the above description does enable one to anticipate the types of processing problems which could occur in converting these liquids to high-octane gasoline, jet fuel and diesel fuel.

2. REFINING PROBLEMS

In contrast to COED liquids, few data have been published concerning the refining H-coal liquids on a large scale. Some key catalytic problems can be anticipated from the product composition data. These are discussed next for the various product fuels.

a. High-Octane Gasoline

The composition of a typical naphtha fraction (C_4-400°F) is given in Table IV-13. Since it is qualitatively similar to that for a COED naphtha, the primary conversions required to reform this fraction to high octane gasoline will involve dehydrogenation and hydroisomerization to aromatics. Both reactions occur readily over conventional reforming catalysts and yield moderate pressure hydrogen. Activity maintenance would not normally be expected to be a problem for such a highly naphthenic naphtha. However, unlike the COED liquids, the H-coal liquids reportedly have a reasonable amount of polynuclear aromatics. For example, Table IV-13 indicates about 8 wt.% of such materials with 6.44 wt.% being indans. While these structures are not as severe as 4 and 5 ring structures for deactivating reforming catalysts, they do adsorb strongly on acidic sites and cause carbon deposition with time. It is expected that operation at higher hydrogen pressures than those used for reforming COED liquids should solve this problem, giving an easily processed naphtha with good C_5^+ liquid yields and high yields of hydrogen.

The middle distillate (400-650°F) and residuum (650°-919°F) fractions are expected to give the greatest amount of problems in processing to high-octane gasoline. This is primarily due to the high concentration of polynuclear

aromatics and heterocyclic nitrogen compounds. The former, as described above, promotes rapid catalyst deactivation by means of carbon deposition. The latter poisons conventional bifunctional catalysts such as those used for catalytic cracking and hydrocracking.

The 400-650°F fraction should be processable to a naphthenic-aromatic naphtha by a moderate hydrotreating operation. This should remove phenols and sulfur and nitrogen compounds to low enough levels so that this heavy naphtha could be further processed either by reforming or by mixing with catalytic cracker feed stock. For conventional cracking operations this requires the basic nitrogen level to be decreased to less than 10-20 ppm to avoid catalyst poisoning.

Processing the 650-919°F fraction presents more formidable problems. As for the middle fraction, the sulfur, nitrogen and polynuclear aromatics must be reduced to an acceptable level for conventional catalytic cracking or hydrocracking. However, the heavier fraction is almost entirely polynuclear atomatics or heterocyclic compounds (Table IV-15). The larger rings such as phenanthrenes, chrysenes, pyrenes and benzanthracenes are particularly diffi-cult molecules for cracking. The heavy fraction also contains about 14 wt.% of heterocycles, most of which are high molecular weight materials which are difficult to desulfurize and denitrogenate. One possible option with the heavier residuum fraction is to distill off a 650-800°F fraction for pro-cessing with the 400-650°F fraction. The remaining heavy residuum fraction could then be used as a blending stock for heavy fuel oils if the sulfur, nitrogen and polynuclear aromatic constraints are met. If the 650-800°F fraction behaves like the COED liquids, conventional hydrocracking will still present a problem.

b. <u>Jet Fuel</u>

The middle distillate and residuum fractions from H-coal liquids are highly aromatic and therefore, as in the case for COED liquids, do not yield a good jet fuel fraction. As for COED liquids, it is likely that a severe hydrotreating process would improve the liquid quality for certain product specifications. This would saturate some aromatics and therefore satisfy the minimum aromatics requirement. The smoke point may still be a problem because of the large concentration of cycloparaffins. Therefore, selective hydrocracking of the cycloparaffins to branched paraffins would be desirable. Even after a severe hydrofining treatment, it is likely that the product would best be used as a jet fuel blending stock since there are still some critical parameters which may not easily be satisfied by this treatment. These include (as shown in Table IV-8) specific gravity, luminosity, boiling range and flash point.

c. <u>Diesel Fuels</u>

As is the case for COED liquids, the 400-650°F fraction from the H-coal process is highly aromatic and therefore is not expected to meet diesel specifications, particularly for density, cetane number and oxidation stability. Severe hydrotreating and more effective hydrocracking will be needed to upgrade H-coal liquids to a diesel fuel.

D. <u>SYNTHOIL LIQUIDS</u>

In the Synthoil process coal is slurried in a recycled aromatic oil and flowed at highly turbulent conditions with hydrogen gas through a fixed bed of cobalt molybdate catalyst (18-25). Depending upon the conditions of operation, either a heavy or a light low-sulfur, fuel oil is produced. Coal conversion levels of 90-98% are common (18). As an example, a Kentucky coal with 5.5%

sulfur and 16% ash can be converted to an oil which flows at room temperature and has 0.2 wt.% sulfur, 0.8 wt.% nitrogen and 0.2 wt.% ash. Process conditions are usually either 2000 or 4000 psig at 450°C depending upon whether the desired product is a light or heavy oil. Usual contact time is two minutes. Oil yields are about 3 bbl/ton of coal with a hydrogen consumption of 4000-5000 SCF/bbl of oil depending upon product quality.

A unique feature of this process is that the ash in the coal reportedly acts to give controlled attrition of the catalyst surface thereby minimizing deposition of mineral matter and carbon. The ash is ultimately separated from the coal liquids by centrifugation. A detailed chemical analysis has only recently been reported for the coal liquids product from the Synthoil process (25) and is summarized below.

1. NATURE OF SYNTHOIL LIQUIDS

A recent study by Woodward et al. (25) reports on the characteristic molecular constituents of Synthoil liquids produced from West Virginia Coal. Although the following discussion pertains to a West Virginian Pittsburgh seam coal, the general trends and compositional types are expected to be similar for other eastern coals. Therefore upgrading problems and procedures would be expected to be similar. As mentioned later, this may not be the case for western coals such as those from Utah or Wyoming.

The Synthoil syncrude discussed in the Woodward study was produced at 4000 psig and 450°C by passing hydrogen gas and a 35 wt.% coal in recycle oil slurry at 25 lb/hr through a 14.5-foot-long Synthoil reactor containing 1/8-inch pellets of cobalt molybdate on silica-stabilized alumina. The product was a brownish-black liquid with a specific gravity of 1.081 and nitrogen and sulfur contents of 0.79 and 0.42 weight percent, respectively. Comparison of the Synthoil syncrude with that produced by the COED process for Utah coal (26)

and western Kentucky coal (27), showed the Synthoil product to be much heavier, and containing a considerably greater amount of carbon residue (Conradson carbon) in both the residuum and total crude oil (25). The Synthoil product also had higher nitrogen content (Utah, 0.48%, western Kentucky, 0.23%) and substantially more sulfur (Utah, 0.05%, western Kentucky, 0.08%). Also unlike the syncrudes produced by the COED process, the nitrogen and sulfur compounds of the Synthoil liquids are concentrated in the heavy ends, somewhat similar to what is found for petroleum crudes.

Additional data comparing Synthoil coal liquids and COED coal liquids for three different coals are given in Table IV-16. Although the starting coals vary in physical and chemical properties, some useful general points can be made. The West Virginia and western Kentucky coals are perhaps most similar in overall properties. The concentration of saturates is lower in both Synthoil fractions compared to the other two coals. The concentration of monoaromatics in the 685-988°F fraction of the Synthoil liquids is also lower than the corresponding fraction for the other two coals, indicating a greater degree of aromaticity. This is corroborated by the low saturates level and the greater amount of polynuclear aromatics in the high-boiling Synthoil fraction. The 685-988°F Synthoil fraction contained 67% aromatics with greater than four rings while the Utah syncrude contained only 40% of these polynuclear aromatics, and the western Kentucky syncrude 49%. For comparison, comparable petroleum distillate fractions contain 17-21% polynuclear aromatics (25). Finally, the level of heteroatomic molecules (S, N, O) is greater in both the low-boiling and high-boiling fractions of the Synthoil liquids than in the COED liquids.

These differences are mentioned to indicate the diversity of composition which can be found among the syncrudes produced from various coals and using

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TABLE IV-16

COMPARISON OF DISTILLATES OF SIMILAR BOILING RANGE FRACTIONS FOR THREE SYNCRUDES

PRODUCED BY THE SYNTHOIL AND COED PROCESSES (25)

Coal Type Boiling Range (^{0}F)	Synthoil West Virginia		COED Western Kentucky (1)		Utah (1)	
	405-685^{0}F	685-988^{0}F	400-716^{0}F	716^{0}F	400-716^{0}F	716^{0}F
Saturates	16.0	9.7	25.0	23.8	27.8	25.8
Monoaromatics	27.3	4.7	42.0	25.1	25.1	14.4
Diaromatics	21.6	22.6	13.0	24.3	17.5	18.4
Polynuclear Aromatics	7.9	41.1	5.4	20.0	7.1	25.1
Heteroatomics	22.2	15.6	4.4	4.5	15.2	7.4
Distillate Wt.% of Syncrude	42.6	27.3	54.2	24.2	45.4	40.3

(1) Neither western Kentucky nor Utah COED syncrudes contained appreciable material boiling above 988^{0}C.

various coal liquefaction process. It would be of interest, in this respect, to liquefy a given seam of coal using the various liquefaction processes to see the exact differences in composition due primarily to processing variations.

In the study by Woodward et al. (25) the West Virginia syncrude was separated by distillation into three primary fractions 405^oF^-, 405°-685^oF and 685°-988^oF. The physical properties for these fractions are given in Table IV-17.

The 405^oF^- fraction contained 35.3 wt.% acids which were almost entirely phenols. This fraction consisted of 61 wt.% hydrocarbons, of which 27.1% was paraffins and cycloparaffins, 3.2% aliphatic olefins, 27.6% monoaromatics and 3.2% diaromatics.

The heavier fractions, 405°-685^oF and 685°-988^oF, were separated into component groups using liquid chromatography. These groups consisted of saturates, monoaromatics, diaromatics and polynuclear aromatic-polar materials. A summary of the separation for the two fractions and comparison with the initial syncrude is given in Figure IV-1. Of particular interest is the fact that the polynuclear aromatic polar compounds represent more than 62% of the 685°-988^oF fraction but only 30% of the 405°-685^oF fraction. It should also be noted that the 405°-685^oF fraction contains about 16% saturates compared to 60-80% found for most conventional petroleum crude fractions in same boiling range. Similarly, the 685°-988^oF fraction contains 10% saturates compared to 40-80% saturates for most petroleum fractions in the same boiling range.

The 405°-685^oF and 685°-988^oF fractions were further separated into specific compounds representative of three broad classes of compounds: monoaromatics, diaromatics and polynuclear aromatic-polar materials. The monoaromatics comprised 27% of the 405°-685^oF fraction and only 5% of the 685°-988^oF distillate. Most of these molecules consisted of a single benzene ring with several (up to six) naphthene rings attached. The average carbon number

TABLE IV-17

PHYSICAL-PROPERTY DATA FOR THREE DISTILLATES FROM

WEST VIRGINIA COAL LIQUID (25)

Property	< 405°F distillate	405° to 685°F distillate	685° to 988°F distillate
Specific gravity at 60°/60°F	0.936	0.990	1.109
Gravity, °API	19.7	11.4	
Pour point, ASTM D-97, °F	< 5	< 5	NA
Color (BuMines description)	brownish black	brownish black	greenish black
Kinematic viscosity, 100°F, ASTM D-445, Cs	2.27	9.56	-
Saybolt viscosity, SUS, 100°F	34	57	NA
Sulfur (bomb), ASTM D-129, wt.%	0.20	0.30	0.44
Nitrogen (Kjeldahl), wt.%	0.423	0.724	1.187
Carbon residue (Conradson), ASTM D-524, wt.%	1.29	2.33	7.42

NA -- Not applicable.

Weight — percent

Distillate [hatched]

Crude [hatched]

SATURATES
LB 16.5
HB 10.1
7.0
2.8

MONOAROMATICS
LB 37.1
HB 8.2
15.8
2.2

DIAROMATICS
LB 15.1
HB 18.7
6.5
5.1

POLYAROMATIC — POLAR
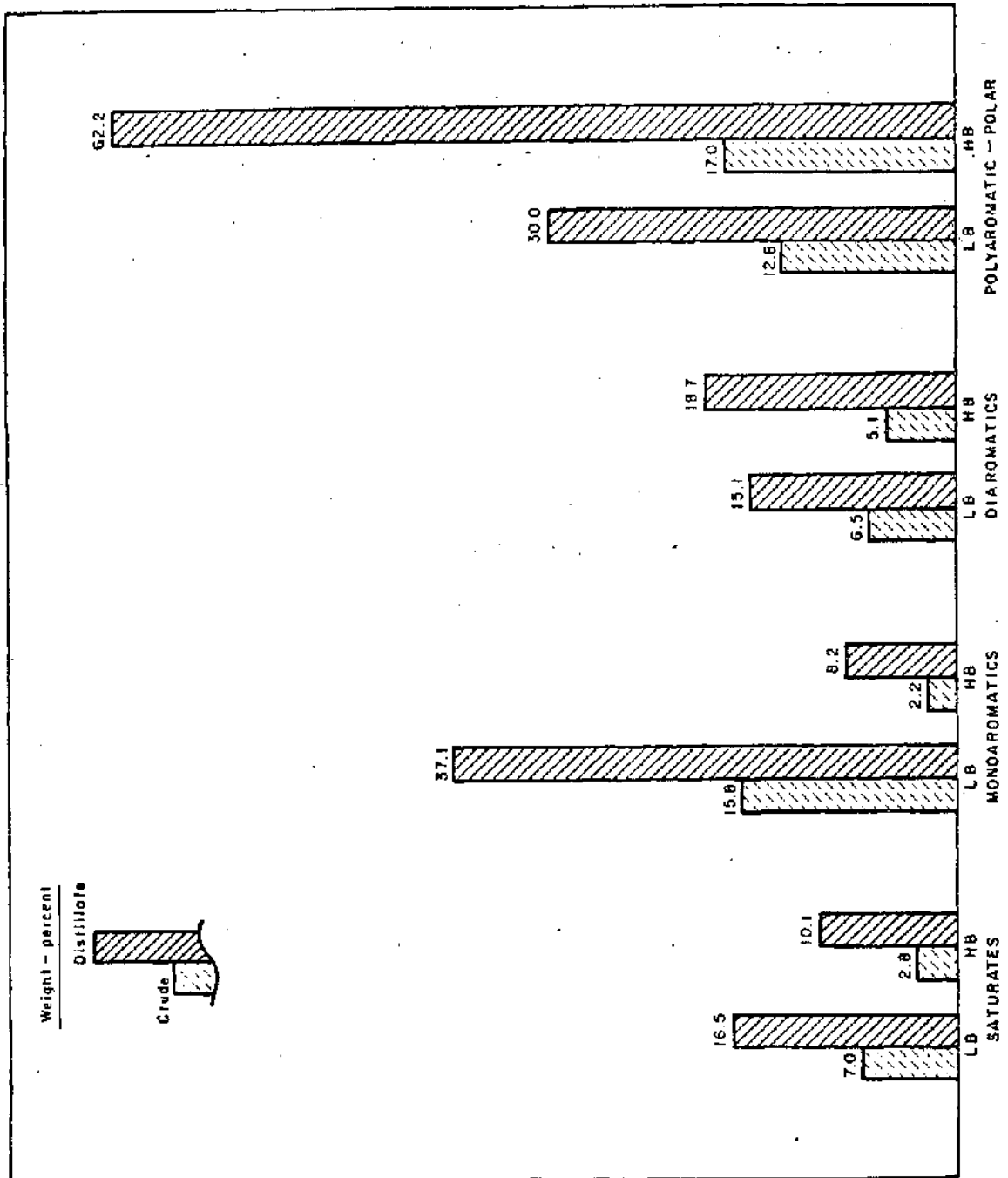LB 30.0
HB 62.2
12.8
17.0

Figure IV-1. Distillate Separation Data by Silica-Alumina Gel Chromatography for the 405° to 685° F (LB) and 685° to 988° F (HB) Distillates (25)

was C_{13} (with a range of C_{10}-C_{28}) for the lower boiling fraction and C_{22} (with a range of C_{15}-C_{30}) for the high boiling fraction.

Diaromatics made up 22% of both fractions. Diaromatics in the 405°-685°F fraction correspond to naphthalenes, diphenylalkanes and their naphthenologs with an average C_{13} carbon number (with a range of C_{10}-C_{26}). In the heavier fraction (685°-988°F) diaromatics were primarily naphthalenes with up to nine naphthene rings attached to the naphthalene nucleus. The average carbon number was C_{20} (with a range of C_{15}-C_{34}).

The chemical constituents of the polynuclear aromatic-polar group were also determined for both high and low boiling fractions. In the low boiling distillate the compounds were chromatographically separated into neutral hydrocarbons (10.3%), weak acids (7.2%), strong acids (9.1%) and bases (3.4%). The hydrocarbon fraction was found to consist of acenaphthalenes, phenanthrenes, anthracenes and their napthenologs.
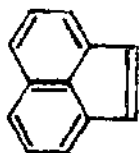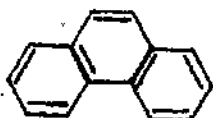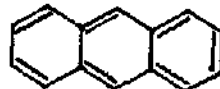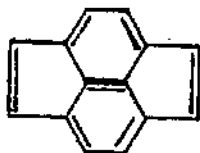
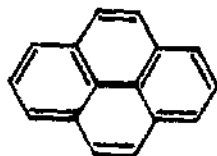ACENAPHTHALENE   PHENANTHRENE   ANTHRACENE
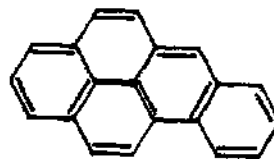
Other compounds included diacenaphthalenes, pyrenes, benzyopyrenes, perylenes, chrysenes and their naphthenologs.
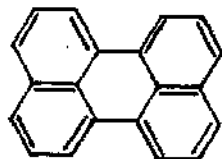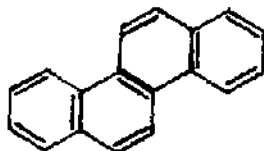
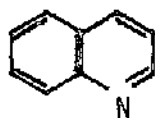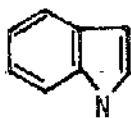DIACENAPHTHALENE   PYRENE   BENZOPYRENE
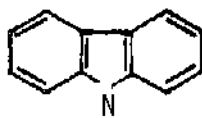
PERYLENE   CHRYSENE

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The nitrogen compounds which were detected consisted of 7.8% of the hydrocarbon fraction or 0.8% of the low boiling distillate. These included quinolines, indoles, carbazoles and acridines.
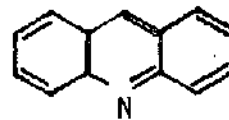

QUINOLINE   INDOLE   CARBAZOLE   ACRIDINE

Oxygenated compounds such as dibenzofurans and naphthenodibenzofurans were also identified but found to make up less than 1% of the distillate.

The weak acid compounds were determined to be indoles, quinolines and carbazoles as well as some oxygenates and sulfur compounds. The strong acids were found to be phenols and nephthenophenols, dinaphthenophenols and indene-ols.

The base fraction consisted primarily of pyridines, quinolines and acridines with quinolines being the major compounds in this group.

Similar to the low boiling fraction, the 685°-$988^{\circ}F$ fraction was separated into hydrocarbons (including neutral and weak acids) (48.4%), strong acids (6.8%) and bases (4.7%). The hydrocarbons were found to be naphthenologs of acenaphthalenes, phenarthrenes, anthracenes and chrysenes.

The strong and weak acids were not readily separated for the high boiling fraction. However, oxygenates and complex nitrogen compounds such as alkylcarbazoles were detected. Approximately 2.6% of the high boiling fraction was found to consist of nitrogen compounds, and 1.4% sulfur compounds. The bases extracted from this fraction were primarily quinolines and acridines. As will be shown below, these are difficult compounds to denitrogenate.

2. REFINING PROBLEMS

Three potential problem areas are expected to affect the required processing steps of Synthoil liquids. The severity of these problems will depend

upon the fraction being processed and the desired product specifications. The problems are high values of Conradson carbon in all fractions, high concentrations of large polynuclear aromatic molecules and the existence of sulfur, nitrogen and oxygen in complex heterocycles. A fourth potential problem is the fact that the Synthoil syncrude contains about 0.2 wt.% ash which can affect processing by depositing on the surface of the catalyst. Each of these points is discussed below for upgrading to the three desired products: high-octane gasoline, jet fuel and diesel fuel.

a. High-Octane Gasoline

The primary objective in producing high-octane gasoline is to make single-ring aromatics and branched-chain paraffins, both of which are high octane components. In this respect the $405^{\circ}F^{-}$ fraction from Synthoil syncrude could be used as a naphtha feedstock, however only after some pretreatment. This distillate would require hydrotreating to convert the high concentration of phenols (35.3%) to single ring aromatics, to reduce the nitrogen (0.423%) and sulfur (0.20%) levels to less than 2 ppm, and to minimize the high level of Conradson carbon (1.29%). The phenols and sulfur and nitrogen compounds poison conventional reforming catalysts. The Conradson carbon level leads to excessive deposition of carbon on the reforming catalysts, thereby affecting activity maintenance. To minimize these problems, the required hydrotreatment may be quite severe because of the high levels of nitrogen and Conradson carbon. It should be noted that in contrast to this light fraction from the Synthoil syncrude, a similar fraction from the COED or H-coal processes would be highly naphthenic and therefore easily converted to gasoline.

The $405-685^{\circ}F$ fraction (middle distillate fraction) also presents several refining problems for conversion to gasoline. It contains almost 30 wt.%

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polynuclear aromatics which are large molecules including acenaphthalene, phenanthrene, anthracene, diacenaphthalene, pyrene, benzopyrene, perylene and chrysene. The average carbon number is C_{13} in a range of $C_{10}-C_{28}$. The structure of these molecules has been shown earlier. They are basic in nature and adsorb strongly on metals and oxides and lead to excessive catalyst deactivation by blocking active sites, as well as by acting as coke precursors. This middle distillate fraction is also low in saturates (16% compared with 60-80% for similar petroleum fractions). It is likely that this fraction could be hydrocracked or catalytically cracked. However, before such processing could be done, hydrotreatment would again be required to lower the sulfur (0.30%) and nitrogen (0.724%) levels and to reduce the amount of Conradson carbon (2.33%). An alternate possibility would be to distill off a lighter fraction and blend the heavy residuum with fuel oil.

The heavy fraction, 685-988°F, is even more problematic for processing than the light and middle distillate fraction. The sulfur level is as large as 0.44%, the nitrogen 1.19% and the Conradson carbon 7.4%. The polynuclear aromatics level is greater than 62%, with most of the molecules being large aromatic rings, highly substituted with naphthenes. Unless this fraction is subjected to a very severe hydrotreatment (similar to a residfining process), it is likely that it would have to be vacuum distilled and the residuum coked.

b. Jet Fuel

The middle distillate from Synthoil syncrude (405°-685°F) can potentially be converted to jet fuel or at least a jet fuel blending stock. However, it will also require a reasonable amount of pretreatment. A comparison of the physical properties for the middle distillate fraction (Table IV-16) with those for JP-5 jet fuel (Table IV-8) shows that the Synthoil middle distillate has a high specific gravity (11.4 °API compared to 36-48 °API for JP-5)

and the sulfur level of 0.3 wt.% is lower than the JP-5 specification of 0.4 wt.%. The primary problem is likely to be the high level of aromatics. The Synthoil fraction contains 37.1% monoaromatics, 15.1% diaromatics and 30.0% polynucleararomatics. This is substantially greater than the tolerable level of 25 volume % for JP-5. As was the case for the COED liquids, high-pressure hydrotreating could saturate many of these aromatic structures to naphthenic materials which not only have better smoke point properties but also give an improved energy density. However, in the presence of substantial amounts of naphthenes it may be necessary to reduce the aromatics level to practically zero, as their smoking properties are enhanced in the presence of naphthenes. Ultimately, the most effective processing step for converting the Synthoil middle distillate fraction to jet fuel would be hydrogenation to naphthenic structures followed by selective cracking of these saturates to branched paraffins and paraffin-substituted single ring aromatics.

c. Diesel Fuels

The Synthoil middle distillate fraction is in the appropriate boiling range for a diesel fuel. However, it is a very aromatic fraction. In view of the diesel fuel specifications presented in Section II of Part 3, it is apparent that the Synthoil fraction would not meet the cetane number and specific gravity requirements (See Table IV-9). As pointed out in the discussion of COED coal liquids, this high aromaticity also gives the fuel an increased oxidation stability which promotes poor burning characteristics in diesel engines.

High pressure hydrotreating and selective cracking to a paraffinic-naphthenic fuel is expected to be necessary to reduce aromaticity and produce a fuel which meets the diesel specifications discussed in Section II.

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E. IMPACTING AREAS AND RECENT RESEARCH DEVELOPMENTS

Although the syncrudes produced from a given coal may vary for the COED, H-Coal and Synthoil processes, it is apparent that the compositions are at least qualitatively similar with respect to various molecular constituents. Therefore, the technical difficulties in converting these syncrudes to high-octane gasoline, jet fuel and diesel fuel, are expected to be similar and to vary primarily in degree. As an example, the COED and H-Coal processes generally give a more naphthenic naphtha which is easier to reform than that which is obtained from Synthoil syncrudes. However, both H-Coal and Synthoil naphthas contain polynuclear aromatics and heterocycles which lead to catalyst deactivation. This problem is most severe for Synthoil liquids.

The high aromaticity of the various syncrudes makes them difficult to process, particularly to jet and diesel fuels which are generally paraffinic in nature. From the previous discussion of the molecular composition of the starting syncrudes and the three primary distillate fractions, it is clear that there are three major technical requirements: selective hydrocracking of polynuclear aromatics, more effective hydrotreating processes (particularly for HDN) and the development of catalysts with improved activity maintenance. Each of these is discussed below in some detail.

1. SELECTIVE HYDROCRACKING OF POLYNUCLEAR AROMATICS

Distillation of COED, H-Coal and Synthoil liquids into light naphtha, middle distillate and residuum oil gives fractions with substantial amounts of molecules containing 3 to 9 condensed aromatic rings, sometimes highly substituted with naphthenes or paraffins. It is essential to selectively hydrocrack these multiring structures with a minimum consumption of hydrogen, as they lead to catalyst deactivation in many conventional petroleum upgrading processes. For the production of jet and diesel fuels the rings must be either

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saturated to form cycloparaffins (naphthenes) or, more preferably, the latter hydrocracked to branched paraffins.

Unfortunately, only a limited amount of work has been done concerning detailed kinetic studies of the catalytic conversion of these large ring structures, primarily because of the experimental difficulties in carrying out a catalytic study with such large aromatic molecules. These difficulties include rapid catalyst deactivation and, more particularly, difficulties in obtaining reliable product analyses. Over the past five years, the development of chromatographic and spectrographic techniques which are capable of giving rapid, accurate analyses (28), have permitted some progress in this area. Pertinent studies have included the hydrocracking of naphthalene, anthracene, phenanthrene and pyrene (29). With structures such as anthracene, it is most desirable to minimize uncontrolled thermal reactions by using an active catalyst which operates at low temperatures, and to selectively crack to single ring aromatics with minimum light gas make. For example, in the case of phenanthrene, it is preferrable to saturate the center ring and subsequently crack only this part of the molecule to form ethyl- and methyl-benzenes.
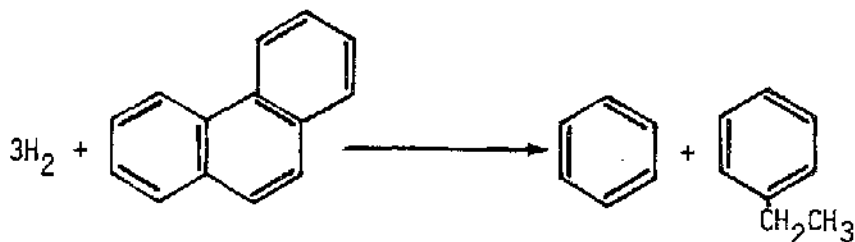
This has been observed with limited selectivity in the work of Wu and Haynes (30). The approach was to use controlled acidity and a valence-stabilized transition metal oxides, in this instance Cr_2O_3 on Al_2O_3. The particular catalyst used in the study had moderate acidity and alumina was used to stabilize the Cr^{+3} state in the reducing environment. Therefore, controlled acidity in the

present of a particular transition metal oxidation state may be one approach to enhancing the selectivity for center-ring cracking reactions.

This is further exemplified by the work of Qader et al. (31) who found that CoS mechanically mixed with $SiO_2 \cdot Al_2O_3$ was more active for hydrocracking aromatic ring structures than either component by itself. This supports the bifunctional mechanism for hydrocracking and further indicates that migrations occur for either hydrogen or one of the hydrocarbon intermediates. In studying the $CoS/SiO_2 \cdot Al_2O_3$ catalyst, these workers also found a marked effect of the Si/Al ratio, high ratios giving more active catalysts. CoS appeared to be better than NiS, WS_2 and MoS_2 for minimizing coke formation, possibly because of its higher hydrogenation activity. All of this suggests that low temperature hydrocracking catalysts will require an optimum ratio of the hydrogenation and cracking functions.

The data are few and there is a need for much more work in this area. It is necessary to discover very active catalysts for cracking the large rings, as the activation energy for the condensation or polymerization reactions is usually larger than the cracking reactions, and therefore lower temperatures favor cracking over condensation to coke precursors. If higher temperatures are required, it may be necessary to quench free-radical intermediates which initiate condensation. One way to do this is by using hydrogen-donors such as tetralin which selectively transfer hydrogen atoms to these intermediates. Some work in this area has recently been reported (32) in conjunction with donor desulfurization of heterocyclic aromatics. As discussed below for catalyst deactivation, donors may be an effective means of minimizing the carbonization of polynuclear aromatics by quenching free-radical thermal reactions.

Advances in catalyst preparative techniques allow the preparation of a variety of oxides, sulfides, oxysulfides and even more complex materials with

controlled physical and chemical properties (33). Pore size distribution, surface area, and acidity are primary parameters for the hydrocracking of large aromatic molecules. Preparative procedures such as gel-precipitation, homogeneous pH charge, aerogels, pyrogels and sol gels are useful for preparing mixed oxides like $TiO_2 \cdot SiO_2$, $Al_2O_3 \cdot MgO$, $ZrO_2 \cdot TiO_2$, etc., with varying pore-size distribution and acidity (33). It is expected that many of these techniques will be important for synthesizing new catalysts.

One of the more important physical properties to control is pore size. With molecules like acenaphthalene, phenanthrene, anthracene, diacenaphthalene, pyrene, benzopyrene, perylene and chrysene, as well as heterocycles such as quinoline, indole, carbazole and acridine among many others, it is crucial to have wide pore catalysts to facilitate the entry of these large molecules to the active sites. Unfortunately, as these pores are made larger by a number of the various preparative procedures mentioned above, the mechanical properties (particularly crush strength and attrition) begin to deteriorate rather quickly. However, recent work has indicated that this might be remedied to some degree (34). For example, doping aluminas with certain alkaline and rare earth cations creates a more rigid lattice network which is apparently translated on a macroscopic scale since the crush strength of the aluminas is improved. It is not certain at this time whether this improvement in mechanical properties is due to the improved lattice properties or simply to enhanced adhesive strength between particulates which make up the alumina structure in the final catalyst pellet.

In terms of chemical properties, the hydrogenation to cracking activity ratio is important for selective hydrocracking. The wealth of novel inorganic materials which have been discovered over the last decade gives the catalytic chemist a vast number of systems from which to choose. These include complex

oxides which may contain both catalytic functions, e.g., zeolites, perovskites like $SrTiO_3$ (perhaps with modified acidity by addition of another oxide like SiO_2 or Al_2O_3), bronzes like $NaWO_3$, oxides containing metal-metal bonded clusters like $Mg_2Mo_3O_8$ or $Co_2Mo_3O_8$; a large number of complex sulfides such as $BaZrS_3$ (perovskite), $FeCr_2S_4$ (thiospinel) and $Al_{0.5}Mo_2S_4$; and a host of carbides (e.g., W_2C, Pt_3SnC, $W_{16}Ni_3C_6$), Nitrides (e.g., Co_3N_2, V_2N, Ti_2AlN, Ni_3AlN), Borides (MoB, $Co_{21}Hf_2B_6$, Ni_3B), Phosphides (Co_2P, FeP_2) and Silicides (Mo_3Si, $TiSi$) (35). These materials have varying thermal and chemical stabilities. As discussed in Parts 1 and 2 of this study chemical stability is especially affected by the presence of sulfur. Depending upon the upgrading step and the level of sulfur in a given fraction these materials will vary in chemical stability. Particularly influenced by a sulfiding environment are metals and multimetallic systems although thermodynamic calculations suggest that the ultrastable Engle-Brewer intermetallic compounds such as $ZrPt_3$ may have enhanced sulfur resistance at low to moderate sulfur levels (36). Unfortunately, many of these materials have not been studied even for simple catalytic reactions, although their structure and chemical properties suggest potential applications. The primary reason for this has been the inability to prepare these compounds in high enough surface area to obtain meaningful catalytic data. Numerous new catalyst preparative procedures have been developed which have direct application to the solution of this problem (33).

Complex oxides, sulfides and oxysulfides are of particular interest because the hydrogenation to cracking activity can be "fine tuned" for these materials by controlling composition (35). There is also some indication that sulfur sensitivity can be affected for some of these materials. Zeolites in combination with amorphous mixed-oxides have significant potential. Work by Dalla Betta et al. (37) has shown that by careful preparative procedures one can put

a highly dispersed transition metal in various parts of the zeolite network. For some metals this results in a modification of electronic properties and therefore catalytic properties. As an example, it is possible to enhance the sulfur tolerance of Pt atoms in certain zeolites because there is an electron withdrawal from the Pt atoms which apparently weakens any interaction with sulfur. This is supported by the fact that interactions with bases like NH_3 are enhanced. Indeed, preliminary work with zeolites in combination with hydrogenation functions such as WS_2 or MoS have shown that they have potential for hydrocracking polynuclear aromatics to single ring structures (38).

In carrying out catalytic studies with model polynuclear aromatic structures it is essential to work with well characterized catalysts. At minimum, this means that the total surface area, average pore diameter and possibly selective adsorption measurement of the active catalytic surface are required. Each of these have been discussed in detail in Section III as well as in Part 1 (39) and therefore will not be treated here. Furthermore, the use of techniques such as Auger electron spectroscopy, X-ray photoelectron spectroscopy, ion scattering spectroscopy and many others which have been developed by workers in catalysis and surface science (40) will find application in elucidating the surface chemical and physical properties of complex catalysts.

Finally, it should be mentioned that hydrocracking the middle distillate, particularly the heavy ends fraction from any of syncrudes discussed in this section is, by the very nature of the system, carried out in liquid phase. In addition to deactivation phenomena (discussed below), contacting of the catalyst with hydrogen and the large polynuclear aromatic structures is a problem and inevitably leads to mass-transfer limitations. More effective contacting can be obtained by the use of homogeneous catalysts (41), molten salts (42) and also by the use of supercritical catalysis (43). Homogeneous catalysts, while

conceptually promising, are fraught with the difficulties of catalyst loss and and recovery. Molten salts have similar problems although in recent work improved catalyst recovery and diminish losses to the 99.9% level for direct coal liquefaction have been reported (44). The probability of success using melts for hydrocracking heavy feedstocks is substantially greater than for coal since losses due to eutectic formation with mineral matter is decreased. The concept of supercritical catalysis is relatively new, however preliminary data suggest that this technique offers a number of possible advantages for hydrocracking heavy fractions. For example, direct extractions of coal at 660°F and 1450 psi with toluene gave products which indicated very limited degradation at these relatively severe conditions (43). Furthermore, gas yields were insignificant. These results may be due to a substantial improvement in contacting at super-critical conditions and also to the significant increase in gaseous diffusivities at these conditions. Catalytic work in this area is limited but some work concerning paraffin isomerization (45) using a CO_2-hydrocarbon solvent at 1000-5000 psig and temperatures up to 200°C showed a five-fold increase in the ratio of isomerization to cracking. Lewis acid catalysts such as $AlBr_3$ and $AlCl_3$ were used in this example. The catalysts can be either homogeneous or heterogeneous.

2. HYDROTREATING PROCESSES

In converting a highly aromatic syncrude to a jet fuel or diesel fuel it is necessary to subject the middle distillate and heavy distillate to severe hydrotreating prior to hydrocracking or catalytic cracking. For the H-Coal and Synthoil syncrudes, it is also necessary to hydrotreat the light naphtha fraction prior to catalytic reforming. The primary reasons for hydrotreating are:

- To reduce oxygen, sulfur and nitrogen compounds, which are catalyst poisons, to acceptable levels for further catalytic processing

To saturate and partially hydrocrack polynuclear aromatics which give rise to catastrophic catalyst deactivation in most conventional petroleum upgrading operations.

The second point has been treated above and therefore the present discussion will be confined to the removal of oxygen, sulfur and nitrogen. Of these, the removal of oxygen is least difficult. This is because in most instances the oxygen atoms are in phenol groups and not in complex furan structures. Therefore, only hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) will be discussed in detail. It should be mentioned that in some instances where the presence of oxygen-containing molecules such as phenols is acceptable, it is desirable to remove only sulfur and nitrogen selectively to minimize hydrogen consumption. For upgrading to gasoline, jet fuel and diesel fuel this is not the case.

a. Hydrodesulfurization

Hydrodesulfurization is kinetically less difficult than HDN, although substituted benzothiophenes and naphthobenzothiophenes present both steric and chemical problems for conventional HDS catalysts (46). Unfortunately, only a few studies have been reported for HDS of large polynuclear heterocycles. These have been carried out over cobalt molybdate catalysts and described in Part 2 of this study (47). This work suggests the following general steps for substituted thiophenes such as 3,7-dimethylbenzo- b- thiophene:

i) Alkyl group migration on the thiophene ring;

ii) Dealkylation from the ring;

iii) Sulfur extraction from the rearranged or demethylated secondary products; and,

iv) Some direct sulfur extraction from the primary reactant.

It was found that the desulfurization step involves C-S bond breaking as an

initial step, and that aromatic saturation is not a prerequisite for C-S bond breaking when the carbon atom is aromatic. This suggests that the appropriate selective catalyst should be able to remove sulfur without doing a significant amount of unnecessary hydrogenation. This would have certain economic benefits due to savings in hydrogen costs.

Much of the work in the HDS area indicates that hydrogenolysis and hydrogenation reactions proceed on separate sites (48). Thus, selective poisoning experiments suggest that hydrogenation occurs on strongly electrophilic sites, whereas desulfurization reactions require weakly electrophilic sites. If this is true, the synthesis of more active catalysts for HDS may require a bifunctional approach. Many of the novel inorganic materials discussed above could find application. The use of catalyst-support interactions, controlled surface acidity and modified physical properties should also be important (48). In terms of new materials, sulfides and oxysulfides are particularly attractive for study. The latter have not been studied much for HDS. However, work by Kolboe and Ambery (46) showed that the addition of oxygen to thiophene during HDS over MoS_2 caused a doubling of the rate of HDS. The effect of oxygen on butene (a proposed intermediate in thiophene HDS) hydrogenation is even greater, increasing by one hundredfold (46). This effect, though unexplained, may be due to one or both of two factors. First, the oxygen may activate molecular hydrogen forming OH · radicals, which ultimately leads to a chain mechanism that produces substantial quantities of atomic hydrogen. Alternatively, the partial pressure of oxygen may produce a surface oxysulfide which has higher catalytic activity for HDS.

Numerous other complex oxides such as the $M_2Mo_3O_8$ (where M=Mg, Zn, Co, Mn, and others) have been suggested as HDS catalysts (49) because of the unusual position of the Mo atoms in these structures. They are located at the apices

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of equilateral triangles with a Mo-Mo distance 2.53A (shorter than in Mo metal). Only recently has a procedure been developed to prepare these materials in high surface area (49). These materials were indeed found to exhibit unusual catalytic properties for hydrogenation and hydrogenolysis reactions, with activities between those observed for metals and oxides. The study of HDS of realistic model compounds such as dibenzothiophene and even larger molecules using these and other complex oxide and oxysulfides could give some leads for new more active HDS catalysts.

Finally, it is worth noting the recent catalytic hydrogen donor HDS work which was reported by Doyle (32). In this study it was found that the combination of an HDS catalyst (cobalt molybdate) with a hydrogen donor such as tetralin synergistically enhanced desulfurization over the rates found by the use of the donor or the catalyst separately. While the mechanism is not completely understood it suggests a promising approach for improving desulfurization. The few experiments which were tried for HDN were unsuccessful, perhaps for reasons which are discussed next.

b. <u>Hydrodenitrogenation</u>

The motivation for removing nitrogen from syncrudes is twofold: to avoid catalyst poisoning in downstream refining steps and to minimize NO_x formation during combustion of the final fuel product. The latter factor is responsible for a more recent intensive interest in HDN studies. Prior to this, catalyst poisoning was the major reason for studying HDN and much greater emphasis was put on HDS because of catalyst poisoning problems in refining and environmental control of SO_x formation during fuel combustion.

Most HDN work has been done with pyridine which is not a realistic model compound for the polynuclear heterocycles reported in the fractions from the syncrudes of the three liquefaction processes. Compounds such as quinoline,

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indole, carbazole and acridine are more relevant. The work which has been done using more complex molecules such as quinoline suggests that C-N hydrogenolysis is the rate-limiting step (50). This should be studied in further detail and confirmed. If true, it suggests that bifunctional systems may play a significant role. For example, a controlled acid function may be used to interact just sufficiently with the basic nitrogen atom, while an adjacent surface site (perhaps a transition metal cation) interacts with the α-carbon atom in the nitrogen heterocycle. This could lead to substantial weakening of the C-N bond in the molecule and perhaps increased activity. It would permit operation of HDN at lower temperatures, where coke formation (see below) is minimal. Catalyst-support interactions and novel sulfides, oxides, and oxysulfides are likely to be important for the synthesis of these materials. It is interesting to note that conventional HDN catalysts usually contain a metal which strongly adsorbs nitrogen, e.g., W in Ni-W, and Mo in Ni-Mo. For feeds which are low in sulfur, chemical stability will not be a severe problem; and this opens up the possibility of metals, multimetallic systems and especially the Brewer-type intermetallic compounds such as $ZrPt_3$ (51).

In using oxide and sulfide catalysts, the conditions for presulfidation could have a significant effect on the optimum HDN activity. For example, Goudriaan and co-workers (52) studied pyridine HDN over Cobalt molybdate catalysts and found the presulfided catalyst to be substantially more active than the oxide. Continuous addition of H_2S further increased activity. From other mechanistic work they concluded that the beneficial effect of H_2S on HDN is twofold. First, the hydrogenation activity of the sulfided catalyst is substantially greater than the oxide for conversion of the heteroaromatic ring to its saturate analog. Secondly, the presence of H_2S had a beneficial effect on the hydrocracking activity of the catalyst. Similar effects were reported by

Mayer (53). It is possible that two effects are in operation, one where the H_2S maintains an optimum surface stoichiometry for the catalyst and the other where H_2S participates in the surface reaction. However, much more work with realistic model compounds at controlled conditions, using well-characterized systems, is needed to clarify these effects. The effects of NH_3, H_2O, O_2, CO and CO_2 should be studied as well.

It has been known for some time that heterocyclic nitrogen compounds promote catalyst deactivation. Kinetic studies with multiring heterocyclic nitrogen compounds are hampered because of side reactions which reportedly lead to unstable intermediates and subsequent coking of the catalyst surface (50). This is shown by the work of Madison and Roberts (54) who studied the pyrolysis of aromatics and related heterocyclics. In one series of experiments these workers studied the liquid phase thermal pyrolysis of molecules such as quinoline, isoquinoline, acridine, indole and carbazole. They found that the substitution of a nitrogen atom in a polynuclear aromatic substantially increased the coking rate. For example, acridine coked 10 times faster than anthracene:

<div align="center">

wt.% COKE (30 min. at 475°C)

</div>
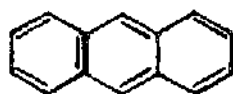
ANTHRACENE   5.6
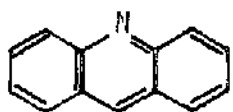
ACRIDINE   56.2

The gas formed contained an equal quantity of hydrogen and methane, indicating extensive decomposition of the aromatic nucleus. Similar effects were found for quinoline versus its aromatic analog, naphthalene, the latter forming no coke under the test conditions while the quinoline formed 4.9 wt.% coke.

<div align="center">

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</div>

These authors feel that replacement of a CH group in naphthalene or anthracene by a nitrogen atom leads to a decrease in the dissociation energy of one or more of the C-H bonds, thereby facilitating condensation. The position of the nitrogen atom also has an effect as shown by the fact that isoquinoline coked more rapidly than quinoline. Acridine coked even faster than the quinoline, which is in agreement with the fact that anthracene cokes more rapidly than naphthalene. These experiments suggest that not only can nitrogen compounds deactivate catalysts by interacting with acidic sites, but also by enhanced coking rates relative to other polynuclear aromatics. Interestingly, sulfur or oxygen anologs were not nearly as active as the nitrogen heterocyclics for forming coke. All of this suggests that more active catalysts (which could be operated at lower temperatures) will have a much greater effect than might be presently anticipated, especially if present activity maintenance is limited largely by coking of nitrogen heterocycles.

   3. ACTIVITY MAINTENANCE

The primary distillates from the COED, H-Coal and Synthoil syncrudes deactivate catalysts in upgrading operations such as reforming, hydrotreating, hydrocracking and catalytic cracking. The most important modes of deactivation include coking, sintering, poisoning by sulfur and nitrogen compounds, and mineral deposition. The problems of HDS and HDN have already been discussed in detail above. Therefore, this section will concentrate on catalyst deactivation by coking, sintering and mineral deposition.

Coking is perhaps one of the major problems in catalyst deactivation. This is particularly true in the presence of polynuclear aromatics, and especially those which contain nitrogen atoms. The high coking rates observed for heterocyclic polynuclear aromatics (discussed above) have also been observed for polynuclear atomatic compounds which do not contain a heteroatom.

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Although the effect is not as severe, Madison and Roberts (54) have observed that ring structures such as anthracene undergo thermal pyrolysis much more readily in liquid phase than in the vapor phase. The gas from the vapor phase pyrolysis was found to be primarily hydrogen, while that from the liquid phase pyrolysis was mainly methane, indicating degradation of the ring structure in the latter case. Differences in liquid and gas phase reactions have also been observed for phenyl radicals in toluene at 80°C (and in the gas phase at 600°C (55). It was found that in solution the radicals add to the aromatic nucleus to form pyrolysis products, while in the gas phase they abstract a hydrogen atom from the methyl group of toluene. The former leads to the formation of substantial hydrocarbon deposits.

Madison and Roberts also found that molecular structure significantly affects coking rates (54). Thus, compounds having an anthracene or chrysene nucleus (e.g., Benz [a] anthracene, Naphthacene, Benzo [a] pyrene) formed coke much more readily than unsubstituted aromatics such as biphenyl, naphthalene, phenanthrene, triphenylene, pyrene, fluoranthrene and decacyclene. The high reactivity of polynuclear atomatics toward $CCl_3 \cdot$ and $CH_3 \cdot$ radicals (56) suggests that thermal free-radical reactions are involved in the coking condensation reactions. Szwarc (56) showed that reactivities of aromatic molecules with $CH_3 \cdot$ radicals correlated well with the energy of excitation of the aromatic nucleus from its singlet ground state to the first excited triplet state. In the latter the hydrocarbon showed diradical character and was reactive toward other radicals. The Madison-Roberts study confirmed this (54), since, with only the exception of pyrene, lower singlet-triplet excitation energies were found for all hydrocarbons possessing the anthracene structure. As discussed above, this structure was shown to correlate with a high coking tendency. These workers feel that the pyrolysis-coking reactions are not

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simply polymerization, as hydrogen is eliminated in the reactions. They feel that easy activation to a diradical facilitates the formation of an activated complex between two molecules, which then can form a condensation product by elimination of a hydrogen molecule.

Two approaches can be taken to avoid catalyst deactivation by polynuclear aromatic coking. First, a more active catalyst for cracking these structures (discussed above) can be formulated which permits operation at low enough temperatures to minimize the thermal free-radical reactions. Secondly, a mechanism exists for quenching the radicals formed. Hydrogen donor and supercritical catalysis are two possibilities and have been previously discussed in detail.

For processing fractions which contain substantial amounts of coke precursors such as polynuclear aromatic, it is sometimes possible to use a catalyst which has high activity maintenance under these conditions. For example, for reforming naphtha to high octane gasoline, Exxon's KX-130 catalyst has high activity maintenance because it minimizes carbon deposition. Similarly, Chevron's Pt-Re catalyst has high activity maintenance because it can tolerate high levels of coke.

Sintering can come about from continued oxidative regeneration of catalysts or by operation at high temperatures in a reactive environment. Sintering models have been developed and have been used to understand the modes of thermal deactivation of catalysts (57). Many of the pertinent sintering models indicate that catalyst stability can be enhanced by controlling the support morphology and/or structure and by enhancing the catalyst-support interaction (58). In this regard, the use of structurally-stabilized solid acids and ultrastable zeolites as the acid function of the catalyst will be important. Similarly, novel preparative procedures such as the cogel

procedures (59) will be useful. For example, the latter reportedly gives complex oxide catalysts such as $NiO \cdot WO_3 \cdot ZrO_2$, $NiO \cdot WO_3 \cdot TiO_2$, cogelled with ultrastable zeolites, which maintain a surface area at high temperatures (e.g., 350 m^2/g after treatment at 1200°C for 2 hrs.).

The final mode of catalyst deactivation to be discussed is by mineral deposition. The mineral content of the syncrudes from the COED, H-Coal and Synthoil liquefaction processes can be as high as 0.2-0.3 wt.%. This consists primarily of silicates, aluminates and components of iron and titanium as well as trace amounts of numerous other elements (60). The deposition of these minerals on a catalyst surface during an upgrading operation not only blocks active sites but can possibly modify the chemical state of the catalyst. For example, small amounts of TiO_2 on a silica or alumina support can cause a marked increase in surface acidity. This can result in increased hydrocracking activity to light gases and consequent liquid product losses and increased use of hydrogen. Other mineral components are not as severe for chemically modifying the catalyst but simply geometrically block active surface area.

The mineral problem is a very difficult one. Little work has been done to understand and solve it. One program which is presently being sponsored by ERDA is being performed at the SANDIA Laboratories in New Mexico (61) to determine the mode of catalyst deactivation which is used in the Synthoil process. However, insufficient data are available at this time. The Synthoil process is in fact operated at very high linear velocities in the turbulent regime to promote "controlled attrition" of carbon and minerals which deposit on the catalyst. Two other approaches to the problem are to use a homogeneous or molten salt catalyst. However, these have the limitations discussed previously and would require major innovation to be practical. The use of

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molten salts is perhaps an exception and work being done at this time at the University of Utah and by the Consolidation Coal Co. (44) may prove this to be the case. The mineral problem is of no concern for the light and middle distillates from the syncrudes and only becomes a problem for the heavy fraction in which it concentrates after distillation.

As one approach to the problem, one might consider novel approaches to regenerating used catalyst which have mineral deposits (especially if they are expensive materials). Ultimately, it would be most effective to develop catalyst systems which would avoid the problem, or to develop an unusually high-yield, separation process which would remove most of this contaminant from the fractions being processed.

F. CONCLUSIONS

Various fractions from COED, H-Coal and Synthoil syncrudes can be processed to high-octane gasoline, jet fuel and diesel fuel using conventional petroleum technology. The processing presents difficulties of a greater or lesser degree depending upon the fraction and the desired product. High octane gasoline is not a significant problem since this product is derived from the light naphtha fractions which are usually either naphthenic or aromatic in nature. The naphthenes are readily dehydrogenated or hydroisomerized by reforming to single ring aromatics which are high-octane constituents. The problems occur in converting the middle distillate or heavy-end fractions to single ring aromatics or to low molecular weight cycloparaffins or branched paraffins, the latter two molecular types being desirable for jet and diesel fuels. The middle distillate and heavy-ends fraction are usually high in Conradson carbon, polynuclear aromatics and high molecular weight heterocycles. These materials are difficult to convert to the desired molecules and also

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facilitate rapid catalyst deactivation in processes such as naphtha reforming, hydrocracking and catalytic cracking. Therefore, these fractions require severe hydrotreating before they can be processed by conventional petroleum technology. Such hydrotreating is costly because it is non-selective leading to excessive use of H_2. There are, therefore, three broad areas which require new scientific and technological development: Selective hydrocracking of polynuclear aromatics, more effective hydrotreating processes and the development of catalysts with improved activity maintenance.

The following is a summary of the results and recommendations presented in this section. It is divided into the abovementioned three research areas. Short and long range programs are indicated.

1. <u>Selective Hydrocracking of Polynuclear Aromatics</u>

    a. <u>Short Range Programs</u>

    ● Development of new bifunctional catalysts which have a controlled ratio of cracking to hydrogenation activities. Emphasis should be on novel inorganic materials particularly complex oxides and oxysulfides, and the use of novel catalyst preparative procedures to control surface acidity and physical properties (particularly pore size distribution, crush strength and attrition).

    ● Improvement of catalyst characterization techniques and comparison of activities of all catalysts on a rate per unit surface area basis. Methods such as the titration of transition metal cations with gases (e.g., NO) should be perfected.

    b. <u>Long Range Programs</u>

    ● Study of model reactions with polynuclear aromatic molecules such as anthracene, chrysene, etc. Investigation of the

properties of novel catalysts (acidity, hydrogenation activity, cracking activity, etc.) which promote center-ring scission and conserve hydrogen.

- Understanding and minimization of thermal free-radical reactions: Study of pyrolysis rates of polynuclear aromatics which are found in various fractions at process conditions, development of hydrogen-donor catalysis.

- Development of surface characterization procedures for complex oxides, sulfides, etc., including the application of spectroscopic tools such as AES, XPS, and SIMS.

- Study of improved methods of solving the mass-transfer contacting problems, including consideration of molten-salt cracking (bifunctional systems) and the use of supercritical catalysis.

2. Hydrotreating Processes

   a. Short Range Programs

   - Development of bifunctional HDS/HDN catalysts. Investigation of complex oxides, sulfides, and oxysulfides, and the concept of dual-sites which interact with C and either S or N. Variation of the ratio of hydrogenation to hydrogenolysis activity by catalyst support interactions and controlled acidity; optimization of physical properties (particularly pore size distribution).

   - Study and optimization of the effects of presulfidation and the effects of NH_3, O_2, H_2O, CO and CO_2 on activity and activity maintenance of HDS and HDN catalysts.

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b. <u>Long Range Programs</u>

- Study of HDS and especially <u>HDN</u> using realistic model compound such as dibenzothiophene, carbazole, acridine, etc.

- Study of the nature of thermal coking reactions for N and S heterocycles. Investigation of routes to minimize these cracking reactions by hydrogen donor effects and supercritical conditions.

3. <u>Activity Maintenance</u>

a. <u>Long Range Programs</u>

- Study of the pyrolysis of polynuclear aromatics and methods to avoid coking reactions.

- Improvement of the sintering resistance of catalysts and supports by catalyst-support interactions and the use of new doping procedures and catalyst preparation (e.g., cogels, ultrastable zeolites).

- Development of novel procedures for catalyst regeneration, including the use of reagents which selectively remove minerals.

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