Exploratory Studies in Catalytic Coal Liquefaction

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ABSTRACT

HRI, in support of their H-coal process, has run catalyst aging tests simulating H-coal conditions with Illinois #6 coal for ~10 days with Cyanamid 1442A ($CoMo/Al_2O_3$), Cyanamid $NiMo/Al_2O_3$, Armak $NiMo/Al_2O_3$, Amocat 1A ($CoMo/Al_2O_3$), and Amocat 1B (Mo/Al_2O_3) catalysts. From each test we obtained fresh catalyst, aged catalyst from the end of the run, and total reactor effluents (less gases) from various times during the run. The catalysts and the corresponding products were examined.

In a test developed at Mobil using a fixed bed high pressure downflow reactor and model compound mixtures, we examined fresh and aged catalysts for hydrogenation, hydrocracking, isomerization, desulfurization, denitrogenation, and deoxygenation. Several minerals were also included in the tests. Activities, selectivities and deactivation are discussed. Fresh commercial catalysts, especially $NiMo/Al_2O_3$, appear to be undesirably active for the H-Coal process. Amocat 1B is the least active. All catalysts age extensively but the used catalysts are still quite active. Activities for all reactions are reduced in the presence of nitrogen compounds. Hydrocracking activity appears to be critical to denitrogenation effectiveness.

Examination of the products of the HRI catalyst aging runs confirms the interpretations of the model compound tests. Also, it is found that $400°F^+$ product mixtures become more complex as catalysts age, and that the catalysts affect especially the highest (largest size) boiling products, but lose the ability to lower molecular weight as they age.

A brief examination of novel hydrogen donor-catalyst systems is also described.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

This final report is one of a series of research efforts under Research Project (RP) 779 that support EPRI's overall coal liquefaction development effort. These projects are either short duration scoping studies, as was this investigation, or studies aimed at obtaining very specific information required by ongoing research or development projects.

During this study, equipment and techniques developed by Mobil (under RP410) for studying the detailed chemistry involved in the direct noncatalytic liquefaction of coal were utilized to carry out a scoping study relating to the direct catalytic liquefaction of coal. In particular, these techniques were employed to characterize the liquid products, coal residues, and spent catalysts from several continuous bench-scale test runs carried out under the H-Coal process development subprogram sponsored in part by EPRI. Materials were obtained from tests in which both commercial and developmental catalysts were evaluated. These findings were supplemented by contacting the same fresh and aged catalysts with mixtures of model compounds in the presence of molecular hydrogen. This provided information relating to the activities, selectivities, and deactivation for the various catalyst functions relating to liquefaction and heteroatom removal.

A brief examination of novel hydrogen donor-catalyst systems was also undertaken to explore alternative methods of heteroatom removal from coal and heavy coal liquids.

PROJECT OBJECTIVES

The primary objective of the study was to obtain an increased understanding of the basic chemistry involved in direct catalytic coal liquefaction. This should result in a better control or process

improvements for this type of operation that is typified by the H-Coal process. In doing so, decreases in cost and/or improvements in the quality of clean power generation fuels may result. A secondary objective was to determine the potential for novel means of improving heteroatom removal from coal liquids, again with a view towards either improving quality or reducing the cost of utility fuel.

PROJECT RESULTS

As a result of the progress made during the contract period of June 1978 through March 1979, evidence was provided for the direct action of catalyst on the heaviest coal liquefaction products as well as the indirect action via transformation of the lighter donor solvents components. Recognition of this progress is important for the development of new or improved liquefaction catalysts. Furthermore, fundamental differences were found between the chemical compounds acting as the dominant hydrogen donors during the catalytic and noncatalytic liquefaction. These results provide leads as to how these processing approaches differ and how these differences may lead to better control of the respective processes.

With regard to the various catalysts obtained from the H-Coal bench-scale tests, information was developed on how these different catalysts function and are affected by the presence of nitrogen-containing compounds and how they deactivate. This information provides guidance for potential improvements of both catalyst, product and process.

On the basis of the promising preliminary results obtained in the scoping study, EPRI has begun a new project (RP1655) to further explore the detailed chemistry of catalytic liquefaction in relation to conversion of coals to clean utility fuels of increased hydrogen content.

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CONTRIBUTORS TO THE WORK

Several individuals and organizations contributed to the work described in this report and we gratefully acknowledge their contributions. They are identified below, along with the studies in which they participated.

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Section 1

SUMMARY

In previous work on coal liquefaction at Mobil, apparatus and techniques were developed for examining the detailed chemistry involved in the thermal dissolution process and in subsequent thermal reactions. In particular, procedures were developed for conducting conversions at precise times, including very short times, for liquid chromatographic fractionation of coal liquids into chemical classes by SESC (sequential elution by solvent chromatography) and for fractionation of recycle solvents by RSMC (recycle solvent multiple characterization). In the work described here, these techniques were applied to the examination of coal liquefaction in the presence of catalysts. The principal purpose was to gain insight into the basic differences in the chemistry of catalyzed and uncatalyzed coal liquefaction, with emphasis on understanding the inherent chemical limitations.

The present project was a limited exploratory scoping study of catalytic coal liquefaction consisting of:

- an examination of the effects of five commerical and developmental type catalysts used in H-Coal investigations,
- studies of the same catalysts and several minerals in model compound conversions, and
- a lower level of effort in scoping of novel heteroatom removal techniques.

This work was co-funded by Mobil and EPRI, prior to more extensive studies on catalytic coal liquefaction fundamentals that have now begun under project RP1655-1.

In our previous studies, we found that coal mineral matter could play two important roles in liquefaction in the absence of added

catalysts. Initial thermal coal fragmentation produces radicals that interact with the solvent to produce soluble products; coal mineral matter can play an important role in catalyzing reactions of hydrogen gas with these initial coal products, and with the solvent. Also the initial products are highly reactive toward further chemical transformations; certain defunctionalization reactions, for example dehydroxylation of polyaromatic ring phenols, can be catalyzed by coal mineral matter.

In the present study, therefore, we looked for two principal modes of catalytic action. First, we anticipated that the added catalyst would result in increased hydrogen donor concentrations, and second the catalyst could interact directly with coal products. Each mode could increase the important coal transformations of molecular weight reduction, hydrogenation, and defunctionalization.

In support of their H-Coal process, HRI ran catalyst aging tests simulating H-Coal conditions with Illinois #6 coal for 11-14 days with Cyanamid 1442A ($CoMo/Al_2O_3$), Cyanamid $NiMo/Al_2O_3$, Armak $NiMo/Al_2O_3$, Amocat 1A ($CoMo/Al_2O_3$), and Amocat 1B (Mo/Al_2O_3). We obtained fresh catalyst, aged catalyst from the end of the run and total reactor effluents (less gases) from various times during each run.

In a test developed at Mobil using a fixed-bed high-pressure downflow reactor and model compound mixtures, we examined fresh and aged catalysts for hydrogenation, hydrocracking, isomerization, desulfurization, denitrogenation, and deoxygenation. Activities, selectivities and deactivation were examined and compared and contrasted to dissolver solids and several minerals. We also isolated and characterized solvent range and heavier products from the HRI samples and related these data to the catalyst activity test data.

Interpretation of the results requires a thorough understanding of the operation of the HRI unit, which is therefore described in some detail. A particularly important factor was that runs were started up with hydrogenated anthracene oil as the solvent; this was slowly replaced over the course of about the first week of

operation. This material had a different hydrogen donor capacity, different ability to maintain products in solution, and a different heteroatom content. It thus affected the progress of reactions as well as the composition of the solvent range material; this made the assessment of the effects due to catalysts more difficult. Other important factors were the batch nature of the recycle operations, run-to-run variations in procedure, the small number of product samples obtained, and the availability of only one aged sample of each catalyst.

In the catalyst testing we identified the extent of phenanthrene hydrogenation as a very useful generalized catalyst activity parameter and it is used extensively in comparing and contrasting catalyst activities and selectivities. It was found that those catalysts (aged commercial) that produced the highest concentrations of hydrogen donors from phenanthrene also produced the most tetralin from naphthalene. Fresh commercial catalysts were so active that they produced large amounts of non-donor aliphatic polycyclic compounds, that are undesirable as solvent components.

The desulfurization activities of all the fresh and aged catalysts were very high in our tests. Several minerals, in particular manganese nodules, showed appreciable activity.

Multi-ring phenols were found to be very easy to deoxygenate; single-ring phenols were less reactive; aromatic ethers were least reactive. Only fresh catalysts gave high conversions of the latter.

Denitrogenation of heterocyclic compounds is more complicated; it proceeds by hydrogenation, without nitrogen removal, then hydrocracking (ring opening) without nitrogen removal, and then a second hydrocracking step in which the nitrogen is finally eliminated. Note that hydrocracking is required for denitrogenation. Basic nitrogen in multi-ring systems was found to be easiest to remove, then non-basic nitrogen; basic nitrogen in single rings was found to be most resistent. Hydrogenation of multi-ring heterocycles was found to be facile. $NiMo/Al_2O_3$ was superior to $CoMo/Al_2O_3$ for oxygen and nitrogen removal; Mo/Al_2O_3 was least active.

One $CoMo/Al_2O_3$ catalyst containing 0.5% SiO_2 was found to have a high initial hydrocracking activity, but this activity was not sustained on aging. $NiMo/Al_2O_3$ catalysts otherwise had the highest activities for hydrocracking and hydrogenation in our tests. Hydrocracking activity was found to decrease more significantly on aging than was hydrogenation activity.

In general, desulfurization was found to be the easiest reaction; deoxygenation is slightly easier than denitrogenation. Product nitrogen contents are critical to suitability for further conversion or use, but coal products contain more oxygen than nitrogen, reflecting the composition of the parent coals. Activities for all reactions were reduced in the presence of nitrogen compounds.

The conclusions on relative catalyst activity, selectivity, and stability based on these model compound studies are similar to those of HRI based on performance in their unit and of Mobil based on our examination of some representative HRI products. Conclusions are not identical because of the difference in the tests.

All catalysts aged extensively in HRI's runs but the used catalysts were still quite active in our tests.

Examination of elemental analyses and boiling point distributions of the coal liquids produced in HRI's catalyst evaluation program showed that catalysts have effects on the heavier as well as the solvent-range products. The pyridine-soluble distillation residues showed significant changes, especially increases in sulfur and nitrogen contents, as the catalysts aged, and the catalysts appeared to lose the ability to reduce molecular weight.

The materials were also examined in detail by gas chromatography, liquid chromatography, and field ionization mass spectrometry. Thermal (SRC) recycle solvents showed large amounts of a few individual compounds such as phenanthrene and pyrene. Catalytically produced solvents contained a more even distribution of components; mixtures became less complex as the catalysts aged in the HRI runs. In a reaction in which we heated an H-Coal solvent with coal in the absence of catalyst, the solvent recovered closely resembled an SRC solvent.

The 800°+F pyridine-soluble chemical functionality distributions of thermal and catalytic materials appeared to be quite similar by SESC (liquid chromatography), although the catalytic products did contain a little more saturated hydrocarbons and less basic nitrogen (which was shown in the model compound tests to be easier to remove catalytically than non-basic nitrogen). The distributions did not undergo major changes as the catalysts aged. However, molecular weight profiles of some SESC fractions of the 800°+F materials did shift to higher ranges with catalyst aging. ^{1}H and ^{13}C-NMR examination of representative fractions indicated that, relative to thermal products, the catalytic products contained more aromatic methyls, more isolated aromatic rings, and less condensed aliphatic rings. In general, the results of product characterization were consistent with the conclusions on catalyst activity, selectivity, and aging in the model compound tests.

We also briefly examined the use of methanol as a hydrogen donor and found that at high ratios of methanol to SRC and with manganese nodule catalysis, there can be substantial reductions in oxygen and sulfur and a lesser removal of nitrogen, even in the absence of H_2. Methanol is initially incorporated with retention of the -OH; the modified SRC is subsequently defunctionalized. An active catalyst and a good physical solvent are necessary to prevent char formation. Such use of methanol does not appear to be superior to H_2 or H_2/CO as a hydrogen source.

The following are the most important general conclusions drawn from the studies reported here:

- There are significant differences between the catalysts, the way they age, and the products they produce; in particular the NiMo catalysts tended to be most active and the unpromoted Mo tended to be least active and to age most rapidly.
- With the commercial type catalysts examined, denitrogenation and hydrocracking activities are closely related and hydrocracking ages more rapidly than hydrogenation.
- The catalysts appear to act directly on the heaviest products as well as on the lighter.

- Catalysis of all reactions was reduced by the presence of nitrogen compounds.
- Fresh catalysts, which would be continually added in the H-Coal process can have such high activities under H-Coal conditions that solvent hydrogenation is excessive and gas yields are very high due to hydrocracking.

The work done in this brief scoping study indicates three particularly important areas for future research in catalytic coal processing. The significant activities of several minerals reported here indicate that research into the efficacy of disposable catalysts should be expanded. The extensive action of catalysts on solvent range material shows that studies should be made on the interdependencies of solvent composition and catalyst activity, selectivity, and aging. Finally the difficulty and criticality of denitrogenation, and its close relationship to hydrocracking with commercial type catalysts, indicate that research into novel methods of nitrogen removal from coal liquids should be expanded. Continuation of our work in these three areas has been begun in this laboratory under Project RP-1655 entitled "Fundamental Studies in the Conversion of Coals to Fuels of Increased Hydrogen Content".

Section 2

INTRODUCTION

In the past three years we have been concerned with the elucidation of the kinetics and mechanisms of thermal coal liquefaction (SRC) and characterization of the recycle solvents and heavy liquid products from that process (2-1,2-2,2-3). During the course of that work, we developed a number of new techniques for the characterization of heavy coal liquids.

Most of the direct coal liquefaction processes currently under development involve catalytic as well as thermal chemistry. Thermal processing alone can provide high yields of boiler fuels. Catalysis is required to produce high yields of distillates having lower heteroatom contents and higher hydrogen contents without exesssive hydrogen consumption and light hydrocarbon production. There remains much to be learned about how catalysts and catalytic processes can be optimized for use in conjunction with coal liquefaction. There is room for much improvement in our understanding and control of these systems.

The bench-scale catalyst aging studies conducted by HRI (2-4) offered an opportunity to apply our techniques to the products of catalytic coal liquefaction, to compare these products with those of thermal coal liquefaction, and to study how the compositions of these products change as the catalyst ages in the H-Coal process. The aging tests were simulations of that process with the exception that no catalyst make up was used; thus the catalytic activity declined.

Accordingly, at the request of EPRI, we received a series of total reactor effluents from the HRI tests at selected times on stream as well as catalysts before and after aging. It was necessary for us

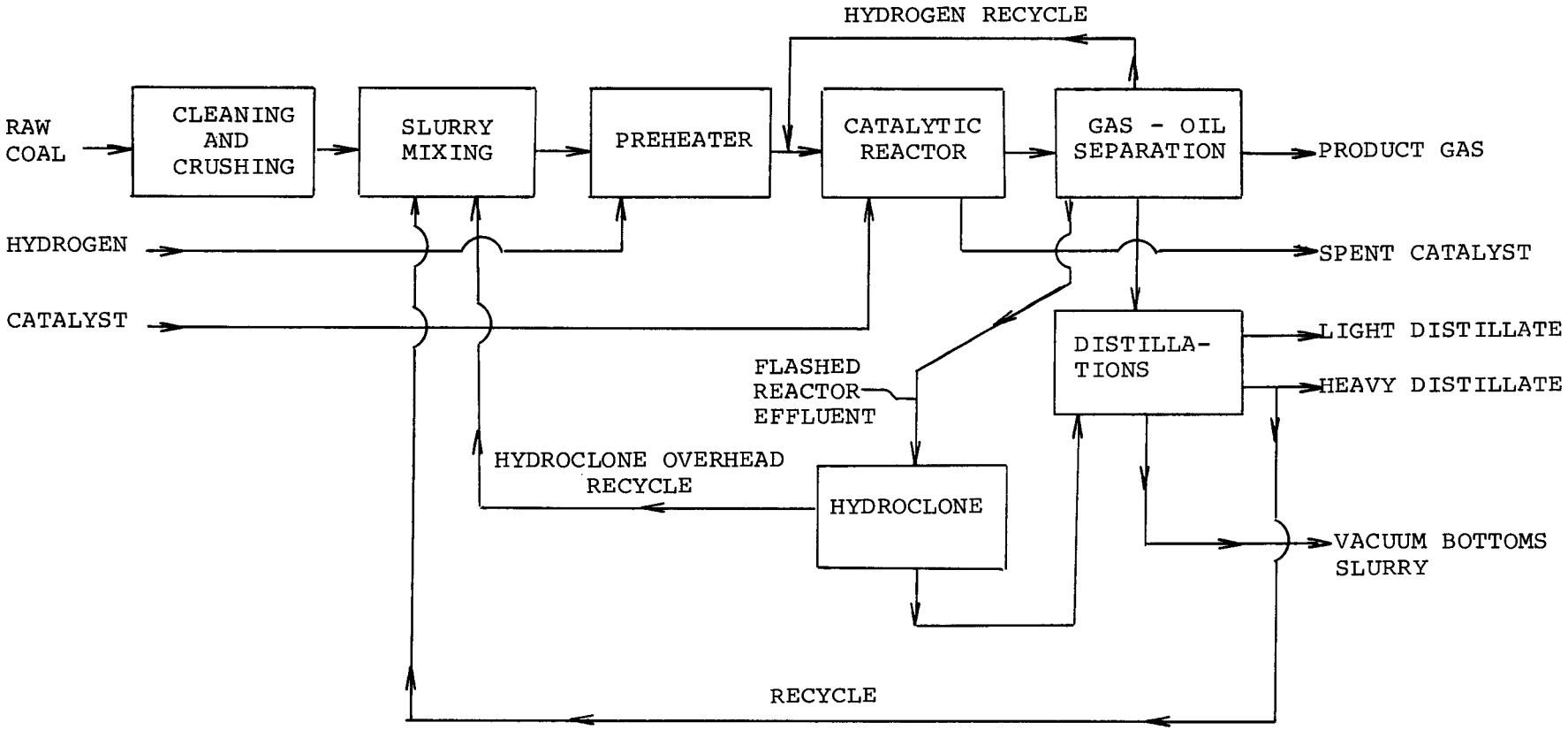
to develop a series of catalyst characterization tests to determine what was affected in the catalyst through interactions with coal liquids. Reactor effluents were characterized as in the past (2-1, 2-2,2-3). This report describes the results of these studies.

Interpretation of many of the results given in this report requires an understanding of the H-Coal process of Hydrocarbon Research, Inc. To aid in this understanding, a general description of the H-Coal process is provided below and was taken from a recent HRI paper (2-5).

> "In the H-Coal process, coal is dried, pulverized, and slurried with coal-derived oil for charging to the coal hydrogenation unit. The heart of the process is the unique reactor design. The coal-oil slurry is charged continuously with hydrogen to a reactor containing a bed of ebullated catalyst wherein the coal is catalytically hydrogenated and converted to liquid and gaseous products. In the ebullated bed the upward passage of the solid, liquid, and gaseous materials maintains the catalyst in a fluidized state. The relative size of the catalyst and coal is such that only the unconverted coal, ash, liquid and gaseous products leave the reactor while the catalyst remains therein. Catalyst can be added and withdrawn continuously so a constant activity can be maintained. The reactor provides a simple means of controlling reactor temperature and an effective contact between the reacting species and the catalyst, permitting a satisfactory degree of reaction at reasonable operating pressure. The liquid product from the reactor is a synthetic crude oil which can be converted to gasoline and furnace oil by conventional refining processes. Alternately, under milder operating conditions, a clean fuel gas and low sulfur fuel oils may be produced. The relative amounts of these products depend on the desired sulfur level in the heavy fuel oil."

A schematic of the H-coal process is shown in Figure 2-1.

Work has been carried out primarily in bench-scale units processing about 25 pounds of coal per day and in a Process Development Unit (PDU) handling about three tons per day. A schematic of the PDU is shown in the Experimental Section. This unit can be run with catalyst addition and withdrawal so that constant catalyst activity can be maintained.



Process Description

Co-Mo on alumina catalyst, ebullated bed. Preheated coal-solvent slurry, under hydrogen pressure is passed through an ebullating bed, at 850°F and 2600-2800 psig operating pressure. Product recovered by vaporization. Ash filtered from bottoms, or bottoms are burned. Principal product is "syn crude" or fuel oil, depending on operating conditions.

Figure 2-1. H-Coal Process

We approached our study of catalytic effects in coal processing, as exemplified by the H-Coal process, in two ways. First, we examined the catalytic properties of fresh and aged catalysts. Second, we studied the chemical composition of the coal liquids produced as catalysts aged in coal processing.

To compare and contrast the activities and selectivities of fresh and used catalysts, we chose to use them for the hydroconversion of model compound mixtures in a fixed-bed flow unit. The results were used to develop catalyst rankings for various reactions of interest. As in all model compound studies, this technique has the advantages of comparative simplicity and specificity. For the present brief scoping study, this outweighed the disadvantage that we were not studying the "real life" system.

Catalytically produced coal liquids have already been examined by others with a number of techniques including elemental analyses and a variety of spectroscopic tools. To add to the information available, we employed our liquid chromatographic procedures for fractionation of solvents and heavier fractions into discrete chemical functionality classes and then examined the fractions in the conventional ways. We also made extensive use of Field Ionization Mass Spectrometry.

Finally in a few batch autoclave runs we examined the thermal reactions of catalytically generated coal products, and briefly evaluated several novel hydrogen donor/catalyst systems.

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Section 3

DEFINITION OF TERMS

Throughout this report we use a few terms that could have ambiguous meanings, especially because of differences in terminology between thermal and catalytic processes. To avoid problems we list below definitions as we intend terms to be interpreted.

SRC. The product of a thermal coal solvent refining process, boiling above 800°F, which is soluble in pyridine, including material extracted by pyridine from the residue.

Residual oil. The product of the H- process, boiling above about 975°F (atmospheric), that is the bottoms from a vacuum distillation.

Solvent-range product. In our autoclave runs the liquids that have an equivalent atmospheric boiling range of 257-650°F. In the H-coal process, the ~400°F-975°F liquids are recycled. In our examination of H-Coal products, the 450-800°F range material were isolated by vacuum distillation.

800°F$^+$ Pyridine solubles. That portion of the H-coal products that we isolated by vacuum distillation followed by Soxhlet extraction with pyridine.

Oils. Organic compounds which are soluble in hexane. In the H-Coal process usually used to designate any liquid, however.

Asphaltenes. Organic compounds which are soluble in benzene but insoluble in hexane.

Asphaltols. Organic compounds which are soluble in pyridine but insoluble in benzene; others have used the term "pre-asphaltenes".

RSMC. Stands for Recycle Solvent Multiple Characterization and designates a fraction isolated from a solvent by liquid chromatography on alumina.

SESC. Stands for Sequential Elution with Specific Solvents Chromatography and designates a fraction isolated from an SRC or 800°F$^+$ pyridine solubles by liquid chromatography on silica.

Section 4

EXPERIMENTAL

In this section we describe the procedure used by HRI in their bench-scale catalyst aging tests (4-1) which generated the samples that we characterized in detail. These samples consisted of fresh and aged catalysts as well as total reactor effluents at selected times on stream. We also describe our procedures for catalyst evaluation that were developed as part of this program. All of the techniques used for characterization of the distillates and heavy coal liquids have been previously described (4-2,4-3,4-4).

DESCRIPTION OF HRI'S BENCH-SCALE TESTING PROCEDURE

Nearly all of the samples and data that were available to us for the present investigation came from HRI's bench-scale unit 177. The design and operation of this unit differ significantly from those of the PDU and of the pilot plant being built in Catlettsburg, Kentucky. In the bench unit, catalyst is not added or withdrawn, the start-up and recycle procedures are different, and product work-up (distillation, solids removal, etc.) are done in batches rather than continuously.

We shall describe the general operation of this unit as well as specifics of the runs from which our samples came. The information was taken from HRI's report (4-1) on the runs and from discussions with A. G. Comolli, E. S. Johanson, and R. F. Bernard of HRI.

Figure 4-1 shows the Bench Unit (adapted from reference 4-1 with product work-up and recycle sections added). This diagram also shows flow rates (g/hr) in various sections, conditions, and product yields for one specific operating period (177-136-6).

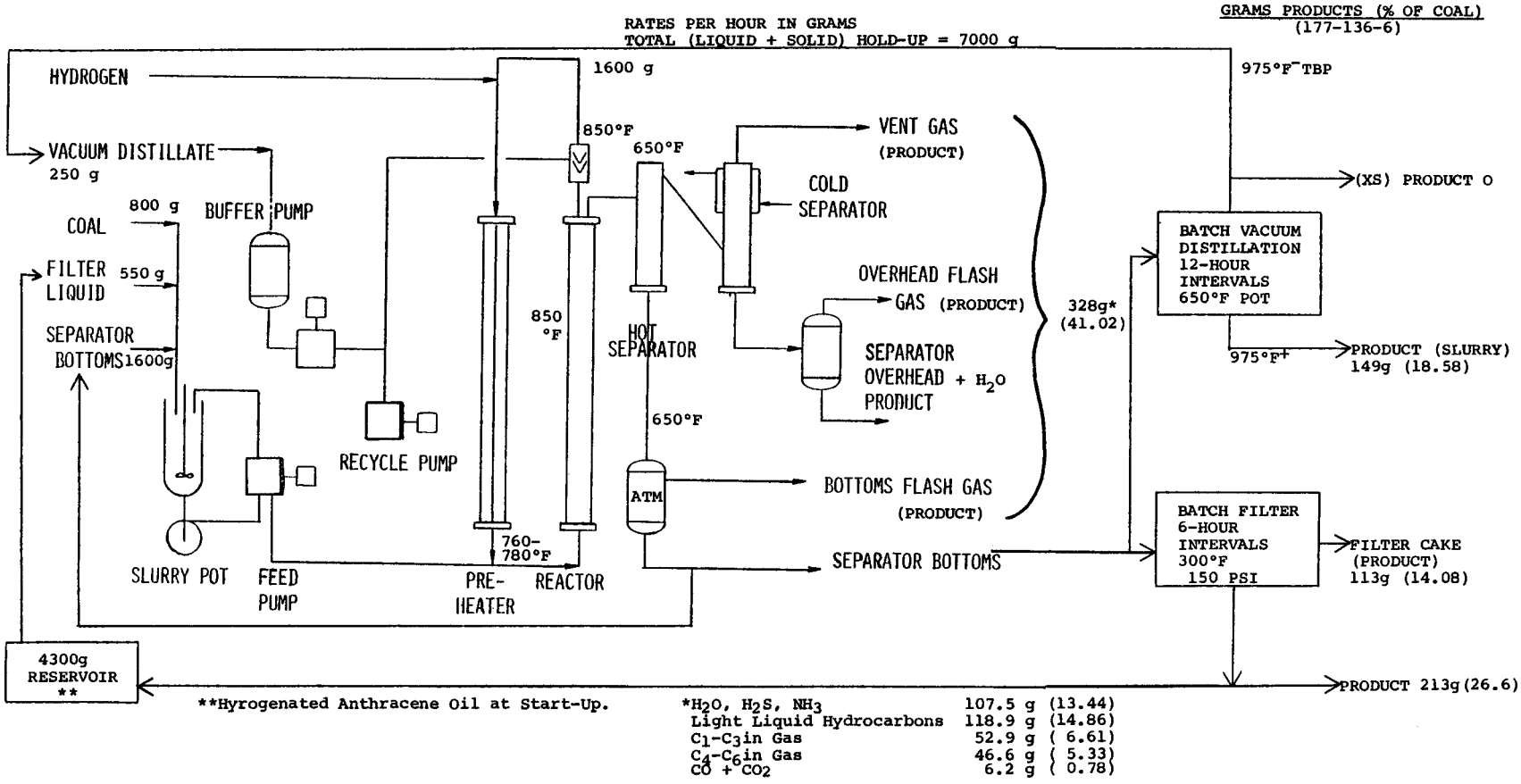


Figure 4-1. HRI Bench Unit Flow Sheet

The five catalysts were all tested at the same conditions of feed and recycle rates, temperature and pressure for an operating period of ten days of coal feed. The first two days of coal operations involved such large changes in the composition of the unit liquid inventory that there was a great deal of uncertainty in calculated product distribution even after including an allowance for the materials present in the inventory. For the third day and later, the changes in the composition were more moderate, corresponding to less than 1 W % yield (on coal) of the distillate or residual oil components, so the performance of the catalysts was compared beginning on the third day of coal operations.

The coal feed rate was set at 50 pounds per hour per cubic foot of reactor, which is intermediate between that for the syncrude and desulfurized fuel oil modes of H-coal operation. The flow of oils recycled to slurry the coal feed was set to obtain about 40 W % residual oil plus solids in the product slurry in operations with all the catalysts. The following operating conditions were used:

Coal feed rate, lbs/hr/ft^3	50.0
Recycle slurry oils, lbs/lb coal	
Vacuum distillate	0.31
Filtered liquid	0.69
Separator bottoms	2.0
Reactor temperature, °F	850
System pressure, psig	2250
Excess hydrogen flow, SCF/lb coal	19

These conditions resulted in a hydrogen partial pressure of about 1800 psi at the reactor outlet.

The base case run with the standard catalyst (HDS 1442A CoMo/Al_2O_3) was extended three days beyond the scheduled ten-day operating period to obtain a better-defined deactivation curve.

The standard catalyst was handled by the same procedures generally used with this catalyst, which do not involve a specific presulfiding operation. The other four catalysts had been evaluated after presulfiding with a hydrogen sulfide-hydrogen mixture, and this pretreatment was incorporated into the H-Coal Bench Unit evaluation of those catalysts.

All catalysts were calcined at 850°F before charging to the reactor. The four catalysts were presulfided *in situ* at atmospheric pressure by the following procedure:

1. With reactor at 200°F, 10% H_2S in hydrogen flow was started at a rate of 5.0 SCFH and this condition was maintained for one hour.

2. Reactor temperature was raised to 450°F over about two hours, while maintaining a H_2S-H_2 flow of 2 SCFH. The reactor was then held at 450°F for two hours while feeding a 5 SCFH of the H_2S-H_2 mixture.

3. The reactor temperature was then raised to 600°F over a period of about 1½ hours while maintaining a H_2S-H_2 flow of 2 SCFH. The reactor was then held at 800°F for two hours while feeding 5 SCFH of the H_2S-H_2 mixture.

4. The reactor and the rest of the H-coal system were pressured to the 2250 psig operating pressure using hydrogen. When the system was pressurized, the start-up-oil, hydrogenated anthracene oil with 0.68 W % dimethyldisulfide added, was introduced to establish liquid levels and flows in the system before further heating to the H-Coal operating temperature of 850°F at which point feed would be started to the system.

In all runs 450 cc of catalyst (settled volume) were charged to the 1000 cc reactor. This procedure provided a minimum of 95 grams of sulfur in the presulfiding gas or 0.26 gram sulfur/gram catalyst. This was three to four times the amount of sulfur required to convert the molybdenum, cobalt, and nickel to the sulfide form.

Start-up for the standard catalyst test was begun by heating the pressure reactor to 300°F while feeding hydrogen. No. 2 fuel oil was then introduced to the system while continuing to heat the reactor. When the reactor temperature reached 650°F, hydrogenated anthracene oil was substituted for the No.2 oil which was purged from the system while the reactor was heating to the 850°F operating temperature.

The reactor diameter was 0.814" and the height was 10 feet, to give a nominal reactor volume of 1000 cc. Expansion of the catalyst charge in the reactor was controlled by the velocity of the fluids passing through the reactor.

Feed coal was slurried with recycle oil and recycle slurry and pumped to reactor pressure with a metering pump. This feed slurry was mixed with hot recycle oil which had been pumped from the reactor outlet and reheated concurrently with make-up hydrogen in a downflow recycle oil heater to 760-780°F to compensate for heat losses. The hydrogen-slurry mixture was then fed to the bottom of the H-Coal reactor. After contacting the catalyst in the reactor, the hot oil recycle stream was separated from the reactor mixture at reactor temperature and the balance of vapors and liquid passed to a hot separator. The temperature of the hot separator was held about 200°F below reactor temperature. The overhead vapors from the hot separator passed to a light product cooler-condenser and cold separator to provide a vent gas stream and a light liquid product after pressure release.

The bottoms slurry from the hot separator (separator bottoms) was flashed at atmospheric pressure and a portion recycled directly as part of the coal slurry medium. The balance was fed to the two recycle oil recovery systems -- a batch vacuum distillation operation and a batch plate filtration operation.

Vacuum distillation was carried out to supply distillate oil to serve as a purge medium for the seal of the hot oil recycle pump which was pumped to reactor pressure by a buffer oil pump. The vacuum bottoms which resulted became a net product of the system. Vacuum distillations were carried out at 12-hour intervals using 5-6 kilograms of hot separator bottoms slurry to supply material to be recycled subsequently over an equal time period. Distillation pressure was 1-2 mm Hg (abs) and final pot temperature was 650°F which resulted in a final overhead temperature of 550-580°F equivalent to an atmospheric boiling point of about 900°F.

The batch plate filtration provided a larger portion of the recycle slurrying medium and was carried out at six-hour intervals to provide slurry oil for the feed coal for the subsequent operating period. The filtration was achieved on a horizontal, approximately 12-inch-free diameter plate, with three thicknesses of Reeves 202 laboratory filter paper as the filter medium. Analysis of the lower papers indicated very little solid penetration through the first layer.

The filtration was performed at 300°F, with a pressure of 150 psig imposed on the liquid by means of bottled nitrogen. Filtration was continued after the breakthrough of nitrogen until collection of additional liquid ended.

The recycled filtration oil was returned to the H-Coal system directly with the feed coal through the slurry feed pump. The final portion of the recycled material returning with the feed coal through the slurry feed pump was separator bottoms which had been neither filtered nor distilled. The recycled vacuum distillate was mixed with feed coal in the H-Coal system when the feed slurry mixed with internal recycle downstream of the preheater.

The net products of the operation were (a) the vent gas stream, (b) the two flash gas streams from pressure release of the liquids condensed at high pressures, (c) light liquids and water from the cold separator, (d) net filtered liquid remaining after recycle slurry oil requirements were met, (e) filter cake, (f) any vacuum distillate remaining after meeting recycle oil requirements and (g) the vacuum bottoms slurry from the vacuum still. All net streams were weighed or metered and analyzed.

Beyond the use of start-up oils, the operation was entirely sustained by the coal feed.

Inspections of the start-up hydrogenated anthracene oil used are given in Table 4-1. The start-up oil was used to establish liquid levels and internal flows. Hydrogenated anthracene oil make-up was used until eight hours of coal operations when recycle oil became available from the vacuum still and filter. The hydrogenated anthracene oil had been prepared by hydrogenation of Allied Chemical 24CB Creosote Oil "Anthracene" at 2700 psi, 750°F, 1.3 V (oil)/H_2/V (cat), with Standard Catalyst HDS-1442A catalyst.

As can be seen in Figure 4-1, there was a 4300 g reservoir for liquid needed to make up fresh coal feed slurry. At the start of a run this was filled with the hydrogenated anthracene oil (HAO); the rest of the system contains additional HAO for a total of 7000 g.

Table 4-1

ANALYSES OF START-UP OIL*

	Allied Chemical 24 CB Creosote (Anthracene) Oil HRI 3836	Hydrogenated Anthracene Oil L-467 Start-Up Oil
Gravity, °API	-3.3	6.5
ASTM Distillation, °F		
IBP	466	432**
10	500	471
20	520	502
30	540	532
40	566	548
50	600	572
60	634	602
70	670	626
80	705	
90	750	
EP	880	
Volume % at 650°F	65	78
Carbon, W %	89.58	90.08
Hydrogen, W %	5.81	8.65
Sulfur, W %	0.59	<0.03***
Nitrogen, W %	-	0.35

*From Reference 4-1.

**ASTM-D-86 atmospheric distillation (IBP-650°F).

***For runs with pre-sulfided catalysts, dimethyldisulfide was added to the hydrogenated anthracene oil to give a sulfur content of 0.7 W %.

Coal feed was started at 200 g/hr and the feed rate was increased by 25 g/0.5 hr every half hour until the design rate was reached. As coal was fed, a weight of "product" was withdrawn. This "product" was composed of hot separator overhead, atmospheric flash distillation overhead, and atmospheric flash bottoms ("separator bottoms") in excess of that which was recycled. When sufficient separator bottoms had been collected, it was filtered. Filtrate was set aside so that the total of this and the two overhead streams equaled the weight of coal added during the period. The rest of the filtrate was returned to the reservoir.

Part of the 7000 g consisted of a smaller reservoir, initially containing HAO, for feeding the external recycle buffer pump. Separator bottoms was also fed to a vacuum still; 250 g/hr of the 975°F⁻ overhead was recycled to the buffer pump and the still bottoms slurry was included as part of the final product.

Thus initially the entire 7000 g in the system was HAO. After each filter or still batch operation, some filtrate and still overhead were recycled; the rest was taken as product along with the other product streams mentioned above. The initial "product", of course, as well as recycled filtrate and vacuum still overhead were substantially HAO. As the run progressed, the initial HAO was slowly replaced with solvent-range coal products. Coal feed rate was initially low and then brought up to the design rate; a total of about 9.4 hours was required before a weight of coal equal to the initial HAO (7000 g) had been fed. However, later in a run about 40 percent of the coal fed was converted to filtrate and vacuum bottoms liquids. If one assumes that such a conversion occurred early in a run, about 24.5 hours should have been required to generate 7000 g of material to dilute and replace the HAO. In each additional 21.9 hours, another 7000 g was produced. If we assume complete mixing in the system, and no conversion of HAO or of the material that replaces it, the liquid composition profile would be as follows:

Time From Initial		Percent of Liquid	
Hours	Days	HAO	From Coal
24.5	1.02	50	50
46.4	1.93	25	75
68.3	2.85	12.5	87.5
90.2	3.76	6.3	93.7
112.1	4.67	3.1	96.9

This indicates the approximate rate at which HAO was replaced in the total liquid inventory in the unit. However, only about 65% of the coal liquids that replaced HAO were in the 450-800°F boiling range of HAO. In this range one would expect a greater contribution of HAO at a given time on stream than would be observed for the entire liquid product:

Time, Days	~% HAO in 450-800°F Cut
2	40
3	25
4	14
5	8
6	5
7	3

Thus at three days the overall liquid that contributed to catalyst behavior was ~90% derived from coal in the run, but the 450-800°F cut that we examined was ~25% HAO derived. This will have little effect on catalyst aging rate but a significant effect on characterization of solvent-range materials.

DESCRIPTION OF CATALYSTS USED IN THE HRI CATALYST AGING STUDIES

Table 4-2 summarizes the analytical information for the five catalysts tested. Each of the runs used 450 cc (settled volume) of catalyst in a 1000 cc reactor. Accordingly, the weight of catalyst charges was proportional to the bulk densities of the catalysts. Consequently for different runs, the catalyst age in pounds of coal per pound of catalyst, differed as a function of time on stream. This introduces an additional complication in interpreting catalyst aging.

Table 4-2* INSPECTION OF CATALYSTS FOR H-COAL BENCH UNIT PROGRAM

HRI No.	3830	3905	3922	3982	3991
Designation	Standard	SN 4475	PA24268	Amocat 1B	Amocat 1A
Run Number	177-130	177-131	177-134	177-136	177-137
Bulk Density, gm/cc, Compacted	0.580	0.585	0.802	0.675	0.714
Particle Density, gm/cc					
In Mercury	0.983	0.994	1.271	1.156	1.186
In Heptane	0.908	0.923	1.183	0.964	1.032
From Weight Dimensions	0.917	1.071	1.117	0.968	1.052
Skeletal Density, gm/cc					
In Mercury, 60,000 psi	2.93	3.37	3.10	3.19	3.36
In Heptane	3.57	3.47	3.67	3.67	3.52
Heptane Wetted Density, gm/cc	1.445	1.451	1.670	1.498	1.547
Heptane Absorbed, cc/gm	0.821	0.795	0.572	0.765	0.685
Average Weight of Particles, Milligram	9.20	10.62	12.46	4.66	4.63
Particle Length, Average, mm	4.69	5.19	4.24	3.04	2.82
Range, mm	2.4-12.0	1.9-10.7	2.2-6.9	1.8-4.0	1.8-3.9
Particle Diameter Average,mm	1.65	1.56	1.83	1.42	1.41
Chemical Analysis by Supplier					
MoO_3, Wt%	16.0	17.2	14.0		
Co , Wt%	3.2				
NiO , Wt%		3.5	3.2		
Na_2O, Wt%	0.02	0.015	0.04		
SO_4 , Wt%		0.3	0.91		
Surface Area, M^2/gm		267	206		
Pore Volume, cc/gm		0.76	0.51		
Crush Strength, lb/mm		1.5	2.1		
Analysis by HRI					
Molybdenum, Wt%	9.73	11.29	9.64	9.34	9.59
Cobalt, Wt%	2.75				2.18
Nickel, Wt%		2.60	2.31	0.01	0.00
Sodium, Wt%		0.03	0.05	0.04	0.03
Iron, Wt%		0.03	0.02	0.10	
Titanium, Wt%					
Crush Strength, lb/mm	3.2	2.6	1.8	2.2	2.3
Attrition Test, % Undersize	3.9		23.0		6.1
Pore Volume (Hg at 60,000 psi)					
D>30 Å, cc/gm	0.691	0.723	0.483	0.561	0.570
Pore Size Distribution, cc/gm					
D = 30-50 Å	0.142	.174	.009	.005	.004
D = 50-100 Å	0.259	.229	.356	.098	.086
D = 100-200 Å	0.036	.029	.016	.381	.394
D = 200-2000 Å	0.120	.121	.015	.051	.054
D > 2000 Å	0.134	.170	.087	.026	.032
Maximum, Å**	55	50	85	125	125
Spectroscopic Analysis, Wt%					
High >10%				Al	Al,Mo
1-10%				Mo	Co
.1-1%					
.01-.1%				Fe,Mg,Ni, Pb,Si,Sn	Ca,Fe,Na, Ni,Si
.001-0.1%				Cr	Mg,Pb,Ga

*From Reference 4-1.
**Position of greatest slope of pore volume against diameter.

HDS-1442A (HRI 3830)

This commercially available catalyst was tested in Bench Unit Run 177-130, and served as the "standard" for the other catalysts tested. This shipment of catalyst had been used with Illinois No. 6 coal in PDU run 5. It is a moderate density, cobalt-molybdate on alumina preparation, and contains 0.691 cc/gram pore volume. The pore size distribution is bi-modal, with about 30% of the pore volume having diameters in the 500-5000 Å range, and 60% of the pore volume having diameters in the 40-100 Å range centered around 55 Å.

SN-4475 (HRI 3905)

This was an experimental catalyst which had shown good denitrogenation performance in HRI fixed bed tests on coal-derived products. SN-4475 is a nickel molybdate, as-received catalyst with physical characteristics very similar to those of the standard catalyst. It was tested in Bench Unit Run 177-131.

PA-24268 (HRI 3922)

This was an experimental catalyst which had shown good denitrogenation performance in fixed bed tests at HRI on coal-derived products. It is a nickel molybdate on alumina catalyst with a particle density about 1.3 times that of the standard catalyst. It was considered advantageous to use a high density catalyst since it should allow higher slurry density in the reactor which corresponds to higher residuum concentration with deeper residuum conversion. The higher density of this catalyst was obtained by a lower amount of pores, 0.483 cc/gram against 0.691 cc/gram for the standard catalyst. The pores of the PA-24268 catalyst were principally in the 70-100 Å diameter range (about 70% of the pore volume), with 15% of the pores in the 5,000-20,000 Å diameter range. The catalyst was somewhat less mechanically stable than the standard, with only 60% as great a crush strength, and much greater loss to undersize (23% against 3.9%) in an 18-hour attrition test in a rotating drum. This catalyst was tested in Run 177-134.

Amocat 1A (HRI 3991)

This catalyst gave about 4-6% deeper conversion to benzene-soluble product than was obtained with the standard catalyst in tests with a stirred tank reactor. Amocat 1A is a cobalt molybdate on alumina catalyst, with a pore size distribution somewhat different from the standard catalyst. The pores are predominately in the 90-200 Å pore diameter range (centered around 125 Å) with consequently smaller amounts of larger and smaller pores. The pore volume was less than that of the standard catalyst, 0.571 cc/gram against 0.691 cc/gram, and the density was about 1.2 times that of the standard catalyst. Amocat 1A was slightly smaller (by about 15%) and about 40% shorter than the standard catalyst. It was also not quite as strong with 70% as great crush strength, but had fairly good attrition resistance, with 6.1% loss to undersize in the attrition test. This catalyst was tested in Run 177-137.

Amocat 1B (HRI 3892)

The only difference between this catalyst and Amocat 1A was that no cobalt was impregnated; it was a molybdenum on alumina catalyst. The catalyst support was the same as that of Amocat 1A, and they both had the same characteristics with respect to size, pore volume, and pore size distribution. In screening tests it was found that less hydrogen was consumed with Amocat 1B than with Amocat 1A with no severe penalty in coal conversion at less severe conditions than those of characteristic H-coal operations. Amocat 1B catalyst was tested in Run 177-136.

BRIEF DESCRIPTION OF HRI AGING RUNS

HDS-1442A - Standard Catalyst (Run 177-130)

This run was smooth and trouble-free with respect to pressure drop, reactor and catalyst control. The catalyst was found in a normal position in the reactor and was recovered easily at the end of operations.

Catalyst SN-4475 (Run 177-131)

The run was smooth and trouble-free with respect to pressure drop, reactor and catalyst control. The catalyst was found in a normal position in the reactor and was recovered easily at the end of the run.

Catalyst PA-24268 (Run 177-134)

Run 177-134 was completed with only minor feed pump difficulties. The pressure drop across the reactor increased a small amount during the run, from 7 to 12 psi. The catalyst was found in a normal position in the reactor and was recovered easily at the end of the run.

There were two prior attempts (177-132 and -133) using this catalyst, one which shut down after nine hours of coal feed with a pressure drop of 400 psi, and another which ran for only five hours and ended with a pressure drop of 150 psi. In both runs it was difficult to maintain the feed flow through the slurry feed pump.

Because of this catalyst's high density the internal recycle flow had been set at a higher than normal rate. However, some expansion tests indicated that the standard recycle flow should be used when testing this catalyst and the rate was readjusted for the next experiment. This proved to be the factor which enabled the run to proceed smoothly to its scheduled shutdown.

Catalyst Amocat 1A (Run 177-137)

The first attempt at operating with this catalyst (Run 177-135) lasted for 17 hours of coal operation. The feed slurry flow failed several times and the operation was interrupted by a pressure drop of 50 psi. Consequently, Run 177-136 was run with Amocat 1B while additional Amocat 1A was obtained.

Because the slurry consistency caused Run 177-135 to fail, the next attempt used a higher ratio of separator bottoms in the feed slurry at the beginning of the coal operations, 3 pounds/pound coal over the first 48 hours of coal feed. That is, the recycle of atmospheric flash separator bottoms to the slurry pot (see Figure 4-1) was initially 3200 g/hour. After 12 hours of operation, this recycle was reduced by 400 g/hour every 12 hours, so that the design rate was reached starting in period 4A. This procedure was used in Runs 177-136 and 177-137. This run was carried out to its scheduled completion while maintaining a normal pressure drop across the reactor. However, there was some difficulty maintaining a normal

recycle flow after 180 hours of the run, apparently because of gas pockets in the internal recycle pump and because the check valves in the pump kept sticking. At the end of the run the catalyst was found lifted to the outlet of the reactor. This probably happened during the wash since the pressure drop had been normal during the run. The catalyst had to be rodded from the reactor.

Catalyst Amocat 1B (Run 177-136)

This run continued smoothly to the end of coal operations at normal pressure drop. During the wash after completion of operations the pressure drop increased to about 50 psi after seven hours, and finally a complete plug appeared after 11 hours of the wash operation. The plug was found in the upper section of the reactor, although the catalyst bed itself had returned to about the normal settled position in the reactor. About 25% of the catalyst was free-flowing and the rest was rodded from the reactor.

COAL FEED IN HRI AGING RUNS

The coal used in these runs was Burning Star Mine, Illinois No. 6 coal, HRI No. 3944, which was a carload shipment also used in PDU Run 5 operations. The coal had been received about four months prior to these catalyst evaluation tests, and had been stored in closed drums during the interval. The coal was dried to 1-2 W % moisture content shortly before use in the bench unit runs.

Table 4-3 gives the analyses of the coal fed to each of the runs. The coal contained 3.4±0.2 W % sulfur, 1.23±0.2 W % nitrogen and 10.4±0.4 W % ash. Thus run to run variations were as much as 12% in sulfur, 33% in nitrogen, and 8% in ash contents.

EXPERIMENTAL PROBLEMS WHICH INFLUENCE OUR INTERPRETATIONS

The following aspects of the catalyst aging runs contribute to the difficulty of accurate assessment of the effect of coal and coal products on catalyst aging and vice versa.

Table 4-3*

ANALYSIS OF ILLINOIS NO. 6 BURNING STAR MINE NO. 2 COAL
HRI NO. 3944, FEED TO BENCH UNIT CATALYST TESTING PROGRAM

Run No. 177	As	130	131	134	136	137
Feed to Periods	Received	1-13	1-10	1-10	1-12	1-11
Hours of Run	-	0-312	0-240	0-232	0-276	0-252
Moisture, Wt %	11.05	1.65	1.58	1.58	2.28	1.83
Proximate, Dry Basis, Wt %						
Ash	11.75	10.85	10.66	10.22	10.00	10.29
Volatile Matter	35.56	34.51	35.83	35.17	37.51	35.27
Fixed Carbon	52.69	54.64	53.51	54.61	52.49	54.44
Ultimate, Dry Basis, Wt %						
Carbon	71.52	70.17	70.05	70.06	70.64	69.72
Hydrogen	5.05	4.81	4.74	4.88	4.94	4.77
Nitrogen	1.36	1.31	1.34	1.12	1.21	1.12
Sulfur (LECO)	3.52	3.47	3.61	3.27	3.38	3.21
Ash	11.75	10.85	10.66	10.22	10.00	10.29
Chlorine	0.10	-	-	-	-	-
Oxygen (Difference)	6.70	9.39	9.60	10.45	9.83	10.89
Sulfur in Ash, Wt %	1.11					
Sulfur (Eschka), Wt %	3.47					
Sulfur Forms, Dry Basis, Wt %						
Pyritic	1.29	1.33				
Sulfate	0.07	0.08				
Heating Value, btu/lb	12,620					
Sieve Analysis, Screen Size (USS)						
+50		0.25			0.12	
50/70		0.23			0.12	
70/100		2.42			9.54	
100/140		8.41			21.49	
140/200		11.56			21.43	
200/325		25.89			20.34	
-325		51.24			26.97	

Mineral Analysis, Wt % Ignited	
Silica, SiO_2	47.83
Alumina, Al_2O_3	18.07
Titania, TiO_2	0.85
Ferric Oxide, Fe_2O_3	17.81
Lime, CaO	7.40
Magnesia, MgO	0.40
Potassium Oxide, K_2O	1.81
Sodium Oxide, Na_2O	0.45
Sulfur Trioxide, SO_3	3.66
Phosphorus Pentoxide, P_2O_5	0.01
Undetermined	1.21
TOTAL	100.00

*(From Reference 4-1)

- The composition of the solvent (450-800°F) changed for several reasons. Initially it consisted of hydrogenated anthracene oil which was hydrogenated under different conditions prior to the run than were used in the aging study. The catalyst activity changed during the run. The initial hydrogenated anthracene oil was gradually replaced by feed-coal derived liquids. Replacement was probably ~90% complete after ~3 days but replacement of HAO in the 450-800°F solvent range we examined was probably only ~75% complete after ~3 days and not 90% complete until ~4.5 days. The composition of the 800^{+} material was essentially all coal-derived after 3 days.

- There were occasional flow interuptions in such streams as the feed slurry and the recycles.

- Catalyst charge volume was constant but catalyst densities differed, so WHSV and catalyst age (in pounds coal/pound catalyst) as a function of time differed.

- The runs were not all the same length.

- Catalyst pretreatment for the base case differed from that for the other four catalysts.

- The recycle of separator bottoms early in the runs with the two Amoco catalysts was greater than in the other runs.

- The feed coal composition varied slightly from run to run.

- The samples of aged catalysts which were examined represented only single points in the aging curve. Thus, nothing can be said about the rate of aging; we can describe only our observations as to the activity and selectivity of the catalysts before and after the termination of the tests.

MOBIL'S EXPERIMENTAL PROGRAM

The following apparatus and techniques have been described in detail previously (4-2,4-3,4-4): liquid chromatographic separation and characterization of $800°F^{+}$ coal products (SESC) and of 450-800°F solvents (RSMC); reactions conducted in high-pressure autoclaves; standard analyses such as gas chromatography, mass spectrometry, determination of elemental composition, surface area, etc.; special techniques applied to coals and coal liquids, such as CP-^{13}C-NMR, polarography, and field ionization mass spectrometry.

Catalyst Evaluations

One new technique was used in this project: catalyst activity and selectivity evaluation in a fixed-bed continuous downflow reactor. A schematic diagram is shown in Figure 4-2. The feed mixture was introduced from either barrel of a Ruska positive displacement pump, mixed with H_2, and passed downward through the reactor. Inlet pressure was maintained by a Hoke regulator and outlet pressure by a Grove loader. Inlet gas flow was maintained by a Brooks electronic mass flow regulator. Exiting product passed through a water-cooled condenser; gases passed into a water bubbler and then a wet test meter. Pressures were read from gauges; temperatures were read and controlled by thermocouples. The system had appropriate vents, valves, check valves, rupture discs, needle valves, etc., and was automatically shut down in the event of power failure or pressure changes in excess of preset limits.

The reactor itself was divided into three sections, independently heated and controlled. Overall the reactor had an annulus 13 1/2 inches long with a 1/8 inch OD centered thermowell; it was 0.56 inches ID stainless steel with 0.095 inch wall thickness. The top 5 inches of the reactor was a preheater containing a close-fitting solid stainless steel rod cut with a helical square 1/8 inch deep by 1/8 inch wide groove through which the feed mixture and H_2 had to pass before entering the central 5.5 inch long reaction section. Below the central section was an empty 3 inch long take-off section.

This reactor was packed as follows: A 2.73 g portion of 30/50 mesh catalyst (ground and sieved from extrudate or from pellets made from finer catalysts) and mixed with an equal volume of 20/30 mesh acid-washed and calcined Vycor, was centered in the reactor. The rest of the reactor, above and below was filled with Vycor; the catalyst/Vycor mixture was separated from the rest by 100 mesh stainless steel screens.

To start a test, the reactor was loaded as described, the system assembled and pressure tested with N_2 at 1500 psi, and the three portions of the reactor heated to reaction temperature under a slow

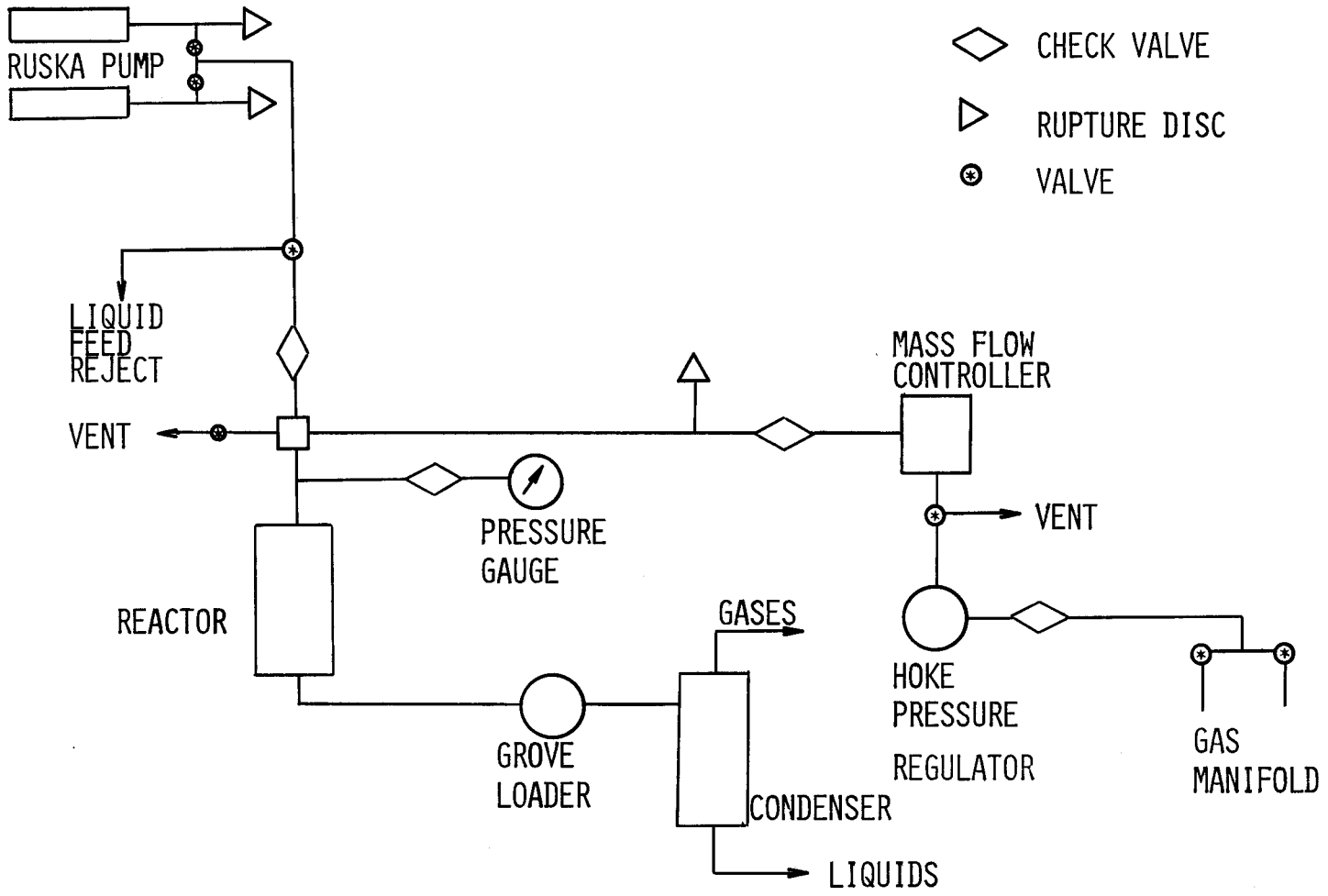


Figure 4-2. Schematic of Flow Reactor System

N_2 flow. The gas was switched to H_2 and the feed pump started at 5.45 ml/hr; assuming a feed density of 1 g/ml, this was a WHSV of 2 hr^{-1}. The H_2 flow rate was 100 ml/min (at STP) or a H_2 circulation of 6100 SCF/BBL; the pressure was 1500 psi total. Under these conditions gases other than H_2 in the exit gas stream were undetectable. Liquid product was collected and weighed.

Liquids were analyzed by gas chromatography on a Dexsil 300 column as already described (4-3); peaks were identified by GC-MS and by comparison to authentic samples. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tennessee.

Tests were ended by stopping the pump, switching to a low N_2 flow, and allowing the reactor to cool. The contents of the three sections of the reactor fill were then saved separately. The catalyst/Vycor central mixture could be separated by sieving.

Three feed mixtures were used, as indicated in Table 4-4, which also summarizes the test conditions. Each contained 0.1 wt % n-heptyl mercaptan to assure that catalysts would remain sulfided. With mix 1 we examined hydrogenation of phenanthrene, desulfurization of benzothiophene, and deoxygenation of a multi-ring phenol (α-naphthol), a single ring phenol (p-cresol), and an ether (dibenzofuran). With mix 2, denitrogenation of basic single-ring (γ-picoline), basic multi-ring (quinoline), and non-basic (indole) nitrogen compounds could be examined. Also the effects of the presence of these compounds on the reactions of the components that were common to both mixes 1 and 2 could be studied. Finally, with mix 3 we examined hydrocracking and hydrogenation of 2-ethylnaphthalene (and hydrogenation of mesitylene which occurred because of the higher temperature at which mix 3 was used).

These model compounds were chosen as being representative of the chemical structures and functionalities in coal and coal liquids, with the further constraints that the mixtures be homogeneous solutions at room temperature and that the compounds and their products be separable and identifiable by gas chromatography. After brief scoping runs at 315-454°C, temperatures were chosen in order to give a broad range of conversions with the catalysts used. Mixes 1 and 2 were generally run at 371°C (700°F) and mix 3 at 413°C (775°F).

Table 4-4

FLOW UNIT TEST CONDITIONS
1500 psig (1400 psi H_2)
2 hr^{-1} WHSV
6100 scf/bbl H_2 Circulation

Mix 1	Wt %	Mix 2	Wt %
Mesitylene	49.9	Mesitylene	45.1
Phenanthrene	10.0	Phenanthrene	9.0
Benzothiophene	10.0	Benzothiophene	9.0
α-Naphthol	10.0	α-Naphthol	9.8
p-Cresol	10.0	γ-Picoline	9.0
Dibenzofuran	10.0	Indole	9.0
n-Heptyl Mercaptan	0.1	Quinoline	9.0
		n-Heptyl Mercaptan	0.1
C	86.3	C	86.0
H	7.8	H	7.7
O	3.5	O	1.1
N	0	N	3.1
S	2.4	S	2.1

Mix 3	Wt %
Mesitylene	89.9
2-Ethylnaphthalene	10.0
n-Heptyl Mercaptan	0.1

Description of Catalysts Which Were Evaluated

The catalysts examined included five pairs of fresh and aged samples from the five bench-scale catalyst testing runs just described. The catalysts were obtained either directly from HRI or from Amoco Oil Company (who also characterized fresh and aged catalysts). Aged catalysts, after washing in anthracene oil during unit shut-down were washed with toluene, Sohxlet extracted with THF, and dried in vacuum at 130°C before we received them. A similar catalyst sample, withdrawn at the end of HRI's run PDU-5, was also obtained. This 30-day run employed addition and withdrawal of the base case catalyst (HDS-1442A); the sample is designated as "equilibrium" catalyst.

The following catalysts were also tested:

Wilsonville Dissolver Solids. The dissolver solids used were high-iron dissolver solids (~15% Fe_2O_3) obtained as blowdown solids from the Wilsonville, Alabama PDU (SN-21273) dated 11/24/76 from Run 97 with Monterey coal. A precise analysis was not available; however, the analyses of two Wilsonville dissolver solids samples from 13 days before and 5 days after our sample was dated are given in Table 4-5.

Burning Star LTA. This low-temperature ash was supplied by Dr. R. G. Jenkins of The Pennsylvania State University. It was prepared using 100 watts power from Burning Star coal.

Iron Pyrite. This sample from an unknown source was used in powdered form because it could not be pelleted.

Red Mud. In aluminum manufacture from bauxite, the ore is treated with strong caustic, dissolving most of the aluminum species and leaving behind an insoluble material that is substantially finely divided oxides of silicon, aluminum, and iron. After neutralization, this material is called red mud. Our sample was obtained from the Aluminum Company of America, and was dried to constant weight at 120°C in vacuum before use. Its BET surface area was 23 m^2/g. Qualitative emission spectroscopy showed the sample to consist primarily (1 to 10% each) of the following: silicon, iron, aluminum, titanium, calcium, and sodium.

Table 4-5

DISSOLVER BLOWDOWN SOLIDS ANALYSES*
ACETONE WASHED SOLIDS FROM V144 EMERGENCY BLOWDOWN TANK
MONTEREY (ILL. 6)

Date - 1976	11 November	29 November
Quantity, lb	400	250
Proximate, wt%		
Moisture	<0.1	<0.1
Ash	70.0	74.8
Volatile	19.7	19.3
Fixed Carbon (by difference)	10.3	5.9
Ultimate, wt%		
Carbon	22.3	19.1
Hydrogen	0.7	0.5
Nitrogen	0.2	0.2
Chlorine	1.0	0.1
Sulfur	3.5	5.4
Ash	69.9	74.7**
Oxygen	2.4	-
Sulfur Forms, wt%		
Pyritic	0.3	0.9
Sulfate	0.2	0.1
Sulfide	3.0	4.4
Organic	0.0	<0.1
Mineral Analysis of Ash, wt%		
Sodium oxide, Na_2O	0.9	0.9
Potassium oxide, K_2O	1.4	0.2
Lime, CaO	25.8	27.2
Magnesia, MgO	0.8	0.3
Ferric oxide, Fe_2O_3	14.7	15.2
Titania, TiO_2	6.5	5.3
Phosphorus pentoxide, P_2O_5	0.7	1.0
Silica, SiO_2	26.1	24.8
Alumina, Al_2O_3	8.5	7.0
Sulfur trioxide, SO_3	14.3	18.1
Undetermined	0.3	<0.1
Carbon Dioxide, CO_2, wt%	9.0	10.4

*From Wilsonville quarterly report, fourth quarter, 1976.

**Ash adjusted to force ultimate to total 100 percent.

Manganese Nodules. Manganese nodules were obtained from Lake Michigan and the Pacific Ocean, washed with hot water and screened to remove debris. The nodules were then ground and sieved to 30/50 mesh for use in our test. Typical properties of such nodules are shown in Table 4-6.

Table 4-6

TYPICAL PROPERTIES OF MANGANESE NODULES

	Lake Michigan	Pacific Ocean
Surface area, m^2/g	200	325
Pore volume, cm^3/g	0.4	0.4
Particle density, g/cm^3	1.5	1.4
Average pore diameter, Å	80	50
Composition, wt %		
Fe	35	15
Mn	10	25
Ni	<0.01	0.6
Cu	0	0.4
SiO_2	40	18
Al_2O_3	5	3
Ash	88	82

Work-up Procedure for HRI Reactor Effluents

We also obtained a number of reactor effluent slurry samples from HRI; these were hot separator bottoms (see Figure 4-1) and represent the total reactor effluent except for the hot separator overhead. Samples were obtained from various times on stream from the catalyst testing bench scale runs. These samples were worked up by vacuum distillation (maximum pot temperature 450°F) and Soxhlet extraction, and analyzed as indicated in Figure 4-3.

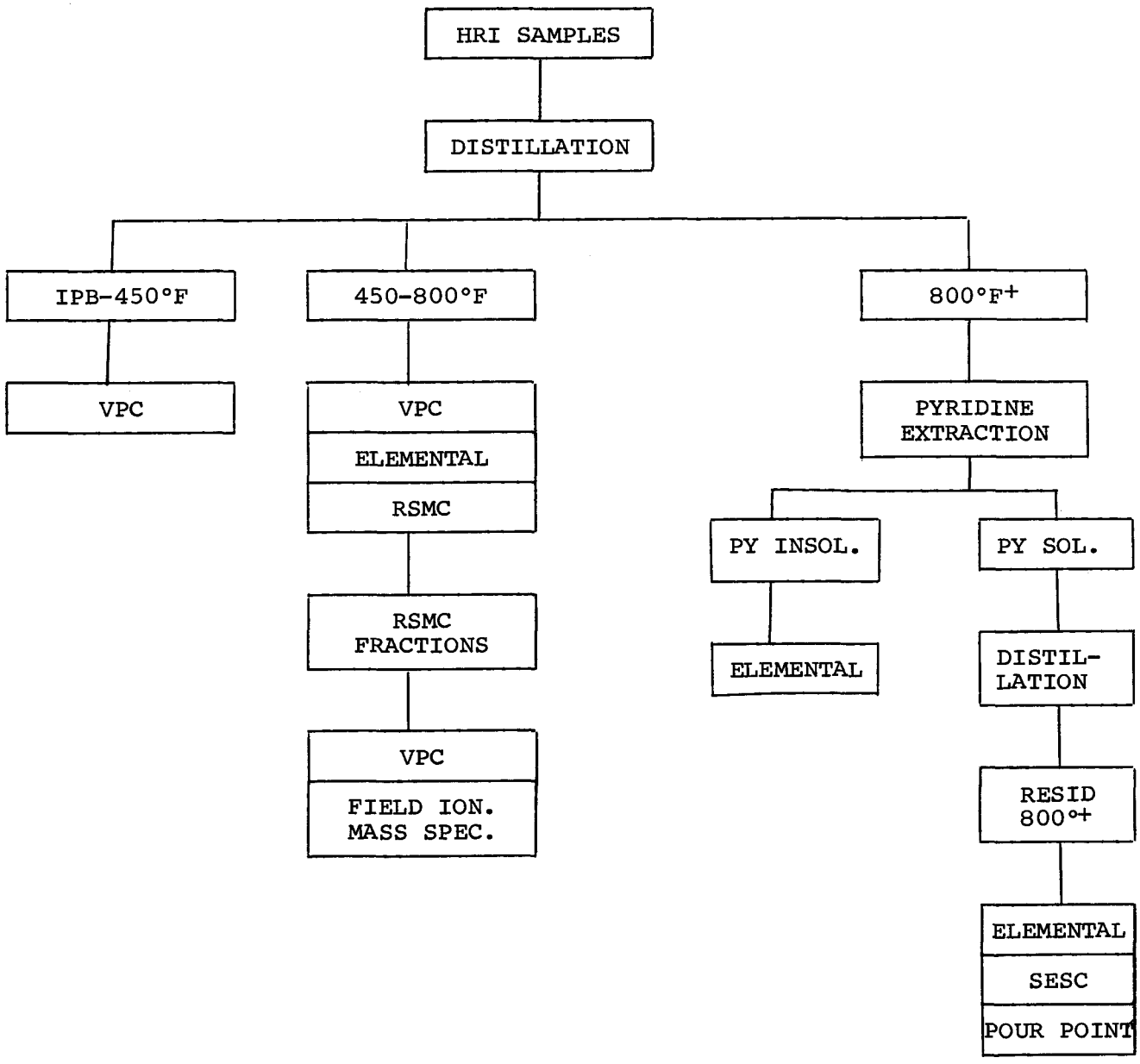


Figure 4-3. Work-Up of Separator Bottoms Samples

REFERENCES

4-1. A. G. Comolli and E. S. Johanson, "Bench Scale Catalyst Evaluation Program," Report FE-2547-28, under contract EX-77-C-01-2547, from HRI to DOE, December 1978.

4-2. D. D. Whitehurst, M. Farcasiu, and T. O. Mitchell, "The Nature and Origin of Asphaltenes in Processed Coals," EPRI Report AF-252, First Annual Report Under Project RP-410, February 1976.

4-3. D. D. Whitehurst, T. O. Mitchell, M. Farcasiu, and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals," EPRI Report AF-480, Second Annual Report Under Project RP-410-1, July 1977.

4-4. D. D. Whitehurst, T. O. Mitchell, M. Farcasiu, and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals," Final Report Under Project RP-410-1, March 1977-January 1979, in preparation.

Section 5

COMPARISONS OF CATALYSTS' ACTIVITIES, SELECTIVITIES, AND AGING

INTRODUCTION

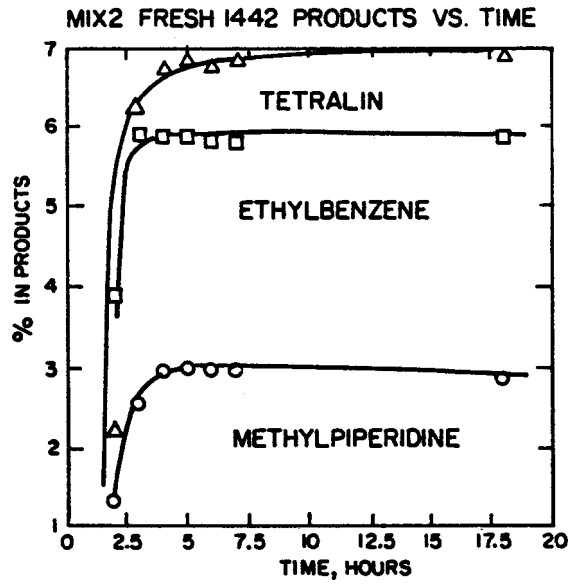
In Section 4 we described the catalysts examined and the procedures used; in this section we will present the results of catalyst testing. We will give first the catalysts' activities and aging for each catalyst function, then selectivity comparisons for fresh and aged catalysts, and finally overall comparisons of the catalysts and comparisons of these results to other available data on the catalysts' performance.

It was found that when a model compound mixture was passed over a fresh commercial catalyst, there was an initial period of up to about five hours when changes in product composition might be observed; thereafter, there were negligible changes. This behavior is shown for the yields of typical products over two fresh catalysts in Figure 5-1. It can be seen that the yields of products typically stabilized (Figure 5-1a) after about 4 hours and in general (Figure 5-1b) there were no changes at longer times such as 36-44 hours on stream. The initial changes can be attributed to reduction or sulfiding of the catalysts and/or to coke deposition in the early stages of a run. All the data used in the discussions to follow were taken after this initial change had occurred.

In addition, when we switched from a nitrogen-containing model compound feed mixture to one without nitrogen (or vice versa) there was a change that required several hours with either fresh or aged catalysts. This is attributed to reversible poisoning of catalytic sites by nitrogen. Feed mixtures could be run in either order with the same results. In the presence of nitrogen*, activities for

*"Nitrogen" indicates "nitrogen-containing compounds".

(5-1a)



(5-1b)

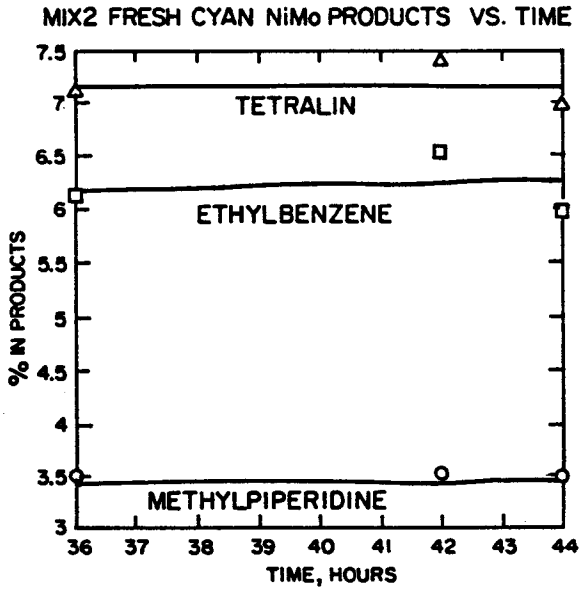


Figure 5-1. Model Compound Reaction Products vs. Time

all reactions were reduced, as will be discussed in more detail later. A typical example is shown in Figure 5-2 which shows the decrease in phenanthrene hydrogenation over fresh catalysts when mixture 2 is substituted for mixture 1. The relative activities of the three catalysts shown remained the same, but the absolute activities decreased.

This figure also introduces a measure of catalyst activity that we found extremely useful. This is the extent of phenanthrene hydrogenation. Fourteen hydrogens are required to convert phenanthrene to perhydrophenanthrene. We define the extent of phenanthrene hydrogenation as the percent actually added of these 14 possible hydrogens that could be added. Thus 9,10-dihydrophenanthrene is 14% hydrogenated. (Of course, so is a 50/50 mixture of phenanthrene and tetrahydrophenanthrene; our measure can be related to the equivalent pure compound but is actually obtained from a weighted average of all the phenanthrenes.) Figure 5-3 shows the percent phenanthrene hydrogenation and the total % H of representative pure compounds.

In Figure 5-4 it can be seen that there is an excellent correlation between phenanthrene hydrogenation and the total hydrogen contents of the liquid products for each mixture. Furthermore, as shown in Figure 5-5 there is a better correlation of heteroatom removal with phenanthrene hydrogenation than with % H in the liquid products. We will use phenanthrene hydrogenation extensively in this report as a generalized measure of catalyst activity.

Table 5-1 shows the percent phenanthrene hydrogenation of mix 1 and mix 2 with fresh, aged, and equilibrium catalysts; the same data are shown graphically in Figure 5-6 for mix 2. It can be seen that phenanthrene hydrogenation ranges from 3-81% for the catalysts and is zero for Vycor so it is a very good parameter on which to base other comparisons. Furthermore there are very clear differences between fresh and aged commercial catalysts, between these and the minerals, and between runs with and without nitrogen in the feeds. A comparison of these data to those in Figure 5-3 indicates the equivalent average type of hydrophenanthrene formed in each case.

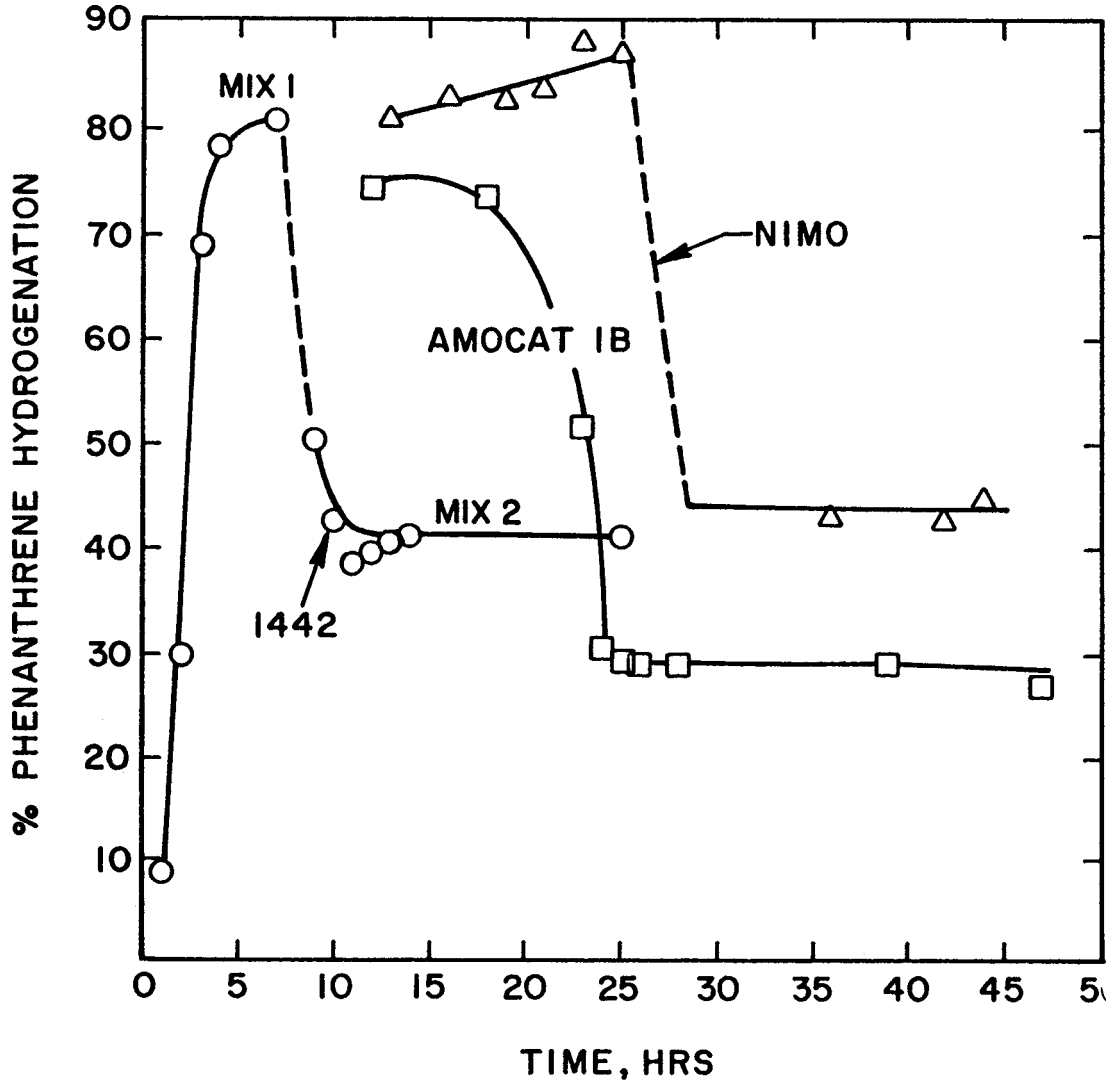
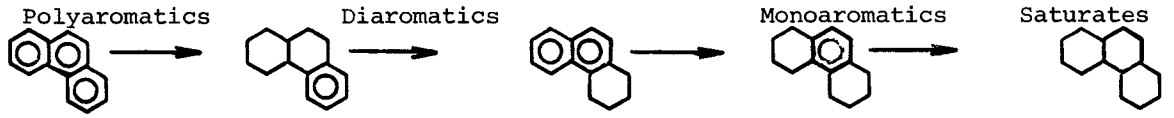


Figure 5-2. Phenanthrene Hydrogenation vs. Time



% Hydrogen				
5.6	6.7	7.7	9.7	12.5
% Hydrogenation				
0	14	29	57	100

Figure 5-3. % Hydrogenation of Phenanthrene as a Selectivity Parameter

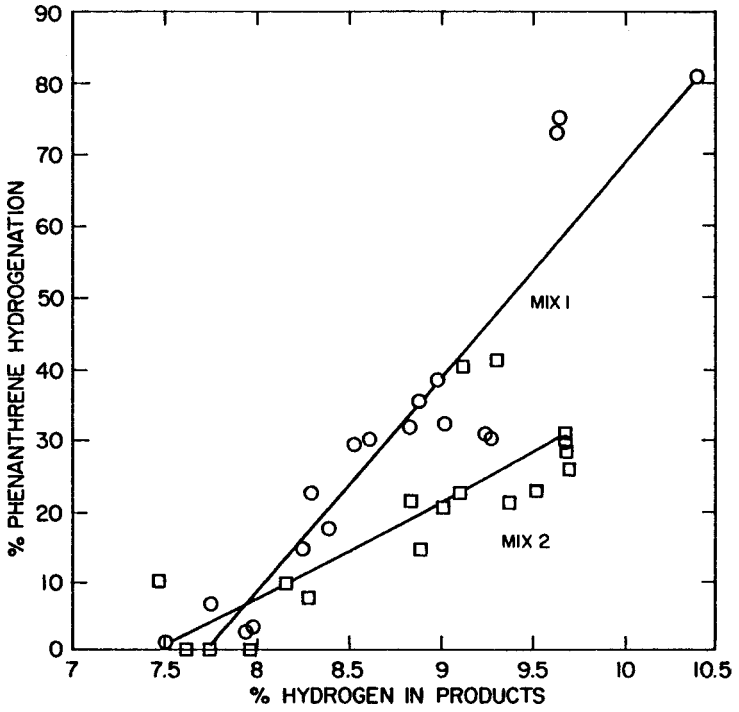
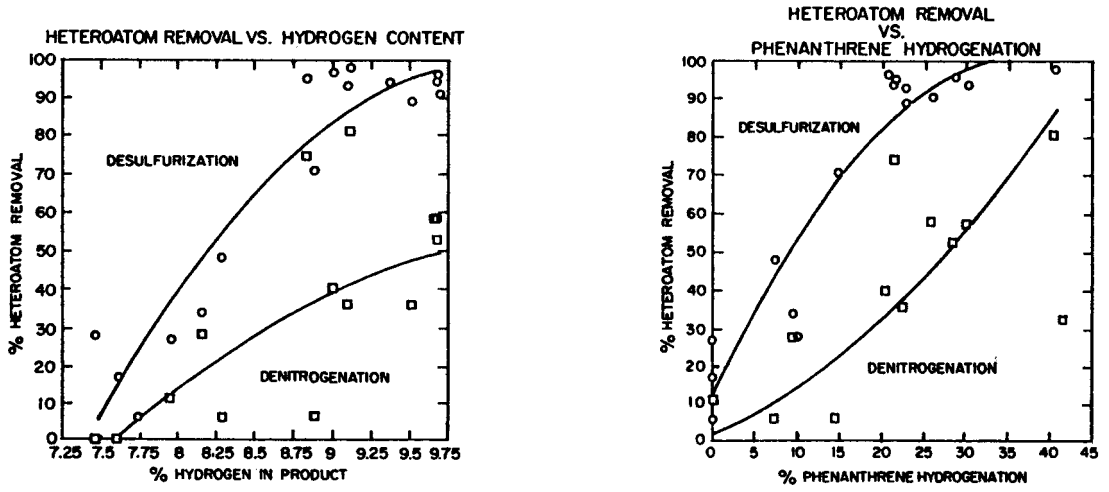


Figure 5-4. Phenanthrene Hydrogenation vs. Hydrogen Content



(a) (b)

Figure 5-5. Heteroatom Removal vs. (a) Hydrogen Content and (b) Phenanthrene Hydrogenation

Table 5-1

PERCENT PHENANTHRENE HYDROGENATION

MIX 1

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	80.8	31.8	29.9
Cyanamid (NiMo)	81.3	38.3	
Armak (NiMo)		35.4	
Amocat 1B (Mo)	74.0	22.5	
Amocat 1A (CoMo)		29.4	
Manganese Nodules	17.6		
Wilsonville Solids	3		

MIX 2

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	40	41	21
Cyanamid (NiMO)	42	21	
Armak (NiMo)		23	
Amocat 1B (Mo)	29	15	
Amocat 1A (CoMo)		23	
Manganese Nodules	8		
Wilsonville Solids	3		

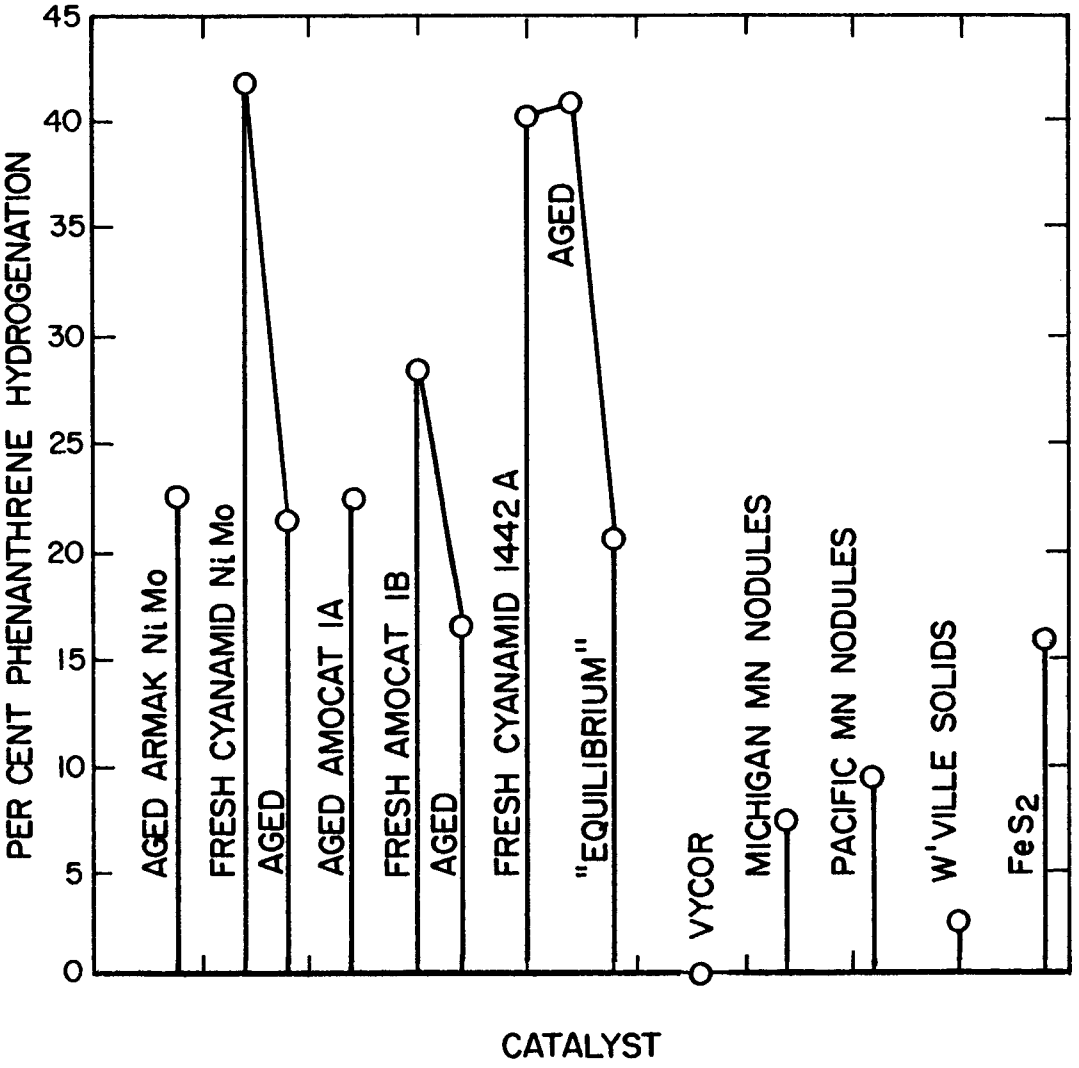


Figure 5-6. Phenanthrene Hydrogenation in Mix 2

DESULFURIZATION

One sulfur compound, benzothiophene, was used in both mix 1 and mix 2 for the examination of desulfurization activities. (Heptyl mercaptan was also present to assure that the catalysts would be sulfided and maintained in that form; it is assumed that heptyl mercaptan conversion was complete in all runs and it was not counted in desulfurization comparisons.) The accepted (5-1) conversion mechanisms are shown below:

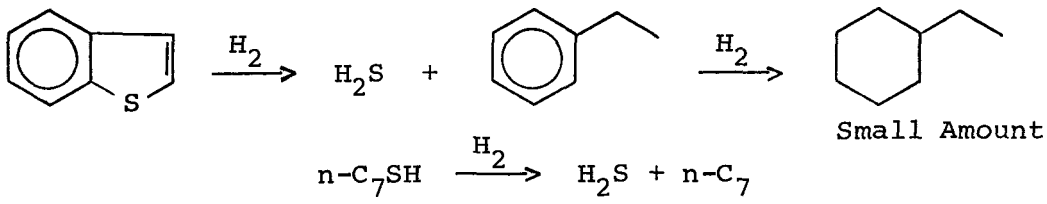
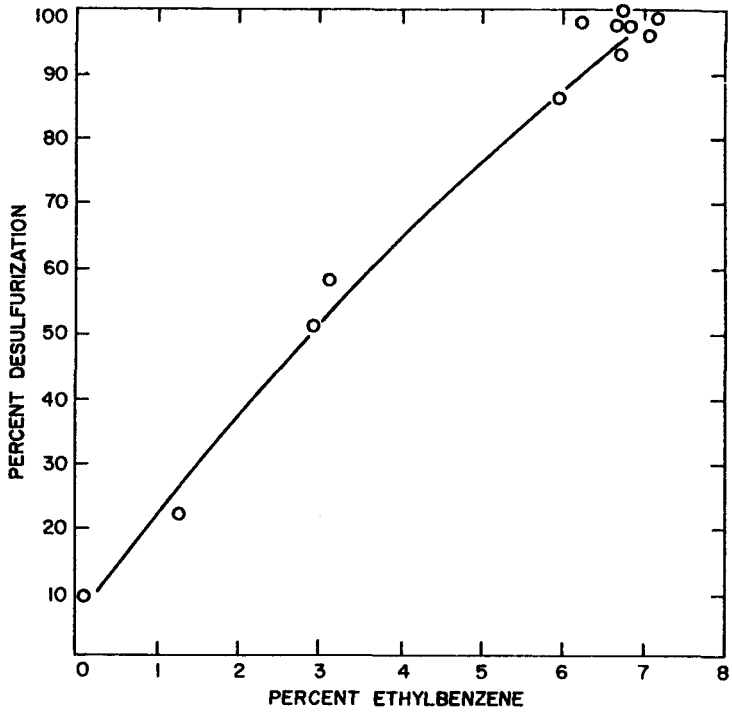


Figure 5-7 shows the correlation of ethylbenzene detected to the percent desulfurization. Linear relationships are evident but there is an indication that especially in the presence of nitrogen some desulfurization does not lead to ethylbenzene formation; ethylcyclohexane would not be produced in significant amounts in the presence of nitrogen compounds, especially at low conversions. Styrene is a possible product, but confirmation was not sought.

Table 5-2 shows the percent desulfurization in our test reactions. The commercial preparations all gave very high conversions; Amocat 1B was noticeably less active than the others. Manganese nodules were quite active and the pyrite surprisingly low in activity; there was no thermal reaction over Vycor. It can be seen that there was little difference between fresh and aged catalysts except for Amocat 1B. However, as can be seen from Figure 5-8, the aged catalysts were considerably less active than the fresh for coal liquids desulfurization (5-2). Benzothiophene desulfurization is too easy to give fine discrimination under the conditions of our test. Figure 5-9 shows the benzothiophene results graphically.



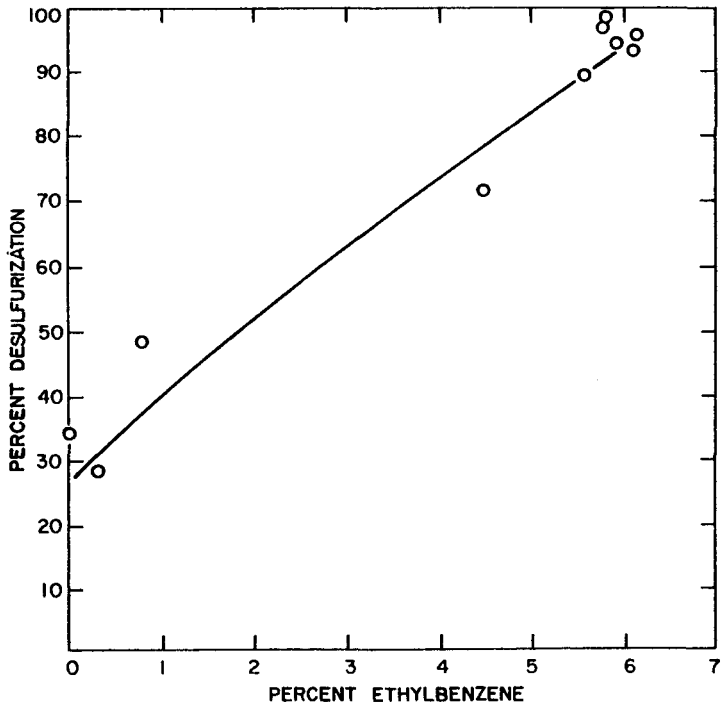


Figure 5-7. Ethylbenzene vs. Desulfurization

Table 5-2

PERCENT DESULFURIZATION

MIX 1

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	98	96	96
Cyanamid (NiMo)	98	97.5	
Armak (NiMo)		93	
Amocat 1B (Mo)	98	86	
Amocat 1A (CoMo)		97.5	
Manganese Nodules	58		

MIX 2

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	98	96	97
Cyanamid (NiMo)	97	95	
Armak (NiMo)		89	
Amocat 1B (Mo)	94	71	
Amocat 1A (CoMo)		93	
Manganese Nodules	48		

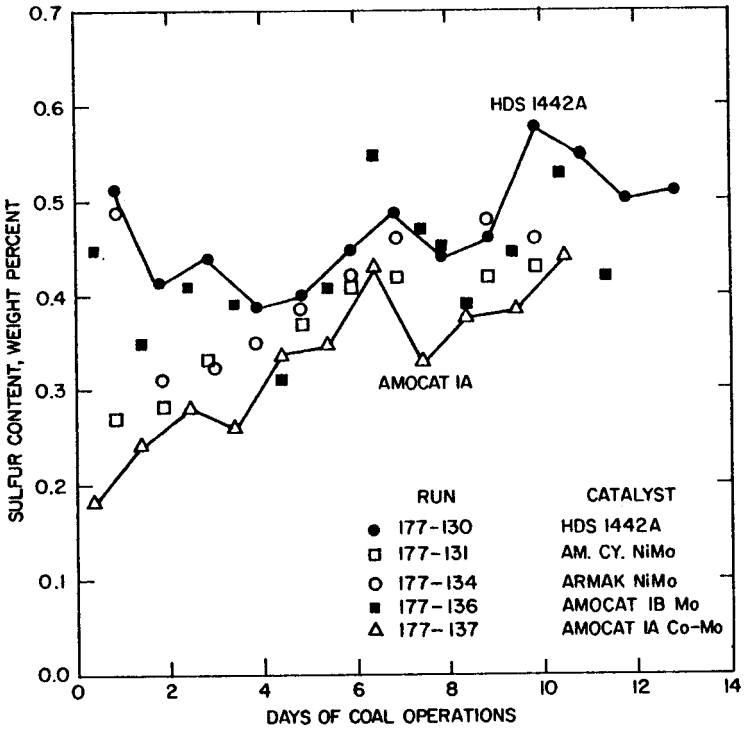


Figure 5-8. Sulfur Content of Residual Oil (Reference 5-2) in HRI Runs

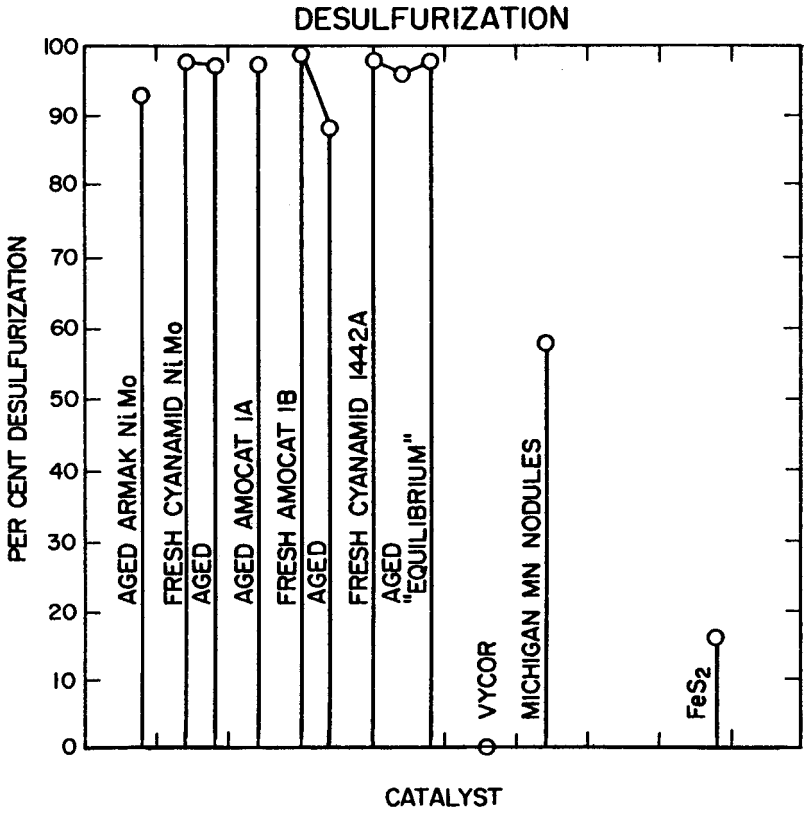
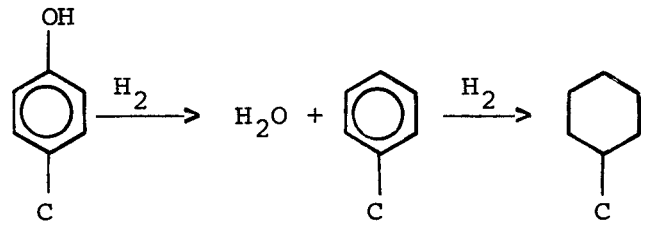


Figure 5-9. Mix 1 -- Desulfurization

DEOXYGENATION

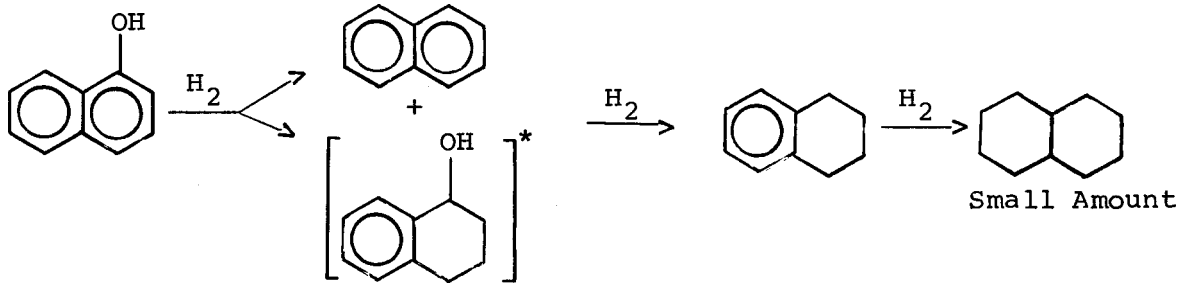
We used three oxygen compounds in mix 1 to follow deoxygenation: p-cresol as representative of single-ring phenols, 1-naphthol as representative of multi-ring phenols, and dibenzofuran as representative of aromatic oxygen heterocyclic ethers. 1-Naphthol was also present in mix 2. The accepted mechanisms (5-1) for the reactions of these compounds are shown in Figure 5-10. Two comments are appropriate. First, there was negligible phenol condensation under these conditions of low temperature and often high donor concentration. Second, there are two possible routes from α-naphthol to tetralin.

Single Ring Phenols



Small Amount

Multi-ring Phenols



Small Amount

*Not detected.

Aromatic Oxygen Heterocycles

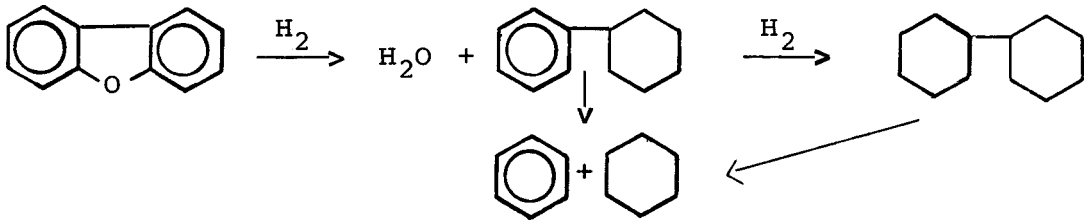


Figure 5-10. Deoxygenation Reactions

Table 5-3 shows the percent deoxygenation with each catalyst with each mixture, and Table 5-4 shows the percent disappearance of each of the oxygen-containing compounds in the feeds. Figure 5-11 shows the total percent deoxygenation of mix 1 vs. phenanthrene hydrogenation and Figure 5-12 shows the disappearance of each of the oxygen compounds in mix 1 vs. phenanthrene hydrogenation.

Several features are apparent. There is a broad range of deoxygenation with these catalysts under these conditions. This is because the three oxygen compounds are very different in ease of deoxygenation. 1-Naphthol is completely deoxygenated by all catalysts but the minerals; it is ~50% converted over Vycor in mix 1. p-Cresol shows an intermediate ease of deoxygenation. Dibenzofuran conversion is quite high with fresh commercial catalysts and quite low with aged commercial catalysts and minerals.

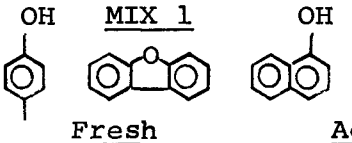
Thus under our conditions some catalysts can convert one compound but not another. In catalytic treatment of coal or coal liquids the products would not be likely to contain multi-ring phenols; they would contain some aromatic ethers and single-ring phenols. In products containing very little oxygen, it would probably be almost entirely single-ring phenols and aromatic ethers. Very little hydrogenation activity is required for conversion of multi-ring phenols; more activity is required for conversion of the other compounds. Even though the first step in cresol conversion is dehydroxylation with catalysts of this type, apparently this can occur only over catalysts having good hydrogenation activity. Overall there is an excellent correlation between deoxygenation and hydrogenation (Figure 5-11).

The extent to which the conversion of these compounds is "consecutive" in our tests is shown in Figures 5-12 and 5-13. In the latter figure (cresol remaining vs. percent deoxygenation), a line has been drawn showing the results that would be obtained if all the 1-naphthol were converted without any conversion of the other two compounds, then all the p-cresol, and then all the dibenzofuran. (This is, of course, on a catalyst activity scale, not a time scale.) The points are below the line partly because gas formation reduces the liquid product yield and raises the product oxygen content slightly.

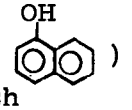
Table 5-3

PERCENT DEOXYGENATION

MIX 1



Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	92	41	47
Cyanamid (NiMo)	89	62	
Armak (NiMo)		58	
Amocat 1B (Mo)	77	39	
Amocat 1A (CoMo)		37	
Manganese Nodules	26		

MIX 2 (only )

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	83	52	66
Cyanamid (NiMo)	77	75	
Armak (NiMo)		46	
Amocat 1B (Mo)	56	67	
Amocat 1A (CoMo)		45	
Manganese Nodules	6		

Table 5-4

PERCENT CRESOL AND DIBENZOFURAN CONVERSIONS

Mix 1 (Cresol)

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	100	66	61
Cyanamid (NiMo)	100	87	
Armak (NiMo)		85	
Amocat 1B (Mo)	100	35	
Amocat 1A (CoMo)		49	
Manganese Nodules	7		
Wilsonville Solids	0		

(Note: α-Naphthol conversion 100% in all cases except 64% with Mix 2 and manganese nodules, 40% Mix 1, 50% Mix 2 } Wilsonville solids).

Mix 2 (Dibenzofuran)

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	~100	~25	~40
Cyanamid (NiMo)	~90	~40	
Armak (NiMo)		~40	
Amocat 1B (Mo)	~70	~10	
Amocat 1A (CoMo)		~10	
Manganese Nodules	~10		
Wilsonville Solids	0		

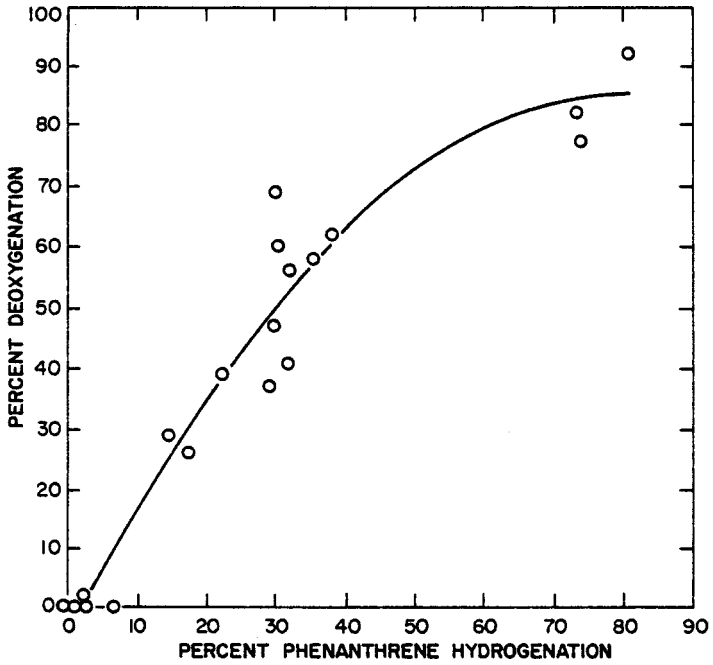


Figure 5-11. Mix 1 Deoxygenation vs. Phenanthrene Hydrogenation

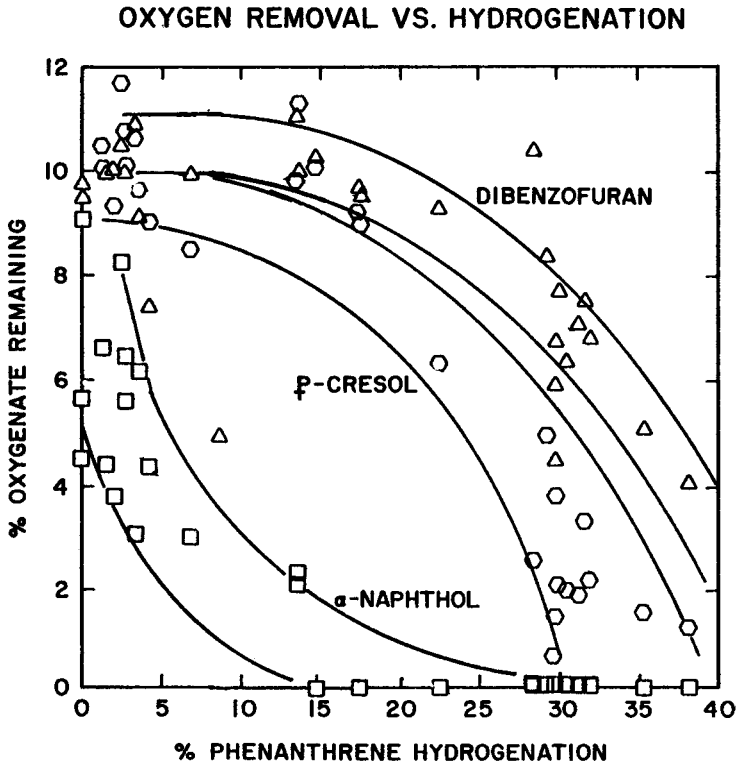


Figure 5-12. Oxygen Removal vs. Hydrogenation

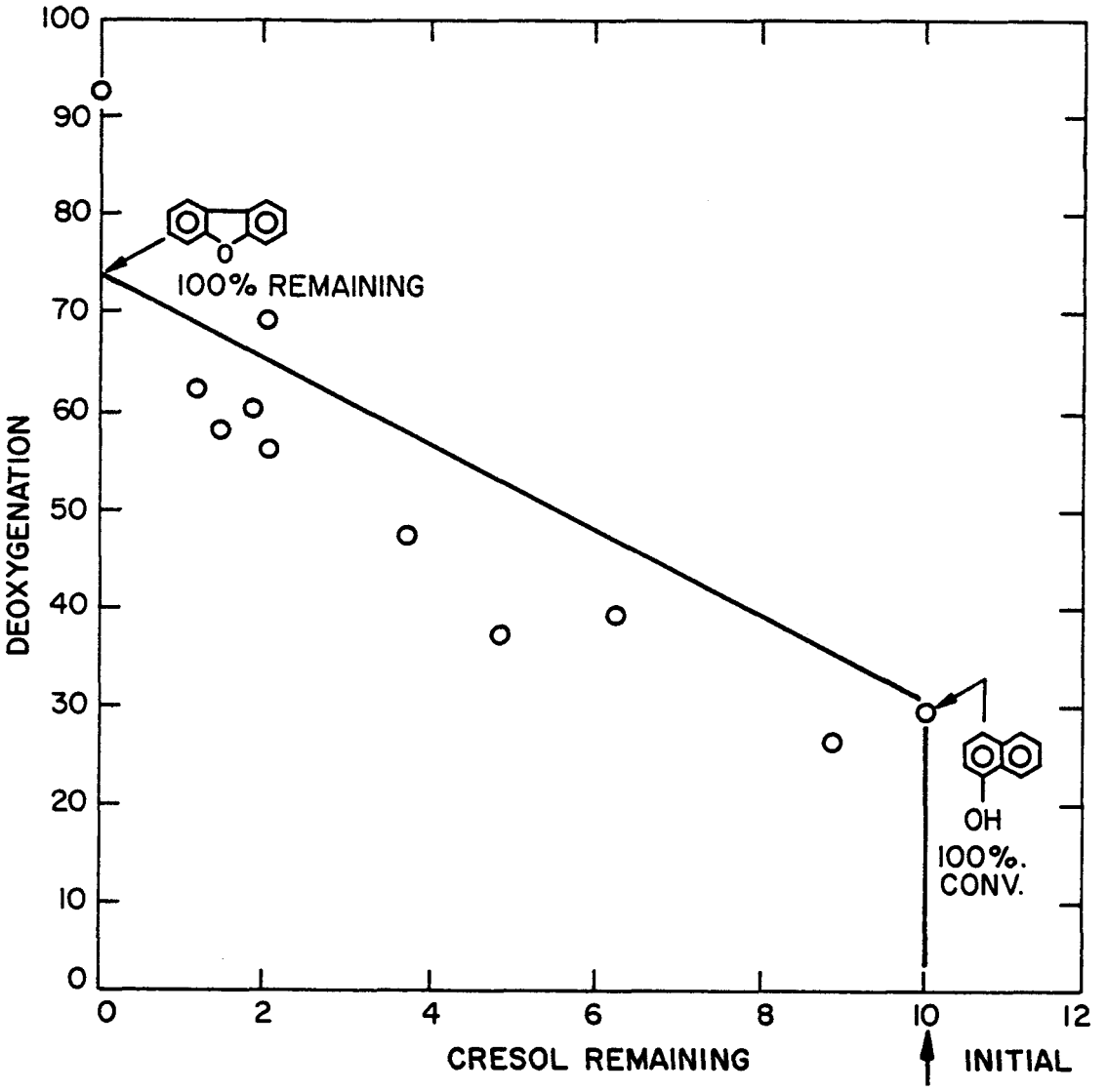


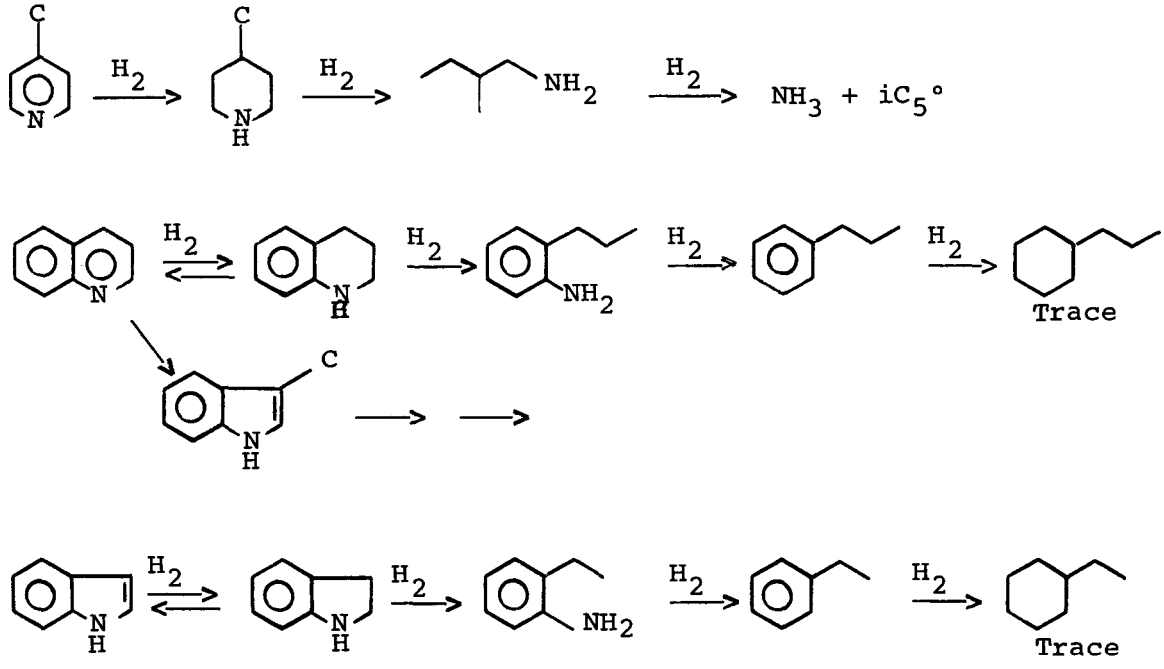
Figure 5-13. Cresol Remaining vs. Deoxygenation Mix 1

The fresh commercial catalysts are very active for conversion of all three compounds except for Amocat 1B. The nickel catalysts show the best retention of activity when aged, and the Amoco catalysts are the poorest. The minerals are very poor, except for 1-naphthol conversion.

It is interesting to note that although 1-naphthol is completely converted over the commercial catalysts, the apparent deoxygenation (as measured by product oxygen content) when nitrogen is present (Table 5-3) is too low, especially over the aged catalysts. Perhaps the water formed is soluble in the amine-containing products.

DENITROGENATION

Denitrogenation is somewhat more difficult to assess than were the other heteroatom removal processes because nitrogen-containing intermediates are formed in the nitrogen removal sequences. The exact mechanisms are not as unambiguously defined as in the other cases (5-1,5-3,5-4,5-5); we will use the mechanisms we believe have the most support, as shown below.



Denitrogenation Reactions

In each case, the sequence involves hydrogenation of the nitrogen-containing ring, followed by hydrocracking of one C-N bond to form an amine or aniline, followed by hydrocracking of the other C-N bond to form NH_3 and a hydrocarbon. Depending upon the initial compound, any of the steps could be rate-determining. In some cases, rates of hydrogenation of other rings may be comparable; perhydroquinoline was observed in some of our product mixtures. Furthermore, hydrogenation of nitrogen-containing rings is reversible; in our runs quinoline and tetrahydroquinoline were found to be at thermodynamic equilibrium (5-4). Finally, isomerizations are possible; we observed methyl indole formation from quinoline. This complexity plus the difficulty in detecting and identifying all these products by gas chromatography makes our data on the nature of the decomposition products somewhat less precise than for the other feed components.

The behavior is similar to that with the oxygen compounds in that the three nitrogen compounds are converted with very different degrees of difficulty. Figure 5-14 shows the disappearance of the three parent compounds as functions of phenanthrene hydrogenation and total nitrogen removal. It is clear that the order of disappearance (on a catalyst activity scale, not a time scale) is quinoline > indole > picoline.

However, as shown in Figure 5-15, conversion of the parent compound does not necessarily result in comparable denitrogenation. Tetrahydroquinoline is readily formed from quinoline; in fact virtually no catalytic activity is required. Figure 5-16 shows that the tetrahydroquinoline concentration we observed was always much greater than the quinoline concentration. Picoline behavior was similar, but a high hydrogenation activity was required, equal to the ability to hydrogenate phenanthrene to a mixture equivalent to hexahydrophenanthrene. Comparatively little indoline (hydrogenated indole) was observed; indoline denitrogenation must be faster than indole hydrogenation. Substituted anilines were observed, at low concentration, with aged commercial catalysts only. The product distributions observed depended partially on the relative hydrogenation and hydrocracking activities, which will be discussed below.

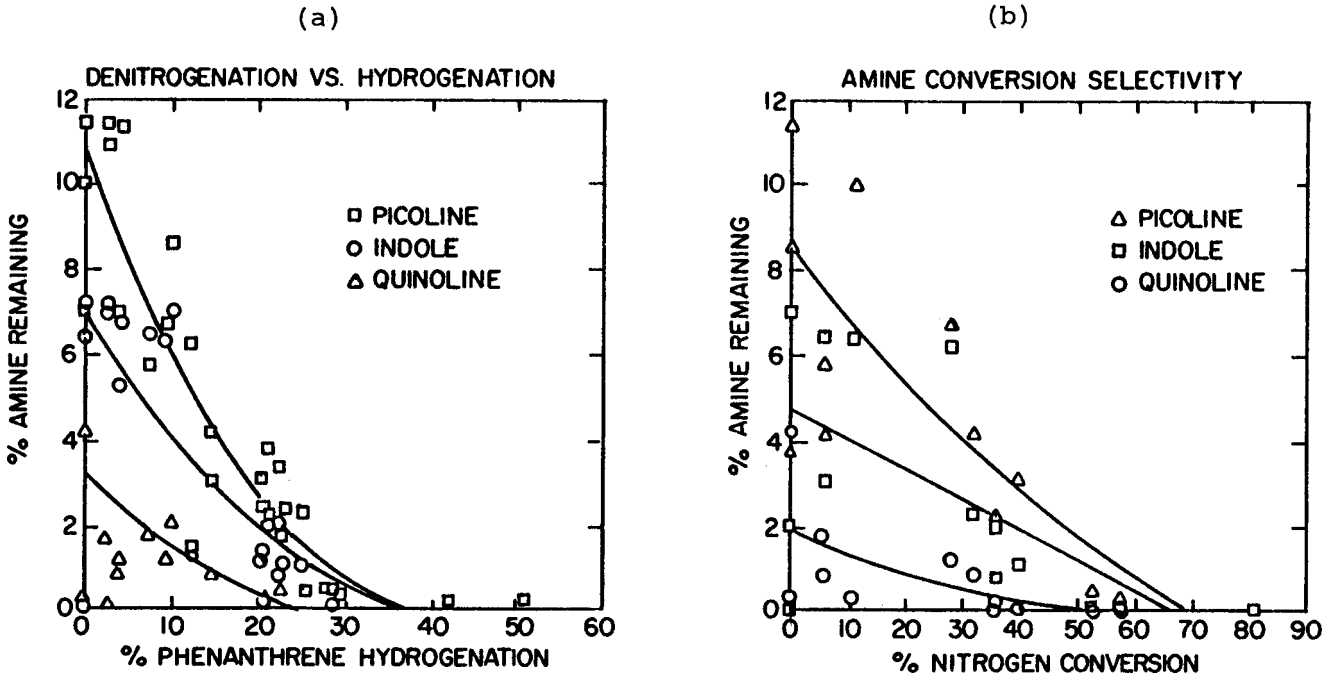


Figure 5-14. Comparisons of Denitrogenation of Three Nitrogen Compounds

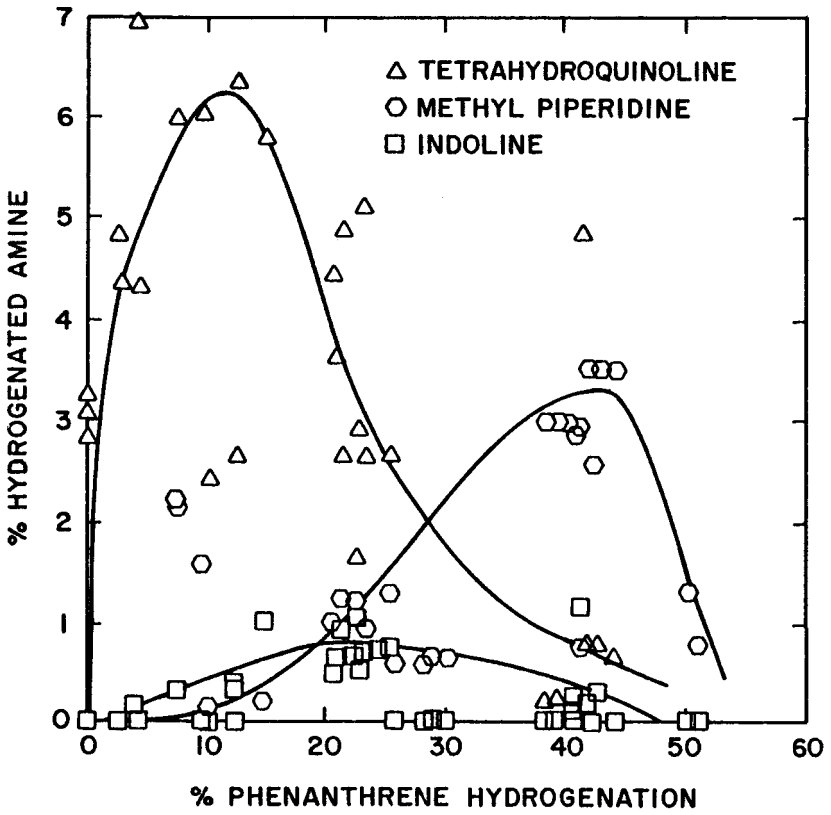


Figure 5-15. Hydrogenation Selectivity (Amines)

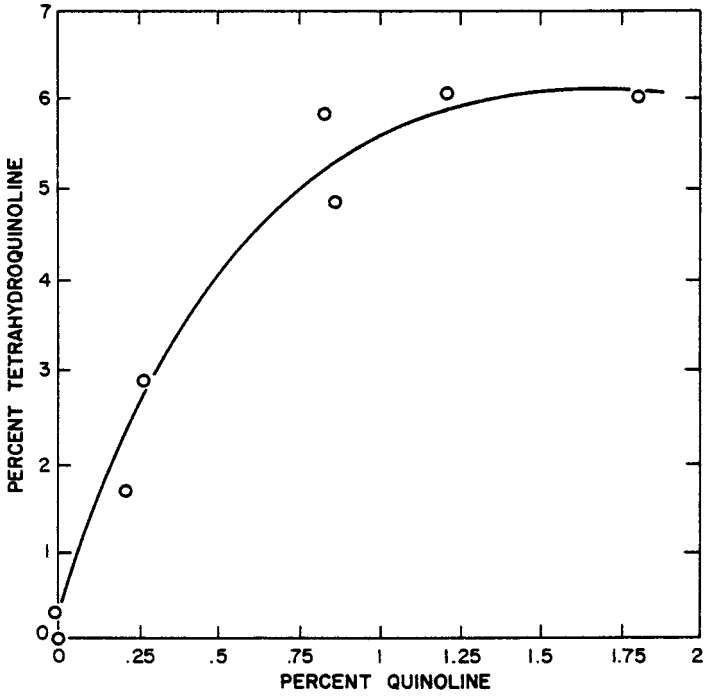


Figure 5-16. Quinoline Selectivity

Figure 5-17 shows the differences in the ease of conversion of the three compounds and the relationship to total denitrogenation. The line shows the behavior that would be observed if all the quinoline were converted with no conversion of the others and all indole were converted with no conversion of picoline. The NiMo catalysts are least selective (above the line). Most points at intermediate activity are slightly below the line because of the presence of hydrogenated amines. Several catalysts (aged Amocat 1B and manganese nodules especially) show much more hydrogenation (disappearance of indole) than hydrocracking (denitrogenation).

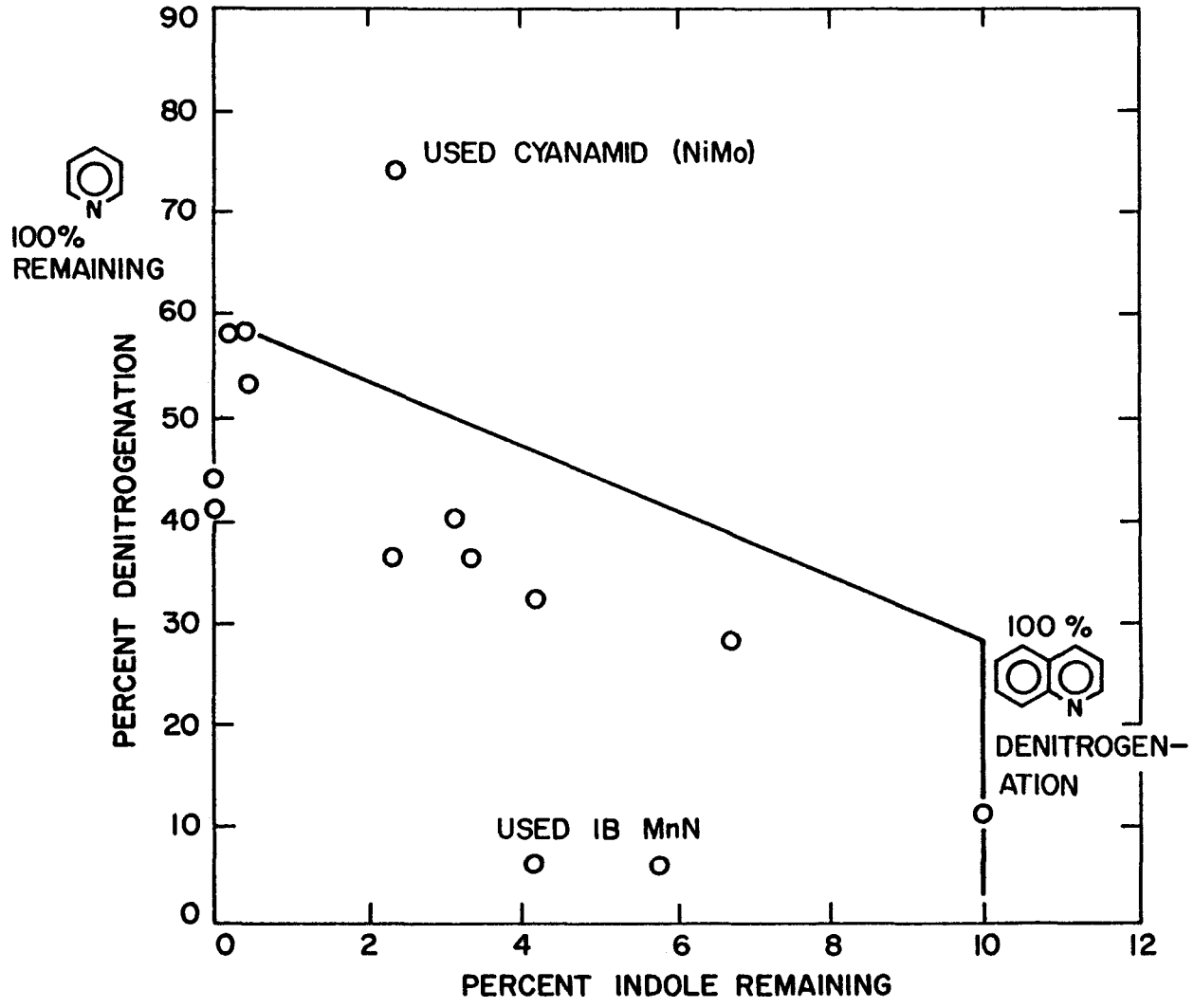


Figure 5-17. Percent denitrogenation vs. percent indole remaining.

Table 5-5 shows the overall denitrogenation activities of the catalysts. The fresh catalysts show high activities, with NiMo being the best and Amocat 1B the lowest. Minerals are very poor. Aged catalysts show much reduced activity with the same relative order. The range is very large with over a factor of 10 difference between the most active (Cyanamid NiMo) and the least active (Amocat 1B).

Table 5-5

MIX 2 PERCENT DENITROGENATION

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	81	32	40
Cyanamid (NiMo)	84	74	
Armak (NiMo)		36	
Amocat 1B (Mo)	58	6	
Amocat 1A (CoMo)		36	
Manganese Nodules	6		

Tables 5-6 and 5-7 show the different catalysts' performance with the three nitrogen compounds. The fresh commercial catalysts gave complete quinoline conversion and almost no tetrahydroquinoline in the products (because further reaction had occurred). The aged commercial catalysts and the minerals still gave high quinoline conversion, complete with the NiMo catalysts, but were not good for tetrahydroquinoline denitrogenation. Aged NiMo catalysts performed very well, but the aged Amocat 1A appeared best for tetrahydroquinoline formation. The fresh commercial catalysts gave high indole and picoline conversions and the minerals very low conversions. Aged commercial catalysts gave intermediate indole and picoline conversions with NiMo catalysts showing the highest activities. Aging had a greater effect on indole conversion. As in the other cases discussed, the "equilibrium" Cyanamid CoMo catalyst was a little more active than the sample from HRI's catalyst aging test.

Table 5-6

MIX 2 PERCENT QUINOLINE CONVERSION AND TETRAHYDROQUINOLINE PRODUCED

Quinoline Conversion

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	100	93	100
Cyanamid (NiMo)	100	100	
Armak (NiMo)		100	
Amocat 1B (Mo)	100	93	
Amocat 1A (CoMo)		98	
Manganese Nodules	85		
Wilsonville Solids	85		

Tetrahydroquinoline Produced*

Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	0.29	4.84	4.44
Cyanamid (NiMo)	0.77	2.67	
Armak (NiMo)		2.93	
Amocat 1B (Mo)	0 ?	5.8	
Amocat 1A (CoMo)		1.68	
Manganese Nodules	6.01		
Wilsonville Solids	4.84		

*Percent of total liquid product.

Table 5-7

MIX 2 PERCENT INDOLE AND PICOLINE CONVERSIONS

	Indole		
Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	100	41	56
Cyanamid (NiMo)	96	67	
Armak (NiMo)		67	
Amocat 1B (Mo)	93	41	
Amocat 1A (CoMo)		52	
Manganese Nodules	18		
Wilsonville Solids	0		

	Picoline		
Catalyst	Fresh	Aged	(Equil.)
Cyanamid 1442 (CoMo)	100	67	84
Cyanamid (NiMo)	94	85	
Armak (NiMo)		89	
Amocat 1B (Mo)	?	56	
Amocat 1A (CoMo)		72	
Manganese Nodules	10		
Wilsonville Solids	0		

HYDROGENATION AND HYDROCRACKING

Hydrogenation was studied with all three model compound feed mixes (see Table 4-4); hydrocracking was studied with mix 3. Considering first the overall hydrogenation of the complex mixtures, Table 5-8 gives some hydrogen contents of the products from mixes 1 and 2 and Figure 5-18 shows the mix 2 results graphically.

It can be seen that in all cases hydrogen contents increased, even over Vycor. In this case, and with the mineral catalysts, this is partially due to thermal heteroatom removal (especially dehydroxylation of the naphthol) which increases the product percent hydrogen without adding any hydrogen to the molecules. Another contributing factor is thermal hydrogenation, especially of nitrogen heterocycles (such as quinoline to tetrahydroquinoline). Note that the hydrogen contents of the mix 2 products is higher than that of the mix 1 products, even though nitrogen decreases catalytic activity for other reactions.

No catalyst or catalyst type (such as NiMo or Mo) consistently gives the most or least hydrogenation under the various conditions examined (fresh, aged, with or without nitrogen). This is because some reactions result in increases in hydrogen and some in decreases.

To understand and compare the results we must examine them in more detail. Table 5-9 shows the tetralin produced and Table 5-10 shows the decalin produced. It can be seen that the fresh catalysts produce decalin at the expense of tetralin, except for Amocat 1B and manganese nodules, which give more tetralin because they are less active. Among the aged catalysts, the NiMo versions produce the most tetralin, and, in general, catalysts produce more tetralin when nitrogen is present.

Figure 5-19 shows the yields of tetralin and decalin as a function of percent phenanthrene hydrogenation. The maximum tetralin yield corresponds to about 25-50% phenanthrene hydrogenation; catalysts having greater hydrogenation activity produce less tetralin. Figure 5-20 shows the interrelationship of naphthalene hydrogenation

Table 5-8

PRODUCT PERCENT H

Catalyst	Fresh	Aged	(Equil.)
	(Mix 1 - Feed = 7.8%)		
Cyanamid 1442 (CoMo)	10.4	8.83	8.62
Cyanamid (NiMo)	10.14	8.98	
Armak (NiMo)		8.88	
Amocat 1B (Mo)	9.64	8.30	
Amocat 1A (CoMo)		8.53	
Manganese Nodules	8.39		
	(Mix 2 - Feed = 8.0%)		
Cyanamid 1442 (CoMo)	9.12	9.30	9.01
Cyanamid (NiMo)	10.13	8.84	
Armak (NiMo)		9.52	
Amocat 1B (Mo)	9.69	8.89	
Amocat 1A (CoMo)		9.10	
Manganese Nodules	8.29		

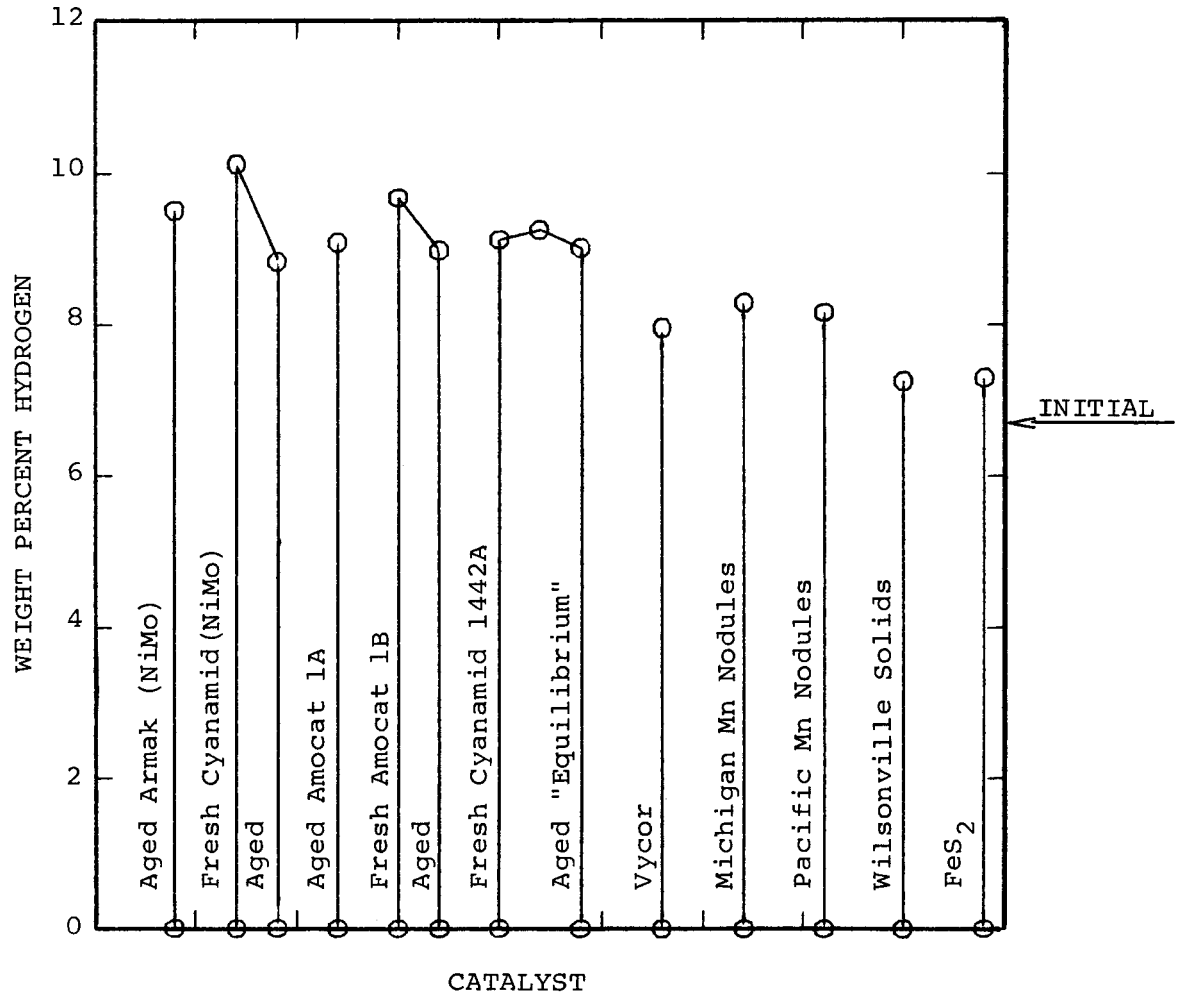


Figure 5-18. Hydrogen Content - Mix 2

Table 5-9

PERCENT TETRALIN PRODUCED

Catalyst	Fresh	Aged	(Equil.)
	(MIX 1)		
Cyanamid 1442 (CoMo)	4.28	5.53	6.29
Cyanamid (NiMo)	4.52	6.72	
Armak (NiMo)		6.77	
Amocat 1B (Mo)	6.32	5.82	
Amocat 1A (CoMo)		6.20	
Manganese Nodules	5.87		
Wilsonville Solids	0.5		
	(MIX 2)		
Cyanamid 1442 (CoMo)	6.77	5.57	6.41
Cyanamid (NiMo)	7.41	7.41	
Armak (NiMo)		7.25	
Amocat 1B (Mo)	6.69	5.04	
Amocat 1A (CoMo)		6.22	
Manganese Nodules	0		
Wilsonville Solids	0.3		

Table 5-10

PERCENT DECALIN PRODUCED

Catalyst	Fresh	Aged	(Equil.)
	(MIX 1)		
Cyanamid 1442 (CoMo)	3.1	0	0.7
Cyanamid (NiMo)	3.2	1.0	
Armak (NiMo)		0	
Amocat 1B (Mo)	0.2	0	
Amocat 1A (CoMo)		0.2	
Manganese Nodules	0		
Wilsonville Solids	0		
	(MIX 2)		
Cyanamid 1442 (CoMo)	0.7	0	0
Cyanamid (NiMo)	0.7	0.4	
Armak (NiMo)		0	
Amocat 1B (Mo)	0.2	0	
Amocat 1A (CoMo)		0.2	
Manganese Nodules	0		
Wilsonville Solids	0		

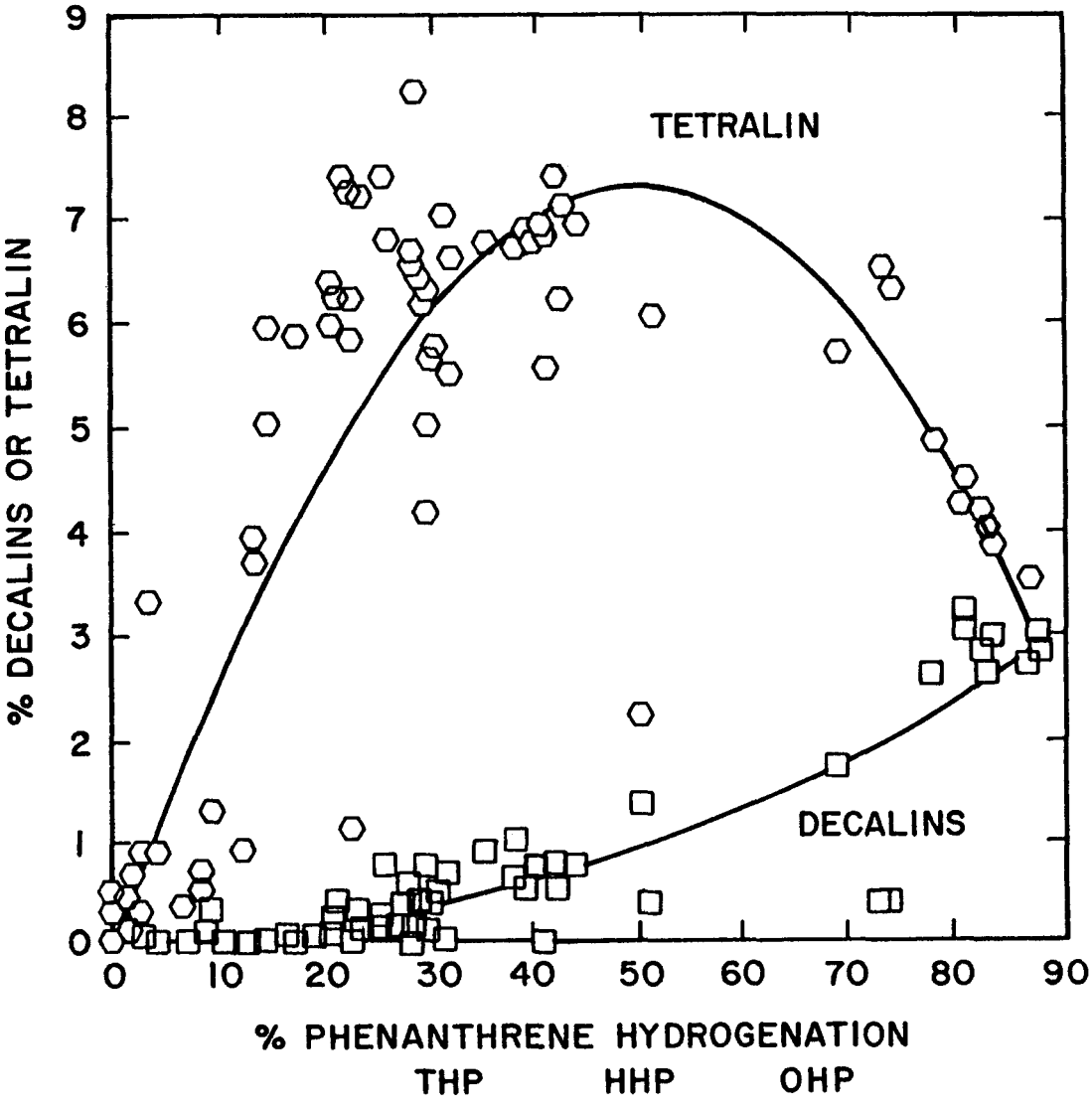


Figure 5-19. Hydrogenation Selectivity (C_{10} Compounds)

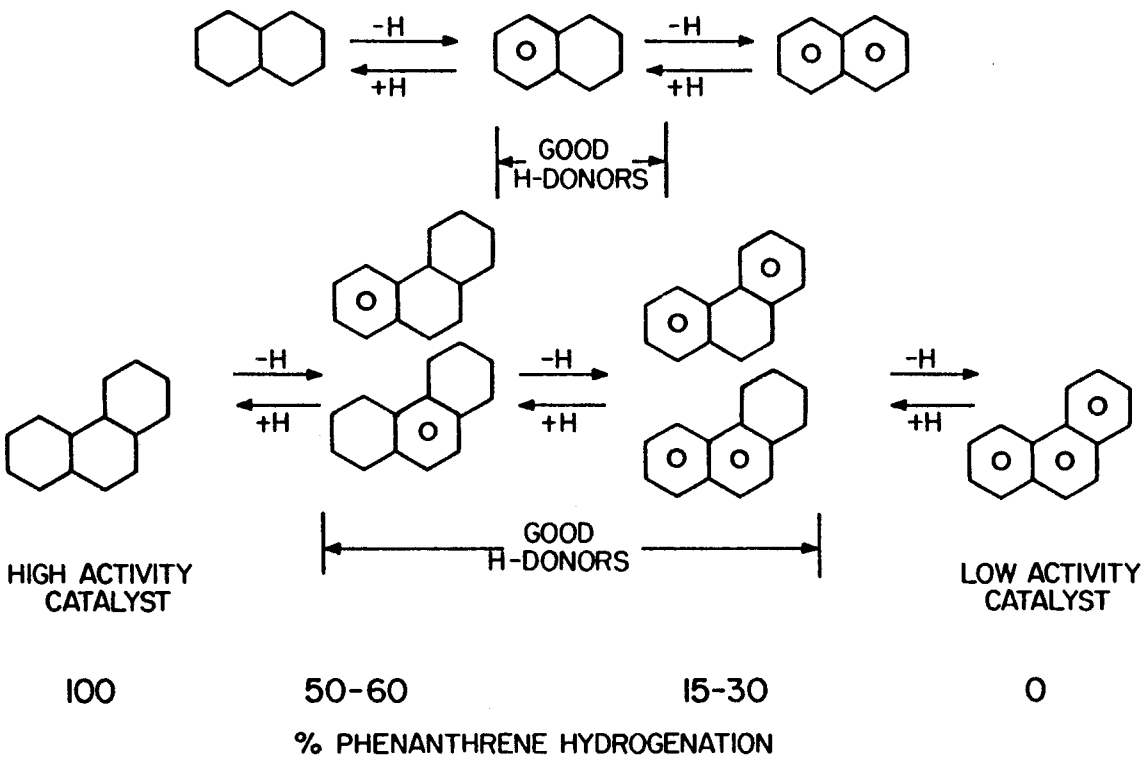


Figure 5-20. Effect of Catalyst Activity on Solvent Hydrogen Donors

to phenanthrene hydrogenation; at 25-50% phenanthrene hydrogenation the best hydrophenanthrene hydrogen donors are produced. Therefore, for catalysts of intermediate activity, maximum yields of hydrogen donors from both two-ring and three-ring systems are produced simultaneously. This is important because it indicates that a properly chosen catalyst could maximize the hydrogen donors formed from a wide variety of aromatics, possibly including high molecular weight species.

Figure 5-21 shows the reactions taking place in mix 3; the ethylnaphthalene undergoes hydrogenation and dealkylation (hydrocracking) and ethyltetralins isomerize. The mesitylene undergoes hydrogenation, isomerization, and dealkylation.

Figure 5-22 shows the ethylnaphthalene conversion over the various catalysts. (In this and subsequent similar figures, the upper values for each commercial catalyst are for fresh catalyst and the lower for aged.) The commercial catalysts all gave very high conversions; Amocat 1B aged much more than the others; the minerals had very low activity. In general only one ring was hydrogenated; very small amounts of decalin and ethyldecalin were formed over the fresh catalysts under these test conditions.

It is interesting to note that there was no ethylnaphthalene hydrogenation over Vycor and very little over manganese nodules. The same results were observed for phenanthrene in mixes 1 and 2. However, with mix 1 Vycor produced some tetralin from the α-naphthol, and manganese nodules gave a high tetralin yield. This is evidence for a direct route from α-naphthol to tetralin that does not involve formation and then hydrogenation of naphthalene.

Figure 5-23 shows the total moles of hydrogen atoms added to mix 3 (including formation of gas) for each catalyst. Figure 5-24 shows the moles of hydrogen atoms used in hydrocracking. The hydrogen required for hydrocracking was only a small portion of the total because hydrogenation of a ring requires 4-6 hydrogens while hydrocracking requires only two, and because the feed was mostly mesitylene which underwent little hydrocracking. A plot showing hydrogenation, only, would be almost identical to Figure 5-23.

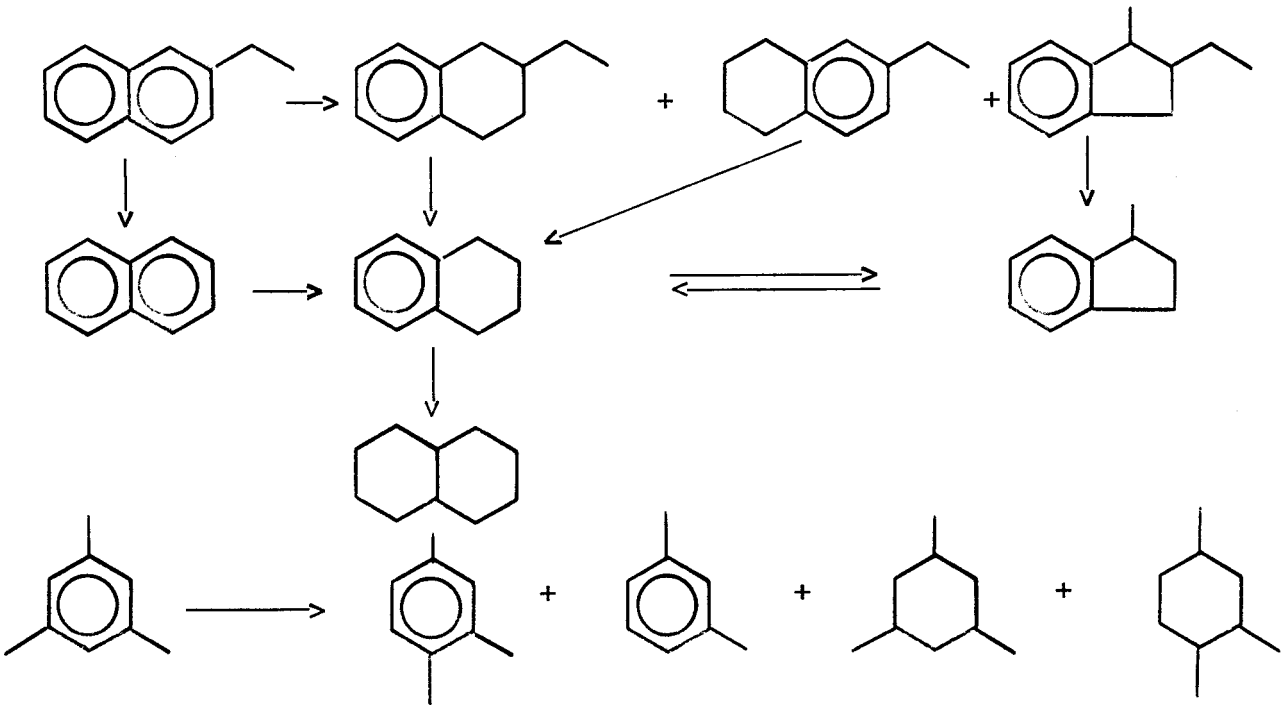


Figure 5-21. Mix 3 reactions.

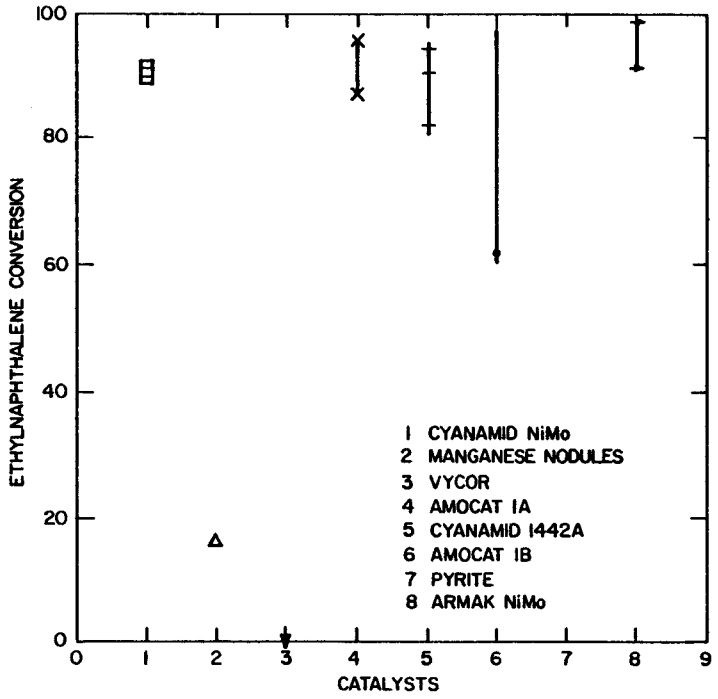


Figure 5-22. Ethylnaphthalene conversion.

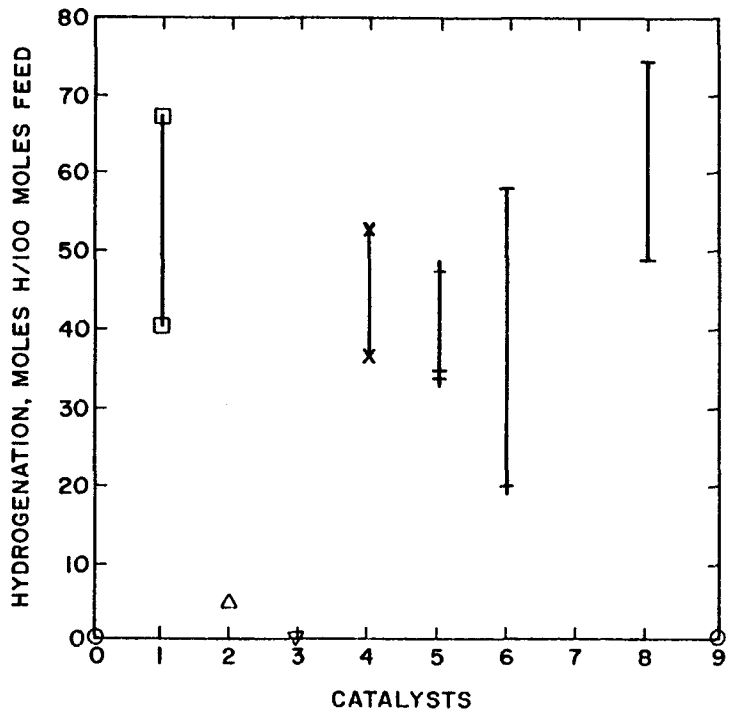


Figure 5-23. Total Hydrogen Added

1 CYANAMID NIMO
2 MANGANESE NODULES
3 VYCOR
4 AMOCAT 1A
5 CYANAMID 1442A
6 AMOCAT 1B
7 PYRITE
8 ARMAK NIMO

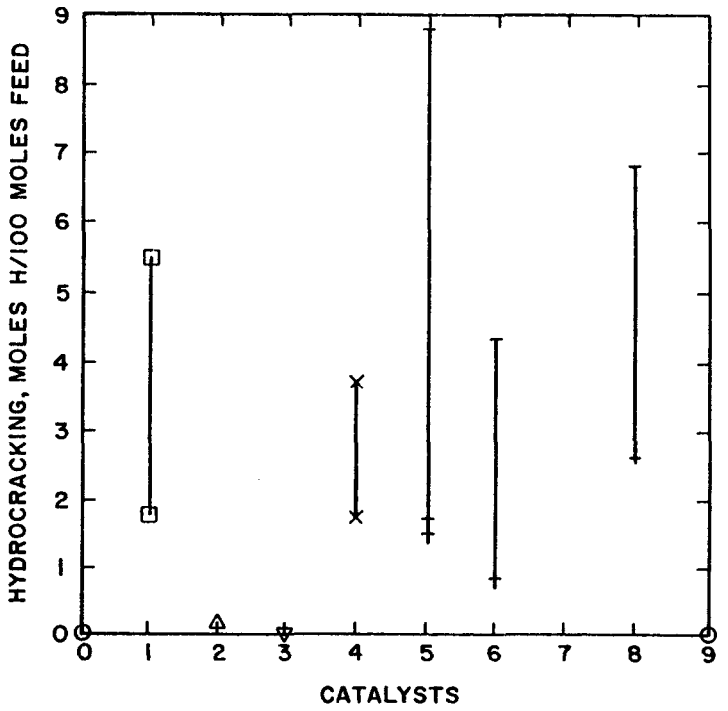


Figure 5-24. Hydrocracking

It can be seen that the NiMo catalysts have the highest activities, fresh and aged, for both reactions, except for the high hydrocracking activity of fresh Cyanamid 1442A. This exception is probably due to the presence of ~0.5% SiO_2 in the Al_2O_3 support of that catalyst (5-6). The effect is lost as the catalyst is aged. The non-nickel catalysts are about equal except that Amocat 1B ages more than the others.

Hydrocracking activity decreases much more than hydrogenation as the catalysts age. Selectivities are shown in Figure 5-25, and hydrogenation vs. hydrocracking is shown in Figure 5-26. (The slopes of the lines are related to the total moles of hydrogenation and hydrocracking that are possible; the shapes of the lines are more significant.) Hydrocracking as a percent of the total hydrogen added was appreciable only with the most active catalysts. The ratio of hydrogenation to hydrocracking decreased with increasing catalyst activity. The difference between fresh and aged catalysts is clear from Figure 5-26. The anomalous behavior of fresh 1442A was explained above.

In these reactions of mix 3 there is very little decalin observed and the ratio of tetralin to naphthalene is virtually constant ($\simeq$0.2) over a broad range of catalyst activities, as shown in Figure 5-27. At equilibrium at 775°F and ~1400 psi H_2, the relative amounts of decalin:tetralin:naphthalene should be about 90:8.5:1.5 (tetralin: naphthalene $\simeq$5.7). The approach to equilibrium at this temperature may be very slow even with fresh commercial catalysts (and the ratio governed by the relative rates of hydrocracking of ethylnaphthalene and ethyltetralin). The tetralin may also be acting as a hydrogen donor.

HETEROATOM REMOVAL SELECTIVITY CHANGES WITH ACTIVITY

In Figure 5-28 we show the percentages of heteroatom removal (mix 2) with each catalyst as functions of the extent of hydrocracking (mix 3) with the same catalyst. Sulfur removal is high even when there is little hydrocracking activity. Nitrogen removal is strongly related to hydrocracking; oxygen removal shows an intermediate response. Hydrocracking activity is required for removing nitrogen from all three of our nitrogen model compounds and is required for deoxygenation of dibenzofuran. It is not required for desulfurization of

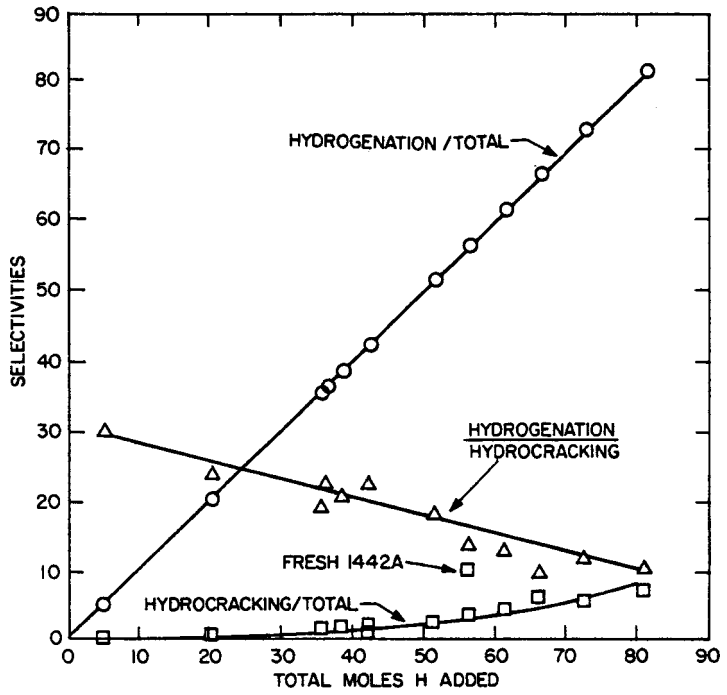


Figure 5-25. Hydrogen Selectivities (all catalysts included)

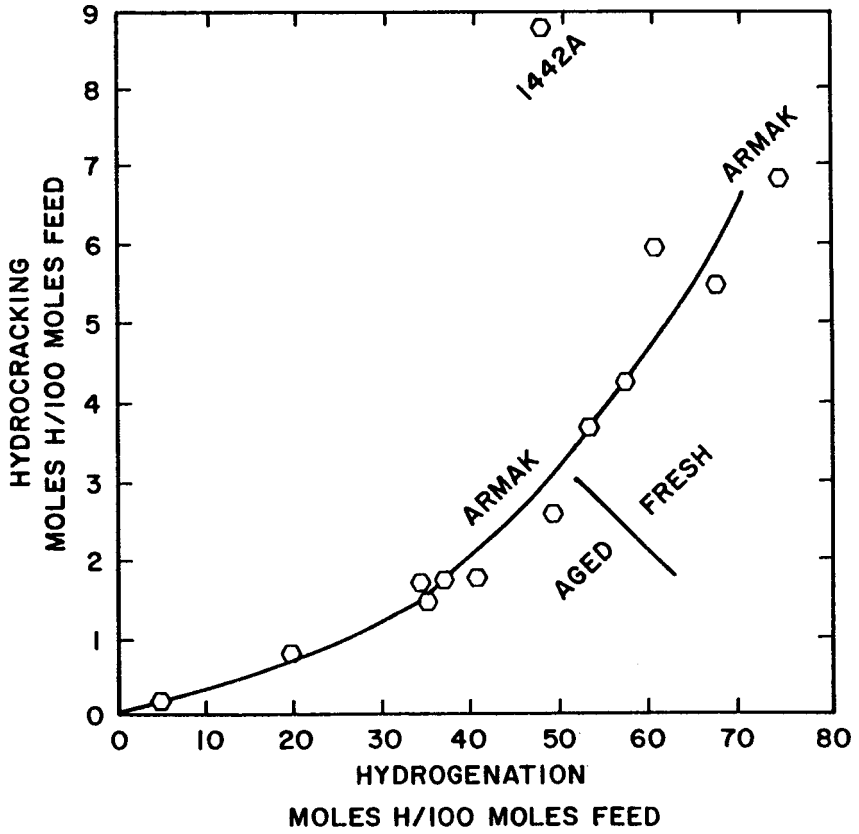


Figure 5-26. Hydrocracking vs. Hydrogenation

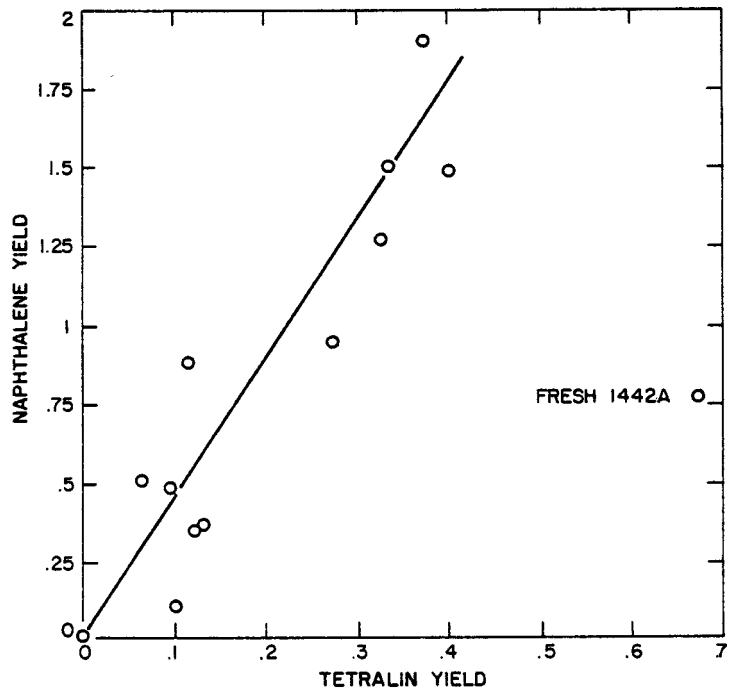


Figure 5-27. Tetralin vs. Naphthalene

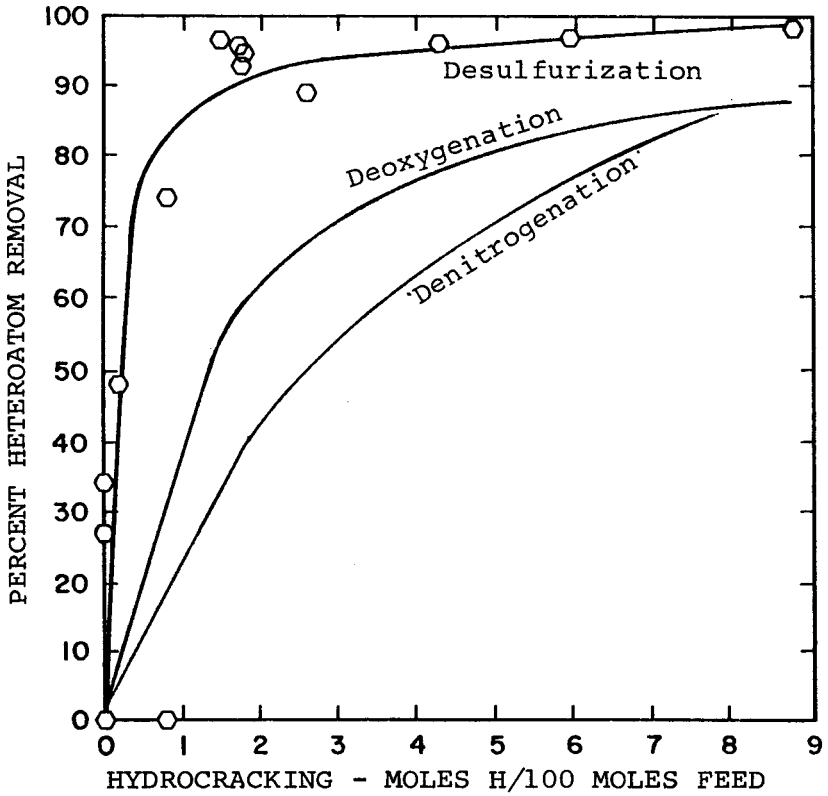


Figure 5-28. Mix 2 Heteroatom Removal vs. Hydrocracking in Mix 3

benzothiophene. With the catalysts presently being considered for coal processing, extensive denitrogenation can not be achieved without hydrocracking. This aids in molecular weight reduction, but leads to hydrocarbon gas formation.

Similar plots can be constructed for comparisons of removal of the heteroatoms. Figure 5-29 shows desulfurization vs. denitrogenation of mix 2. Along the X-axis we show first the extents of denitrogenation equivalent to complete conversion of the quinoline (23% of the nitrogen) with no conversion of the other amines, then conversion of the indole (an additional 35% of the nitrogen) and then the picoline. There is actually some overlap, but ease of denitrogenation does vary in that order, as discussed earlier. Thus a catalyst that can convert quinoline but not the other nitrogen compounds converts essentially all of the benzothiophene; a catalyst that cannot convert quinoline cannot convert benzothiphene.

Figure 5-30 shows desulfurization vs. deoxygenation of mix 1. A catalyst that can convert α-naphthol, but not the other oxygen compounds, can convert essentially all of the benzothiophene. A catalyst that cannot convert α-naphthol cannot convert benzothiophene.

Figure 5-31 shows deoxygenation of mix 1 vs. denitrogenation of mix 2 for the various catalysts. Nitrogen removal is considered the chief problem in heteroatom removal, primarily because of the undesirable aspects of nitrogen in subsequent processing or use. However, it can be seen that aside from multi-ring aromatic phenols, oxygen is as difficult to remove as nitrogen. A catalyst capable of converting indole is required to convert dibenzofuran, and a catalyst capable of converting picoline is required to convert cresol. In fact, because of the much higher oxygen contents of coals, coal liquids contain more oxygen than nitrogen.

Overall Catalyst Comparisons

It must be recognized that catalyst comparisons are valid only for the exact conditions of a given test, and extrapolations from limited data must be very tentative. We have three sets of data as shown on page 5-40.

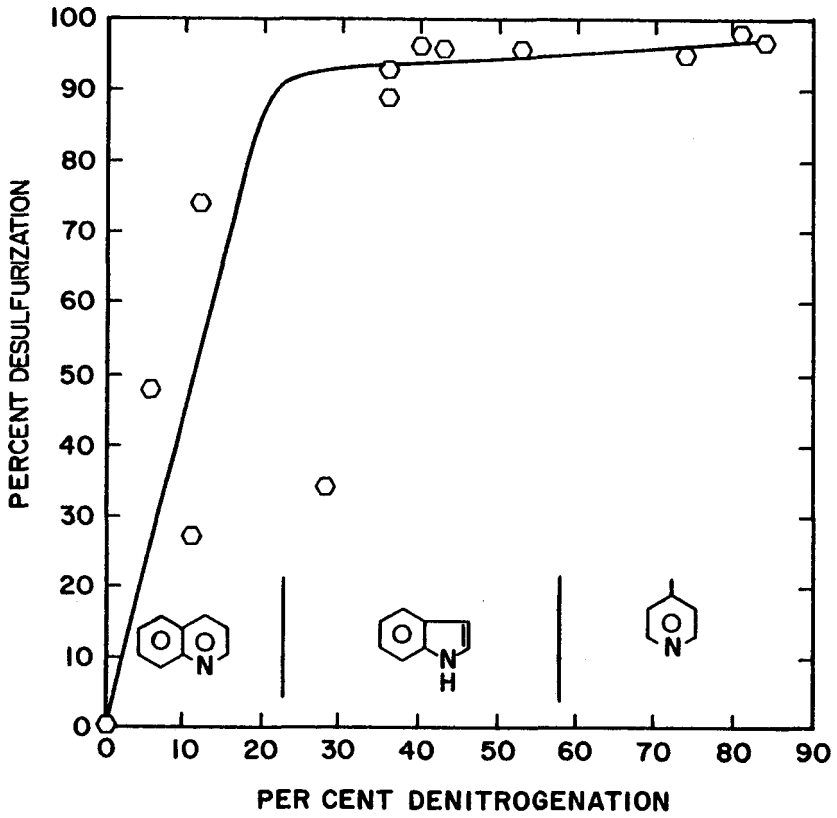


Figure 5-29. Mix 2 - Desulfurization vs. Denitrogenation

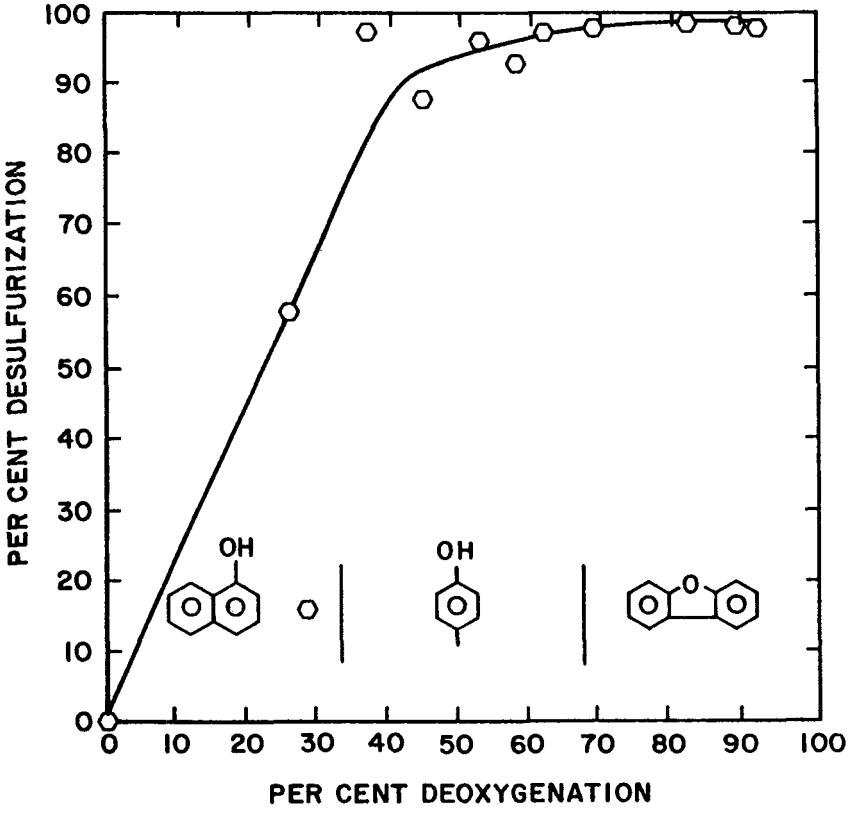


Figure 5-30. Mix 1 - Desulfurization vs. Deoxygenation

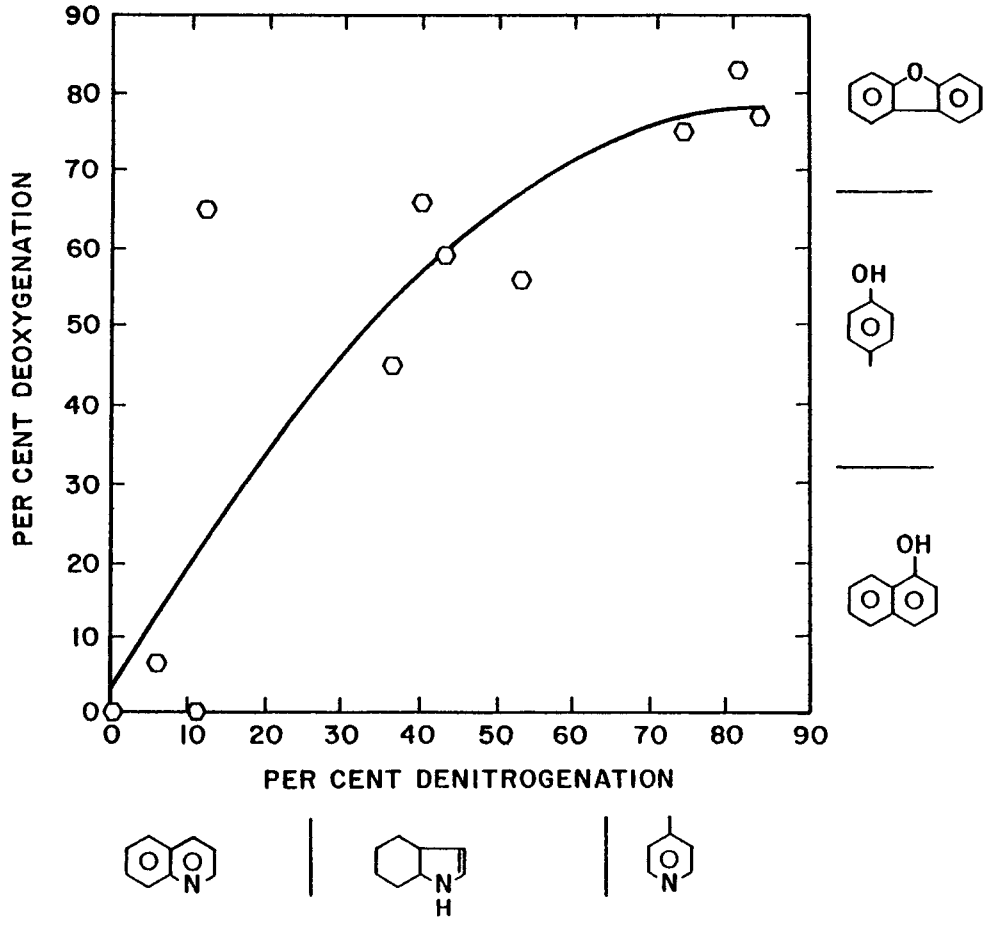


Figure 5-31. Deoxygenation vs. Denitrogen

1. HRI interpreted (5-2) analyses of the products in their catalyst aging studies. We will use their conclusions on the ~400-975°F distillates.

2. Mobil distilled samples of HRI flash separator bottoms to isolate 450-800°F solvent range cuts. Analyses are given in detail in Section 6 of this report; we will use the data from ~7-14 days on coal.

3. From the model compound studies just described we will take hydrocracking data from mix 3, data on desulfurization and deoxygenation from mix 2, and on denitrogenation and hydrogenation from mix 1. Only aged catalysts will be considered.

There are a number of problems associated with comparisons of these sets of data, as will be evident from the disagreements in the rankings. Although the first two sets come from the same runs, we are examining different products and different catalyst ages. For instance, we have only the sample from the fourteenth day of operation with the standard catalyst in the second set. The third set, of course, comes from runs in which the feeds and conditions, especially temperature, were also totally different.

As will be discussed in more detail in Section 6, there are factors other than catalyst activity that affect the compositions of the solvent-range materials, especially those in the narrower boiling range examined at Mobil. This range contains the hydrogenated anthracene oil used for start-up, which is low in heteroatom and hydrogen content. Its replacement rate was discussed in Section 4. Second, this boiling range is essentially an intermediate that is being formed from coal and residual oil and being further converted to produce lighter materials. The heavier precursors contain more heteroatoms and less hydrogen, while for the lighter products the reverse is true. Thus, changes in the relative rates of formation and destruction of this cut could result in changes in elemental analyses that do not truly reflect changes in catalyst hydrogenation or heteroatom removal activites.

In the following tables, catalysts are ordered with the most active at the top and least active at the bottom. In instances where differences were minor or inconsistent, the catalysts are enclosed in

brackets; ranking within brackets is tentative. The ranges of N,S, O, or H contents of the coal liquids are given to show the magnitudes and differences in the numbers being compared.

For more details on the relative rates of aging of these catalysts and on selectivities for specific reactions, see earlier discussions in this section. For more details on the properties of coal liquids produced over these catalysts see Section 6.

Table 5-11 gives comparisons of denitrogenation with the five catalysts in the three different cases. The NiMo catalysts are most active, the unpromoted Mo catalyst is least active, and the CoMo catalysts are intermediate. All three sets of data agree.

Table 5-11

DENITROGENATION COMPARISONS

Ranking by H-Coal Product Analyses (Mobil)	Ranking by H-Coal Product Analyses (HRI)	Ranking by Model Compound Study
Armak NiMo	[Armak NiMo	Cyanamid NiMo
Cyanamid NiMo	Cyanamid NiMo]	[Armak NiMo
[Amocat 1B Mo	Amocat 1A CoMo	Amocat 1A CoMo
Cyanamid 1442 CoMo	[Cyanamid 1442 CoMo	Cyanamid 1442 CoMo]
Amocat 1A CoMo]	Amocat 1B Mo]	Amocat 1B Mo
Range, %S 0.19-0.58	0.14-0.32	

(Note: Most active catalysts at top.)

Table 5-12 gives the deoxygenation comparisons; HRI did not report on deoxygenation. The Cyanamid 1442 CoMo appears to be good upon examination of the coal liquids. However, the oxygen contents of the solvent-range liquids decreased late in the HRI runs, probably because not as much fresh, high oxygen, solvent-range material was being produced; we have only a fourteen-day sample from the Cyanamid 1442 CoMo run. The low oxygen content is probably not a result of high deoxygenation activity. Disregarding that data point, the comparisons are about the same as for denitrogenation.

Table 5-12

DEOXYGENATION COMPARISONS

Ranking by H-Coal Product Analyses (Mobil)	Ranking by H-Coal Product Analyses (HRI)	Ranking by Model Compound Study
Cyanamid 1442 CoMo(?)	(no data available)	[Cyanamid NiMo
[Armak NiMo		Armak NiMo
Cyanamid NiMo		Cyanamid 1442 CoMo]
Amocat 1A CoMo]		[Amocat 1B Mo
Amocat 1B Mo		Amocat 1A CoMo]
Range, %O 0.72-1.48		

(Note: Most active catalysts at top.)

Table 5-13 shows the results for desulfurization. In this case, the HRI data are probably most meaningful. There was only one model compound used in our tests and all conversions were high, although agreement with the HRI data is quite good. The solvent range cuts isolated and analyzed by Mobil, in addition to the limitations already cited, had very low sulfur contents; analytical errors could be large relative to the values reported. The HRI data indicate that Amocat 1A was the most active and the Cyanamid 1442 was the least; the others were intermediate and about equal. All differences were small.

Table 5-13

DESULFURIZATION COMPARISONS

Ranking by H-Coal Product Analyses (Mobil)	Ranking by H-Coal Product Analyses (HRI)	Ranking by Model Compound Study
Armak NiMo	Amocat 1A CoMo	[Amocat 1A CoMo
Amocat 1B Mo	[Cyanamid NiMo	Cyanamid NiMo
[Cyanamid 1442 CoMo	Armak NiMo	Cyanamid 1442 CoMo]
Amocat 1A CoMo	Amocat 1B Mo]	Armak NiMo
Cyanamid NiMo]	Cyanamid 1442 CoMo	Amocat 1B Mo
Range, %S 0.05-0.16	0.34-0.46	

(Note: Most active catalysts at top.)

Table 5-14 shows hydrogenation comparisons. HRI (5-2) reported that the hydrogen contents of the liquid products made with the different catalysts in their program varied considerably, depending upon the boiling range examined. Catalysts would be ranked differently for each range except that Amocat 1B consistently gave products with the least hydrogen. There is no consistent pattern shown in the three sets of data in Table 5-14, except that Amocat 1B was also least active for phenanthrene hydrogenation in our test. Hydrogenation apparently is particularly sensitive to the exact nature of the feeds, conditions, and products examined.

Table 5-14

HYDROGENATION COMPARISONS

Ranking by H-Coal Product Analyses (Mobil)	Ranking by H-Coal Product Analyses (HRI)	Ranking by Model Compound Study
[Amocat 1A CoMo Armak NiMo Amocat 1B Mo]	[Varies with product boiling range]	[Armak NiMo Cyanamid 1442 CoMo]
Cyanamid NiMo	Amocat 1B Mo	[Amocat 1A CoMo Cyanamid NiMo Amocat 1B Mo]
Cyanamid 1442 CoMo		
Range, %H 8.3-9.05		

(Note: Most active catalysts at top.)

No information directly showing relative hydrocracking abilities is available from the coal processing studies except that the two NiMo catalysts gave a slightly lower boiling point distribution than the others, and the Cyanamid 1442 CoMo gave the highest. Table 5-15 shows that the NiMo catalysts were better for ethylnaphthalene dealkylation; no clear distinction could be made for the others. Recall that we did observe very high initial hydrocracking activity with the Cyanamid 1442 CoMo, but this activity was not sustained.

Table 5-15

HYDROCRACKING COMPARISON

Ranking by Model Compound Study
[Armak NiMo Cyanamid NiMo]
[Cyanamid 1442 CoMo Amocat 1B Mo Amocat 1A CoMo]

(Note: Most active catalysts at top.)

To summarize these comparisons, the two NiMo catalysts are more active than the others for denitrogenation, deoxygenation, and hydrocracking, and they are very active for desulfurization. The Cyanamid 1442 and Amocat 1A CoMo catalysts appear to be quite similar and generally about in the middle of the rankings. The Amocat 1A Appears to be slightly more active than Cyanamid 1442 for denitrogenation and hydrogenation, and slightly less active for deoxygenation and perhaps hydrocracking. Amocat 1A, however, appears to be the most active desulfurization catalyst. Amocat 1B appeared to have the lowest activity for all five reactions.

Of course which catalyst is "best" or "worst" depends upon many factors. A catalyst choice would depend upon the coal used, the reaction conditions, and the products desired. The work done to date is not sufficient for such choices to be made. The HRI runs considered here were done with a high sulfur coal, at high temperature, and at a coal feed rate intermediate between their syncrude and fuel oil modes. Under these conditions they concluded (5-2) that Amocat 1A and the Cyanamid NiMo catalysts gave the best overall performance; the principal criteria were minimization of residual oil yield and maximization of desulfurization. For a low sulfur coal and with low hydrogen consumption considered critical, Amocat 1B might be the catalyst of choice. If denitrogenation were the over-riding factor, the Armak NiMo catalyst might be chosen.

Future research should be concentrated in two areas. First, general studies like those reported here should be continued so that the strengths and weaknesses of catalyst candidates can be catalogued. This work should include studies of deoxygenation, desulfurization, denitrogenation, cracking, hydrogenation, hydrogen consumption, aging, distillate and boiler fuel yields, etc. The effects of temperature and pressure should also be assessed. Model compounds should be used to study inherent catalyst abilities, but coals must be used to reveal coking and poisoning effects, and the influence of catalyst support structure.

Second, decisions must be made on specific cases (for instance, the production of low-sulfur boiler fuel from one specified coal, the production of low-nitrogen high-hydrogen distillate from another specified coal, etc). Once such vital decisions are made, hopefully in light of such studies as were described above, then these specific cases must be studied in greater detail. Particular attention must be given at this point to optimizing the reaction conditions and catalyst properties simultaneously.

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Section 6

COMPOSITIONAL CHANGES WITH CATALYST AGING

INTRODUCTION

In the past three years we have developed a number of techniques for the chemical characterization of coal liquefaction products (6-1 through 6-3). The catalyst evaluation study at HRI (6-4) gave us a unique opportunity to compare the compositional information we had obtained for thermal coal liquefaction to that for catalytically-derived coal liquids. The effect of catalyst deactivation on coal liquefaction product compositions could also be assessed. In addition, we have attempted to determine the relevance of thermal reactions between solvent and coal during the catalytic process.

Our previous studies of thermal coal liquefaction showed that the initial transformations of coal were the result of thermal fragmentation of the coal to produce radicals which interacted with the solvent to produce soluble products. These initial products are highly reactive toward further chemical transformation and the selectivity for these transformations is controlled by the chemical nature of the solvent, and the temperature and time of reaction. In the absence of added catalysts, coal mineral matter plays an important role in catalyzing the reactions of hydrogen gas with coal products. In addition, certain defunctionalization reactions can be accentuated by coal mineral matter, for example, dehydroxylation of polyaromatic ring phenols. In thermal reactions, aromatic ring hydrogenation activity was very low and recycle-solvents always contained less than the thermodynamically allowed concentrations of hydrogen donors.

In the present study, two effects of the added catalyst in the H-Coal process were anticipated. First, the added catalyst should allow the formation of higher concentrations of hydrogen donors (hydroaromatics), although the high temperature of the H-Coal process would tend to limit their concentrations at equilibrium and hydrocracking should be accentuated. This higher concentration of hydrogen donors should promote more extensive conversion of the coal liquids (molecular weight reduction, desulfurization, and deoxygenation).

The second effect is that the catalyst could act directly on the initial products of coal and increase their rate of conversion.

The various catalysts could promote both of these effects differently and also age differently. The purpose of this study was to shed some light on these areas.

Because of time limitations in this brief study, detailed examination of product compositions were carried out only on a few selected samples. Gross product distributions and compositions were determined for all samples which were received. Before discussing the results of these studies it is appropriate to review how the samples were produced, as this is critical to the interpretations of changes in chemical composition.

As discussed in Section 4, all of the aging runs were started up with hydrogenated anthracene oil and with fresh catalysts; the flow rates were not held constant for the different catalysts and internal recycle streams varied greatly. Interpretations were also affected by our own limitations in product separations. For example, the distillations had to be limited to 800°F. Higher temperatures would have caused the distillation pot temperature to exceed 450°F. This could possibly cause thermal alteration of the products in the pot and thus confuse the results.

These experimental difficulties caused the following confusions in interpretation:

- Because the anthracene oil was hydrogenated at a lower severity than was employed in the H-coal simulation, the start-up solvent itself changed in composition due to further hydrocracking during the HRI study.

- The liquids produced from the feed coal replaced the start-up solvent slowly because of the large solvent inventory. This was discussed in detail in Section 4 of this report.

- As the catalysts aged, both hydrogenated anthracene oil hydrocracking and catalytic reactions of coal liquids caused changes in compositions.

- The hydrogenated anthracene oil, although considered to be the solvent, also contained ~10% 800^{+}°F materials. This affected the composition of the 800^{+}°F product at early times on stream.

- In the H- Coal aging runs, some recycle streams were obtained in batch operations rather than continuously. This caused significant fluctuations in the product compositions.

- Only one sample (14 days) was obtained for the base case (Cyanamid $CoMo/Al_2O_3$-1442A) and only two samples (7 and 10 days) were obtained for the Cyanamid $NiMo/Al_2O_3$ (4475); thus not many conclusions with regard to these catalysts are possible.

There is one potentially confusing factor that requires elaboration. The relatively narrow 450-800°F boiling cut range we examined is in some respects an intermediate in the overall reaction. Fresh material formed in this range from coal and heavier products is high in heteroatom content and low in hydrogen. Also, the 450-800°F material is destroyed in the formation of lighter materials. Therefore, changes in the actual or relative rates of formation and destruction of 450-800°F liquids could result in changes in the elemental analyses that do not truly reflect changes in catalyst activity for hydrogenation or heteroatom removal.

For instance, for Amocat 1B and Armak catalysts especially, we observed decreases in oxygen contents after about 7 days on coal. This is not likely to reflect an increase in deoxygenation activity. More likely it is caused by a decrease in the formation of fresh 450-800°F product (that has a high oxygen content). In the following discussion, relative catalyst activities are given at a time on stream before this occurred, and subsequent changes are noted.

Keeping these limitations in mind, we describe below our interpretations of the changes in composition of coal-derived liquids as the reactions progressed and catalysts aged in the H-Coal process.

Gross Product Distribution

The samples which were obtained from HRI for this study are listed below:

Sample Description				
Unit	Run #	Day on Stream	Catalyst	Metals
177-130-14A			Cyanamid 1442A	$CoMo/Al_2O_3$
177-131-7AB			Cyanamid 4475	$NiMo/Al_2O_3$
177-131-10A				
177-134-2A/B			Armak PA24268	$NiMo/Al_2O_3$
177-134-7A				
177-134-10A				
177-136-3A			Amocat 1B	Mo/Al_2O_3
177-136-7A				
177-136-10A				
177-137-4A			Amocat 1A	$CoMo/Al_2O_3$
177-137-7A				
177-137-10A				
L-467			Hydrogenated Anthracene Oil (start-up solvent)	

All samples consisted of the total product effluent after the hot separator (hot separator bottoms - see Figure 4-3 for exact details).

On receipt of the samples we sent them to Mobil's Paulsboro analytical laboratory for analytical distillation. They were distilled to obtain 450°-, 450-800°F, and 800°+F products. The vacuum residues were further separated at our laboratory into pyridine-soluble and pyridine-insoluble materials. A schematic diagram of these separation procedures and the corresponding analyses obtained for each

fraction are presented in Figure 6-1. Also noted in this figure is the way in which in one run, the fractions were recombined and reacted with coal (AC-525); this establishes the thermal background reactions which must occur between coal and solvent in the absence of catalysts.

The gross product distributions we obtained for the various samples are given in Table 6-1. These can be compared with HRI's reported gross product distributions which are shown in Figures 6-2a and 6-2b (Reference 6-4).

The data shown in Table 6-1 indicate that the hydrogenated anthracene oil start-up solvent contained 10.6% 800°$^+$F material. This material contaminated the coal-derived 800°$^+$F products at short times on stream.

In all cases the coal was converted >90% to pyridine-soluble form. The yield of 450-800°F distillate, however, varied significantly. The NiMo/Al_2O_3 catalysts appeared to have the lowest hydrocracking activities (as judged by 450-800°F yield) of all the catalysts. The Mo/Al_2O_3 catalyst showed the most change in hydrocracking activity during the tests. These two observations are in agreement with the results of our activity and selectivity tests which were described in Section 5.

ELEMENTAL ANALYSES OF FRACTIONATED PRODUCTS

Although direct comparisons between thermal processes, such as SRC, and the H-Coal process are difficult to obtain, we have attempted to give a general comparison in Table 6-2 for the various fractions. Products derived from different coals had to be used for this comparison due to lack of appropriate samples; however, all data are for bituminous coals from the Interior Province.

From Table 6-2 it can be seen that the heteroatom contents in all fractions are higher in the thermal processes. The H/C molar ratio of all fractions is higher in the case of the catalytic process. This indicates that the catalyst acts directly on high molecular

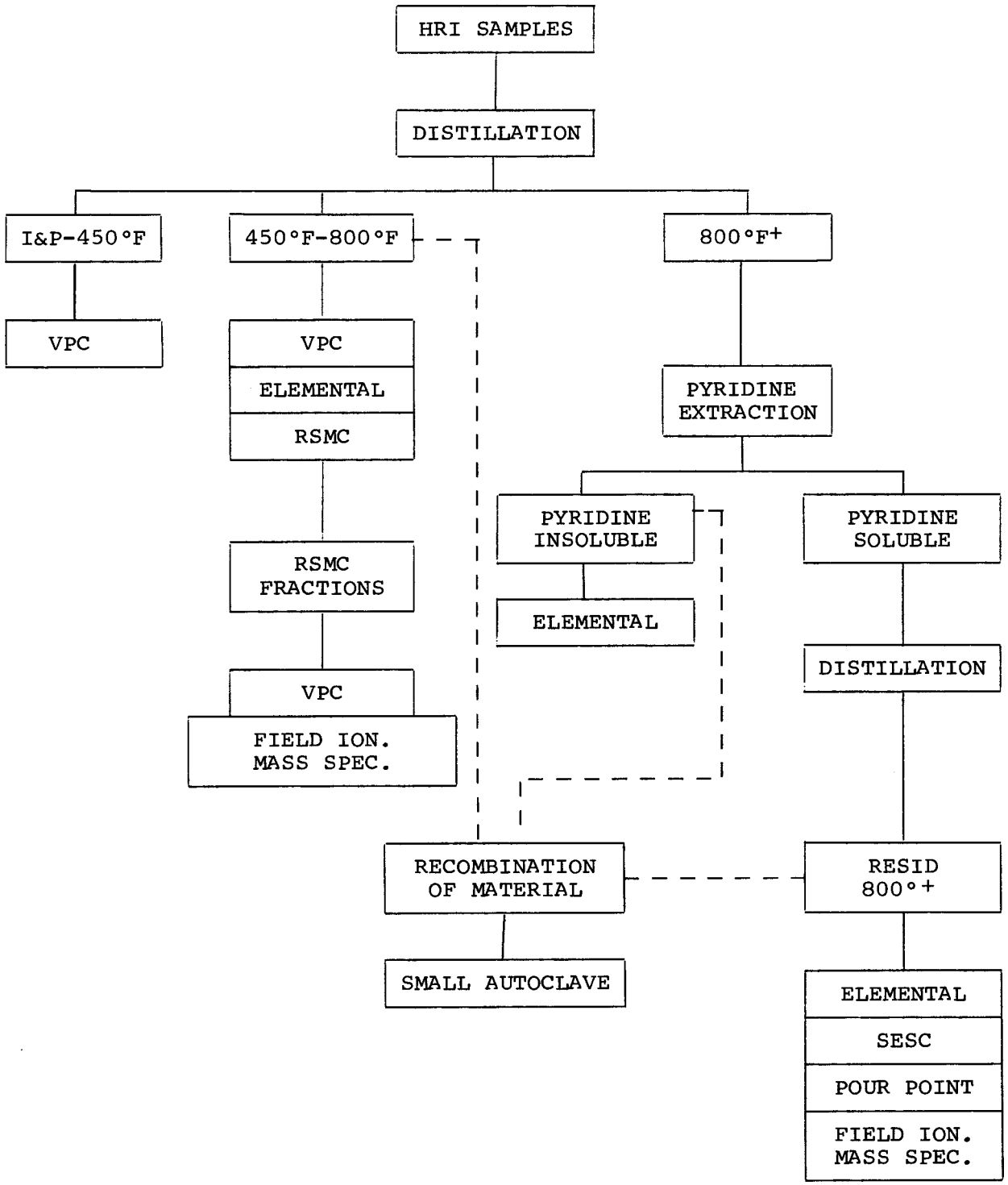


Figure 6-1. Mobil Work-Up of HRI Samples

Table 6-1

HRI DISTILLATION: MATERIAL BALANCE (WT%)

Hydrogenated Anthracene Oil

Sample Number	L-467
IBP-450°F	2.02
450-800°F	87.35
800°+ Py.Sol.	10.61
800°+ Py. Insol.	

Cyanamid 1442A ($CoMo/Al_3O_3$)

Sample Number	177-130-14A
IBP-450°F	3.39
450-800°F	37.77
800°+ Py Sol.	49.35
800°+ Py. Insol.	9.46

Cyanamid SN4475 ($NiMo/Al_2O_3$)

Sample Number	177-131-7AB	177-131-10A
IBP-450°F	7.49	8.51
450-800°F	39.11	33.35
800°+ Py. Sol.	43.67	47.42
800°+ Py. Insol.	9.70	10.70

Armak PA24268 ($NiMo/Al_2O_3$

Sample Number	177-134-2A/B	177-134-7A	177-134-10A
IBP-450°F	21.63	3.64	4.39
450-800°F	40.13	41.19	39.70
800°+ Py. Sol.	28.40	45.44	46.81
800°+ Py. Insol.	9.82	9.70	9.07

Amocat 1B (Mo/Al_2O_3)

Sample Number	177-136-3A	177-136-7A	177-136-10A
IBP-450°F	3.33	8.02	4.57
450-800°F	52.30	40.31	42.23
800°+ Py. Sol.	37.62	44.25	45.27
800°+ Py. Insol.	7.98	7.42	7.90

Amocat 1A ($CoMo/Al_2O_3$)

Sample Number	177-137-4A	177-137-7A	177-137-11A
IBP-450°F	5.03	4.09	3.16
450-800°F	46.03	43.75	44.10
800°+ Py. Sol.	39.56	43.00	43.73
800°+ Py. Insol.	9.38	9.15	9.00

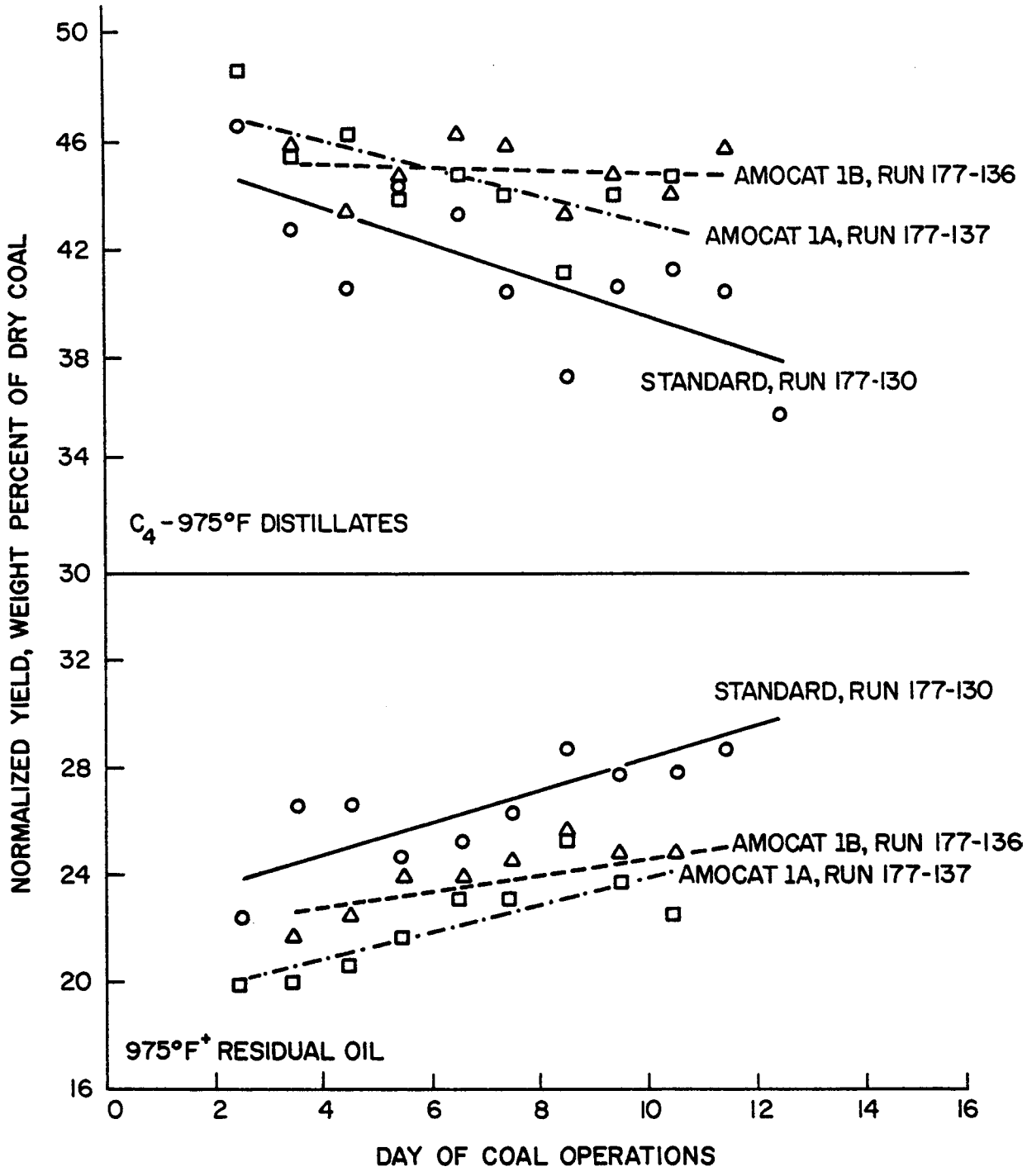


Figure 6-2a. Distillates and Residual Oil Yields
(From Reference 6-4)

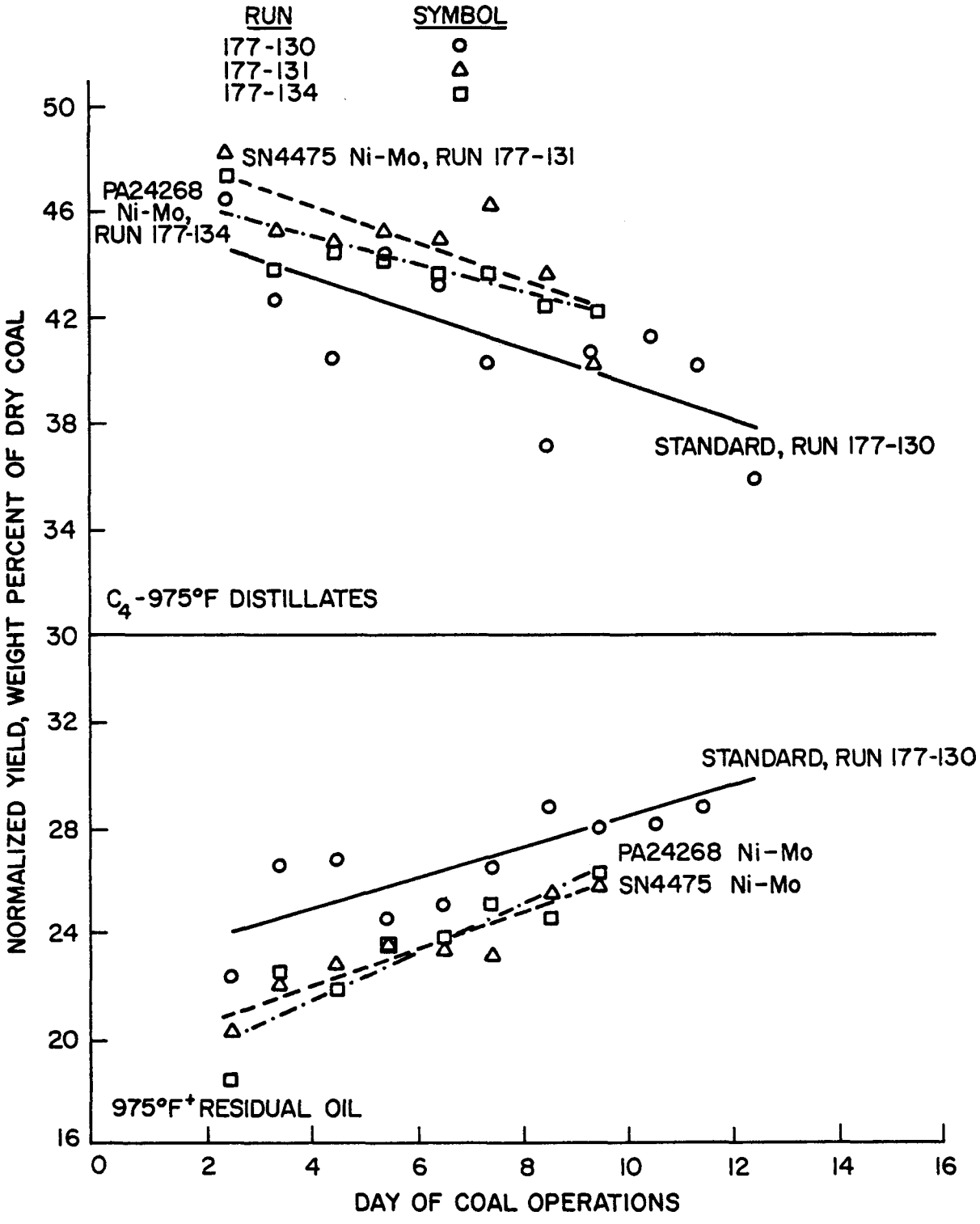


Figure 6-2b. Distillates and Residual Oil Yields
(From Reference 6-4)

Table 6-2

ELEMENTAL ANALYSES OF THERMAL AND CATALYTIC COAL LIQUEFACTION PRODUCTS

	Solvent		Pyridine-Sol. Residue		Pyridine-Insoluble Residue	
	SRC	H-COAL	SRC	H-COAL	SRC	H-COAL
Boiling Range Compared	IBP-850°F	450-800°F	850+°F	800+°F		
Coal	W.Kentucky 9-14	Ill. No.6 Burning Star	Ill. No.6 Monterey	Ill. No.6 Burning Star	Ill. No.6 Burning Star	Ill. No.6 Burning Star
Carbon	87.37	89.31	87.4	88.2	33.32	25.20
Hydrogen	7.74	8.65	5.8	6.8	1.69	1.38
Oxygen	3.60	1.05	3.5	2.8	-	(.28)*
Nitrogen	0.82	0.65	1.7	1.6	.66	.45
Sulfur	0.24	0.14	1.0	0.4	6.14	5.50
Ash					58.35	67.19
C/H	1.06	1.16	.80	.93	.61	.66

*Oxygen by difference.

weight coal products as well as on the lower (solvent range) products. We will provide further data to support this conclusion later.

The elemental analyses of the starting anthracene oil and the various fractions of products obtained from HRI are given in Tables 6-3 through 6-8.

Catalyst Aging Effects on 450-800°F Elemental Analyses

Inspection of these data provides some information on the relative activities of the various catalysts and how these change with time on stream. If we take, for example, the elemental composition of the 450-800°F boiling cut, the following conclusions can be drawn about the different catalysts:

Desulfurization of 450-800°F Liquid Products

- All catalysts were very effective for the removal of sulfur even after 10-14 days on stream without regeneration.
- The relative activities after 10 days were Armak >> Amocat 1B ~ Amocat 1A ~ 1442A > 4475 (although the range of results was small -- .08-.16 % S in products).
- All catalysts aged at about the same rate.

Denitrogenation of 450-800°F Liquid Products

- Aging rates for all catalysts were higher than for desulfurization and all catalysts aged at about the same rate.
- After 10 days on stream the relative activities for the various catalysts were: Armak > 4475 ~ Amocat 1B > 1442 ~ Amocat 1A. (The range of results was again very small -- .4-.55% N in the products.)

Deoxygenation of 450-800°F Liquid Products

- The oxygen contents of the solvent-range products were higher than the N or S contents, reflecting the higher oxygen contents of the coal.

Table 6-3

ELEMENTAL ANALYSES OF HYDROGENATED ANTHRACENE OIL START-UP SOLVENT

	450-800°F	800+°F Pyridine Soluble
C	89.16	87.92
H	8.29	7.76
O	0.87	3.07
N	0.31	1.08
S	0.09	0.20
Ash		
C/H	1.12	1.06

Table 6-4

ELEMENTAL ANALYSES OF 177-130 PRODUCTS (Cyanamid 1442A)
(14 days on stream)

	450-800°F	800+°F Pyridine Soluble	800+°F Pyridine Insoluble
Sample	14A	14A	14A
C	89.31	88.12	25.20
H	8.65	6.08	1.38
O	1.05	3.28	(.28)*
N	0.65	2.02	.45
S	0.14	0.50	5.50
Ash		0.13	67.19
C/H	1.16	0.83	.66

*Oxygen by difference.

Table 6-5

ELEMENTAL ANALYSES OF 177-131 PRODUCTS (Cyanamid 4475)

	450-800°F		800+°F Pyridine Soluble		800+°F Pyridine Insoluble	
Sample	7AB	10A	7AB	10A	7AB	10A
C	89.89	88.95	88.92	88.97	25.04	28.62
H	8.51	8.84	6.39	6.41	1.25	1.53
O	.92	1.20	2.91	2.74	(1.27)	(.24)*
N	0.44	0.45	1.51	1.55	0.42	.48
S	0.16	0.16	0.26	0.36	5.33	4.93
Ash			0.19	0.14	66.69	64.20
C/H	1.14	1.19	0.86	0.865	0.60	0.64

*Oxygen by difference.

Table 6-6

ELEMENTAL ANALYSES OF 177-134 PRODUCTS (Armak PA24268)

	450-800°F			800+°F Pyridine Soluble			800+°F Pyridine Insoluble		
Sample	2A/B	7A	10A	2A/B	7A	10A	2A/B	7A	10A
C	89.12	88.60	88.58	88.57	88.79	88.75	28.25	27.30	25.00
H	8.60	9.02	8.88	6.56	6.60	6.39	1.87	1.48	1.39
O	0.72	1.13	1.08	3.01	2.69	2.02	(-)	(2.37)	(1.15)*
N	0.19	0.38	0.41	1.23	1.43	1.58	0.48	0.35	0.46
S	0.05	0.08	0.09	0.41	0.48	0.56	5.15	5.33	5.28
Ash	-	-	-	.05	0.13	0.50	67.72	63.17	66.72
C/H	1.16	1.22	1.20	0.89	0.89	0.86	0.79	0.65	0.67

*Oxygen by difference.

Table 6-7

ELEMENTAL ANALYSES OF 177-136 PRODUCTS (Amocat-1B)

	450-800°F			800+°F Pyridine Soluble			800+°F Pyridine Insoluble		
Sample	3A	7A	10A	3A	7A	10A	3A	7A	10A
C	89.40	89.28	89.30	88.35	88.55	88.23	24.32	25.44	27
H	8.44	8.78	8.98	6.89	6.62	6.75	1.46	1.36	1.4
O	1.08	1.48	1.31	2.58	2.70	2.82	(1.52)	(1.32)	(.5)*
N	0.39	0.51	0.45	1.69	1.51	1.64	.48	.45	0.5
S	0.11	0.12	0.11	0.30	.35	0.38	5.26	5.69	6.11
Ash	-	-	-	0.11	0.13	0.12	66.96	65.74	64.5
C/H	1.12	1.18	1.21	.94	.90	.92	.72	.64	.62

*Oxygen by difference.

Table 6-8

ELEMENTAL ANALYSES OF 177-137 PRODUCTS (Amocat-1A)

	450-800°F			800+°F Pyridine Solube			800+°F Pyridine Insoluble		
Sample	4A	7A	10A	4A	7A	10A	4A	7A	10A
C	89.74	89.53	89.52	88.59	88.64	88.63	25.70	24.53	24.08
H	8.26	9.05	8.24	6.84	6.71	6.74	1.44	1.40	1.39
O	.90	1.11	1.06	3.04	3.18	3.12	(1.11)	(1.05)	(.83)*
N	0.36	0.51	0.58	1.32	1.26	1.46	0.38	0.39	0.37
S	0.14	0.13	-	.20	.24	.20	4.89	6.09	5.85
Ash				<.05	<.05	<.05	66.48	66.54	67.48
C/H	1.10	1.21	1.10	.93	.91	.91	.67	.68	.69

*Oxygen by difference.

- Product oxygen contents rapidly increased for about seven days then tended to decrease.
- Amocat 1B was the least effective and the others were about equal to one another.

Hydrogen Content of 450-800°F

- With all catalysts the hydrogen content of the liquids increased up to seven days; with Armak and Amocat 1A the hydrogen content then decreased.
- Up to seven days the relative activity for hydrogenation was Amocat 1A ~ Armak > Amocat 1B > 4475 ~ 1442A. (Hydrogen contents ranged from 8.5 to 9%.)

Catalyst Aging Effects on 800°+F Pyridine-Soluble Products

Catalyst aging also had an effect on the composition of the 800°+F pyridine-soluble products. This is illustrated in Figure 6-3 for Amocat 1B (Run 177-136).

The observed changes are, of course, complicated by the replacement of the start-up solvent by coal products but this replacement was much more rapid in the case of 800°+F products than for the 450-800°F products. After three days the changes were rather modest which indicates that up to that time replacement of anthracene oil by coal products was the major reason for compositional changes. Also, as mentioned earlier, changes in the rates of formation or destruction of a given product range may cause changes in the observed elemental composition. The effect is probably largest in the solvent range, however.

The most noticeable changes occurred in the hydrogen content of the products, which decreased in the case of the 800°+F products and increased for 450-800°F products. This may indicate that a selective loss of the ability to hydrogenate large molecules had occurred. Desulfurization and denitrogenation showed similar trends. Deoxygenation was not affected as much for either product after ~ three days. The relative catalytic activities of the various catalysts for alteration of the 800°+F pyridine-soluble products (see Tables 6-3 through 6-8) are given below:

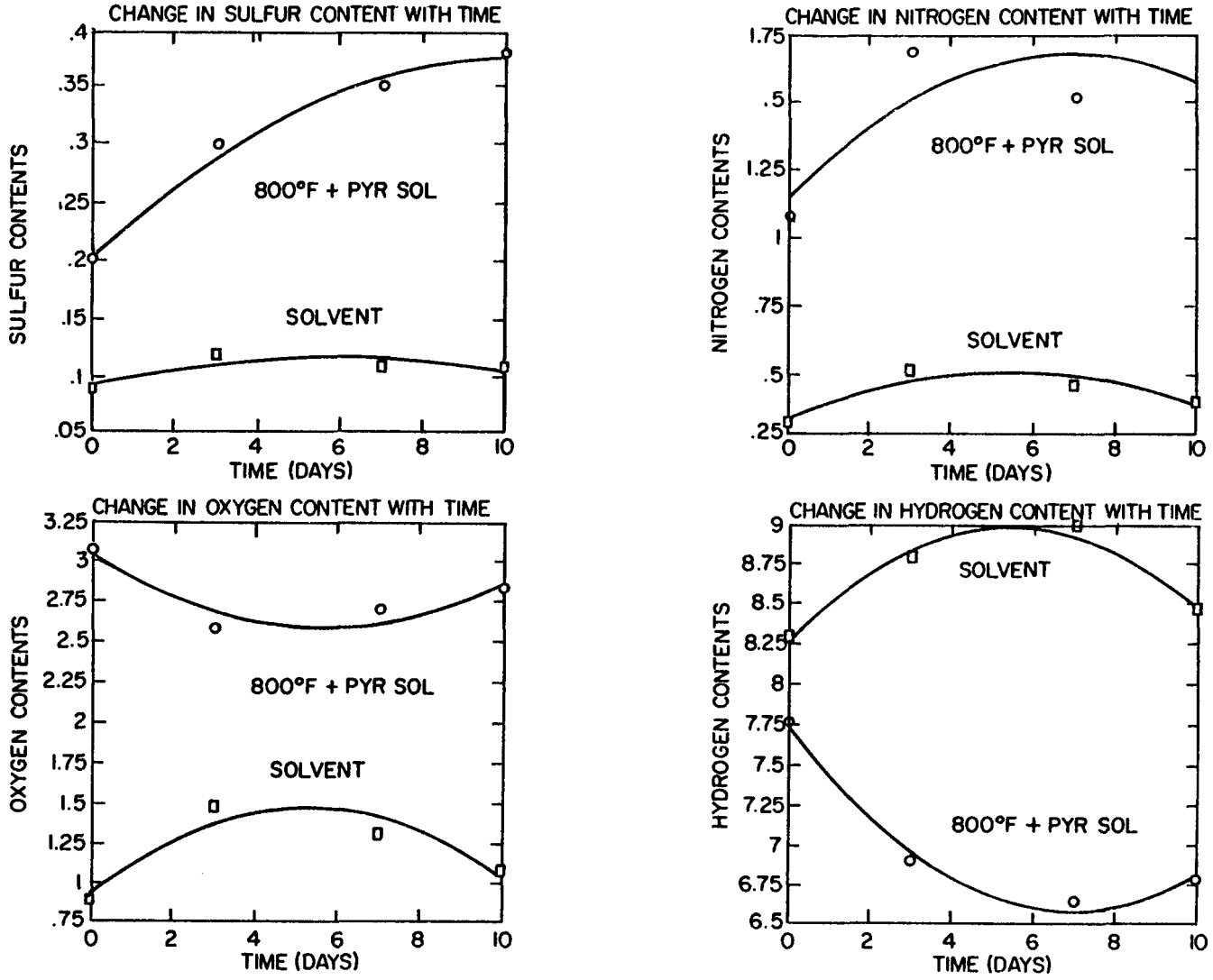


Figure 6-3. Changes in Elemental Composition of Run 177-136 Products With Time on Stream

Desulfurization

All catalysts were similar, Amocat 1A was the best; Armak was the worst. Aging was minor.

Denitrogenation

Armak ~ Amocat 1A > 4475 ~ Amocat 1B > 1442A.
Aging was minor.

Deoxygenation

4475 ~ Amocat 1B > Armak ~ Amocat 1A ~ 1442A.
Armak oxygen contents decreased steadily.

Hydrogenation

Amocat 1A ~ Armak ~ Amocat 1B > 4475 > 1442.
Aging was minor.

These data are in general agreement with those of HRI as shown in Figure 6-4 for the residual oil (6-4). Note the range of scatter in the HRI data; conclusions are difficult to draw.

DETAILED COMPOSITIONAL VARIATION

General Comments

In order to obtain a more thorough understanding of the compositional changes which occurred on aging of the catalysts, we concentrated our efforts primarily on Amocat 1B, as this catalyst was shown by our catalyst activity tests (see Section 5) to undergo the most change with time on stream.

Unfortunately most of our work concentrated on the differences in composition between the 3-day and 10-day samples. After the work had been carried out we concluded that the solvent-range products (450-800°F) were still heavily contaminated with the starting hydrogenated anthracene oil at three days. The 800°+F products were affected less in this regard.

The method of study involved liquid chromatographic separation of both the 450-800°F and 800°+F pyridine-soluble products. The procedures used have been previously described (6-1,6-3) but for ease of discussion a description of the various fractions is

Figure 6-4a

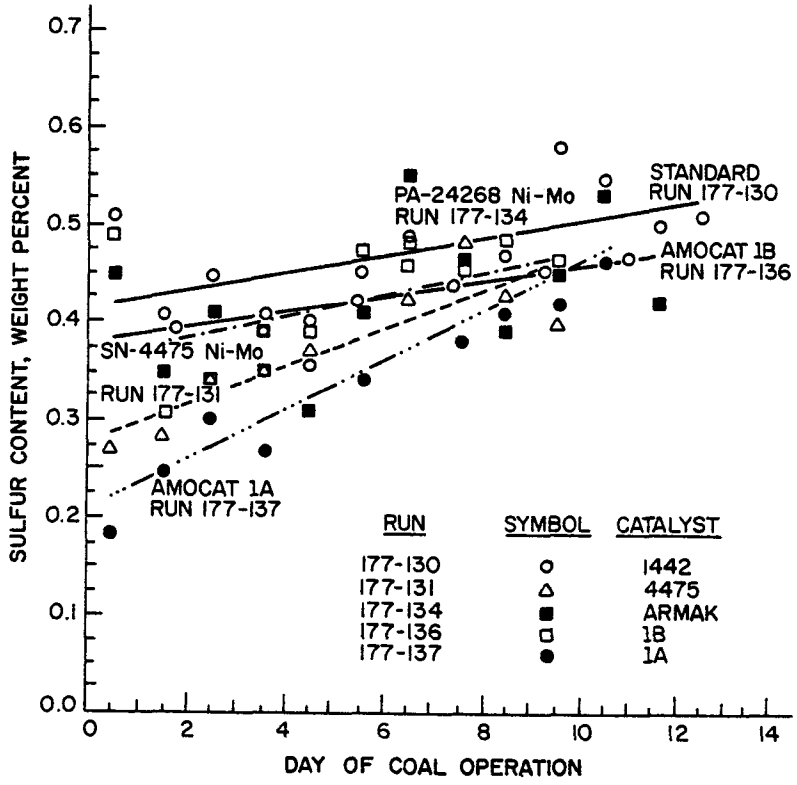


Figure 6-4b

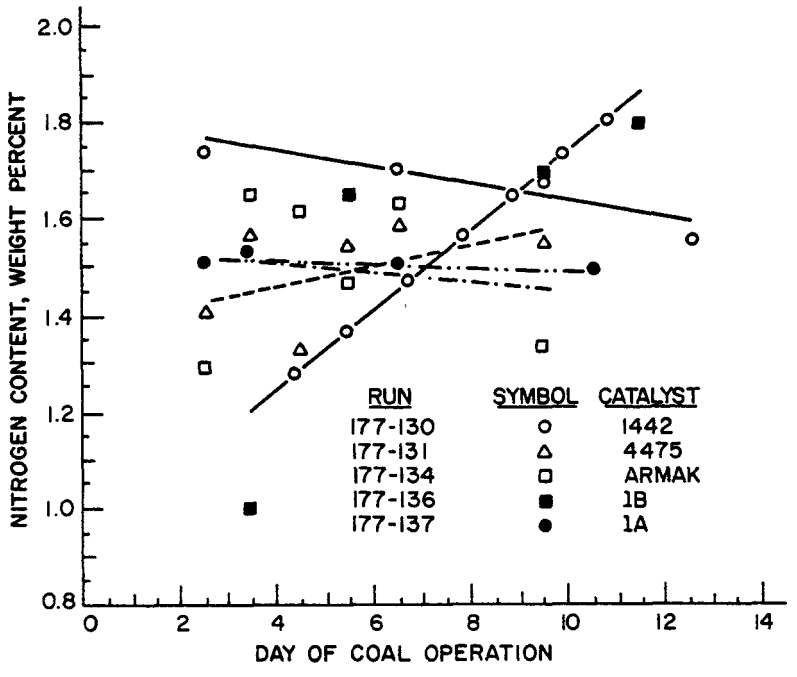


Figure 6-4. Sulfur and Nitrogen Contents of Residual Oil (975°F$^+$) (Reference 6-4)

provided in Figure 6-5. Each chromatographic fraction was further characterized by a variety of techniques. In the case of the 450-800°F products, gas chromatography of the whole product was also used. The distribution of these products at various times in HRI's run 177-136 is presented below.

	Weight Percent of the Products			
			800°F+	
Time on Stream	IBP-450°F	450-800°F	Pyridine Soluble	Pyridine Insoluble
Start-up	1.3	87.9	10.8	-
3 Days	3.3	51.8	37.5	7.9
10 Days	4.6	41.5	45.3	7.9

Composition of the 450-800°F Products of Run 177-136

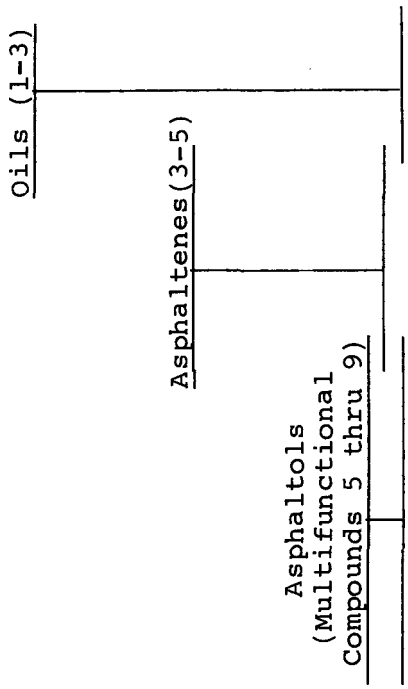
Gas chromatographic analysis of the whole solvent-range product provided a great deal of information about the general course of the reaction. One can immediately see how the presence of a catalyst causes the formation of a much more complex solvent than is produced in thermal reactions. Figures 6-6 and 6-7 show, respectively, the gas chromatograms of thermally-derived and catalytically-derived whole solvents and fractions thereof.

The elemental analyses of solvent-range products also show catalytic alteration of the composition (see below):

	Weight Percent of Solvent				
Thermally Generated Recycle Solvent	C	H	O	N	S
(SN6663, Wilsonville, Alabama)	87.4	7.7	3.6	0.8	0.3
Hydrogenated Anthracene Oil	89.2	8.3	0.9	0.3	0.1
177-136-3A	89.4	8.4	1.1	0.4	0.1
177-136-10A	89.3	9.0	1.3	0.5	0.1

The data in Section 5 show that Wilsonville solids and pyrite have low but appreciable activities for hydrogenation, desulfurization, and phenol dehydrogenation. Assuming comparable activity for coal mineral matter, the solvent from thermal conversion of a fully demineralized coal would be expected to be a little less hydrogenated and to contain a little more sulfur and phenols.

SRC FRACTIONATION (SESC)



Classical Description	Fraction	Elution Solvent	Major Compounds
Oils (1-3)	1	Hexane	Saturates
	2	Hexane/15% Benzene	Aromatics
Asphaltenes (3-5)	3	Chloroform	Polar aromatics; nonbasic N, O, S-heterocyclics
	4	Chloroform/10% Et_2O	Simple phenols
Asphaltols (Multifunctional Compounds 5 thru 9)	5	Et_2O/3% EtOH	Basic nitrogen heterocyclics
	6	MeOH	Highly-functional molecules (>10 wt % heteroatoms)
	7	$CHCl_3$/3% EtOH	Polyphenols
	8	THF	Increasing O content and increasing basicity of nitrogen
	9	Pyridine	
	10		Non-eluted, unknown materials

RECYCLE SOLVENT FRACTIONATION (RSMC)

RSMC Fraction	Solvent	Chemical Species
1	Petroleum ether	Saturated hydrocarbons
2	95% Petroleum ether 5% Benzene	Monoaromatic hydrocarbons with aliphatic substituents. (Includes tetralin and possibly ethers of the diphenyl ether type.)
3	85% Petroleum ether 15% Benzene	Diaromatic hydrocarbons. (Includes naphthalene and substituted naphthalenes.)
4	Tetrahydrofuran; 1% Ethanol	Polyaromatic hydrocarbons. (Mainly anthracene and phenanthrene and dibenzofuran type ethers.)
5	Tetrahydrofuran; 10% Water	Phenols and basic nitrogen compounds
6	(Non-eluted)	Polyfunctional Compounds

Figure 6-5. Fractions obtained by liquid chromatographic analysis

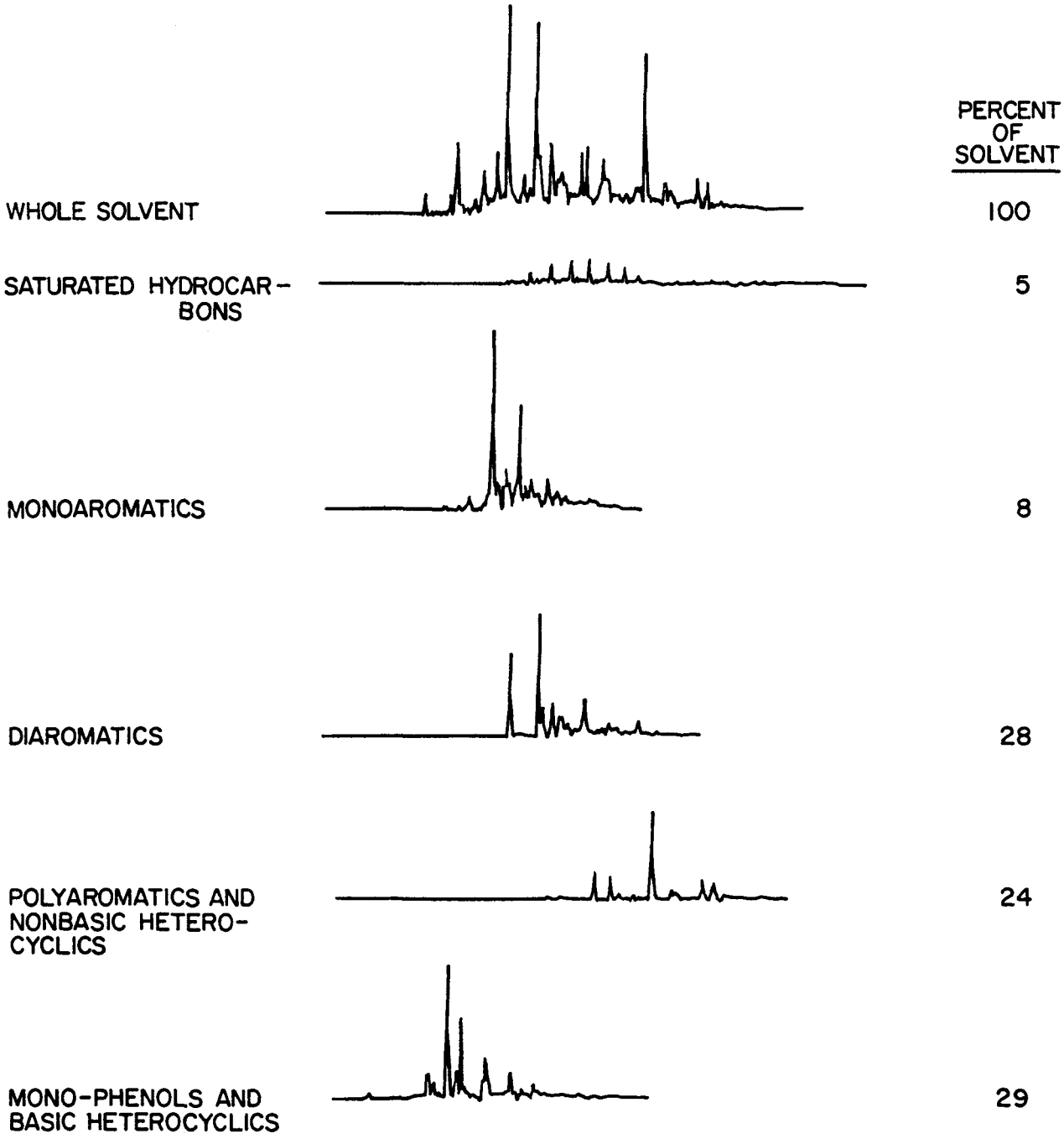


Figure 6-6. Gas Chromatograms of Thermal Coal Liquefaction Solvent and Fractions Thereof (Kentucky 9,14 SN6663)

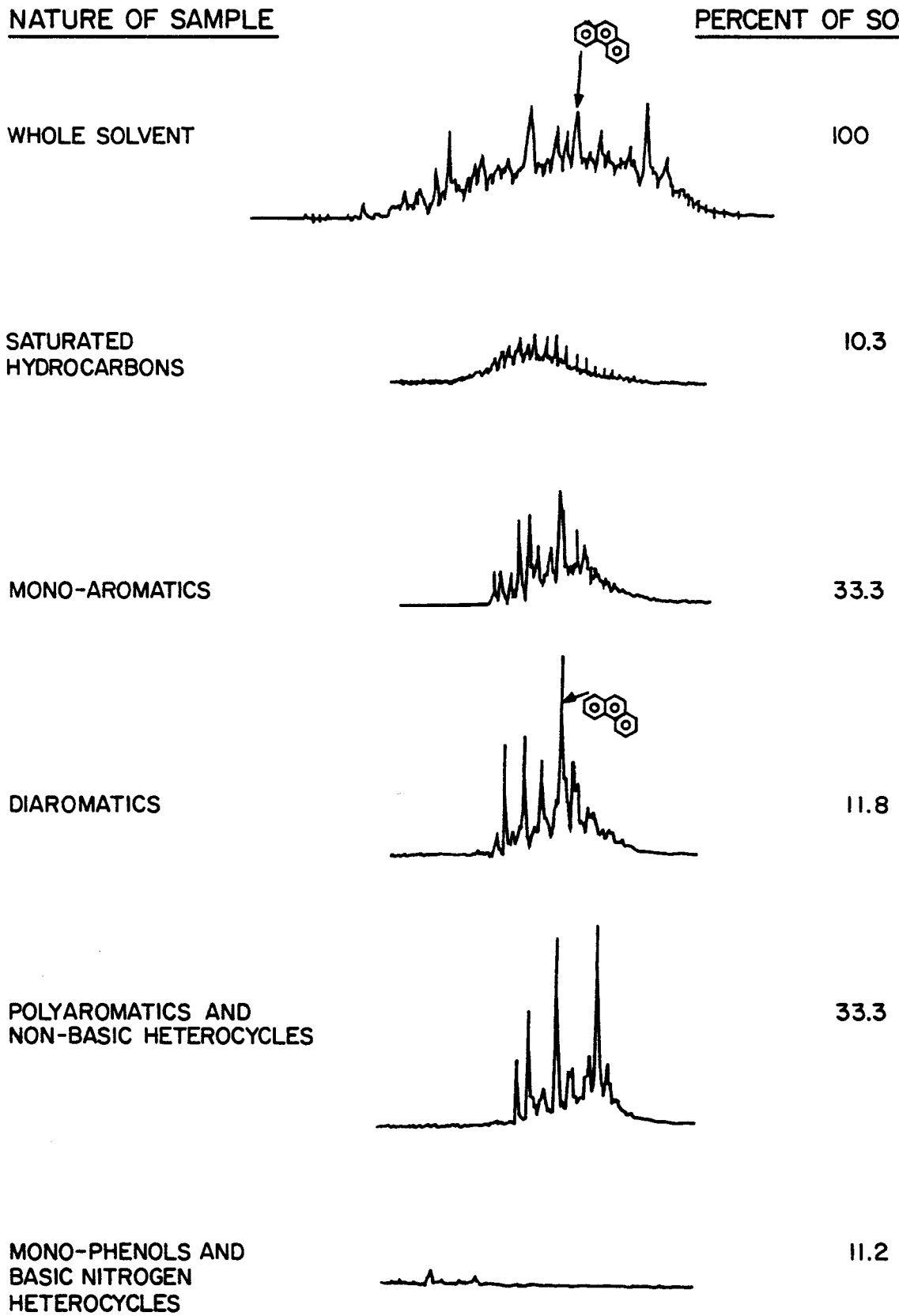
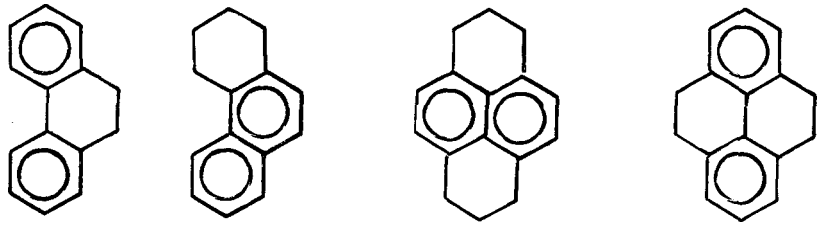


Figure 6-7. Gas Chromatograms of Catalytic Coal Liquefaction Solvent and Fractions Thereof (HRI 177-136-10A)

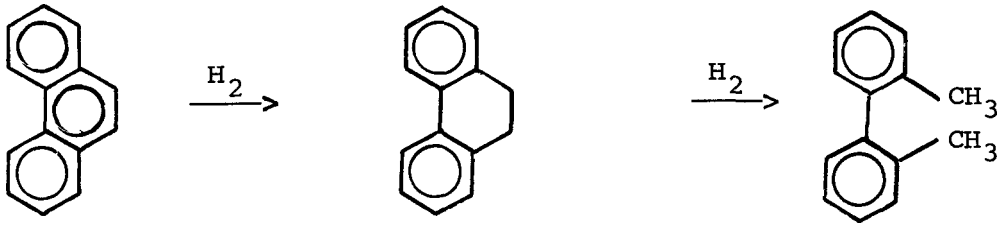
Gas chromatographic analyses of the solvent at various times on stream during run 177-136 (see Figure 6-8) show the smooth replacement of the hydrogenated anthracene oil during the course of the first seven days after which time the composition remains fairly constant and is similar to the steady-state solvent produced in HRI's PDU-5 at equilibrium conditions.

Liquid chromatographic fractionation (RSMC) of the solvent at various times on stream provided additional information on the compositions. The results shown in Table 6-9 indicate that the catalytically-derived solvents are lower in phenol content and have higher contents of the fractions that could contain hydroaromatics (RSMC-2 and 3). Hydroaromatics which are expected to be found in these fractions have ring structures such as the following:



etc.

The complexity of the fractions shown in Figure 6-7 indicates that these structures must be heavily substituted with alkyl (mostly methyl) groups. Such substitution can only result from ring-opening reactions of larger ring structures via hydrocracking. GC mass spectroscopic analysis of 177-137-10A RSMC-3 showed it to contain alkyl naphthalenes and dimethylbiphenyls as the major constituents. Our catalytic studies with model compounds showed that a significant reaction path for hydrogenation and hydrocracking is as follows for phenanthrene.



The pyrene ring system undergoes similar transformations.

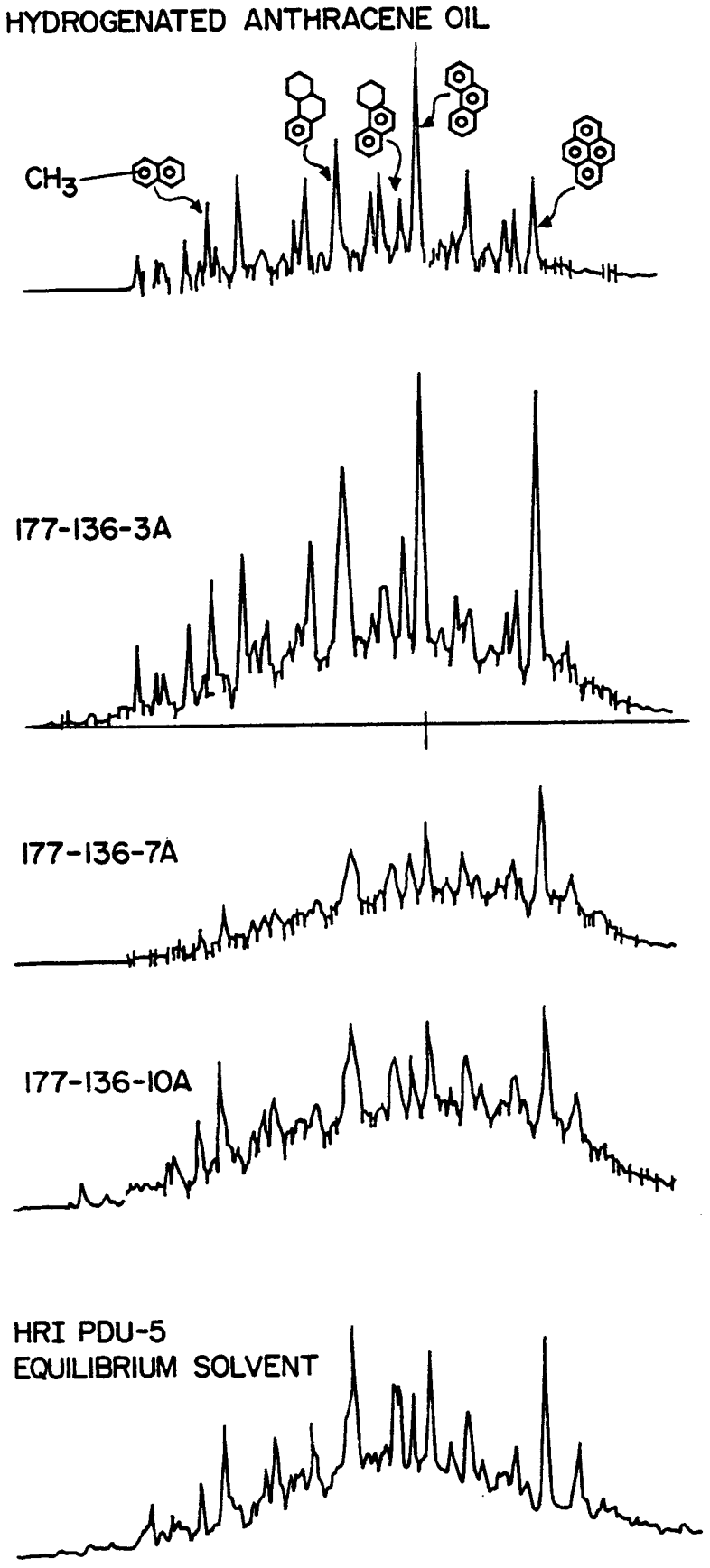


Figure 6-8. Gas Chromatographs of Solvents

Table 6-9

H-COAL PRODUCTS

(Solvent Range -- 450-800°F bp)

Classes of Substances	Weight Percent In Initial Solvent (Hydrogenated Anthracene Oil)	177-136-3A (3 days)	177-136-10A (10 days)	Composition of an SRC Solvent of Similar Volatility (SN6663)
Saturated hydrocarbons	9.4	10.3	11.0	5.0
Monoaromatic hydrocarbons (hydroaromatic)	32.5	33.3	26.7	7.6
Diaromatic hydrocarbons (including some hydroaromatic)	24.6	11.8	23.0	27.6
Trianol poly-aromatic hydro-carbons	29.6	33.3	30.0	24.2
Phenols and basic H compounds	3.8	11.2	9.3	28.8
H/C ratio all solvents	1.11	1.13	1.2	1.0
% O in all solvents	0.87	1.08	1.3	3.6

Field Ionization Mass Spectrometry (at SRI) of RSMC fractions gave some additional composition information.

RSMC fraction 2, from a number of solvents from the HRI runs, consists chiefly of the following four homologous series:

Tetralins and cyclohexylbenzenes	15-45%
Benzenes	0-12%
Decahydropyrenes and hexahydrophenanthrenes	5-15%
Octahydrophenanthrenes and cyclohexylcyclohexenes	25-55%

Typically 85-90% of the entire fraction can be accounted for by parents and alkyl homologs of these series.

RSMC fraction 3 is chiefly the following:

Phenylbenzofurans, 9,10-dihydrophenanthrenes, and octahydrobenzphenanthrenes	0-30%
Naphthofurans, tetrahydrophenanthrenes, and biphenyls	30-60%
Naphthalenes, tetrahydronaphthofurans, and naphthothiophenes	10-15%

Typically 85-95% of the fraction can be accounted for by parents and alkyl homologs of these series.

RSMC fraction 4 is chiefly the following:

Pyrenes and fluoranthenes	20-30%
Dihydropyrenes, phenylnaphthalenes, and tetrahydrobenzphenanthrenes	10-20%
Phenanthrenes and tetrahydropyrenes	20-30%
Dihydrophenanthrenes* and phenylbenzofurans	10-20%
Naphthofurans and benzophenanthrenes	0-15%

*Other than 9,10-dihydrophenanthrenes.

Typically 70-85% of the fraction can be accounted for by parents and alkyl homologs of these series.

It is clear that FIMS confirms that fraction RSMC-2 is substantially monoaromatic hydrocarbons, RSMC-3 is substantially diaromatic hydrocarbons, and RSMC-4 is substantially hydrocarbons and furans containing three or more conjugated or fused aromatic rings. There may be some furans and thiophenes in RSMC-3.

Composition of 800°+F Pyridine-Soluble Products from Run 177-136

As noted above, the most marked changes which occurred in the elemental composition of the 800°+F pyridine-soluble products were noted during the first three days of the tests when anthracene oil replacement was a major contributor to compositional change. Between three and ten days the changes in elemental composition of the 800+°F products were minimal.

The elemental analyses of 177-136 products and several thermally-derived vacuum residues (6-3) are compared in Table 6-10. AC-70 was a run with Monterey coal using our 40% tetralin synthetic recycle solvent (6-1,6-2,6-3) at 800°F, ~1000 psi H_2, for one hour. AC-172 was a similar run conducted at 858°F. AC-525 will be discussed later.

The two thermal SRCs (AC-70 and 172) both have higher concentrations of heteroatoms even though the solvent had high concentrations of hydroaromatics (40% tetralin). It thus appears that the catalyst in the HRI runs was acting directly on these heavy fractions.

Table 6-10

ELEMENTAL ANALYSES OF THE PYRIDINE-SOLUBLE
VACUUM RESIDUES FROM H-COAL AND THERMAL REACTIONS

		C	H	O	N	S
Catalytic Products	Hydrogenated Anthracene Oil Residue	87.9	7.8	3.1	1.1	0.2
	177-136-3A	88.3	6.9	2.6	1.7	0.3
	177-136-10A	88.2	6.8	1.6	2.8	0.4
Thermal Products	AC-70 (800°F)	85.0	5.9	5.8	1.7	1.51
	AC-172 (858°F)	86.6	5.7	4.7	1.9	1.0
	AC-525 (850°F)	91.1	5.2	1.0	1.5	0.5

Liquid chromatographic fractionation (SESC) of the 800+°F pyridine-soluble products provided additional compositional detail. The results shown in Table 6-11 again point to little change in the composition of the 800+°F products between three and ten days on stream. The only difference between products of a high temperature thermal conversion (AC-172) and the catalytic conversion was slightly higher concentrations of saturated hydrocarbons and polyfunctional compounds in the catalytic products. These latter compounds may have been lost due to charring in the thermal reaction.

The elemental analyses of individual SESC fractions also give indication of little change in the product composition between three and ten days on stream. Table 6-12 shows that corresponding chemical class fractions had almost identical elemental analyses at the two times.

Again comparing a typical thermally-derived product (AC-58, same chemical class) the heteroatom content is higher and the hydrogen content is lower.

Some rather interesting compositional changes were noted, however, by Field Ionization Mass Spectrometry (FIMS). Figure 6-9 shows the molecular profile analysis of the SESC-3 fraction of the 800+°F products obtained at three and ten days and compares these profiles to one of a corresponding thermally-derived product. These profiles are clearly different. The product obtained at three days has a lower molecular weight distribution and the thermal product has a higher molecular weight distribution. The ten-day sample has a distribution which has features of both of the above profiles. This indicates that after ten days on stream the catalyst may have lost some of its ability to lower the molecular weight of soluble products (hydrocracking activity). Our catalyst activity tests described in Section 5 did indicate that the catalyst used in these conversions (Amocat 1B) did lose a substantial portion of its hydrocracking activity.

Table 6-11

SESC FRACTIONATION OF H-COAL AND SRC PRODUCTS

(800°F Range Material)

SESC Fractions	Classes of Substances	H-Coal Vacuum Residues 177-136-3A Product* After 3 Days	(Mw)	H-Coal Vacuum Residues 177-36-10A Product* After 10 Days	(Mw)	Typical Composition of an SRC AC-170 (800°F)	(Mw)	Typical Composition of an SRC AC-172 (858°F)	Thermal Reaction Under H-Coal Conditions AC-525 SRC
1	Saturated hydrocarbons	3.0		3.4		0.6		0.7	5
2	Aromatic hydrocarbons	34.8		32.0		9.7		34.4	37
3	Heterocyclic compounds	28.2	(370)	26.8	(422)	29.8	(430)	44.2	39
4	Monophenols	19.6	(514)	20.2	(465)	24.5	(490)	6.5	[
5	Basic N Compounds	1.8		2.0		7.3		2.5	19
6	Very polar compounds	1.5		1.9		4.5		2.3	]
7-9	Polyphenols	11.5		15.3		23.6		9.3	
	H/C Ratio Total Product	0.93		0.92		0.8		0.8	

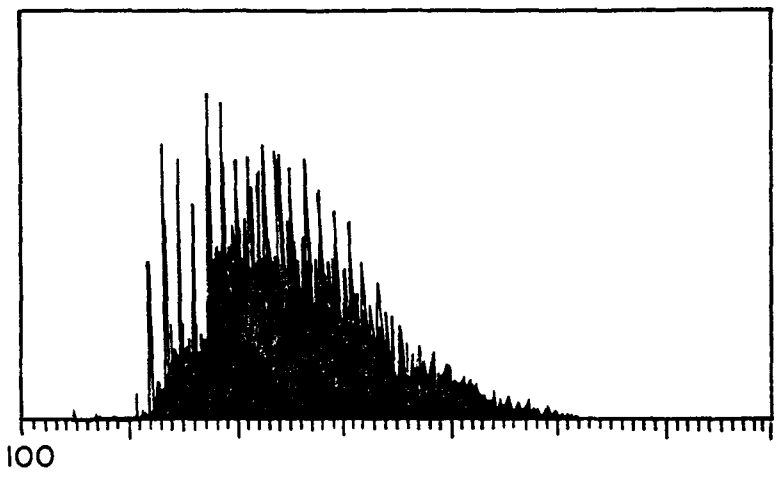
*A major portion of this product has seen extensive recycle.

Table 6-12

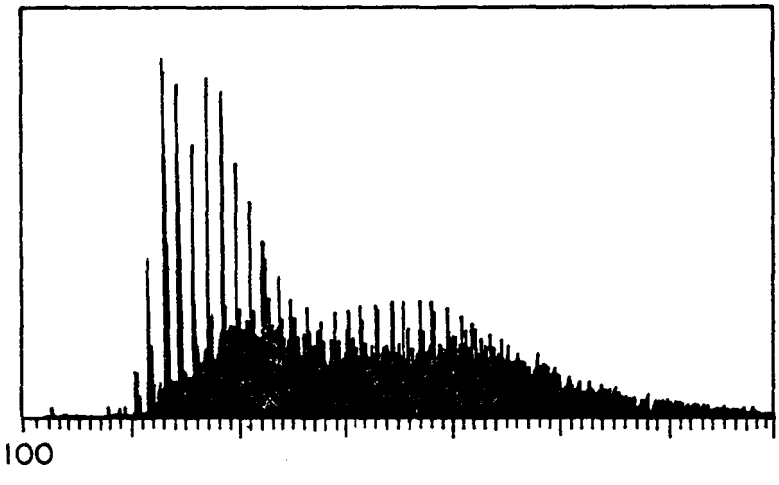
ELEMENTAL ANALYSIS OF SESC FRACTIONS OF 800^{+} RESIDUES

Thermal vs. Catalytic

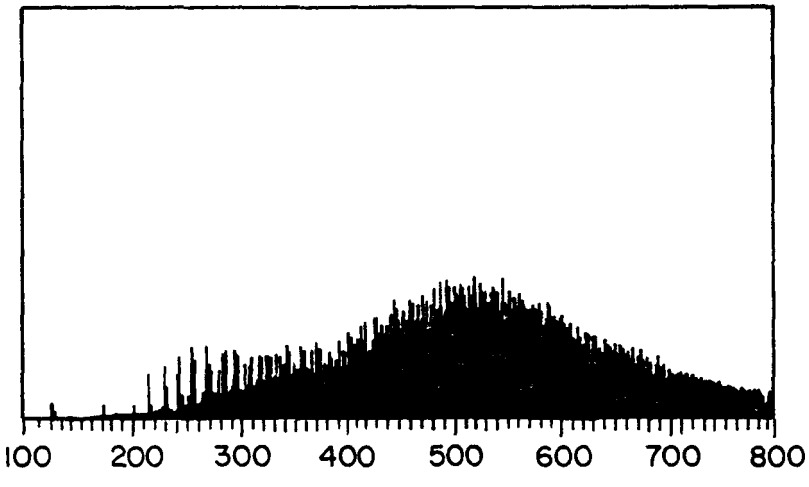
Sample 177-136-3A	% C	% H	% O	% N	% S
SESC-3	87.9	6.7	3.6	1.5	0.3
SESC-4	85.1	6.6	5.1	2.6	0.5
SESC-7	85.9	5.4	6.2	2.4	-
SESC-8	81.8	5.3	9.2	2.0	-
Sample 177-136-10A					
SESC-3	88.0	6.7	3.4	1.6	0.3
SESC-4	86.2	6.3	4.4	2.6	0.6
SESC-7	85.8	5.5	6.2	2.4	-
SESC-8	81.6	5.3	8.2	2.1	-
AC-58 SESC-3	86.3	6.3	4.6	1.0	1.8



3 DAYS ON STREAM
177-136-3A
Avg. MW = 370 (VPO)



10 DAYS ON STREAM
177-136-3A
Avg. MW = 422 (VPO)



TYPICAL THERMAL PRODUCT
AC-58
Avg. MW = 430 (VPO)

Figure 6-9. Change in Molecular Weight Distribution of 800^{+}°F Heterocyclics (SESC-3) With Catalyst Age (Amocat 1B)

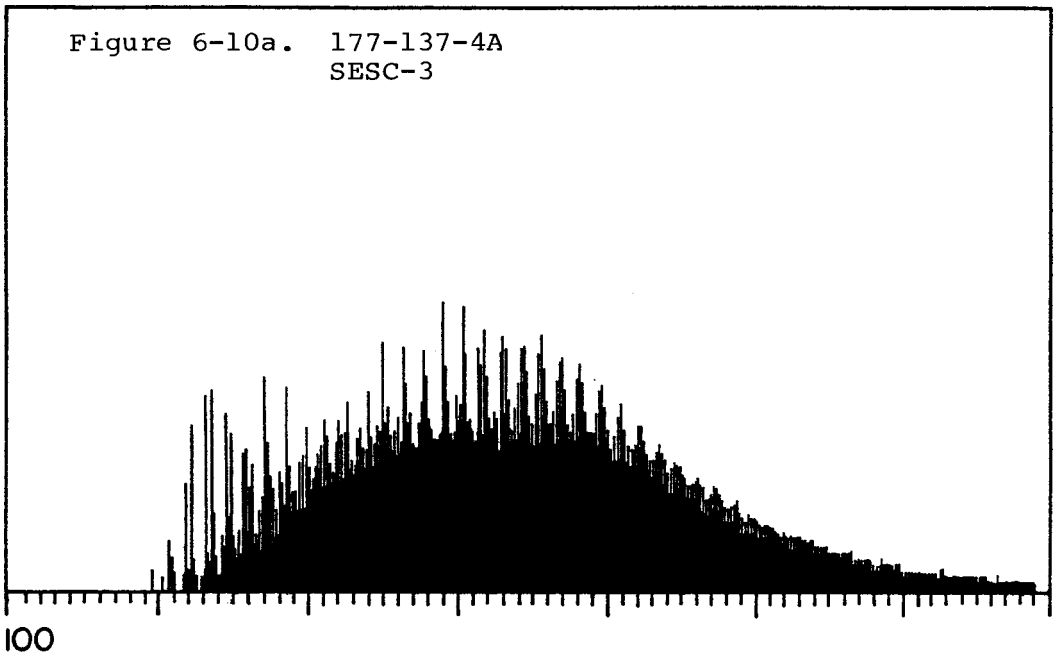
To check for generality of this finding, we fractionated the 800+°F products of 177-137 (Amocat 1A, CoMo/Al_2O_3) at four and eleven days on stream. The FIMS analyses of fractions SESC-3 and SESC-4 at these two times of conversion are presented in Figures 6-10 and 6-11. The profiles of these fractions at the two different times show some shift to higher molecular weight but, in general, they are very similar and both have a lower molecular weight distribution than the thermally produced product. This would indicate that the hydrocracking activity of the catalyst used for these conversions (Amocat 1A) was not lowered as much as with the former catalyst (Amocat 1B). This conclusion was verified by our independent measurement of catalyst activities as described in Section 5.

CONVERSIONS OF COAL UNDER SIMULATED H-COAL CONDITIONS IN ABSENCE OF A CATALYST

Because only minor changes in composition occurred during the HRI studies, we attempted to determine how the composition would change if the catalyst became completely ineffective. To do this we reconstituted the total product effluent from run 177-136-3A, mixed it with coal and reacted the mixture under simulated H-Coal conditions but with no catalyst. The reconstitution of this mixture was shown earlier in this section (see Figure 6-1). The three product fractions were combined in the ratio of the original mixture. In the H-coal reactor the concentrations of the various product fractions, coal, and catalyst are as follows:

	Weight Fraction
Coal	1
450-800°F (solvent)	2.1
800+°F Pyridine soluble (recycle)	1.5
800+°F Pyridine insoluble (recycle)	0.3
Catalyst	0.9

Thus, the total coal liquid/solids ratio is 2.8/1. The conditions chosen for our simulated conversion were 850°F, 2250 psi H_2 and 100 minutes. This is probably a little longer than the average



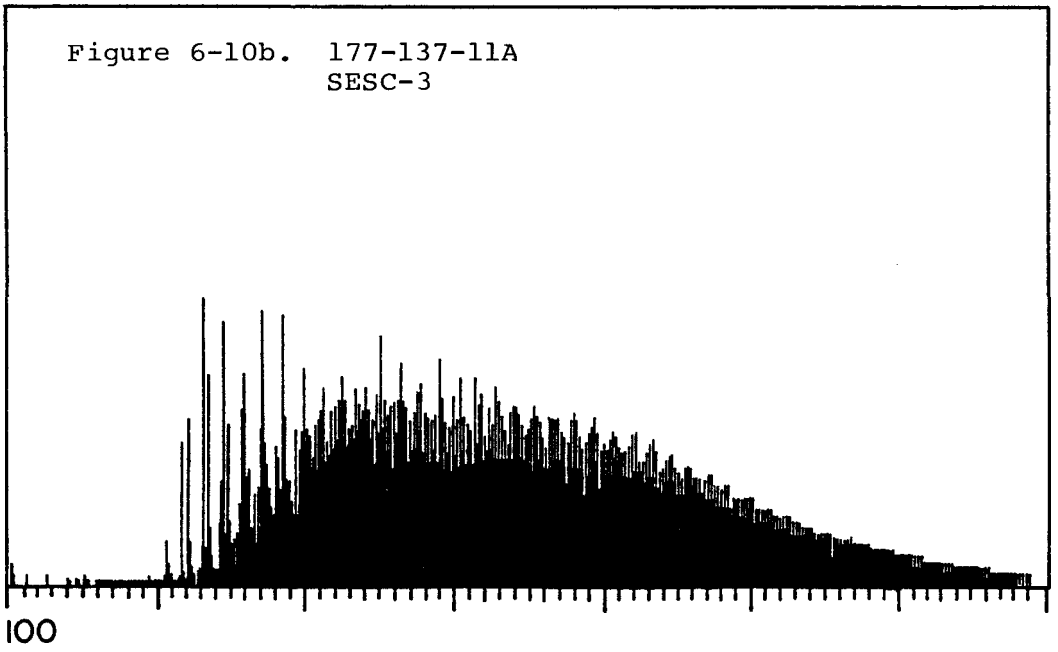
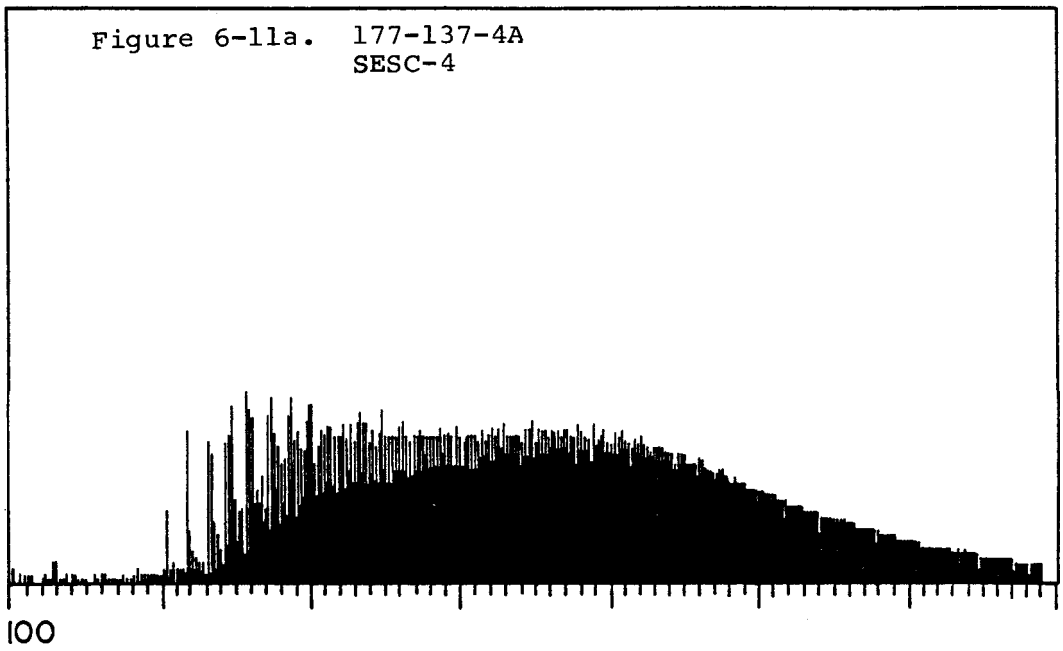


Figure 6-10. FIMS Analyses of Fraction 3 From Run 137



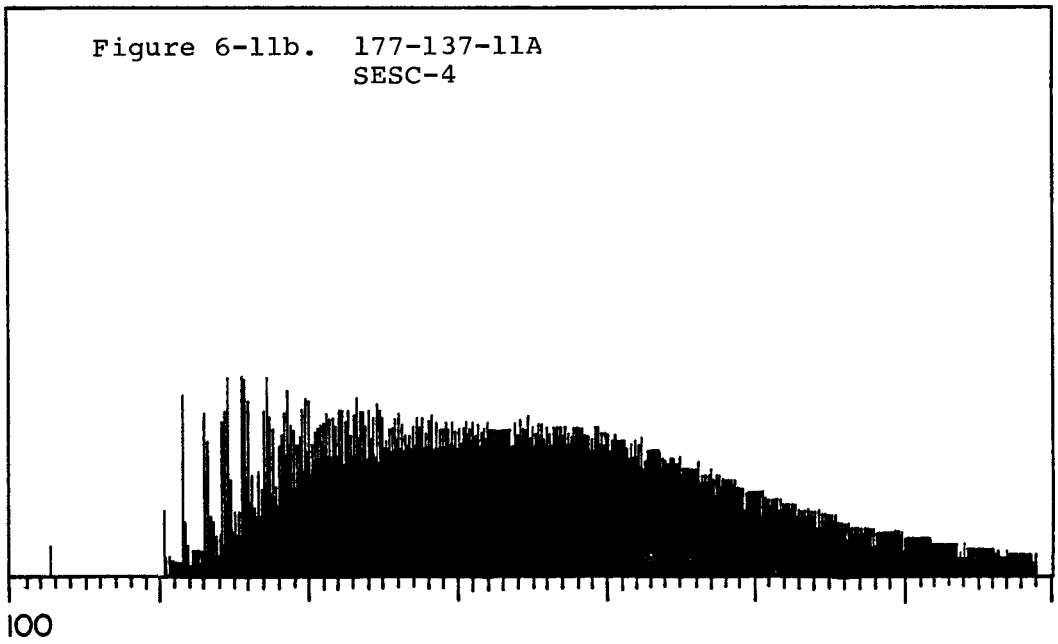


Figure 6-11. FIMS Analyses of Fraction 4 From Run 137

time any liquid molecule would spend in the unit at >800°F, as estimated from volumes, recycles, and throughput. (The time per pass is much shorter, but most molecules eventually make many passes when recycle through the still, filter, and preheater are considered; our estimate is crude because we don't know, for example, the volume of the reactor occupied by gases.)

The conversion (AC-525) was carried out in our small autoclave (6-3) in order to minimize experimental difficulties such as long heat-up times of a portion of the mixture and difficulty in injection of such heavy slurries. The balance of this run is presented in Table 6-13.

Table 6-13

BALANCE OF SIMULATED H-COAL CONVERSION WITHOUT CATALYST

		Weight Charged (grams)	Weight Recovered (grams)
Pyridine Insoluble Solids	Coal	2.00	
	Pyridine Insol. Residue	0.6	2.03
Solvent	450⁻°F	0	.17
	450-800°F	4.17	3.71
(Recycle) Vacuum Residue	800⁺°F Pyridine Sol.	3.03	3.20
Gases and loss		-	0.7
Total		9.8	9.8

From the data it is clear that either coal did not convert or massive charring occurred in this run. We believe the latter is more likely.

The elemental analysis of the 800⁺°F pyridine-soluble product of this run was shown in Table 6-10. This analysis indicates a much lower hydrogen content and lower heteroatom content in this run than would be observed in a run under comparable conditions but with a solvent that will not char. Charring would tend to lower

the overall heteroatom content as phenolic and non-basic nitrogen-containing compounds are the most prone to condensation reactions (6-3). The SESC analysis of this heavy fraction also indicates that the phenolic components of the sample are depleted (see Table 6-11).

We have previously shown (6-3) that solvents which contain high concentrations of heavy phenolic materials will char if they are used to dissolve coal.

The aromatic hydrogen content of the 800$^+$°F product of the non-catalytic reaction (AC-525) was much higher than that of catalytic reactions (177-136 -- three and ten day samples). This is shown in Table 6-14.

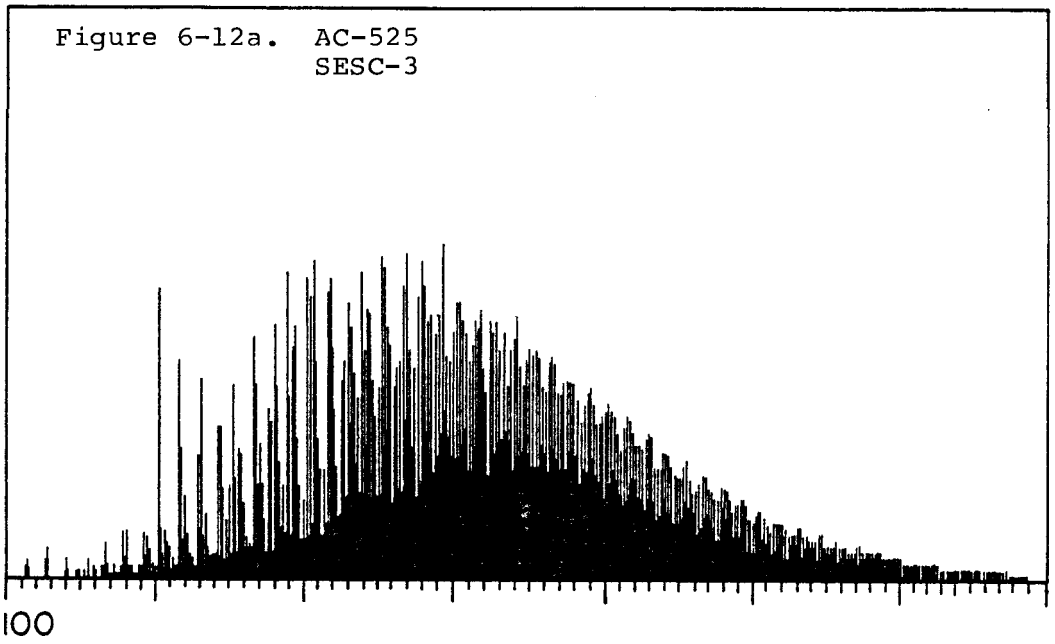
Table 6-14

THERMAL VS. CATALYTIC 800$^+$°F RESIDUE COMPOSITIONS

Sample	Percent of 800$^+$ Residue	Percent Aromatic H
HYDROAROMATIC HYDROCARBONS		
177-136-3A-SESC-2	35	37
177-136-10A-SESC-2	32	38
AC-525-SESC-2*	~42	66
NON-BASIC AROMATIC HETEROCYCLES		
177-136-3A-SESC-3	28	36
177-136-10A-SESC-3	27	36
AC-525-SESC-3	~40	60

*May contain ~5% saturates.

FIMS analysis of SESC fractions of this run show molecular weight profiles typical of thermal processes (a shift toward higher molecular weight). Figure 6-12a and 6-12b present the FIMS analyses of AC-525 SESC fractions 3 and 4.



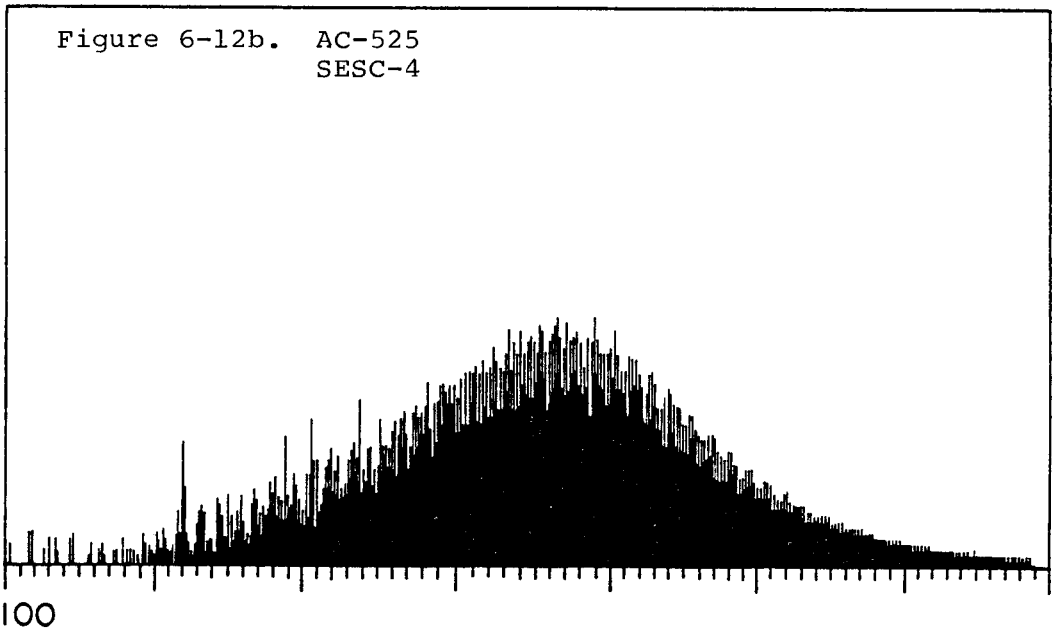


Figure 6-12. FIMS Analyses of Fractions From AC-525

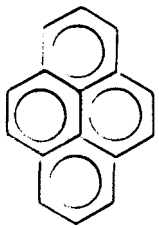
We examined the FIMS data on SESC fraction 2 in the AC-525 product in some detail. These data were consistent with molecules like those shown in Figure 6-13 (and homologs having additional alkyl substitution totaling up to three carbons). This examination of a simple fraction shows the kinds of carbon skeletal structures probably making up the bulk of the products in the HRI runs. These particular compounds of course are highly aromatic because of the nature of our run AC-525.

These data again indicate that the catalyst acts directly on the heavy products as well as solvent-range products, because the 800^{+}°F catalytic products change considerably if they are heated in the absence of a catalyst.

The solvent-range products of run AC-525 also underwent major changes on reaction with coal. Figure 6-14 compares the gas chromatographs of the 450-800°F material before and after reaction. The disappearance of hydroaromatic hydrogen donors is clearly evident. Another rather striking feature is the decrease in complexity of the spectra on reaction with coal. The solvent-composition changed substantially and after reaction resembled a thermal coal liquefaction solvent (methylnaphthalene, phenanthrene, and pyrene as major constituents).

In summary, all of the compositional changes show that during the H-Coal process the catalyst acts both on high and low molecular weight components. Without a catalyst (or if the catalyst completely loses activity), the process would become extremely unstable because of the high temperatures. Char formation would become massive and molecular weights would shift to higher values.

In the runs we investigated in detail no major changes occurred in the coal product compositions at up to ten days on stream. The major effect noted was replacement of the hydrogenated anthracene oil start-up solvent by coal-derived solvents. Comparison of catalytic and thermal coal liquefaction processes at the same temperature shows that catalytic processes produce products which are richer in hydrogen, lower in sulfur and oxygen content and lower overall



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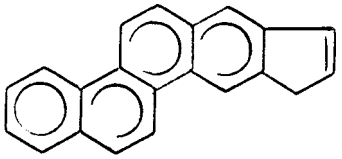

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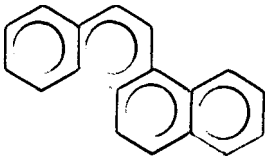

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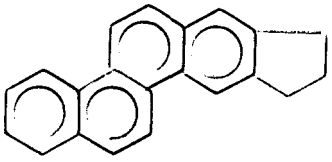

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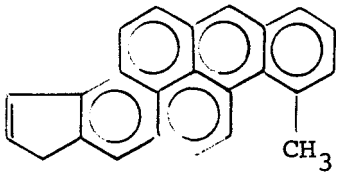

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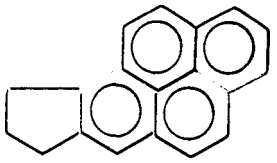

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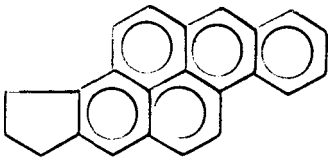

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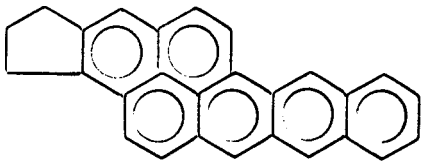

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Figure 6-13. Structures Consistent With FIMS Analysis of AC-525 (SESC-2)

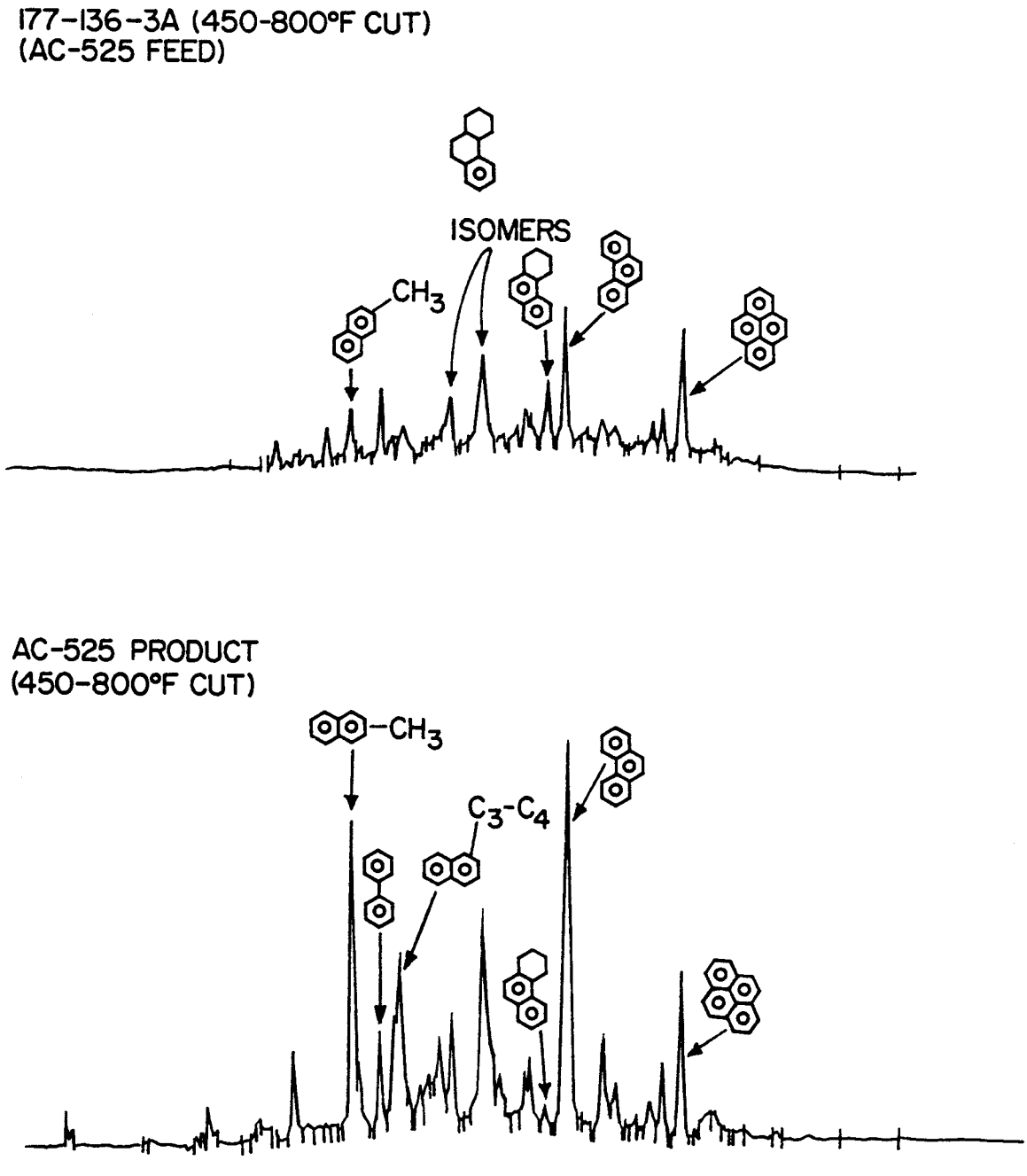


Figure 6-14. Gas Chromatographs of AC-525 Solvent

in molecular weight distribution. The nitrogen contents of the 800^{+}°F soluble products are about the same for both reactions. More of the nitrogen is present as non-basic nitrogen in high temperature processes than in lower temperature processes (see Table 6-11).

As we showed in Section 5, non-basic nitrogen like indole is harder to remove catalytically. Thus the higher temperature is detrimental to denitrogenation in subsequent processing.

CONSIDERATION OF STRUCTURAL DIFFERENCES BETWEEN CATALYTIC AND THERMAL 800^{+}°F LIQUEFACTION PRODUCTS

Although it is not possible to make precise comparisons of the skeletal structures resulting from thermal and catalytic coal liquefaction, some gross comparisons can be useful. In the following text we have tried to integrate our observations on the compositions of products of Illinois #6 coal in both processes and construct some models of structures which fit these observations.

In deriving these structures we have attempted to draw one common assemblage of ring structures and functionality and show how this is modified by different processing parameters. A number of aspects considered are listed below:

- The skeletal structure of the product is assumed to be represented by the skeletal structure of fraction SESC-3 (heterocyclic compounds).
- The observed weight average molecular weights of 800^{+}°F products from both thermal and catalytic liquefaction of Illinois #6 coal were not grossly different and were about 480. Elemental analyses of SESC-3 fractions predicts that an average structure of this molecular weight would have 35 carbons. Therefore in all of the structures which we derived the same carbon number was used.
- Aromatic C and H contents as determined by ^{1}H and ^{13}C-NMR for all of the structures derived were matched as closely as possible.
- Elemental analyses were essentially identical to observed values, with the exception of AC-525 products where only the total product analyses were available. The heteroatom content was assumed to be higher in SESC-3 than the total SRC for AC-525 as shown.

- In catalytic coal liquefaction products, the aromatic ring structures were assumed to be close to thermodynamic equilibrium; which means that the aromatic rings are predominantly isolated (tetralin/naphthalene = 85/15).

- In thermal and liquefactions conducted under mild conditions with sufficient H-donors the aromatic ring structures are mostly condensed with a low probability of more than 2 or 3 fused rings.

- In high severity-low donor solvents the aromatic ring structures become highly condensed.

- In mild thermal conversions less than one aromatic methyl group for every three molecules at this molecular weight was observed by selective oxidation (6-3). Therefore, no aromatic methyls were used in the thermal conversion products.

- Hydrocracking of aliphatic ring structures was observed in catalytic coal conversion processes. Thus, one aromatic methyl per molecule was assumed to be produced via this reaction.

- Since Fraction SESC-3 was used as a model, the nitrogen heterocycles were assumed to be non-basic. Using these considerations the structures shown in Figure 6-15 were derived. For the three process variations we have investigated:

  (1) Mild thermal coal liquefaction with reasonable H-donor contents in the solvent (SRC).

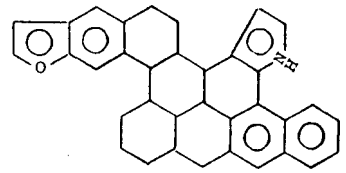
  (2) H-Coal process (equilibrium catalyst).

  (3) H-Coal process (inactive or non-existent catalyst).

One striking feature of this treatment is that indeed one can draw skeletal structures which are common for the three process variations and still conform to the general analytical observations of the products.

The difference in chemistry between the three examples is consistent with these structures and enables one to envision what transformations occur via different processes. One can see how the different coal liquids can undergo various catalytic and thermal reactions (hydrogenation, dehydrogenation, and hydrocracking) so that they have different properties (especially aromaticity) but the same skeletal structure. Furthermore, all the reactions are reversible, including the type of hydrocracking depicted. We have shown (6-3) in a study of solvent condensation reactions that aromatic methyl groups can be incorporated into rings.

SRC Conditions (800°F)
Synthetic Solvent (40% Tetralin)



Wt. Avg. Molecular Weight = 483
% Aromatic C = 63
% Aromatic H = 39

	%	Empirical Formula	Aromatic	Aliphatic
C	86.35	35	22	13
H	6.32	31	12	19
O	4.64			
N	0.95	2		
S	1.81	(2.0)		

Comments

(Patterned after AC-58 SESC-3)

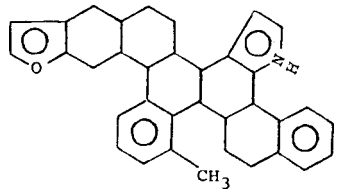
Very few aromatic methyls

Fused aromatic rings

More condensed aliphatic rings

Easily dehydrogenated

H-Coal Conditions (850°F)
H-Coal Solvent



Wt. Avg. Molecular Weight = 487
% Aromatic C = 57
% Aromatic H = 32

	%	Empirical Formula	Aromatic	Aliphatic
C	86.2	35	20	15
H	7.1	35	12	23
O	3.4			
N	1.6	2		
S	0.3	(1.6)		

Comments

(Patterned after HRI 177-136-10A SESC-3)

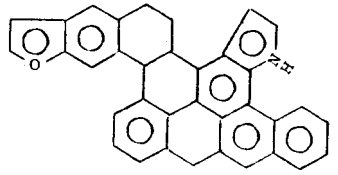
Some Aromatic methyls

Single aromatic rings

Less condensed aliphatic rings

Easily dehydrogenated

H-Coal Conditions No Catalyst (850°F)
H-Coal Solvent



Wt. Avg. Molecular Weight = 473
% Aromatic C = 86
% Aromatic H = 65

	Observed* Analysis For Whole SRC	Basis For Structure	Empirical Formula	Aromatic	Aliphatic
C	91.1	88.8	35	30	5
H	5.2	4.9	23	15	8
O	1.0	3.3			
N	1.5	2.5	2		
S	.5	.5			

Comments

(Patterned after AC-525 whole SRC)

Aromatic methyls should be absent

Highly condensed aromatic rings

Less condensed aliphatic rings

Reaching limit of dehydrogenation

*Elemental analysis of whole 800°F+ product. Forty-two percent of which is hydrocarbon. Thus the heteroatom percent is approximately two times larger in the non-hydrocarbon products.

Figure 6-15. Postulations of the Average Structures of Heterocyclic Fractions of 800+°F Products (SESC-3)

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Section 7

NOVEL HYDROGEN SOURCES AND HETEROATOM REMOVAL

INTRODUCTION

A recurrent theme in our previous work on coal liquefaction (7-1 through 7-3) has been the criticality of minimizing hydrogen consumption while simultaneously maximizing heteroatom removal. As can be seen from the previous sections of this report, with the catalysts currently being explored for coal liquefaction and product upgrading, H_2 gas is the principal hydrogen source (even when hydrogen donors or shuttlers are important) and extensive hydrogenation and hydrocracking are required for heteroatom removal. Research on altering this situation would clearly be beneficial. We describe here very brief efforts in this direction.

BACKGROUND

In coal liquefaction, extensive removal of N and S are almost always desirable; requirements for oxygen removal, aromatics saturation and molecular weight reduction depend upon the intended use of the products. Excessive hydrocracking is almost invariably detrimental.

Different types of catalytic sites are required, such as metallic and acidic, and the critical balance is difficult to maintain when there are differing aging and poisoning characteristics of the different functions. Furthermore, each heteroatom is found in relatively easy or difficult to remove forms. Finally, proper solvent characteristics (7-3) must be maintained and these may not be the same for optimizing both coal dissolution and product upgrading.

The limitations of presently known catalysts for heteroatom removal have been summarized (7-4). Significant problems are poor selectivity (and thus excessive hydrogen consumption) and rapid catalyst

aging (thus high catalyst costs). Interest in producing a clean boiler fuel from coal presents different problems from those that have been addressed in the past. For boiler use, the quality of the fuel is judged primarily by its sulfur content and its pumpability at a reasonable temperature. Since the BTU content is secondary, oxygen content is not of major concern. The nitrogen content of the fuel becomes a problem if NO_x emission standards are imposed; coal liquids (SRC) do produce more NO_x on combustion than conventional fuels because the nitrogen levels are considerably higher.

Thus, for boiler fuel production via catalytic processing, new criteria must be chosen when evaluating catalysts. With conventional catalysts and processes, the removal of oxygen from feedstocks proceeds at a faster rate than the removal of sulfur or nitrogen. In addition, aromatic rings containing phenolic or heterocyclic oxygen must generally be saturated before the oxygen is rejected (7-5). The added hydrogen (which is retained in the fuel) does not increase the value of the fuel in proportion to its cost. Catalysts are known which effect hydrogenolysis of phenolic groups without ring saturation (7-6,7-7) but these have not been extensively studied for coal liquid hydrogenation. Selective catalytic removal of nitrogen and sulfur without oxygen removal is a reasonable goal for boiler fuel.

If higher hydrogen addition is desired (e.g., for turbine fuel applications where high-hydrogen liquids are needed) then catalysts of higher activity need to be developed such that the saturation of aromatic rings can be accomplished under milder conditions. For example, at lower temperatures the thermodynamics are more favorable, allowing lower H_2 pressures, which saves in equipment investment.

Nitrogen removal proceeds via the same mechanism as oxygen removal. The aromatic rings must be saturated before the nitrogen is rejected (7-5). Additional problems occur with nitrogen, however. Basic nitrogen species inhibit the rate of other hydrogenative reactions (e.g., desulfurization) (7-8). The thermodynamics of aromatic nitrogen ring saturation are less favorable than those of hydrogenation of hydrocarbon aromatics at the temperatures employed for

coal liquid upgrading. Thus, aromatic compounds without heteroatoms are saturated preferentially resulting in nonselective hydrogen consumption as discussed above. A temperature maximum for catalytic denitrogenation of pyridine (750°F) was said to be due to equilibrium constraints (7-9). Thus for denitrogenation, development of catalysts which resist poisoning by nitrogen compounds and which are more active, thus allowing lower temperature operation, is warranted.

The existing commercial catalysts for desulfurization are quite effective on coal liquids. With these catalysts, however, low activity requires higher temperatures than is desired from thermodynamic constraints. Note that the mechanism of sulfur removal differs from that of oxygen and nitrogen removal in that aromatic ring saturation is not necessarily required for sulfur rejection (7-10). It would also be advantageous to use an inexpensive catalyst that could be discarded (or used as an ore, etc.) rather than regenerated.

We will not consider further here the use of only "conventional" catalysts (such as CoMo, NiMo, NiW, etc. on Al_2O_3) and hydrogen sources (such as H_2 gas and hydroaromatic donors), but will turn to nonconventional concepts.

One technique that has been considered for both coal liquefaction and heteroatom removal is the use of secondary alcohols (7-11) or methanol (7-11,7-12) with caustic catalysis. Alcohol/caustic systems were found to be more effective than tetralin for coal solubilization, and for desulfurization at 300-450°C in the absence of H_2. Methanol is potentially the least expensive alcohol available. Aqueous NaOH + $Ca(OH)_2$ at mild conditions (100-250°C) has been examined for desulfurization (7-13) and is reported to remove some organic sulfur as well as pyrite. The use of soluble caustic, however, is expensive and recycle would be complicated.

NOVEL APPROACHES EXAMINED UNDER THE CONTRACT

In the very limited time available in this contract, two alternatives were considered: methanol as hydrogen donor and manganese nodules as an inexpensive disposable catalyst. We cited above reports that

alcohols such as methanol have been used as donors, although in conjunction with caustics. With the caustics a different mechanism may be involved and the process could be costly and difficult to operate. We chose to investigate other catalysts.

Mobil has had experience with the use of manganese nodules as demetallation and desulfurization catalysts (7-14,7-15). These materials are plentiful in ocean and lake bed deposits and potentially are very inexpensive. They could thus be used only until their activity dropped to an unacceptable level and not regenerated. Their subsequent value as ores would not be reduced. In Section 4 of this report, we described the manganese nodules used in the present work; in Section 5 we demonstrated their activity for the important reactions in coal dissolution and product upgrading.

Beneficial effects of water in heteroatom removal have been indicated in several instances. Work at Mobil's Paulsboro Laboratory initially showed some advantages to inclusion of water during denitrogenation of recycle solvents (7-16). Later results were less conclusive (7-17). Two significant differences in the data are apparent, however; the feedstocks were different and the promising results were obtained at a lower temperature (675°F vs 720°F). Equilibrium limitations on partially hydrogenated species could be more severe at the higher temperatures.

Another indication can be found by comparing the results of liquefaction of lignites and subbituminous coals via the solvent-refined lignite (SRL) process vs the solvent-refined coal (SRC) process. The significant difference between these two processes is the reducing agent: H_2O/CO for SRL and H_2/H-donor for SRC. The analysis (7-18) of typical products from these two processes shows that the ratio of C/N is changed considerably during the SRL process but is essentially unaffected in the SRC process. The basic ash components of lignite could possibly aid the hydrolysis of nitrogen compounds. It should be mentioned that with MeOH and caustic no change in C/N ratio is observed (7-11).

A number of reactions were conducted to test some of the above concepts. In each case a 300 cc stainless steel autoclave was charged with a short-contact time solvent-refined coal obtained from the Wilsonville SRC pilot demonstration unit operated by Southern Services, Inc. The indicated amounts of donor compound (methanol or tetralin), solvent (2-methylnaphthalene or decalin) and a catalyst, if used, were added. The unit was sealed, pressure tested with argon, charged with one atmosphere argon and heated in 1-2 hours to the indicated temperature with stirring. In two cases H_2 or H_2/CO were then added. The system was held for two hours at the indicated temperature and total pressure with stirring, and then quenched within 1-2 minutes by forcing water through a cooling coil in contact with the autoclave contents. The vessel was opened and the contents washed out with tetrahydrofuran; the residue and catalyst were Soxhlet extracted with tetrahydrofuran, the extract added to the other liquids, and the solvent removed with a rotary evaporator. Distillation under vacuum yielded the SRC product (800°F+ material). The feed was entirely THF soluble.

In order to compare these data with a more conventional coal conversion, one conversion was conducted using no catalyst and a typical hydroaromatic hydrogen donor (Run 70). The feed was a Monterey coal similar to the one from which the feed to the other runs was generated. It contained 2.70% organic S. In this run ~25 g coal was injected as a ~2:1 slurry in a synthetic solvent (~2% γ-picoline, 18% p-cresol, 38% tetralin, 42% 2-methylnaphthalene) into preheated solvent (same mixture) and stirred at 800°F for 90 minutes under 1333 psi H_2. It was then quenched and worked up as described above, except that pyridine was used for the extraction. The solvent:coal ratio during the run was ~6:1. The apparatus and procedure have previously been described more fully (7-2).

RESULTS

It can be seen (Table 7-1) that in these runs the best desulfurization was obtained with manganese nodules plus methanol and methylnaphthalene (Run 145); the next best was with manganese nodules plus tetralin and methylnaphthalene (Run 153) or with manganese nodules and H_2

Table 7-1

EXPLORATION RUNS WITH NOVEL CATALYSTS OR HYDROGEN SOURCES

RUN	70[a]	143	144	145	153	173	174	175	176	177	178	179	SRC Feed[b]
Feed[b]	MT Coal	5g SRC	5g SRC	5g SRC	5g SRC	20g SRC	20g SRC	20g SRC	20g SRC	20g SRC	20g SRC	20g SRC	
Catalyst[c]	-	5g 13X	-	5g Mn Nod	4.9g Mn Nod	10g Mn Nod	10g Mn Nod	10g Mn Nod	10g Mn Nod	10g Mn Nod	10g Mn Nod	10g Mn Nod	
Donor	Tetralin	25g MeOH	25g MeOH	25g MeOH	25g Tetralin	100g MeOH	10g MeOH	10g MeOH	-	20g MeOH	-	20g MeOH	
Solvent[d]	(SS*43)	50g MeN	50g MeN	50g MeN	50g MeN	-	90g Decalin	90g Decalin	100g MeN	90g MeN	100g MeN	90g MeN	
Temp., °F	800	890→800[e]	914→800[f]	800 ± 16	804	570	794	800	800	800	800	800	
Time, min.	90	120	40 + 80	120	120	90	35[j]	26[j]	90	90	90	90	
Press., psig[g]	1333(H_2)	2100	950	2065	530	2000	1100	2000	1550	600	1550	700	
Gas[h]	H_2	Ar	Ar	Ar	Ar	Ar	Ar	Ar	1:1H_2:CO[i]	Ar	H_2[i]	Ar	
Char Yield	-	56	62	5	7.6	24	54	37	3	18(?)	2	39	
SRC Yield	69	40	40	76	68	65	20	44	67	31(?)	72	42	
SRC (%)													
C	85	86.6	91	88.6	87.9	82.9	85.4	85.0	85.9	86.7	86.3	87.3	82.3
H	5.9	5.7	6	5.9	5.8	6.0	6	6.1	5.6	5.7	5.5	5.3	6.3
O	5.8	4.3	1.7	2.9	4.1	7.4	5.8	5.1	5.2	4.4	5.3	4.7	7.7
N	1.7	1.5	1.0	1.3	1.3	1.2	1.6	1.6	1.6	1.4	1.7	1.2	1.5
S	1.5	1.8	1.13	0.5	0.8	1.8	1.2	1.4	1.2	1.4	0.8	1.2	1.9
H/C	0.83	0.79	0.79	0.80	0.79	0.87	0.84	0.86	0.79	0.79	0.77	0.73(?)	0.9
Arom. C	44	-	-	46	-	-	-	-	-	-	-	-	36
% SRC - SESC 1	5.4			2.7	2.3	4.2			4.0				0.9
2	18.0			21.4	17.4	6.0			16.3				10.1
3	19.7			25.6	17.4	12.1			15.4				12.2
4	21.8			9.3	11.4	8.9			18.0				18.0
5	9.0			7.5	13.0	8.8			11.3				14.2
6	6.4			5.1	13.9	7.3			10.0				9.4
7	0.7			1.9	4.2	5.1			2.4				3.8
8	5.6			4.2	8.6	6.2			5.3				7.7
9	13.4			22.3	11.9	41.5			17.4				23.8

a. See Reference 7-2 for description of Run 70.
b. SRC was Monterey short-contact time SRC (77-D-13) obtained from Wilsonville; THF soluble portion only.
c. 13X = Linde 13X molecular sieve (NaX zeolite); Mn Nod = Manganese Nodules (see Section 4).
d. SS*43 ≈ Mobil's Standard Synthetic Solvent (see Reference 7-2); MeN = 2-Methylnaphthalene.
e. Temperature lowered because of increasing pressure.
f. Temperature 914°F for 40 minutes then 800°F for 80 minutes.
g. Total pressure at temperature, except in Run 70; autogenous except in Runs 70, 176, 178.
h. Argon used for pressure test; 0 psig at start.
i. 700 psi gas added at 800°F.
j. System failed.

with methylnaphthalene (Run 178). Selective loss of sulfur relative to oxygen was promoted in all runs containing Mn nodules. Catalytic conversion using 13X catalyst (Run 144) showed no such improvement over the selectivity of thermal conversion (Run 70).

In one run (173) using a large amount of methanol, no other solvent, and a much lower temperature, the SRC oxygen content was about the same as the feed. (This temperature was within the range cited earlier for work with methanol and caustic.) In all other runs, deoxygenation occurred despite a large amount of oxygen introduced into the products as methanol.

The SRC with the lowest nitrogen content was produced in the run with high temperature and no catalyst (144) but less SRC than char was found. The next best was the run with only methanol and manganese nodules at low temperature (173) but this is probably partially an artifact caused by methanol incorporation.

A few continuous flow reactions were done with model compound mixtures as described in Sections 4 and 5. When methanol was added to mix 1 or mix 2 and passed over the commercial catalysts or manganese nodules in the flow unit, there were sometimes very slight indications of more oxygen or nitrogen removal. These were so minor and inconsistent that they are not reported and no further work is planned.

The H/C mole ratios of the SRC's produced in the autoclave runs decreased smoothly with the overall extent of reaction as indicated by the decreasing oxygen contents. The H/C ratio was highest in Run 173 (methanol incorporation) and when decalin was used as the dispersing solvent (Runs 174 and 175). In the decalin cases this may have been due only to the shorter times; we have shown that H/C decreases with time (7-2). Note that the H/C was quite high in conventional Run 70 with coal, our standard synthetic solvent, and H_2. The low H/C for Run 179 is probably an experimental error. ^{13}C-NMR indicates no significant difference in aromatic carbon content between Run 70 and the most promising methanol/manganese nodules run (145).

Char formation is particularly high in runs with decalin (174 and 175), without catalyst (Run 144) or with 13X zeolite (143). Charring was also extensive in several scoping runs (not reported further) with water, methylnaphthalene, SRC, and 13X zeolite. Charring is worse at high temperature (143 and 144). The high residue yield in 173 is probably not char but material made insoluble because of methanol incorporation. Similar residue (or char) may be formed in the runs with relatively low methanol/SRC ratios.

H_2/CO or H_2 prevent char formation when manganese nodules are present even if there is no donor. The H_2 run (178) does show some desulfurization; neither H_2 or H_2/CO shows much effect in oxygen or nitrogen removal. H_2/CO is no better than H_2 and no better than methanol except that it gives less char than methanol unless large excesses of methanol and manganese nodules are used.

It is clear that manganese nodules are beneficial. With methanol and no catalyst (144) the SRC quality was improved but the yield was very poor due to massive charring. With 13X zeolite the quality and yield were low. All the runs with manganese nodules and methanol (unless decalin was the solvent) gave more heteroatom removal than was observed in Run 70, even though in the latter case the coal mineral matter was present and the H_2 pressure was high.

Examination of the SESC fraction distributions shows that methanol is incorporated into the SRC's, especially at low temperature and high methanol/SRC (173). There is a general decrease in fractions 4-6 (asphaltenes) and a substantial increase in fraction 9 (asphaltol) and a residue which was probably highly functional material rather than char. This indicates that the incorporation occurs with retention of the -OH group, rather than by formation of ethers or esters.

At low temperature, the incorporation is permanent and results in high oxygen content and H/C mole ratio. There is an indication that the nitrogen content might be reduced slightly more than would be observed from dilution alone because the S-content is still high.

We did not examine the methanol balances, but they must have been low.

At higher temperature with the right catalyst (manganese nodules), this modified SRC is defunctionalized and ultimately contains less oxygen and sulfur than if methanol had not been used. Comparing runs 145 and 153 with manganese nodules and methylnaphthalene, methanol gives a higher SRC yield with a better elemental analysis, but tetralin gives an SRC with a more desirable functionality distibution.

It is clear that when methanol is used the proper balance of methanol and other solvent components such as methylnaphthalene is necessary to maintain the physical dissolution properties of the solvent and prevent formation of insoluble materials. Comparisons of runs 177 and 179 to 145 show also that high methanol/SRC and manganese nodules/SRC ratios are necessary in order to obtain the benefits of methanol without residue formation.

The following conclusions are drawn from this brief scoping study:

- It is possible to use materials other than H_2 gas or hydroaromatics as the principal source of hydrogen.
- The activity shown by manganese nodules, in these runs and in those described in Section 5 of this report, indicates that beneficial inexpensive disposable catalysts can be developed.
- The specific novel system of methanol and manganese nodules does not appear promising, as results are good only at impractical high ratios of these materials to SRC.

Novel hydrogen sources and disposable catalysts appear to have promise in coal liquefaction and should be investigated further. The most benefit could be derived if a system could be discovered with which selective denitrogenation occurs. We are continuing these investigations under EPRI Contract RP 1655-1 entitled "Fundamental Studies in the Conversion of Coals to Fuels of Increased Hydrogen Content".

/LMCole
1979

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APPENDIX

This appendix contains three tables, showing the conditions and results of the conversions of three different model compound mixtures over the catalysts investigated. We give before Tables A-1 and A-2 an explanation of abbreviations.

Abbreviations in Table A-1, Conversions of Mix 1:

RUN NO	Run Number
SAMP NO	Sample Number
MIX NO	(See Experimental, Section 4)
BENZ or CYCLOHEX	Benzene or Cyclohexane
METHYLCYCLOHEX	Methylcyclohexane
TRIMETHYLCYCLOHEX	Trimethylcyclohexane
?	Unidentified Minor Component
NAPH A/O BENZTHIO	Naphthalene and/or Benzothiophene
CYCLOHEXCYCLOHEX	Cyclohexylcyclohexane
CYCLOHEXBENZ	Cyclohexylbenzene
PHP	Perhydrophenanthrene
DBF or PHP	Dibenzofuran or Perhydrophenanthrene
OHP	Octahydrophenanthrene
DHP + OHP	Dihydrophenanthrene plus Octahydrophenanthrene
THP	Tetrahydrophenanthrene
TIME	Hours Since Start of This Catalyst
CATALYST	See Key at End of Appendix
DES	Percent Desulfurization
DEN	Percent Denitrogenation
DEO	Percent Deoxygenation
% PHENAN HYDROG	Percent Phenanthrene Hydrogenation (see Page 5-3)

Table A-1

RUN NO	9.00	28.00	28.00	1.00	1.00	1.00	1.00
SAMP NO	2.00	2.00	4.00	1.00	2.00	3.00	4.00
MIX NO	1.00	1.00	1.00	1.00	1.00	1.00	1.00
PARAFFINS		0.02	0.06	0.01			
PARAFFINS		0.04	0.06	0.06	0.07	0.08	0.02
BENZ OR CYCLOHEX		1.18	1.36	0.22	0.17	0.27	0.21
METHYLCYCLOHEX		3.54	4.05	1.37	1.96	2.36	2.25
TOLUENE		1.12	1.22	1.41	1.45	1.43	1.19
TRIMETHYLCYCLOHEX		0.41	0.42	0.13	0.09	0.10	0.12
?		0.32	0.28	0.08	0.04		
ETHYLBENZENE	0.24	7.15	7.23	6.72	6.72	7.14	6.79
XYLENES							
CUMENE (RUN 1 ONLY)				2.77	0.91	0.22	0.14
MESITYLENE	53.29	52.88	52.87	53.16	53.20	53.19	53.17
P-CRESOL	10.51			1.42	1.90	2.10	1.83
T-DECALIN		0.25	0.25	0.37	0.32	0.47	0.40
C-DECALIN		0.12	0.12	0.19	0.10	0.18	0.15
TETRALIN	0.37	6.32	6.54	5.04	5.77	6.61	7.03
NAPH A/O BENZTHIO	5.66	0.14	0.17	0.62	0.60	0.69	0.74
CYCLOHEXCYCLOHEX		0.26	0.26				
?		0.26	0.26				
CYCLOHEXBENZ		0.34	0.33				
?							
?							
?							
?							
PHP		0.12	0.14				
PHP		1.17	1.19				
α-NAPHTHOL OR PHP	6.74	0.63	0.67				
DBF OR PHP	10.18	5.21	5.47	6.96	7.68	8.70	9.13
OHP	0.11	1.63	1.64	0.75	0.78	1.23	1.33
OHP	0.13	0.35	0.40	1.46	1.51	1.99	2.07
DHP + OHP		3.10	3.12	1.04	1.33	1.87	2.08
THP		0.61	0.66	1.05	1.03	1.41	1.55
PHENANTHRENE	10.63	0.06	0.28	2.17	2.15	2.58	2.98
TIME	12.00	12.00	18.00	0.75	2.00	4.00	5.00
CATALYST	1.00	5.00	5.00	6.00	6.00	6.00	6.00
DES		98.00	99.00		99.50	99.00	
DEN							
DEO		77.00	82.00		60.00	56.00	
o/o H IN PRODUCT	7.51	9.64	9.63		9.25	9.02	
o/o PHENAN HYDROG	1.28	74.05	73.24	29.89	30.53	32.04	31.27

Table A-1 (continued)

RUN NO	1.00	1.00	4.00	4.00	4.00	4.00	4.00
SAMP NO	9.00	11.00	1.00	2.00	3.00	4.00	5.00
MIX NO	1.00	1.00	1.00	1.00	1.00	1.00	1.00
PARAFFINS				0.03	0.01	0.01	0.01
PARAFFINS	0.10			0.03	0.05	0.06	0.08
BENZ OR CYCLOHEX	0.21			0.84	2.10	2.58	2.95
METHYLCYCLOHEX	2.49	0.52	0.17	2.25	3.60	3.95	4.27
TOLUENE	0.78	0.30	0.23	0.13	1.42	1.29	1.20
TRIMETHYLCYCLOHEX	0.08			0.29	1.11	1.97	2.57
?				0.18	0.74	1.30	1.70
ETHYLBENZENE	7.06	5.94	1.24	4.62	6.30	6.35	6.22
XYLENES							
CUMENE (RUN 1 ONLY)	0.24			0.13	0.11	0.11	0.10
MESITYLENE	53.21	53.29	53.29	53.00	52.18	51.32	50.72
P-CRESOL	3.74	2.51	0.30	0.59			
T-DECALIN	0.51	0.01	0.57	0.38	1.22	1.85	2.20
C-DECALIN	0.23			0.21	0.54	0.78	0.90
TETRALIN	6.29	8.26	0.71	4.19	5.73	4.88	4.28
NAPH A/O BENZTHIO	0.72	0.50	3.62	2.28	0.57	0.25	0.15
CYCLOHEXCYCLOHEX			0.20		0.39	0.41	0.45
?			0.22	0.19	0.49	0.67	0.70
CYCLOHEXBENZ			0.19	0.35	0.59	0.46	0.51
?							
?							
?							
?					0.12	0.16	0.19
PHP					0.22	0.35	0.41
PHP				0.31	1.73	2.79	3.23
α-NAPHTHOL OR PHP				0.21	0.73	1.05	1.17
DBF OR PHP	7.97	12.49	4.96	6.15	4.11	2.49	1.88
OHP	0.93	0.90	0.17	0.79	1.37	1.00	0.76
OHP	1.76	2.37	0.15	0.48	0.20	0.27	0.24
DHP + OHP	1.23	2.06		1.68	3.22	2.23	1.80
THP	1.27	1.47	0.11	0.78	0.74	0.53	0.24
PHENANTHRENE	2.63	3.83	2.07	2.20	0.83		0.14
TIME	25.00	31.00	1.00	2.00	3.00	4.00	7.00
CATALYST	6.00	6.00	7.00	7.00	7.00	7.00	7.00
DES	96.00						98.00
DEN							
DEO	47.00						92.00
o/o H IN PRODUCT	8.62						10.40
o/o PHENAN HYDROG	29.91	28.45	8.56	29.76	68.83	77.99	80.79

Table A-1 (continued)

RUN NO	14.00	14.00	14.00	22.00	29.00	6.00	10.00
SAMP NO	2.00	3.00	5.00	2.00	1.00	2.00	2.00
MIX NO	1.00	1.00	1.00	1.00	1.00	1.00	1.00
PARAFFINS			0.01			0.01	
PARAFFINS	0.52		0.54			0.01	
BENZ OR CYCLOHEX			0.07			0.44	0.34
METHYLCYCLOHEX	0.05				1.80	3.50	3.37
TOLUENE					0.93	0.32	0.31
TRIMETHYLCYCLOHEX						0.35	0.27
?						0.20	0.15
ETHYLBENZENE	3.12	3.00	2.91	1.29	6.82	6.83	6.73
XYLENES		0.45					
CUMENE (RUN 1 ONLY)	0.53						
MESITYLENE	53.29	53.29	53.29	53.29	53.29	52.94	53.02
P-CRESOL	8.95	9.18	10.07	10.64	3.26	1.21	1.47
T-DECALIN						0.76	0.70
C-DECALIN						0.25	0.21
TETRALIN	5.87	5.86	5.96	3.33	5.53	6.72	6.77
NAPH A/O BENZTHIO	1.45	1.56	1.72	7.72	1.10	0.28	0.38
CYCLOHEXCYCLOHEX	1.73	1.82	1.90			0.11	0.13
?				0.44		0.12	0.14
CYCLOHEXBENZ						0.11	0.34
?							
?							
?							
?	0.03		0.16	0.33			
PHP							
PHP						0.40	0.26
α-NAPHTHOL OR PHP				3.06		0.20	0.16
DBF OR PHP	9.54	9.76	10.31	10.97	8.81	7.40	7.98
OHP		0.17	0.08		0.94	1.41	1.30
OHP	2.61	2.58	2.43	0.67	2.50	1.23	1.50
DHP + OHP		0.05			1.31	3.37	2.94
THP	0.53	0.51	0.46		1.32	1.30	1.44
PHENANTHRENE	6.21	6.68	7.68	10.80	2.78	1.39	1.93
TIME	12.00	16.00	20.00	12.00	9.00	12.00	12.00
CATALYST	8.00	8.00	8.00	10.00	11.00	12.00	13.00
DES	58.00		51.00		96.00	97.50	93.00
DEN							
DEO	26.00		29.00		41.00	62.00	58.00
•/• H IN PRODUCT	8.39		8.25	7.98	8.83	8.98	8.88
•/• PHENAN HYDROG	17.59	17.36	14.69	3.33	31.75	38.31	35.44

Table A-1 (continued)

RUN NO	7.00	8.00	31.00	31.00	31.00	31.00	31.00
SAMP NO	2.00	2.00	2.00	3.00	4.00	5.00	6.00
MIX NO	1.00	1.00	1.00	1.00	1.00	1.00	1.00
PARAFFINS							
PARAFFINS							
BENZ OR CYCLOHEX	0.02	0.04	2.56	2.69	3.02	2.55	2.58
METHYLCYCLOHEX	1.00	1.21	5.64	5.73	6.36	5.44	5.43
TOLUENE	0.32	0.41	0.45	0.44	0.50	0.32	0.19
TRIMETHYLCYCLOHEX			3.42	3.27	3.55	3.74	3.88
?			2.58	2.48	2.54	3.04	3.15
ETHYLBENZENE	5.96	6.66	7.35	6.84	7.42	5.78	5.40
XYLENES							
CUMENE (RUN 1 ONLY)							
MESITYLENE	53.29	53.29	49.87	50.02	49.74	49.55	49.41
P-CRESOL	6.29	4.90					
T-DECALIN	0.17	0.30	2.26	1.96	2.13	2.44	2.22
C-DECALIN		0.26	0.95	0.67	0.77	0.55	0.60
TETRALIN	5.82	6.20	4.52	4.03	4.21	3.85	3.00
NAPH A/O BENZTHIO	1.90	0.98					
CYCLOHEXCYCLOHEX			0.85	0.53	0.70	0.76	0.38
?	0.18		1.06	0.68	0.79	0.85	
CYCLOHEXBENZ			0.70	0.33	0.45		
?							
?							
?							
?			0.36	0.08	0.24		
PHP		0.16	0.67	0.28	0.51	0.60	0.29
PHP			3.77	3.21	3.57	4.00	3.71
α-NAPHTHOL OR PHP			1.48	1.14	1.37	1.55	1.24
DBF OR PHP	9.51	9.18	3.12	2.39	2.81		
OHP	0.33	0.69	1.23	0.72	0.99	1.40	1.91
OHP	3.01	2.98	0.39	0.20	0.33	0.64	
DHP + OHP	0.21	0.83	2.21	1.74	1.83	0.93	
THP	0.68	1.21	0.56	0.19	0.42		
PHENANTHRENE	5.44	4.01					
TIME	12.00	12.00	13.00	16.00	19.00	21.00	23.00
CATALYST	14.00	15.00	16.00	16.00	16.00	16.00	16.00
DES	86.00	97.50	98.00				
DEN							
DEO	39.00	37.00	89.00				
o/o H IN PRODUCT	8.30	8.53	10.14				
o/o PHENAN HYDROG	22.51	29.35	81.25	83.32	82.72	83.89	88.55

Table A-1 (continued)

RUN NO	31.00	32.00	32.00	32.00	51.00
SAMP NO	7.00	1.00	2.00	3.00	2.00
MIX NO	1.00	1.00	1.00	1.00	1.00
PARAFFINS					
PARAFFINS					
BENZ OR CYCLOHEX	2.68				
METHYLCYCLOHEX	5.51				
TOLUENE	0.32				
TRIMETHYLCYCLOHEX	4.03				
?	3.33				
ETHYLBENZENE	6.41	0.22			1.26
XYLENES					
CUMENE (RUN 1 ONLY)		0.24			
MESITYLENE	49.26	53.29	53.29	53.29	53.29
P-CRESOL		9.04	10.15	9.02	10.20
T-DECALIN	2.09				
C-DECALIN	0.67				
TETRALIN	3.54	0.92	0.26	0.49	1.54
NAPH A/O BENZTHIO		5.10	5.55	9.35	8.07
CYCLOHEXCYCLOHEX	0.63	0.18			0.54
?	0.64	0.17			
CYCLOHEXBENZ		0.58			
?					
?					
?					
?					
PHP	0.44				
PHP	3.67				
α-NAPHTHOL OR PHP	1.35	4.50	4.43	4.51	4.82
DBF OR PHP	0.96	7.74	10.02	9.80	7.82
OHP	0.78	0.17			
OHP	0.18	0.19	0.23		0.59
DHP + OHP	1.03	0.28			
THP		0.12			
PHENANTHRENE		7.28	8.46	6.96	11.89
TIME	25.00	4.00	7.00	10.00	13.00
CATALYST	16.00	17.00	17.00	17.00	30.00
DES	98.00		67.00		16.00
DEN					
DEO	90.00		19.00		29.00
%/% H IN PRODUCT	9.97		7.34		8.10
%/% PHENAN HYDROG	87.27	4.23	1.51		2.68

Abbreviations in Table A-2, Conversions of Mix 2:

RUN NO	Run Number
SAMP NO	Sample Number
MIX NO	(See Experimental, Section 4)
BENZ or CYCLOHEX	Benzene or Cyclohexane
TOL or METHYLCYCLOHEX	Toluene or Methylcyclohexane
TRIMETHYLCYCLOHEX	Trimethylcyclohexane
?	Unidentified Minor Component
NAPH A/O BENZTHIO	Naphthalene and/or Benzothiophene
CYCLOHEXCYCLOHEX	Cyclohexylcyclohexane
CYCLOHEXBENZ	Cyclohexylbenzene
PHP	Perhydrophenanthrene
OHP	Octahydrophenanthrene
DHP + OHP	Dihydrophenanthrene plus Octahydrophenanthrene
THP	Tetrahydrophenanthrene
TIME	Hours Since Start of This Catalyst
CATALYST	See Key at End of Appendix
DES	Percent Desulfurization
DEN	Percent Denitrogenation
DEO	Percent Deoxygenation
% PHENAN HYDROG	Percent Phenanthrene Hydrogenation (see Page 5-3)

Table A-2

RUN NO	9.00	28.00	28.00	28.00	28.00	28.00	28.00
SAMP NO	4.00	7.00	8.00	9.00	10.00	12.00	14.00
MIX NO	2.00	2.00	2.00	2.00	2.00	2.00	2.00
PARAFFINS		0.84	0.86	0.90	0.85	0.08	0.10
PARAFFINS		0.16	0.05	0.04			0.03
BENZ OR CYCLOHEX		0.47	0.11	0.07	0.05	0.04	0.03
TOL OR METHYLCYCLOHEX		0.14					
METHYLPIPERIDINE		0.77	0.64	0.66	0.64	0.61	0.58
ETHYLCYCLOHEXANE		0.09					
ETHYLBENZENE		5.65	5.56	5.62	5.68	5.66	5.64
XYLENES							
PICOLINE	6.38						
TRIMETHYLCYCLOHEX		1.00	1.19	1.28	1.29	1.32	1.27
?							
MESITYLENE	46.89	45.89	45.70	45.61	45.60	45.57	45.62
T-DECALIN		0.28	0.02	0.13	0.08	0.14	0.30
C-DECALIN		0.08	0.06	0.28	0.06	0.21	0.24
O-ETHYLANILINE							
O-PROPYLANILINE							
TETRALIN	0.27	6.07	6.22	6.49	6.62	6.69	6.58
NAPH A/O BENZTHIO	5.09	0.92	0.89	0.98	1.02	1.09	1.12
INDOLINE							
3-*METHYLINDOLE*	1.84	0.88	1.27	1.49	1.55	1.63	1.62
? (FROM INDOLE)	2.30	0.19	0.10				
QUINOLINE	0.27						
INDOLE	10.02	0.15	0.23	0.34	0.38	0.47	0.44
?	0.64	0.44					
TETRAHYDROQUINOLINE	2.86						
CYCLOHEXCYCLOHEX		0.15	0.24	0.35	0.36	0.39	0.44
DIPHENYL ETHER		0.19	0.17	0.27	0.27	0.32	0.28
CYCLOHEXBENZ		0.22	0.17	0.28	0.30	0.33	0.30
PHP							
PHP		0.30					
α-NAPHTHOL OR PHP	5.97	0.20					
PHP		1.92	0.13				
OHP		1.01	0.57	0.64	0.73	0.75	0.65
OHP		1.25	1.79	2.01	2.27	2.35	2.45
DHP + OHP		1.66	1.10	1.07	1.09	1.13	0.92
THP		0.96	1.03	1.14	1.34	1.39	1.29
PHENANTHRENE	7.43	1.66	2.56	2.82	3.24	3.40	3.49
TIME	22.00	23.00	24.00	25.00	26.00	28.00	39.00
CATALYST	1.00	5.00	5.00	5.00	5.00	5.00	5.00
DES	27.00		94.00			96.00	
DEN	11.00		58.00			53.00	
DEO			48.00			56.00	
•/• H IN PRODUCT	7.96		9.68			9.69	
•/• PHENAN HYDROG		51.12	30.11	28.93	28.66	28.52	28.06

Table A-2 (continued)

RUN NO	28.00	1.00	2.00	3.00	3.00	11.00	12.00
SAMP NO	16.00	13.00	2.00	3.00	4.00	2.00	2.00
MIX NO	2.00	2.00	2.00	2.00	2.00	2.00	2.00
PARAFFINS	0.95	0.96		0.36	0.17	0.24	0.92
PARAFFINS	0.04					0.19	0.06
BENZ OR CYCLOHEX							0.10
TOL OR METHYLCYCLOHEX							0.47
METHYLPIPERIDINE	0.57	0.31	0.54	1.01	0.67		
ETHYLCYCLOHEXANE							
ETHYLBENZENE	5.80	4.90	4.35	5.78	5.50		
XYLENES						92.50	93.69
PICOLINE		1.52	1.08	1.12	1.40		
TRIMETHCYCLOHEX	1.31	0.94	0.80	0.93	0.47	0.93	
?						0.45	
MESITYLENE	45.58	45.95	46.09	45.96	46.42		0.27
T-DECALIN	0.42						0.18
C-DECALIN	0.35						
O-ETHYLANILINE							0.79
O-PROPYLANILINE						0.70	
TETRALIN	6.81	0.90	1.11	6.41	5.98	0.14	0.33
NAPH A/O BENZTHIO	1.20	0.46		1.50	1.27		
INDOLINE			0.54	0.88	0.48		2.86
3-METHYLINDOLE	1.62	2.54	2.21	1.58	1.29	0.79	
? (FROM INDOLE)							0.34
QUINOLINE		1.27	0.45		0.22	0.44	
INDOLE	0.40	1.48	1.77	3.13	2.46		
?					0.12		
TETRAHYDROQUINOLINE		2.67	5.11	4.44	3.64	3.62	
CYCLOHEXCYCLOHEX	0.34						
DIPHENYL ETHER	0.22						
CYCLOHEXBENZ	0.27				0.15		
PHP							
PHP							
α-NAPHTHOL OR PHP							
PHP							
OHP	0.54		0.34		0.11		
OHP	2.26	2.00	3.48	2.73	2.83		
DHP + OHP	0.84	0.40	0.60		0.27		
THP	1.35	1.01	1.38	0.92	0.91		
PHENANTHRENE	3.86	9.05	6.39	5.23	5.73		
TIME	47.00	30.00	11.00	16.00	20.00	12.00	13.00
CATALYST	5.00	6.00	6.00	6.00	6.00	6.00	6.00
DES	91.00			96.50			
DEN	58.00			40.00			44.00
DEO	61.00			66.00			
°/° H IN PRODUCT	9.70			9.01			9.74
°/° PHENAN HYDROG	25.82	12.63	22.89	20.52	20.68		

Table A-2 (continued)

RUN NO	12.00	13.00	21.00	5.00	5.00	5.00	5.00
SAMP NO	4.00	2.00	4.00	1.00	2.00	3.00	4.00
MIX NO	2.00	2.00	2.00	2.00	2.00	2.00	2.00
PARAFFINS	1.05	1.21	0.39	0.54	1.65	1.52	1.65
PARAFFINS	0.14			0.70	0.37	0.16	0.14
BENZ OR CYCLOHEX	0.23			0.61	0.40	0.15	0.11
TOL OR METHYLCYCLOHEX	0.20			0.33	0.07		
METHYLPIPERIDINE		2.21	1.26	1.32	2.55	2.97	2.98
ETHYLCYCLOHEXANE	0.35			0.42	0.17	0.21	0.20
ETHYLBENZENE			5.93	3.91	5.89	5.87	5.83
XYLENES	97.12	82.90		0.37			
PICOLINE		14.87	2.05				
TRIMETHCYCLOHEX			0.51	0.37	2.30	2.68	2.67
?							
MESITYLENE	0.76		46.38	46.52	44.59	44.21	44.22
T-DECALIN			0.07	1.02	0.35	0.40	0.36
C-DECALIN				0.36	0.18	0.23	0.17
O-ETHYLANILINE							
O-PROPYLANILINE							
TETRALIN			6.24	2.24	6.23	6.75	6.87
NAPH A/O BENZTHIO	0.16		0.99	1.54	0.52	0.26	0.25
INDOLINE			0.94				
3-METHYLINDOLE			1.38	0.14	1.06	1.18	1.21
? (FROM INDOLE)				0.23			
QUINOLINE			0.35				
INDOLE			3.80	0.34	0.10		
?				0.27	0.07		
TETRAHYDROQUINOLINE			4.89		0.14	0.22	0.25
CYCLOHEXCYCLOHEX					0.33	0.55	0.61
DIPHENYL ETHER					0.18	0.29	0.33
CYCLOHEXBENZ			0.31		0.02	0.09	0.11
PHP				0.12			
PHP			0.15	1.24	0.12	0.19	0.23
α-NAPHTHOL OR PHP				0.47	0.10	0.09	0.11
PHP			0.16	0.34	1.16	0.20	0.26
OHP			0.28	0.17	0.98	1.13	1.30
OHP			2.73	0.40	0.47	0.81	0.90
DHP + OHP					2.09	2.88	3.09
THP				0.31	1.59	1.89	2.04
PHENANTHRENE			6.24	2.10	1.55	1.07	1.11
TIME	22.00	12.00	40.00	2.00	3.00	4.00	5.00
CATALYST	6.00	6.00	6.00	7.00	7.00	7.00	7.00
DES	98.30		94.00				
DEN		41.00	11.00				
DEO			45.00				
•/• H IN PRODUCT	9.72	9.95	9.37				
•/• PHENAN HYDROG			21.25	50.19	42.25	38.21	39.22

Table A-2 (continued)

RUN NO	5.00	5.00	5.00	15.00	15.00	22.00	29.00
SAMP NO	5.00	6.00	8.00	2.00	3.00	5.00	3.00
MIX NO	2.00	2.00	2.00	2.00	2.00	2.00	2.00
PARAFFINS	1.60	1.53	0.14	0.65	0.50		0.46
PARAFFINS	0.12	0.12	0.11				
BENZ OR CYCLOHEX	0.11	0.10	0.10				
TOL OR METHYLCYCLOHEX							
METHYLPIPERIDINE	2.96	2.96	2.86	2.23	2.14	1.59	0.75
ETHYLCYCLOHEXANE	0.22	0.20	0.19				
ETHYLBENZENE	5.80	5.82	5.86	0.80	0.72		6.17
XYLENES							
PICOLINE				6.46	6.48	6.25	2.35
TRIMETHCYCLOHEX	2.71	2.65	2.65				0.65
?							
MESITYLENE	44.18	44.24	44.24	46.89	46.89	46.89	46.24
T-DECALIN	0.43	0.35	0.41			0.13	
C-DECALIN	0.26	0.17	0.26			0.19	
O-ETHYLANILINE							
O-PROPYLANILINE				2.55	2.44		
TETRALIN	6.77	6.84	6.95			1.31	5.57
NAPH A/O BENZTHIO	0.27	0.25	0.28	6.23	6.28	3.76	1.45
INDOLINE				0.34	0.33		1.17
3-*METHYLINDOLE*	1.23	1.19	1.34				1.40
? (FROM INDOLE)							
QUINOLINE				1.81	1.78	1.21	0.86
INDOLE				5.81	5.79	6.74	4.19
?							
TETRAHYDROQUINOLINE	0.29	0.23	0.30	6.01	5.99	6.05	4.84
CYCLOHEXCYCLOHEX	0.65	0.61	0.70	0.20			
DIPHENYL ETHER	0.37	0.33	0.43	0.14	0.55	0.15	
CYCLOHEXBENZ	0.14	0.11	0.18	0.24	0.37	0.19	0.89
PHP							
PHP	0.26	0.20	0.32				
α-*NAPHTHOL OR PHP*	0.13	0.06	0.19	4.08	3.94	2.88	
PHP	0.29	0.19	0.37	0.29	0.28	0.36	
OHP	1.33	1.19	1.45			0.36	
OHP	0.91	0.81	1.05	0.80	0.76	0.69	2.69
DHP + OHP	3.10	3.03	3.21				0.57
THP	2.01	0.19	2.18				1.17
PHENANTHRENE	1.03	0.99	1.24	8.89	8.36	8.56	0.61
TIME	6.00	7.00	18.00	13.00	16.00	21.00	24.00
CATALYST	7.00	7.00	7.00	8.00	8.00	10.00	11.00
DES	98.00			48.00		34.00	96.00
DEN	81.00			5.80		28.00	32.00
DEO	83.00			6.40			52.00
%H IN PRODUCT	9.12			8.29		8.16	9.30
%PHENAN HYDROG	40.24	40.87	40.70	7.51	7.59	9.61	41.20

Table A-2 (continued)

RUN NO	6.00	6.00	6.00	10.00	7.00	8.00	31.00
SAMP. NO	4.00	5.00	6.00	4.00	4.00	4.00	9.00
MIX NO	2.00	2.00	2.00	2.00	2.00	2.00	2.00
PARAFFINS	0.72	0.85	0.78		0.11	0.44	1.70
PARAFFINS	0.02	0.02	0.07			0.02	0.09
BENZ OR CYCLOHEX	0.04	0.03	0.01			0.02	0.09
TOL OR METHYLCYCLOHEX						0.03	
METHYLPIPERIDINE	0.93	1.30	1.24	0.56	0.20	1.25	3.51
ETHYLCYCLOHEXANE							0.31
ETHYLBENZENE	6.16	6.11	6.13	5.59	4.47	6.11	6.13
XYLENES							
PICOLINE	1.06	1.03	1.10	0.77	3.05	2.02	4.52
TRIMETHCYCLOHEX	1.32	1.26	1.29	1.28	0.18	0.43	
?							
MESITYLENE	45.57	45.63	45.60	45.61	46.71	46.46	46.89
T-DECALIN	0.20	0.18	0.19			0.10	0.50
C-DECALIN	0.09		0.17			0.07	0.27
O-ETHYLANILINE							
O-PROPYLANILINE							
TETRALIN	7.20	7.42	7.41	7.25	5.04	6.22	7.12
NAPH A/O BENZTHIO	0.58	0.59	0.61	0.62	2.27	1.03	0.18
INDOLINE	0.69	0.73	0.63	0.62	1.03	1.06	0.32
3-METHYLINDOLE	1.54	1.78	1.81	1.54	0.56	1.05	0.99
? (FROM INDOLE)							
QUINOLINE					0.83	0.22	
INDOLE	2.39	2.31	2.33	2.34	4.18	3.38	0.29
?							
TETRAHYDROQUINOLINE	2.67	2.67	2.67	2.93	5.80	1.68	0.79
CYCLOHEXCYCLOHEX	0.16	0.16	0.14			0.11	0.39
DIPHENYL ETHER						0.11	0.17
CYCLOHEXBENZ	0.21	0.18	0.12			0.30	
PHP							
PHP							0.47
α-NAPHTHOL OR PHP	0.15	0.39	0.04			0.18	0.21
PHP						0.15	0.30
OHP	0.50	0.46	0.35	0.34		0.20	1.40
OHP	2.02	2.02	1.87	2.04	2.07	2.57	0.73
DHP + OHP	0.86	0.83	0.71	0.65		0.21	3.40
THP	1.06	1.04	0.86	0.92	0.33	0.79	1.49
PHENANTHRENE	4.83	4.72	4.60	46.00	6.21	5.72	1.00
TIME	17.00	23.50	24.00	22.00	22.00	22.00	36.00
CATALYST	12.00	12.00	12.00	13.00	14.00	15.00	16.00
DES			95.00	89.00	71.00	93.00	84.00
DEN			74.00	36.00	6.00	36.00	84.00
DEO			75.00		67.00	45.00	66.00
o/o H IN PRODUCT			8.84	9.52	8.89	9.10	10.18
o/o PHENAN HYDROG	23.30	25.34	21.39	22.65	14.80	22.52	42.66

Table A-2 (continued)

RUN NO	31.00	31.00	33.00	51.00
SAMP NO	10.00	11.00	2.00	4.00
MIX NO	2.00	2.00	2.00	2.00
PARAFFINS	2.09	2.03		
PARAFFINS	0.11	0.08		
BENZ OR CYCLOHEX	0.09	0.06		
TOL OR METHYLCYCLOHEX				
METHYLPIPERIDINE	3.52	3.48		0.65
ETHYLCYCLOHEXANE	0.23	0.27		
ETHYLBENZENE	6.49	5.96	0.22	
XYLENES				
PICOLINE	4.43	4.56	7.20	9.58
TRIMETHCYCLOHEX				
?				
MESITYLENE	46.89	46.89	46.89	46.89
T-DECALIN	0.47	0.44		
C-DECALIN	0.26	0.32		
O-ETHYLANILINE				
O-PROPYLANILINE				
TETRALIN	7.41	6.95	0.30	0.48
NAPH A/O BENZTHIO	0.21	0.30	5.52	11.09
INDOLINE	0.24			
3-METHYLINDOLE	1.10	0.57		
? (FROM INDOLE)				
QUINOLINE			1.72	11.34
INDOLE	0.29		11.40	5.78
?				
TETRAHYDROQUINOLINE	0.77	0.65	4.84	
CYCLOHEXCYCLOHEX	0.40			
DIPHENYL ETHER	0.13			
CYCLOHEXBENZ				
PHP				
PHP	0.42	0.37		
α-NAPHTHOL OR PHP	0.19	0.24	5.23	5.46
PHP	0.29			1.62
OHP	1.39	1.29		
OHP	0.86		0.42	0.39
DHP + OHP	3.30	3.90		
THP	1.47	0.34		
PHENANTHRENE	1.10	0.30	8.72	8.75
TIME	42.00	44.00	27.00	20.00
CATALYST	16.00	16.00	17.00	30.00
DES	97.00		-33.00	
DEN	84.00			
DEO	77.00		-20.00	
o/o H IN PRODUCT	10.13		7.27	
o/o PHENAN HYDROG	41.95	44.07	2.62	15.98

CATALYST KEY

1. Vycor
5. Fresh Amocat 1B
6. Equilibrium 1442A (PDU-5)
7. Fresh 1442A
8. Lake Manganese Nodules
10. Pacific Ocean Manganese Nodules
11. Used 1442A (177-130)
12. Used Cyanamid NiMo (177-131)
13. Used Armak NiMo (177-134)
14. Used Amocat 1B (177-136)
15. Used Amocat 1A (177-137)
16. Fresh Cyanamid NiMo
17. Wilsonville Reactor Solids
30. Iron Pyrite
37. Fresh Armak NiMo
38. Fresh Amocat 1A

Table A-3

RUN NUMBER	62.20	62.40	71.20	72.30	68.20	74.20	64.20
PARAFFIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIMETHYLCYCLOHEXANE	0.00	0.00	2.40	0.50	1.28	0.00	0.71
TRIMETHYLCYCLOHEXANE	0.00	0.00	2.48	0.69	1.23	0.00	0.83
XYLENES	0.00	0.00	0.38	0.20	1.48	0.00	0.29
MESITYLENE	89.49	80.41	84.48	89.24	76.40	89.14	89.65
TRIMETHYLBENZENE	1.39	10.12	2.61	0.00	11.61	2.02	0.00
DECALIN	0.00	0.00	0.00	0.00	0.59	0.00	0.00
DECALIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00
METHYLINDAN	0.00	0.00	0.00	0.00	0.33	0.00	0.00
TETRALIN	0.00	0.00	0.27	0.12	0.60	0.00	0.12
UNKNOWN	0.00	0.00	0.09	0.06	0.24	0.00	0.03
NAPHTHALENE	0.00	0.00	1.03	0.33	0.66	0.08	0.32
ETHYLDECALIN	0.00	0.00	0.47	0.20	0.53	0.00	0.16
ETHYLHEXAHYDRONAPHTH	0.00	0.00	0.16	0.00	0.25	0.06	0.00
ETHYL METHYL INDAN	0.00	0.00	1.03	1.77	0.68	0.36	1.59
ETHYLTETRALIN	0.00	0.00	3.36	6.00	2.33	0.86	4.75
ETHYLTETRALIN	0.00	0.00	1.23	0.00	1.30	0.15	0.00
ETHYLNAPHTHALENE	9.12	9.47	0.00	0.89	0.48	7.32	1.54
TEMP, °F	775	775	775	775	775	775	775
CATALYST	1	1	5	6	7	8	11

Table A-3 (continued)

RUN NUMBER	59.20	59.40	59.60	69.20	65.20	63.20
PARAFFIN	0.00	0.00	0.00	0.00	0.00	0.00
TRIMETHYLCYCLOHEXANE	0.87	1.40	0.37	1.53	0.08	0.73
TRIMETHYLCYCLOHEXANE	1.34	1.78	5.77	2.23	0.11	1.04
XYLENES	0.16	1.83	0.00	0.22	0.17	0.23
MESITYLENE	88.03	84.13	84.05	85.22	91.65	89.33
TRIMETHYLBENZENE	0.00	2.12	0.00	1.89	0.00	0.00
DECALIN	0.00	0.00	0.00	0.00	0.00	0.00
DECALIN	0.00	0.00	0.00	0.00	0.00	0.00
METHYLINDAN	0.13	0.29	0.00	0.00	0.00	0.00
TETRALIN	0.07	0.06	0.00	0.11	0.09	0.09
UNKNOWN	0.00	0.07	0.00	0.05	0.00	0.03
NAPHTHALENE	0.50	0.66	0.27	0.82	0.09	0.43
ETHYLDECALIN	0.22	0.21	0.14	0.40	0.00	0.23
ETHYLHEXAHYDRONAPHTH	0.00	0.00	0.00	0.12	0.00	0.00
ETHYL METHYL INDAN	1.78	1.22	2.43	1.38	1.65	1.51
ETHYLTETRALIN	6.03	3.11	6.68	4.13	3.03	5.26
ETHYLTETRALIN	0.00	0.39	0.00	1.09	0.00	0.00
ETHYLNAPHTHALENE	0.86	2.74	0.29	0.82	3.13	1.12
TEMP, °F	775	850	700	775	775	775
CATALYST	12	12	12	13	14	15

RUN NUMBER	61.20	61.40	61.60	66.20	67.20	70.20
PARAFFIN	0.00	0.00	0.44	0.00	0.00	0.00
TRIMETHYLCYCLOHEXANE	0.79	3.50	5.66	0.00	4.17	1.93
TRIMETHYLCYCLOHEXANE	0.89	3.66	4.89	0.00	4.19	2.09
XYLENES	0.23	0.52	4.82	0.00	0.81	0.47
MESITYLENE	86.92	82.99	71.87	90.02	81.45	83.70
TRIMETHYLBENZENE	0.00	0.00	4.72	0.00	2.08	2.16
DECALIN	0.00	0.11	0.61	0.00	0.00	0.00
DECALIN	0.00	0.00	0.21	0.00	0.00	0.00
METHYLINDAN	0.00	0.09	0.10	0.00	0.00	0.00
TETRALIN	0.11	0.35	1.52	0.00	0.30	0.29
UNKNOWN	0.00	0.13	0.13	0.00	0.19	0.11
NAPHTHALENE	0.72	1.50	1.08	0.00	1.50	0.95
ETHYLDECALIN	0.37	0.58	0.24	0.00	0.60	0.46
ETHYLHEXAHYDRONAPHTH	0.12	0.12	0.11	0.00	0.15	0.62
ETHYL METHYL INDAN	2.43	1.20	0.54	0.00	0.89	1.51
ETHYLTETRALIN	6.86	4.29	1.47	0.00	2.70	4.25
ETHYLTETRALIN	0.00	0.00	0.30	0.00	0.85	1.05
ETHYLNAPHTHALENE	0.56	0.97	1.28	9.98	0.12	0.41
TEMP, °F	700	775	850	775	775	775
CATALYST	16	16	16	30	37	38