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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 to 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) 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 will give 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 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. INTRODUCTION

The objective of this program is to examine distillate products from DOE sponsored liquefaction processes as potential feeds to commercial petroleum refining processes. The ultimate effect is to provide a new source of transportation fuels and environmentally acceptable fuel oils.

Chemical analysis has disclosed that, in comparison to petroleum gas oils, coal derived distillates contain large amounts of cyclic hydrocarbons and large amounts of heterocyclic structures, such as pyridines, phenols, benzofurans, carbazoles, and thiophenes. It is desirable to know the effects of these potential catalyst poisons and coke formers on yield structure and product quality; and the processing severity required relative to a petroleum distillate derived from a Middle East crude.

To answer these questions, distillates from the H-Coal, Exxon Donor Solvent (EDS), and SRC-II processes have been processed in research pilot plants. The naphthas from these processes have been hydrotreated and reformed. The 400°F^+ distillates have been converted by hydrotreating, hydrocracking and fluid catalytic cracking. During the first year of the program, covered by this report, experimental work on the H-Coal distillates has been completed. Detailed results are given in Interim Reports FE-2566-12, FE-2566-20, and FE-2566-23, which are appended to this Annual Report by title. Detailed results from processing EDS and SRC-II distillates will be presented in subsequent Interim Reports and the Final Report.

2. NAPHTHA HYDROTREATING AND REFORMING

Table 1 gives inspections of naphthas from the three liquefaction processes. They 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 heterocyclic constituent. These naphthas are very unstable toward oxidation. The as-received H-Coal naphtha was rerun to remove storage impurities and color bodies. However, the color redeveloped almost immediately.

These naphthas were hydrotreated over a commercial catalyst to reduce the sulfur and nitrogen to below 1 wt-ppm. Operating conditions used were more severe than required for processing the Middle East naphtha of the base case. The liquid hourly space velocity was only one eighth, pressure was 450 psi greater, and temperature was 55°F higher. Results obtained with H-Coal naphtha are given in Table 2. Results for the other two naphthas were similar. Targets for sulfur and nitrogen reduction were met. The oxygenates, identified as methyl phenols, tended to persist at low levels. Mass spectrometer results suggest that in the case of H-Coal naphtha, olefins were saturated to paraffins, and the polar heterocyclics (principally phenols) were converted to naphthenes. Research octane number (RON) dropped 13 points. Chemical hydrogen consumption was 480 standard cubic feet per barrel (SCF/B).

The high naphthene content of the hydrotreated naphthas make them very responsive to catalytic reforming. Figure 1 shows the yield-octane curve generated by reforming the hydrotreated H-Coal naphtha at various temperatures over a commercial reforming catalyst. The pressure employed was the same as specified for reforming a Middle East naphtha. However, the space velocity was 50% greater and the temperature was 90°F lower relative to base case conditions specified for producing 100 RON gasoline. The dotted line illustrates, for comparison, the yield estimate for reforming a straight run Middle East naphtha. At 100 RON the yield of gasoline from H-Coal naphtha is 89.5 vol-% vs. 76.7 vol-% from the petroleum naphtha. Hydrogen yield from H-Coal naphtha is also higher, amounting to 1625 SCF/B vs. 1285 SCF/B from the petroleum naphtha.

Analyses of the H-Coal hydrotreated naphtha feed and of reformates made at three levels of severity (Table 3) show that up to 97.7 RON, the octane improvement derives exclusively from the dehydrogenation of naphthenes to aromatics. Only at the very highest severity does dehydrocyclization of paraffins contribute. The realized hydrogen yields of 1250-1700 SCF/B are several times the 480 SCF/B required for hydrotreatment.

3. DISTILLATE HYDROTREATING AND FLUID CATALYTIC CRACKING

Table 4 gives inspections of the 400°F$^+$ distillates provided from the H-Coal and EDS processes before and after rerunning. Their aromatic contents range from 86 to 91%. Like the naphthas, they contain substantial amounts of heterocyclic compounds. However, the distillation end points, relative to typical petroleum vacuum gas oils, are low. Both of the coal derived distillates contain heptane insolubles. These were low in the case of H-Coal distillate, and were eliminated by rerunning. They amounted to 6.45% in the EDS product, and could not be eliminated by rerunning. Mass spectrometric analysis has identified these insolubles as oxygenated polycyclic aromatics.

These distillates, after rerunning, were cracked in a once through riser-type research scale fluid catalytic cracking (FCC) unit (Figure 2). An equilibrium zeolitic catalyst withdrawn from a commercial FCC unit was employed. Temperature and catalyst/oil ratio were close to values specified in a base case for cracking Middle East gas oil. Results are shown in Table 5. Low conversions and gasoline yields and high carbon yield and high octane numbers were observed. These results are consistent with the aromatics and heterocyclic natures of the charge stocks.

The H-Coal 400°F$^+$ distillate was hydrotreated at two levels of severity to provide upgraded feedstocks for catalytic cracking. Preliminary hydrotreating will substantially improve its processability. Nitrogeneous poisons are reduced. Polycyclic aromatic structures are partially hydrogenated to provide points for catalytic attack on carbon-carbon bonds. The properties of the treated feedstocks are given in Table 6. The mild severity treatment required 1130 SCF/B hydrogen, and made little or no 400°F$^-$ naphtha. The severe hydrotreatment required 3640 SCF/B hydrogen, and generated 51.6% naphtha.

Figure 3 illustrates the effect of hydrotreatment on the response of the H-Coal rerun distillate to fluid catalytic cracking. Volume percent conversion, volume percent yield of C_5^+ gasoline, and weight percent yield of carbon are plotted for the untreated stock and the two hydrotreated stocks versus hydrogen content. For comparison, a similar correlation obtained by hydrotreating a California refinery FCC charge stock is shown in dashed lines. The comparison indicates that the coal derived stocks will respond as well as petroleum derived stocks of similar hydrogen content. However, it should be emphasized that the boiling ranges of the hydrotreated coal stocks and the hydrotreated California feeds are very different.

4. DISTILLATE HYDROCRACKING

The data of Table 6 show that mild hydrotreating of a coal-derived distillate will produce environmentally acceptable fuel oil. The yield of 650°F$^-$ distillate in a single pass will depend on the end point of the original charge stock. For complete conversion, a hydrocracking stage may be added with recycle of unconverted heavy ends.

In one instance the rerun H-Coal 400°F$^+$ distillate was hydrotreated with continuous vacuum fractionation of the product to remove 80.5 wt-% of 375-600°F fuel oil and 2.8 wt-% naphtha. Sulfur and nitrogen contents of the products were less than 3 and 12 wt-ppm, respectively. Relative to a base case for processing Middle East distillate, the pressure was 500 psig higher, while space velocity and temperature were essentially the same. The vacuum column bottoms comprising 15.4 wt-% of the original H-Coal distillate were hydrocracked in a second stage reactor system shown in Figure 4. The product was vacuum fractionated, and the 600°F$^+$ bottoms recycled. Space velocity was one quarter that specified for a base case second-stage hydrocracking. Pressure was 500 psi higher, and temperature was the same. Overall product distribution for the two-stage operation is shown in Table 7. Most of the naphtha was made in the second stage. Most of the hydrogen was consumed in the first stage, 1240 SCF/B. An additional 340 SCF/B, based on original feed, was consumed in the second stage.

Figure 5 compares the yield pattern obtained from this two-stage operation with that from single-stage hydrocracking of a Middle East gas oil at substantially the same conditions. The higher yield of fuel oil and lower yield of naphtha from the H-Coal distillate correspond to the difference in boiling range of the two stocks. The H-Coal distillate contains 76 vol-% of material boiling below 650°F, while this has been substantially all removed from the petroleum gas oil.

For complete conversion of coal-derived distillate to gasoline, two-stage hydrocracking is necessary. In this study, the H-Coal distillate first was mildly hydrotreated. Liquid yield was virtually 100%. The liquid product was hydrocracked in a series flow system shown in Figure 5. The series flow reactor system, which includes a second catalytic reactor, provides for continuous product fractionation and recycle of the 375°F$^+$ bottoms. Operating conditions were somewhat more severe than required for a typical Middle East gas oil.

Overall product distribution is given in Table 8. The gasoline produced was 92 RON clear. Hydrogen consumption was 880 SCF/B in the first stage, and 3000 SCF/B in the series flow second stage. Figure 7 compares this distribution with that obtained by two-stage hydrocracking of Middle East gas oil at the same pressure. The lower yield of naphtha and higher yield of light ends from H-Coal distillate correspond to the higher temperature and lower space velocity required to achieve complete conversion to 375°F$^-$ material.

Of the hydrogen required for hydrocracking to gasoline, 1100 SCF/B can be recovered by reforming the hydrocracker naphtha to 100 RON. Steam reforming of the C_1-C_3 gases will provide another 1200 SCF/B. Including the butanes in the steam reformer feed should result in hydrogen balance.

5. CONCLUSIONS

These studies show that hydrotreating, hydrocracking, fluid catalytic cracking and reforming are applicable to coal-derived distillates. In general the liquids will require hydrogen pretreatment before cracking or reforming to reduce excessive amounts of nitrogen, to enhance processability, and to make the products more environmentally acceptable. Hydrogen is consumed to partially saturate polynuclear aromatics. This renders the stock more susceptible to cracking, and less prone to form coke on catalysts.

The advanced commercial catalysts employed for petroleum conversion are suitable for refining coal derived distillates to premium value products. Process conditions required are within commercially practicable ranges. Hydrogen requirements can be partially met by reforming naphthas and steam reforming light gases.

6. 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.

TABLE 1

INSPECTIONS OF PRIMARY COAL NAPHTHAS

	RERUN H-COAL NAPHTHA	*EDS PROCESS NAPHTHA*	*SRC-II NAPHTHA*
°API AT 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	9.1
AROMATICS	18.6	25.3	18.1
OLEFINS	5.5	9.9	8.4
NAPHTHENES	55.5	42.9	36.6
PARAFFINS	16.2	13.2	27.8
RON (CLEAR)	80.3	83.2	80.8

UOP 197D-2B

TABLE 2

HYDROTREATING H-COAL PRIMARY NAPHTHA

	RERUN H-COAL NAPHTHA	*HYDROTREATED H-COAL NAPHTHA*
°API AT 60°F	43.7	46.8
IBP, °F	132	153
EP, °F	396	393
S, WT-ppm	1,289	0.5
N, WT-ppm	1,930	0.6
O, WT-ppm	5,944	34
Cl, WT-ppm	23	4
MS TYPES, VOL-%		
POLARS	4.2	—
AROMATICS	18.6	17.6
OLEFINS	5.5	—
NAPHTHENES	55.5	63.4
PARAFFINS	16.2	19.0
RON (CLEAR)	80.3	66.8
H_2 CONSUMPTION, SCF/B		480

UOP 197D-3B

TABLE 3

REFORMING HYDROTREATED H-COAL NAPHTHA

		REFORMING SEVERITY		
	(FEED)	*LOW*	*MED.*	*HIGH*
C_5+ YIELD, VOL-%		92.5	91.1	88.1
RON (CLEAR)	66.8	94.2	97.7	102.6
MS TYPES, VOL-%				
AROMATICS	19.4	65.8	71.7	83.3
NAPHTHENES	64.6	16.4	9.4	5.0
PARAFFINS	16.0	17.8	18.9	11.7
H_2 YIELD, WT-%		2.5	3.0	3.4
SCF/B		1,250	1,500	1,700

UOP 197D-4

TABLE 4

INSPECTION OF COAL DERIVED 400°F+ DISTILLATES

PROCESS:	*H-COAL*		*EDS*	
	(a)	*(b)*	*(a)*	*(c)*
°API AT 60°F	7.4	8.9	3.5	8.0
IBP-650°F, VOL-%	76.0	81.0	54.0	55.0
650°F-EP, VOL-%	23.0	18.0	31.0	43.0
EP, °F	857	769	930	940
H, WT-%	—	9.14	8.66	8.97
C, WT-%	—	89.32	89.22	87.93
S, WT-%	0.10	0.08	0.49	0.20
N, WT-%	0.35	0.41	0.71	0.49
O, WT-%	0.50	0.52	1.93	2.84
AROMATICS (FIA), VOL-%	91	90	—	86
HEPTANE INSOL., WT-%	0.37	0.05	6.45	4.14
CON. CARBON, WT-%	0.41	<0.01	6.60	0.95

a) AS RECEIVED
b) RERUN, 94 VOL-% OVERHEAD
c) RERUN, 84 VOL-% OVERHEAD

UOP 197D-5

TABLE 5

FLUID CATALYTIC CRACKING OF COAL DERIVED 400°F+ DISTILLATES

PROCESS:	*H-COAL*	*EDS*
CONVERSION, VOL-%*	30.6	45.9
C_4^-, WT-%	4.3	6.4
CARBON, WT-%	11.1	12.8
C_5+ GASOLINE, VOL-%	15.5	27.2
RON, CLEAR	99.4	96.8

*100%—VOL-% 400°F+ CYCLE OIL

UOP 197D-6

TABLE 6

HYDROTREATED FCC CHARGE STOCKS FROM 400°F+ H-COAL DISTILLATES

HYDROTREATMENT	*MILD*	*SEVERE*
°API AT 60°F	16.8	29.2
IBP — 400°F, VOL-%	2.0	0
400-650°F, VOL-%	89.0	99.0
650° —EP, VOL-%	5.5	—
EP, °F	710	670
H, WT-%	10.68	12.88
S, WT-ppm	6.7	0.2
N, WT-ppm	856	2
AROMATICS (FIA), VOL-%	73	12

UOP 197D-7

TABLE 7

TWO-STAGE HYDROCRACKING OF H-COAL DISTILLATE TO FUEL OIL

PRODUCT DISTRIBUTION

	WT-%	*VOL-%*
C_1-C_4	4.0	—
C_5-375°F	12.0	15.3
375-600°F	85.5	91.2
H_2S, H_2O, NH_3	1.0	—
	102.5	106.5
HYDROGEN CONSUMPTION	2.5	—

UOP 197D-8

TABLE 8

TWO-STAGE HYDROCRACKING OF H-COAL DISTILLATE TO GASOLINE

PRODUCT DISTRIBUTION

	WT-%	*VOL-%*
C_1-C_3	12.4	—
C_4	16.1	27.5
C_5+	76.9	97.9
H_2S, H_2O, NH_3	0.9	—
	106.3	125.4
HYDROGEN CONSUMPTION	6.3	—

UOP 197D-9

FIGURE 1

YIELD OCTANE CURVE FOR UPGRADED H-COAL NAPHTHA

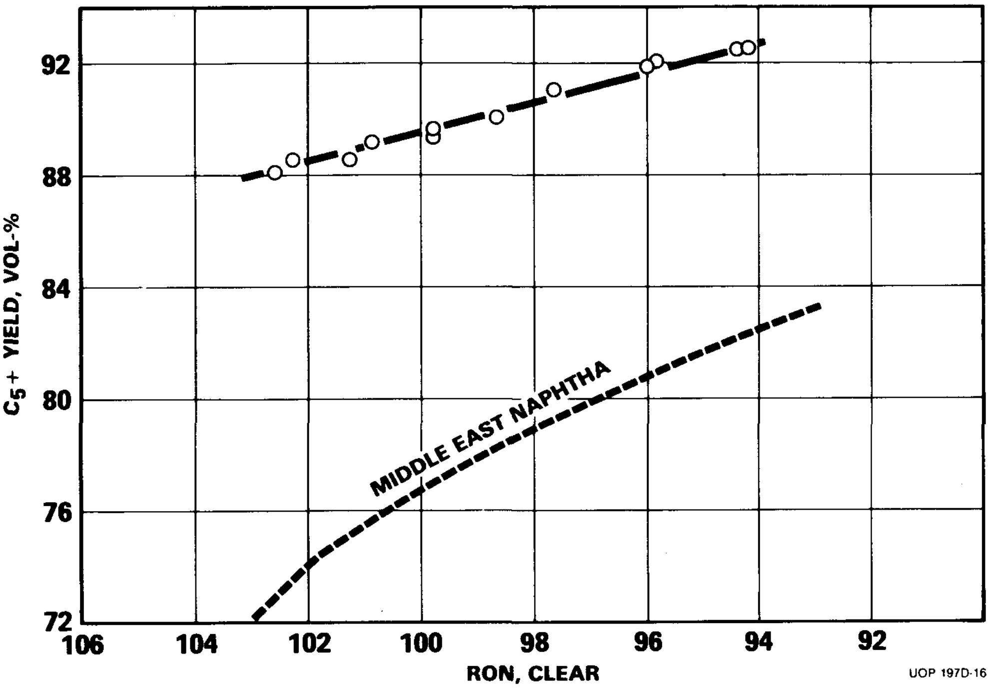


FIGURE 2

SMALL SCALE FLUID CATALYTIC CRACKER

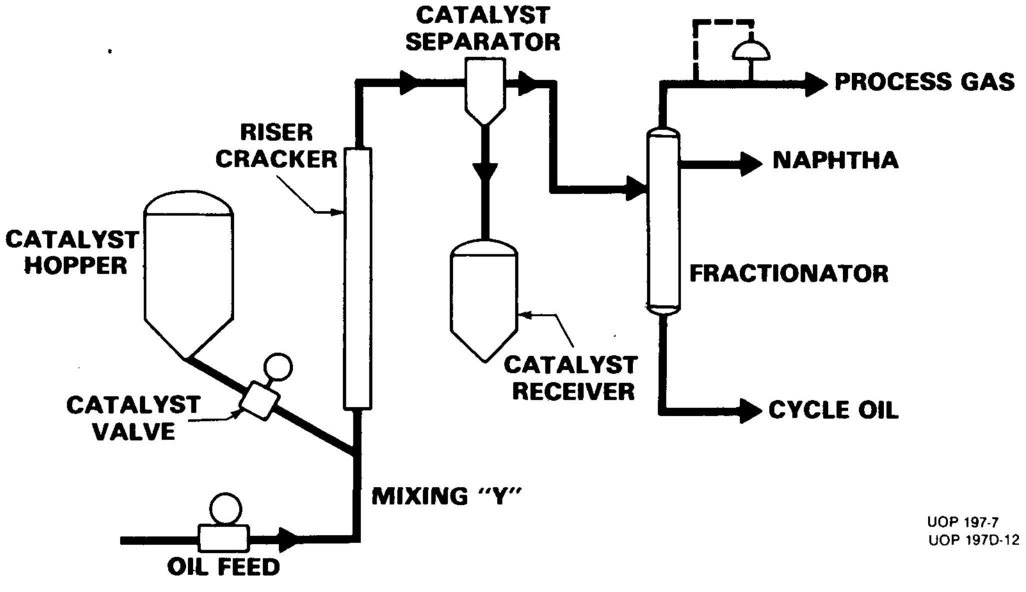


FIGURE 3

FCC PRODUCT DISTRIBUTION

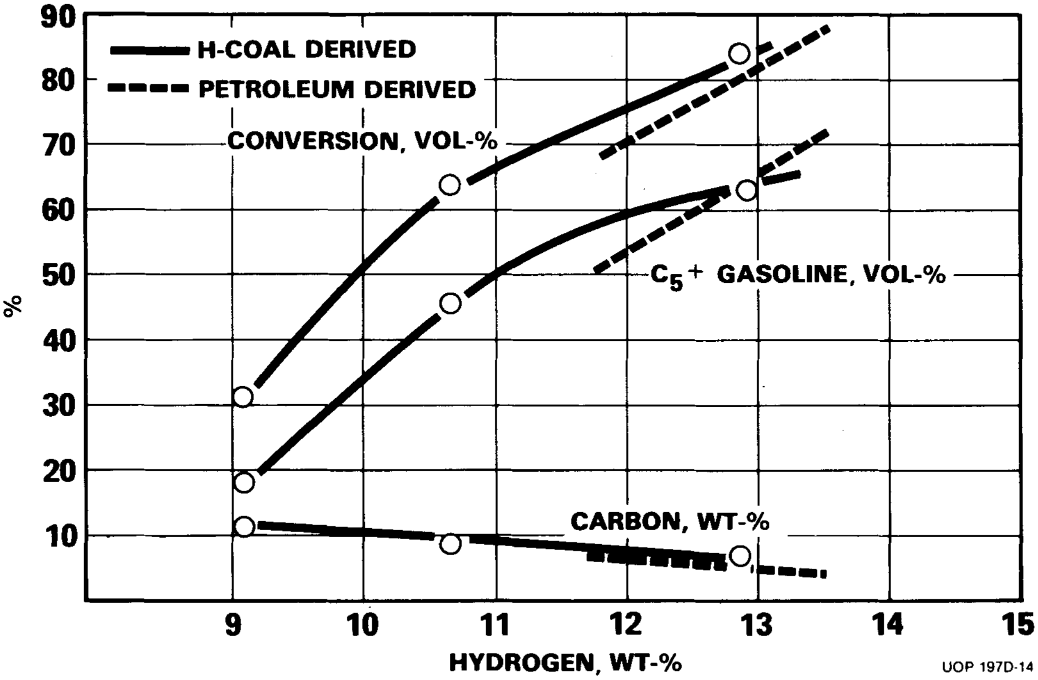
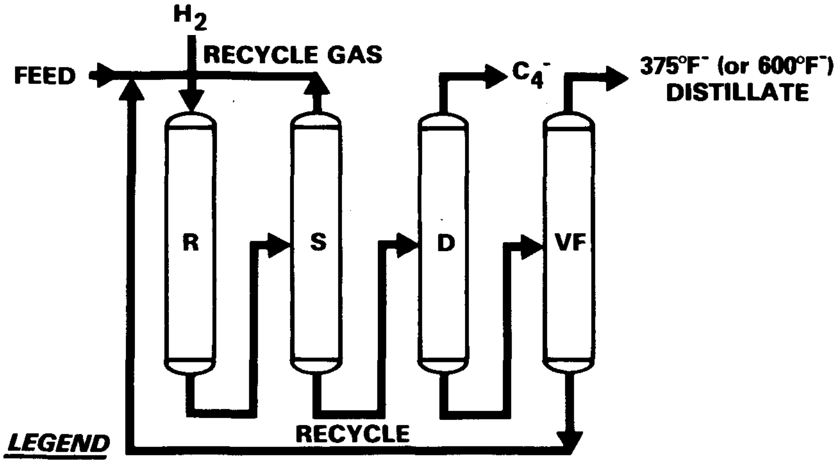


FIGURE 4

BENCH-SCALE UNIT FOR SECOND-STAGE HYDROCRACKING



LEGEND

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

FIGURE 5

PRODUCT DISTRIBUTION IN HYDROCRACKING TO FUEL OIL

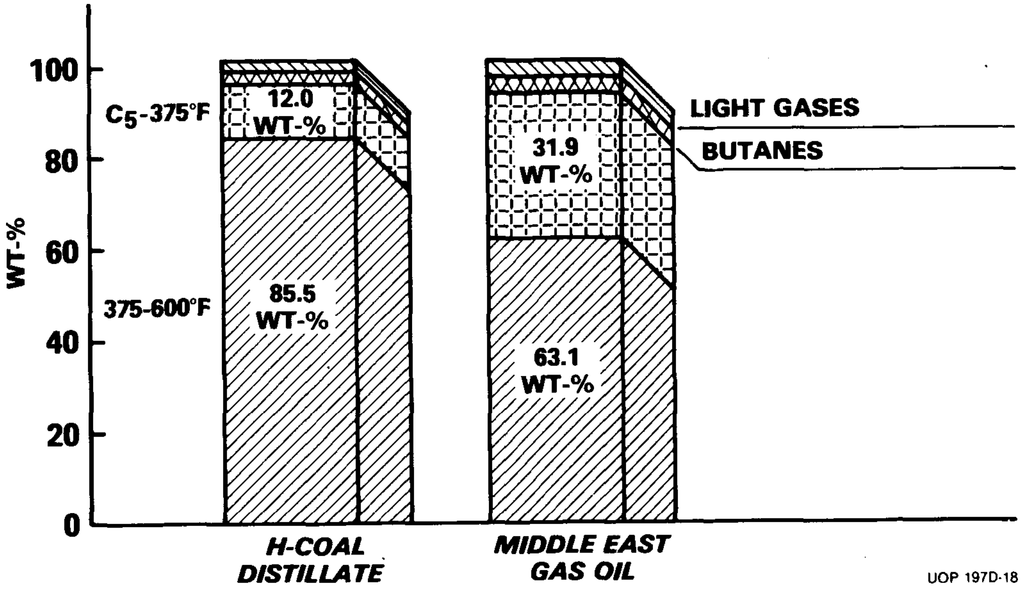


FIGURE 6

BENCH-SCALE UNIT FOR SERIES FLOW SECOND-STAGE HYDROCRACKING

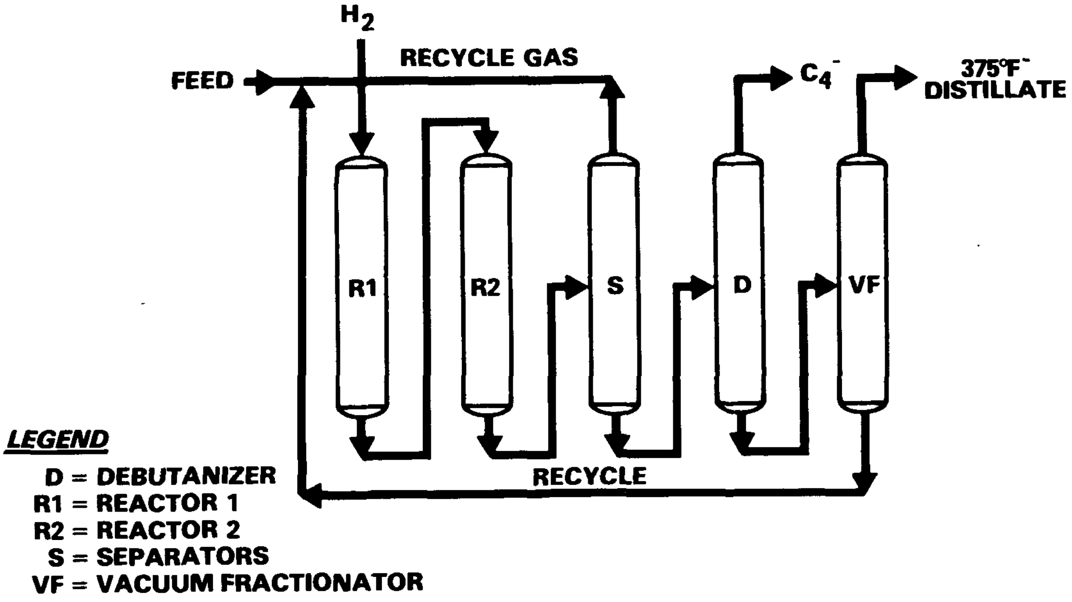
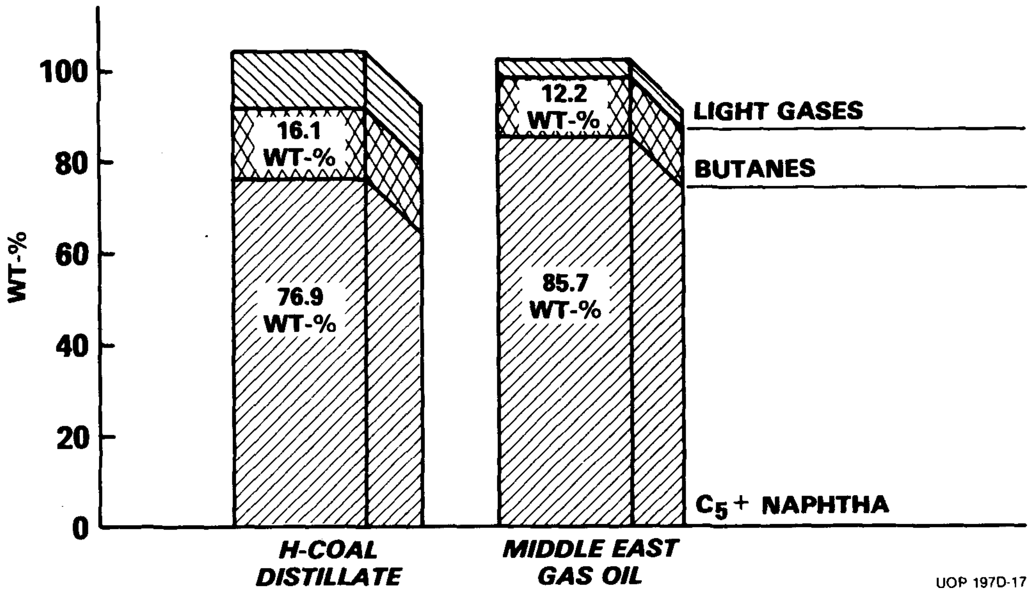


FIGURE 7

PRODUCT DISTRIBUTION IN HYDROCRACKING TO GASOLINE



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