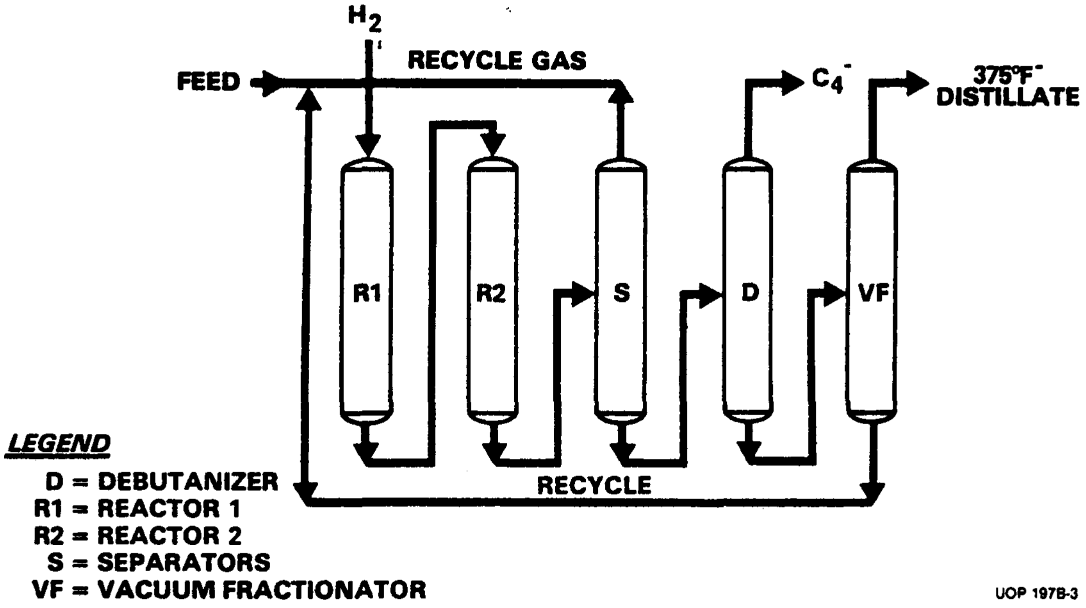


FIGURE 2

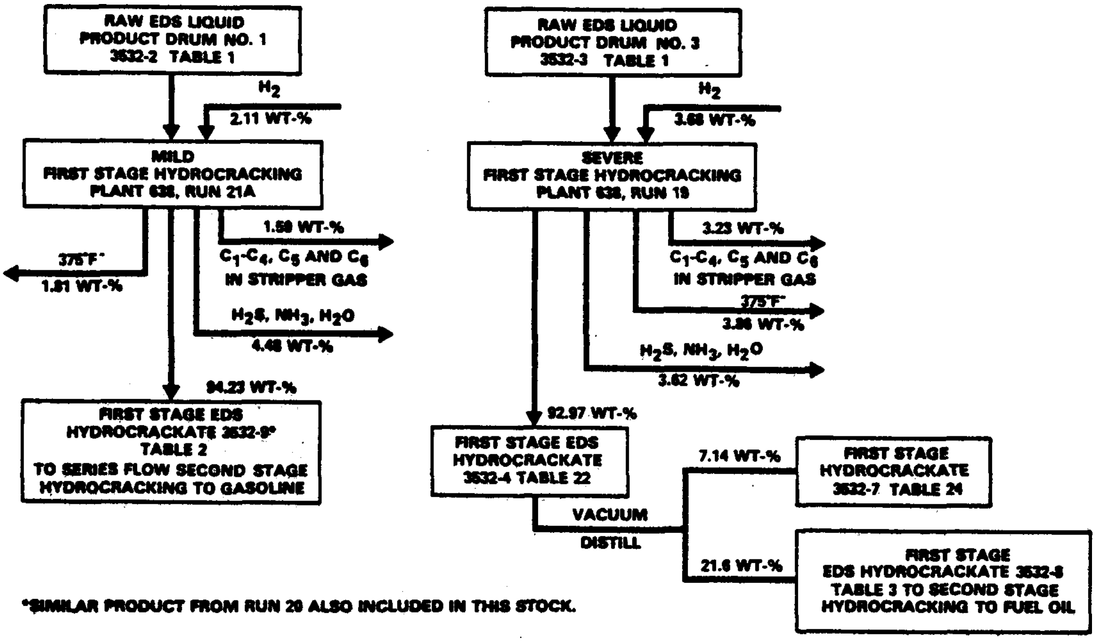
BENCH-SCALE UNIT FOR SERIES FLOW SECOND-STAGE HYDROCRACKING



Errata, Report 2566-33, p. 100

FIGURE 13

PREPARATION OF EDS LIQUID PRODUCT FOR SECOND STAGE HYDROCRACKING



*SIMILAR PRODUCT FROM RUN 20 ALSO INCLUDED IN THIS STOCK.

UOP 1970-23

Sample 3532-10
Cut #1 of Exxon Donor Solvent Feedstock 3532-5

z No. (C_nH_{2n-z})	Possible Compound Types	Wt-%[a] of Total Feed	Average Molecular Weight
	Saturates		
	Paraffins	3.44	268
	Naphthenes		
	1 Ring	2.92	266
	2 Rings	3.23	250
	3 Rings	1.83	248
	4 Rings	0.18	232
	Aromatic Hydrocarbons (C_nH_{2n-z})		
z=6	Alkylbenzenes	0.88	155
8	Indans/Tetralins	12.58	158
10	Dinaphthene Benzenes	2.67	183
12	Naphthalenes	11.74	156
14	Acenaphthenes/Biphenyls	9.69	190
16	Fluorenes	6.34	211
18	Phenanthrenes	6.75	209
20	Aceanthrenes	4.62	232
22	Pyrenes	5.56	239
24	Chrysenes	1.87	250
26	Benzofluoranthenes	0.47	274
28	Benzopyrenes	0.38	273
	Aromatic Oxygenates ($C_nH_{2n-z}O$)		
6^0	Phenols	3.92	137
8^0	Naphthenophenols	2.17	161
10^0	Benzofurans	0.33	196
12^0	Naphthols	0.38	162
14^0	Naphthenonaphthols/Hydroxybiphenyls	0.45	207
16^0	Dibenzofurans/Hydroxyfluorenes	2.97	215
18^0	Hydroxyanthracenes	1.22	231
20^0	Hydroxynaphthenoanthracenes	1.21	249
22^0	Hydroxypyrenes	1.68	253
24^0	Hydroxychrysenes	0.16	268

[a] Values accurate only to tenth of a percent-shown to 2 places for normalization only. Estimated accuracy ± 5%.

z No.	Possible Compound Types	Wt-%[a] of Total Feed	Average Molecular Weight
	Aromatic Dioxygenates $(C_nH_{2n-z}O_2)$		
6^{O_2}	Hydroxyphenols	0.20*	129
14^{O_2}	Hydroxynaphthenonaphthols	0.33*	229
16^{O_2}	Hydroxydibenzofurans	0.66*	235
18^{O_2}	Dihydroxyanthracenes	0.27*	253
20^{O_2}	Dihydroxynaphthenoanthracenes	0.05*	265
22^{O_2}	Dihydroxypyrenes	0.06*	254
	Aromatic Trioxygenate $(C_nH_{2n-z}O_3)$		
16^{O_3}	Dihydroxydibenzofurans	0.02*	217
	Aromatic Sulfur-Oxygen $(C_nH_{2n-z}S,O)$		
$10^{O,S}$	Hydroxybenzothiophenes	0.18*	179
$18^{O,S}$	Hydroxyacenaphthenothiophenes	< 0.01*	240
	Aromatic Nitrogens $(C_nH_{2n-z}N)$		
5^N	Pyridines/Amines	0.12	135
7^N	Naphthenopyridines	0.14	156
9^N	Indoles	0.11	159
11^N	Quinolines	0.28	160
13^N	Naphthenoquinolines	0.39	199
15^N	Carbazoles	1.09	193
17^N	Acridines	0.67	215
19^N	Naphthenobenzoquinolines	0.14	244
21^N	Benzocarbazoles	0.68	244
23^N	Benzacridines	0.29	262
Non-Volatiles and Loss		4.40	

*Estimated due to lack of sensitivity data.

Carbon Number Distribution of Aromatic Hydrocarbons on 100 Wt-% Basis

C#	z#= 6	8	10	12	14	16	18	20	22	24	26	28
10	0.04	3.25	0.02	3.57								
11	0.71	5.93	0.10	5.36								
12	0.49	4.98	0.56	3.41	1.08							
13	0.14	2.70	0.98	2.51	3.06	0.40						
14		1.73	1.35	2.11	4.09	1.43	2.00					
15		0.82	0.85	0.83	2.92	1.64	2.41					
16		0.39	0.35	0.46	2.20	2.25	2.11	0.72	1.25			
17				0.23	1.35	1.88	1.59	2.15	1.63			
18					0.55	1.50	1.17	2.25	1.65	0.52		
19						0.73	0.80	1.27	1.42	0.86		
20						0.16	0.46	0.52	1.02	0.96	0.05	
21							0.07	0.36	1.01	0.49	0.31	0.31
22									0.48	0.11	0.37	0.29
23									0.28			
	1.38	19.80	4.21	18.48	15.25	9.99	10.61	7.27	8.74	2.94	0.73	0.60

$\Sigma = 100.0$

Carbon Number Distribution of Aromatic Oxygenates

(Eluting with Aromatic Hydrocarbons)

C#	z#= 16^{O}	18^{O}	22^{O}
13	9.42		
14	20.22		
15	21.05		
16	13.57	5.26	
17	9.42	7.48	
18	4.99	1.66	4.71
19			2.22
	78.67	14.40	6.93

$\Sigma = 100.0$

Carbon Number Distribution of Aromatic Oxygenates on 100% Basis

In Polar Fraction

C#	z#= 6^{O}	8^{O}	10^{O}	12^{O}	14^{O}	16^{O}	18^{O}	20^{O}	22^{O}	24^{O}
7	0.90									
8	10.36									
9	11.27	2.32								
10	7.06	5.65		0.50						
11	2.45	4.53		1.47						
12	0.49	2.98	0.39	1.06						
13		1.63	0.90	0.13	0.63	0.14				
14		0.71	0.93		1.01	1.56	0.36			
15		0.23	0.49		1.29	2.52	1.34			
16					0.82	1.67	1.28	0.70	0.76	
17						1.70	2.19	2.46	2.53	
18						1.07	1.52	3.33	3.28	
19							0.51	2.51	2.87	0.39
20								1.07	1.97	0.95
21									1.12	
	32.53	18.05	2.71	3.16	3.75	8.66	7.20	10.07	12.53	1.34

$\Sigma = 100.0$

Carbon Number Distribution of Aromatic Dioxygenates on 100% Basis

In Polar Fraction

C#	z#= $6^{O}2$	$14^{O}2$	$16^{O}2$	$18^{O}2$	$20^{O}2$	$22^{O}2$
6	0.61					
7	7.45					
8	4.90					
13		2.04	3.16			
14		4.90	8.27			
15		6.12	10.10	1.84		
16		5.82	7.86	3.37		
17		1.22	6.94	5.71	0.71	2.35
18		0.82	4.39	4.18	1.43	1.53
19			1.12	2.14	1.02	
	12.96	20.92	41.84	17.24	3.16	3.88

$\Sigma = 100.0$

Aromatic Trioxygenates

C#	z#= $16^{O}3$
13	78.57
14	21.43
	100.00

$\Sigma = 100.0$

Carbon Number Distribution of Aromatic Oxygenates on 100% Basis

Aromatic Sulfur-Oxygen Compounds

C#	z#=	$10^{O,S}$	$18^{O,S}$
9		20.83	
10		47.50	
11		27.50	
15			4.17
		95.83	4.17

Σ = 100.0

Carbon Number Distribution of Aromatic Nitrogens on 100% Basis

In Polar Fraction

C#	z#=	5^N	7^N	11^N	13^N	15^N	17^N	19^N	21^N	23^N
9		1.84								
10		2.17	0.13							
11		1.32	1.25	1.58						
12			1.45	3.42						
13				3.23						
14				1.84	4.21					
15				0.66	5.53		3.03			
16					5.07		5.20			
17					0.92	0.33	3.49	0.66	2.90	
18						2.57	2.50	7.18	4.08	0.26
19						0.33	0.20	6.85	3.75	2.37
20								3.29	1.18	4.67
21								0.86	3.55	4.55
22										1.58
		5.33	2.83	10.73	15.73	3.23	14.42	18.84	15.46	13.43

Σ = 100.0

Carbon Number Distribution of Aromatic Nitrogens on 100% Basis

Eluting with Aromatic Hydrocarbons

C#	z#= 7^N	9^N	11^N	13^N	15^N	17^N	21^N
10			2.37				
11	2.37						
12		5.42					
13	1.69				6.44		
14					15.94	0.68	
15				2.37	20.36	4.41	
16					6.10	1.69	0.33
17					2.03	5.42	
18						5.76	4.75
19							6.79
20							5.08
	4.06	5.42	2.37	2.37	50.87	17.96	16.95

$\Sigma = 100.0$

Miscellaneous Averages and Summaries

Aromatic Hydrocarbons (C_nH_{2n-z})

Average C#	14.79
Average z#	14.39
Average MW	192.67

Aromatic Oxygenates ($C_nH_{2n-z}O$)

Eluting with aromatic hydrocarbons

Average C#	15.56
Average z#	16.70
Average MW	248.33

In Polar Fraction

Average C#	12.56
Average z#	12.34
Average MW	179.51

2 Oxygens per Molecule ($C_nH_{2n-z}O_2$)

In Polar Fraction

Average C#	14.82
Average z#	14.99
Average MW	224.50

3 Oxygens per Molecule ($C_nH_{2n-z}O_3$)

Average C#	13.21
Average z#	16.00
Average MW	217.00

Aromatic Sulfur-Oxygen ($C_nH_{2n-z}S,O$)

Average C#	10.28
Average z#	10.45
Average MW	181.47

Aromatic Nitrogenates

Eluting with aromatic hydrocarbons

Average C#	15.37
Average z#	15.58
Average MW	213.60

In Polar Fraction

Average C#	16.75
Average z#	16.54
Average MW	231.96

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