

Upgrading Coal Liquids

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FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

PREFACE

Our current dependence on petroleum is a natural result of economic forces: petroleum products until recently were much cheaper than liquid hydrocarbons derived from other sources such as coal, oil shale, and tar sands. We have also developed over the years transportation and domestic uses for liquid fuels that could be produced from petroleum at a relatively low cost. As the supply of petroleum becomes shorter, the alternative of synthetic fuels, derived from hydrocarbon resources other than petroleum, becomes more attractive, provided that they can be upgraded to suit our needs. If synthetic fuels could not be refined to suit our existing uses, we would be forced at an extraordinarily high expense to reinvent, redesign, and replace much of our end use equipment. Therefore, both production and upgrading of synfuels are critical to the goal of developing alternative energy resources.

Although coal can be used directly in many stationary power plants equipped with appropriate environmental safeguards, it must be converted to a liquid before it can serve as a substitute for present-day transportation fuels or home heating oils. Liquids have been obtained from coal for many years. However, as a direct result of recent energy shortages, a major effort is now being made to develop new and improved coal liquefaction technologies.

Typically, liquids derived from coal are lower in hydrogen content and contain more impurities than do petroleum products. These impurities consist of atoms other than hydrogen and carbon, that is, nitrogen, sulfur, oxygen, and inorganic materials. Upgrading of coal liquids to make specification fuels typically involves both hydrogen addition and removal of impurities.

This book presents results of studies representative of the type of work in progress today on the upgrading of coal liquids. Information is presented on composition of coal liquids, the chemistry of upgrading, a variety of processing routes, catalyst evaluations, biological tests, and cost studies. Most of the chapters in this book were originally presented at the 179th National Meeting of the American Chemical Society in March

of 1980; many of them have been revised and updated. It is our hope that this book will serve as a convenient reference for those currently involved in related research areas and will serve as a building block for future work.

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November 7, 1980

The Composition of Liquids From Coals of Different Rank

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Among the many reports in the literature on coal liquefaction, several indicate a relationship between the rank of the coal and the complexity of the hydrocarbon groups in the coal and in its liquefaction products. This subject was reviewed in some detail in previous reports (1,2) and will only be summarized and updated here.

Background

Early German work indicated that the lower-rank brown coals (lignite) are more reactive, require less hydrogen pressure, and produce smaller polynuclear hydrocarbon units (3) than bituminous coals. Also, the asphaltene content of the coal liquids decreases with the coal rank to a minimum for sub-bituminous coals. Early work by the U.S. Bureau of Mines produced similar results (4). Low-rank coals were found to be so reactive that, at a reaction temperature of 430° C, high hydrogen pressure was required to prevent repolymerization of reactive fragments to coke. More recent studies have shown that the product from the liquefaction of a Utah sub-bituminous coal with hydrogen donor solvent (5) contains less benzene insoluble material than that from Pittsburgh bituminous coal.

Although the literature suggests that the complexity of hydrocarbon groups in coal and coal liquefaction products can differ substantially with the rank of the coal, specific data are limited and sometimes appear to be contradictory. A recent report on the comparison of solvent-refined lignite and solvent-refined sub-bituminous and bituminous coals (6) indicates hardly any difference among the products in terms of gross combustion analysis; acid and basic titres; molecular weight; and nuclear-magnetic resonance, ultraviolet, and electron-spin-resonance spectra. Only the nitrogen content of the coal was reflected in the solvent-refined products. However, in another recent study of a lignite, a bituminous coal, and an anthracite coal, analysis of the organic compounds trapped in the coals and contained in the products of selective

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oxidation indicated an increased condensation of aromatic rings with increasing rank (7). Analysis was performed by gas chromatography/time-of-flight mass spectrometry and high-resolution mass spectrometry. Furthermore, an extensive, detailed study revealed compositional differences in the pyridine extracts of three coals of different rank and also in their liquefaction products produced by the Synthoil process (8). For example, larger quantities of saturates and higher percentages of lower ring-number saturate compound types were observed in the two higher rank coal extracts. However, the ring distributions of the aromatic fractions from the coal extracts indicated slightly higher average ring numbers for the higher rank coals.

Similar results were obtained in a study characterizing liquid products obtained from six coals of different rank by treatment of the coals with NaOH-alcohol for 1 hour at 300° to 350° C (9). Characterization by elemental analysis, molecular-weight determination, and proton NMR indicated that the younger (lower-rank) coals gave simpler products with primarily two-ring, tetralin-type nuclei and more abundant ether linkages than the higher-rank bituminous coals which yielded products with five to six rings, about two of which were naphthenic. Similarly, in Japanese studies of pyridine extracts of coals of different rank (10), analysis by proton NMR indicated more condensed aromatic rings with less substitution and shorter aliphatic chains in the higher-rank-coal extracts. Extracts from bituminous coals contained an average of four or five aromatic rings with side chains averaging three or four carbons in length, whereas a lignite extract had an average of one or two aromatic rings with seven- or eight-carbon, aliphatic side chains. Finally, a study using carbon-13 NMR to characterize a hard-coal-tar pitch and a brown-coal-tar pitch indicated a predominance of fused-aromatic-ring systems with small amounts of methyl and hydroaromatic methylene groups for the hard-coal-tar pitch (11). The results for the brown-coal-tar pitch indicated primarily long, straight-chain aliphatics estimated at 25 to 40 carbon atoms in length.

The coal liquids characterized at the Bartlesville Energy Technology Center previous to this study have come from different projects in which the primary objective was the development of a specific process. This precluded a systematic study of the relationship of coal rank to coal liquid composition, which is the objective of this study.

Eight coal liquids prepared from six coals (1,2) of widely differing rank were characterized by procedures previously developed for petroleum (12,13,14) and by ASTM methods. The liquids were prepared and upgraded by hydrogenation in a batch autoclave under conditions intended to minimize cracking of the hydrocarbons (especially those of cyclic and aromatic structure) and yet produce most of the liquid hydrocarbons potentially obtainable from a given coal. The extent of the hydrogenation/hydrogenolysis (henceforth referred to as hydrogenation) of the raw coal liquids

was adjusted as required to decrease the nitrogen content to about 0.2 to 0.3 weight-percent with the additional intent of providing a predominantly hydrocarbon liquid for analysis. Details of the coal liquid preparations have been reported previously (1,2). This report covers the characterization of the coal liquids and possible implications in relation to refining.

Experimental Procedures

Coal Liquid Preparations. The coal liquids were produced in two stages as previously described in detail (1). In the first stage, crude coal liquids were produced by hydrogenation of a coal/tetralin slurry in a batch autoclave with 60-100 mesh Cyanamid Aero HDS-3A catalyst (3.2 wt-pct NiO and 15.1 wt-pct MoO₃ on an alumina support) at about 2,500 psig total pressure over a temperature program which increased slowly to a maximum of 400° C. In subsequent runs with a given coal, filtered product liquid from the previous run was used to slurry the coal. After the tetralin content of the liquid product decreased to 5 percent or less, three or four additional runs were made. All liquids with less than 5 percent tetralin were combined as the crude coal liquid.

In the second stage of coal liquid preparation, the crude coal liquids were upgraded in the batch autoclave with presulfided Aero HDS-3A catalyst under conditions designed to decrease the nitrogen content to a targeted range of 0.2 to 0.3 weight percent. One exception was a sample of liquid from the Wyodak coal which, for comparison purposes, was upgraded on the same time-temperature program as that required to upgrade the Illinois No. 6 run 2 crude liquid. In every case the maximum temperature employed was 400° C or less.

Distillations. The upgraded coal liquids were distilled with a metal-mesh-spinning-band still under the conditions shown in Figure 1 to produce cuts at 200°, 325°, and 425° C. Asphaltenes were then precipitated from each >425° C residuum dissolved in benzene by addition of 50 volumes of normal pentane (15). Further distillations on the asphaltene-free materials, at 202° C and 4 micron pressure using a wiped-wall molecular still, produced 425° to 540° C distillate cuts and residua fractions.

Separations and Analyses. After removal of trace amounts of acids and bases from the <200° C distillates by extraction methods (16), a chromatographic separation with silica gel provided a check for the presence of olefins. No olefins were detected; thus, the acid- and base-free distillates were analyzed by ASTM D2789-71, Standard Method of Test for Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry. The separation and analysis scheme for this distillate is shown in Figure 2.

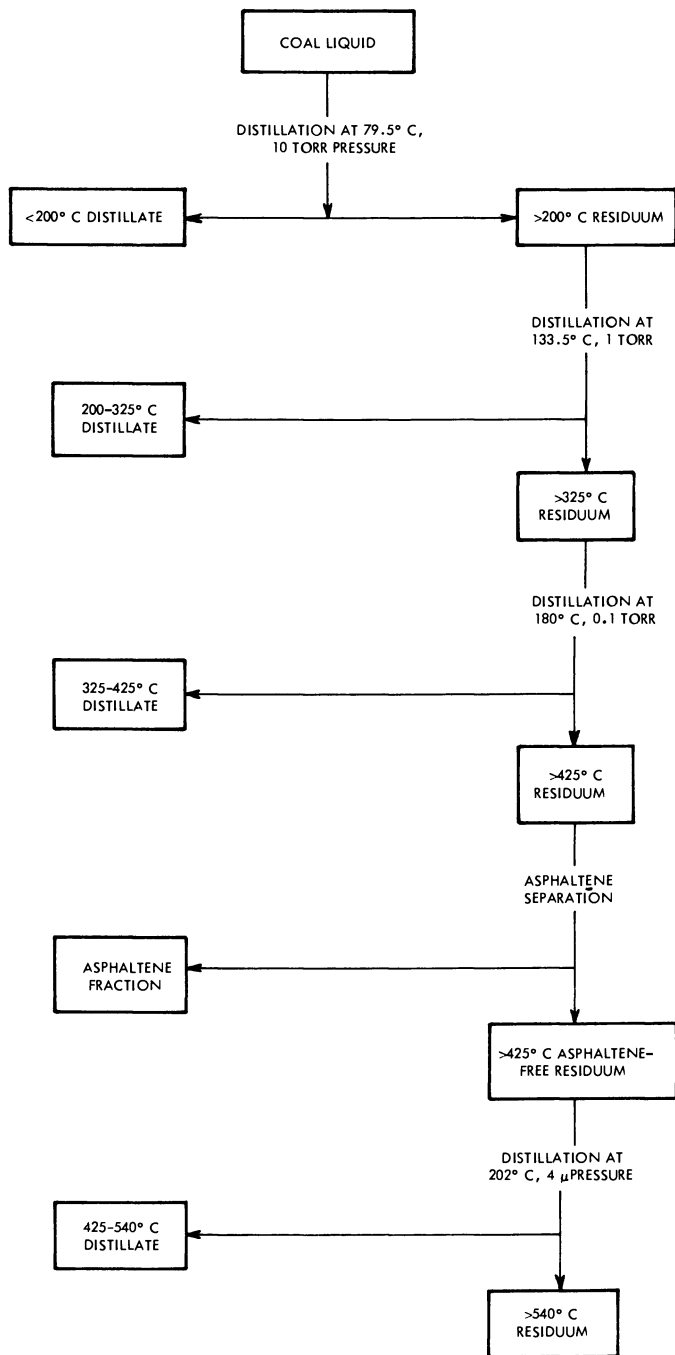


Figure 1. Distillation scheme for coal liquids

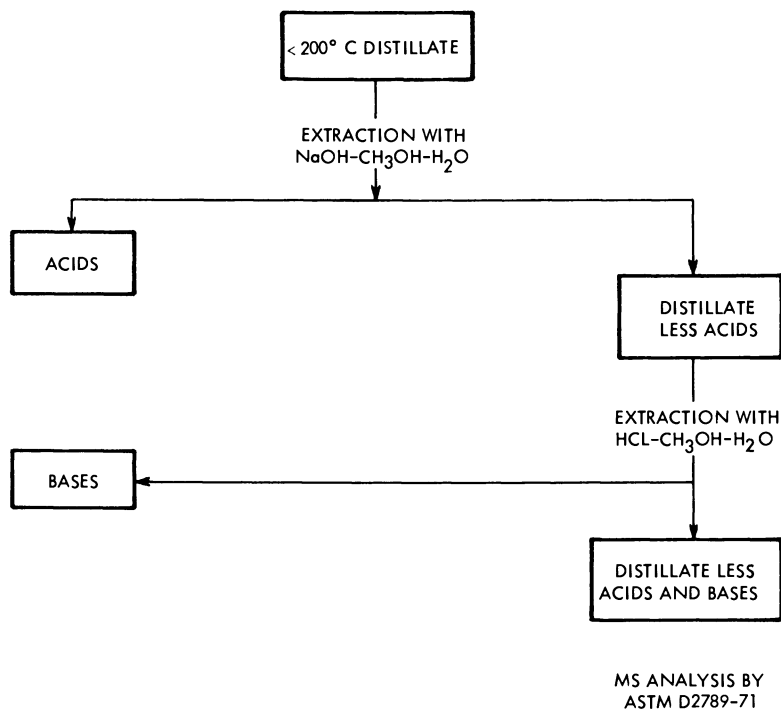


Figure 2. Separation and analysis scheme for < 200° C coal liquid distillates

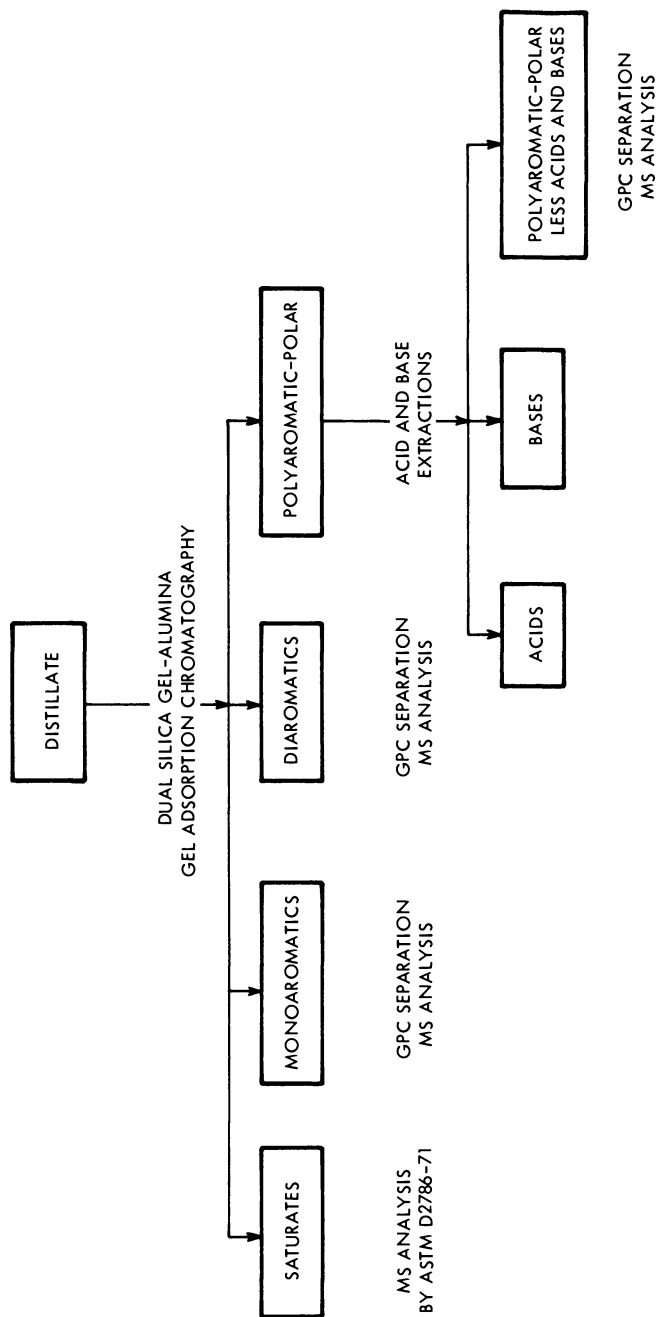


Figure 3. Characterization scheme for 200°–325° C, 325°–425° C, and asphaltene-free 425°–540° C coal liquid distillates

The higher-boiling distillates were characterized by methods adapted from the characterization of heavy ends of petroleum (12, 14). A schematic of the procedure is shown in Figure 3. Details of the procedures have been reported previously (12,14,16,17). Analyses of subfractions of aromatic concentrates separated by gel-permeation chromatography (GPC) were performed on a low-resolution CEC 21-103C mass spectrometer (MS) using low-ionizing-energy electrons to produce predominantly molecular ions. Compound-type assignments were made by means of previously established GPC-MS correlations and high-resolution mass spectral data for selected fractions. High-resolution, 70 eV, mass spectra were obtained on an AEI MS 3074 mass spectrometer. High- and low-resolution field-ionization spectra of selected fractions, primarily poly-aromatic-polar concentrates, were obtained at Oklahoma State University on a CEC Model 21-110 B mass spectrometer fitted with a razor blade source (18).

Results

Properties of Coals and Coal Liquids. Descriptions and analyses of the six coal samples used to prepare the coal liquids are summarized in Table I. Physical and chemical property data for the eight coal liquids prepared from the six coals are summarized in Table II. Included in Table II are data for repeat runs on Illinois No. 6 and Wyodak coals. The repeat run for the Illinois No. 6 coal was made because of changes in the procedure instituted during the first liquefaction run, Illinois No. 6 run 1. The changes involved a switch from CoMo to NiMo catalyst and a decrease in the maximum temperature from 425° to 400° C (1). Also, upgrading of the first Illinois crude liquid did not achieve the targeted value of 0.2 to 0.3 percent nitrogen. The second Wyodak coal liquid was prepared from the same crude liquid as the first by upgrading according to the time-temperature profile used for the Illinois No. 6 run 2 liquid. It was noted previously, that the lower-rank coals reacted more readily and under milder conditions than those of higher rank for both the initial liquefaction and the upgrading of the raw coal liquids (1). Thus, the second Wyodak run was made to determine the effects of increased upgrading upon liquefaction-product composition.

Distillation Results and Distillate Properties. Distillation results for the upgraded coal liquids are also summarized in Table II. The results showed no large differences for the liquids, except for the extensively upgraded second Wyodak liquid which had a higher percentage of low-boiling material. Asphaltene content of the six "normally" upgraded liquids ranged from about 1 to 7 percent. Inclusion of the second Wyodak and first Illinois liquids extended the range of asphaltene content from 0.1 to 14 percent. The asphaltene content correlated with the nitrogen content of the liquids, thus supporting the use of nitrogen content to monitor the extent of coal-liquid upgrading.

Table I. Analysis of Coals, Weight Percent

Source -----	PA-WV	Illinois	W. KY	Montana	Wyoming	N. Dakota
Seam -----	Pittsburgh	No. 6	--	(Colstrip)	(Wyodak)	Beulah Std. II
Rank -----	hvb A	hvb B/C	hvb B/C	Rosebud subb. A	Lower subb. C	Lignite
Proximate analysis, (as received):						
Moisture.....	1.7	7.8	2.9	4.2	10.9	28.0
Volatile matter	35.9	34.2	38.4	34.4	39.5	31.0
Fixed carbon ..	55.1	51.4	48.8	48.5	42.7	33.3
Ash	7.3	6.6	9.9	12.9	6.9	7.7
Ultimate analysis, (moisture free):						
Hydrogen	5.1	4.9	4.9	4.3	4.8	4.5
Carbon	76.9	75.2	70.2	65.2	66.8	63.5
Nitrogen	1.5	1.6	1.4	0.6	1.0	0.9
Sulfur	1.6	1.5	4.3	1.8	0.5	1.3
Oxygen (diff) .	7.6	9.7	8.8	14.5	19.2	19.1
Ash	7.4	7.1	10.2	13.5	7.8	10.7

hvb B/C -- high volatile bituminous B or C
subb. -- subbituminous

Table II. Properties of Crude and Upgraded Coal Liquids

Coal	Illinois No. 6		W. Ky.	Colstrip	Wyodak	Lignite
	Run 1	Run 2				
Nitrogen, wt-pct.....	0.44	1.10	1.28	0.64	0.48	0.43
Oxygen, wt-pct.....	.59	1.34	2.09	1.61	1.08	1.55
Sulfur, wt-pct.....	<.01	<.01	.02	<.01	<.01	<.01
			<u>Crude Liquids</u>			
Sp. gr., 60/60° F ...	0.993	1.006	0.989	0.987	Run 1	Run 2
SUS vis. @ 100° F....	441	129	89	263	0.955	0.922
SUS vis. @ 130° F....	189	65	-	123	96	56
Pour point, °F.....	+5	<+5	<+5	+20	+70	+65
Carbon, wt-pct.....	89.2	90.1	88.2	88.1	88.9	88.0
Hydrogen, wt-pct.....	10.8	9.9	10.7	10.6	11.0	11.9
Sulfur, wt-pct.....	<.01	.03	.02	<.01	<.01	<.01
Nitrogen, wt-pct.....	.20	.444	.287	.192	.095	.250
Oxygen, wt-pct ¹28	.50	.32	.34	.17	.61
Distillation, wt-pct:			<u>Upgraded Liquids</u>			
<200° C.....	10.0	12.3	16.6	11.5	13.9	12.3
200°-325° C.....	21.7	27.3	26.1	21.5	26.7	24.0
325°-425° C.....	20.3	20.7	22.8	21.1	21.3	20.7
425°-540° C ³ ...	26.6	19.1	19.7	20.9	25.2	21.0
>540° C.....	16.2	6.4	9.3	18.4	11.2	15.0
Asphaltenes, wt-pct ...	4.7	14.3	5.2	6.6	1.2	6.7

¹ Determined by neutron activation analysis.² Upgraded on same temperature-time program as Illinois No. 6 Run 2.³ Asphaltenes removed from >425° C residuum.

Table III lists the specific gravity, nitrogen content, and sulfur content of the various distillation fractions obtained from each of the eight coal liquids. Nitrogen content increased for the higher-boiling distillates as expected. All sulfur values were low as expected. Nitrogen contents of the asphaltenes from the bituminous-coal liquids were higher than those from the lower-rank-coal liquids.

Separation, Characterization and Analysis of the Distillate Fractions. Results from the analyses of the <200° C coal-liquid distillates (after removal of trace quantities of acids and bases) are summarized in Table IV. Results from the dual silica-gel/alumina-gel adsorption chromatography separations of the 200° to 325° C, 325° to 425° C, and 425° to 540° C coal-liquid distillates are summarized in Table V. Data for the acid and base extracts of the polyaromatic-polar adsorption fractions are also included in Table V. Summary data on analysis of the saturate fractions are listed in Table VI. Data in Table VI show a trend toward higher percentages of zero- and one-ring saturates in lower-rank coals.

Summary data from GPC-MS characterization of the coal liquid monoaromatic, diaromatic, and polyaromatic-polar concentrates are given in Tables VII, VIII, and IX. The detailed characterization data for adsorption concentrates of each distillate are too extensive for this report and are being published elsewhere (19). Compound type assignments for selected fractions from the GPC separations were checked by high-resolution electron-impact MS. Also, the quantitative results for selected adsorption fractions were checked by high- and low-resolution FI/MS. Some typical results are shown in Table X. In general, the results were consistent except for the indication in the high-resolution EI and FI spectra of very small amounts of additional compound types containing S, NO, NO₂, and O₂ in some of the polyaromatic-polar fractions. Also, the EI results for the -15N and -17N series are somewhat high, probably due to interference from fragment ion peaks.

The characterization results from all fractions for each coal liquid were combined and expressed in terms of compound types containing the same number of total rings (aromatic and naphthenic). This scheme was chosen because of the different degree of saturation of aromatic rings in the upgrading of the crude liquids from different coals, and the fact that liquefaction and upgrading reaction conditions were chosen to minimize hydrocarbon ring cracking reactions. The results are summarized in Tables XI and XII.

Discussion

Adsorption Chromatographic Fractions. Examination of the data of Table V shows a tendency for distillates of lower-rank-coal liquids to contain more saturate material and less polyaromatic-

polar material. However, liquids from the highest- and lowest-rank coals, Pittsburgh and lignite, respectively, do not follow the trend. No trend is readily observed in the 200° to 325° C monoaromatic content of the various coal liquids, although the relatively low values for the Pittsburgh and Wyodak run 2 liquids partially balance their high saturate contents. The 325° to 425° C distillates show a slight trend toward lower monoaromatic content in the lower-rank coal liquids, whereas the 425° to 540° C distillates show an opposite trend (increased monoaromatics for the lower-rank coal liquids) with the exception of the Pittsburgh and lignite liquids. The diaromatic content for each distillate shows a slight trend to lower values for the lower-rank coal liquids with the exception of the Pittsburgh and lignite values for the 200° to 325° C and 325° to 425° C distillates. No trend was observed for the 200° to 325° C distillate polyaromatic-polar (PAP) contents except that the Illinois No. 6 run 1 and lignite values are relatively high. The total liquids from these two coals contained the highest oxygen content (Table II) and the Illinois run 1 liquid was also high in nitrogen. Because of the low PAP content of the 200° to 325° C distillates in general, no attempt was made to separate acids and bases. Thus, the relatively higher PAP values for Illinois run 1 and lignite probably reflect the high oxygen (and nitrogen for Illinois run 1) contents through increased amounts of acids (and bases for Illinois run 1). Correlation of the 200° to 325° C PAP content with the oxygen content of the total crude (oxygen data was not available for the 200° to 325° C distillate) gave a fair correlation coefficient of 0.79.

The polyaromatic-polar contents for the 325° to 425° C and 425° to 540° C distillates show a trend to lower values for the lower-rank coal liquids with the exception of the Pittsburgh and lignite liquids again. No readily apparent reason could be ascertained for the somewhat anomalous behavior of the Pittsburgh and lignite coal liquids. However, in the liquefaction of the Pittsburgh coal a slightly higher pressure was employed (1). This, plus the lower production of water and CO₂ in the Pittsburgh liquefaction, resulted in higher partial pressure of hydrogen and significant upgrading of the crude coal liquid in the liquefaction step. The relatively low nitrogen content of the Pittsburgh crude liquid (0.44 wt-pct) is also consistent with significant upgrading in the liquefaction step. Because of the low nitrogen content of the Pittsburgh crude liquid, a relatively short and low-temperature upgrading was required to bring the nitrogen content down to 0.20 wt-pct, which is at the low end of the desired range (0.2 to 0.3 wt-pct). A net increased upgrading of the Pittsburgh liquid is consistent with lower levels of polyaromatic-polar material and higher levels of saturates and monoaromatics as was observed.

An explanation of the lignite results is likewise not entirely straightforward. Clearly, the lignite coal was more reactive than the higher-rank coals toward liquefaction and upgrading requiring significantly shorter runs (1). The high oxygen content and rel-

Table III. Distillation Fractions of Upgraded Coal Liquids

Coal	Pittsburgh	Illinois No. 6		W. Ky.	Colstrip	Wyodak		Lignite
		Run 1	Run 2			Run 1	Run 2	
<200° C distillate: Sp. gr. Sulfur, wt-pct.... Nitrogen, wt-pct.	0.829 <.01 .003	0.825 <.01 .068	0.827 <.01 .001	0.832 <.01 .096	0.822 <.01 .023	0.819 <.01 .003	0.810 <.01 <.001	0.822 <.01 .007
200°-325° C: Sp. gr. Sulfur, wt-pct.... Nitrogen, wt-pct.	.915 .01 .016	.937 .03 .102	.926 <.01 .021	.919 .02 .062	.918 <.01 .030	.909 <.01 .012	.897 <.01 .002	.916 <.01 .104
325°-425° C: Sp. gr. Sulfur, wt-pct.... Nitrogen, wt-pct.	.983 <.01 .076	1.018 <.01 .396	1.001 <.01 .159	.993 .02 .200	.982 <.01 .119	.972 <.01 .072	.952 <.01 .004	.983 <.01 .304
425°-540° C: Sp. gr. Sulfur, wt-pct.... Nitrogen, wt-pct.	1.045 <.01 .272	1.079 <.01 .594	1.061 <.01 .415	1.049 <.01 .415	1.032 <.01 .233	1.026 <.01 .176	1.001 <.01 .029	1.032 <.01 .412
>540° C resid: Nitrogen, wt-pct.	.420	.709	.576	.565	.348	.275	.052	.518
Asphaltenes: Nitrogen, wt-pct.	.722	1.104	1.004	1.036	.579	.393	.194	.714
>425° C resid: Sulfur, wt-pct.... Nitrogen, wt-pct. Asphaltenes, wt-pct	<.01 .374 9.9	.01 .829 35.9	<.01 .560 17.9	0.04 .573 15.3	.02 .332 14.3	<.01 .219 3.3	<.01 .024 .4	<.01 .501 15.7

† Asphaltene-free.

Table IV. Composition of the <200 °C Distillate Hydrocarbons from Eight Coal Liquids, Weight Percent Total Coal Liquid Basis

Compound Type	Coal Liquid	Pittsburgh	Illinois No. 6		Western Kentucky	Colstrip	Wyodak		Lignite
			Run 1	Run 2			Run 1	Run 2	
O-Ring Paraffin		0.78	0.87	0.77	3.46	1.19	1.76	2.07	1.12
1-Ring Paraffin		4.34	6.20	5.52	7.52	5.41	6.58	9.89	6.18
2-Ring Paraffin		2.91	2.15	2.57	2.81	2.55	2.93	4.65	2.43
Alkylbenzenes		1.49	1.93	1.82	2.25	1.27	1.86	1.36	1.85
Indans/Tetralins		.47	1.08	.71	.57	1.05	.77	.34	.73
Naphthalenes		.01	.06	.02	-	.03	-	-	-

Table V. Fraction Yields from Adsorption Chromatography and Acid-Base Separations, Weight Percent

Coal Liquid Fraction	Illinois No. 6						Western Kentucky	
	Pittsburgh		Run 1		Run 2		Crude	Distillate
	Crude	Distillate	Crude	Distillate	Crude	Distillate		
200 - 325° C Distillate								
Saturates	11.91	54.9	7.92	29.0	11.75	42.1	11.82	45.3
Monoaromatics	7.77	35.8	15.02	55.0	13.81	49.5	12.01	46.0
Diaromatics	1.36	6.3	2.37	8.7	1.54	5.5	1.31	5.0
Polyaromatic-Polar	.36	1.7	2.00	7.3	.80	2.9	.65	2.5
Loss	.30	1.3	.0	.0	.0	.0	.31	1.2
325 - 425° C Distillate								
Saturates	5.44	26.8	2.11	10.2	3.87	17.2	4.92	21.6
Monoaromatics	10.17	50.1	6.91	33.4	9.70	43.1	9.46	41.5
Diaromatics	2.52	12.4	6.42	31.0	5.09	22.6	4.47	19.6
Polyaromatic-Polar	2.13	10.5	5.26	25.4	3.67	16.3	3.97	17.4
PAP Hydrocarbons	1.93	9.53	4.82	23.3	3.40	15.10	3.58	15.7
PAP Acids	.11	.56	.11	.51	.11	.47	.11	.47
PAP Bases	.05	.24	.14	.66	.10	.43	.09	.38
Loss	.08	.40	.19	.90	.23	1.10	.17	.80
425 - 540° C Distillate								
Saturates	2.26	8.8	.53	3.2	.80	3.6	2.17	11.8
Monoaromatics	5.76	22.4	1.30	7.9	1.80	8.1	2.36	12.8
Diaromatics	5.78	22.5	3.60	21.8	4.82	21.7	4.36	23.7
Polyaromatic-Polar	11.87	46.2	11.06	67.0	14.79	66.6	9.27	50.4
PAP Hydrocarbons	11.77	45.8	10.91	66.1	14.54	65.5	9.05	49.2
PAP Acids	.07	.29	.08	.50	.13	.59	.10	.55
PAP Bases	.05	.18	.07	.40	.10	.45	.04	.21
Loss	.01	.03	.01	.10	.01	-	.32	1.7

Table V. Continued

Coal Liquid Fraction	Wyodak				Run 1		Run 2		Lignite		
	Colstrip		Distillate		Crude	Distillate	Crude	Distillate	Crude	Distillate	
	Crude	Distillate	Crude	Distillate	Crude	Distillate	Crude	Distillate	Crude	Distillate	
200 - 325° C Distillate											
Saturates	10.75	50.0	15.06	56.4	22.73	75.0	11.71	48.8	11.71	48.8	
Monoaromatics	8.92	41.5	10.12	37.9	6.24	20.6	10.13	42.2	10.13	42.2	
Diaromatics	1.01	4.7	1.01	3.8	.51	1.7	1.02	4.2	1.02	4.2	
Polyaromatic-Polar	.77	3.6	.51	1.9	.48	1.6	1.15	4.8	1.15	4.8	
Loss	.05	.2	.0	.0	.34	1.1	.0	.0	.0	.0	
325 - 425° C Distillate											
Saturates	5.84	27.7	6.99	32.8	11.77	61.6	5.22	25.2	5.22	25.2	
Monoaromatics	8.52	40.4	8.48	39.8	4.22	22.1	7.87	38.0	7.87	38.0	
Diaromatics	3.19	15.1	3.11	14.6	1.64	8.6	3.29	15.9	3.29	15.9	
Polyaromatic-Polar	3.42	16.2	2.73	12.8	1.47	7.7	4.06	19.6	4.06	19.6	
PAP Hydrocarbons	3.17	15.0	2.56	12.0	1.34	7.0	3.62	17.5	3.62	17.5	
PAP Acids	.09	.41	.08	.37	.10	.52	.16	.76	.16	.76	
PAP Bases	.08	.37	.03	.13	.01	.03	.18	.88	.18	.88	
Loss	.21	1.0	.05	.25	.02	.15	.36	1.7	.36	1.7	
425 - 540° C Distillate											
Saturates	3.15	15.6	4.96	19.7	8.86	35.0	2.70	13.8	2.70	13.8	
Monoaromatics	3.47	17.2	4.96	19.7	5.46	21.6	2.88	14.7	2.88	14.7	
Diaromatics	4.38	21.7	4.79	19.0	3.74	14.8	3.49	17.8	3.49	17.8	
Polyaromatic-Polar	9.19	45.5	10.48	41.6	7.24	28.6	10.29	52.5	10.29	52.5	
PAP Hydrocarbons	8.79	43.5	10.21	40.5	6.93	27.4	10.09	51.5	10.09	51.5	
PAP Acids	.12	.59	.09	.34	.14	.55	.11	.58	.11	.58	
PAP Bases	.03	.14	.03	.11	.02	.06	.11	.54	.11	.54	
Loss	.26	1.2	.16	.63	.15	.60	.22	1.1	.22	1.1	

1 Total coal liquid basis.

Table VI. Summary of Ring Distributions of the Saturate Concentrates from Eight Coal Liquids, Weight Percent Total Coal Liquid Basis

Mass Z Series	Ring Number	Pittsburgh	Illinois No. 6		Western Kentucky	Colstrip	Wyodak		Lignite
			Run 1	Run 2			Run 1	Run 2	
+2	0	1.79	2.07	1.86	4.79	4.42	5.69	6.22	3.59
0	1	10.02	8.74	9.60	12.32	9.79	14.06	19.62	11.92
-2	2	7.63	5.02	7.28	7.87	7.24	9.91	15.95	7.80
-4	3	4.67	2.22	3.77	4.22	4.13	4.94	10.04	3.42
-6	4	2.17	1.38	1.89	2.17	2.21	2.33	5.25	1.72
-8	5	1.01	.06	.70	.84	.82	1.03	2.13	.66
-10	6	.25	.06	.09	.30	.25	.28	.67	.17
MA	1	.10	.23	.09	.20	.06	.06	.06	.07

Table VII. Semiquantitative Analysis of the Monoaromatic Concentrates from Eight Coal Liquids, Weight Percent Total Liquid Basis

Mass Z Series	Ring Number	Pittsburgh		Illinois No. 6		Western Kentucky		Colstrip		Wyodak		Lignite	Probable Compound Types
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2		
-6	1	1.96	2.46	3.13	2.47	1.87	2.75	1.91	2.41	Alkylbenzenes.			
-8	2	4.03	7.64	5.78	7.53	4.90	5.36	3.05	5.90	Alkylindans/tetralins.			
-10	3	5.47	8.37	7.13	8.51	5.42	6.79	4.25	6.95	Alkylindanaphthenobenzenes.			
-12	4	6.06	4.28	4.62	5.03	4.52	5.16	3.48	4.33	Alkyltrinanaphthenobenzenes.			
-14	5	3.57	1.77	2.54	2.12	2.75	3.05	2.33	2.07	Alkyltetranaphthenobenzenes.			
-16	6	1.86	.61	1.15	.96	1.36	1.47	1.32	.92	Alkylpentanaphthenobenzenes.			
-18	7	.70	.22	.42	.34	.61	.67	.61	.31	Alkylhexanaphthenobenzenes.			
-20	8	.29	.08	.16	.15	.21	.29	.26	.14	Alkylheptanaphthenobenzenes.			
-22	9	.10	.03	.05	.05	.07	.13	.10	.05	Alkyloctanaphthenobenzenes.			
-24	10	.02	.01	tr	.02	tr	.03	tr	.02	Alkylnonanaphthenobenzenes.			
0,-14	-				.01					Unknown.			
-2,-16	-				.06					Unknown.			
-4,-18	-				.01					Unknown.			
-6,-20	-				.03	.02				Unknown.			
-8,-22	-				.01					Unknown.			
-10,-24	-				.06					Unknown.			
NA		.62	.59	.55	.31	.37	.37	.26	.20	Material not analyzed, insufficient sample.			
Loss		.00	.20	.00	.21	.15	.12	.05	.15	Material lost in GPC separations.			

1. Contains small amounts of oxygenates also, probably benzofuran types.

Table VIII. Semiquantitative Analysis of the Diaromatic Concentrates from

Mass Z Series	Ring Number	Pittsburgh	Illinois No. 6		Western Kentucky	Colstrip	Wyodak	
			Run 1	Run 2			Run 1	Run 2
-12	2	¹ 0.23	0.77	0.49	0.46	0.35	0.34	0.18
-14	2 or 3	.92	2.69	2.05	¹ 1.71	1.28	¹ 1.41	.87
-16	3 or 4	¹ 1.86	3.17	2.80	¹ 2.39	1.94	¹ 2.10	1.34
-18	4 or 5	1.91	2.26	2.20	¹ 1.97	1.72	1.81	1.25
-20	5 or 6	1.66	1.55	1.79	¹ 1.59	1.32	1.37	.93
-22	6 or 7	1.10	.97	1.11	1.00	.94	.91	.59
-24	7 or 8	¹ .62	.39	.50	.50	.53	.52	.33
-26	8 or 9	.31	.15	.21	.21	.27	.27	.15
-28	9 or 10	.14	.05	.06	.07	.09	.12	.05
-30	10 or 11	.03	.01	.02	.02	.01		.01
-6,-20	-							.01
-8,-22	-			tr		tr		.01
-10,-24	-		.04	.01	.01	.01	.02	.03
-12,-26	-	.01				tr		
-14,-28	-					tr		
-16,-30	-							.01
-18,-32	-							.01
-8(0)	2	.04						
-10(0)	2 or 3	.29						
-12(0)	3	.32						
-14(0)	3 or 4		.01					
-16(0)	3 or 4		.08					
-18(0)	4		.15					
-20(0)	4 or 5		.02					
NA	-	.24	.13	.22	.17	.14	.07	.12
Loss	-	.00	.02	.00	.02	.01	.02	.00

¹ Contains small amounts of oxygenates also, probably benzofuran or dibenzofuran types.

Eight Coal Liquids, Weight Percent Total Coal Liquid Basis

Lignite	Probable Compound Types
0.35	Alkyl naphthalenes.
1.46	Alkyl naphthenonaphthalenes and/or diphenylalkanes.
2.09	Alkyl dinaphthenonaphthalenes and/or naphthenodiphenylalkanes.
1.65	Alkyl trinaphthenonaphthalenes and/or dinaphthenodiphenylalkanes.
1.06	Alkyl tetranaphthenonaphthalenes and/or trinaphthenodiphenylalkanes.
.57	Alkyl pentanaphthenonaphthalenes and/or tetranaphthenodiphenylalkanes.
.27	Alkyl hexanaphthenonaphthalenes and/or pentanaphthenodiphenylalkanes.
.12	Alkyl heptanaphthenonaphthalenes and/or hexanaphthenodiphenylalkanes.
.05	Alkyl octanaphthenonaphthalenes and/or heptanaphthenodiphenylalkanes.
.01	Alkyl nonanaphthenonaphthalenes and/or octanaphthenodiphenylalkanes.
	Unknown.
	Unknown.
	Unknown.
	Unknown.
	Unknown.
	Unknown.
tr	Alkyl benzodihydrofurans.
.01	Alkyl benzofurans.
.02	Alkyl naphthenobenzofurans.
tr	Alkyl dinaphthenobenzofurans.
tr	Alkyl trinaphthenobenzofurans and/or alkyl dibenzofurans.
	Alkyl naphthenodibenzofurans.
	Alkyl dinaphthenodibenzofurans.
.15	Not analyzed, insufficient sample in GPC fractions.
.00	Material lost in GPC separations.

Table IX. Semiquantitative Analysis of the Polyaromatic-Polar Concentrates

Mass Z Series	Ring Number	Pittsburgh	Illinois No. 6		Western Kentucky	Colstrip	Wyodak	
			Run 1	Run 2			Run 1	Run 2
-16	3	0.67	¹ 1.18	0.64	¹ 0.45	¹ 0.67	0.50	¹ 0.45
-18	3 or 4	¹ 1.07	¹ 1.57	¹ 1.12	¹ 1.05	¹ 1.25	¹ 1.18	¹ .73
-20	4 or 5	¹ 1.79	¹ 1.86	¹ 1.59	¹ 1.49	¹ 1.70	¹ 1.75	¹ 1.32
-22	4-6	¹ 2.30	¹ 2.59	¹ 2.48	¹ 2.16	¹ 2.36	¹ 2.31	¹ 1.71
-24	4-7	¹ 2.51	¹ 2.42	¹ 3.02	¹ 2.07	¹ 2.23	¹ 2.20	¹ 1.68
-26	≥5	¹ 1.64	¹ 1.61	¹ 2.14	¹ 1.39	¹ 1.52	1.49	.98
-28	≥5	¹ .90	¹ 1.15	¹ 1.56	¹ .89	¹ .93	.94	.56
-30	≥5	¹ .40	¹ .85	¹ 1.14	¹ .56	¹ .54	.58	.34
-32	≥6	¹ .21	.53	¹ .75	.30	.23	.29	.16
-34	≥6	.04	.21	.33	.05	.03	.17	.05
-36	>6	tr	.10	.15	.01	.01	.05	tr
-38	>6	tr	-	-	tr	-	-	-
-8(0)	2	-	-	-	.02	-	-	-
-10(0)	2	-	-	-	.01	.01	-	-
-12(0)	3	.03	-	.01	.04	.02	² .03	tr
-14(0)	4	.06	.04	.03	.11	.09	² .05	.06
-16(0)	3-5	.22	² .23	.14	.32	.36	² .45	.11
-18(0)	4-6	.11	.31	.18	.25	.15	.16	-
-20(0)	5-7	-	.12	.05	.10	tr	.01	-

¹ Contains small amounts of oxygenates also.

² Contains significant amounts of hydrocarbon material also.

from Eight Coal Liquids, Weight Percent Total Coal Liquid Basis

Lignite	Probable Compound Types
0.52	Alkylacenaphthalenes/Fluorenes.
¹ 1.44	Alkylnapthenoacenaphthalenes/Fluorenes and/or Alkylphenanthrenes/Anthracenes.
¹ 1.92	Alkyldinaphthenoacenaphthalenes/Fluorenes and/or Alkylnapththenophenanthrenes/Anthracenes.
¹ 2.25	Alkyltrinaphthenoacenaphthalenes/Fluorenes and/or Alkyldinaphthenophenanthrenes/Anthracenes and/or Alkylpyrenes/Fluoranthenes.
¹ 2.06	Alkylaromatics and/or Alkylnapththenoaromatics.
¹ 1.41	Alkylaromatics and/or Alkylnapththenoaromatics.
¹ .87	Alkylaromatics and/or Alkylnapththenoaromatics.
.51	Alkylaromatics and/or Alkylnapththenoaromatics.
.09	Alkylaromatics and/or Alkylnapththenoaromatics.
.01	Alkylaromatics and/or Alkylnapththenoaromatics.
.01	Alkylaromatics and/or Alkylnapththenoaromatics.
-	Alkylaromatics and/or Alkylnapththenoaromatics.
-	Alkyldihydrobenzofurans.
.03	Alkylbenzofurans.
.03	Alkylnapththenobenzofurans.
.14	Alkyldinaphthenobenzofurans.
.38	Alkyldibenzofurans and/or Alkyltrinaphthenobenzofurans.
.23	Alkylnapththenodibenzofurans and/or Alkyltetranaphthenobenzofurans.
.01	Alkyldinaphthenodibenzofurans and/or Alkylpentanaphthenobenzofurans.

Table IX. Continued

Mass Z Series	Ring Number	Pittsburgh	Illinois No. 6		Western Kentucky	Colstrip	Wyodak	
			Run 1	Run 2			Run 1	Run 2
-5N	1	-	-	.01	-	.01	-	-
-7N	2	-	-	.02	-	.02	-	-
-9N	2 or 3	-	-	.02	-	.02	-	-
-11N	3	-	-	.02	-	.01	.01	-
-13N	4	.01	.10	tr	.04	tr	.01	-
-15N	3 or 5	.07	.45	.09	.22	.02	.01	.02
-17N	4	.16	.42	.44	.37	.05	.03	.02
-19N	5	.13	.26	.36	.28	.02	.06	.02
-21N	4 or 6	.07	.16	.17	.13	.01	.02	.01
-23N	5	.02	.09	.12	.08	.01	.02	-
-25N	6	.01	.09	.11	.04	tr	.01	-
-27N	5 or 7	tr	.02	.04	.01	-	-	-
-29N	6	tr	.01	tr	tr	-	-	-
-31N	7	-	tr	-	-	-	-	-
Acids		.19	.19	.24	.21	.21	.17	.24
Bases		.10	.20	.20	.13	.11	.06	.02
NA		.78	.24	.84	.83	.45	.57	.23
Loss		.87	1.32	1.25	.28	.34	.59	.48

Table IX. Continued

Lignite	Probable Compound Types
-	Alkylpyridines/Anilines.
-	Alkyl naphthenopyridines/Anilines.
.04	Alkyldinaphthenopyridines/Anilines and/or Alkylbenzopyrroles.
.04	Alkyl naphthenobenzopyrroles.
.18	Alkyldinaphthenobenzopyrroles.
.36	Alkylcarbazoles and/or Alkyltrinaphthenobenzopyrroles.
.41	Alkyl naphthenocarbazoles.
.23	Alkyldinaphthenocarbazoles.
.05	Alkylbenzocarbazoles and/or Alkyltrinaphthenocarbazoles.
.03	Alkyl naphthenobenzocarbazoles.
.01	Alkyldinaphthenobenzocarbazoles.
tr	Alkyldibenzocarbazoles and/or Alkyltrinaphthenobenzocarbazoles.
-	Alkyl naphthenodibenzocarbazoles.
-	Alkyldinaphthenodibenzocarbazoles.
.27	
.29	
1.31	Not analyzed due to insufficient sample in GPC fractions.
.37	

Table X. Comparison of Field Ionization and Low-Voltage Electron-Impact Mass Spectral Results for Two Adsorption Concentrates, Weight Percent Concentrate Basis

Pittsburgh 325-425° C Monoaromatic Concentrate			Western Kentucky 325-425° C Polyaromatic-Polar Concentrate		
Z Series	FI	EI	Z Series	FI	EI
-6H	0.25	0.29	-14(0)	0.79	1.52
-8(0)	.22	-	-26H	1.44	.65
-20H	.02	-	-28(0)	.46	-
-8H	6.08	4.92	-16(0)	5.20	4.94
-10(0)	.20	-	-28H	.64	.32
-10H	29.39	27.07	-16H	6.10	3.60
-12(0)	.50	-	-18(0)	6.19	6.96
-12H	40.03	42.15	-30H	.22	-
-14(0)	1.16	-	-18H	19.29	17.48
-14H	17.30	19.42	-20(0)	3.21	2.82
-16(0)	.25	-	-20H	19.00	18.67
-16H	3.95	4.94	-22(0)	1.59	-
-18H	.66	-	-8(0)	.06	-
			-22H	23.99	21.89
			-24(0)	1.29	-
			-10(0)	.09	-
			-24H	5.13	4.51
			-26(0)	.60	-
			-12(0)	.21	-
			-15N	2.69	4.59
			-17N	1.29	4.33
			-21N	.01	.06
			-23N	.04	-
			-25N	.41	-
			-27N	.06	-

Table XI. Comparison of Six Coal Liquids Based on Ring Number and Asphaltene and Residuum Content, Weight Percent Total Coal Liquid Basis

No. of Rings	Coal Liquid	Pittsburgh	Illinois No. 6	Western Kentucky	Colstrip	Wyodak	Lignite
			Run 2			Run 1	
0		1.8	1.9	4.8	4.4	5.7	3.6
1		12.1	12.2	15.7	11.7	16.9	14.4
2		12.9	17.4	16.9	13.8	17.0	15.0
3		15.2	17.1	15.8	14.8	15.6	15.3
Sum 0 to 3		42.0	48.6	53.2	44.7	55.2	48.3
>4		32.2	31.9	27.9	27.6	29.6	24.5
Asphaltenes		4.7	6.8	5.2	6.6	1.2	6.7
>540° C Resid		16.2	7.5	9.3	18.4	11.2	15.0
Acids		.2	.2	.2	.2	.2	.3
Bases		.1	.2	.1	.1	.1	.3
Other ¹		4.6	4.8	4.1	2.4	2.5	4.9

¹ Includes unknowns, material not analyzed due to insufficient sample, and material lost in separations.

Table XII. Ring Number Distributions for Coal Liquids Produced from Illinois No. 6 and Wyodak Coal Using Different Processing Conditions, Weight Percent Total Coal Liquid Basis

No. of Rings	Coal Liquid	Illinois No. 6		Wyodak	
		Run 1	Run 2	Run 1	Run 2
0		2.1	1.9	5.7	6.2
1		11.4	12.2	16.9	21.6
2		16.1	17.4	17.0	20.1
3		17.3	17.1	15.6	16.9
>4		27.0	31.9	29.6	26.4
Asphaltenes		14.3	6.8	1.2	.1
>540° C Resid		6.4	7.5	11.2	6.3
Acids		.2	.2	.2	.2
Bases		.2	.2	.1	tr
Unknown and losses		5.0	4.8	2.5	2.2

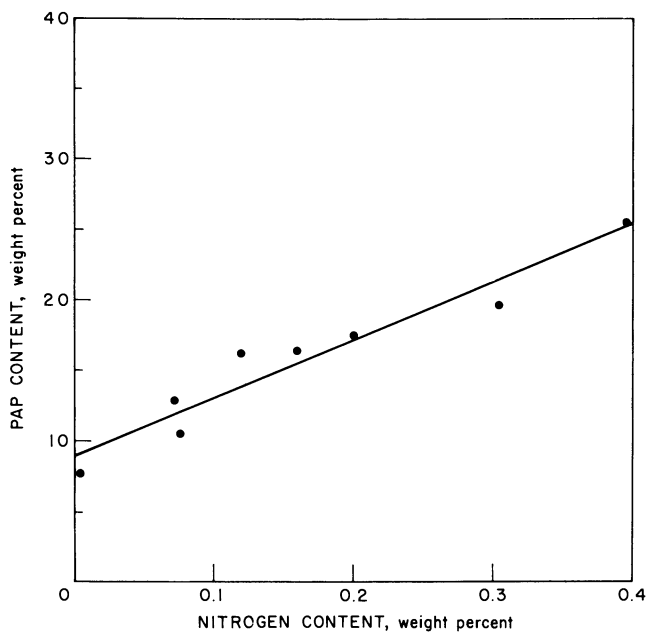


Figure 4. Polyaromatic-polar vs. nitrogen content, 325°–425° C distillate

atively low nitrogen content of the lignite coal may have resulted in a tractable liquid with less hydrogenation of polyaromatic ring systems due to the shorter reaction times. Also, with the exception of the first Illinois No. 6 run, only one upgraded coal liquid had a higher nitrogen content. Also, only one coal had a lower consumption of hydrogen in the liquefaction and upgrading runs (1). These considerations are all consistent with less hydrogenation of aromatic ring systems and thereby a relatively high polyaromatic content.

Linear regression results for the correlation of the PAP contents of the 200° to 325° C, 325° to 425° C, and 425° to 540° C distillates with the distillate nitrogen content gave correlation coefficients of 0.85, 0.96, and 0.93, respectively, indicating very good correlations. Data for the middle distillate are plotted in Figure 4. Thus, the trend in PAP content may very well be more dependent on nitrogen content than on coal rank for these liquids.

Acid Fractions. The acid contents, as shown in Table V, account for about 0.4 to 0.6 percent of the 325° to 425° C coal liquid distillates except for the lignite liquid (0.76). The acid content for the 425° to 540° C distillates mostly fall in the range of 0.50 to 0.59 percent except for Pittsburgh (0.29) and Wyodak run 1 (0.34). The total acids from the 325° to 425° C and the 425° to 540° C distillates plus the oxygenate material from the 200° to 325° C distillate (19) expressed on a total liquid basis, correlated fairly well with the total coal liquid oxygen content (Table II) (correlation coefficient 0.82). The data are plotted in Figure 5.

Base Fractions. The base contents of the 325° to 425° C distillates were quite low (range 0.03 to 0.88 wt-pct) but correlated well with the nitrogen contents of these distillates, as shown in Figure 6 (correlation coefficient 0.90). Similarly, the bases in the 425° to 540° C distillates were low (range 0.06 to 0.54 wt-pct) and correlated fairly well with the distillate nitrogen content (coefficient 0.79).

Ring Number Distributions. Examination of the data in Table XI shows the ring number distributions to be similar for all coal liquids. Differences among the liquids from the several coals doubtless were minimized because the upgrading was adjusted to eliminate nitrogen to about the same level in most of the liquids. The greater reactivity of the lower-rank coals and the lesser required upgrading of their crude liquids was clear from the previously reported preparations (1). Some scatter in compositional data could be expected because of the variation in individual preparations. However, since conditions generally were such as to avoid significant cracking of hydrocarbons, especially hydrocarbon ring structures (20,21,22), differences or similarities in basic hydrocarbon structures should be valid. One of the largest uncertainties

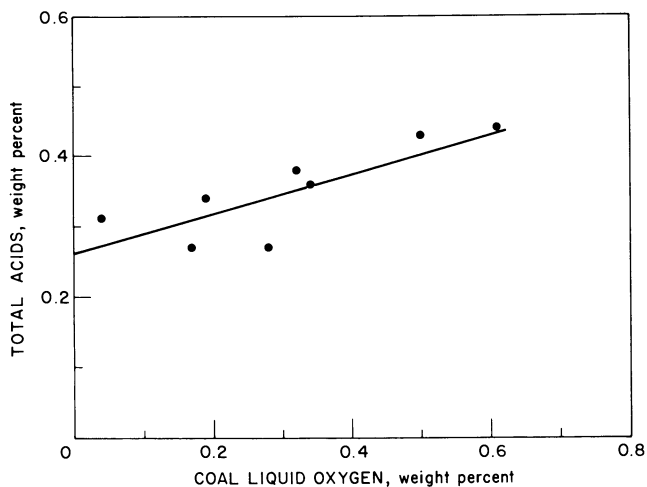


Figure 5. Total acids vs. coal liquid oxygen

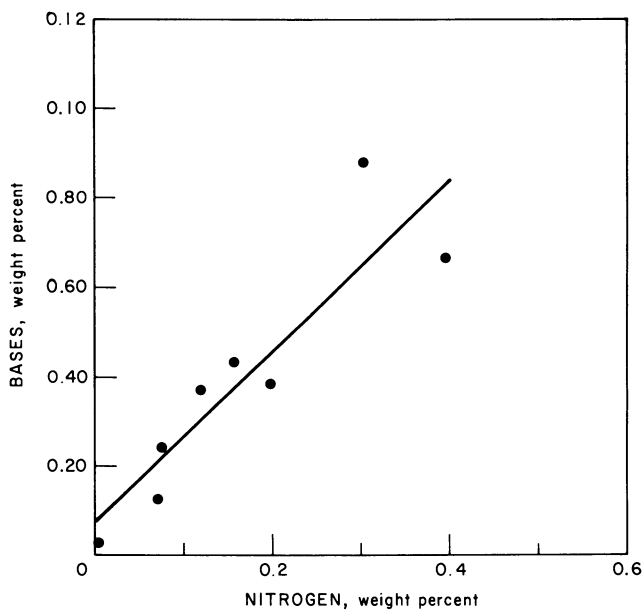


Figure 6. Bases vs. nitrogen content, 325°–425° C distillate

is the extent of hydrogenation of aromatic hydrocarbon rings originally present in the coal. Total consumption of hydrogen was approximately constant and independent of coal rank (1), so that hydrogen consumed by reaction with combined oxygen in lower-rank coals was counterbalanced by increased saturation of aromatic rings in the coals of higher rank. With the catalyst and conditions used, many of the polynuclear aromatic structures originally present could be expected to hydrogenate partially to yield hydroaromatics in the upgraded liquids. The uncertainty in the extent of hydrogenation of aromatics is circumvented in part by counting total rings per molecule in the several distillate fractions.

Comparison of the data from the two Illinois No. 6 liquefaction and upgrading runs summarized in Table XII indicates little difference in the products in terms of ring-number distributions, especially in the lower-ring-number compounds. The largest effect in switching from CoMo to NiMo catalyst and decreasing the maximum reaction temperature from 425° to 400° C appears in the compound types containing four or more rings and in the asphaltene content. The second Illinois run with NiMo at 400° C maximum temperature produced more >4-ring compound-type material at the expense of the asphaltenes.

Extent of Upgrading. As seen in Table XII, the ring-number data for the two Wyodak runs show that the extent of upgrading was an important factor in final product composition. The more extensive upgrading (Wyodak run 2) produced considerably higher yields of low-ring-number compound types. This was due only in a small part to more complete conversion of heteroatomic-ring compounds to hydrocarbons. Beyond that, some hydrocarbon cracking must have occurred. Our compositional data are not of sufficient detail to determine the relative importance of ring-opening cracking reactions to the breaking of alkyl linkages between rings in contributing to the higher yields of low-ring-number compounds although the literature suggests hydrocarbon ring-opening reactions with similar catalysts at these temperatures are not very significant (20,21,22), amounting to less than 10 percent for phenanthrene in a flow reactor (21) and less than 5 percent for anthracene after 200 minutes at 390° C in a batch autoclave reactor (20).

Comparison of the data for the Illinois run 2 and Wyodak run 2 liquids shows significantly higher yields of low-ring-number compound types for the liquid from the lower-rank Wyodak coal. However, since the Wyodak coal was more reactive, the extent of upgrading as seen in the nitrogen contents is much greater for the Wyodak coal even though the same upgrading time-temperature profile was followed in each case. These differences are in contrast to the data from the six coal liquids in Table XI which were upgraded to about the same nitrogen content, and for which no clear trend in terms of yields of compounds of equal ring number as a function of coal rank was evident.

Effect of Coal Rank on Coal Liquid Composition. Further comparison of the Illinois run 2 data with those for the Wyodak runs are interesting. For example, the total saturate content of the Illinois run 2 coal liquid (25.2 wt-pct) is considerably lower than that of the Wyodak run 1 liquid (38.2) even though its total reaction time for liquefaction and upgrading was almost twice as long (1). The Wyodak run 2 coal liquid, which was upgraded on the same time-temperature profile as the Illinois run 2 liquid, has an even higher saturate content (59.9). This trend in the total coal liquid saturate content (Illinois run 2 < Wyodak run 1 < Wyodak run 2) holds true for each of the distillates (Tables IV and V) and, with only a rare exception, for each saturate compound type within each distillate calculated on a distillate basis (19). Thus, the extent of upgrading and the rank of the coal (at least for Illinois No. 6 and Wyodak) both appear to affect coal liquid saturate content in a significant manner. To investigate this possible relationship in a more quantitative manner, an arbitrary scale of 0 to 12 was used to express the rank of the coals. The arbitrary scale was devised for two reasons. First, no one coal property defines the rank over the entire range. Second, although the ranks of the coals used in this study fall in the range determined by BTU values, the exact BTU values were not available. Thus, meta-anthracite, anthracite, and semianthracite coals were assigned 0 through 2 scale values; low-volatile bituminous and medium-volatile bituminous were assigned 3 and 4; high-volatile bituminous A through C were given 5 through 7 scale values; and so on with lignite and brown coals assigned values of 11 and 12. A plot of the total saturate contents of the six coal liquids upgraded to the same approximate nitrogen level versus the arbitrary coal rank scale value reveals considerable scatter in the data, as shown in Figure 7 (correlation coefficient, $r = 0.55$). A similar plot of saturate content versus total liquefaction plus upgrading reaction time as measured from 325° C and higher showed even more scatter (Figure 8) and a poorer correlation ($r = 0.27$). However, multiple linear regression analysis using the eight coal liquid saturate content (S) as the dependent variable, coal rank scale value as one independent variable (R) and total reaction time as a second independent variable (RT) gave a much improved multiple correlation coefficient of 0.83. The resulting equation was as follows:

$$S = 4.79(R) + 1.07(RT) - 27.04$$

The t-values for the coefficients were 3.14 and 2.35, respectively, and the F-value was 5.52. These results, of course, do not prove the dependence of coal liquid saturate content upon reaction time and coal rank, but they are consistent with that interpretation.

Further comparisons of data in Table V for the Illinois run 2 and the two Wyodak runs show a reverse trend in monoaromatic, diaromatic and polyaromatic-polar contents in the 200° to 325° C,

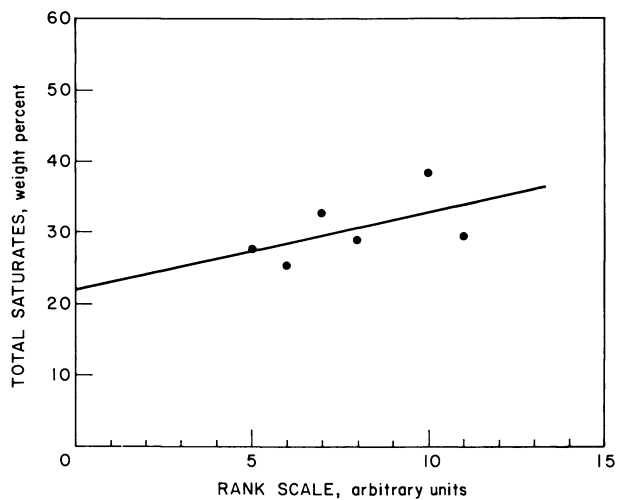


Figure 7. Total saturates vs. coal rank

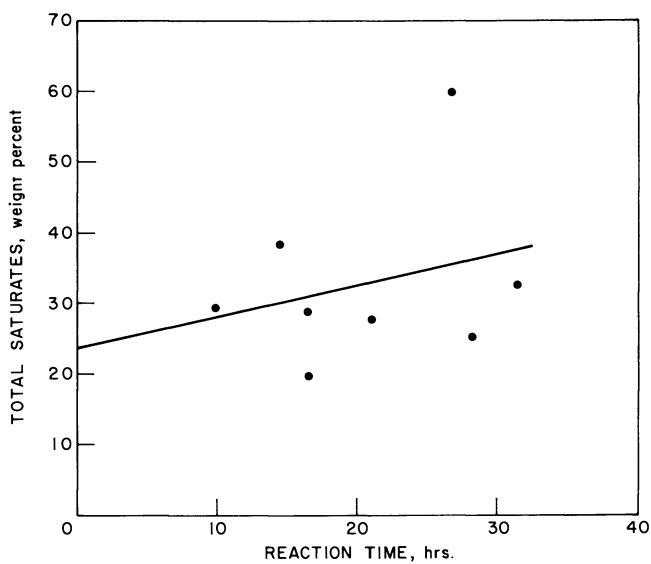


Figure 8. Total saturates vs. $> 325^{\circ} \text{C}$ reaction time

325° to 425° C, and 425° to 540° C distillates on a total coal liquid basis (Illinois run 2 > Wyodak run 1 > Wyodak run 2) with the exception of the 425° to 540° C monoaromatics which follow the same trend as the saturate contents.

In a further effort to determine the effect of coal rank on coal liquid composition, compound types containing zero to three rings were grouped together, and the sums are listed in Table XI. No clear trend is apparent although there does appear to be some slight correlation with the Colstrip and lignite data excluded. Least-squares analysis of total 0- to 3-ring compound type content as a function of coal rank scale value gave a rather poor correlation coefficient of 0.48, indicating considerable scatter in the data as seen in Figure 9. Eliminating the values for the Colstrip and lignite liquids improved the correlation considerably ($r = 0.87$). Expressing the 0- to 3-ring compound content (0-3 RC) as a function of total reaction time (Figure 10) also resulted in a rather poor correlation ($r = 0.35$). However, as for the saturate content, inclusion of the coal rank scale factor as a second independent variable resulted in a much improved multiple correlation coefficient of 0.89. The coefficients in the model are shown below:

$$(0-3 \text{ RC}) = 2.92(R) + 0.71(RT) + 12.9$$

The t -values for the coefficients of 3.92 and 3.21, respectively, and the F -value of 9.05 each indicate a good correlation.

To further investigate the complexity of the coal liquids as a function of rank, 0- and 1-ring compound-type contents were summed and plotted versus coal rank scale value, as shown in Figure 11. Although the correlation was better than for the 0- to 3-ring results, the correlation coefficient of 0.65 indicated only a fair correlation. Zero- plus 1-ring content correlated quite poorly with total reaction time as indicated by the correlation coefficient of 0.20. However, expressing 0- plus 1-ring content (0-1 RC) as a linear function of both rank and reaction time resulted in a much improved correlation as shown by the multiple correlation coefficient of 0.90. The resulting coefficients in the model are shown below:

$$(0-1 \text{ RC}) = 2.22(R) + 0.42(RT) - 7.90$$

The t -values for the coefficients (4.63 and 2.97, respectively) and the F -value (11.26) also indicate a good correlation. It may be noteworthy also, that the ratio of the two independent variable coefficients (5.3) is of the same order of magnitude as for the 0- to 3-ring results (4.1). In general, these results lend support to the conclusion that the complexity of the coal liquids in terms of average number of rings per molecule increases with increasing rank of coal (i.e. for decreasing coal rank scale value) and with decreasing total liquefaction and upgrading reaction time.

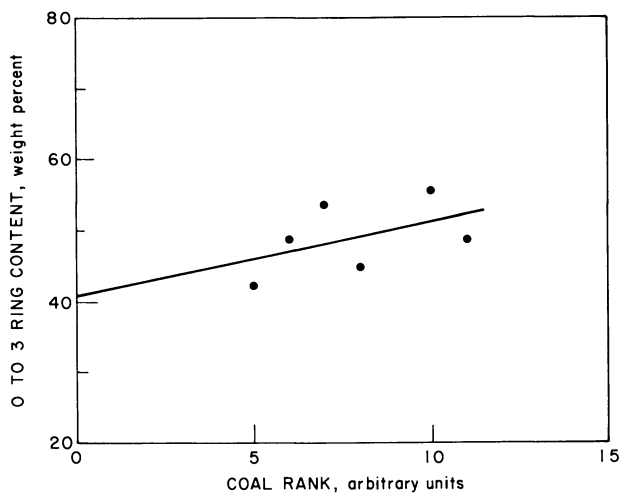


Figure 9. Zero- to 3-ring content vs. coal rank

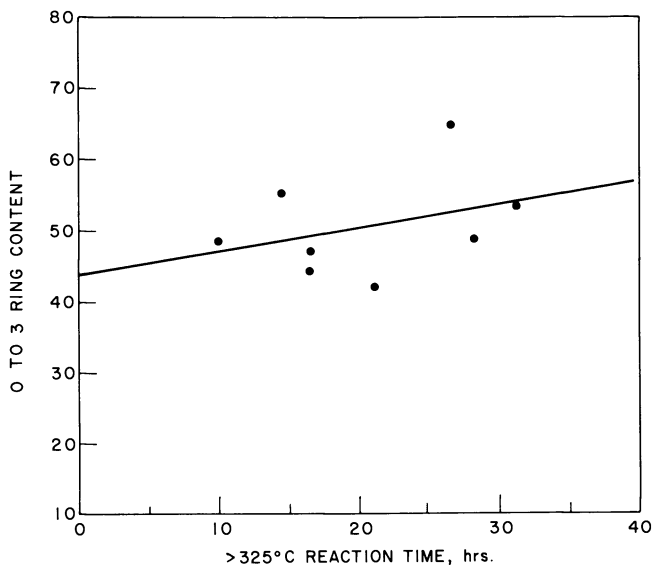


Figure 10. Zero- to 3-ring content vs. > 325° C reaction time

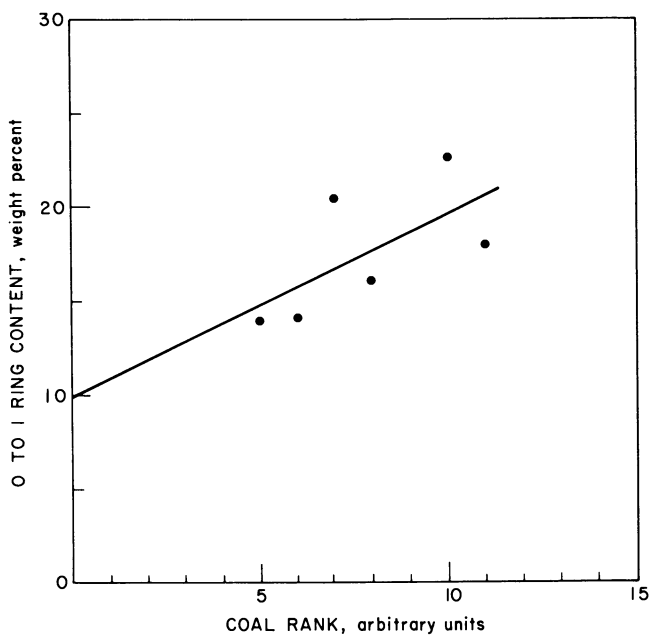


Figure 11. Zero- to 1-ring content vs. coal rank

Summary and Conclusions

The studies showed the coal liquids upgraded to about the same level of nitrogen removal have similar compositions in many respects. The differences in compositions that were observed did not vary consistently with the coal rank alone. Although the ranks of the coals used in this study covered the full range of practical interest for liquefaction, selection of additional coal samples covering an even greater range of coal rank might be of value in determining any possible dependence of coal liquid composition upon coal rank.

Acid and base contents of the coal liquids although quite small, correlate well with coal liquid oxygen and nitrogen contents, respectively. Polyaromatic-polar content correlates well with nitrogen content. Coal liquid composition in terms of saturate content, 0- to 1-ring compound-type content, and 0- to 3-ring compound-type content correlated rather poorly with an arbitrary coal-rank scale. However, inclusion of a second independent variable, total liquefaction and upgrading reaction time, gave much improved correlation coefficients. Results from two upgrading runs on the same raw coal liquid indicated the extent of upgrading to be an important factor in each of these compositional parameters. More extensive upgrading produced larger amounts of saturates due to increased hydrogenation of aromatics, and larger amounts of lower-ring-number compound types due in part to greater removal of heteroatoms. Also, significant amounts of lower-ring-number compound types must have resulted from cracking of alkyl linkages between ring systems and/or hydrocarbon ring-opening cracking reactions. The relative importance of these factors could not be determined from our studies.

Furthermore, considering the results of this compositional study in conjunction with the results of the preparations of the coal liquids, 1) liquids from lower-rank coals were more easily upgraded, 2) for a given raw coal liquid, increased severity of upgrading produced larger amounts of low-ring-number compound types, and 3) coal rank alone could not account for the observed variations in complexity of the coal liquids.

Finally, the results show that liquids of comparable suitability as feedstocks for production of refined fuels can be produced from coals of different rank.

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Abstract

Eight coal liquids prepared from six coals of widely differing rank were compared with respect to their suitability as potential feedstocks for production of refined fuels. The compositions of the liquids were determined by methods adapted from those developed for characterization of petroleum crudes. The coal liquids were prepared and upgraded by hydrogenation in a batch autoclave. The reaction conditions employed were selected to minimize hydrocarbon ring-opening reactions and, at the same time, to produce most of the hydrocarbon liquids potentially available from the coals. The degree of hydrogenation of the raw coal liquids was varied as required to decrease the nitrogen content to about the same level and to provide a predominantly hydrocarbon liquid for analysis. Distilled fractions of the upgraded coal liquids boiling up to 540° C were characterized by a combination of separation and analytical techniques including adsorption chromatography; gel permeation chromatography; separations of acids, bases, and asphaltenes; and high- and low-resolution mass spectrometry. In general, the results show that liquids of comparable suitability as feedstocks for production of refined fuels can be produced from coals of different rank.

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Chemical Composition of Raw and Upgraded Anthracene Oil and the Chemistry of Coal-Liquids Upgrading

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Nonconventional fossil-fuel-derived materials such as coal liquids, shale oil, tar sands, and petroleum-heavy ends are potentially significant alternatives to conventional petroleums. Unlike conventional petroleums, nonconventional feedstocks are characterized by the presence of significant quantities of polynuclear aromatic hydrocarbons and heteroatom-containing polynuclear aromatics (1-12). These differences in chemical composition necessitate that synthetic crudes be subjected to hydrogenation/hydrogenolysis in order to remove most of the polynuclear aromatic hydrocarbons and the sulfur-, nitrogen- and oxygen-containing aromatic compounds prior to refining (13,14, 15). Detailed molecular analysis of feedstocks and products is thus a prerequisite to the development of efficient and economical technologies for upgrading nonconventional crudes. In this regard, the principle intent of our characterization of raw and upgraded anthracene oil was to support the development of catalysts for upgrading coal-derived liquids (16). It is important to note that during the course of this study, significant advances have occurred (17-24) in regard to the elucidation of reaction networks and chemical kinetics involved in hydrodenitrogenation and hydrodesulfurization through elegant studies employing known compounds. Consequently, the compositional data for feedstock and upgraded anthracene oil are qualitatively related to the results obtained in these mechanistic studies.

Experimental

Upgrading and Sample Selection. Anthracene oil was hydro-treated using flow-through trickle-bed reactors containing

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Co-Mo-alumina catalysts (16). The selection of four hydrotreated samples for analysis, termed reactor-samples 1 through 4 reflects the following considerations. The variations in hydro-treating conditions presented in Table I should not drastically

TABLE I. Conditions For Hydrotreating Anthracene Oil

	REACTOR-SAMPLE			
	1	2	3	4
Reactor Temperature ($^{\circ}$ F)	700	600	700	700
Reactor Pressure (psig)	1000	1000	1020	507
Space time (hrs)	1.48	2.50	0.75	0.75
Catalyst	Nalco Sphericat Harshaw HT 400			

alter the gross composition of the four samples. However, the differences in reaction conditions should be sufficient to indicate the effect of changes in temperature, pressure, and space time on product distribution.

Reagents. Amberlyst A-29 anion-exchange and Amberlyst-15 cation-exchange resins were obtained from Rohm and Haas, Inc. Attapulgas clay (LVM, 60/80 mesh) was obtained from Engelhard Minerals. Pentane (99%, Phillips Petroleum) was purified by flash distillation and by percolation through activated silica gel; reagent-grade 1,2-dichloroethane was percolated through activated silica gel. Benzene and methanol were flash distilled. Reagent-grade 2-propylamine was used without purification. Solutions of HCl in CH_3OH were prepared by mixing 10 volumes of concentrated HCl with 90 volumes of absolute CH_3OH . Solutions of KOH in CH_3OH were prepared by dissolving 10g of KOH in 90 ml of absolute CH_3OH . Solutions of ferric chloride in methanol were prepared by dissolving 10g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 90 ml of absolute CH_3OH .

Separations Apparatus. Separations were performed using water-jacketed liquid-chromatographic columns allowing continuous sample elution via solvent recycling (25). The solvent was removed from each fraction using a roto-evaporator and a room-temperature water bath (*ca.* 25°C) until a constant sample weight ($\pm 0.02\text{g}$) was obtained.

Preparation of Resins and Adsorbents. A volume of Amberlyst A-29 anion-exchange resin was added to a liquid-chromatographic

column and washed first with a volume of HCl in CH₃OH equivalent to 6 times the volume of resin taken and second with deionized water until the eluent was neutral. The resin was then removed from the column and extracted in a Soxhlet extractor for 24 hrs. with each of the following solvents: methanol, benzene, and pentane. After the pentane extraction, the resin was vacuum dried.

Amberlyst-15 cation-exchange resin was activated in the manner described for the anion-exchange resin except that the sequence of acid/base washings were reversed. Also, the rate of addition of both the acidic and basic methanolic solutions were governed by the heat generated.

Methanolic ferric chloride solution was slurried with Attapulgas clay for 1 hr. and the excess solution removed by filtration. The ferric chloride coated Attapulgas Clay was washed several times with pentane, then Soxhlet extracted with pentane for 48 hrs., and then vacuum dried.

Separation Procedures. Cation- and anion-exchange and complexation chromatography were used to separate samples of both the feedstock and upgraded anthracene oil into acidic, basic, neutral-nitrogen-containing, and hydrocarbon plus ether fractions (25).

A pentane slurry of anion-exchange resin (150 ml) was added to a chromatographic column filled with pentane and the resin was packed using a vibrator. The resin bed was then extracted by recycling pentane under an argon atmosphere for 5 to 10 hrs. A weighed sample (ca. 20g) was quantitatively transferred to the column and the unreactive material eluted under an argon atmosphere with pentane for ca. 48 hours at a rate of 6 to 10 drops per minute. After the unreactive compounds were removed, the acids were recovered in two subfractions. Weak acids were eluted by substituting benzene for pentane. The strong acids were recovered using CH₃OH saturated with CO₂ as the eluent. The two subfractions were combined to yield a total acid fraction.

The acid-free sample was quantitatively transferred to the cation-exchange resin (ca. 150 ml) wet-packed as described above. Unreactive materials were eluted under an argon atmosphere with pentane for ca. 48 hours at a rate of 6 to 10 drops per minute. The reactive materials were recovered by eluting the resin with benzene and then with an 8% 2-propylamine in methanol solution (V/V). The two eluents were combined to yield the total base fraction.

A chromatographic column was wet-packed to half capacity with a pentane slurry of Amberlyst A-29 (ca. 100-125 ml) and a glass-wool plug positioned on top of the resin bed. The remaining volume of the column was wet-packed with a pentane slurry of ferric chloride coated on Attapulgas Clay (120-125 ml). The acid-and base-free material was quantitatively transferred to

the column and the hydrocarbons plus ethers were eluted with pentane under an argon atmosphere for *ca.* 12 hrs. The neutral-nitrogen-containing compounds were desorbed from the ferric chloride/Attapalagus Clay by elution with 1,2-dichlorethane.

Analytical Methods. Field-ionization and 70-eV electron-impact mass spectra (FI/MS and EI/MS) were obtained for the various fractions using a CEC 21-110B mass spectrometer equipped with a modified combination FI/EI ion source. The 70-eV EI/MS were recorded at a static resolution of *ca.* 21,000 (90% valley definition) on Ilford Q2 photographic plates and FI/MS were produced with an emitter potential of 6.8 kV and a counter-electrode potential of -300 to -500 V. Field-ionization mass spectra were oscillographically recorded at dynamic resolutions sufficient to resolve two ions differing by *ca.* 1 part in 2,000 and 7,000 with approximately 90% valleys. Samples were introduced into the ion source (270°C) via the batch-inlet system (300°C). For each sample, the precise ion masses obtained from the high-resolution 70 eV EI/MS were used to assign most-probable formulas to the molecular ions observed in the low- and high-resolution FI/MS (8,11). The ion intensities in the latter spectra were converted into the weight percents of the individual homologs for each compound type as previously described (11).

The hydrocarbon plus ether fractions were analyzed using an LKB 9000P GC/MS and a Perkin-Elmer 3920 GC. Both analyses employed a 5% OV-101 on Gas Chrom Z AW-DMSC (100/120) glass column (12'X1/8"). The initial column temperature was maintained at 100°C for 5 minutes following sample injection (0.2 µl). The temperature was then increased to 200°C at a rate of 1°C per minute and maintained constant until elution was essentially complete. The absence of a data system interfaced to the LKB 9000P GC/MS precluded exhaustive structure elucidation. However, major components and compound types were identified by comparing mass spectra of the column effluents with standard API Project 44 mass spectra and by the *m/z* values observed in individual spectra in relation to the molecular weights observed in the group-type analyses. Semiquantitative analyses were calculated from the FID gas chromatograms obtained using the PE 3920 GC.

The base fractions were subjected to GC/MS analysis using a Finnigan 4000 interfaced to a Finnigan (INCOS) 2400 data system. The GC separations were obtained using a 30m SP2100 column, 8 lb head pressure, a 10 ml system sweep, and a 80 ml/min split. The column temperature was increased from 100 to 250°C at 2°C per minute. The limited availability of reference mass spectra for nitrogen-containing aromatics precluded extensive use of pattern recognition for structure elucidation. Consequently individual components and compound types were identified using both their relative retention times and mass spectra.

Results and Discussion

General. The weight percentages of the acidic, basic, neutral-nitrogen containing and hydrocarbon plus ether (or neutral) fractions obtained from the separation of the feedstock and upgraded anthracene oil are presented in Table II. Unfortunately the total yield of gaseous products was not determined in this hydrotreating study. However, other studies suggest that the assumption of a 5% production of gaseous products is reasonable (26). This assumption was employed in calculating both the weight percentages in Table II and the carbon-number distributions for reactor samples 1 through 4. It should be noted that all fractions were found to be volatile in the all-glass-inlet system of the mass spectrometer.

TABLE II. Summary of Separation Data for Feedstock and Upgraded Anthracene Oil and Reaction Conditions

Fraction	Weight Percentages				
	Feedstock	Reactor Samples ^a			
		1	2	3	4
Acids	14.9	2.5	4.3	3.0	2.8
Bases	9.5	7.5	6.1	10.1	8.6
Neutral Nitrogen	1.7	1.5	1.7	1.9	0.8
Neutrals	73.9	83.5	82.9	80.0	82.8
Temperature (°F)		700	600	700	700
Pressure (psig)		1000	1000	1020	507
Space Time (hrs)		1.48	2.50	0.75	0.75

^aAssumes a 5% weight loss due to formation of gaseous products.

As seen in Table II, the composition of the raw anthracene oil is dominated by aromatic hydrocarbons plus ethers (neutrals) and acids. Comparison of columns 3 through 6 of Table II with column 2 reveals significant decreases and increases in the weight percentages of acids and neutrals, respectively, and insignificant changes in the amounts of bases and neutral nitrogens independent of the reaction conditions. The distribution of compound classes is not markedly affected by the variations in reaction conditions. Indeed, it is impossible to clearly determine the extent to which the variations in the weight percentages

of the various compound classes in the four reactor samples reflect changes in reaction conditions and/or experimental imprecision in the separations.

Acids. The carbon-number distribution obtained for the oxygen-containing acids in the anthracene oil is presented in Table III. Singly, doubly, and triply oxygenated compounds possessing 1 through 3 aromatic rings account for 75%, 24%, and 1% of the feedstock oxygen-containing acids, respectively. Based upon studies of the chemical composition of coal tars (27-30), the chemistry associated with ion-exchange chromatography, and the carbon numbers for at least the first homologs in the Z(0), Z(0₂), and Z(0₃) series, these acids are attributed to the presence of hydroxylated aromatics derived from aromatic hydrocarbons by substitution of 1 through 3 hydroxyl groups for an aromatic hydrogen. It is interesting to note that hydroxylated aromatics such as phenols, -6(0); naphthalenols, -12(0); fluorenols, -16(0), -diols, -16(0₂), and -triols, -16(0₃); phenanthrenols/anthracenols, -18(0), and -diols, -18(0₂); and pyrenols/fluoranthenols, -22(0), and -diols, -22(0₂), account for 81% of the acids. Thus, the hydroxylated hydroaromatics such as indanols, -8(0), acenaphthenols, -14(0), and dihydro-pyrenols, -20(0), comprise only 19% of the acids. This preference for hydroxylated aromatics parallels the preference for aromatic hydrocarbons over hydroaromatic hydrocarbons (see below).

As seen in Table III, the distribution of weight percentages in each specific Z series is dominated by the first three homologs. The initial carbon number for each compound type corresponds to the value for the parent-ring structure. Thus, the parent hydroxylated aromatics and their homologs possessing up to 2 carbons exocyclic to the ring structure account for *ca.* 87% of the oxygen-containing acids. This result parallels the one observed for the aromatic hydrocarbons (see below). The data in Table III reveal that the ratio of parent to alkylated homologs is considerably lower for the phenol series, -6(0), than for the other oxygenated series. This result may reflect the precursor coal since GC/MS analysis of coal pyrolysates (31) revealed that the ratio of phenol to alkylated phenols decreases rapidly with the age of the coal. Finally, it is interesting to note that acids in the -12(0), -18(0) plus -18(0₂), and -22(0) plus -22(0₂) Z series account for 9%, 3%, and 23% of the acids whereas the aromatic-ring equivalent hydrocarbon -12, -18, and -22 series account for 14%, 24%, and 26% of the hydrocarbons.

The data in Table IV demonstrate the occurrence of extensive phenol deoxygenation. The reactivity of -18(0) through -22(0) and -18(0₂) and -22(0₂) compounds appears to be independent of

Table III. Carbon-Number Distribution for C_{N-2N+Z}^H , C_{N-2N+Z}^H , C_{N-2N+Z}^H , and C_{N-2N+Z}^H Acids Present in Anthracene oil.

-Z	Parent Formula	Weight Percents ($\times 10^1$) for Carbon Number																	
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	Total			
6(0)	$C_6H_6^0$	6.1	14.6	10.6	3.3	1.5	0.3	0.6										40.0	
8(0)	$C_9H_{10}^0$			1.6	1.4	0.7	0.6	0.3										4.6	
12(0)	$C_{10}H_8^0$			3.1	3.4	1.8	1.0	1.0										10.3	
14(0)	$C_{12}H_{10}^0$					3.5	4.8	3.5	2.0	0.8	0.2							14.8	
16(0)	$C_{13}H_{10}^0$						5.3	3.1	2.0	0.9	0.6	0.2						12.1	
18(0)	$C_{14}H_{10}^0$							1.3	0.9	0.6	0.3							3.1	
20(0)	$C_{15}H_{10}^0$									1.8	1.2	0.7	0.3					4.0	
22(0)	$C_{16}H_{10}^0$										0.8	0.3	0.3					1.4	
16(0 ₂)	$C_{12}H_8O_2$					11.1	10.0	4.6	1.6	0.6								27.9	
18(0 ₂)	$C_{14}H_{10}O_2$								0.3									0.3	
22(0 ₂)	$C_{16}H_{10}O_2$										0.2	0.1						0.3	
16(0 ₃)	$C_{12}H_8O_3$							0.5	0.6	0.2								1.3	

the experimental conditions. However, the weight percentages for the lower Z(0) and Z(0₂) series reveal that the increased reaction time did not overcome the effect of decreasing the reactor temperature. Comparison of the data for reactor-samples 3 and 4, with those for the feedstock and reactor-sample 1 shows a very small effect of decreasing H₂ pressure, space time, and catalyst change on deoxygenation.

TABLE IV. Summary Data For Oxygen-Containing Acids In Feedstock and Upgraded Anthracene Oil

-Z	Parent Formula	Weight Percent in				
		Feedstock	Reactor-Samples			
			1	2	3	4
6(0)	C ₆ H ₆ O	4.0	0.1	0.9	0.3	0.8
8(0)	C ₉ H ₁₀ O	0.5	0.2	0.5	0.4	0.2
12(0)	C ₁₀ H ₈ O	1.0	0.0	<0.1	0.0	0.0
14(0)	C ₁₂ H ₁₀ O	1.5	<0.1	0.5	0.3	0.3
16(0)	C ₁₃ H ₁₀ O	1.2	0.1	0.5	0.3	0.3
18(0)	C ₁₄ H ₁₀ O	0.3	0.0	<0.1	0.0	0.0
20(0)	C ₁₆ H ₁₂ O	0.4	0.0	0.2	0.1	0.2
22(0)	C ₁₆ H ₁₀ O	0.1	0.0	0.1	0.1	<0.1
16(0 ₂)	C ₁₂ H ₈ O ₂	2.8	0.0	0.4	0.0	<0.1
18(0 ₂)	C ₁₄ H ₁₀ O ₂	0.1	0.0	0.0	0.0	0.0
22(0 ₂)	C ₁₆ H ₁₀ O ₂	0.1	0.0	0.0	0.0	0.0

The group-type MS analysis shows that the extent and/or pattern of aliphatic substitution affects the ease of deoxygenation. For example, Table V presents the weight percentages of phenol and its alkylated homologs in the feedstock and in the reactor samples. Comparison of the values in columns 3 through 6 with the entries in column 2 shows that the extent of deoxygenation decreases as the number of alkyl carbons increases independent of the reaction conditions. The extent to which this phenomenon reflects the number of carbons in and the structure of each alkyl side chain and the pattern of alkyl substitution on the aromatic ring cannot be elucidated because the molecular-ion-group type analysis does not distinguish between isomeric homologs in a given Z series.

The data in Table V indicate the gross effect of changes in reaction conditions on deoxygenation of the homologs in the -6(0)

Table V. Weight Percents of Phenols Present in Feedstock and Hydrotreated Anthracene Oil

Formula	Weight Percents ($\times 10^1$) in				
	Feedstock	Reactor Sample			
		1	2	3	4
C_6H_6O	9.1	0.0	1.0	0.4	1.1
C_7H_8O	14.6	0.0	2.3	0.8	2.1
$C_8H_{10}O$	10.6	0.0	2.8	0.8	2.3
$C_9H_{12}O$	3.3	0.1	1.5	0.6	1.3
$C_{10}H_{14}O$	1.5	0.3	0.7	0.4	0.6
$C_{11}H_{16}O$	0.3	0.3	0.5	0.3	0.4
$C_{12}H_{18}O$	0.6	0.2	0.3	0.2	0.3

series. Comparison of the weight percentages for each homolog in reactor-samples 1 and 2 shows that the decrease in deoxygenation resulting from a $100^\circ F$ decrease in reaction temperature was not compensated by the 1 hr. increase in space time. The results for reactor samples 3 and 4 show that a decrease in H_2 pressure reduces oxygen removal. Assuming similar chemical/physical properties for the two catalysts, comparison of the data for reactor-samples 2, 3, and 4 with those for reactor-sample 1 suggests that overall reactivity in deoxygenation of phenols is adversely affected by decreases in temperature, pressure, and space time. Although the extent of hydrodeoxygenation under the various reaction conditions decreases with increasing alkyl-carbon number, the dependence of reactivity on reaction conditions rises as the alkyl-carbon number diminishes.

The same nitrogen-containing-compound types were observed in the acidic and neutral-nitrogen fractions from the anthracene oil and the four reactor samples. The feedstock acids also contain compounds possessing both a nitrogen and an oxygen. Thus, the analytical data for these Z(N) compounds in both the acidic and neutral-nitrogen fractions and the results for the Z(N,O) compounds in the acids were combined to obtain a single carbon-number distribution for the feedstock and for each reactor sample. These results are summarized in Table VI.

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ACS Symposium Series; American Chemical Society: Washington, DC, 1981.

Table VI. Summary Data for $C_N H_{2N+Z} N$ and $C_N H_{2N+Z} NO$ Compounds Present in the Acid and Neutral-Nitrogen Fractions from Feedstock and Hydrotreated Anthracene Oil

-Z	Parent Formula	Range in N	Weight Percent				
			Feedstock	Reactor Sample			
				1	2	3	4
9(N)	$C_8 H_7 N$	9-12	0.2	<0.1	0.1	0.1	0.1
15(N)	$C_{11} H_7 N$	12-16	1.8	1.6	1.4	1.9	1.6
17(N)	$C_{13} H_9 N$	14-17	0.2	0.2	0.2	0.4	0.1
19(N)	$C_{13} H_{11} N$	14-18	0.2	0.2	0.1	0.1	0.1
21(N)	$C_{15} H_9 N$	16-17	0.3	0.3	0.2	0.2	0.1
11(N,O)	$C_9 H_7 NO$	9-10	0.5	<0.1	0.1	<0.1	0.0
17(N,O)	$C_{13} H_9 NO$	13-14	0.1	0.0	<0.1	0.2	<0.1

Based upon the chemistry associated with the separation, the carbon numbers for the first homolog in each Z(N) series, and analyses of other coal tars (28,30,32), the data for these nitrogen-containing compounds in Table VI are reasonably attributed to the presence of pyrrolic nitrogen types. For example, the carbon number for the first homolog in the -9(N), -15(N), and -21(N) series are those expected for indoles, carbazoles, and benzocarbazoles, respectively. The maximum number of homologs in the various Z(N) series is ≤ 4 with the parent compound dominating the distribution, e.g., the distribution in the -15(N) series is 55, 24, 15, 5, and 1 weight percent for carbazole and its $C_1, C_2, C_3,$ and C_4 alkylated homologs.

Definitive conclusions concerning structures for the nitrogen plus oxygen-containing compounds are not possible. Based upon the formulas for the first members in each series, hydroxyazanaphthalenes and hydroxyazaphenanthrenes/anthracenes are tentatively suggested to account for the -11(N,O) and -17(N,O) series, respectively.

Comparison of the weight percentages in Table VI for the reactor samples with those for the feedstock reveals a net non-reactivity for compounds containing the pyrrolic nucleus. The -11(N,O) and -17(N,O) compounds seem to be more reactive than the Z(N) compounds.

Bases. Carbon-number distributions for the nitrogen and nitrogen plus oxygen-containing compounds present in the base fractions from the feedstock and from reactor-samples 1 and 2 are presented in Tables VII and VIII, respectively. As seen in Table VII, the base fraction from anthracene oil contains -5(N) through -23(N) and -27(N) compound types. These series are indicated to be composed principally of compounds possessing the pyridine nucleus based upon the chemistry associated with the separation, the formulas for the first homolog observed in each series, GC/MS analysis, and other compositional data for anthracene oil and coal tars (27-30). The available data preclude a clear deduction of structures for the NO-containing compounds. However, the initial carbon numbers for these Z(N,O) series, tentatively suggest the presence of azaoaromatics phenomenologically derived from furans by replacement of aromatic-ring CH by nitrogen. The nitrogen compound types possess from 1 through 5 aromatic rings while the nitrogen plus oxygen types have 3 through 4 rings.

The data in Table VII reveal that 2-, -11(N), 3-, -17(N), and 4-, -21(N), aromatic-ring compounds account for 23, 28, and 15% of the anthracene-oil bases. The ring equivalent -12, -18, and -22 hydrocarbons account for 14, 24, and 26% or a total of 64% of the anthracene-oil hydrocarbons. Thus, both the distribution and total percentage of 2-, 3-, and 4-ring aromatic compounds is similar for the bases and hydrocarbons. In contrast, the 2-, 3-, and 4- ring-aromatic compounds account for only 9, 3, and 23% or a total of 35% of the acids.

Similar to the results obtained for both the acids and neutrals the first three homologs in each Z(N) and Z(N,O) series account for 88% of the anthracene-oil bases. An unambiguous determination of the contribution of azaaromatics and hydroazaaromatics is precluded by the possible presence of both compound types in a given Z(N) series. In this regard, dihydro and tetrahydro -15(N) compounds should contribute minimally to the weight percentages at carbon numbers ≥ 12 in the -13(N) and -11(N) series, respectively, because such compounds should be chemically unstable relative to the fully aromatic compounds in the -15(N) series, the hexahydro analogs in the -9(N) series, or biphenyls in the -13(N) series derived from opening of the cyclopentano ring in -15(N) azafluorenes. The situation is considerably more complicated for the more negative Z(N) series. For example, the dihydro and tetrahydro 3-ring azaaromatics could contribute to carbon numbers ≥ 13 in the -15(N) and -13(N) series, respectively; the data for the -9(N) series demonstrates a negligible amount of octahydro 3-ring azaaromatics. It is important to note that GC/MS analysis indicates a negligible contribution of dihydro and tetrahydro 3-ring azaaromatics possessing 13 carbons to the -15(N) and -13(N) series. Based upon such considerations, the weight percentages of the -5(N),

Table VII. Carbon-Number Distribution for C_NH_{2N+Z}N and C_NH_{2N+Z}NO Bases in Anthracene Oil

-Z	Parent Formula	Weight Percents (X10 ¹) for Carbon Number																	Total
		8	9	10	11	12	13	14	15	16	17	18	19						
5(N)	C ₅ H ₅ N	0.4	0.2																0.6
7(N)	C ₈ H ₉ N	1.0	2.0	0.7	0.6	0.2													4.5
9(N)	C ₈ H ₇ N	0.3			0.2	0.3													0.8
11(N)	C ₉ H ₇ N		8.5	6.0	4.1	1.8	1.0	0.5	0.2	0.1									22.2
13(N)	C ₁₁ H ₉ N				1.2	1.4	2.5	1.2	0.3	0.1									6.7
15(N)	C ₁₁ H ₇ N				4.3	2.9	1.0	0.5	0.2	0.1									9.0
17(N)	C ₁₃ H ₉ N					14.5	7.7	3.4	1.1	0.4	0.1								27.2
19(N)	C ₁₄ H ₉ N						1.0	1.8	1.3	0.8	0.4	0.1							5.4
21(N)	C ₁₅ H ₉ N							8.9	3.2	1.4	0.5	0.2							14.2
23(N)	C ₁₆ H ₉ N								2.8	0.7	0.2								3.7
27(N)	C ₁₉ H ₁₁ N																0.3	0.3	
11(N,0)	C ₁₀ H ₉ NO				0.5	0.5	0.3	0.2	0.1										1.6
19(N,0)	C ₁₃ H ₇ NO					0.2	0.2	0.1	0.1										0.6
21(N,0)	C ₁₅ H ₉ NO							0.1	0.4										0.5

Table VIII. Carbon-Number Distributions for $C_{H_{2N+Z}N}$ and $C_{H_{2N+Z}NO}$ Bases Present in Reactor-Samples 1 and 2

-Z	Parent Formula	Reactor Sample	Weight Percents ($\times 10^1$) for Carbon Number																
			6	7	8	9	10	11	12	13	14	15	16	17	18	19	Total		
5(N)	C_{5H_5N}	1	0.3	0.8	2.0	2.4	1.0	0.5	0.2	0.1							7.3		
		2	0.1	0.3	1.2	1.2	0.5	0.2	0.1	0.1							3.7		
7(N)	C_{7H_9N}	1				1.5	3.0	2.9	1.6	0.6	0.5	0.2					10.3		
		2				2.3	2.2	1.9	1.1	0.6	0.2	0.2	0.1	0.1			8.7		
9(N)	C_{8H_7N}	1						0.1	0.4	8.8	3.3	1.1	0.4	0.2			14.3		
		2						1.3	0.3	5.5	2.4	1.1	0.5	0.2			11.3		
11(N)	C_{9H_7N}	1				0.5	0.9	1.2	0.9	0.6	0.3	0.4	0.3	0.4	0.2		5.7		
		2				0.3	0.5	0.7	0.5	0.4	0.2	0.7	0.5	0.5	0.3		4.6		
13(N)	C_{11H_9N}	1						0.1	0.4	3.3	2.6	0.4	0.6	0.3			7.7		
		2						0.1	0.2	2.5	1.7	1.1	0.4	0.3			6.3		
15(N)	C_{11H_7N}	1						0.1	0.8	1.0	1.0	1.9	1.2	1.0	0.5		6.5		
		2						0.8	1.2	0.9	2.2	1.5	1.3	0.6	0.2		8.7		
17(N)	C_{13H_9N}	1							2.5	2.5	1.8	1.0	1.0	0.3	0.3		9.4		
		2							1.9	1.5	1.1	0.8	1.2	0.5	0.4		7.4		
19(N)	C_{14H_9N}	1							0.1	1.0	0.7	2.2	0.7	0.2			4.9		
		2							0.1	0.5	0.4	1.5	0.7	0.3			3.5		
21(N)	C_{15H_9N}	1								2.0	1.0	0.8	0.2	0.2			4.2		
		2								0.4	0.5	0.5	0.2	0.3	1.9		4.2		
23(N)	C_{16H_9N}	1											0.3	0.1	0.2		0.6		
		2											0.2	0.2	0.2		0.6		
27(N)	$C_{19H_{11}N}$	1															0.2		
		2															0.2		
11(N,0)	C_{10H_9NO}	1							0.3	0.6	0.4	0.3					1.6		
		2							0.2	0.3	0.2	0.2					0.9		
19(N,0)	C_{13H_7NO}	1								0.1	0.1	0.1	0.1				0.3		
		2								0.1	0.2	0.2					0.5		
21(N,0)	C_{15H_9NO}	1									0.1	0.1	0.6				0.7		
		2											0.1				0.1		

-9(N), -11(N), and -13(N) series; the first three homologs in the -15(N) series; the first two homologs in the -17(N) through -27(N) series; and the Z(N,0) series lead to an estimate of 84% azaaromatics in the feedstock-base fraction.

It is interesting to note that the anthracene-oil-base fraction contains heterocyclic compound types containing two nitrogens (33). This appears to be the first report of numerous $C_N H_{2N+Z} N_2$ compounds in coal liquids. Minor amounts of dinitrogen compounds have been previously observed in these materials (34).

The analytical results for the base fractions from reactor-samples 3 and 4 are similar to those for the base fractions from reactor-samples 1 and 2. Thus, comparison of the data in Tables VII and VIII shows that hydrotreating markedly increased the compositional complexity of the bases. The occurrence of extensive hydrogenation/hydrogenolysis of azaaromatics during the upgrading process is demonstrated: 1) by the increase in both the weight percentages and number of homologs for the -5(N), -7(N), -9(N), and -13(N) series, 2) by the decrease in the amounts of the other Z(N) series, and 3) by the alterations in the weight percentages at a given carbon number across the various Z(N) series. However, the reaction conditions and catalysts were incorrect for effective hydrodenitrogenation of the intermediates produced from the reactant bases. It is thus important to note that the weight percentages of the four base fractions in Table II mask this observation. Indeed, the values in Table II could be interpreted as reflecting only limited reactivity of the feedstock bases under the specified reaction conditions. This situation constitutes another example (11) of the importance of detailed molecular characterization in coal-liquids upgrading. It also demonstrates the difficulty of using the yields of chromatographic or solubility fractions in such endeavors.

The distribution of bases in the upgraded anthracene oil reflects the various rate constants for the hydrodenitrogenation networks under the specified reaction conditions and catalysts. Consequently, the chemistry of the first homologs in the -11(N) and in the -17(N) series, which account for 0.9 and 1.4% of the feedstock, respectively, is qualitatively considered in terms of the reaction networks for hydrodenitrogenation of known compounds. For ease of presentation, the discussion is formulated in terms of the relevant analytical data for the feedstock and reactor-sample 1.

By GC/MS analysis, quinoline (I) and isoquinoline (II) comprise the first homolog in the -11(N) Z series. Table IX presents mole data, calculated per 100g of feedstock, for the bases comprising the 129-139 molecular-weight series. It is interesting to note that the moles of I and II in the feed are *ca.* 2.2×10^{-3} and 4.4×10^{-3} , respectively, by GC/MS. In addition GC/MS analysis reveals the absence of II in the base fractions from

TABLE IX. Moles of Bases at Molecular Weights 129-135
In Feed and Reactor-Sample 1

Mass	Formula	Moles $\times 10^3$, ^a	
		Feedstock	Reactor Sample 1
129	C ₉ H ₇ N	6.6	0.4
133	C ₉ H ₁₁ N	0.2	1.1
135	C ₉ H ₁₃ N	0.2	1.8
139	C ₉ H ₁₇ N	-	0.006
TOTAL		7.0	3.3

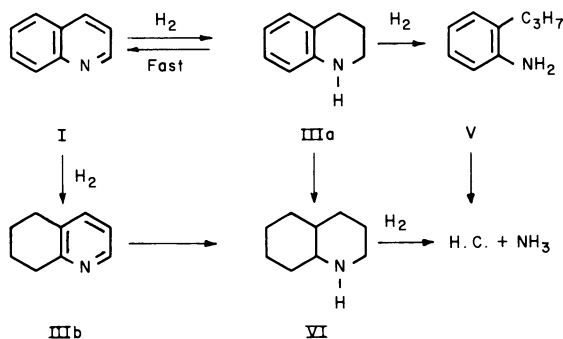
^aCalculated per 100g of feed.

the reactor samples. In regard to the C₉H₁₁N compounds, GC/MS shows the presence of 1,2,3,4-tetrahydroquinoline (IIIa) and the absence of both 5,6,7,8-tetrahydroquinoline (IIIb) and tetrahydroisoquinolines (IV). Finally, the GC/MS analysis confirms the presence of minor and significant amounts of 2-propylaniline (V) in the feedstock and reactor-base fractions, respectively. These results are at least qualitatively consistent with those obtained from reaction of I with H₂ a) in a batch reactor using MoS₂ as the catalyst (35) and b) in a high-pressure/high-temperature liquid-phase reactor using a variety of metal catalysts (17,19,21) and from the MoS₂ catalyzed reaction of II with H₂ (35).

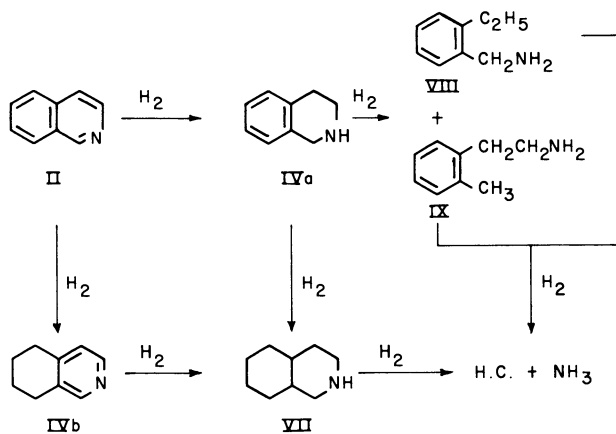
As shown in Scheme 1 (17,19,21), rapid catalytic addition of H₂ to I produces IIIa and IIIb. The presence of IIIa and the absence of IIIb in the products is at least qualitatively consistent with the fact that the former is kinetically favored while the latter is thermodynamically favored (17,19,21). Structure-reactivity relationships provide a preference for hydrogenolysis of the N-C(2) bond rather than the C(8a)-N bond in IIIa producing V rather than 3-phenylpropylamine. Both IIIa and IIIb are converted to decahydroquinoline (VI), mass 139; the rate constant for the latter conversion is significantly greater than the one for the former (17,19,21). The absence of significant amounts of VI in the products is consistent with its facile conversion to hydrocarbons and NH₃ (17,19,21,35).

The only nitrogen containing compounds observed from the MoS₂ catalyzed reaction of H₂ and II were IV and decahydroisoquinoline (VII) (35). VII is a minor product. As shown in

Scheme 1. Known reaction network for hydrodenitrogenation of quinoline



Scheme 2. Proposed reaction network for hydrodenitrogenation of isoquinoline



Scheme 2, II reacts with H_2 producing either IVa or IVb. Hydrogenolysis of either the N-C(3) bond or the N-C(2) bond in IVa produces either 2-ethylbenzylamine (VIII) or 2-(2-methylphenyl)ethylamine (IX), respectively. Since VIII and IX contain a benzylic and aliphatic NH_2 group, respectively, their denitrogenation should be facile. In contrast, the NH_2 group in V, see Scheme 1, is aromatic and, hence, as observed would be expected to undergo hydrogenolysis less readily. Alternatively, hydrogenation of IVa and IVb produces VII which in turn suffers hydrogenolysis producing hydrocarbons plus NH_3 .

The weight percentages of the homologs containing 13 carbons in the -17(N) series in Tables VII and VIII demonstrate that hydrotreating significantly reduced the amount of 3-ring azaaromatics. Results from the GC/MS analyses of the base fractions from the feed and reactor-sample 1 allow the weight percentages of the C-13 homologs in the -7(N) through -17(N) series in the feedstock and in reactor-sample 1 to be considered in terms of the chemistry of the $C_{13}H_9N$ compounds.

Of the eight possible $C_{13}H_9N$ isomers, GC/MS determined the presence of six and possibly seven isomers in the feedstock and five isomers in reactor-sample 1. Thus, unlike the hydrocarbons, the anthracene-oil bases contain both the anthracene and phenanthrene ring structure. Unfortunately, the lack of both GC-retention times and 70-eV reference spectra for the isomeric azaanthracenes and azaphenanthrenes precludes identification and quantification of the individual isomers.

Table X presents for both the feedstock and reactor-sample 1 the moles of azaanthracenes plus azaphenanthrenes and their variously hydrogenated analogs. These values were calculated from the weight percents in Tables VII and VIII for the C-13 homologs in the -7(N) through -17(N) series as follows. Since GC/MS of the feedstock bases did not identify partially hydrogenated azaphenanthrenes or azaanthracenes, the weight percents of $C_{13}H_{11}N$, $C_{13}H_{13}N$, $C_{13}H_{15}N$, and $C_{13}H_{17}N$ in Table VII reflect the presence of other compounds such as alkylated azafluorenes, phenylpyridines, quinolines, and indoles, respectively. Consequently, the moles of masses 181 through 189 for the feed are entered as zero in Table X. The GC/MS data for reactor-sample 1 reveal the presence of at least nine $C_{13}H_{11}N$ (m/z 181), five $C_{13}H_{13}N$ (m/z 183), and eight $C_{13}H_{15}N$ (m/z 185) isomers attributable to the presence of compounds resulting from the addition of 2, 4, and 6 hydrogens, respectively, to the 3-ring azaaromatics. The contributions of these compounds to the weight percents of the C-13 homologs in the -15(N), -13(N) and -11(N) series were estimated from the selected ion chromatograms to be

Table X. Moles of Azaanthracenes/Azaphenanthrenes and Their Hydrogenated Analogs at Molecular Weights 179-189 in Feed and Reactor-Sample 1.

Mass	Formula	Moles $\times 10^a$ In	
		Feedstock	Reactor-Sample 1
179	$C_{13}H_9N$	8.1	1.4
181	$C_{13}H_{11}N$	0.0	0.2
183	$C_{13}H_{13}N$	0.0	1.0
185	$C_{13}H_{15}N$	0.0	0.1
187	$C_{13}H_{17}N$	0.0	4.7
189	$C_{13}H_{19}N$	0.0	0.3
Total		8.1	7.7

^aCalculated per 100g of feed.

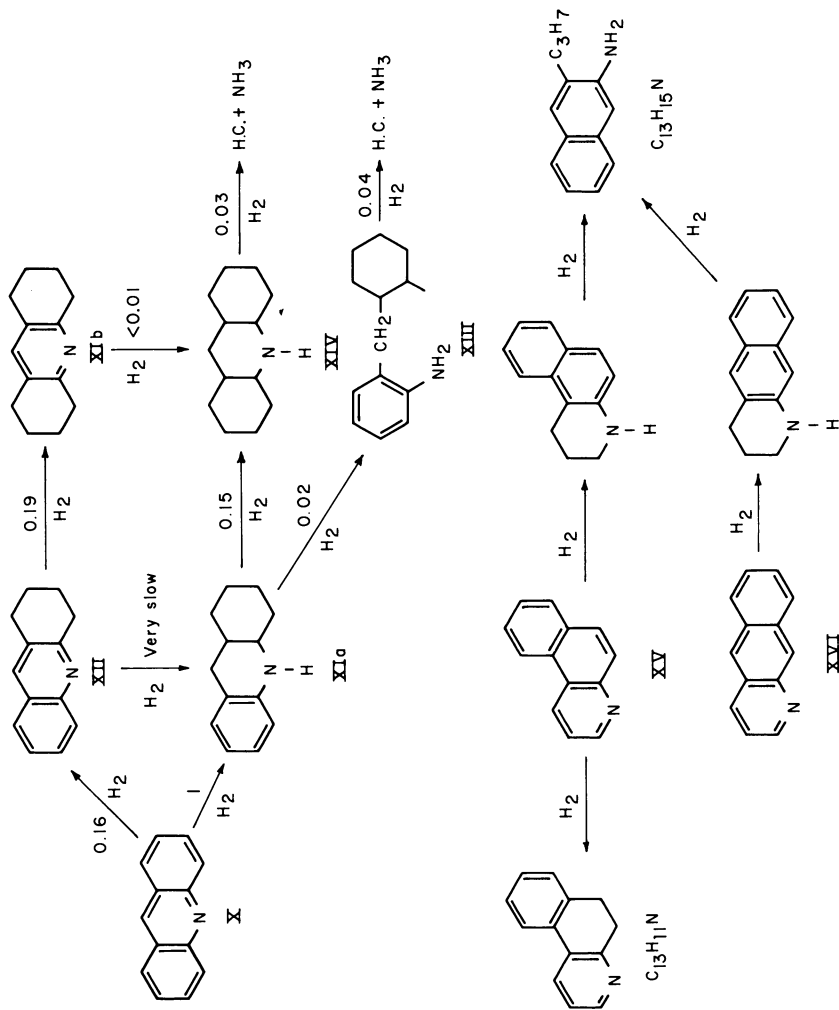
40, 54, and 17 percent, respectively. These values and the weight percentages at C-13 in the -15(N), -13(N), and -11(N) series in Table VIII were used to calculate the moles of $C_{13}H_{11}N$, $C_{13}H_{13}N$, and $C_{13}H_{15}N$ for reactor-sample 1 in Table X.

At least four octahydro-(*m/z* 187) and three decahydro-(*m/z* 189) 3-ring azaaromatics and were identified in the reactor-sample-1 bases by GC/MS. Thus, in Table X the moles of $C_{13}H_{17}N$ and $C_{13}H_{19}N$ in reactor-sample 1 were calculated using the weight percentages at C-13 in the -9(N) and -7(N) series, respectively, from Table VIII.

The results in Table X reveal that hydrotreating under the reaction conditions and catalyst specified in Table I reduced the moles of azaanthracenes and azaphenanthrenes by *ca.* 83%. However, it is important to note that the decrease of 6.7 millimoles in reactants (mass 179) essentially equals, within the limits of data precision, the increase of 6.3 millimoles in products (masses 181 through 189). Consequently, for the given catalyst, the reaction conditions were insufficiently severe to convert intermediate products to hydrocarbons and NH_3 .

The chemical implications of the data in Table X are considered in terms of the hydrogenation mechanisms in Scheme 3. The reaction network for hydrodenitrogenation of acridine (X) was reported by Zawadski, Shih, Katzer, and Kwart (36); the

Scheme 3. Reaction network for hydrogenation of acridine and proposed extension to other $C_{13}H_9N$ isomers



relative rates shown with the arrows in Scheme 3 were calculated from the first-order rate constants for Co-Mo/Al₂O₃ catalyst at 693°F and 1999 psig (37). The hydrogenation of X to form 1,2,3,4,4a,9,9a,10-octahydroacridine (XIa) is kinetically favored over its conversion to 1,2,3,4-tetrahydroacridine (XII). Furthermore, the rate of production of XII is approximately equal to its rate of conversion to 1,2,3,4,5,6,7,8-octahydroacridine (XIb). The rate of hydrogenolysis of a C-N bond in XIa producing 2-(2-methylcyclohexyl)aniline (XIII) is considerably less than the rates of formation of XIa, XIb, XII and perhydroacridine (XIV). The rates of C-N bond hydrogenolysis in XIII and XIV leading to hydrocarbons plus NH₃ are also considerably smaller than the rates of ring hydrogenation.

Unfortunately, the mechanisms for hydrodenitrogenation of the remaining C₁₃H₉N isomers and the isomeric distribution of the molecular formulas in Table X are unknown. However, relating the results for acridine to the structures of the remaining C₁₃H₉N isomers using structure-reactivity considerations leads us to postulate in general: 1) that hydrogenation of carbon-carbon and carbon-nitrogen bonds will be facile compared to hydrogenolysis of carbon-nitrogen bonds and 2) that production of tetrahydro and octahydro analogs should be facile. The absence of dihydro- and hexahydroacridines (C₁₃H₁₁N and C₁₃H₁₅N, respectively) in the products from hydrogenation of X are consistent with aromaticity considerations and the anticipated low rates of Co-Mo catalyzed hydrogenolysis of carbon-carbon single bonds in compounds such as XII. However, as seen in Scheme 3, C₁₃H₁₁N compounds are reasonably expected intermediates in the reaction of compounds such as 1-azaphenanthrene (XV). In addition, hydrodenitrogenation of compounds such as XV and 1-azaanthracene (XVI) is anticipated to involve C₁₃H₁₅N compounds as shown in Scheme 3.

The present hydrotreating studies were conducted in the temperature range 600-700°F. The lower hydrogen pressures in the present study and the existence of C₁₃H₉N isomers in addition to acridine in the feed are two of a number of factors precluding any attempt at quantitatively interpreting the data in Table X. However, the presence of significant amounts of C₁₃H₁₃N and C₁₃H₁₅N compounds in the products, as shown in Table X, is at least qualitatively consistent with the acridine results and the proposed extension of this network to other C₁₃H₉N isomers. Table X demonstrates the production of lesser amounts of C₁₃H₁₁N and C₁₃H₁₅N compounds from the reaction of C₁₃H₉N with hydrogen. The formation of these compounds in this and other coal-liquid-

hydrotreating studies (38) is at least qualitatively explained in terms of the hydrodenitrogenation networks proposed in Scheme 3 for compounds such as X, XV, and XVI. Thus, the existence of $C_{13}H_{11}N$ and $C_{13}H_{15}N$ isomers in the products indirectly supports the presence of compounds such as XV and XVI in the reactants. The failure to observe perhydro analogs of $C_{13}H_9N$ isomers in the base fraction from reactor-sample 1 could reflect their retention on the anion-exchange resin (39).

Neutrals. Table XI presents compositional data for the furan and thiophene compound types present in the neutral fractions from the feed and the products. Results for only two reactor samples are given because of insignificant variations in the analytical data for these Z(0) and Z(S) compound types between the four upgraded liquids. Dibenzofurans and dibenzothiophenes were identified by GC/MS.

The weight percents in Table XI indicate that the furans were markedly resistant to both hydrogenation and hydrogenolysis under the experimental conditions. It should be noted that on a 100g basis the moles at C-16 and C-17 in the -22(0) series are 2.8×10^{-3} and 1.8×10^{-3} less in product 1 than in the feed. However, this decrease approximates the increase of 1.8×10^{-3} and 1×10^{-3} moles of C-16 and C-17 homologs in the -18(0) series in product 1. Similar results are observed for reactor-sample 3. This result suggests the hydrogenation of benzonaphthenofurans produces tetrahydroderivatives.

The weight percents in Table XI demonstrate that the thiophenes were very reactive toward sulfur removal under all experimental conditions. The absence of partially hydrogenated thiophenes in the products is consistent with the mechanism of dibenzothiophene desulfurization (18,22).

Table XII presents compositional data for the aromatic hydrocarbons present in the anthracene oil. Compounds in the -12(H), -14(H), -18(H), and -22(H) series account for 78% of the aromatic hydrocarbons. The -12(H) compounds identified by GC/MS include naphthalene, 1- and 2-methylnaphthalene and at least 5 naphthalenes possessing 2 alkyl carbons. By GC/MS, acenaphthene and biphenyl account for 94% and 6%, respectively, of the first homolog in the -14(H) series. The parent member of the -18(H) series ($C_{14}H_{10}$) was preparatively isolated using GC and identified by UV and NMR to be $\geq 98\%$ phenanthrene. The dominance of phenanthrene over anthracene in both high- and low- temperature coal tars has been previously noted (29,30,40,41,42,43). Thus, phenanthrene and presumably its alkylated homologs comprise the -18(H) Z series and account for 15.4% of the anthracene oil. The initial homolog in the -22(H) series, $C_{16}H_{10}$, is comprised of 58%

Table XI. Carbon-Number Distribution for $C_N H_{2N+Z} O$ and $C_N H_{2N+Z} S$ Neutrals in Anthracene Oil and in Reactor-Samples 1, 2, and 3

-Z	Parent Formula	Sample ^a	Weight Percents ($\times 10^1$) at Carbon Number															
			8	9	10	11	12	13	14	15	16	17	18	Total				
16(O)	$C_{12}H_8O$	F				2.1	1.4	0.9	0.3								4.7	
		R1				2.3	1.5	0.7	0.3								4.8	
		R3				2.0	1.4	0.8	0.3								4.5	
18(O)	$C_{14}H_{10}O$	F							0.1	0.1							0.2	
		R1							0.1	0.5	0.2						0.8	
		R3							0.1	0.6	0.2						0.9	
22(O)	$C_{16}H_{10}O$	F												1.3	0.8		2.1	
		R1											0.7	0.4	0.2		1.3	
		R3											0.5	0.3	0.1		0.9	
26(O)	$C_{18}H_{10}O$	F															0.1	
		R1															0.1	
		R3															0.1	
10(S)	C_8H_6S	F	0.2	0.1													0.3	
		R1	0.0	0.0													0.0	
		R2	0.0	0.0													0.0	
16(S)	$C_{12}H_8S$	F				0.8	0.2	0.1									1.1	
		R1				0.1	0.1	0.0									0.2	
		R2				0.4	0.1	0.0									0.5	
22(S)	$C_{16}H_{10}S$	F														0.2	0.2	
		R1														0.1	0.1	
		R2														0.1	0.1	

^aF=Feedstock; R1=Reactor-Sample 1, R2=Reactor-Sample 2, R3=Reactor-Sample 3.

Table XII. Carbon-Number Distribution for C_NH_{2N+Z} Compounds Present in Anthracene Oil

-Z(H)	Parent Formula	Weight Percents ($\times 10^1$) for Carbon Number																		
		9	10	11	12	13	14	15	16	17	18	19	20	Total						
6	C_6H_6	0.5	0.4																0.9	
8	C_9H_{10}	2.0	1.4	0.8															4.2	
12	$C_{10}H_8$	48.3	23.1	13.0	6.4	2.3	0.3												93.4	
14	$C_{12}H_{10}$				52.6	18.3	13.5	3.7	2.7	1.4	0.4								92.6	
16	$C_{12}H_8$							25.9	18.5	7.4	2.6	1.0	0.5						55.9	
18	$C_{14}H_{10}$									104.1	31.8	13.2	4.1	1.1					154.3	
20	$C_{15}H_{10}$									13.9	23.7	9.1	3.4	3.3					53.4	
22	$C_{16}H_{10}$										121.3	26.6	16.3	2.7	1.6				168.5	
24	$C_{18}H_{12}$											16.3	3.8	1.6					21.7	
26	$C_{18}H_{10}$												1.3	1.2	1.6				4.1	
28	$C_{20}H_{12}$														3.3				3.3	

fluoranthene and 42% pryene by GC/MS. It should be noted that combination of the GC/MS and group-type MS analyses shows that the eight parent compounds indane, naphthalene, acenaphthene, biphenyl, fluorene, phenanthrene, pyrene, and fluoranthene account for *ca.* 35 weight percent of the anthracene oil. Finally, the hydrocarbons possess from 1 through 5 aromatic rings.

The compositional data for the aromatic hydrocarbons present in the upgraded anthracene oil are presented in Table XIII. Comparison of the data in Tables XII and XIII reveals significant increases and decreases in the amounts of hydroaromatic and aromatic hydrocarbons, respectively, under all reaction conditions. This is especially evident by the presence and absence of the hydroaromatic -10(H) series in the products and feeds, respectively, and by the large increase in the weight percentage of the -8(H) compounds in the products compared to the feeds. The presence of significant amounts of dihydro-, tetrahydro-, and octahydrophenanthrenes in the products is indicated by GC/MS, by the increase in the weight percents at C-14 in the -16(H) and -14(H) series, and by the presence of $C_{14}H_{18}$, -10(H).

The following procedure was adopted to obtain a first estimate of the contribution of hydroaromatic hydrocarbons to both the feed and products. As seen in Table XIV, the homologs possessing 14 or more carbons in the -14(H) and -16(H) series and the homologs containing in excess of 15 carbons in the -18(H) and -20(H) series were assumed to correspond to compounds resulting from the addition of various amounts of hydrogen to aromatic hydrocarbons of the same carbon number in more negative Z(H) series. The compounds in the -12(H) series containing 16 but not 14 or 15 carbons were assumed to be hydroaromatics. This assumption appears to be reasonable because the former homolog can be ascribed to the presence of compounds such as decahydro-pyrene whereas the latter two homologs would suggest the presence of unstable compounds such as hexahydrophenanthrene. The calculated amounts for each Z(H) series in the reactor samples were averaged to obtain the results presented in column 5 of Table XIV. As seen in column 4 the range in carbon numbers is the same for all reactor samples.

The previous assumptions probably produce upper limits to the weight percents of hydroaromatic hydrocarbons. However, comparison of the values in columns 3 and 5 of Table XIV reveals that the increased contribution of these compounds in the products compared to the feed must be quantitatively significant. Furthermore, the deficiencies associated with these necessary assumptions should be minimized by considering the ratio of aromatic to hydroaromatic hydrocarbons in the products relative to the corresponding ratio for the feed. Thus, the hydroaromatic to aromatic hydrocarbon ratio in the products relative to the feed is *ca.* 5 to 1.

The following examples further illustrate the qualitative information which can be deduced concerning the chemical

Table XIII. Carbon-Number Distributions for the C_nH_{2N+Z} Compounds Present in Reactor-Samples 1 through 4

-Z(H)	Parent Formula	Reactor Sample	Weight Percents ($\times 10^1$) for Carbon-Number																		Total	
			9	10	11	12	13	14	15	16	17	18	19	20								
6	C_6H_6	1	2.5	1.9	1.0	0.9														6.3		
		2	2.1	1.9	1.2	0.5															5.7	
		3	1.8	1.8	1.1	0.6															5.3	
		4	2.6	2.1	1.0																	5.7
8	C_9H_{10}	1	5.2	32.3	14.2	10.6	6.0	2.0													70.3	
		2	4.1	18.4	9.5	6.5	5.2	2.2													45.9	
		3	3.8	42.7	19.2	14.3	8.0	3.2														91.2
		4	4.9	25.4	11.6	7.9	3.3	1.3														54.4
10	C_9H_8	1				29.9	10.0	14.9	5.0	2.1											61.9	
		2				18.4	5.9	5.6	2.9	0.9											33.7	
		3				36.5	13.9	26.3	7.5	4.0											88.2	
		4				24.0	6.7	9.9	3.3	1.4											45.3	
12	$C_{10}H_8$	1				39.2	22.5	14.4	7.3	2.7	2.2	12.5									100.8	
		2				45.6	24.1	17.2	7.2	3.0	1.5	3.4									102.0	
		3				20.0	12.4	9.3	5.2	2.9	4.0	19.1									72.9	
		4				44.5	23.0	16.0	7.1	3.1	1.7	5.2									100.6	
14	$C_{12}H_{10}$	1						35.1	14.4	33.3	9.0	5.5	2.9	1.4							101.6	
		2				48.6	17.5	22.6	8.0	2.8	2.1	0.9									102.5	
		3				23.5	11.5	34.1	10.9	4.8	3.2	1.8									89.8	
		4				43.0	18.2	35.8	10.7	4.4	2.5	0.8									115.4	
16	$C_{12}H_8$	1																			1.4	
		2																			3.2	
		3																			0.9	
		4																			1.0	
																				0.6		
																					0.1	

Table XIII. Continued

-Z(H)	Parent Formula	Reactor Sample	9	10	11	12	13	14	15	16	17	18	19	20	Total	
18	C ₁₄ H ₁₀	1													157.2	
		2	72.5	24.4	39.1	11.5	6.7	2.0	1.0						181.1	
		3	79.4	28.2	52.3	12.1	6.7	1.6	0.8							139.5
		4	59.4	21.0	35.7	11.9	7.5	2.4	1.6							152.7
20	C ₁₅ H ₁₀	1	87.9	26.0	23.9	8.4	4.7	1.3	0.5						58.7	
		2		8.7	27.3	8.5	10.4	2.2	1.6						69.6	
		3		7.7	40.2	10.7	7.7	1.7	1.6						50.9	
		4		7.2	21.8	7.2	10.3	2.4	2.0						55.0	
22	C ₁₆ H ₁₀	1			11.1	23.7	8.1	9.5	1.8	0.8					89.0	
		2			61.3	12.8	9.2	2.9	2.8						81.5	
		3			47.2	14.1	13.9	3.7	2.6						75.7	
		4			52.5	11.3	8.1	1.0	2.8						121.5	
24	C ₁₈ H ₁₂	1			89.9	17.0	9.7	2.6	2.3						8.5	
		2			5.1	1.8	1.6								11.5	
		3			6.9	2.6	2.0								11.6	
		4			6.3	2.4	2.9								10.8	
26	C ₁₈ H ₁₀	1			6.9	2.2	1.7								5.1	
		2			2.5	1.5	1.1								2.6	
		3			0.7	0.7	1.2								7.4	
		4			3.5	2.7	1.2								3.2	
28	C ₂₀ H ₁₂	1			1.2	1.0									1.0	
		2													1.3	
		3													2.1	
		4													1.6	

Table XIV. Semiquantification of Hydroaromatic $C_N H_{2N+Z}$ Compounds Present in Feedstock and Upgraded Anthracene Oil

-Z(H)	Feedstock		Products	
	Range In N	Weight Percent Hydroaromatics	Range In N	Av. Weight Percent ^a Hydroaromatics
8	9-11	0.4	9-14	6.5 \pm 2.0
10	-	-	12-16	5.7 \pm 2.4
12	-	-	16	1.3 \pm 0.8
14	14-18	2.2	14-18	4.9 \pm 0.9
16	14-18	3.0	14-20	7.4 \pm 0.2
18	16-18	1.8	16-20	6.3 \pm 0.7
20	16-19	4.0	16-20	5.0 \pm 0.8
Total		11.4		37.1 \pm 3.5
Wt.% Hydrocarbons		65.2		74.6 \pm 1.4
Aromatics/Hydro- aromatics		4.7		1.0 \pm 0.1

^aValues are the averages of the total weight percents for each Z(H) series in column 1 for reactor-samples 1 through 4.

processes occurring during hydrotreating. As previously noted, dihydrophenanthrene ($C_{14}H_{12}$), tetrahydrophenanthrene ($C_{14}H_{14}$), and octahydrophenanthrene ($C_{14}H_{18}$) which are produced in chromia-alumina hydrotreating of phenanthrene (44) were tentatively identified in the product mixtures. Other C-14 compounds (44) involved in this process are 2-ethylbiphenyl, $C_{14}H_{14}$, 2-butyl-naphthalene, $C_{14}H_{16}$, and 6-butyltetralin, $C_{14}H_{20}$. The reaction network (44) is illustrated in Scheme 4. Based upon bond-energy considerations, hydrogenolysis of the C_9-C_{10} bond in 9,10-dihydrophenanthrene is expected to be facile compared to hydrogenolysis of the C_8-C_9 bond producing, as shown in Scheme 4, 2,2'-dimethylbiphenyl rather than the reported (44) 2-ethylbiphenyl. Thus, the question of C_9-C_{10} versus C_8-C_9 bond hydrogenolysis should be reexamined. It is significant to note that the reaction network allows for the eventual introduction of phenanthrene and its partially hydrogenated analogs into the biphenyl, naphthalene, and tetralin pools. For the C_{14} hydrocarbons ranging in mass from 178 to 188 amu, Table XV presents moles in the feed and the change in the moles between each reactor sample and the feed. The data reveal that the amount of phenanthrene has decreased in all reactor samples. The smaller decrease in moles of $C_{14}H_{10}$ in reactor samples 2 and 4 compared to reactor sample 1 is qualitatively consistent with the reaction conditions in Table I. The extent to which the anomalously large decrease in the millimoles of $C_{14}H_{10}$ in reactor-sample 3 and the variations in the millimoles of the other C-14 hydrocarbons between reactor samples reflects inaccuracies in the analytical procedures and a complex interdependence of reaction conditions and catalyst properties on reactivity cannot be delineated. However, the values in column 8 of Table XV reveal that all 4 reactor samples contain more moles of C-14 compounds in the -8(H) through -16(H) series (masses 188 through 180) than does the feed on a 100g basis. Furthermore, for each reactor sample the values in column 9 show that the total increase in moles of $C_{14}H_{12}$, $C_{14}H_{16}$, $C_{14}H_{18}$, and $C_{14}H_{20}$ exceeds the decrease in moles of $C_{14}H_{10}$. Thus, the mechanism for hydrogenation of phenanthrene over chromia-alumina appears to be at least qualitatively applicable to the conditions specified in Table I and other compounds contribute to the amounts of C-14 compounds in the -8(H) through -18(H) series. In this regard, phenanthrene is a product in the hydrocracking of pyrene (45).

Acenaphthene (XVII) and biphenyl (XVIII) comprise the first homolog ($C_{12}H_{10}$) in the -14(H) series of the feedstock and reactor samples by GC/MS. Tetrahydroacenaphthene (XIX), $C_{12}H_{14}$,

Table XV. Moles of Hydrocarbons at Molecular Weights 178-188 in the Feed and the Changes in Moles of These Compounds Between Products and Feed

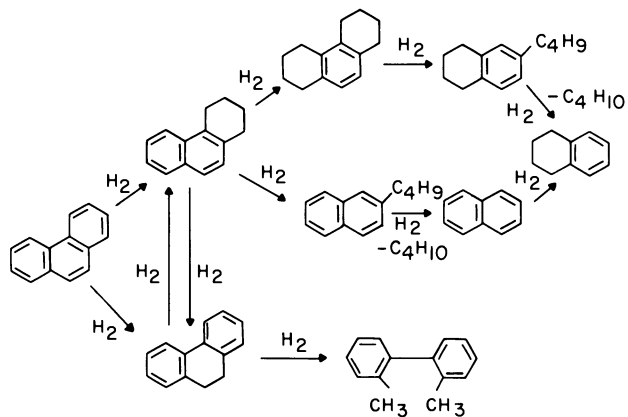
Sample ^{a,b}	Moles ($\times 10^3$) at Mass ^c					Total Columns		
	178 (C ₁₄ H ₁₀)	180 (C ₁₄ H ₁₂)	182 (C ₁₄ H ₁₄)	184 (C ₁₄ H ₁₆)	186 (C ₁₄ H ₁₈)	188 (C ₁₄ H ₂₀)	3-7	2-7
Feed	58	10	7	1	0	0	18	76
Δ RS-1	-18	10	11	0.3	8	1	30.3	12.3
Δ RS-2	-14	17	5	0.4	3	1	26.4	12.4
Δ RS-3	-25	6	11	0.4	14	2	33.4	8.4
Δ RS-4	-9	4	12	0.5	5	1	22.5	13.5

^a $\Delta RS(i) = M(j)R(i) - M(j)F$ where $M(j)$ = Moles of the j th component in the i th reactor sample R and in the feed F .

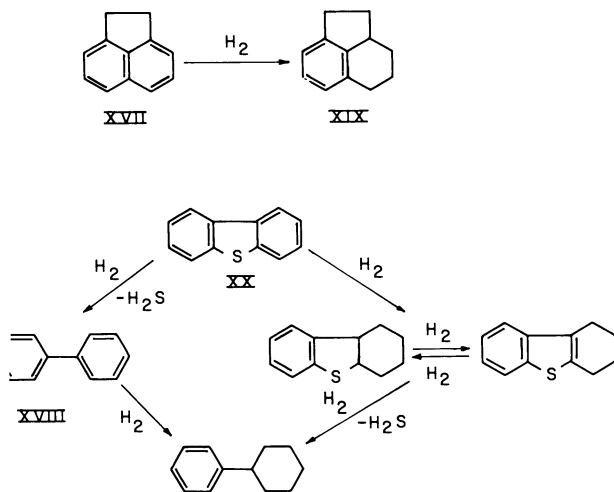
^b Reaction conditions specified in Table I.

^c Calculated per 100g of feed.

Scheme 4. Reaction network for the hydrogenation/hydrogenolysis of phenanthrene



Scheme 5. Reaction network for the hydrodesulfurization of dibenzothiophene and for the hydrogenation of acenaphthene and biphenyl



in the -10(H) series, was similarly identified in the products. The changes in the amounts of XVII, XVIII, XIX and dibenzothiophene (XX) between the feed and reactor-sample 1 are considered in terms of the reaction mechanisms in Scheme 5. The network for hydrodesulfurization of XX is the one developed by Gates and co-workers (18,22).

By GC, XVII and XVIII account for 94% and 6%, respectively, of the $C_{12}H_{10}$ compounds in the feed. XVIII and XIX were unresolved in the gas chromatograms of the products. However, the $C_{12}H_{10}$ compounds in reactor-sample 1 were estimated to consist of 52% of acenaphthene and 48% biphenyl assuming equal 70-eV EI sensitivities for the parent ions of XVIII and XIX and using the total weight percentages of XVII, XVIII, and XIX by GC. On a 100g basis, the weight percentages of the $C_{12}H_{10}$ compounds in Tables XII and XIII when combined with these percentages for XVII and the weight percentage of $C_{12}H_{14}$ in Tables XII and XIII result in a decrease of ca. 20 millimoles of XVII and an increase of ca. 19 millimoles of XIX between feed and products. This surprisingly good agreement suggests, as shown in Scheme 5, that tetrahydroacenaphthene is a primary product of the hydrogenation of acenaphthene, at least under the conditions specified in Table I.

It should be noted that 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4,10,11-hexahydrodibenzothiophene shown in Scheme 5 were not detected, as expected (22), in the four reactor samples. Combining the percentage contributions of XVIII to the $C_{12}H_{10}$ hydrocarbons in the feed and products with the weight percentages of the latter compounds in Tables XII and XIII results in an increase of ca. 9 millimoles of biphenyl in reactor-sample 1 compared to the feed. This value significantly exceeds the ca. 4 millimole decrease in XX between products and reactants. The mass-balance discrepancy is undoubtedly larger because of the expected conversion of XVIII to cyclohexylbenzene (23). Although the $C_{12}H_{16}$ isomers were not rigorously identified and quantified by GC/MS, the maximum increase in millimoles of the latter between products and reactants is 6.6 based upon the weight percentage of $C_{12}H_{16}$ compounds in reactor-sample 1. These results suggest that other compounds are precursors to biphenyl.

Conclusions

The following are the salient conclusions resulting from this study.

1. The reaction conditions and catalyst used in the upgrading experiments produced extensive deoxygenation of hydroxy-

lated aromatic hydrocarbons. In fact, the significant reactivity precludes inferences concerning the mechanism of hydrodeoxygenation of these compounds.

2. Compounds containing the pyrrole nucleus exhibited a marked net non-reactivity. This result parallels the significantly reduced reactivity of carbazole in complex mixtures (46). It is thus important to note that carbazole exhibits appreciable reactivity in a carrier oil at 367°C and 136 atm using a presulfided Ni-Mo/Al₂O₃ catalyst (19). It may also be significant to note that a substituted carbazole was one of the products from the catalytic hydrogenation of indole in furnace oil (47).

3. Compounds in the feed possessing the pyridine nucleus exhibited significant reactivity. However, the reaction conditions and the catalysts were inadequate for the effective conversion of the intermediate nitrogen-containing products to hydrocarbons plus ammonia.

4. The analytical data for quinoline appears to be at least qualitatively consistent with its known (17,19,21) hydrodenitrogenation mechanism. A mechanism for the hydrodenitrogenation of isoquinoline is proposed based upon the analytical data.

5. The compositional data for 3-ring azaaromatic hydrocarbons appear to be consistent with the network for hydrodenitrogenation of acridine (36) and, based upon considerations of structure-reactivity, our proposed extension of it to other C₁₃H₉N isomers.

6. Considerable hydrodesulfurization of the thiophene type compounds is consistent with the known reactivity of dibenzothiophene (18,22). The furans exhibited a net nonreactivity.

7. The amount of hydroaromatic hydrocarbons significantly increased upon hydrotreating. The ratio of aromatic to hydroaromatic hydrocarbons in the feed relative to the products is α . 5 to 1.

8. The yields of phenanthrene, dibenzothiophene, acenaphthene, and biphenyl appear to be reconcilable with their known (44,18,22) or expected chemistry.

9. The composition of anthracene oil is dominated by parent aromatic compounds possessing 2, 3, and 4 aromatic rings.

10. The present study provides another example (11) of the importance of detailed molecular characterization in understanding and controlling the chemical/physical phenomena involved in

coal-liquids upgrading and the inherent difficulty of simply using the yields of fractions obtained from chromatographic separation or solvent extraction of coal liquids in such endeavors.

11. Additional (19) experiments should be conducted to quantitatively determine the applicability of reaction networks for the hydrogenation/hydrogenolysis of individual compounds to coal liquids and to establish mechanisms for reaction of other compound types.

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Catalytic Upgrading of SRC-II Syncrude

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Chevron Research Company, under a contract sponsored by the U.S. Department of Energy (DOE), is conducting a program to determine the feasibility and estimate the costs of using modern petroleum processing technology to produce distillate fuels, such as high octane gasoline, jet fuel, and diesel, from a number of synthetic crude feedstocks. Pilot plant tests for the key processing steps are being conducted to the extent needed to make reasonable estimates of commercial plant performance.

The first feedstock studied under this contract was Paraho shale oil. In a series of recent papers (1-4) and a DOE report (5), three basic shale oil processing routes for the production of transportation fuels were studied: hydrotreating followed by hydrocracking, hydrotreating followed by fluid catalytic cracking (FCC), and severe coking followed by hydrotreating. It was concluded that shale oil can be refined to high quality transportation fuels via modern state-of-the-art refining technology and that it can serve as a substitute for crude oil in a refinery equipped with modern hydrotreating facilities. The key to successful shale oil refining is the initial hydrotreating step which removes contaminants (nitrogen, sulfur, oxygen, olefins, and metallic contaminants) and permits the use of conventional conversion and refining processes to make finished products.

This chapter reports results of a similar study to determine the feasibility of converting solvent refined coal (SRC) to transportation fuels. The next chapter discusses upgrading of H-Coal process products.

The SRC process, in its two forms, is one of the major processes under current study in programs sponsored by the DOE for conversion of coal to either (1) a solid deashed low sulfur product or (2) a low boiling liquid.

In the original SRC process (6), now designated as SRC-I, coal is dissolved under moderate hydrogen pressure in an

internally generated heavy aromatic solvent to yield a product from which most of the mineral matter is removed by filtration. Solvent is recovered for reuse by vacuum distillation. The distillation residue (known as SRC or SRC-I) is a solid under ambient conditions. Research on the upgrading of SRC-I is reported in other chapters of this book.

In an alternate version of the process (7), designated SRC-II, a portion of the coal solution is recycled as solvent in place of the distillate solvent of the SRC-I process. The filtration step is eliminated; and, typically, the process operates at a higher pressure, higher temperature, and longer residence time than the SRC-I process. Hydrogen consumption and the conversion of dissolved coal is increased, and the primary product is a liquid rather than the solid product of the SRC-I process. The liquid product of the SRC-II process is the feedstock that is the subject of the work described in this chapter.

In a previous paper (8), we presented results of hydro-treating SRC-II process product at several severities, and preliminary cost estimates were given. In the present chapter, previous results are summarized; and results of further downstream processing pilot plant studies are presented, together with process engineering studies and updated cost estimates. More details of this study are given in a DOE report. (9)

Feeds

The Pittsburg and Midway Coal Mining Company provided the SRC-II process products that were used as feeds in these studies. They were produced in the Fort Lewis, Washington, pilot plant from a West Virginia coal (Pittsburg Seam, Blacksville No. 2 Mine of the Consolidated Coal Company). Three fractions of SRC-II were provided. These were reblended in a ratio recommended by the DOE to constitute the net whole liquid process product from "typical" SRC-II operation as best could be estimated at the time this project was started (April 1978).

Table I shows the inspections of the reconstituted SRC-II process product. Chloride was not removed from the samples before hydroprocessing. However, it was shown that water washing can remove most of the chloride. It is our understanding that this would typically be done at the upstream (SRC) processing facility in a commercial situation.

Processing of SRC-II

Pilot plant tests were made to hydrotreat the whole SRC-II process product blends to remove nitrogen, sulfur, oxygen, and metals using fixed catalyst beds.

TABLE I

PROPERTIES OF SRC-II PROCESS PRODUCT

Inspections	
Gravity, °API	18.6
Aniline Point, °F	<30
Sulfur, Wt %	0.29
Total Nitrogen, Wt %	0.85
Basic Nitrogen, Wt %	0.7
Oxygen, Wt %	3.79
Hydrogen, Wt %	10.46
Hydrogen/Carbon Atom Ratio	1.47
Chloride, ppm	50
Pour Point, °F	Below -80
Ramsbottom Carbon, Wt %	0.70
Hot Heptane Insolubles, Wt %	0.50
Benzene Insolubles, Wt %	<0.03
Ash, Wt %	0.004
Molecular Weight	132
TBP Distillation, °F	
St/5	56/189
10/30	241/379
50	424
70/90	473/562
95/99	642/820

Two Chevron catalysts were evaluated: ICR 106 (containing nickel, tungsten, silica, and alumina) and ICR 113 (containing nickel, molybdenum, silica, and alumina). Although ICR 113 is somewhat less active than ICR 106, it is also a less expensive catalyst and, therefore, may be the catalyst of choice for cases in which lower severities of hydrogenation are needed.

Results of several long pilot plant runs were previously reported (8), including one of over 3000 hours in length. The runs were terminated voluntarily when the catalysts were still active and clearly commercial length runs would be expected.

For convenience, pilot plant tests at 0.5 LHSV and 2300 psia hydrogen with ICR 106 catalyst will be referred to as "high severity." Those at 1.5 LHSV and 2300 psia with ICR 106 catalyst will be referred to as "intermediate severity," and those at 1.0 LHSV and 1750 psia with ICR 113 catalyst will be referred to as "moderate severity."

For the process engineering studies, these severity definitions were broadened, based on the hydrogen consumption required. If the hydrogen consumption for the whole oil hydro-treater was over 2750 SCF/bbl, the severity was referred to as high. If the hydrogen consumption was between 1750 and 2750 SCF/bbl, the severity was referred to as intermediate. If the hydrogen consumption was 1750 SCF/bbl or lower, the severity was referred to as moderate.

At high severity, the nitrogen, sulfur, and oxygen were all removed to the lower limit of our ability to measure with the analytical techniques employed (Dohrmann nitrogen, Dohrmann sulfur, neutron activation for oxygen). The product was water-white in appearance.

Table II compares yields and whole liquid product properties obtained at both high and intermediate severities with ICR 106. Results are shown both when the catalyst is fairly fresh and after aging. Table III shows results with partially aged ICR 113 catalyst at moderate severity. (Similar results were obtained with ICR 106 at 1.5 times the space velocity used here.)

Figure 1 shows how product nitrogen varies with hydrogen consumption, while Figure 2 shows the same kind of relationship with product aromatics. These plots are useful in further characterizing severity for the design studies discussed later.

Product Properties

Naphtha - Table IV shows properties of the naphtha product at the high and intermediate severities. The naphtha produced at the highest severity is essentially free of nitrogen, sulfur, and oxygen and can be fed directly to a catalytic reformer. The naphtha produced at the lower severities is

TABLE II
HYDROTREATING OF SRC-II
COMPARISON OF YIELDS AND LIQUID PRODUCT PROPERTIES
AT HIGH AND INTERMEDIATE SEVERITIES
WITH ICR 106 CATALYST

Severity Catalyst Condition Avg. Cat. Temp., °F	2300 psia H ₂							
	High (0.5 LHSV)				Intermediate (1.5 LHSV)			
	Fresh		Aged		Fresh		Aged	
	750		776		750		768	
	Wt %	Vol %	Wt %	Vol %	Wt %	Vol %	Wt %	Vol %
No Loss Prod. Yields								
C ₁	0.17		0.22		0.08		0.12	
C ₂	0.29		0.37		0.16		0.20	
C ₃	0.37		0.53		0.17		0.24	
iC ₄	0.03	0.05	0.05	0.08	0.02	0.02	0.02	0.03
nC ₄	0.18	0.28	0.21	0.34	0.09	0.14	0.12	0.19
C ₅ -180°F	4.7	6.1	5.6	7.1	5.1	6.5	5.4	6.9
180-300°F	26.5	32.3	27.1	32.7	25.6	30.8	24.5	29.3
300-550°F	61.4	67.9	60.6	66.6	58.6	62.4	58.6	62.0
550°F-EP	5.8	6.1	4.4	4.7	7.9	8.0	8.4	8.3
Total C ₅ [†]	98.4	112.4	97.8	111.0	97.1	107.7	96.9	106.6
H ₂ Cons. (Chemical), SCF/Bbl	3100		2900		2000		2000	
Inspections of Whole Liquid Product								
Gravity, °API	39.3		38.4		34.1		32.7	
Aniline Point, °F	116.9		105.4		67.5		54.8	
Sulfur, ppm	5		3		5		21	
Nitrogen, ppm	0.25		0.27		20		52	
Hydrogen, Wt %	13.7		13.5		12.4		11.8	
Oxygen, ppm*	40		40		630		680	
Group Type, LV %								
Paraffins	6.4		7.5		7.8		8.4	
Naphthenes	89.9		79.4		57.2		47.7	
Aromatics	4.3		13.1		35.0		43.9	
TBP Distillation, °F								
St/5	65/181		65/181		59/175		66/179	
10/30	215/276		215/277		109/279		213/286	
50	365		364		370		380	
70/90	410/499		410/498		435/518		442/528	
95/99	546/648		543/657		570/685		581/705	

*Includes dissolved water.

TABLE III
 HYDROTREATING OF SCR-II WITH
 AGED ICR 113 CATALYST AT MODERATE SEVERITY
 750°F--1750 PSIA H₂
 8000 SCF/BBL RECYCLE GAS RATE

Catalyst	ICR 113	
LHSV	1.0	
	Wt %	Vol %
No Loss Prod. Yield		
C ₁	0.10	
C ₂	0.19	
C ₃	0.19	
iC ₄	0.02	0.03
nC ₄	0.08	0.13
C ₅ -180°F	3.8	4.8
180-350°F	31.8	37.5
350°F-EP	61.1	61.9
Total C ₅ ⁺	96.6	104.2
H ₂ Consumption (Chemical), SCF/Bbl	1740	
Whole Liquid Product Properties		
Gravity, °API	29.9	
Aniline Point, °F	38.1	
Sulfur, ppm	8	
Nitrogen, ppm	453	
Hydrogen, Wt %	11.4	
Oxygen, ppm	2800	
Group Type, LV %		
Paraffins	7.1	
Naphthenes	43.5	
Aromatics	49.4	
TBP Distillation, °F		
St/5	59/181	
10/30	216/309	
50	401	
70/90	454/545	
95/99	608/746	

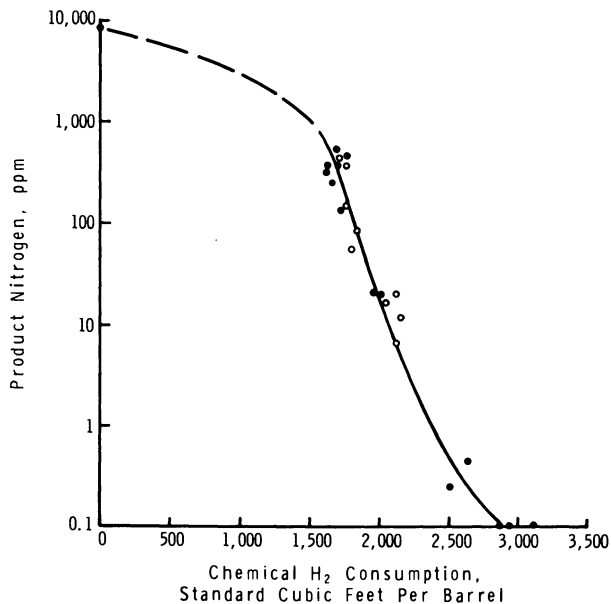


Figure 1. Product nitrogen vs. hydrogen consumption hydrotreating of SRC-II at 750° F: (●) ICR 106 catalyst, (○) ICR 113 catalyst

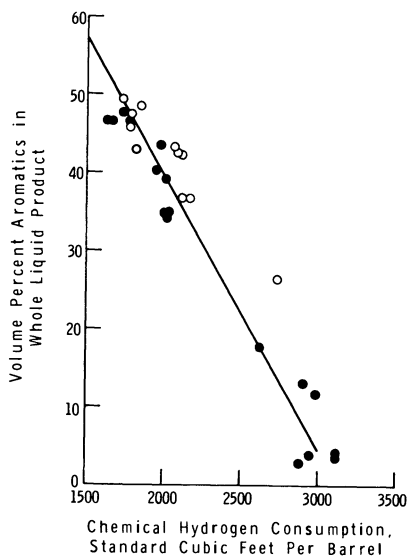


Figure 2. Product aromatic content vs. hydrogen consumption; hydrotreating whole SRC-II oil at various severities; group type calculated from GC or MS of individual fractions: (●) ICR 106, (○) ICR 113

TABLE IV
 HYDROTREATING OF SRC-II WITH ICR 106 CATALYST
 NAPHTHA PRODUCT PROPERTIES
 2300 PSIA H₂

Severity Condition of Catalyst	High		Intermediate	
	Fresh	Aged	Fresh	Aged
Inspections, C ₅ -180°F Product				
Gravity, °API	60.7	58.6	59.9	59.9
Group Type, LV %				
Paraffins	31.2	26.2	30.0	32.8
Naphthenes	65.4	66.3	62.3	58.0
Aromatics	3.4	7.4	7.7	9.1
Olefins		0.1		0.1
Octane Number				
F-1 Clear	81.1	82.2	81.5	81.1
F-2 Clear	77.0		77.4	
Inspections, 180-300°F Product				
Gravity, °API	51.6	49.9	49.0	48.4
Aniline Point, °F	108.8	96.8	87.4	79.2
Nitrogen, ppm	0.1	0.1	2.1	2
Oxygen, ppm	<20	<20	280	300
Group Type, LV %				
Paraffins	7.1	10.1	10.1	11.3
Naphthenes	90.1	79.5	75.8	69.3
Aromatics	2.8	10.4	14.1	19.4
Octane Number				
F-1 Clear	66.0	68.4	69.2	72.0
F-2 Clear	66.0	66.9	67.3	68.5
TBP Distillation, °F				
St/5	98/177	157/184	159/184	147/183
10/30	180/220	206/233	203/232	202/232
50	246	252	252	251
70/90	269/294	277/299	280/302	279/301
95/99	303/ -	306/317	310/323	308/319

considerably higher in nitrogen content, but it can be further processed in a conventional naphtha hydrotreater before reforming. Table V shows product properties at moderate severity.

Jet Fuel - Table VI shows the properties of the 300-550°F product obtained at the two higher severities. These properties can be compared with current commercial (Jet A) specifications (10) shown in Table XVII. Also included in Table XVII are the properties of the kerosene fraction from the refining schemes to be discussed later. One product inspection of particular interest is the JFTOT thermal stability rating of the jet boiling range product (ASTM D 1660). The product from the high severity ICR 106 tests easily passes this test at 280°C with a No. 1 rating, even when the smoke point is 20 mm, the minimum range of the current commercial specification. Current jet specification requires a No. 1 rating at 260°C, a temperature considerably less severe than the 280°C used here. Therefore, smoke point appears to be the limiting specification, and jet fuel produced from SRC-II is expected to pass the thermal stability specification at any condition that the smoke point is acceptable.

One property outside current limits is the API gravity. This specification was originally set because of limitations of available fuel flow controllers. Today's controllers are no longer limited in this way, but there has been no incentive to lower the specification because until now, there was no available product below 37°API which met the other specifications. Also, the gravity specification could be met by adjusting the boiling range of the jet fuel fraction by including product boiling below 300°F.

The gravimetric heat of combustion, while within current specifications, is slightly below the present commercial production range: 18,500 to 18,650 Btu per pound. However, freezing point and hydrogen content are more favorable than those of the average jet fuel produced today. The kerosene boiling range product would, therefore, make an excellent blend stock for upgrading marginal jet fuels. The volumetric heat of combustion, which determines the range of an existing plane with fixed fuel tanks, is quite high because the fuel is unusually dense.

A recent study by Franck et al. at the Institut Francais du Petrole (11) indicates that naphthenic hydrocarbons with two or three rings (molecular weight between 120 and 200) give the best compromise among the different properties of jet fuels. Of the types of compounds studied, these are the only ones to show, simultaneously, the following properties: (1) high caloric value by volume, (2) satisfactory calorific value by weight, (3) acceptable thermal stability, (4) very low freezing

TABLE V
 PROPERTIES OF PRODUCT FRACTIONS
 HYDROTREATERS OF SRC-II WITH
 AGED ICR 113 CATALYST
 AT MODERATE SEVERITY

Catalyst	ICR 113
LHSV	1.0
Inspections	
C ₅ -180°F Naphtha	
Gravity, °API	60.9
Group Type, LV %	
Paraffins	31.6
Naphthenes	60.3
Aromatics	8.1
Octane Number	
F-1 Clear	81.4
180-350°F Naphtha	
Gravity, °API	45.5
Aniline Point, °F	79.1
Total Nitrogen, ppm	126
Oxygen, ppm	1700
Group Type, LV %	
Paraffins	8.0
Naphthenes	69.2
Aromatics	22.8
Octane Number	
F-1 Clear	69.3
F-2 Clear	67.1
TBP Distillation, °F	
St/5	161/182
10/30	213/230
50	269
70/90	301/337
95/99	347/362
350°F+ Product	
Gravity, °API	20.7
Aniline Point, °F	<32
Total Nitrogen, ppm	529
Oxygen, ppm	3400
Smoke Point, mm	8
Cetane No.	<21
Pour Point, °F	-38
Group Type, LV %	
Paraffins	4.7
Naphthenes	26.6
Aromatics	68.8
TBP Distillation, °F	
St/5	329/362
10/30	381/417
50	452
70/90	497/586
95/99	648/765

TABLE VI
 HYDROTREATING OF SRC-II WITH ICR 106 CATALYST
 300-550°F PRODUCT PROPERTIES
 2300 PSIA HYDROGEN

Severity Condition of Catalyst	High		Intermediate	
	Fresh	Aged	Fresh	Aged
Inspections of 300-550°F Product				
Gravity, °API	34.6	33.3	28.5	27.3
Aniline Point, °F	122.3	110.2	60.3	41.8
Nitrogen, ppm	0.1	0.1	19	40
Oxygen, ppm	<50	<50	970	1400
Smoke Point, mm	22	20	11	-76
Freeze Point, °F	<-94	-81	-76	-76
Group Type, LV %				
Paraffins	3.3	3.9	4.0	4.3
Naphthenes	92.6	81.1	47.1	36.7
Aromatics	4.0	15.0	48.8	59.0
TBP Distillation, °F				
St/5	266/304	277/312	264/313	281/318
10/30	316/365	329/373	332/382	334/386
50	404	403	419	421
70/90	451/504	442/497	460/510	459/507
95/99	520/560	516/542	526/550	522/544
Viscosity				
cSt at -40°F	12.79	11.92	13.17	
cSt at 100°F		1.64	1.59	
Existent Gum, mg/100 ml	2	0	High	High
Flash Point, Tag Closed, °F	132	134	142	142
Neutralization No. (Acid), mg/g	0.02	0.05	0.03	0.05
Naphthalenes, %	0.1	0.2	0.9	1.3

point, (5) acceptable low temperature viscosity, (6) low volatility and high flash point, and (7) acceptable flame characteristics. Our results show that these observations apply, in particular, to the jet produced by hydroprocessing SRC-II.

Heating Oil - The 300°F+ bottoms prepared at moderate severity could be marketed as No. 2 heating oil or as a heating oil blending component if a product other than transportation fuel is desired. Table XVII includes the properties of the No. 2 oil fraction from the refinery studies at moderate hydrotreating severity compared with the 1978 ASTM specifications. Specific gravity is the only specification not met. Hydrotreating to meet the gravity specification would produce acceptable jet fuel, usually a more valuable product. Therefore, heating oil from SRC-II is only acceptable for applications where high specific gravity is not a problem. Because of the high heating value on a volumetric basis, the high density may be advantageous in some applications. The low cetane number of this fraction makes it unattractive as a diesel fuel, although it could, under certain circumstances, be used as a diesel blending stock. (Diesel fuel could be prepared by high severity hydrotreating. This option is discussed in the next chapter, together with the discussion of hydroprocessing of H-Coal syncrudes.)

Another analysis of interest for heating oil is a thermal stability test. Although there is no ASTM requirement, the test used in these studies is a Chevron adaption of Du Pont Test Method 21-61. (12) In Du Pont's method, a test blotter is used to rate the stability. However, because evaluation of the result is visual and subjective, Chevron has found that better repeatability is obtained by evaluating the test filters using a reflectometer. As a reference point, a reflectance of 80% or higher is recommended as a passing rating for automotive diesels. (This is comparable to a test blotter rating of No. 6 or below by the Du Pont method.) The 90% reflectance measured for the heating oil product is, therefore, quite satisfactory.

Processing of Hydrotreated SRC-II

If the SRC-II is hydrotreated at an intermediate or moderate severity, further processing will be necessary to upgrade the product to specification transportation fuels. A number of pilot plant tests have been made to determine the conditions and to demonstrate the feasibility of these processing steps.

Naphtha Hydrotreating - At both the moderate and intermediate severities, it is necessary to further hydrotreat the naphtha before it can be fed to a bimetallic reforming catalyst. Table VII summarizes results of further hydrotreating of

TABLE VII
 HYDROFINING OF PARTIALLY HYDROTREATED ST-400° F
 SRC-II NAPHTHA WITH ICR 113 CATALYST

Average Cat. Temperature, °F	700	
LHSV	2.0	
Total Pressure, psig	638	
H ₂ Mean Pressure, psia	505	
Recycle Gas, SCF/Bbl	2695	
	Wt %	Vol %
No Loss Prod. Yields		
C ₁	0.01	
C ₂	0.01	
C ₃	0.02	
iC ₄	0.01	0.01
nC ₄	0.01	0.01
Total C ₅ ⁺	99.8	100.2
H ₂ Cons. (Chemical), SCF/Bbl	108	
	Feed	Whole Liquid Product
Inspections		
Gravity, °API	41.6	41.8
Aniline Point, °F	67.6	70.0
Sulfur, ppm	4	4
Total Nitrogen, ppm	225	0.2
Oxygen, ppm	3000	<10
Hydrogen, Wt %		12.8
Octane No., F-1 Clear	74.4	71.2
Group Type, LV %		
Paraffins	8.2	8.9
Naphthenes	61.0	61.8
Aromatics	30.8	30.2
TBP Distillation, °F		
St/5	135/184	101/182
10/30	216/260	199/247
50	309	294
70/90	359/406	345/399
95/99	414/436	411/437

a St-400°F partially hydrotreated naphtha with ICR 113 catalyst. The table shows run conditions, yields, hydrogen consumption, and product properties. The naphtha boiling range would be varied, depending on the desired product slate. Lower boiling range naphthas would be easier to hydrotreat and reform and higher boiling naphthas more difficult to process.

Jet Fuel Hydrogenation - The jet boiling range product from hydrotreating at the lower severities requires further hydrotreating (hydrogenation) before it can be marketed as jet fuel.

Table VIII shows results of hydrogenating a jet boiling range product containing 63% aromatics and 173 ppm of nitrogen using ICR 106 catalyst. (Note: Some cracking occurred during this processing step and about 10% of the product boils below 300°F. It would be necessary to remove some of this material by distillation before the product would have an acceptable jet flash point.)

Extinction Recycle Hydrocracking - If maximum gasoline is desired rather than jet fuel, one possible option is hydrocracking of the hydrotreated SRC-II boiling above the gasoline boiling range. Experiments were made to demonstrate the feasibility of hydrocracking the 350°F+ product fraction prepared at moderate severity. Properties of this stock are shown in Table IX. Pilot plant tests were made for a two-stage hydrocracking process. In these experiments, the first stage contained ICR 106 catalyst. Product nitrogen was reduced to less than 0.5 ppm. The second stage used ICR 202 catalyst (containing a Group VIII metal, silica, and alumina) and operated in the extinction recycle mode at 60% per pass conversion. All of the product boiling above 350°F was recycled until completely converted to 350°F- product.

First-stage studies were made over an extended period of time with some variations in process conditions. Denitrified products from these studies were blended and used as second-stage feed. Table X shows the inspections of this blend and also the processing conditions and yields that correspond to making a second-stage feed of this quality.

Table XI shows the second-stage yields and product properties. Although the hydrogen consumption is high, a considerable amount of this hydrogen would be recovered when the heavier naphtha product is fed to a catalytic reformer to be converted to high octane gasoline.

Other Processing Options

Another processing option for maximum gasoline is use of the catalytic cracking process rather than hydrocracking as the major conversion process. Our experiments indicate that conversions in catalytic cracking of SRC-II are low unless the

TABLE VIII
 HYDROGENATION OF 300-550°F PARTIALLY
 HYDROTREATED SRC-II WITH ICR 106

Average Cat. Temperature, °F	727
LHSV	2.0
Total Pressure, psig	1696
H ₂ Mean Pressure, psia	1527
Recycle Gas, SCF/Bbl	5609

	Wt %	Vol %
No Loss Prod. Yields		
C ₁	0.02	
C ₂	0.04	
C ₃	0.20	
iC ₄	0.05	0.09
nC ₄	0.05	0.08
Total C ₅ +	120.0	108.4
H ₂ Cons. (Chemical), SCF/Bbl	1386	

	Feed	Whole Liquid Product
C ₅ + Product Inspections		
Gravity, °API	24.6	36.5
Aniline Point, °F	33.3	110.9
Nitrogen, ppm	173	0.15
Smoke Point, mm	9	22
Freeze Point, °F		-84
Group Type, LV %		
Paraffins	4.3	4.4
Naphthenes	32.4	82.0
Aromatics	63.3	13.6
TBP Distillation, °F		
St/5	242/309	31/228
10/30	332/393	291/358
50	429	388
70/90	467/516	419/476
95/99	533/554	500/546
Fraction Below 300°F, Wt % (TBP)	3.5	10.8

TABLE IX
 FEED FOR HYDROCRACKER
FIRST-STAGE PILOT PLANT TESTS

	<u>350°F+ From Hydrotreated Whole SRC-II</u>
Gravity, °API	22.0
Aniline Point, °F	<32
Sulfur, ppm	6.3
Nitrogen, ppm	608
Oxygen, ppm	4700
Group Type, LV %	
Paraffins	5.1
Naphthenes	26.9
Aromatics	68.0
TBP Distillation, °F	
St/5	317/363
10/30	380/418
50	452
70/90	494/568
95/99	612/715
Overlap, Wt % Below 350°F by TBP	2.2

TABLE X

FIRST-STAGE HYDROCRACKER WITH ICR 106 CATALYST
 FEED - PARTIALLY HYDROTREATED SRC-II

Feed Nitrogen, ppm	608	
Feed Aromatics, %	68	
Avg. Cat. Temp., °F	695	
LHSV	1.0	
Total Pressure, psig	1600	
H ₂ Mean Pressure, psia	1425	
Recycle Gas, SCF/Bbl	5000	
		<u>Wt % Vol %</u>
No Loss Prod. Yields		
C ₁	0.03	
C ₂	0.07	
C ₃	0.25	
iC ₄	0.03	0.04
nC ₄	0.07	0.11
Total C ₅ ⁺	100.5	104.2
H ₂ Cons. (Chemical), SCF/Bbl	900	
Whole Liquid		
Product Properties (Feed to Second Stage)		
Gravity, °API	27.7	
Aniline Point, °F	63.3	
Sulfur, ppm	5.5	
Nitrogen, ppm	0.4	
Group Type, LV %		
Paraffins	4.5	
Naphthenes	46.3	
Aromatics	49.2	
TBP Distillation, °F		
St/5	52/274	
10/30	344/396	
50	428	
70/90	469/536	
95/99	579/684	

TABLE XI
HYDROCRACKING OF DENTRIIFIED 350°F+
SRC-II WITH ICR 202 CATALYST
AT 350°F RECYCLE CUT POINT

Avg. Cat. Temp., °F	592	
LHSV	1.10	
Per Pass Conversion	58.2	
Total Pressure, psig	1398	
H ₂ Mean Pressure, psia	1219	
Recycle Gas, SCF/Bbl	5859	
	<u>Wt %</u>	<u>Vol %</u>
No Loss Prod. Yields		
C ₁	0.01	
C ₂	0.10	
C ₃	2.27	
iC ₄	12.8	20.2
nC ₄	2.4	3.6
C ₅ -180°F	19.8	25.5
180-350°F	66.0	74.4
Total C ₅ +	85.8	99.9
H ₂ Cons. (Chemical), SCF/Bbl	1918	
Product Inspections		
C ₅ -180°F		
Gravity, °API	73.4	
Octane No.		
F-1 Clear	90.5	
F-2 Clear	84.3	
Group Type, LV %		
Paraffins	61.8	
Naphthenes	32.3	
Aromatics	5.9	
180-350°F		
Gravity, °API	48.0	
Aniline Point, °F	110.7	
Octane No.		
F-1 Clear	69.6	
F-2 Clear	68.8	
Group Type, LV %		
Paraffins	8.8	
Naphthenes	83.7	
Aromatics	7.5	
TBP Distillation, °F		
St/5	160/195	
10/30	200/232	
50	269	
70/90	317/344	
95/99	350/358	

feed to the catalytic cracker is severely hydrotreated prior to catalytic cracking. Our work and the work of others (13) indicate that hydrocracking is a less costly route for cases in which a high conversion to gasoline is desired.

Engineering Studies

Refinery Plans - The pilot plant studies for this project encompassed a wide range of initial hydrotreating severities. Figures 1 and 2 delineate this range by relating product nitrogen and aromatics to hydrogen consumption. Figure 3 further characterizes the initial hydrotreating severities by focusing on the product boiling above naphtha.

As discussed previously, the highest severity operation (about 3000 SCF/bbl hydrogen consumption) produces specification kerosene jet fuel and naphtha suitable for single-stage reforming.

The Case 1A refining plan, then, is the rather simple scheme shown in Figure 4 based on this high severity operation.

As severity is decreased, aromatics and nitrogen in the product rise and the kerosene and naphtha must be further hydrotreated to make jet fuel and reformer feed. This type of operation constitutes Case 2A, with initial severity corresponding to about 2000 SCF of hydrogen consumed per barrel (Figure 5). The case was included to see if the reduction in the initial hydrotreating cost was larger than the increased cost due to the need for additional lower severity downstream processing.

The next two cases produce motor gasoline as the only desired product. Flow schemes are shown in Figures 6 and 7. In Case 3A, fluid catalytic cracking is evaluated. To eliminate all net products heavier than gasoline, it was necessary to use high severity initial hydrotreating to obtain high enough conversion in the catalytic cracker.

Case 4A uses hydrocracking as the downstream conversion process to produce motor gasoline. Initial hydrotreating severity was chosen to provide a reasonably optimum hydrocracker based on the pilot plant work for this project and our general processing correlations. Desired severity fell in the intermediate range at about 2500 SCF/bbl hydrogen consumption. (Engineering studies based on the pilot plant work discussed previously showed there is no particular advantage of operating the hydrotreater at moderate severity and providing a second hydrotreater for the hydrocracking feed.)

Case 5A uses moderate severity hydrotreating without further downstream cracking conversion to produce motor gasoline and No. 2 heating oil as shown in the alternate arrangement of Figure 8. This case was included to give some idea of the

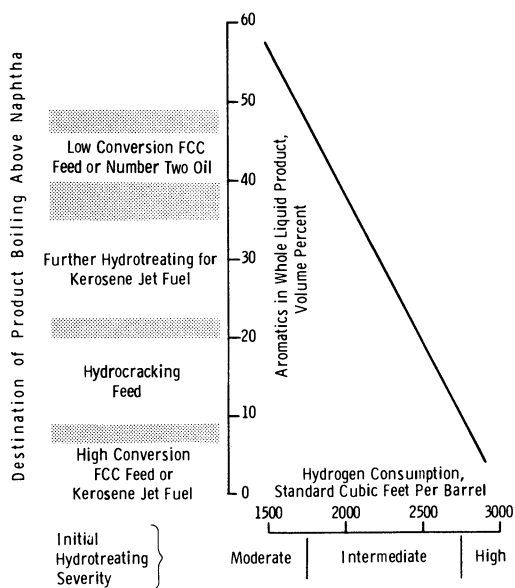
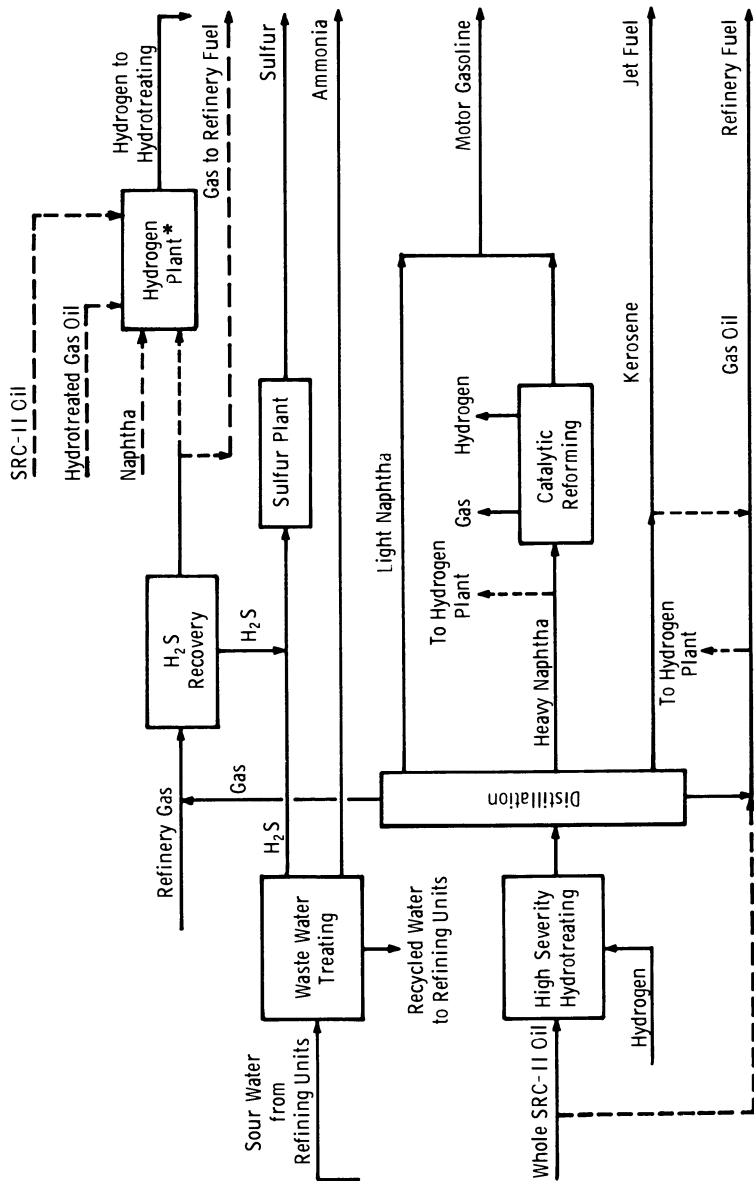
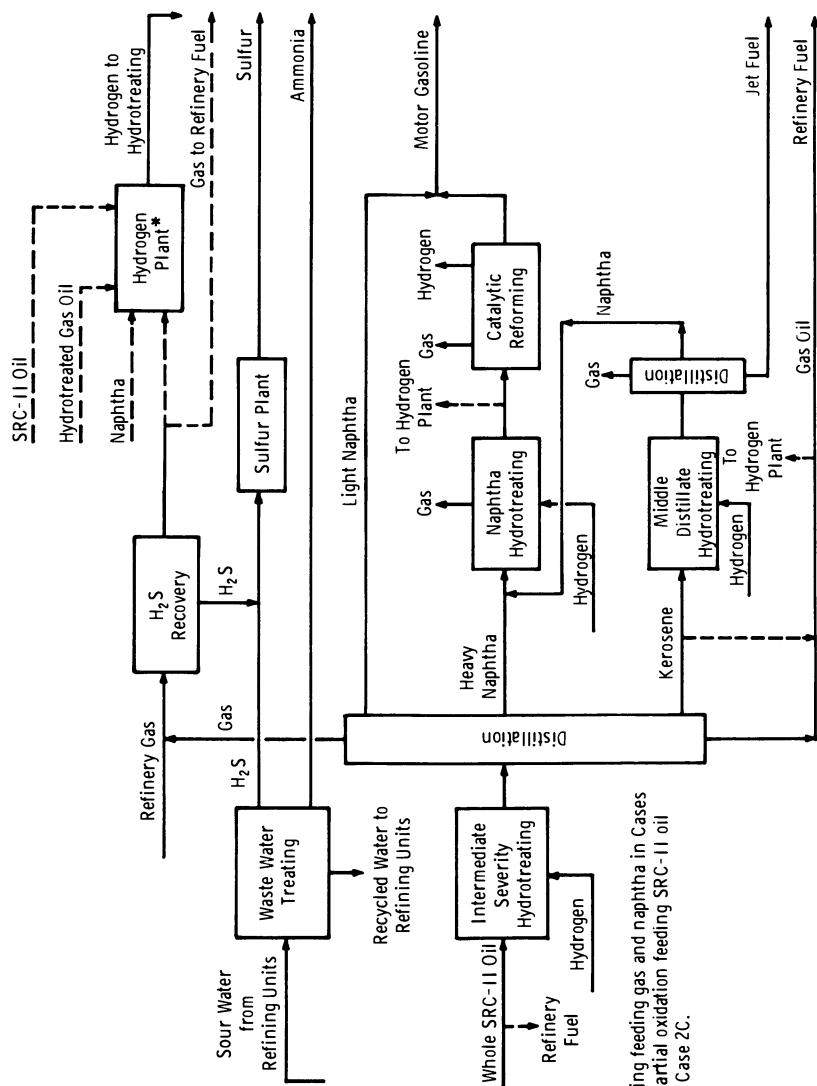


Figure 3. Characterization of severities; initial hydrotreating of SRC-II oil



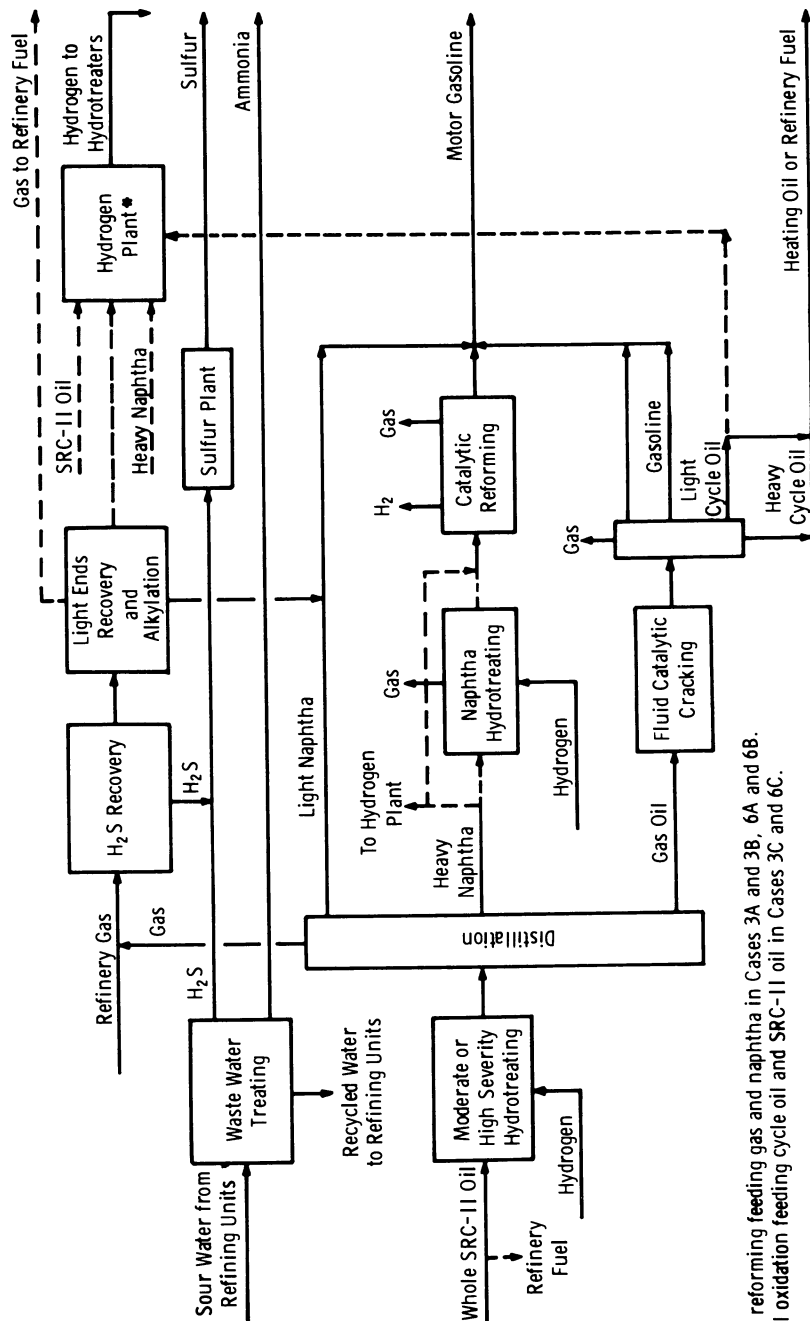
* Steam reforming feeding gas and naphtha in Cases 1A, 1B, and 1D
 Partial oxidation feeding gas oil and SRC-II oil in Case 1C.

Figure 4. Flow diagram: refining of SRC-II oil by high severity hydrotreating, case 1



* Steam reforming feeding gas and naphtha in Cases 2A and 2B. Partial oxidation feeding SRC-II oil and gas oil in Case 2C.

Figure 5. Flow diagram: refining of SRC-II oil by intermediate severity hydrotreating, case 2



• Steam reforming feeding gas and naphtha in Cases 3A and 3B, 6A and 6B.
 Partial oxidation feeding cycle oil and SRC-II oil in Cases 3C and 6C.

Figure 6. Flow diagram: refining of SRC-II oil by hydrotreating and fluid catalytic cracking, case 3

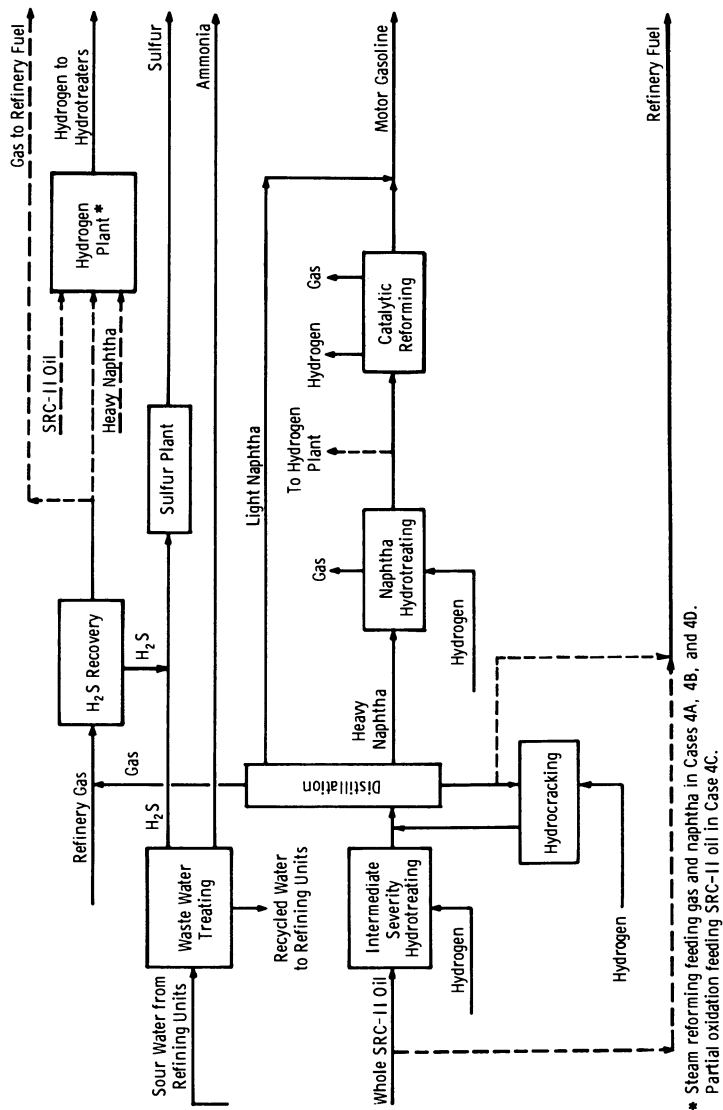
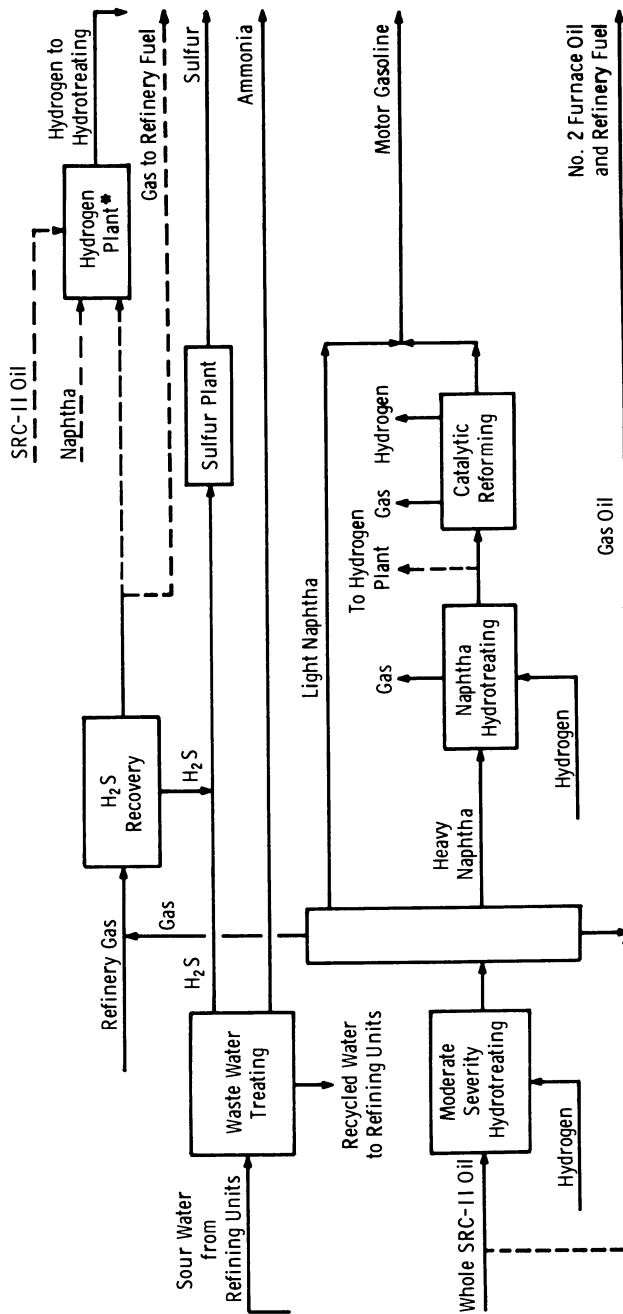


Figure 7. Flow diagram: refining of SRC-II oil by hydrotreating and hydrocracking, case 4

* Steam reforming feeding gas and naphtha in Cases 4A, 4B, and 4D. Partial oxidation feeding SRC-II oil in Case 4C.



* Steam reforming feeding gas and naphtha in Cases 5A, 5B, and 5D.
 Partial oxidation feeding SRC-II oil in Case 5C.

Figure 8. Simplified flow diagram: refining of SRC-II oil by moderate severity hydrotreating, case 5

effect on refinery cost of relaxing the ground rule to make only transportation fuels.

The appendix shows yields and product properties from each of the hydrotreaters and hydrocrackers estimated for the studies.

Stock Balances - Tables XII-XVI show detailed stock balances for each of the five cases. Yields are based directly on pilot plant results and general petroleum processing correlations where appropriate. The primary basis is to make a constant 50,000 BPCD of desired products in each case. This capacity was selected for the first series of studies because it matches the maximum feasible throughput for a single SRC-II plant as presently conceived. The refineries are stand-alone grass roots facilities, that is, complete new installations, including all necessary supporting facilities, such as utility plants, tankage, and required environmental control equipment. Another objective for this series was to meet refinery furnace fuel and hydrogen plant feed requirements with internally supplied clean fuels, ensuring minimum air emissions. Boiler plants, however, were assumed to be coal fired in compliance with present DOE regulations. Other options for fuel and hydrogen plant feed are examined in the complete DOE report. (9)

Estimates of finished gasoline production were made by using correlations for catalytic reforming of naphtha and blending of gasoline components. Correlations could be used in this case because the properties of the reformer feeds distilled from the pilot plant hydrotreater products were well within Chevron's range of experience on petroleum stocks. Gasoline blending objectives were to make a single unleaded pool meeting accepted industry specifications for quality with minimum octane numbers of 93 (Research + Motor)/2. These octane numbers are typical of those projected for the early 1980's. Table XVII lists the refinery product inspections.

Each plan represents a completely feasible and reasonably efficient refining arrangement. A more detailed optimization of conditions, cut points, and other factors, while not within the scope of this study, would be carried out in the course of a normal refinery design.

Cost Estimates - Plant investment costs were developed using cost correlations based on actual plants constructed by Standard Oil Company of California. The important bases for these estimates are summarized in Table XVIII. Costs for the overall Case 1 refinery are broken down and detailed in Table XIX. Investments are categorized as "onplot," those directly concerned with the individual refinery process plants, and "offplot," for auxiliary or supporting facilities, such as utility plants, tankage, etc. The estimating allowances shown

TABLE XII
STOCK BALANCE - CASE 1A
REFINING SRC-II OIL BY HIGH SEVERITY HYDROTREATING TO PRODUCE
50,000 BARRELS PER CALENDAR DAY OF MOTOR GASOLINE PLUS JET FUEL
DOE CONTRACT EF-76-C-01-2315

	Processing					Products				
	Refinery Input	High Severity Hydrotreating	Catalytic Reforming	Hydrogen Manufacture	H ₂ S Recovery and Sulfur Plant	Offplot Boiler Plant	Refinery Fuel	Motor Gasoline	Kerosene Jet Fuel	By-Products
Whole SRC II Oil*	59,860	(59,860)				(1,870)				
Coal, Equivalent Fuel Oil	1,870									
Fuel Gas, Equivalent Fuel Oil		795								
Isobutane		1,380	115	(510)			910			
Normal Butane		1,410	15	(520)			160	725		
C ₅ /C ₆ Light Gasoline		3,795	10				160			
180-300°F Heavy Gasoline		18,615	(10,070)	(8,545)				3,795		
300-550°F Kerosene		38,370					2,570		35,800	
550°F+ Bottoms		3,000					3,000			
Reformate (97.5 F-1 Clear)			8,940					8,940		
Total Liquid Product		67,365	9,080				6,800	14,200	35,800	
Total Liquid Feed		(59,860)	(10,070)	(9,575)						
Liquid Gain (Loss)		7,505	(990)	(9,575)			(105)			
Fuel		(625)	(545)	(5,525)			6,695			
Hydrogen, Millions of Standard Cubic Feet Per Calendar Day		(174.9)	17.0	157.9						
Tons Per Calendar Day										
Hydrogen Sulfide		29.1								
Sulfur		-								
Ammonia		96								
										26.2
										96

*Including 4.6 LV & Butanes
Note: Parentheses () Denote a Negative Quantity, i.e., Consumption

TABLE XIII

STOCK BALANCE - CASE 2A
REFINING OF SRC-II OIL BY INTERMEDIATE SEVERITY HYDROTREATING TO PRODUCE
50,000 BARRELS PER CALENDAR DAY OF MOTOR GASOLINE PLUS JET FUEL
DOE CONTRACT EF-7-6-C-01-2313

Feeds and Products, Barrels per Calendar Day	Processing						Products				
	Refinery Input	Intermediate Severity Hydrotreating	Middle Distillate Hydrotreating	Naphtha Hydrotreating and Catalytic Reforming	Hydrogen Manufacture	H ₂ S Recovery and Sulfur Plant	Offplot Boiler Plant	Refinery Fuel	Motor Gasoline	Kerosene Jet Fuel	By- Products
Whole SRC II Oil*	59,020	(59,020)					(1,250)				
Coal, Equivalent Fuel Oil	1,250										
Fuel Gas, Equivalent Fuel Oil	645		205	145	(735)		995	650			
Isobutane	1,360			25	(730)			650			
Normal Butane	1,360			20							
C ₅ /C ₆ Light Gasoline	3,775		3,170	(13,100)	(6,930)			3,775			
180-300°F Heavy Gasoline	16,860										
300-550°F Kerosene	35,075		(34,115)				960				
550°F* Bottoms	4,535						4,535				
Hydrotreated Kerosene		33,025								33,025	
Reformate (97 F-1 Clear)				11,900				11,900			
Total Liquid Product	63,616		36,400	12,090	-						
Total Liquid Feed	(59,620)		(34,115)	(13,100)	(8,395)			6,490	16,975	33,025	
Liquid Gain (Loss)	4,590		2,285	(1,010)	(8,395)						
Fuel	(530)		(250)	(770)	(4,940)			6,490			
Hydrogen, Millions of Standard Cubic Feet Per Calendar Day	(117.1)		(41.5)	18	140.9						
Tons Per Calendar Day											
Hydrogen Sulfide	28.7						(28.7)				26
Sulfur											96
Ammonia	96										

*Including 4.6 LV % Butanes

Note: Parentheses () Denote a Negative Quantity, i.e., Consumption

TABLE XIV

STOCK BALANCE - CASE 3A
REFINING SRC-II OIL BY HIGH SEVERITY HYDROTREATING AND FLUID CATALYTIC CRACKING
TO PRODUCE 50,000 BARRELS PER CALENDAR DAY OF MOTOR GASOLINE
DOE CONTRACT BE-76-C-01-2313

Feeds and Products, Barrels per Calendar Day	Processing							Products			
	Refinery Input	High Severity Hydrotreating	Fluid Catalytic Cracking	Light Ends Recovery	Catalytic Reforming	Hydrogen Mfg.	H ₂ S Recovery and Sulfur Plant	Offplot Boiler Plant	Refinery Fuel	Motor Gasoline	By- Products
Whole SRC II Oil*	59,130										
Coal, Equivalent Fuel Oil	1,890							(1,890)			
Fuel Gas, Equivalent Fuel Oil		785	310	1,910	260				3,265		
Propane			1,575	(1,515)		(220)				2,230	
Isobutane		1,365	1,130	(1,130)	220	(500)				535	
Butylene			1,800	(1,800)/1,300	65	(510)				1,470	
Normal Butane		1,395	745	(745)/535	60						
			720	(720)/525							
C ₆ /C ₇ Light Gasoline		3,750			(27,230)	(6,330)				3,750	
80,000# Heavy Gasoline		33,560	11,665							11,665	
FCC Light Gasoline			6,295							6,295	
FCC Heavy Gasoline											
400°F+ Bottoms		25,690	(25,690)								
FCC Cycle Oil			3,415						3,415		
Reformate (98.5 F-1 Clear)		-	-		24,055					24,055	
Total Liquid Product		66,545	27,595	4,270	24,660	-			6,680	50,000	
Total Liquid Feed		(59,130)	(25,690)	(5,910)	(27,230)	(7,560)					
Liquid Gain (Loss)		7,415	1,905	(1,640)	(2,570)	(7,560)					
Fuel		(625)	(385)	-	(1,470)	(4,400)			6,680		
Hydrogen, Millions of Standard Cubic Feet per Calendar Day		(172.7)			47.0	125.7					
Tons Per Calendar Day											
Hydrogen Sulfide		28.8					(28.8)				25.9
Sulfur							25.9				96
Ammonia		96									

*Including 4.6 LV & Butane
Note: Parentheses () Denote a Negative Quantity, i.e., Consumption

TABLE XV
 STOCK BALANCE - CASE 4A
 REFINING OF SRC-II OIL BY INTERMEDIATE SEVERITY
 HYDROTREATING AND SINGLE-STAGE ISOCRACKING TO PRODUCE
 50,000 BARRELS PER CALENDAR DAY OF MOTOR GASOLINE
 DOE CONTRACT EF-76-C-01-2315

	Processing						Products			
	Refinery Input	Intermediate Severity Hydrotreating	Hydrocracking	Naphtha Hydrotreating and Catalytic Reforming	Hydrogen Manufacture	H ₂ S Recovery and Sulfur Plant	Offplot Boiler Plant	Refinery Fuel	Motor Gasoline	By- Products
Feeds and Products, Barrels per Calendar Day	56,520	(56,520)								
Whole SRC II Oil*	1,110									
Fuel Gas, Equivalent Fuel Oil		675	470	475	(3,325)			1,620	3,245	
Isobutane		1,320	5,235	100				85	1,200	
Normal Butane		1,320	1,335	85	(1,546)					
C ₅ /C ₆ Light Gasoline		3,700	10,795	(34,515)	(4,325)				14,494	
180-300 F Heavy Gasoline		17,085	21,755							
300°F+ Bottoms		38,615	(32,625)					5,990		
Reformate (96 F-1 Clear)				31,060					31,060	
Total Liquid Product		62,715	39,590	31,720	(9,910)			7,695	50,000	
Total Liquid Feed		(56,520)	(32,625)	(34,515)						
Liquid Gain (Loss)		6,195	6,965	(2,795)						
Fuel		(570)	(230)	(1,880)	(5,015)			7,695		
Hydrogen, Millions of Standard cubic Feet Per Calendar Day		(142.0)	(52.5)	49.0	145.5					
Tons Per Calendar Day										
Hydrogen Sulfide		27.7				(27.7)				25
Sulfur		92				25				92
Ammonia										

*Including 4.6 LV % Butanes.

Note: Parentheses () Denote a Negative Quantity, i.e., Consumption

TABLE XVI

STOCK BALANCE - CASE 5A
 REFINING SRC-II OIL BY MODERATE SEVERITY HYDROTREATING TO PRODUCE
 50,000 BARRELS PER CALENDAR DAY OF MOTOR GASOLINE PLUS NUMBER TWO HEATING OIL
 DOE CONTRACT EF-76-C-01-2315

Feeds and Products Barrels per Calendar Day	Processing						Products			
	Refinery Input	Moderate Severity Hydrotreating	Naphtha Hydrotreating and Catalytic Reforming	Hydrogen Manufacture	H ₂ S Recovery and Sulfur Plant	Offplot Boiler Plant	Refinery Fuel	Motor Gasoline	Number Two Oil	By- Products
Whole SRC II Oil*	56,200	(57,200)				(860)				
Coal, Equivalent Fuel Oil	860									
Fuel Gas, Equivalent Feed Oil		490	215							
Isobutane		1,320	35	(260)			705	875		
Normal Butane		1,320	30	(260)			220	875		
C ₅ /C ₆ Light Gasoline		3,165					215			
180-300°F Heavy Gasoline		17,405	(12,800)	(4,605)				3,165		
300°F* Bottoms		36,585								
Reformate (96.5 F-1 Clear)			11,590						33,495	
Total Liquid Product		60,285	11,870	-				11,590		
Total Liquid Feed		(57,200)	(10,800)	(5,125)			4,230	16,505	33,495	
Liquid Gain (Loss)		3,085	(930)	(5,125)			(145)			
Fuel		(410)	(740)	(2,945)			4,095			
Hydrogen, Millions of Standard Cubic Feet Per Calendar Day		(101.1)	17.0	84.1						
Tons Per Calendar Day										
Hydrogen Sulfide		26.7			(26.7)					24.0
Sulfur					24.0					88
Ammonia		88								

*Including 4.6 LV & Butanes
 Note: Parentheses () Denote a Negative Quantity, i.e., Consumption

TABLE XVII
REFINERY PRODUCT INSPECTIONS
REFINING OF SRC-II OIL
DOE CONTRACT FF-76-C-01-2315

	ASTM Method	1978 Specifications	Case				
			1	2	3	4	5
<u>Inspections of Motor Gasoline</u>							
Reid Vapor Pressure, Pounds	D 323	-	10	10	10	10	10
Doctor Test	D 484	Negative	Negative	Negative	Negative	Negative	Negative
Sulfur, Weight Percent	D 1266	0.03 Max	<0.03	<0.03	<0.03	<0.03	<0.03
Octane Number,							
Research Unleaded	D 2699	93 Min.*	94	94	95.3	93.3-94	94-94.5
Motor Unleaded	D 2700	84 Min.*	84	84	84	84.6-85	84
Distillation Temperature, °C							
At 50% Distilled	D 86	116 Max.	102-107	112-116	112	96-104.5	113
End Point		215.5 Max.	215.5	215.5	215.5	215.5	215.5
<u>Inspections of Kerosene Jet Fuel</u>							
Specific Gravity, Relative to Water at 15.5°C	D 287	0.8398-0.7753	0.845-0.855	0.855-0.858	-	-	-
Aromatics, Volume Percent	D 1319	20 Max.	10	16	-	-	-
Flash Point, °C	D 56	37.8 Min.	38-54	49-54	-	-	-
Freezing Point, °C	D 2386	-40 Max.	-70	-60	-	-	-
Smoke Point, Millimeters	D 1322	20 Min.	21	20	-	-	-
Mercaptan Sulfur, Weight Percent	D 1323	0.003 Max.	<0.001	<0.001	-	-	-
Distillation Temperature, °C	D 86						
At 10% Recovered		204.4 Max.	170-182	175-182	-	-	-
At 20% Recovered		-	182-188	184-188	-	-	-
At 50% Recovered		-	204	202-204	-	-	-
At 90% Recovered		-	246	246	-	-	-
Final Boiling Point		300	277	277	-	-	-
Viscosity, Centistokes at -20°C	D 445	8 Max.	5.2-5.7	5.5	-	-	-
Net Heat of Combustion, Btu/Pound	D 1405	18,400 Min.	18460-18570	18,375-18,400	-	-	-
Copper Strip Corrosion after Two Hours at 100°C	D 130	No.1 Max.	No. 1A	No. 1A	-	-	-
Naphthalenes, Volume Percent	D 1840	3 Max.	0.15	0.25	-	-	-
Existent Gum, Milligrams per Hundred Milliliters	D 381	7 Max.	0	0	-	-	-
Thermal Stability, Jet Fuel Thermal Oxidation Test, Rating at 280 °C	D 1660	(See Text)	No. 1	No. 1	-	-	-
<u>Inspections of No. 2 Heating Oil</u>							
Specific Gravity, Relative to Water at 15.5°C	D 287	0.8762 Max.	-	-	-	-	0.919-0.925
Flash Point, °C	D 93	38 Min.	-	-	-	-	43-47
Pour Point, °C	D 97	-6 Max.	-	-	-	-	-50
Water and Sediment, Volume Percent	D 1796	0.05 Max.	-	-	-	-	<0.01
Carbon Residue on 10% Bottoms, Weight Percent	D 524	0.35 Max.	-	-	-	-	<0.05
Distillation Temperature at 90% Recovered, °C	D 86	282-338	-	-	-	-	304
Viscosity, Saybolt Seconds Universal at 38°C	D 445	32.6-97.9	-	-	-	-	33
Kinematic Viscosity, Centistokes at 38°C	D 445	2.0-3.6	-	-	-	-	2
Copper Strip Corrosion after Two Hours at 100°C	D 130	No. 3 Max.	-	-	-	-	No. 1A
Sulfur, Weight Percent	D 2662	0.5 Max.	-	-	-	-	<0.001
Thermal Stability, Percent Reflectance after 90 Minutes at 150°C	(See Text)		-	-	-	-	90

*Average Market Projections for the Early 1980's

TABLE XVIII

BASES FOR COST ESTIMATES AND COMPARISONS
REFINING OF SRC-II OIL
DOE CONTRACT EF-76-C-01-2315

General

Estimated processing costs include annual capital charges and operating costs required to refine SRC-II oil using conventional refining processes. No allowance is included in these estimates for (a) coal resource costs, (b) mining or handling of coal, (c) conversion of coal to oil by the SRC-II process, (d) SRC-II oil transportation to the refinery, (e) refined product distribution and transportation from the refinery, or (f) community facilities, electric power generation or other support facilities (except for a small "infrastructure" allowance for roads, power lines, water supply, and disposal lines from the refinery to connect to existing services a few miles away). Notes apply to all subsequent cost tables. Item numbers are keyed to comparative cost summaries.

Investment Costs

Investment estimates are based on:

1. First quarter, 1980 costs. (Excludes escalation during planning, design, and construction periods.)
2. Mid-Continent refining location.
3. Tankage equivalent to ten days of SRC-II oil feed, fifteen days of motor gasoline blend components, fifteen days of light products, and ten days of intermediate products.
4. Cost correlations based on actual plants constructed by Standard Oil Company of California from the 1960's through mid-1970's. In addition to adjustments for inflation, size and known differences in plant location, the base estimates include allowances for:
 - a. Accuracy of the cost correlations.
 - b. A less favorable field labor productivity and materials purchasing situation that will likely be experienced if the U.S. enters into a significant program of synthetic fuels plant construction.
 - c. Changes in plant design philosophy to provide for improved operating efficiency, better reliability, increased safety, additional energy conservation, and stricter environmental requirements.
5. Adding an estimating allowance of about 10% of total onplot and offplot investment to account for the cost of additional items which the history of major projects shows are encountered as the detailed project engineering proceeds.

Working Capital Includes

6. Value of feed and product inventories in storage, assuming tanks are half full.
7. Estimated value of spare catalyst and spare parts.
8. Estimated value of accounts receivable less accounts payable for thirty days.

Capital Charge Factor

9. Overall processing costs are based on a capital charge equal to 30% of total investment (including working capital and initial catalyst costs) per year. This capital charge factor is approximately equivalent to a 15% after tax discounted cash flow rate of return on investment based on:
 - a. 51% income tax.
 - b. Four-year construction period.
 - c. Investment payments equal to 10%, 15%, 25%, and 50% of total investment during the four years of construction.
 - d. 50% of design capacity during first year of operation; 100% in second year and thereafter.
 - e. 10% investment tax credit.
 - f. Sum of the years' digits depreciation; 13-year tax life of refining equipment.
 - g. 20-year project life.

Utilities and Operating Costs

10. Refinery fuel and steam are internally supplied. Boiler plant fuel is purchased coal (amounts shown on stock balances).
11. Process water is conserved by treatment in the WWT plants and then returned to the refining units. Net make-up water cost estimated at \$300 per million gallons.
12. Maintenance cost estimated at 2-1/2% of onplot plus offplot per year.
13. Property taxes and insurance estimated at 2-1/2% of onplot plus offplot per year.
14. Operating labor cost estimated at 110,000 dollars per shift position per year. Sixty-five percent is then added to cover support labor (technical service, administration, security, etc.) and supplies.
15. Power cost estimated at three cents per kilowatt-hour.
16. Coal cost estimated at eight dollars per equivalent fuel oil barrel. (Net heating value of six million British thermal units.)

TABLE XIX
ESTIMATES OF INVESTMENTS AND UTILITIES: CASE 1A
REFINING OF SRC-II OIL BY HIGH SEVERITY
HYDROTREATING TO PRODUCE 50,000 BARRELS PER
CALENDAR DAY OF MOTOR GASOLINE PLUS JET FUEL

	Size	Investment, Millions of Dollars	Initial Catalyst, Millions of Dollars	Net Power Required, Megawatts	Catalysts and Chemicals, Millions of Dollars per Year	Labor, Shift Positions
<u>Onplot Facilities</u>						
High Severity Whole Oil Hydrotreater	63,000 Barrels per Operating Day	15 ^a	12	6.5	5	2.5
Hydrogen Manufacture	2 x 88 Million of Standard Cubic Feet per Operating Day	161	2	1	1	6
Reformer	11,000 Barrels per Operating Day	17	3	-	-	2
WWT Plant	500 Gallons per Minute	12	-	0.5	-	1
Hydrogen Sulfide Recovery	2,700 Pounds per Hour	4	-	-	-	0.5
Sulfur Production and Tail Gas Treating	30 Tons per Operating Day	6	-	-	-	1
Subtotal		369	17	8	6	12.5
Estimating Allowance		37				
<u>Offplot Facilities</u>						
Boiler and Miscellaneous Utility Plant	790,000 Pounds per Hour Steam	89	-	-	-	
Cooling Tower	36,000 Gallons per Minute	6	-	0.5	-	
Electrical Distribution	30,000 Kilovolt- Amperes	9	-	-	-	
Feed and Product Storage Tanks	1.7 Million Barrels	31	-	-	-	
Interconnecting and Tankfield Pipeways Plus Blending Facilities	-	36	-	0.5	-	
Site Development	110 Acres	6	-	-	-	
Relief and Flare System	-	7	-	-	-	
Buildings and Maintenance Equipment	-	17	-	-	-	
Waste Disposal	-	18	-	-	-	
Land Purchase and Infrastructure Allowance	-	7	-	-	-	
Subtotal		226	-	1	-	8
Estimating Allowance		23				
<u>Working Capital</u>						
Feed Inventory	Half Full	20				
Intermediate and Finished Product Inventory	Half Full	29				
Spare Catalyst and Parts	-	10				
Accounts Receivable Minus Payable	30 Days	1				
Subtotal		60				

Note: No allowance is included in these estimates for (a) coal resource costs, (b) mining or handling of coal, (c) conversion of coal to oil by the SRC-II process, (d) SRC-II oil transportation to the refinery, or (e) refined product distribution and transportation from the refinery.

See Table 17 for estimating bases.

on the tables are included to cover the cost of additional items which the history of major projects shows are encountered as the detailed project engineering proceeds.

The investments shown are estimated for an urban mid-continent location. As mentioned above, the estimate for the boiler plant is based on coal-fired burners with attendant stack gas sulfur dioxide (SO₂) removal facilities. As indicated on Table XX, no allowance is made for (a) coal resource costs, (b) coal mining or handling, (c) conversion of coal to oil by SRC-II process, (d) SRC-II oil transportation to, or (e) refined product distribution and transportation from the refinery. These additional costs are not required to evaluate refinery processing costs. However, they should be included if it is desired to determine the overall economics of a specific synthetic crude oil refining project.

Detailed estimates similar to Table XIX were carried out for each case. The results are summarized and compared on Table XX. Factors used for labor, maintenance, taxes, and insurance are typical of those used for analyzing long-term, large scale commercial projects. The capital charge factor, the yearly rate at which the investment is charged to the project, was chosen to provide about a 15% after-tax discounted cash flow (DCF) rate of return on investment based on reasonable and commonly used assumptions for projects of this type and magnitude. These assumptions are summarized on Table XVIII.

Other Studies - The complete DOE report (9) includes a sixth case not discussed in this paper. This case is a refinery scheme for production of gasoline by catalytic cracking of a lower hydrogen content feed than in Case 3A. In this case, No. 2 heating oil was a second major product.

Conclusions - The overall conclusion of our studies is that initial hydrotreating severity does not significantly affect refining cost at constant product distribution. Product distribution itself is the major determinant of refining cost, as shown by the following:

<u>Product Slate</u>	<u>Refining cost, Dollars Per Barrel of Product</u>
Motor Gasoline and Heating Oil	10
Motor Gasoline and Jet Fuel	14
Motor Gasoline	16

TABLE XX

COMPARATIVE COST SUMMARY
REFINING OF SRC-II OIL
"GRASS ROOTS" REFINERIES PRODUCING
50,000 BARRELS PER CALENDAR DAY OF DESIRED PRODUCTS
DOE CONTRACT EF-76-C-01-2315

Refinery Furnace Fuel and Hydrogen Plant Feed Supplied by Internally Generated Hydrotreated Products

Case	1A		2A		3A		4A		5A	
	Motor Gasoline Plus Kerosene Jet Fuel		Intermediate Plus Downstream Hydrotreating		Severe Hydrotreating Plus Fluid Cata- lytic Cracking		Intermediate Severity Hydro- treating Plus Hydrocracking		Motor Gasoline Plus No. 2 Oil	
Desired Products	Severe Hydrotreating		Intermediate Plus Downstream Hydrotreating		Severe Hydrotreating Plus Fluid Cata- lytic Cracking		Intermediate Severity Hydro- treating Plus Hydrocracking		Motor Gasoline Plus No. 2 Oil	
Major Processing	370		360		460		410		230	
Investment Costs, Millions of Dollars	230		210		260		230		170	
Onplot Investment	60		60		70		70		40	
Offplot Investment	20		10		20		20		10	
Estimating Allowance	60		70		60		90		60	
Initial Catalyst	60		70		60		90		60	
Working Capital	60		70		60		90		60	
Total Investment Costs	740		710		900		820		510	
Operating Costs, Millions of Dollars Per Year	6		5		7		5		5	
Catalysts and Chemicals	15		14		18		15		10	
Maintenance	15		14		18		16		10	
Taxes and Insurance	4		4		5		4		3	
Labor	2		3		3		4		2	
Power	5		4		6		3		2	
Boiler Plant Coal	47		44		57		47		32	
Total Operating Costs	47		44		57		47		32	
Total Processing Cost, Dollars Per Barrel of Desired Products*	14.5		14		18		16		10	
Volume Ratio of Desired Products to SRC-II Feed	0.835		0.847		0.843		0.885		0.874	

*Based on a Capital Charge at 15% Value of Money and Rounded to the Nearest Half Dollar Per Barrel

In all cases, the cost of hydrogen manufacture is at least 40% of the total.

A number of variations on the basic six cases were explored and results are also given in the DOE report (9):

- . Single versus two-stage hydrocracking.
- . Burning SRC-II oil versus hydrotreated products in refinery furnaces.
- . Hydrogen production by partial oxidation of SRC-II oil versus steam reforming of refinery gases and naphtha.
- . Separate naphtha and middle distillate versus whole oil initial hydrotreating.
- . Partial integration with the SRC-II process versus grass roots facilities.

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Disclaimer

The work described in the paper was sponsored by the United States Government. Neither Chevron, nor the United States, nor the United States Department of Energy (DOE), nor any of their employees, nor any of their contractors, subcontractors, or their employees makes any warranty, express or implied, or assumes any legal liability of responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. By acceptance of this article, the publisher and/or recipient acknowledges royalty-free license in and to any copyright covering this paper.

Abstract

The SRC-II process is one of several coal liquefaction processes currently under development in programs funded by the Department of Energy (DOE). Product from this process is a distillate that is relatively attractive as a feed for conversion to transportation fuels. Essentially all of the nitrogen, sulfur, and oxygen can be removed in a single catalytic hydro-treating stage to yield a naphtha that is an excellent feed for a catalytic reformer and a middle distillate fraction that is a

premium jet fuel smoke point and stability specifications. Only 5-6% of the hydrotreated SRC-II product boils above the jet boiling range. In this chapter, several possible refining routes for the production of distillate fuels from SRC-II process product are considered, based on results from several demonstration pilot plant tests. In all cases, the initial hydrotreating step is the key step in processing sequence. High hydrogen consumption, however, leads to refining costs for this feedstock of from \$10 to \$16 per barrel, depending on the ratio of gasoline to distillate fuels produced.

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Catalytic Upgrading of H-Coal Syncrudes

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Chevron Research Company, under a contract sponsored by the U.S. Department of Energy (DOE), is conducting a program to determine the feasibility and estimate the costs of refining a number of synthetic crude feedstocks to distillate fuels such as high octane gasoline, jet, and diesel fuels using commercial petroleum processing technology. Pilot plant tests for the key processing steps are being conducted to the extent needed to make reasonable estimates of commercial plant performance. The previous chapter describes results with SRC-II process products.

Another route used to liquefy coal is the H-Coal process, which was developed by Hydrocarbon Research Institute. It differs from the SRC-II process in that a catalyst is employed in the liquefaction step. (1,2) Several recent upgrading studies on this material have again shown the importance of hydrotreating.

For example, de Rosset and coworkers (3,4) studied the hydrotreating, hydrocracking, and catalytic reforming of various H-Coal distillates. They concluded that nitrogen, sulfur, and oxygen can be removed to acceptable levels by conventional hydrotreatment with lower-than-normal space velocities. Catalytic reforming to high octane gasolines proceeded at mild conditions and high yields.

Conser, Garrett, and Weiszmann (5) evaluated several schemes involving hydrotreating, hydrocracking, and FCC for processing H-Coal liquid to produce gasoline and middle distillate in various ratios and compared and contrasted results to petroleum refining. They concluded that while the processing schemes are not the same as in a crude oil refinery, upgrading of coal liquids to acceptable end products is certainly technically feasible. They observed, however, that the properties

of the products from a coal oil refinery can be significantly different from products made in a crude oil refinery. Typically, the products are very aromatic. The No. 2 fuel oil would not meet heating oil or diesel transportation fuel gravity requirements without further extensive hydrogenation. They suggested that probably the coal oil distillate can best be blended with Crude Oil No. 2 fuel oil stocks after it has been hydrotreated or it can be used directly, possibly with modified burner systems. In the cases they studied, hydrotreating followed by hydrocracking appeared to be more attractive than hydrotreating followed by FCC.

Caldwell and Eyerman (6) hydrotreated and hydrocracked several coal-derived distillates and naphthas, including those from H-Coal, and evaluated these oils as potential petrochemical feedstocks. High yields of aromatics were obtained upon reforming.

In the present chapter, results are presented from a study of the refining steps needed to produce distillate fuels from H-Coal liquids. The approach has been similar to that used in the SRC-II work described in the previous chapter: analyze the starting material, choose reasonable processing steps, make appropriate pilot plant tests, and analyze the products.

Syncrude Properties

H-Coal naphthas and distillates derived from Illinois No. 6 (Burning Star Mine) and Wyodak coals were supplied by Hydrocarbon Research, Inc. The naphthas and distillates were blended in the appropriate proportions to obtain a whole syncrude derived from each coal. Properties of these syncrudes are shown in Table I. For comparison, Table I also shows properties of the SRC-II syncrude used in the study described in the previous chapter. The SRC-II syncrude was derived from a West Virginia coal (Pittsburgh Seam, Blacksville No. 2 Mine of the consolidated Coal Company). The H-Coal and SRC-II syncrudes are not directly comparable because the coals used to derive these syncrudes differ.

The important properties of these syncrudes include the hydrogen content, boiling range, and impurities. Apparently, the type of coal greatly influences these properties. The Wyodak H-Coal syncrude is richer in hydrogen and contains fewer heteroatoms than the Illinois H-Coal syncrude. In contrast, the SRC-II syncrude contains the least hydrogen and the most

TABLE I
 PROPERTIES OF WYODAK H-COAL,
 ILLINOIS H-COAL, AND SRC-II SYNCRUDES

	Wyodak H-Coal Syncrude	Illinois H-Coal Syncrude	SRC-II Syncrude
Gravity, °API	35.1	25.8	18.6
Aniline Point, °F	<32	<30	
Molecular Weight	~130	147	132
Viscosity, cSt At 100°F	1.225	1.645	2.196
Ramsbottom Carbon, Wt %	0.23	0.29	0.70
Hot C ₇ Insolubles, Wt %	0.068	0.35	0.0469
Ash, ppm	<20	90	40
Pour Point, °F	-	-	<-80
Bromine No.	26	42	70
Maleic Diene No., cg I ₂ /g	3.19	10.4	30.7
Carbon, Wt %	86.20	86.96	84.61
Hydrogen, Wt %	12.74	11.39	10.46
Sulfur, Wt %	0.041	0.32	0.29
Oxygen, Wt %	0.85	1.80	3.79
Total Nitrogen, Wt %	0.17	0.46	0.85
Basic Nitrogen, Wt %	0.13	0.30	0.70
Iron, ppm	9.0	~22	7.5
Chloride, ppm	3	32	50
Hydrogen/Carbon Atom Ratio	1.76	1.56	1.47
H ₂ O, ppm	<500	2217	6000
TBP Distillation, °F (Simulated by Chromatography)			
St/5	53/156	56/177	56/189
10/30	173/261	213/333	241/379
50	354	404	424
70/90	429/535	476/588	473/562
95/99	602/785	654/765	642/820

heteroatoms, which could be the result of either the coal or the different liquefaction process. The Illinois H-Coal syncrude contains a significant amount of compounds which are insoluble in hot heptane and which could not be removed by filtration through diatomaceous earth. Some of these heptane-insoluble compounds, which include both asphaltene-like hydrocarbons and ash, may have formed during the two years this syncrude was stored.

These H-Coal and SRC-II syncrudes are low boiling and do not contain residuum. As shown in Figure 1, much of each syncrude boils in the jet fuel range. Only about 25 vol % boils below the start of the jet fuel range (250°F), and about 5 vol % boils above the end of the jet fuel range (600°F).

The Illinois H-Coal syncrude contains the greatest amount of iron. This iron could be from corrosion during processing or storage, rather than from the coal itself. We have observed high iron contents in California gas oils which contain acidic and corrosive oxygen. In California gas oils, the iron is soluble in the oil as iron naphthenates (iron salts of organic acids).

The Illinois H-Coal and SRC-II syncrudes contain large amounts of chloride, 32 parts per million (ppm) and 50 ppm, respectively. The Wyodak H-Coal syncrude contains only 3 ppm. Because the exit line from the pilot plants which processed the SRC-II syncrude occasionally plugged with ammonium chloride, we water washed the Illinois H-Coal syncrude prior to hydrotreating. It is our understanding that chloride will be removed by water washing at a commercial coal liquefaction facility.

Experimental

The syncrudes were hydroprocessed in pilot plants to support estimates for four refining cases. The four refining cases were designed to produce a high yield of jet, diesel or heating fuel, or feedstock to a catalytic reformer for gasoline production. The first three cases are discussed here. The case for the manufacture of a maximum quantity of gasoline is described in another paper (7) and a forthcoming DOE report. (8)

The syncrudes were hydrotreated in fixed bed, downflow pilot plants. They have high and low pressure product separators, recycle hydrogen facilities, and extensive control and

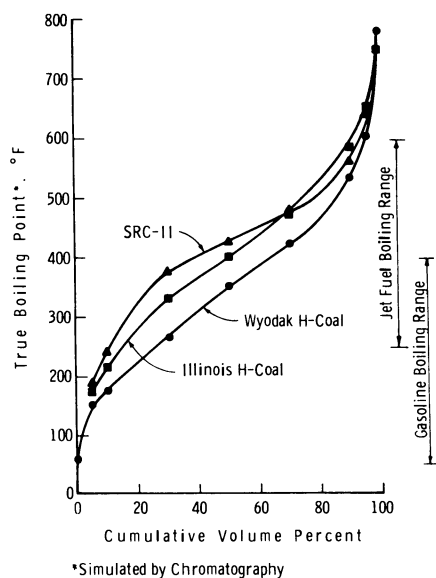


Figure 1. True boiling point distillations for Illinois H-coal, Wyodak H-coal, and SRC-II syncrudes

monitoring instrumentation. These units generally give good recovery (within 2 wt %) and provide an accurate measure of the hydrogen consumption.

Two proprietary Chevron catalysts were used in different pilot plant simulations of the syncrude hydrotreater: ICR 106 and ICR 113. The ICR 106 catalyst contains nickel, tungsten, silica, and alumina; and the ICR 113 catalyst contains nickel, molybdenum, silica, and alumina. An equal volume of inert, nonporous alumina was placed on top of the catalysts. This alumina served as a preheating zone. These catalysts operated satisfactorily for over one-half year (4000 hours) with the Illinois H-Coal syncrude.

Syncrude Refinery Plans

For the manufacture of jet, diesel, or heating fuels from the H-Coal syncrudes, the refinery plan is very simple, as shown on Figure 2 for the jet or diesel fuel cases. The major product fuel oils are simply distilled from the hydrotreated effluent. For the jet and diesel fuel cases, the syncrude hydrotreater is operated at high severity and the by-product naphtha can be fed to a second stage of a catalytic reformer. For the heating fuel case, the syncrude hydrotreater operates at moderate severity. Here, the naphthas contain heteroatoms and must be further refined in a first stage of a two-stage catalytic reformer. For the manufacture of gasoline, the refinery is more complicated since an extinction-recycle hydrocracker is needed to convert all the distillate to gasoline. As indicated above, the latter case is discussed elsewhere. (7,8)

Refining Results

The three cases (jet, diesel, and heating fuel) are presented separately.

Preparation of Jet Fuel - When the Illinois H-Coal and SRC-II syncrudes are hydrotreated at severe conditions [2300 psia hydrogen partial pressure; 0.5 liquid hourly space velocity (LHSV), volumes of feed per volume of catalyst per hour; between 750°F and 800°F average catalyst temperature; 800 standard cubic feet per barrel (SCF/bbl) recycle gas rate], the

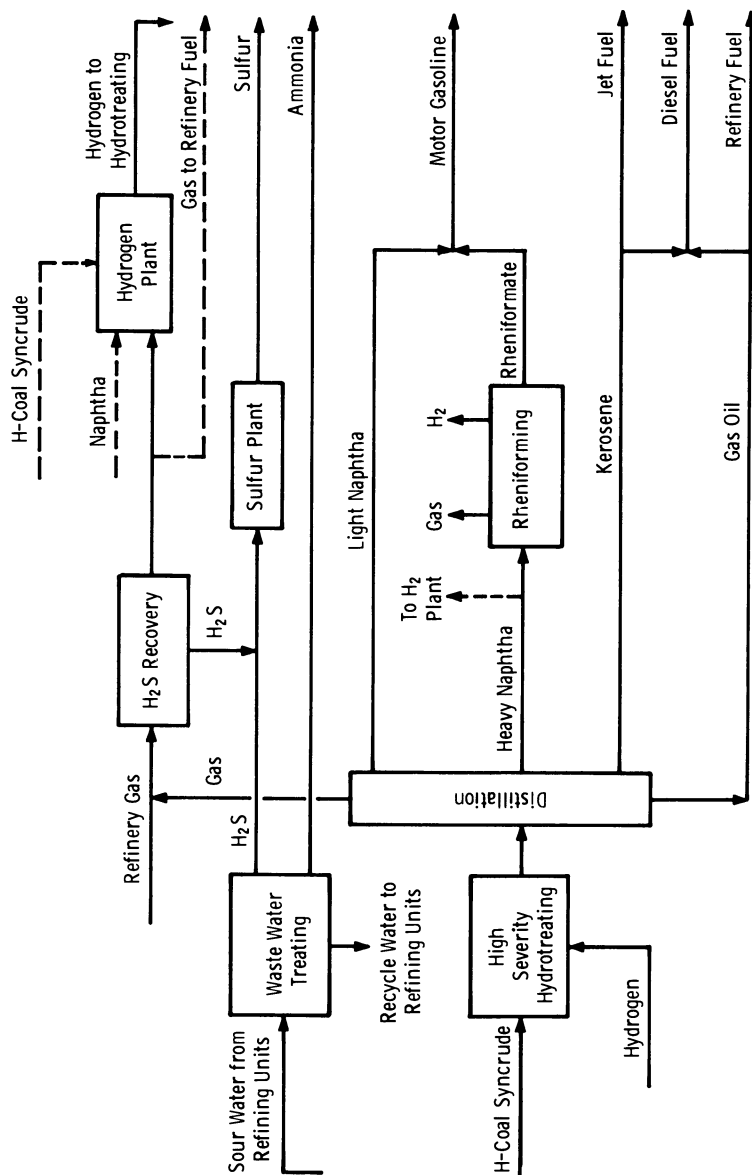


Figure 2. Simplified flow diagram: refining of H-coal syncrude by high severity hydrotreating

250–600°F product meets almost all jet fuel properties, as shown in Table II. The Wyodak syncrude is easier to hydro-process and produces specification jet fuel at 1.0 LHSV and the above conditions. The only property which was not met consistently was the API gravity. If need be, the gravity specification could be met for the jet product from all of these syncrudes by adjusting the end point of the jet fuel. Specification jet fuel was made on this catalyst after 4000 hours of operation.

Yield periods for these three syncrudes, refined to specification jet fuel, are shown in Table III. Accurate yields of the very small 600°F⁺ portion were not determined for these periods. The yields in Table III show this cut combined with the jet cut. The yield of the 600°F⁺ cut is approximately 5 vol % for the Illinois H-coal syncrude and 2.5 vol % for the Wyodak H-Coal and SRC-II syncrudes. Properties of the jet fuels are shown in Table IV.

Properties of the naphthas produced from the syncrudes in the above tests are shown in Table V. Dinaphthenes are found in the 300–350°F naphtha and, surprisingly, in the 250–300°F naphtha. High levels of these compounds can make coal-derived naphthas difficult to reform. (9) A combination gas chromatographic-mass spectrometric (GC-MS) analysis of the 250–300°F naphtha from hydrotreated Illinois H-Coal found that the dinaphthenes are 8-carbon atom compounds (1.8% octahydropentalene) and 9-carbon atom compounds (0.7% bicyclo 3.3.1 nonane, 0.4% methyloctahydropentalene, 1.0% octahydroindenes, and 2.6% unidentified compounds). These dinaphthenes should not yield naphthalene when reformed. If the initial point of the jet fuel is 300°F or less, the 300°F⁻ naphtha should be easy to reform.

Preparation of Diesel Fuel - The same severely hydro-treated 250°F⁺ products from the three syncrudes described in the jet fuel case meet all specifications for No. 1D fuel oil, as shown in Table VI. The cetane test is accurate to about two numbers. Probably all three hydrotreated syncrudes just meet the ASTM required minimum of 40. Conventional additives could be used to improve the cetane numbers, as shown by experimental results discussed elsewhere. (8)

Diesel Fuel No. 1 is used in small engines which require frequent speed or load adjustments. Diesel Fuel No. 2 is more

TABLE II
 COMPARISON OF SEVERELY HYDROTREATED PRODUCTS FROM
 ILLINOIS H-COAL, WYODAK H-COAL,
 AND SRC-II SYNCRUDES WITH
 ASTM JET FUEL SPECIFICATIONS

Product	Jet A Specification ASTM D 1655-78	250-600°F Products From		
		Illinois H-Coal	Wyodak H-Coal	Severely HDT SRC-II ¹
Gravity, °API	37-51	37	39.7	36.3
Smoke Point, mm	>20	23	21	22
Freeze Point, °F	<-40	-53	<-40	-75
Thermal Stability, JFTOT at 260°C	No. 1 or No. 2 ΔP <25 mm	No. 1 ΔP=0		No. 1 ΔP=0
Aromatics, LV %	<20	2.3	3.6	5.0
Existent Gum, ppm	<7	1	1	2
Cu Strip Corrosion, 2 Hr at 212°F	No. 1	No. 1	No. 1	No. 1
End Point, D 86, °F	<570	554	<554	<554
Flash Point, °F	>100	108	>100	>100

¹Estimated from data obtained on products with slightly different boiling ranges.

TABLE III
 YIELDS FROM SEVERE HYDROTREATING OF ILLINOIS H-COAL,
 WYODAK H-COAL, AND SRC-II SYNCRUDES

	Illinois H-Coal Syncrude		Wyodak H-Coal Syncrude		SRC-II Syncrude	
	Wt %	Vol %	Wt %	Vol %	Wt %	Vol %
Catalyst Temperature, °F	750		752		750	
LHSV	0.5		1.0		0.5	
Total Pressure, psig	2,495		2495		2,499	
H ₂ Pressure, psia	2,232		2257		2,306	
Total Gas In, SCF/Bbl	10,127		9043		17,054	
Recycle Gas, SCF/Bbl	7,921		7743		13,752	
No. Loss Yields	Wt %	Vol %	Wt %	Vol %	Wt %	Vol %
C ₁	0.05		0.08		0.17	
C ₂	0.08		0.11		0.29	
C ₃	0.13		0.19		0.37	
iC ₄	0.02	0.03	0.03	0.05	0.03	0.05
nC ₄	0.06	0.09	0.08	0.12	0.18	0.28
C ₅ -180°F	3.64	4.55	8.68	10.28	4.74	6.07
180-250°F	13.39	15.84	17.01	19.02	15.37	18.90
250-300°F	10.56	12.26	12.84	14.09	11.12	13.41
300-350°F	12.59	14.04	13.32	14.05	~10.94	12.82*
350°F ⁺	61.28	64.10	48.66	48.74	~56.25	61.20*
300°F ⁺	73.87	78.14	61.98	62.82	67.19	74.02
250°F ⁺	84.43	90.40	75.30	76.91	78.31	87.43
Total C ₅ ⁺	101.48	110.80	100.52	106.21	98.41	112.40
Actual/No Loss Recovery	101.17/103.61		105.93/102.19		105.44/105.01	
H ₂ Cons. (Gross), SCF/Bbl	2,206		1,340		3,302	
H ₂ Cons. (Chem.), SCF/Bbl	2,146		1,228		3,109	
Run, (Hours)	76-171 (222-246)		76-173 (331-355)		76-165 (251-275)	

*Estimated yields of 300-350°F and 350°F⁺ portions from 76-165 (323-347) yield period.

TABLE IV
 PROPERTIES OF FUEL OILS FROM HYDROTREATING
 ILLINOIS H-COAL, WYODAK H-COAL, AND SRC-II SYNCRUDES

	Illinois H-Coal Syncrude				Wyodak H-Coal Syncrude				SRC-II Syncrude			
	750		2232		752		2257		750		2306	
	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0
Catalyst Temperature, °F												
LHSV												
H ₂ Pressure, psia												
Boiling Range, °F												
Gravity, °API												
Aniline Point, °F												
Molecular Weight												
Sulfur, ppm												
Smoke Point, mm												
Cetane No.												
Existent Gum, mg/100 ml												
Freeze Point, °F												
Pour Point, °F												
Cloud Point, °F												
Flash (Tag Closed), °F												
Flash (P-M), °F												
Cu Strip corrosion												
Viscosity, cSt												
At -40°F												
At 100°F												
Group Types by MS, LV %												
Paraffins												
Naphthenes												
Aromatics												
Distillation, LV %, °F												
Run (Hours)												

*Simulated by chromatography

**Measured at other hours but at these conditions

TABLE V
 PROPERTIES OF NAPHTHAS FROM SEVERELY HYDROTREATING ILLINOIS H-COAL,
 WYODAK H-COAL, AND SRC-II SYNCRUDE

	Illinois H-Coal Synchrude				Wyodak H-Coal Synchrude				Mixed SRC-II Synchrude				
	750		0.5		752		1.0		750		0.5		
	2495	2232	2497	2237	2497	2237	2499	2306	180-300**	180-350**	300-350***	300-350***	
Catalyst Temperature, °F													
LHSV													
Total Pressure, psig													
H ₂ Pressure, psia													
Boiling Range, °F													
Gravity, °API	64.6	53.9	50.3	43.2	65.8	54.8	51.3	44.3	60.7	53.1	51.6	50.2	46.8
Research Octane No.	78.8**	0.2**	0.3**	0.5**	79.0	70.0	0.25		81.1	71.6	65.4	59.5	
Sulfur, ppm													
Group Types, LV %													
Paraffins	37.8	12.1	6.2	4.8	38.3	17.1	14.9	15.1	31.2	6.1	9.6	5.7	
Mononaphthenes	60.2	86.0	85.8	59.9	60.1	81.0	78.5	51.1	65.4	91.4	86.8	86.7	
Dinaphthenes	0.0	0.0	6.2**	33.6**	0.0	0.0	4.6	31.0	0.0	0.0	0.0	6.9	24.3
Aromatics	2.0	1.9	1.8	1.7	1.6	1.8	2.0	2.8	3.4	2.5	3.6	0.7	
TBP Distillation, LV %													
°F*													
St/5	39/76	55/177	208/246	253/293	23/83	154/178	210/246	253/295		136/179	139/178	131/180	
10/30	91/151	181/214	250/263	299/317	98/157	181/207	250/263	301/318		183/219	184/226	186/225	
50	165	226	278	329	168	223	278	329		226	246	285	
70/90	179/187	232/250	287/303	344/355	182/188	230/249	286/304	343/354		231/251	269/292	292/331	
95/EP	189/212	256/266	308/319	360/367	190/200	255/264	308/319	360/369		257/269	303/316	343/360	
Run (Hours)		76-171 (222-246)				76-173 (331-355)					76-165 (251-275)		

*Simulated by chromatography.

**From different hours, but at these conditions.

***Calculated from other cuts.

TABLE VI
 COMPARISON OF SEVERELY HYDROTREATED PRODUCTS FROM
 ILLINOIS H-COAL, WYODAK H-COAL
 AND SRC-II SYNCRUDES WITH
 ASTM DIESEL FUEL SPECIFICATIONS

Property	Diesel Specifications ASTM D 975-78			250°F [†] Products		
	No. 1D	No. 2D		Illinois H-Coal	Wyodak H-Coal	From SRC-II
	All Climates	Typical Climates	Cold Climates			
Cetane No.	>40	>40	>40	~42	~41	~38
Cloud Point, °F	Varies	Varies	<10	-50	-20	<-80
Sulfur	<0.5	<0.5	<0.5	0.001	0.002	0.002
Flash (P-M), °F	>100	>125	>125	116	~115	~115
Ash, Wt %	<0.01	<0.01	<0.01	<0.002	<0.002	<0.002
D 86, 90%, °F	<550	540-560	<560	511	499	492
Viscosity at 40°C, cSt	1.3-2.4	1.9-4.1	1.7-4.1	1.678	1.441	1.606
Viscosity at 100°F, SUS	<34.4	32.6-40.1	-	32.1	<32	<32
Cu Corrosion	<No. 3	<No. 3	<No. 3	No. 1	No. 1	No. 1
Aromatics	-	-	-	2.7	3.6	3.8
				300°F [†] Products		
Flash, (P-M) °F				130	~130	130
D 86, 90%, °F				534	<499	~503
Viscosity at 40°C, cSt				1.898	1.701	1.869

widely used in engines in heavy mobile or industrial service. The minimum flash point for No. 2D fuel is 125°F. To meet this specification, the hydrotreated syncrudes were cut at 300°F. The products from these hydrotreated syncrudes lack paraffins and have low cloud points. Therefore, they are excellent cold climate No. 2D fuels, as shown in Table VI. For diesel fuel used in typical climates, the 300°F⁺ products have viscosities and D 86 90% points just below the ASTM minimums. To meet this specification, the initial point could be adjusted upward.

The yield periods for the preparation of diesel fuel are shown in Table III. These yield periods are the same as shown above in the jet fuel case. Properties of diesel fuel cuts and naphthas are shown in Tables IV and V, respectively.

In summary, specification No. ID fuel can be made from the 250°F⁺ hydrotreated products from all three syncrudes. The 300°F⁺ hydrotreated product could be used as cold climate specification No. 2D fuel. Also, the 300°F⁺ hydrotreated product almost meets the specification of typical climate No. 2D fuel.

Preparation of Heating Fuel - The specifications for heating fuel require less severe hydroprocessing than the specifications for jet or diesel fuels. The Illinois H-Coal and SRC-II syncrudes can be hydrotreated at moderate severity (1.5 LHSV, approximately 1800 psia H₂, 750-800°F, 8000 SCF/bbl recycle gas) over ICR 106. The Wyodak H-Coal syncrude is easier to hydroprocess, and the less expensive and less active ICR 113 catalyst can be used. As shown in Table VII, the 250°F⁺ hydro-treated products from these syncrudes have very low pour points and should make excellent cold climate fuels. However, all three products have viscosities just below the ASTM minimum of 1.8 cSt required for cold climate or 2.0 cSt required for typical climate. Also, only the Wyodak H-Coal product has a gravity above the ASTM minimum of 30°API. If attempts are made to increase the viscosity by reducing the hydrotreating severity or by raising the initial point, the gravity will fall below the minimum of 30°API. As they are, these 250°F⁺ hydrotreated products are very close to the ASTM standards. Small adjustments may have to be made to the burner nozzles to accommodate the slightly heavier and slightly less viscous fuel.

The yields for the preparation of heating fuel are shown in Table VIII. The naphtha and heating fuel oil properties are shown in Tables IX and X, respectively.

TABLE VII
 COMPARISON OF MODERATELY HYDROTREATED PRODUCTS
 FROM ILLINOIS H-COAL, WYODAK H-COAL,
 AND SRC-II SYNCRUDES WITH
 ASTM SPECIFICATIONS FOR HEATING FUEL

Property	No. 2 Fuel Oil Specifications D 396-78		250°F [†] Products From		
	Typical Climate	Cold Climate	Illinois H-Coal	Wyodak H-Coal	SRC-II
Gravity, °API	>30	>30	27.7	32.7	~27
Flash, °F	>100	>100	116	114	>100
Pour, °F	<20	<0	<-80	-45	<-80
D 86, 90%, °F	540-640	<640	560	527	~550
Viscosity at 100°F, cSt	2.0-3.6	1.8-3.6	1.767	No. 1	~1.6
Cu Corrosion	<No. 3	<No. 3	No. 1	No. 1	No. 1
Sulfur, ppm	<5000	<5000	2	0.8	4
Aromatics, LV %	-	-	54	49	58

TABLE VIII
 YIELDS FROM MODERATELY HYDROTREATING
 ILLINOIS H-COAL, WYODAK H-COAL,
 AND SRC-II SYNCRUDES TO MAKE HEATING FUEL

	Illinois H-Coal		Wyodak H-Coal		SRC-II	
	Wt %	Vol %	Wt %	Vol %	Wt %	Vol %
Aromatics C ₅ ⁺ Liquid Products, LV %	43.7		~35		49.8	
Catalyst Temperature, °F	775		750		750	
Catalyst	ICR 106		ICR 113		ICR 106	
LHSV	1.5		1.5		1.5	
Total Pressure, psig	2073		1998		2001	
H ₂ Pressure, psia	1859		1862		1763	
Total Gas In, SCF/Bbl	8747		8735		9880	
Recycle Gas, SCF/Bbl	7792		8206		8066	
No Loss Yields	Wt %	Vol %	Wt %	Vol %	Wt %	Vol %
C ₁	0.10		0.04		0.10	
C ₂	0.11		0.06		0.17	
C ₃	0.11		0.10		0.19	
iC ₄	0.02	0.03	0.02	0.03	0.02	0.03
nC ₄	0.04	0.06	0.11	0.15	0.09	0.14
C ₅ -180°F	5.89	7.25	6.86	8.06	4.29	5.51
180-250°F	11.82	13.81	14.03	15.57	32.75	38.55
250-300°F	8.94	10.11	78.33	76.83		
300-350°F	10.44	11.40				
350°F ⁺	62.39	61.43			59.85	60.65
300°F ⁺	72.83	72.83				
250°F ⁺	81.77	82.94	78.33	76.83		
Total C ₅ ⁺	99.49	104.02	99.23	100.46	96.64	104.52
Actual/No Loss Recovery	98.92/101.48		98.96/100.74		101.63/102.78	
H ₂ Cons. (Gross), SCF/Bbl	955		528		1814	
H ₂ Cons. (Chem.), SCF/Bbl	880		415		1725	
Run (Hours)	76-171 (1967-1991)		66-203 (1366-1390)		76-165 (1283-1307)	

TABLE IX
 PROPERTIES OF NAPHTHAS FROM MODERATELY HYDROTREATED
 ILLINOIS H-COAL, WYODAK H-COAL, AND SRC-II SYNCRUDES

	Illinois H-Coal		Wyodak H-Coal		SRC-II	
	ICR 106	ICR 113	ICR 106	ICR 113	ICR 106	ICR 106
Catalyst						
Catalyst Temperature, °F	775	750	750	750	750	750
LHSV	1.5	1.5	1.5	1.5	1.5	1.5
Total Pressure, psig	2073	1998	1998	2001	2001	2001
H ₂ Pressure, psia	1859	1862	1862	1763	1763	1763
Boiling Range, °F	180-250	250-300	300-350	180-250	180-350	180-350
Gravity, °API	61.6	51.8	45.9	65.0	59.8	45.7
Research Octane No.				54.2		72.2
Motor Octane No.				71.3		67.7
Sulfur, ppm		0.18	0.26			
Oxygen, ppm						3200
Nitrogen, ppm						119
Group Types, LV %						
Paraffins	33.6	11.5	9.5			11.3
Mononaphthenes	60.3	75.4	61.9			60.0
Dinaphthenes	0.0	0.0	4.5			5.5**
Aromatics	6.2	13.1	24.1			23.2
Distillation, LV %, °F						
	TBP*	TBP*	TBP*	TBP*	D. 86	D. 86
St/5	46/90	157/179	212/245	252/291	200/203	214/228
10/30	101/161	183/218	251/273	300/320	204/206	232/245
50	176	226	283	332	208	261
70/90	188/195	235/250	293/305	345/357	213/220	282/309
95/EP	198/208	256/269	311/321	362/367	227/264	319/365
Run (Hours)		76-171 (1967-1991)		66-203 (1366-1390)		76-165 (1283-1307)

*Simulated by chromatography

**Measured at other hours but at the these conditions

TABLE X
 PROPERTIES OF HEATING FUELS FROM MODERATELY HYDROTREATED
 ILLINOIS H-COAL, WYODAK H-COAL, AND SRC-II SYNCRUDES

Catalyst	Illinois H-Coal		Wyodak H-Coal	SRC-II
	ICR 106	ICR 113		
Catalyst Temperature, °F	775	750	750	750
LHSV	1.5	1.5	1.5	1.5
Total Pressure, psig	2073	2998	2001	2001
H ₂ Pressure, psia	2859	2862	1763	1763
Boiling Range, °F	250+	300+	250+	350+
Gravity, °API	27.7	25.4	32.7	20.6
Aniline Point, °F	49.2	46.0	72.3	<32
Molecular Weight		190		175
Sulfur, ppm	2.0*	4.0*	0.8	
Oxygen, ppm	590*	650*		5500
Nitrogen, ppm	<-80*	<-80*	6.7	702
Pour Point, °F	-50	-38	-4.5	-55
Cloud Point, °F	116	148	114	
Flash Point (P-M), °F	1A		1A	1A*
Cu Strip Corrosion				
Viscosity, cSt	12.67*	21.64*		
At 100°F	1.767*	2.085*		2.235
Group Types by MS, LV %				
Paraffins	3.4	4.0		5.2
Naphthenes	43.1	39.9		28.0
Aromatics	53.5	56.0		66.8
Distillation, LV %, °F	D 86	D 86	D 86	D 86
St/5	311/324	360/366	397/413	392/408
10/30	339/381	376/400	418/439	413/428
50	430	441	466	449
70/90	483/560	487/562	508/586	484/566
95/EP	601/664	605/685	642/667	622/691
Run (Hours)	76-171 (1967-1991)		66-203 (1366-1390)	76-165 (1283-1307)

*Measured at other hours, but these conditions

At moderate severity, the hydrotreating catalysts foul, as shown in Figure 3 by the rise in nitrogen content of the products versus time. In commercial operation, the catalyst temperature would be raised; and the product nitrogen content would be held constant. Commercial run lengths appear feasible, even at moderate severity.

Stability of Hydrotreated H-Coal Syncrudes

The stability of the products from coal-derived syncrudes must be examined carefully. Many unique compounds are present in these syncrudes: peri-condensed aromatics and naphthenes, oxygen compounds, and asphaltene-like hydrocabons. Traces of these compounds may remain in the hydrotreated product; and their effect on jet, thermal, and oxidation stabilities cannot be predicted from the behavior of petroleum products.

For jet fuels, a visual rating of No. 1 or No. 2 is required at 260°C in the jet fuel thermal oxidation stability test (JFTOT-ASTM D 3241). Also, a pressure drop of less than 25 mm Hg is required in this test, As shown in Table XI, the 250°F⁺ product from hydrotreated Illinois H-Coal syncrude passes both parts of the JFTOT test, even when the jet fuel is not refined enough to pass three other specifications: aromatic content, smoke point, and gum content. When jet fuels are prepared from coal-derived syncrudes, the smoke point appears to be the limiting specification. The gum content and end point specifications are met when the jet fuels are distilled at 600°F.

Diesel fuel and heating fuels should pass both oxidation and thermal stability tests. As shown in Table XII, the raw Wyodak H-Coal syncrude has a very poor oxidation stability; but the hydrotreated Wyodak H-Coal syncrude has an excellent oxidation stability. The oxidation stability of hydrotreated Illinois H-Coal products is also excellent, even without additives.

The thermal stability test used at Chevron is an adaptation of Du Pont Test Method 21-61 (10) and is described in the previous chapter.

As shown in Table XII, the thermal stability of the raw Wyodak H-Coal syncrude is also very poor; but the thermal stability of the hydrotreated Wyodak H-Coal syncrude is excellent. The thermal stability of hydrotreated Illinois H-Coal

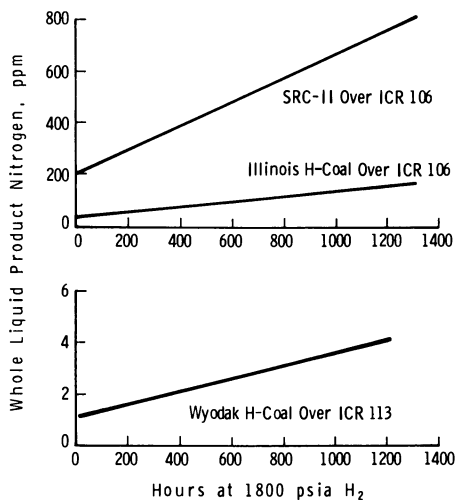


Figure 3. Fouling during the hydrotreating of Illinois H-coal, Wyodak H-coal, and SRC-II syncrudes at 1.5 LHSV and 1800 psia H₂

TABLE XI

TEST FUEL STABILITY TEST RESULTS FOR
ILLINOIS H-COAL SYNCRUDE HYDROTREATED
AT TWO SPACE VELOCITIES

Property	Jet A Specification ASTM D 1655-78	Hydrotreated Illinois H-Coal Syncrude	
		1.0 LHSV 250°F [†]	0.5 LHSV 250-600°F
Aromatics, LV %	<20	28	2.7
Smoke Point, mm	>20	14	23
Gum Content	<7	~500	1
JFTOT at 260°C Rating ΔP, mm Hg	No. 1 or No. 2 <25	No. 1 0	No. 1 0

TABLE XII
 OXIDATION AND THERMAL STABILITY TEST
 RESULTS FOR RAW AND HYDROTREATED (HDT)
 H-COAL SYNCRUCES

	Raw Wyodak	HDT Wyodak	HDT Illinois	
	H-Coal Whole Product	H-Coal Whole Product	300 °F†	H-Coal 300 °F†
Rolling Range				
LHSV	-	1.5	0.5	1.0
H ₂ Pressure, psia	-	1800	2300	2300
Aromatics, LV %	~45	45	2.7	25.3
Nitrogen, ppm	1700	5	<0.5	<0.5
Oxidation Stability Test				
Color As Is	8	<1.0	<0.5	<0.5
Color After 6 Hr O ₂ Blow	8+	<1.5	<0.5	1.0
Filter Residue After 6 Hr O ₂ Blow, ppm	270	1	1	1
Thermal Stability Test				
Reflectance, %	7.5	96.0	93.0	92.0
				300 °F†
				1.5
				53.9
				43
				<3.0
				<3.0
				2

product also is better than the requirements for automotive diesel engines.

Products which were evaluated in JFTOT and thermal stability tests were distilled and stored in glass. Petroleum- or coal-derived fuels which have been distilled or stored in metal equipment sometimes fail these tests due to contamination by metals.

Based on the results, the stability of these hydrotreated products does not appear to be a problem. Other properties (smoke point, cetane number, and viscosity) appear to be important properties to consider when the refining severity is selected.

An Alternative to Whole Oil Hydrotreating: Hydrotreating of Rerun Illinois H-Coal

When we compared the Illinois H-Coal, Wyodak H-Coal, and SRC-II syncrudes, we observed the expected differences in the amount of hydrogen consumed to reach a given level of aromatics, as shown in Figure 4. Based on the hydrogen content, gravity and low levels of heteroatoms in the Illinois H-Coal syncrude, when compared to the SRC-II syncrude, we hoped that the Illinois H-Coal syncrude would be easier to hydroprocess. That is, the Illinois H-Coal syncrude should require a smaller syncrude hydrotreater, operated at a higher LHSV than the SRC-II syncrude. The observed processability of the Illinois H-Coal syncrude, as measured by the aromatics remaining in the C_5^+ liquid product, was not better than the SRC-II syncrude (Figure 5). It appears as if the heptane-insoluble compounds in the whole Illinois H-Coal syncrude are serious catalyst poisons. These compounds may have formed during the two years this syncrude was stored.

The whole Illinois H-Coal syncrude was redistilled at 600°F cut point to yield a rerun Illinois H-Coal syncrude and distillation bottoms (Table XIII). The yield of the rerun syncrude is 83.3 wt % (87.1 vol %). Although the nominal cut point of the distillation was 600°F, the products appear to be cut at close to 550°F. The distillation bottoms could perhaps be used to manufacture hydrogen by partial oxidation or used as refinery fuel since it contains only 0.18 wt % sulfur.

As shown in Figure 5, the rerun Illinois H-Coal syncrude is amazingly easy to hydroprocess, when compared to the whole

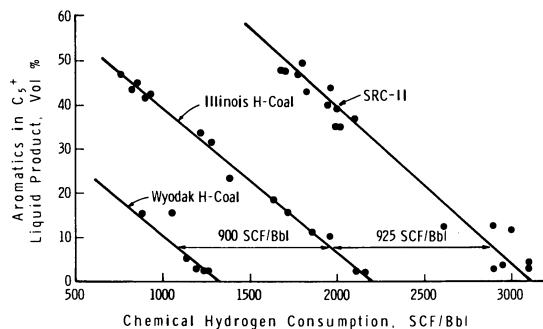


Figure 4. Product aromatic content vs. hydrogen consumption for Illinois H-coal, Wyodak H-coal, and SRC-II syncrudes

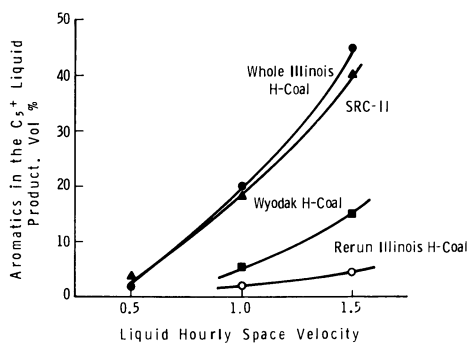


Figure 5. The processability of coal-derived syncrudes over ICR 106; 750° F and N2300 psia H₂

TABLE XIII
 PROPERTIES OF THE RERUN ILLINOIS H-COAL
 SYNCRUDE AND DISTILLATION BOTTOMS

	Rerun Syncrude	Distillation Bottoms
Yield, Wt %/Vol %	83.8/87.1	16.2/12.9
Gravity, °API	28.2	0.1
Molecular Weight	136	262
Ramshotom Carbon, Wt %	0.30	5.94
Hot C ₇ Insolubles, Wt %	0.0054	7.49
Ash, ppm	<0.002	0.17
Bromine No.	31	52
Carbon, Wt %	86.13	88.27
H ₂ , Wt %	11.44	8.99
Sulfur, Wt %	0.14	0.18
Nitrogen, Wt %	0.33	1.18
Oxygen, Wt %	1.96	1.38
Chloride, ppm	34	
H ₂ /Carbon Atom Ratio	1.58	1.21
°BP Distillation, LV %, °F (Simulated by Chromatography)		
St/5	101/175	388/568
10/30	181/194	585/629
50	335	721
70/90	417/508	779/856
95/99	538/589	904/1018

Illinois H-Coal syncrude. The product from the syncrude hydro-treater contains less than 5 vol % aromatics, even at 1.5 LHSV.

The yields from the rerun Illinois H-Coal syncrude are shown in Table XIV. Properties of the jet and diesel fuels are shown in Tale XV. The 250°F⁺ product from the rerun Illinois H-Coal syncrude meets all jet fuel specifications without additional distillation.

Rerunning these syncrudes appears to have three advantages. The size of the Illinois H-Coal syncrude hydrotreater can be reduced, perhaps to one-third of the original size. Distillation of the hydrotreated syncrude to meet jet fuel gum and end point specifications can be eliminated. Hydrogen can be manufactured from the least valuable component of the syncrude.

Summary

H-Coal syncrudes derived from Illinois No. 6 and Wyodak coals can be refined with current hydroprocessing technology to specification jet and diesel fuels. These syncrudes can also be refined to heating fuels which are ideal for cold climates. Although the raw H-Coal syncrudes fail heating and diesel fuel stability tests, the hydrotreated products pass these tests and the stringent jet fuel thermal oxidation stability test. The yields of these fuels are excellent. For example, the yields of diesel, jet, and heating fuels from a single-stage hydrotreater are 80 vol % or higher. Most of the remaining light product is naphtha, which can be reformed to gasoline.

When 15 vol % of the bottoms is removed from the Illinois H-Coal syncrude, the rates of the hydrotreating reactions are increased. The rerun Illinois H-Coal syncrude can be refined to jet or diesel fuel in a unit one-third of the size needed for the whole Illinois H-Coal syncrude.

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TABLE XIV
 YIELDS FROM HYDROTREATING
 RERUN ILLINOIS H-COAL PRODUCT OVER ICR 106

Catalyst Temperature, °F	752	748		
LHSV	1.0	1.5		
Total Pressure, psig	2,501	2,492		
H ₂ Pressure, psia	2,155	2,311		
Total Gas In, SCF/Bbl	9,627	10,519		
Recycle Gas, SCF/Bbl	8,040	8,027		
No Loss Product Yields	Wt %	Vol %	Wt %	Vol %
C ₁	0.06		0.04	
C ₂	0.09		0.06	
C ₃	0.16		0.10	
iC ₄	0.02	0.03	0.01	0.01
nC ₄	0.07	0.10	0.04	0.06
C _F -180°F	3.84	4.61	3.59	4.28
180-250°F	15.93	17.96	15.19	17.04
250-300°F	13.05	14.52	-	-
300-350°F	13.34	14.27	-	-
350°F ⁺	53.91	54.60	-	-
250°F ⁺	80.30	83.39	81.53	84.43
Total C ₅ ⁺	100.08	105.98	100.32	105.76
Actual/No Loss Recovery	105.28	102.62	108.51	102.71
Gross H ₂ Cons., SCF/Bbl	2,013		2,068	
Chem. H ₂ Cons., SCF/Bbl	1,877		1,937	
Whole Product Properties	(403 Hours)			
Gravity, °API	42.5		41.8	
Aniline Point, °F	114.7		110.4	
Sulfur, ppm	1.1		1.3	
Nitrogen, ppm	0.56		1.0	
Gum, ppm	1.0			
Group Types, LV % by MS				
Paraffins	6.1		3.1	
Naphthenes	92.1		92.1	
Aromatics	1.8		4.8	
Run (Hours)	76-173 (403-426)		76-173 (463-475)	

TABLE XV
 PROPERTIES OF JET AND DIESEL FUELS
 MADE FROM REFURN ILLINOIS H-COAL SYNCRUDE

LHSV	1.0			1.5
Catalyst Temperature, °F	750			750
Total Pressure, psig	2501			2492
H ₂ Pressure, psia	2155			2311
Boiling Range, °F	250+	300+	350+	250+
Gravity, °API	38.3	35.9	34.1	37.8
Aniline Point, °F	126.0	127.4	129.5	21
Smoke Point, mm	22	22		21
Freeze Point, °F	-58			-51
Cloud Point, °F		<-80		
Viscosity, cSt				
At -4°F	4.595	5.963	7.709	4.707
At 100°F	1.454	1.690	1.943	1.523
Group Types, LV % by MS				
Paraffins	2.6	3.1	3.8	2.9
Naphthenes	94.8	93.6	92.4	91.4
Aromatics	2.6	3.3	3.8	5.7
Distillation, LV %, °F	D 86	D 86	D 86	TBP*
St/5	290/310	343/356	310/350	211/257
10/30	320/346	362/386	362/388	273/338
50	381	400	405	382
70/90	418/474	432/483	460/505	428/496
95/EP	495/536	501/538	526/576	519/575
Run (Hours)	76-173 (403-427)		76-173 (463-475)	

*Simulated by chromatography

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Abstract

The net liquid product from the H-Coal liquefaction was refined to liquid fuels by commercial catalysts in pilot plants which are used to support the design of Chevron's commercial hydroprocessing plants. Both the commercial and pilot plants use Chevron's advanced state-of-the-art technology. Liquids derived from two different coals were studied: Illinois No. 6 coal (Burning Star Mine) and Wyodak coal. One hydrotreating stage, operated at several severities, upgraded the whole product to either jet, diesel, or heating fuels. In addition, a naphtha was produced, which can be used for hydrogen production or as feed to a catalytic reformer. The kerosene jet fuel meets all critical specifications, including smoke point and stability. The maximum yield of jet derived from the Illinois syncrude is almost 90%. The diesel and heating fuels meet most specifications. The Wyodak H-Coal syncrude proved to be considerably easier to upgrade than the Illinois H-Coal syncrude.

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Hydrotreatment and Biological Test of SRC-II Coal Liquid

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Distillate coal liquid from the SRC-II process has been hydrotreated at several levels of severity in a bench-scale continuous flow unit at the Bartlesville Energy Technology Center. The purpose was two fold with the immediate goal to survey process conditions with a commercially available catalyst to provide samples upgraded to varied degrees for detailed characterization analyses and investigation for biological activity. Long-range goals are to contribute to a data base to evaluate raw material sources, liquefaction or other production processes, characterization of feedstocks for further refining to transportation and other end-use fuels, selection of refining processes, and estimation of type and quality of end products expected from combinations of these steps.

The liquid feed and products have been screened for biological activity by the Ames test at Lovelace Biomedical and Environmental Research Institute, Albuquerque, New Mexico.

Experimental Materials and Procedures

The SRC-II liquid was obtained from the Pittsburg and Midway Coal Mining Co. The liquid was produced from Material Balance Run No. 77 SR-12 on coal from the Pittsburg seam from Consol's Blacksville No. 2 Mine in West Virginia. The middle (177-288° C) and heavy (288-454°C) distillates were blended to the same ratio as produced by the material balance run, e.g., 75.5 percent middle distillate and 24.5 percent heavy distillate. The feed contained 0.23 wt-pct sulfur, 1.06 wt-pct nitrogen and 3.29 wt-pct oxygen and boiled between 185 and 380° C (5-95 percent) by simulated distillation.

The bench-scale hydrogenation unit was designed for operation at up to 3,000 psig and 450° C, with once-through flow of hydrogen, down-flow of gas and liquid over a fixed-bed catalyst. Reactor temperature, pressure, and hydrogen flow and liquid level in the high-pressure product separator were controlled automatically. Liquid product was withdrawn periodically from a low-pressure

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TABLE I. Process Conditions and Results

Sample Period	Sp. gr., 60°/60°	Liquid Product			Approx. H ₂ Cons., SCF/bbl	Catalyst tempera- ture, °C	Liquid feed rate, LHSV
		Hydrogen, wt-pct	Nitrogen, wt-pct	Sulfur wt-pct			
(Feed)	1.003	8.42	1.057	.25	3.29	-	-
1	0.921	10.81	0.352	.01	.59	1,930	0.50
2	.948	10.06	.631	.02	1.65	1,270	1.0
3	.902	11.54	.033	.01	.17	2,670	0.50
4	.953	9.80	.700	.02	1.58	970	0.50
5	.887	12.24	.001	.01	.09	2,880	0.50
6	.877	12.39	.001	.01	.03	3,250	0.50
7	.868	12.82	.001	.01	.06	5,010	0.35
8	.962	9.68	.742	.01	2.00	980	1.0

separator, and the combined high- and low-pressure effluent gas was sampled for analysis.

The catalyst was 100 ml of American Cyanamid HDS-3A, a 1/16-inch diameter extrudate of nickel-molybdenum-alumina. It was diluted with inert, granular alpha-alumina to provide a bed depth of 18 inches in the middle section of a 0.96-inch ID vertical reactor with a 5/16-inch OD internal thermocouple well. The catalyst was progressively more dilute toward the top of the bed to minimize exothermic temperature effects, and end sections were packed with alpha-alumina to provide for preheat and cooling zones.

The catalyst was presulfided and operated for about 100 hours on a petroleum gas oil (200-500° C boiling range, 0.8 wt-pct sulfur) to check controls and provide some catalyst aging before exposure to the coal liquid.

Operating conditions selected as likely to maintain catalyst activity and provide the range of upgrading desired were 2,000 psig pressure, 325 to 400° C, and 0.5 to 1.0 LHSV (volume liquid feed/volume bulk catalyst/hour). Hydrogen flow was held constant at a rate corresponding to 10,000 SCF/bbl to 0.5 LHSV or 5,000 SCF/bbl at 1.0 LHSV. Variation in hydrogen flow rate in on- through operation has little effect at more than 5,000 SCF/bbl. Operation at each condition was for approximately 24 hours to allow 8-12 hours for equilibration plus time to accumulate about 750 ml of liquid product. Table I shows the sequence of reactor conditions and essential process results.

Period 4 was a test of a very mild condition after a weekend shutdown. Period 7 was a test of the liquid feed pump at a low rate. Period 8 was a brief test for decline in activity from period 2, although the entire operation was too short for significant life testing. Periods in the order of 2,1,3,5, and 6 were intended to cover the desired range of increasing upgrading.

The liquid feed and products were screened for chemical mutagens by use of the Ames assay (1, 4).

Results and Discussion

The results in Table I show the expected trends as hydro- treating severity was increased with reaction temperatures in the range of 310 to 400° C. Specific gravity of the product liquid at 375° C decreased from 1.00 for the feed to 0.89 while nitrogen decreased from 1.06 wt-pct to less than .001 wt-pct and oxygen decreased from 3.29 wt-pct to 0.09 wt-pct. Hydrogen content increased from 8.42 wt-pct in the liquid feed to 12.24 wt-pct over this same range of nitrogen removal. Calculated hydrogen consumptions for this range of conditions varied from 970 to 2,880 SCF/bbl which is within the ranges reported by others (2, 3). Precise hydrogen content of the liquid product, used in calculation of hydrogen consumption, was determined by NMR through the courtesy of Phillips Petroleum Company. Analysis of the effluent gas did not include hydrocarbons heavier than ethane.

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TABLE II. Simulated Distillation of Liquid Feed and Products

Sample Period	Temp., °C.	at wt-percent distilled		wt-pct converted to below 185° C
		50	95	
(Feed)	185	255	379	-
1	112	239	361	15
2	131	247	369	9
3	101	235	344	18
4	133	248	375	8
5	96	229	331	21
6	98	225	329	22
7	94	221	326	21
8	156	252	379	7

Contributions of the heavier hydrocarbons to hydrogen consumption are small for hydrotreating at conditions which cause very little cracking of hydrocarbons since most of the consumed hydrogen goes into the liquid product.

The distillation range of the liquid products was shifted downward as hydrotreating severity was increased (Table II). The magnitude of the shift of the simulated distillation is shown in the last column which indicates 8 to 22 percent of the feed is converted to material boiling below the five percent point of the feed.

The increase in product material boiling below 185° C results largely from saturation of aromatic rings and olefins and from removal of heteroatoms. Some hydrocarbons boiling lower than the feed would be formed by cleaving of heteroatom linkages, with very little cracking of hydrocarbons expected. For example, all product liquids had initial boiling points close to that of benzene/cyclohexane.

The results of the Salmonella/Typhimurium Mutagenicity (Ames) assay for the feed and liquid products are given in Table III. The assay was run essentially as described by Ames (1). The assay employs specially constructed strains of Salmonella Typhimurium which are reverted by a wide variety of mutagens from requiring histidine in their growth media back to bacteria capable of synthesizing histidine.

Some chemicals require metabolic activation (addition of microsomal enzymes) prior to showing mutagenic activity; thus, data are given as number of revertants without/with metabolic activation. The Ames test has thus far demonstrated a strong correlation between positive carcinogenesis in animal tests and mutagenicity in the Ames test (1, 4). However, positive results from the Ames test do not conclusively show human risk.

The untreated SRC-II was tested at five concentrations with Salmonella strains TA 98 and TA 100, generally considered the most sensitive strains. In the results indicated in Table III, an increase in the number of revertants greater than two times the background (no SRC-II feed or product) is sometimes considered to indicate a definite positive (mutagenic) response. The plates which showed a positive response by this criteria are underlined.

Activity decreased with decreasing concentration for the untreated feed but was still nearly double the activity of the background at a concentration of 5 ug per plate. A product dose of one hundred micrograms was selected as a satisfactory screening test since a strong response was observed for the untreated SRC-II at this concentration and since no appreciable cytotoxicity was noted. The hydrogenation periods are listed in order of increasing severity of processing. Activity was decreased essentially to the background level when nitrogen content was decreased to 0.35 wt-pct, oxygen content was decreased to 0.59 wt-pct and hydrogen content was increased from 8.4 to 10.8 wt-pct. This occurred at

TABLE III. Results of the Ames Assay

Sample	Concentration, ug/plate	Number of Revertants	
		Without/With Metabolic Activation	TA 100
Feed	250	30/1822	144/322
Feed	100	34/1122	163/348
Feed	50	27/547	150/306
Feed	25	21/316	150/204
Feed	5	31/113	134/178
Background	0	21/60	144/142
8	100	151/131	134/257
4	100	19/111	176/232
2	100	23/178	151/226
1	100	16/64	158/218
3	100	10/40	161/194
5	100	22/64	162/194
6	100	19/70	128/186
7	100	17/65	153/218
Background	0	25/66	169/220

process conditions of 325^o C and 0.5 LHSV feed rate, which had been planned as the lowest reaction temperature expected to give substantial upgrading.

A preliminary screening of crude petroleums from the Wilmington and Prudhoe Bay fields and shale oils from Utah have been performed. This screening indicates that the coal liquids were more mutagenically active than the shale oils and petroleum crudes. The shale oil and petroleum crudes tested were not significantly different from the background which agreed with the work of Calkins, et. al. (5). However, there is the possibility that fractions obtained from these materials may exhibit significant mutagenic activity.

A more complete investigation will require testing of fractions to identify more active components. Since nitrogen and oxygen compounds and aromatic ring structures are important in this respect, it is suspected that mutagenically active components are likely to be in higher-boiling fractions. This aspect will be studied when screening the fractions for active components. Tests on mammalian systems are also needed before making assessments concerning potential human risk.

Summary

Distillate coal liquid from the SRC-II process was hydro-treated in a bench-scale process unit to provide a range of mildly upgraded products for compositional characterization and screening for mutagenicity. Hydrogen content of the liquid was increased from 8.4 to 12.24 wt-pct over the range of process conditions which removed essentially 100 percent of the nitrogen and 95 percent of the oxygen. Results of the Ames assay indicated mutagenic activity of the liquid product decreased by an order of magnitude for 35 percent removal of nitrogen and 52 percent removal of oxygen. Liquid product with 67 percent nitrogen removal and 82 percent oxygen removal showed no mutagenic activity distinguishable from that of the background samples. The full range of effect in decreasing mutagenic activity by the Ames assay was covered by relatively mild hydrotreatment, but assessment of potential human risk must be confirmed using additional mammalian tests.

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LC-Fining of Solvent-Refined Coal

SRC-I and Short-Contact-Time Coal Extracts

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Cities Service's involvement in coal liquefaction technology developed from the proprietary catalytic hydrogenation process which is called LC-Fining (Lummus-Cities Fining). Research on catalytic hydrogenation began at Cities Service more than 20 years ago. The process was originally developed for upgrading bitumen from tar sands. The first commercial applications of the process were not in synthetic fuels, but rather in upgrading petroleum residua.

The process was first demonstrated at Cities Service's Lake Charles refinery with the construction of a 2500 BPD unit. The unit was later expanded to 6000 BPD with no increase in the size of the catalytic reactors. Maximum sulfur removal from delayed coker feedstock was achieved by this expansion.

Petroleos Mexicanos (PEMEX) licensed the process and built an LC-Fining unit at their Salamanca, Mexico refinery. This unit was designed to process 18,500 BPD of petroleum residua. The LC-Finer was started-up in September of 1973 and a successful performance test was completed in November of 1974. The PEMEX unit has been used to process very high metal content feedstocks (more than 300 ppm V and Ni) which are not feasible in competing technology such as fixed bed catalytic reactors.

From May, 1976 through September, 1979, the Department of Energy (DOE) sponsored a process development unit (PDU) program to determine the feasibility and the optimum operating conditions for upgrading coal extracts to higher quality liquid products using Cities' LC-Fining process (1 - 4). C-E Lummus, Cities' exclusive licensing agent for LC-Fining, performed the pilot plant studies in their facilities in New Jersey under a subcontract agreement.

The PDU results from the LC-Fining program on coal extracts were encouraging. DOE extended the original contract twice in order to accommodate an expanded scope of work. Several different types of bituminous and sub-bituminous coal extracts were successfully processed in the PDU. Various extract to solvent feed ratios were used over a wide range of process conditions in runs

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up to 41 days in length. A foreign solvent is usually added to the coal extract before being processed in the reactor. In one PDU run, unconverted SRC-I and process derived solvent were recycled through the LC-Finer in order to maximize SRC-I conversion (greater than 85%). In another run, a short contact time (SCT) coal extract obtained from Wilsonville containing ~7 weight % ash and native process solvent was run for 25 days.

SRC-I is a clean burning, solid coal extract which is low in ash, low in sulfur, but moderately high in nitrogen. The original goal of the LC-Fining work was to produce a distillate product from SRC-I with a greatly reduced nitrogen content. The 2.1 wt.% nitrogen content of SRC-I was reduced to less than 0.3 wt.% in the 390-850°F distillate products. Recently, the emphasis on nitrogen removal was relaxed and a greater emphasis was placed on maximum production of distillate products.

The PDU work on the original and extended DOE contracts for upgrading coal extracts was completed at a cost of \$2.8MM. The LC-Fining PDU program is now being continued under a new two year contract (\$7.3MM), again sponsored by DOE, but with C-E Lummus as the prime contractor. The ultimate objective of this work is to optimize the Two-Stage Liquefaction (TSL) concept for coal conversion (Figure 1). The catalytic expanded bed hydroprocessing portion of the contract (\$2.3MM) is being managed by Cities Service. This program will study a wider range of process conditions and help to identify catalyst and process improvements.

As a part of the new contract, C-E Lummus will operate a fully integrated TSL pilot plant to demonstrate the conversion of coal to distillate products using an internally generated solvent. The TSL pilot plant consists of coal liquefaction, C-E Lummus anti-solvent deashing, and LC-Fining pilot units. Process solvent and unconverted coal extract may be recycled between units to produce a maximum quantity of quality liquids with a low hydrogen consumption. The information learned from the hydroprocessing and TSL programs should be beneficial to the design and operation of the proposed 6,000 ton per day SRC-I demonstration plant to be located at Newman, Kentucky.

Objectives

One of the objectives of this work was to determine the effect of higher reactor pressure and space velocity on conversion and product quality. Heretofore, only temperature had been used to adjust or maintain conversion and product quality. Two different coal extract types were used in this study - namely, whole filter feeds obtained from Wilsonville short contact time coal extract (SCT) operations (Wilsonville run numbers 145 and 146 with 287 and 580 pounds of Indiana V coal feed per hour, respectively), and a conventional solvent refined coal (SRC-I)/Koppers heavy residue creosote oil (KC-Oil) feed blend. The SRC-I was obtained from the Fort Lewis, Washington SRC-I facility.

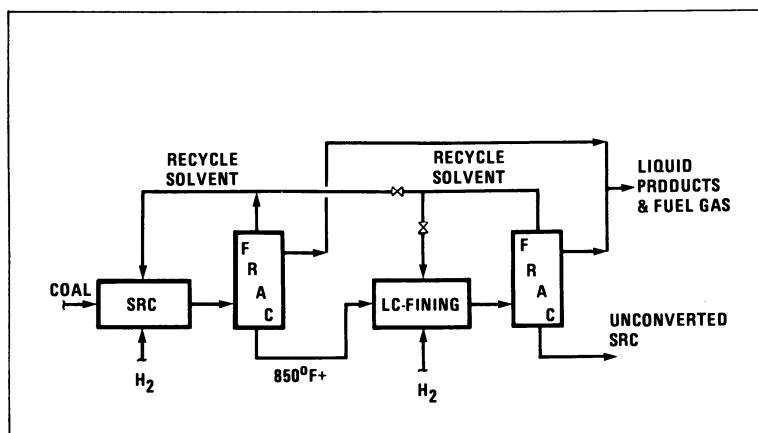


Figure 1. Simplified block flow diagram: 2-step liquefaction

Another objective was to determine whether product differences were obtained with the two feedstocks and also to correlate the higher pressure/space velocity results with previous data.

Data are also presented in this paper which describe the results of a solvent boiling range study when processing SRC-I. A run was also made to establish a thermal baseline wherein the SRC-I was processed over an inert 1/32 inch Shell catalyst support.

Experimental Section

The operation of an LC-Finer is best described by means of a process flow schematic (Figure 2). The LC-Finer reactor maintains the catalyst (typically American Cyanamid 1442B cobalt molybdenum 1/32 inch extrudate or Shell 324 nickel molybdenum 1/32 inch extrudate) in constant motion, suspended by the recirculation of copious volumes of liquid. This recirculation results in a 35-50% bed expansion and the reactor operates at a uniform temperature with essentially no pressure drop. In a commercial unit there is a recycle of hydrogen rich gas along with a distillate liquid stream which is combined with the fresh SRC. The PDU differs from the commercial unit design in that there is no recycle gas or liquid streams. The bed expansion is maintained with an external recirculation loop. It should be noted that the PDU fractionator separates the liquid product into a light oil (L.O.) and a heavy oil (H.O.). The combination of these two oil streams is designated as total liquid product (TLP).

Results and Discussion

Several technical papers have previously been presented or published which describe in detail the results of the initial studies involved in expanded bed hydroprocessing of coal extracts (5 - 9). Four DOE Interim Technical Progress Reports have also been published and are available for distribution (1 - 4). The authors wish to refer to the above publications for an extensive description of the work areas involved and the conclusions derived from the prior PDU results.

PDU Operation - Current Study. This paper will present the results of several alternate processing modes utilizing the expanded catalyst bed (LC-Finer) for hydroprocessing coal extracts. Neither distillate yield nor C₁-C₄ gas yield data from either the SRC unit or the SCT thermal step of the TSL process have been included in this analysis. The specific PDU runs are as follows:

PDU Run 2LCF-10 (31 days operation with catalyst activity

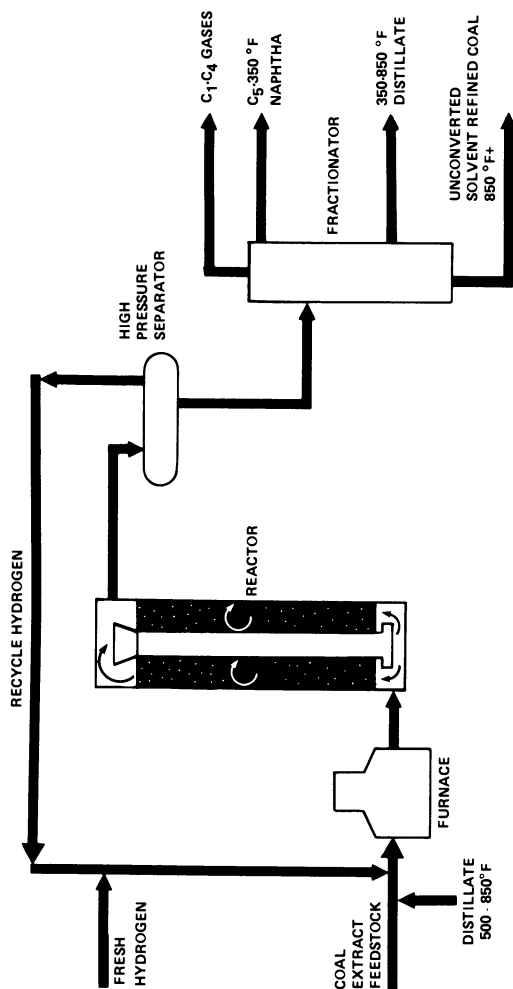


Figure 2. *LC-fining process*

- check points)
 50/50 Volume % SRC-I/KC-Oil
 Cool Zone Operation
- PDU Run 2LCF-12 (19 days operation)
 50/50 Volume % SRC-I/KC-Oil
 Feed Blend contained 1 Wt% Ash
- PDU Run 2LCF-13 (8 days operation)
 Non-deashed SCT (Wilsonville Run 146)
- PDU Run 2LCF-14 (11 days operation)
 Deashed SCT (Wilsonville Run 146)
- PDU Run 2LCF-16 (25 days operation with catalyst activity check points)
 Non-deashed SCT (Wilsonville Run 145)
 Higher pressure and space velocity
- PDU Run 2LCF-17 (32 days operation with catalyst activity check points)
 70/30 Volume % SRC-I/KC-Oil
 Higher pressure and space velocity
- PDU Run 2LCF-20 (24 days operation with catalyst activity check points)
 50/50 volume % SRC-I/KC-Oil
 Various IBP-850°F Solvents
- PDU Run 2LCF-21 (10 days operation)
 70/30 volume % SRC-I/KC-Oil
 Thermal baseline using inert catalyst

Since total reactor pressure and space velocity are proprietary operating parameters within the DOE contract, relative total reactor pressures (P_{rel}) between 1.0 and 1.35 together with relative volumetric space velocities (SV_{rel}) between 1.0 and 3.0 will be used. All runs prior to PDU Run 2LCF-16 were made at a nominal total reactor pressure of $P_{rel} = 1.0$ and a nominal volumetric space velocity of $SV_{rel} = 1.0$.

A short contact time (SCT) coal extract, as prepared at Wilsonville, is obtained by feeding the coal slurry through only the slurry preheater and transfer lines. The conventional solvent refined coal has a residence time in the slurry preheater, transfer lines, and dissolver. The SCT coal extract is, consequently, reacted at higher temperatures to produce similar yields of SRC-type product at very high flow rates. The SCT coal extract used for the studies reported herein was received as non-deashed material which would have been used as a feedstock for the U.S. Filter or Kerr-McGee Critical Solvent Deashing at Wilsonville.

The SCT coal extract was topped before use to correspond to the 500°F-680°F nominal IBP KC-Oils employed previously as a solvent for SRC-I operation. The topped SCT simulated the recycle of a 500-850°F or 600-850°F solvent fraction. Wilsonville Run 146 was topped to a nominal 500°F IBP, and Wilsonville Run 145 was topped to a nominal 600°F IBP. The deashed SCT coal extract used for PDU Run 2LCF-14 was deashed in the Lummus Engineering Development Center at Bloomfield, New Jersey using the Lummus Antisolvent Deashing Process.

Table 1 presents the feed blend properties for selected periods of PDU Runs 2LCF-10, -12, -13, -14, -16, and -17. Table 2 presents the feed blend properties for PDU Runs 2LCF-20 and -21.

Catalyst Activity. As discussed previously, the major objective of this work was to determine the effect of varying the operating parameters of volumetric space velocity and total reactor pressure. Since catalyst activity effects the relative comparisons of the data, it must first be established whether catalyst deactivation is also a correlating factor and to what extent.

Some catalyst activity loss was noted for the two life runs previously reported (2, 3) - PDU Run LCF-36 (once-through operation) and PDU Run 2LCF-3 (once-through/recycle/once-through operation). The loss in catalytic activity was determined by operating the PDU under identical conditions at the beginning and end of a specific run (i.e., catalyst activity check points). A similar operating technique was used for PDU Runs 2LCF-10, -16, and -17 which are included in this report. The catalyst activity relationship at the beginning and end of a run was applied as a proration to the intermediate data to remove the catalyst deactivation factor. Thus the intermediate data would then reflect the data only as a function of temperature or other operating variable changes.

However, several assumptions are inherent in this interpretation of the data. First, it is assumed that the change in the observed effect (such as conversion of 850°F+, percentage denitrogenation, etc.) is linear with respect to time. Thus a linear delta-effect per period of time could be established and intermediate data could be adjusted to a "fresh" activity corresponding to that observed at the reference period and at any desired temperature. Second, it is assumed that the intermediate process parameter variations had no adverse effect on the catalyst deactivation function. For example, operation at constant temperature for a given interval of time would produce the same catalyst deactivation as varying temperatures (within limits) over the same interval of time.

With the advent of PDU Runs 2LCF-16 and -17, total reactor pressure and volumetric space velocity were introduced as process

TABLE 1

Run No./Periods (2LCF-) Type of Coal Extract	Feed Blend Properties SRC-I and SCT Coal Extracts				
	10/1-9	12/All	17/1-9	13/All	14/3-9B SCT
Composition					
Solvent (500°F+), Wt%	45.9	43.7	21.8	-	-
Coal Extract, Wt%	54.1	56.3(a)	78.2	-	-
850°F+, Wt% (by distill'n)	53.5	56.4	72.5	-	-
Gravity of Blend, °API	-12.7	-13.4	-13.0	-13.4	-11.3
Elemental Content, Wt.% of Blend					
Carbon	89.17	89.15	87.79	81.36	86.11
Hydrogen	6.37	6.37	6.07	6.87	7.12
Nitrogen	1.13	1.30	1.39	1.28	1.44
Sulfur	0.44	0.49	0.58	1.56	0.95
Ash, Wt.% of Blend	0.10	0.98	0.22	6.05(b)	0.14(c)
Distillate Fractions, Wt% (ash-free)					
IBP-500°F	4.0	4.3	2.7	0.9	-
500-650°F	18.0	19.6	12.2	21.7	11.0
650-850°F	24.4	18.9	13.7	28.9	28.9
850°F+	53.5	56.2	71.2	43.5	60.0

(a) SRC-I (N-024) and high ash SRC (N-084) were 53.4 wt% and 2.9 wt%, respectively.
 (b) SCT from Wilsonville Run 146 (580 lb of coal/hour). Topped by Lummus.
 (c) SCT from Wilsonville Run 146 (580 lb of coal/hour). Topped and deashed by Lummus.
 (d) SCT from Wilsonville Run 145 (287 lb of coal/hour). Topped by Lummus.

TABLE 2
 Feed Blend Properties
 Solvent Study and Thermal Baseline Study

Run No./Periods (2LCF-) Type of Coal Extract	Solvent Study				Thermal	
	20/7-8	20/13-16	20/9-12	20/17-20	21/1-4	21/5-9
Composition	SRC-I					
Solvent (500°F+), Wt%	48.3	49.9	50.4	55.6	25.3	25.3
Description, IBP °F	500	580	660	740	500	500
Coal Extract, Wt%	51.7	50.1	49.6	44.4	74.7	74.7
850°F+, Wt% (by distill'n)	54.7	49.8	51.9	52.7	70.0	70.1
Gravity of Blend, °API	-11.6	-10.8	-14.3	-13.3	-14.6	-15.2
Elemental Content, Wt.% of Blend						
Carbon	89.46	89.94	89.69	90.41	88.43	88.18
Hydrogen	6.76	6.73	6.57	6.34	6.42	6.40
Oxygen	-	2.38	2.33	2.21	3.54	3.50
Nitrogen	1.24	1.18	1.20	1.22	1.56	1.52
Sulfur	0.37	0.35	0.33	0.28	0.50	0.49
Ash, Wt% of Blend	0.09	0.08	0.08	0.10	0.12	0.13
Distillate Fractions, Wt% (ash-free)						
500-650°F	11.0(a)	17.1(a)	-	-	6.9(a)	7.7(a)
650-850°F	34.3	33.0	48.1(b)	47.2(b)	23.1	22.1
850°F+	54.7	49.9	51.9	52.8	70.0	70.2
(a) IBP-650°F						
(b) IBP-850°F						

parameters. Two separate data interpretations were considered with respect to catalyst activity for PDU Runs 2LCF-16 and -17.

Figures 3 and 4 show the weight percent 850°F+ conversion as a function of the relative space velocity for PDU Run 2LCF-16 (SCT feedstock) and PDU Run 2LCF-17 (SRC-I feedstock), respectively. The 780°F check points used to measure catalyst activity are defined by the symbols C_B and C_E , where the subscripts B and E refer to the beginning and end of the run. It was concluded that higher pressure was significantly contributing to a reduction in catalyst deactivation and both PDU Runs 2LCF-16 and 2LCF-17 were assumed to have a negligible catalyst deactivation.

In the second interpretation, the proprietary LC-Fining correlations were used to correct for the effects of space velocity on 850°F+ conversion. Factors are available which delineate the change in 850°F+ conversion resulting from a change in space velocity. Thus, for PDU Run 2LCF-16, the 850°F+ conversion data for points C_B and C_E were adjusted by a space velocity factor to correspond to $SV_{rel} = 1.0$. This adjustment resulted in an indicated change in the weight percent 850°F+ conversion from 81.6 to 79.2 at C_B and 64.3 to 73.9 at C_E . By analogy, PDU Run LCF-36 showed a decline in weight percent conversion from 55.0 at C_B to 46.7 at C_E and PDU Run 2LCF-10 showed a decline in weight percent 850°F+ conversion from 47.4 at C_B to 38.1 at C_E . PDU Run LCF-36 was a 33-day once-through life run and PDU Run 2LCF-10 was a 31-day once-through life run (cool zone operation). Both of these runs also included 780°F catalyst activity check points. In summary:

PDU Run	<u>Δ-Conversion</u> Weight % 850°F+
2LCF-10 (SRC-I)	-9.3
LCF-36 (SRC-I)	-8.3
2LCF-16 (SCT), higher pressure	-5.3
2LCF-17 (SRC-I), higher pressure	Nil

The PDU runs at the higher pressure (2LCF-16 and -17) show a reduced catalyst deactivation.

The space velocity adjustment for the liquid product fractions lighter than 850°F becomes more complex and increases the uncertainty associated with adjusting data to a common basis. The PDU data prior to PDU Run 2LCF-16 was obtained through operations at a nearly constant $SV_{rel} = 1.0$ and the more simplified linear approach to data adjustment will suffice. Therefore, it was assumed that the Δ-conversion noted above was not sufficiently large to negate the interpretation of essentially no activity decline for higher pressure operation (PDU Runs 2LCF-16 and -17). Two other SCT runs (PDU Runs 2LCF-13 and -14) were evaluated with no activity decline measured due to their shorter run length.

Space Velocity and Total Reactor Pressure. In order to

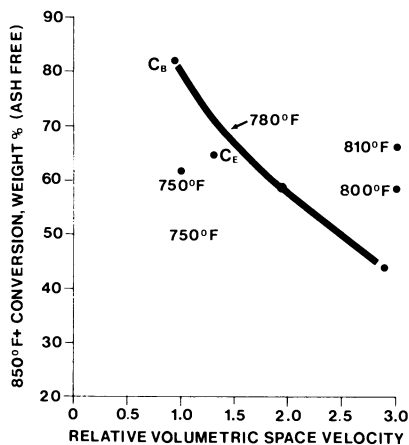


Figure 3. Non-deashed short-contact-time coal extract; 850°F+ conversion vs. relative space velocity, PDU Run 2LCF-16: (○) $P_{rel} = 1.0$, (●) $P_{REL} = 1.35$, data points with no temperature notation were obtained at 780°F

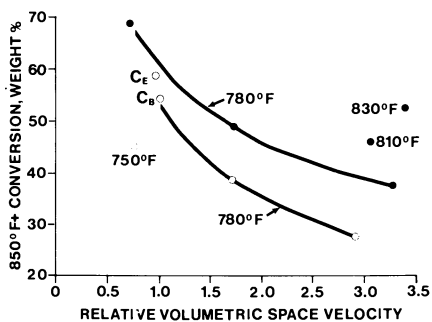


Figure 4. SRC-I extract; 850°F+ conversion vs. relative space velocity, PDU Run 2LCF-17: (○) $P_{rel} = 1.0$, (●) $P_{rel} = 1.35$, data points with no temperature notation were obtained at 780°F

minimize process parameter perturbations, PDU runs prior to PDU 2LCF-16 were conducted at a nominally constant relative volumetric space velocity ($SV_{rel}=1.0$) and a constant relative total reactor pressure ($P_{rel}=1.0$). The main objective of PDU Run 2LCF-16 and -17 was to determine the effect of higher space velocity and higher total reactor pressure on SCT and SRC-I coal extracts, respectively.

Referring to Figures 3 and 4, it will be noted that several different sets of operating conditions were employed for a given 850°F+ conversion. For example, the data for PDU Run 2LCF-17 (Figure 4) show that 45.0 weight percent 850°F+ conversion may be attained at the following combinations of process parameters:

SV_{rel}	P_{rel}	T °F
2.1	1.35	780
1.34	1.0	780
0.75	1.0	750

Conversely, the data for PDU Run 2LCF-16 (Figure 3) show that at $SV_{rel}=3.0$, the 850°F+ conversion will be 43.0 at 780°F, 58.6 at 800°F, and 66.3 at 810°F, all at $P_{rel}=1.35$. It became apparent that the weight percent 850°F+ conversion could be used as a correlating factor for the lighter liquid and gas product fractional distributions. Inherent in this corollary is the fact that for a given weight percent 850°F+ conversion, the light product fractional distribution is relatively constant.

Product Distribution (Comparison - SRC-I and SCT Coal Extracts). Sufficient data has been accumulated and analyzed by linear regression concerning the product distribution for LC-Fining of SRC-I and SCT coal extracts to allow a comparison to be made between the two types of coal extract. Figures 5 through 8 present the comparisons of product distribution for PDU Runs 2LCF-10, -12 and -17 on SRC-I coal extract and PDU Runs 2LCF-13, -14, and -16 on SCT coal extract. The specific data points which determine the slope of these curves are shown in detail on figures to be found in a DOE Interim Technical Progress Report (4). All of the process results described for PDU Runs 2LCF-12, -13, and -16 have been calculated on a deashed basis.

Figures 5, 6, and 7 show that the non-deashed SCT coal extract (PDU Runs 2LCF-13 and -16), when compared to deashed SCT coal extract (PDU Run 2LCF-14), shows the greatest 500°F+ and 650°F+ conversion together with the highest C_5 -500°F weight percent yield for a given 850°F+ conversion in the LC-Finer. The SRC-I run made with one weight percent ash (PDU Run 2LCF-12) was uniformly low in 500°F+ and 650°F+ conversion and also C_5 -500°F weight percent yield.

Since relatively less conversion to distillates occurs in the first stage SCT thermal step of the TSL process, it is not surprising that the SCT distillate produced in the LC-Finer is

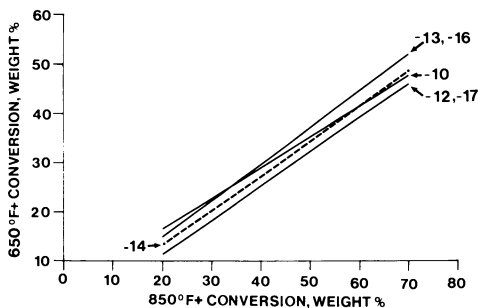


Figure 5. Comparison of SRC-I and SCT coal extracts; 650° F+ conversion vs. 850° F+ conversion: (—) PDU 2LCF-13, -16 (non-deashed SCT), (---) PDU 2LCF-14 (deashed SCT), (—) PDU 2LCF-10, -12, -17 (SRC-I)

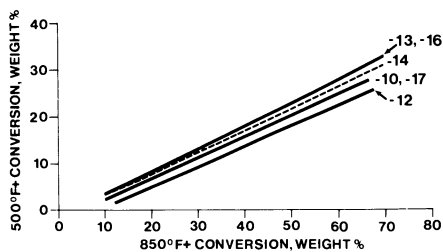


Figure 6. Comparison of SRC-I and SCT coal extracts; 500° F+ conversion vs. 850° F+ conversion: (—) PDU 2LCF-13, -16 (non-deashed SCT), (---) PDU 2LCF-14 (deashed SCT), (—) PDU 2LCF-10, -12, -17 (SRC-I)

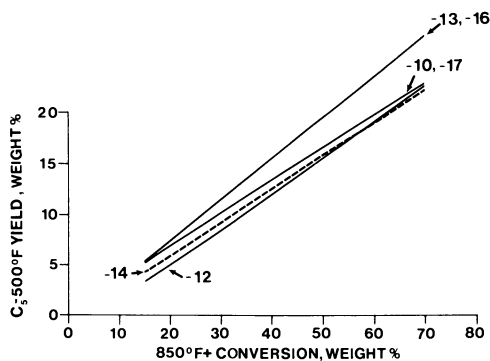


Figure 7. Comparison of SRC-I and SCT coal extracts; C₅-500° F yield vs. 850° F conversion: (—) PDU 2LCF-13, -16 (non-deashed SCT), (---) PDU 2LCF-14 (deashed SCT), (—) PDU 2LCF-10, -12, -17 (SRC-I)

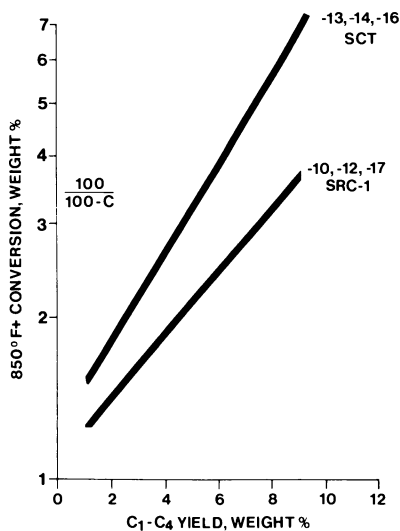


Figure 8. Comparison of SRC-I and SCT extracts; C₁-C₄ yield vs. 850° F conversion

greater than that obtained from conventional SRC. However, these results do not imply that the total distillate yield for the overall TSL process has been optimized.

A comparison of the C_1 - C_4 weight percent yield from the LC-Finer (Figure 8) shows that the SCT runs (PDU 2LCF-13, -14, and -16) produce less C_1 - C_4 gas yield than the SRC-I runs (PDU 2LCF-10, -12, and -17) at a given 850°F+ conversion.

Denitrogenation (Comparison - SRC-I and SCT Coal Extracts).

Figure 9 shows a comparison between the SRC-I and SCT runs in the LC-Finer with respect to percentage denitrogenation for the total liquid product. This plot also indicates the relative rate of loss in denitrogenation activity when the normalized specific run data is plotted against time as equivalent periods of operation at $SV_{rel}=1.0$. It will be recalled that PDU Runs 2LCF-16 and -17 were made to evaluate the effect of increased space velocity.

In preparation for making a denitrogenation comparison, the nitrogen content of the total liquid product was normalized to 780°F, $SV_{rel}=1.0$, and $P_{rel}=1.0$ using proprietary LC-Fining correlations. The normalizing procedure also resulted in a change in the 850°F+ conversion which in turn resulted in a change in the amount of total liquid product produced. The normalized results incorporating the above noted procedure are plotted in Figure 9.

The LC-Finer runs made with SCT feedstock (PDU Runs 2LCF-13, -14, and -16) show a higher percentage feedstock denitrogenation than the runs made with SRC-I/KC-Oil solvent feed blends (PDU Run 2LCF-10, -12, and -17). It should be emphasized that the excellent percentage denitrogenation observed in the LC-Finer is representative of the total liquid product which contains an unconverted 850°F+ fraction.

These results are not meant to suggest that the percentage denitrogenation for the overall TSL process will necessarily be the same as obtained in the LC-Finer.

Solvent Boiling Range Study. Earlier studies (9) utilizing the LC-Fining process for upgrading coal extracts had shown a beneficial effect from using a heavier boiling range solvent (500-850°F versus 680-850°F). This preliminary work indicated an enhanced denitrogenation of the SRC-I with the 680-850°F solvent. A more definitive solvent boiling range study was made (PDU Run 2LCF-20) wherein four prehydrogenated KC-Oil solvents were compared at $P_{rel} = 1.2$: 500-850°F, 580-850°F, 660-850°F, and 740-850°F.

Figure 10 shows the conversion of 850°F+ material based on feed. The temperature and solvent conditions are indicated at their corresponding data points. The catalyst had maintained its conversion activity when Periods 8 and 24 were compared. These two points, near the beginning and at the end of the run, were processed with the same solvent at 780°F temperature. They showed the same conversion level, indicating no catalyst activity

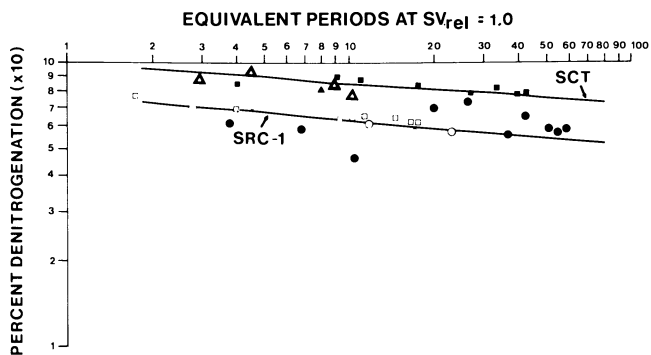


Figure 9. Percentage denitrogenation vs. equivalent time: SRC-1 (○) 2LCF-10, (●) 2LCF-17, (□) LCF-12; SCT (△) 2LCF-13, (▲) 2LCF-14, (■) 2LCF-16; data normalized to 780° F, $P_{rel} = 1.0$, $SV_{rel} = 1.0$

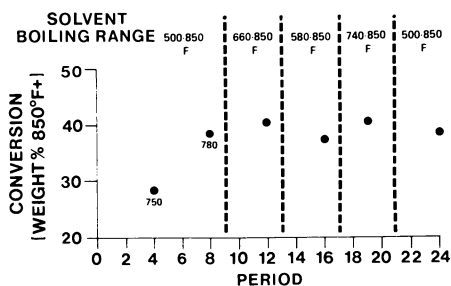


Figure 10. Conversion of 850° F+; PDU Run 2LCF-20; 50/50 vol % SRC/KC-oil solvent

loss. Although there were slight space velocity variations during the course of the run ($SV_{rel} \approx 2.0$), the variations would not significantly alter the conversions if normalized to a single value.

The 660-850°F and 740-850°F solvents gave a slightly higher 850°F+ conversion compared to the 500-850°F solvent. A slightly lower conversion was observed with the 580-850°F. The differences, however, are minor and fall within the experimental scatter of the data. Therefore, the four solvents were essentially equivalent at the given processing conditions.

The nitrogen data plotted as a percentage denitrogenation is shown in Figure 11 for PDU Run 2LCF-20. A straight line has been drawn through the Period 8 and Period 24 data points where the solvent and operating conditions were similar. From the line, a measure of the catalyst activity decline can be determined and linear adjustments applied to the data to compensate for the change in activity.

The percent denitrogenation data is shown in Figure 12 on a fresh catalyst basis corrected for catalyst deactivation. Here the effect of solvent type on nitrogen removal is easily observed. The denitrogenation improved with the higher initial boiling solvents. The 580-850°F solvent showed a 7% improvement, the 660-850°F solvent a 13% improvement, and the 740-850°F solvent a 28% improvement when compared to the 500-850°F solvent.

Although the 740-850°F solvent appears to give the best denitrogenation results, there is a process related problem when using this solvent. Due to the narrow cut range, it was calculated that a sufficient quantity of this material would not be produced in the LC-Fining reactor for use as a recycle solvent. The upgrading unit would not be in solvent balance. Therefore, one of the wider boiling range solvents would be more suitable for process purposes. The data base using the 500-850°F solvent was large and could be valuable for comparisons if the 500-850°F solvent was chosen for future studies. With these considerations in mind, the 500-850°F solvent was selected for use in the support program for Two-Stage Liquefaction.

Thermal Baseline Study. PDU Run 2LCF-21 (Thermal Baseline) processed a 70/30 volume percent SRC-I/500°F IBP KC-Oil feed blend over an inert 1/32 inch Shell catalyst support. The inert support was the extrudate base for the modified Shell 324 catalyst and had been calcined at 1100-1150°C. The purpose of this run was to determine the extent of conversion and denitrogenation in the absence of an active catalyst ingredient - nickel and molybdenum (Ni/Mo).

All the product fractions exhibit lower gravities and higher viscosities and higher heteroatom contents than comparative fractions processed over the more active Shell 324 Ni/Mo catalyst. Particularly outstanding are the higher oxygen levels in the C₅-390°F and 390-500°F fractions produced from converted mater-

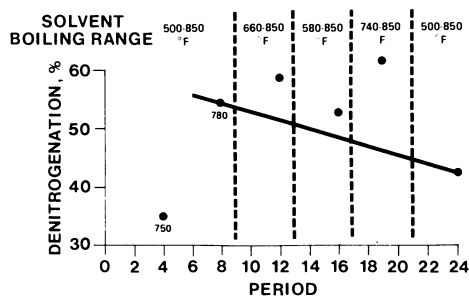


Figure 11. Percent denitrogenation; PDU Run 2LCF-20; 50/50 vol % SRC/KC-oil solvent

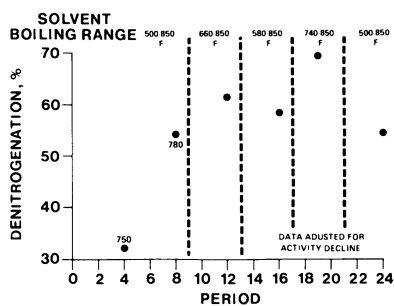


Figure 12. Percent denitrogenation; PDU Run 2LCF-20; 50/50 vol % SRC/KC-oil solvent

ial. The data from the run at 780°F showed oxygen levels of 8.1 wt.% and 4.9 wt.% for the naphtha and light distillate, respectively. These are in contrast to levels of approximately 1.6 wt.% and 0.6 wt.% in the corresponding fractions under similar run conditions with an active Ni/Mo catalyst.

The table below summarizes the 850°F+ conversion for PDU Run 2LCF-21.

PDU Run 2LCF-21/Period	4	6	11
Run Temperature, °F	750	780	810
SV _{rel}	1.6	1.7	1.9
Normalized Conversion, Vol.% (780°F, 1.9 SV _{rel})	11.2	13.4	12.9

The normalized conversions averaged 12.5 vol.%. Under similar conditions with a more active Shell 324 Ni/Mo catalyst, the 850°F+ conversion would be approximately 40 vol.%.

The denitrogenation in PDU Run 2LCF-21 was nearly zero. The amount of nitrogen in the liquid product was approximately equal to that present in the feed blend.

Conclusions

The following conclusions do not imply that the C₁-C₄ gas yield, C₅-500°F liquid yield, 500°F+ conversion, and 650°F+ conversion have been optimized for the TSL process which contains a first stage coal dissolution (SRC-I or SCT) followed by LC-Finer hydrotreating. The conclusions are directly applicable only to the LC-Finer.

1) Short contact time coal extracts show a greater percentage denitrogenation in the total liquid product than SRC-I coal extract when processed by LC-Fining. Also, short contact time coal extracts show a lower C₁-C₄ gas yield.

2) The 850°F+ conversion is a correlating parameter for comparing C₁-C₄ gas yield, C₅-500°F liquid yield, 500°F+ conversion, and 650°F+ conversion. Various combinations of the operating parameters of space velocity, total reactor pressure, and temperature achieve the same 850°F+ conversion. Thus, the product distribution can then be related to 850°F+ conversion with only minor variations between specific experimental runs. No difference in product distribution (at a given 850°F+ conversion) was noted for runs made with SRC-I/prehydrogenated KC-Oil at 70/30 and 50/50 nominal weight ratio feed blends.

3) Higher pressure operation in the LC-Finer tends toward a decrease in the catalyst deactivation rate for conversion. This is believed to be due to a lower coking rate at a higher hydrogen partial pressure.

4) Non-deashed short contact time coal extracts show a higher 500°F+ and 650°F+ conversion than SRC-I coal extracts at a given 850°F+ conversion in the LC-Finer. Deashed short contact

time coal extracts very closely resemble SRC-I coal extract in liquid product distribution.

5) The data obtained from higher pressure and higher space velocity operations in the LC-Finer correlate well with the previously reported data at $SV_{rel}=1.0$ and $P_{rel}=1.0$. The space velocity and pressure data presented in this report have expanded the operability of LC-Fining to produce a product with a given 850°F+ conversion and level of nitrogen removal. Judicious selection of space velocity, pressure, and temperature allow the upgrading of coal extracts by LC-Fining to be more closely integrated with the operation of the coal liquefaction portion of TSL.

6) No effect of solvent boiling range (500-850°F to 740-850°F) was noted for 850°F+ conversion at a 780°F operating temperature. The denitrogenation was improved with a heavier boiling solvent.

7) The thermal effect upon 850°F+ coal extract conversion is less than would have been expected from petroleum residuum considerations. A substantial portion of the 850°F+ conversion of coal extracts is catalytic in nature.

Abstract

The concept of Two-Stage Liquefaction (TSL) hinges on recognition of the fact that the deashed solid coal extract obtained from a first stage coal dissolution can be efficiently upgraded to liquid fuels by a second stage application of conventional hydrocracking or hydroprocessing technology extensively developed and demonstrated in the petroleum industry over the last 20 years (LC-Fining). That is, by judicious hydrocracking of the SRC product from the first stage, in the presence of a selective catalyst and under optimum conditions of temperature, space velocity, and reactor pressure, the production of middle distillate liquid fuels can be enhanced, the formation of light hydrocarbon gases can be minimized, and the overall use of hydrogen is reduced. In addition, the operation of a separate stage of LC-Fining provides wide operating latitude to tailor the overall product slate distribution (i.e., ratio of liquids to solids) and the product quality to both current and future market product.

This study describes the results of processing both conventional solvent refined coal extract (SRC-I) and short contact time coal extract. Both coal extracts have been run at several space velocities, temperatures, and total reactor pressures for comparative purposes. The effect of catalyst deactivation has also been considered. The short residence time coal extract was run in both a deashed and non-deashed mode of operation.

The versatility of the TSL process scheme has been enhanced by the relative ease of processing the two different coal extracts in the LC-Fining operation.

Acknowledgement

This work was supported by the U.S. Department of Energy under Contract No. DE-AC22-76ET10135 (Formerly EX-76-C-01-2038). We appreciate the technical advice from Dr. E. Moroni of DOE and Mr. R. H. Long of CE Lummus. The excellent technical assistance of Mr. K. Moy of C-E Lummus is also gratefully acknowledged.

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Catalyst Assessment for Upgrading Short-Contact-Time SRC to Low Sulfur Boiler Fuels

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Solvent refined coal (SRC) can be upgraded via catalytic hydroprocessing into low sulfur fuels (1,2). Reduced process cost can be affected by several factors, including the following: higher catalyst activity, improved utilization of hydrogen, and optimized SRC concentration in the feedstock. To this end, a series of commercial and proprietary catalysts was evaluated for the hydroprocessing of 50 wt % W. Kentucky short contact time SRC (SCT SRC). The commercial catalysts tested were alumina-based and were known to have good hydro-treating activity for heavy petroleum or coal-derived liquids. The rates of hydrogenation and pore size distribution will be discussed. A developmental catalyst with relatively high desulfurization and efficient hydrogen utilization was tested in a constant temperature aging run to establish process conditions needed to produce 0.4 wt % sulfur boiler fuels.

Experimental

The experiments were conducted in a continuous down-flow fixed bed pilot unit. The feedstock, 50 wt % W. Kentucky/SRC recycle solvent blend, was prepared in a charge reservoir and transferred to a weigh cell by gravity flow. Both the charge reservoir and weigh cell were kept at 350°F. After the reactor, hydrogen and light gases were separated from hydro-treated oil through high (300°F) and low (75°F) temperature separators in series. To maintain fluidity of the high SCT SRC concentration blend, all lines and valves from the charge reservoir to the high temperature separator were heat-traced to 340-420°F. The detailed description of the pilot unit is

available elsewhere (1). The selection of SCT SRC as the feed was based on a recent finding that the hydrogen utilization efficiency for production of hydrogen-rich coal liquids can be improved by coupling mild short resident time hydroliquefaction (to produce SCT SRC) with catalytic hydroprocessing (3).

The catalysts were presulfided with a 10% H₂S/H₂ mixture and tested at a reactor pressure of 2000 psig and a hydrogen circulation of 5000 scf/B. Each catalyst was subjected to a standard sequence of temperatures and liquid hourly space velocities, ranging from 720–800°F and 0.5–2.0 hour⁻¹, respectively

Results and Discussions

Fresh Catalyst Properties. Three Mobil catalysts were tested and have been identified as HCL-1, -2, and -3. Because of the proprietary nature of these catalysts, properties have been excluded. The major properties of the four commercial and two developmental catalysts are shown in Table 1. The four commercial catalysts evaluated were NiMo/Al₂O₃: Harshaw's 618X and HT-500, and American Cyanamid's HDN-1197 and HDS-1443. The NiMo catalysts were tested in a greater number than the CoMo catalysts because it had been thought that improved hydrogenation activity was needed to treat the highly refractory SRC. Also, nickel-promoted hydroprocessing catalysts form less coke than cobalt-promoted catalysts, possibly resulting in better stability. The 618X, HT-500, and HDS-1443 catalysts all have similar metals loading; their major difference is found in surface area, going from relatively low to medium to high, respectively. The shift in surface area can also be seen in the different pore size distributions. Harshaw 618X has a well-defined distribution with 77% of its pore volume in the 100–200Å diameter region. HT-500 has a broader distribution and smaller median size, having half of its pore volume in the 80–100Å region. HDS-1443 has a bimodal distribution: it has most of its pores in 30–80Å, but it also has some 200Å+ pores. HDN-1197 has a higher metals loading than the other NiMo catalysts and also most of its pores in the 30–80Å region.

Two developmental catalysts were evaluated in this study. These include Amocat 1A and 1B, recently developed by Amoco for testing in the H-Coal^R Process (4). Both catalysts were made of the same support and had primarily 100–200Å pores with some macropores (>1000Å). Amocat 1B is an unpromoted Mo/Al₂O₃ while 1A is CoMo/Al₂O₃.

Fresh Activity Comparisons. The nine catalysts have been divided into two groups in order to simplify the activity comparisons. Group A is made up of the more active desulfurization catalysts and includes Mobil HCL-2, Mobil HCL-3, American Cyanamid HDS-1443, and Amocat 1A. Group B included Mobil HCL-1, Harshaw 618X, American Cyanamid HDN-1197, and Amocat 1B.

For the activity comparisons, the heteroatom removals (and CCR reduction) are plotted versus reactor temperature at a liquid hourly space velocity of 1.0. Consequently, catalyst activity can be compared on the basis of temperature requirements for achieving specific liquid product heteroatom (or CCR) contents.

The comparisons of desulfurization activities are shown in Figure 1 and Figure 2 for Group A and Group B catalysts, respectively. At the 80% desulfurization level, Mobil HCL-2 is 10-15°F more active than HDS-1443, followed by HCL-3, Harshaw 618X, and Amocat 1A (Figure 1). Surface area and pore size distribution seem to be important parameters for the fresh catalyst activity. The relatively high fresh activity of HDS-1443 may be partially explained by its high surface area and presence of macropores (Table 1). The presence of macropores may be responsible for the improvement of the relative positions of HDS-1441 and Amocat 1A at more severe conditions (0.5 LHSV).

The importance of pore size distribution also explains the low activity of HT-500, which has 75% of its pore volume in the 30-100Å region. Cyanamid HDN-1197 seems to have a high desulfurization activity (Figure 2). However, it yields an inhomogeneous product, probably due to its high hydrogenation activity coupled with its small pore size. Inhomogeneous products have also been observed in the upgrading of regular SRC by small pore catalysts (1). The SCT SRC, with its high polar asphaltenes content, is particularly susceptible to "front end, back end" incompatibility.

The ranking of deoxygenation activity was very similar to that of the desulfurization activity (Figure 3). The results may suggest that, like desulfurization, the deoxygenation reaction could occur without pre-hydrogenation. The comparison of denitrogenation activities is shown in Figure 4. Mobil HCL-3 was the most active catalyst followed by Mobil HCL-2 and Harshaw 618X.

The CCR reduction activity for the nine catalysts is similarly plotted as a function of temperature in Figure 5 and Figure 6. Mobil HCL-2, HCL-3, and Amocat 1B are the most active catalysts. Generally, heteroatom removal can be achieved with only minor changes in chemical structure. However CCR reduction in SCT SRC occurs with significant alteration of GEC classes, primarily toward the formation of less polar compounds. The classes of W. Kentucky SCT SRC, separated by GEC (gradient elution chromatography), are given in Table 2 and show that 75% of the SRC is polar and noneluted polar asphaltenes.

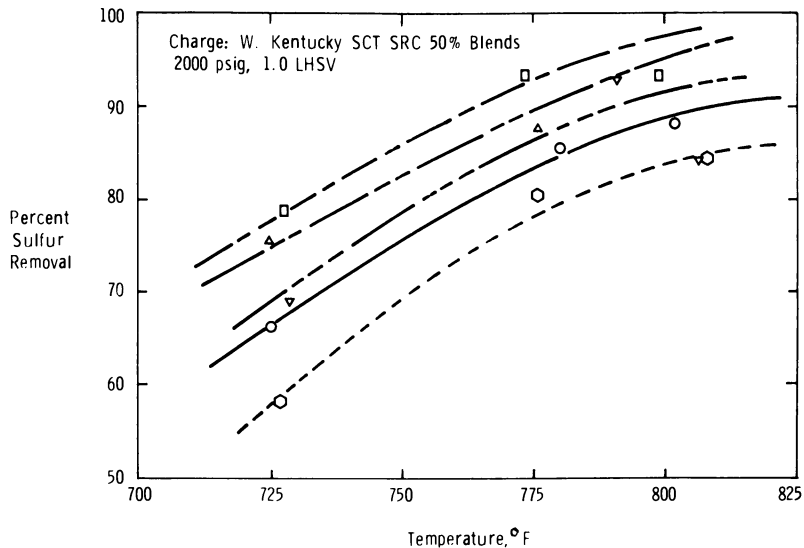


Figure 1. Comparison of desulfurization activities, Group A catalysts: (○) Harshaw 618X, (□) Mobil HCL-2, (△) HDS-1443, (▽) Mobil HCL-3, (○) Amocat 1A

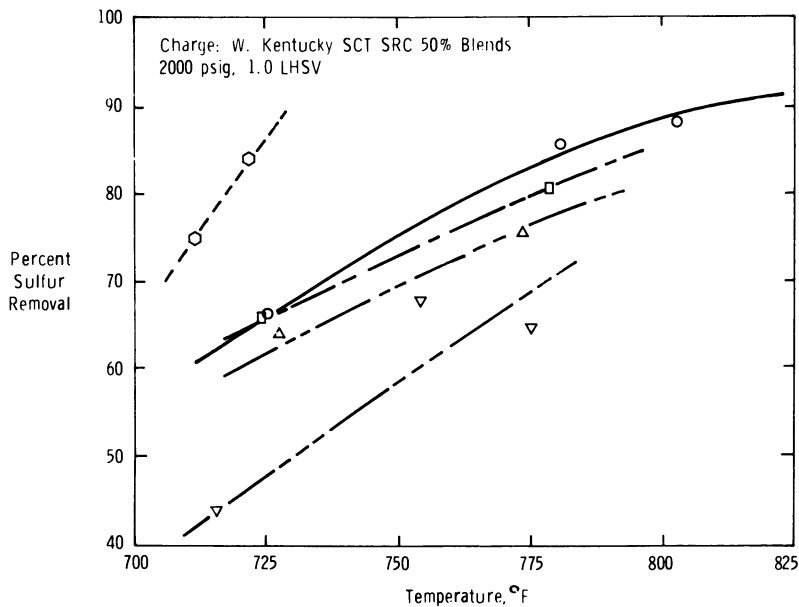


Figure 2. Comparison of desulfurization activities, Group B catalysts: (○) Harshaw 618X, (□) HT-500, (△) Mobil HCL-1, (▽) Amocat 1B, (○) HDN-1197

Table I
Fresh Catalyst Properties

	<u>Harshaw 618X</u>	<u>Harshaw HT-500</u>	<u>Cyanamid HDN-1197</u>	<u>Cyanamid HDS-1443</u>	<u>Amoco* 1B</u>	<u>Amoco 1A</u>
<u>Compositions, Wt %</u>						
Ni	2.7	2.4	3.7	2.9	0	-
CoO-	-	-	-	-	-	2.9
MoO ₃	14.8	14.0	21.7	15.5	14.9	19.7
<u>Physical Properties</u>						
Surface Area, m ² /g	140	193	130	306	167	154
Pore Volume, cc/g	0.60	0.511	0.379	0.764	0.67	0.662
Pore Diameter, Å	172	104	117	100	160	172
<u>Pore Size Dist., cc/g</u>						
0-30Å	0.025	0.005	0.059	0.165	>0.027	0.065
30-80Å	0.037	0.125	0.123	0.355		0.046
80-100Å	0.036	0.252	0.112	0.020	0.063	0.063
100-200Å	0.464	0.123	0.035	0.033	0.419	0.385
200Å+	0.038	0.007	0.050	0.192	0.153	0.103

* Amoco's Analyses

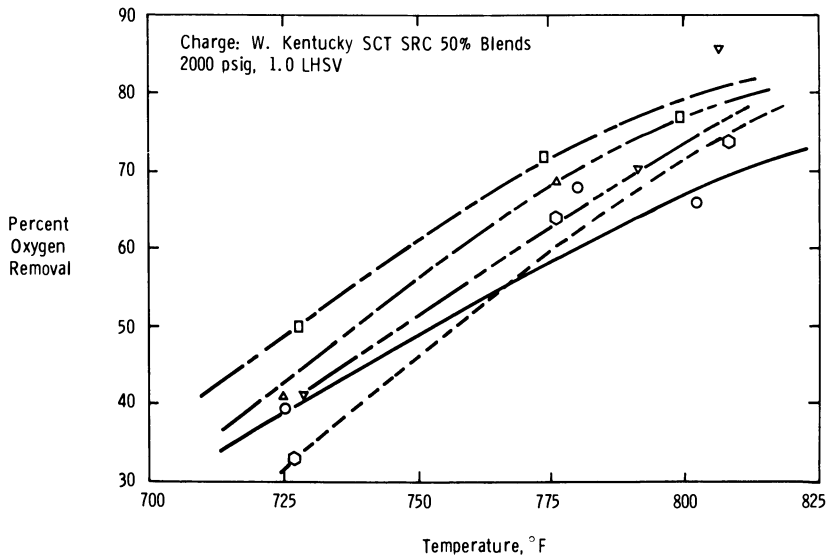


Figure 3. Comparison of deoxygenation activities, Group A catalysts: (○) Harshaw 618X, (□) Mobil HCL-2, (△) HDS-1443, (▽) Mobil HCL-3, (◇) Amocat 1A

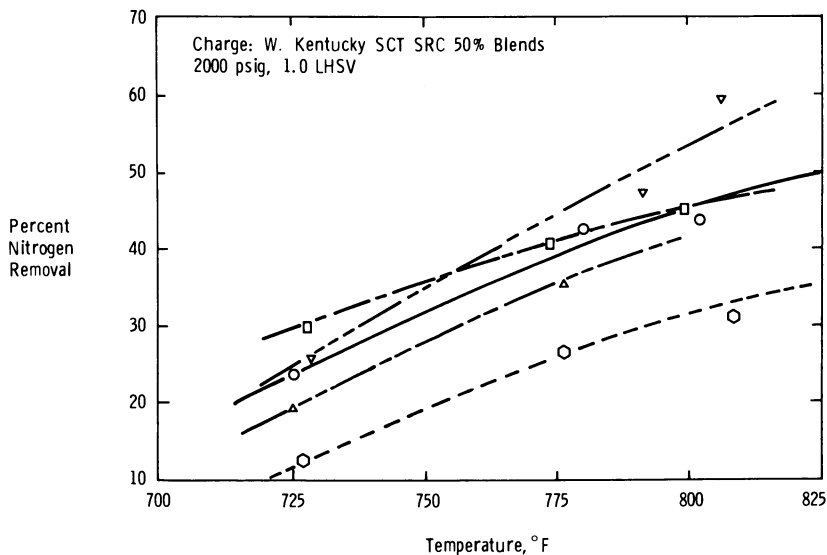


Figure 4. Comparison of denitrogenation activities, Group A catalysts: (○) Harshaw 618X, (□) Mobil HCL-2, (△) HDS-1443, (▽) Mobil HCL-3, (◇) Amocat 1A

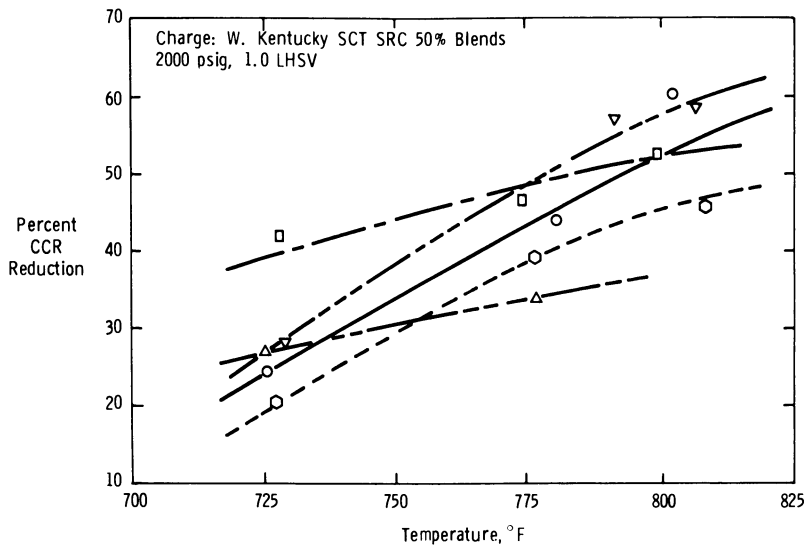


Figure 5. Comparison of CCR reduction activities, Group A catalysts: (○) Harshaw 618X, (□) Mobil HCL-2, (△) HDS-1443, (▽) Mobil HCL-3, (⊙) Amocat 1A

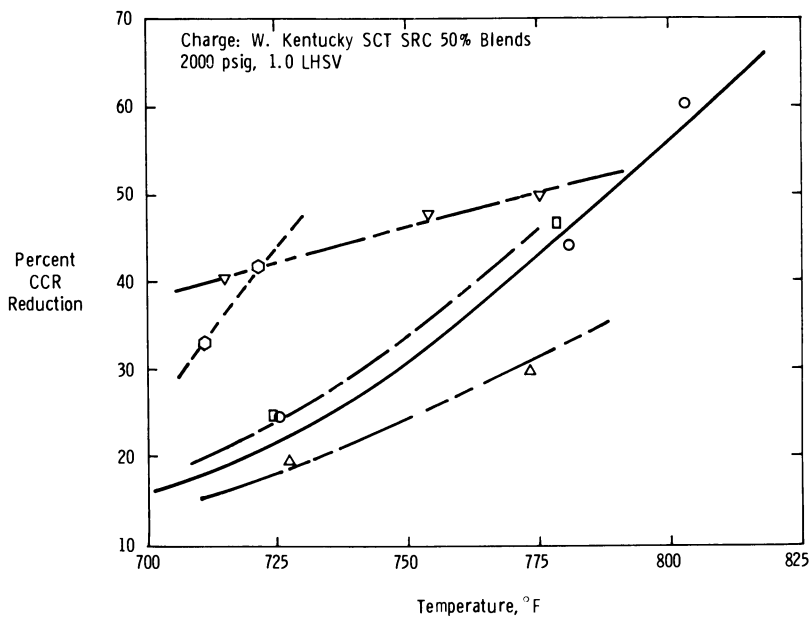


Figure 6. Comparison of CCR reduction activities, Group B catalysts: (○) Harshaw 618X, (□) HT-500, (△) Mobil HCL-1, (▽) Amocat 1B, (⊙) HDN-1197

Table II
GEC Analyses of W. Kentucky SCT SRC

Saturates	0.3 wt %
Aromatic Oils	0.4 wt %
Resins/Asphaltenes	24.8 wt %
Polar Asphaltenes	45.1 wt %
Non-Eluted Asphaltenes	29.4 wt %
	<u>100.0</u>

The conversion of polar asphaltenes (lumped with non-eluted asphaltenes) as a function of process severity, expressed by hydrogen content in the liquid product, is shown in Figure 7. Amocat 1B and HDS-1443 show a significantly high conversion of polar asphaltenes at a given process severity. It is worth noting that Amocat 1B and HDS-1442, the Co-Mo version of HDS-1443, have been found to be active catalysts for coal hydro-liquefaction (4).

Hydrogen consumption is a major economic factor in any coal liquid hydroprocessing operation. In Figure 8, the total hydrogen consumption is plotted vs. total liquid product (TLP) sulfur content. Three selectivity curves have been drawn from Figure 8: the solid curve represents Harshaw 618X, and the dashed curves are for Amocat 1A and 1B. To a rough approximation HCL-2, HDS-1443, and Amocat 1A are "low" hydrogen consumption catalysts; Harshaw 618X and Mobil HCL-3 are relatively "high" hydrogen consumption catalysts. At the same level of desulfurization Harshaw 618X uses approximately 500 scf/B more than Amocat 1A. However, Amocat 1B, a low desulfurization activity catalyst, shows a very high hydrogen consumption.

Analyses of Used Catalysts. The analyses of five used catalysts tested with 50% W. Kentucky SCT SRC are given in Table 3. The coke and iron depositions appear to be strongly dependent upon catalysts; Harshaw 618X and HDS-1443 are high, but Amocat 1A and 1B are low in coke deposition. Since surface area measurements can include contribution by contaminants (particularly coke), these values have no clearcut meaning. Besides the coke deposition, metal deposition on the catalysts contributes to the catalyst deactivation.

Table III
Used Catalyst Properties as Received

	Harshaw 618X	Harshaw HT-500	Cyanamid HDS-1443	Amocat 1B	Amocat 1A
Surface Area, M ² /g	132	147	201	137	125
Pore Volume, cc/g	0.349	0.253	0.568	0.510	0.487
Pore Diameter, Å	106	69	113	149	156
Iron, Wt Pct	0.61	0.30	0.35	0.77	0.61
Coke, Wt Pct	20.6	23.0	18.0	12.8	13.0

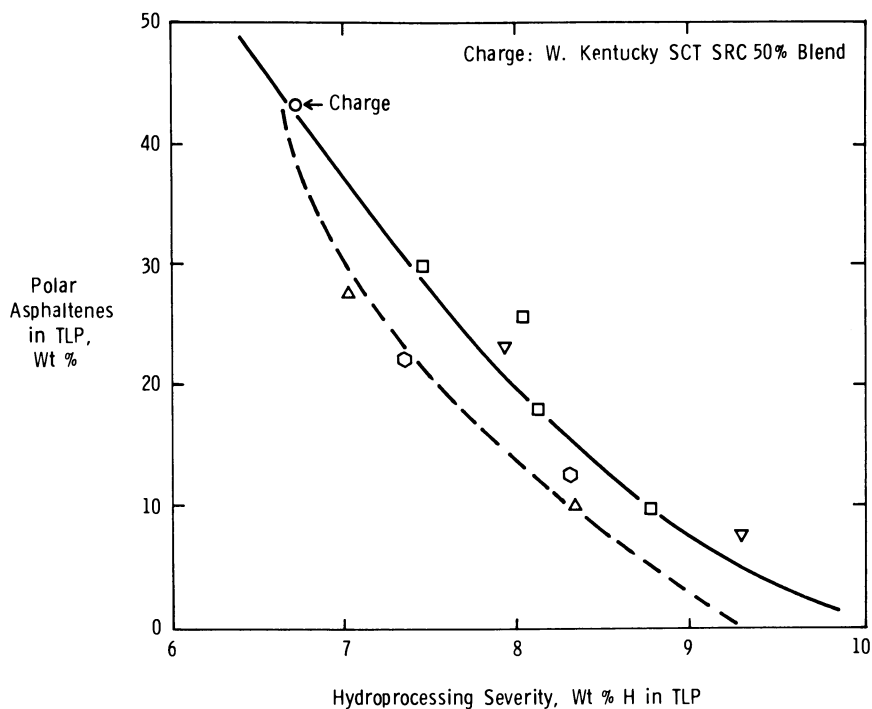


Figure 7. Polar asphaltene conversion as a function of hydroprocessing severity: (\square) Harshaw 618X, (\triangle) Amocat 1B, (∇) Mobil HCL12, (\circ) HDS-1443

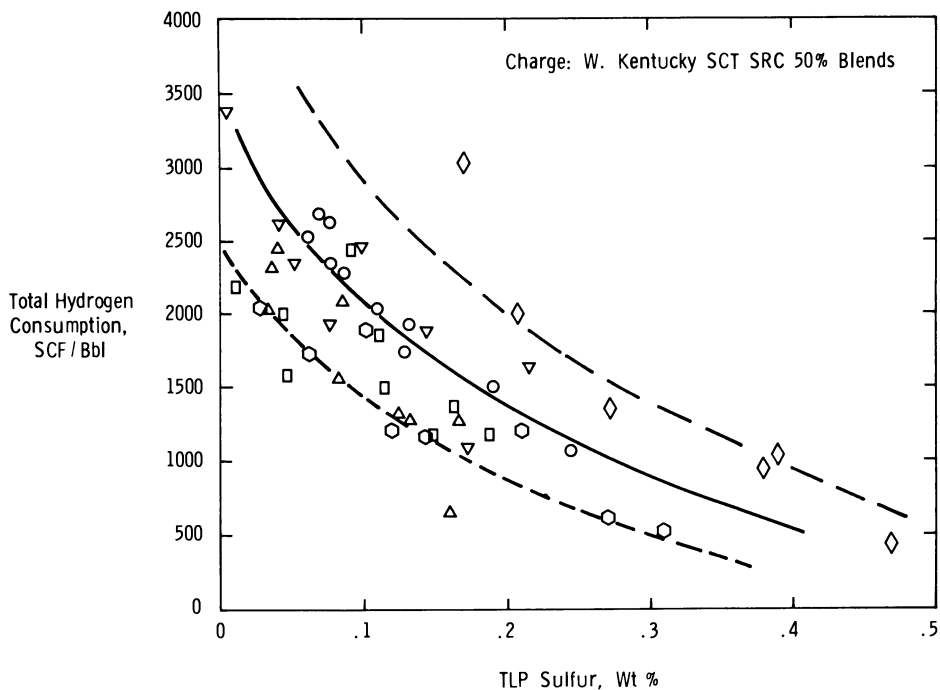


Figure 8. Total hydrogen consumption as a function of sulfur in liquid product: (○) Harshaw 618X, (□) Mobil HCL-2, (△) HDS-1443, (▽) Mobil HCL-3, (○) Amocat 1A, (◇) Amocat 1B

The deposition of metal contaminants on a used Harshaw 618X catalyst was analyzed with a scanning electron microscope (SEM). The SEM x-ray emission spectra for fresh and used catalysts at different locations in the catalyst particle are shown in Figure 9. The used catalyst, tested after our standard procedure, showed a large buildup of iron and titanium in a narrow band (<2 microns) of the catalyst exterior. Other contaminants (e.g., K, Ca, Si) were detected at lower concentrations. As shown in Figure 9(b), strong intensities of deposited metals were clearly shown in the x-ray emission spectrum taken near the extrudate external surface. The intensities were substantially reduced in analyses made away from the exterior edge, as shown in Figures 9(c) and 9(d). These results indicate that the hydroprocessing of coal liquids is well suited to ebullated bed reactors; the motion of the fluidized catalysts may provide a continuous, partial regeneration by mildly abrading the metals-rich pellet exterior.

Aging Run. Based on the fresh activity evaluation, Amocat 1A was tested in an aging run for the hydroprocessing of 50% W. Kentucky SCT SRC. The run was made at constant conditions (2000 psig, 775°F, 0.5 LHSV) and was smoothly operated for 15 days. The run was then terminated due to incipient plugging in the reactor. The results are shown in Figure 10, where sulfur content in the liquid products has been plotted vs. days-on-stream. During this first four days the temperature was varied to obtain an activation energy estimation, and these data have been omitted.

A simple deactivation equation was used for a fixed bed reactor:

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{k_0 e^{-E/RT} e^{-t/\tau}}{\text{LHSV}}$$

where C_{A0} and C_A are the initial and final concentrations of reactant (i.e., heteroatom or CCR). Here, k_0 is the fresh preexponential factor, LHSV is liquid hourly space velocity, E is activation energy, T is reaction temperature, t is time on-stream and τ is catalyst deactivation time constant. The estimated values for τ , k_0 , and E are as follows:

	$\frac{k_0}{1}$ Wt %-hr	$\frac{E}{\text{Btu}}$ lb mole	$\frac{\tau}{\text{Days}}$
Sulfur	1.992×10^{13}	69,900	18.3
Nitrogen	3.368×10^5	34,600	36.1
Oxygen	6.895×10^9	57,800	8.9
CCR	2.553×10^7	50,400	21.9

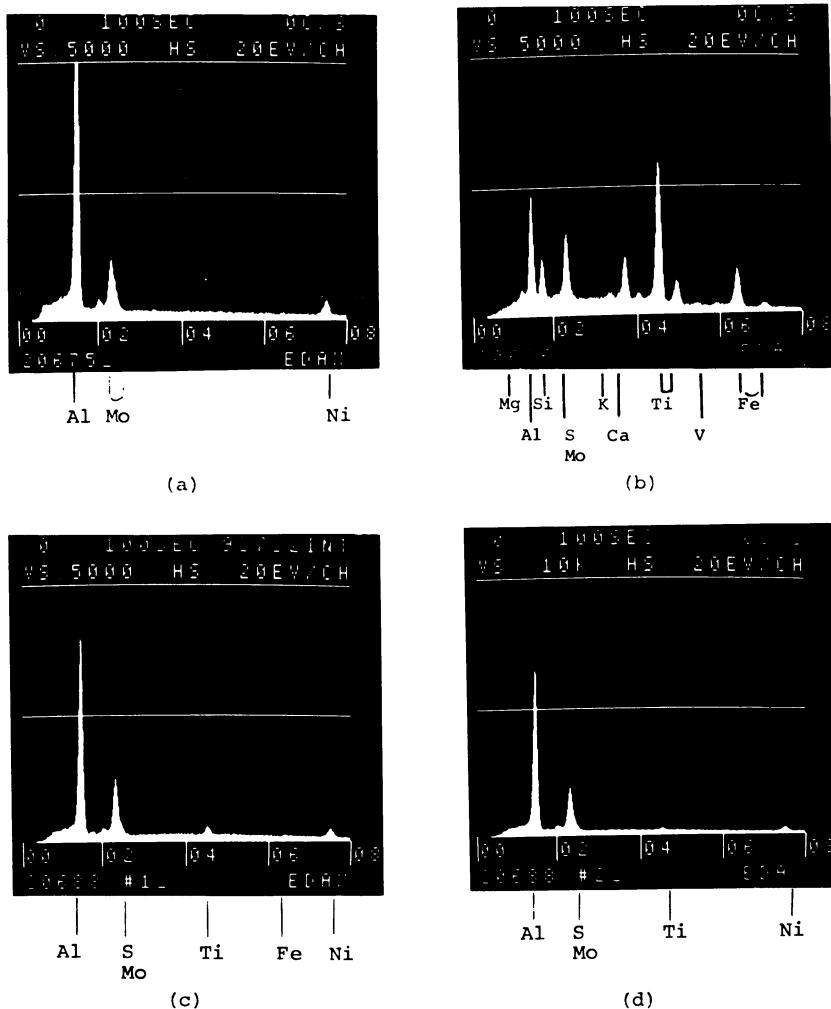


Figure 9. SEM examination of fresh and used Harshaw 618X: a) x-ray emission spectrum taken of external surface of fresh catalyst showing presence of Al, Mo, and Ni; b) x-ray emission spectrum taken of external surface of used catalyst showing presence of Mg, Al, Mo, K, Ca, Ti, and Fe; c) x-ray spectrum taken at 0–20 μ from the edge of the cross section of used catalyst showing presence of Al, Mo, Ti, Fe, and Ni; d) x-ray emission spectrum taken at 60–80 μ from the edge of the cross section of used catalyst showing presence of Al, Mo, Ti, and Ni

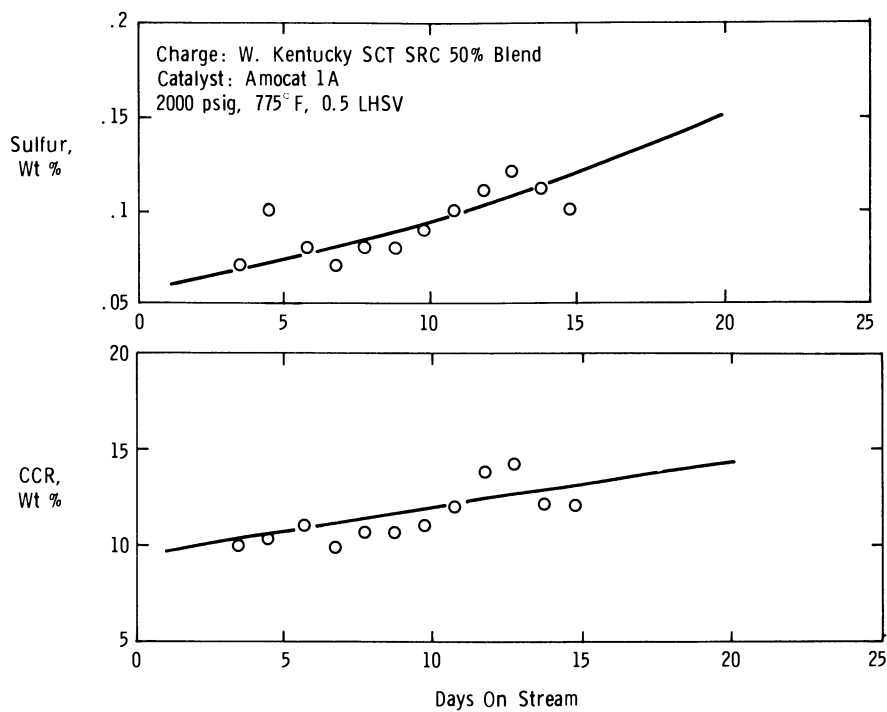


Figure 10. Aging run with W. Kentucky SCT SRC: (○) experimental data, (—) model-predicted data

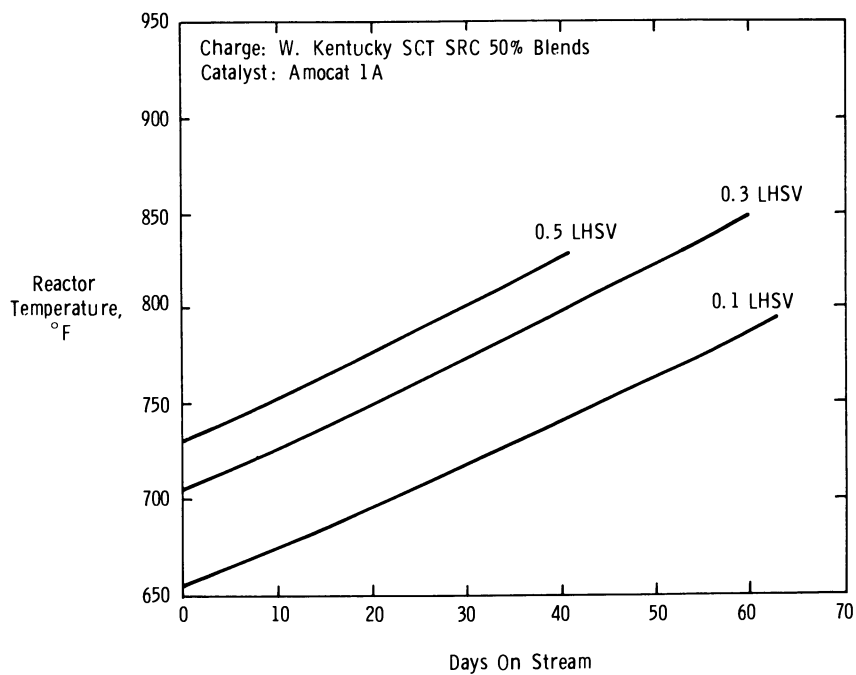


Figure 11. Design variables for fixed-bed reactor, product sulfur concentration: 0.15 wt % in TLP and 0.4 wt % in 900° F+

The temperature rise necessary to maintain a constant product sulfur concentration is about 2-3°F/day. The measured and model-predicted values for sulfur and CCR are shown in Figure 10.

The simulated operating conditions for the fixed bed reactor to produce a 900°F⁺ fuel with a sulfur content of 0.4 wt % are shown in Figure 11, using a charge of 50% W. Kentucky SCT SRC. Figure 11 shows the reactor temperature required to achieve these sulfur levels as a function of days-on-stream and LHSV. The temperature rise is 2.5-3.0°F/day. The cycle length, a function of both LHSV and the limit of reactor temperature, can be determined from Figure 11. For example, at 0.3 LHSV and a maximum reactor temperature of 850°F, the cycle length is 60 days.

Conclusions

Short contact time SRC can be upgraded via catalytic hydroprocessing into low sulfur boiler fuels. However, the solid SCT SRC feedstock requires solvent dilution to reduce its viscosity. Furthermore, even for a 50 wt % W. Kentucky SCR SRC blend, all pilot unit lines and valves have to be heat-traced above 350°F in order to achieve smooth mechanical operations.

Catalytically, the SCT SRC is more susceptible to form an inhomogeneous product than the regular SRC, particularly where small pore catalysts are used. The upgrading costs can be significantly reduced through increased activity as well as efficient hydrogen utilization. A proprietary catalyst, Mobil MCH-2, and a developmental catalyst, Amocat 1A, were observed to have these two important properties. For hydroprocessing of the 50 wt % W. Kentucky SCR SRC blend, the aging rate was moderate with a 2-3°F/day of temperature rise required to keep constant desulfurization activity. The catalysts are believed to be deactivated by coke and metal depositions on the surface. A large buildup of iron and titanium was found in a narrow band of the catalyst exterior of a spent catalyst. Improved catalyst aging is likely to occur by the use of an ebullated bed reactor, primarily by decreased interparticle coke formation as well as by mild abrasion of metal contaminants.

Acknowledgement

This work was performed under EPRI/Mobil research project RP 361-2. Dr. W. C. Rovesti is the EPRI project manager.

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Hydrotreating of SRC-I Product

Optimization of Process Variable Space

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In the Solvent Refined Coal Process, coal is dissolved in a coal-derived solvent to produce a filterable liquid. This is accomplished by means of a mild liquid phase hydrogenation of the coal. The liquid is separated from the insoluble minerals and unreacted organic matter by filtration. The solvent is recovered for recycle by vacuum distillation, and the SRC is obtained as a black shiny solid at room temperature. Some of the sulfur present in the coal is removed in the form of hydrogen sulfide gas.

The present sulfur standards (0.97 percent sulfur in SRC) are being met by conventional SRC processing. New Source Performance Standards (NSPS) recently proposed by the Environmental Protection Agency (EPA) would require a sulfur content of 0.5 to 0.6 percent in SRC for most coals. The proposed NSPS could be met using the conventional SRC process with the application of severe operating conditions (e.g., a reaction temperature of 450°C, a H₂ pressure of 2,000 psig or 13.9 MPa and a long reaction time of 30 to 60 minutes). This would result in an unreasonably high hydrogen consumption and operating cost. Therefore, a modification of the conventional SRC process is necessary to meet the proposed NSPS with minimum hydrogen requirements.

For the coal studied here, a bituminous Western Kentucky #9/14 coal, dissolution of the coal has been shown to occur very rapidly, requiring less than 30 minutes to liquefy most of the coal (~90 percent). However, a relatively long reaction time (120 min.) is required to reduce its sulfur level low enough to meet even the current standards (1). A new short residence time two-stage SRC type process has been suggested by Auburn University (2) for solvent refining this coal. This process has been shown to have the potential of producing a low-sulfur solid SRC product that meets the proposed NSPS. It involves the dissolution of the coal

in the presence of an inexpensive mineral additive (first stage), and then subsequent hydrotreating of the filtered liquid from the first stage in the presence of a presulfided Co-Mo-Al catalyst (second stage).

The objective of the present work is to evaluate the effect of a wide range of process or reaction variables--reaction temperature, hydrogen partial pressure, catalyst loading, and reaction time--on hydrodesulfurization and hydrogenation of filtered liquid product (coal-derived liquid) obtained from the coal dissolution stage in the presence of a commercial presulfided Co-Mo-Al catalyst. The selectivity for desulfurization over hydrogenation (S_e) is used to rate the effectiveness of the above mentioned process variables. S_e is defined as the fraction of sulfur removal per unit (g) of hydrogen consumed, that is,

$$S_e = \frac{\frac{S_o - S_f}{S_o}}{H_2 \text{ used, g}}$$

where S_e : Selectivity,

S_o : Original sulfur content of the coal liquids, and

S_f : Sulfur content of the hydrotreated coal liquids.

The purpose of this study is to identify a set of operating conditions for hydrotreating reactions at which maximum selectivity is attained for a specified sulfur content of the solid SRC product.

There are many different types of search routines used to locate optimum operating conditions. One approach is to make a large number of runs at different combinations of temperature, reaction time, hydrogen partial pressure, and catalyst amount, and then run a multivariable computer search routine (like the Hooke-Jeeves method or Powell method). A second approach is to formulate a mathematical model from the experimental results and then use an analytical search method to locate the optimum. The formulation of a mathematical model is not an easy task, and in many cases, this is the most critical step. Sometimes it is impossible to formulate a mathematical model for the system, as in the case of the system studied here, and an experimental search must be performed.

The experimental strategy used here is to perform a series of small experiments instead of a single comprehensive experiment. An univariate search was made in which only one variable was changed at a time. The information obtained in the earlier experiments performed during the univariant

search was used to plan subsequent experiments. By doing so, the results were available quickly, and the experimental error was checked and minimized during the course of experimentation.

In the first step of the univariate search a series of experiments were performed in which base values were used for the initial hydrogen partial pressure, reaction time and reaction temperature, and only the amount of catalyst used was varied. The amount of catalyst which yielded the best performance (i.e., maximum selectivity) and best satisfied practical constraints was selected. In the next step a series of experiments was performed in which the selected amount of catalyst was used, base values were used for temperature and time, and only the initial hydrogen partial pressure was varied. An initial hydrogen partial pressure was selected as was done for the amount of catalyst in the first step.

The dependence of selectivity (Se) on the reaction time and temperature was modeled using empirical expressions for desulfurization and hydrogen consumption kinetics. The same values selected for initial hydrogen partial pressure and amount of catalyst in the first two steps of the univariate search were used in determining these kinetic expressions. An univariate search does not necessarily lead to an optimum for a multivariable space; that is, convergence to an optimum is not guaranteed. For this reason a series of experiments were made to map the region close to the identified optimum conditions to test whether a local optimum, at least, had been located.

Experimental

Reagents and Materials. Light recycle oil (LRO) and Western Kentucky #9/14 coal were obtained from the Wilsonville SRC Pilot Plant, operated by Southern Company Services, Inc. The LRO contains 0.26% sulfur, and the Western Kentucky #9/14 coal is analyzed to be 67% C, 4.9% H, 3.10% S, and 12% mineral matter. The coal was dried overnight at 100°C and 25 inches Hg vacuum before use.

The coal liquid is obtained by reacting Kentucky #9/14 coal-LRO slurry for 60 minutes at 410°C in an autoclave reactor under 2000 psig (13.9 MPa) hydrogen pressure. The product from the autoclave is collected and filtered using Watman #51 filter paper to remove the mineral matter and undissolved coal. The liquid product is saved and used for further hydrotreating studies. The analysis of the filtered product from the coal dissolution step is given in Table I.

Table I

Analysis of the Liquid Product Used in Hydrotreating Stage

Distillation Product Distribution, %	
Distillate (Oil)	61.6
SRC	38.4
Sulfur Distribution, %	
Distillate (Oil)	0.21
SRC	0.97
Total Liquid	0.54
Tetralin/Naphthalene Ratio	0.24

Distillation is performed under < 1 mm Hg pressure
 Distillate: 270°C - fraction of vacuum distillation
 SRC: 270°C + fraction of vacuum distillation

Table II

Effect of Catalyst Amount on Hydrotreating
 of Kentucky #9/14 Coal Liquid

Coal Liquid = 100 g, Time = 30 min., T = 410°C, P = 2000 psi
 (13.9 MPa)H₂, 1000 RPM, Reactor - Autoclave

Amount of Catalyst, g	1.0	5.0	10.0	15.0
H ₂ Used, g	0.11	0.17	0.18	0.21
Total Sulfur S _f , %	0.36	0.22	0.20	0.17
$Se = \frac{S_o - S_f}{S_o} \times \frac{H_2 \text{ Used, g}}{H_2 \text{ Used, g}}$	3.0	3.5	3.5	3.3
SRC Conversion, %	16	21	22	24

S_o = 0.54%

Co-Mo-Al is a commercial catalyst from Laporte Industries, Inc. (Comox 451). The catalyst was ground and screened to -325 mesh before use. Presulfided Co-Mo-Al was prepared by collecting the solid residue after reaction of creosote oil (S = 0.64 percent) with Co-Mo-Al in the autoclave reactor. The sulfur content of the presulfided Co-Mo-Al was 2.76%.

Hydrogen gas cylinders (6000 psi grade) were supplied by Linde.

Equipment. A commercial 300 ml magne-drive autoclave (Autoclave Engineers) reactor was used for all reaction studies and has been previously described (3-6). Varian gas chromatographs (Model 920 and 1800) were used for analysis of gas samples and products from the hydrotreating reactions. A LECO sulfur determinator (Model 532) was used for analysis of sulfur in the products.

Procedure. One hundred grams of coal liquid was combined with a predetermined amount of presulfided Co-Mo-Al catalyst and charged to the autoclave. Reaction temperature for the runs varied from 360 to 435°C, depending on the run. A stirring setting of 1000 rpm was used, and the initial total pressure was varied from 1500 (10.4 MPa) to 2500 (17.3 MPa) psig. The heat-up rate was about 12 to 20°C/min, thus requiring a total heat-up time of about 20-25 minutes. After a specified reaction time, a gas sample was taken; the autoclave was cooled to below 100°C; and the reaction products were collected. The filtered liquid product was vacuum distilled under <1.0 mm Hg pressure to recover the process solvent added prior to the reaction. The 270°C + fraction obtained by vacuum distillation was defined as the solvent refined coal (SRC). A sulfur analysis was performed on each fraction.

The conversion of SRC to oil and gases is defined as

SRC Conversion, % =

$$\frac{(\text{Amt of SRC})_{\text{original liquid}} - (\text{Amt of SRC})_{\text{hydrotreated liquid}}}{(\text{Amount of SRC})_{\text{original liquid}}}$$

and is used as a constraint.

Results and Discussion

Effect of Catalyst Loading. The effect of the amount of Co-Mo-Al catalyst present in the hydrotreating reaction is tabulated in Table II. It was observed that increasing

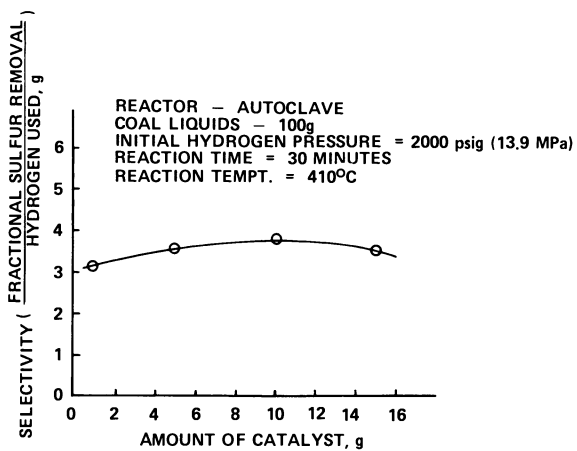


Figure 1. Effect of amount of catalyst (Co-Mo-Al) on selectivity

the amount of Co-Mo-Al from 1 g to 15 g increases the sulfur removal by 52 percent, increases hydrogen consumption by 87 percent, and increases SRC conversion from 16 to 24 percent. Figure 1 shows the variation of selectivity versus the amount of catalyst used while keeping the other reaction variables constant. The selectivity for hydrodesulfurization increased slightly (from 3.0 to 3.5) when the amount of catalyst was increased from 1 g to 5 g. The conversion of SRC to oil and gases increased from 16 to 21 percent with an increase in catalyst amount from 1 g to 5 g. Since a higher selectivity was observed with 5 g of catalyst than with 1 g, the use of 5 g of catalyst was preferred over 1 g. The selectivity only varied by 0.2 (~6 percent) as the amount of catalyst was increased from 5 g to 10 g to 15 g, and the conversion of SRC increased from 21 to 24 percent. The above variation in selectivity and the conversion of SRC is within the limits of experimental error; standard deviations for selectivity and conversion of SRC were + 7.2 percent (+ 0.25) and + 10.1 percent (+ 2.5), respectively (Table III). A maximum in selectivity (3.5) did occur with 5 g or 10 g of catalyst present; however, the significance of this maximum is questionable. The significance of the increase in SRC conversion to oil and gases with the increase in catalyst amount from 5 g to 10 g to 15 g is also questionable because it is within the range of experimental error (Table III). Thus, when 5 g or more of catalyst were used, both selectivity and SRC losses (that is, its conversion to oil and gases) were observed to be relatively insensitive to the amount of catalyst loading at the base reaction conditions used (Table II). The amount of catalyst was held constant throughout the remainder of the study at 10 g.

Effect of Pressure. The purpose of this part of the study was to evaluate the sensitivity of selectivity and SRC conversion to the initial hydrogen partial pressure. This was done to provide a basis for selection of the initial hydrogen partial pressure for use throughout the remainder of the study. The effect of changes in hydrogen partial pressure with reaction on desulfurization kinetics were computed throughout the study as described in the following section. Table IV shows the effect of the initial hydrogen partial pressure on selectivity, sulfur removal, hydrogen consumption, and SRC conversion. It was observed that increasing the hydrogen partial pressure by 1500 psig (10.4 MPa) decreased the selectivity by 72 percent, increased hydrogen consumption by a factor of 2.6, enhanced sulfur removal by a factor of 1.9, and did not affect SRC conversion

Table III

Reproducibility of the Hydrotreating Reaction

Coal Liquid = 100 g, Time = 30 min., T = 410°C,
 P = 2000 psi (13.9 MPa)H₂, 1000 RPM,
 Reactor - Autoclave, Amount of Catalyst = 10 g

H ₂ Used, g	0.18	0.18	0.20
Total Sulfur S _f , %	0.20	0.18	0.19
$Se = \frac{S_o - S_f}{\frac{S_o}{H_2 \text{ Used, g}}}$	3.5	3.7	3.2
SRC Conversion, %	22	27	25

Table IV

Effect of Hydrogen Partial Pressure on Hydrotreating
of Kentucky #9/14 Coal Liquid

Coal Liquid = 100 g, Co-Mo-Al = 10 g, T = 410°C, 1000 RPM,
 Reaction Time = 30 min., Reactor - Autoclave

Pressure, Psig H ₂	1000	1500	2000	2500
H ₂ Used, g	0.08	0.13	0.18	0.22
Total Sulfur S _f , %	0.35	0.30	0.20	0.19
SRC Sulfur, % S _f	0.66	0.57	0.49	0.45
$Se = \frac{S_o - S_f}{\frac{S_o}{H_2 \text{ Used, g}}}$	4.4	3.4	3.5	2.9
SRC Conversion, %	22	19	22	21

appreciably. For initial hydrogen pressures of 1500, 2000, and 2500 psig, the variation of selectivity was within the range of experimental error. Use of a 1000 psig hydrogen pressure gave the maximum selectivity. However, at 1000 psig the sulfur requirements set by the proposed NSPS (0.5 to 0.6 percent SRC sulfur) were not met (SRC sulfur content at 1000 psig is 0.66%). The use of a 2000 psig hydrogen partial pressure gave a slightly higher selectivity than was obtained with either 1500 or 2500 psig, and a sufficient amount of sulfur was removed. Therefore, a hydrogen pressure of 2000 psig was chosen for further studies.

Effect of Reaction Time and Temperature. The amount of catalyst (10 g of Co-Mo-Al in 100 g of coal liquids) and the initial hydrogen partial pressure (2000 psig) determined above were used to study the effect of reaction time and temperature. Hydrodesulfurization and hydrogen consumption kinetics were determined, as outlined in the following paragraphs.

In order to determine the rate equation for hydrodesulfurization, a semi-logarithmic plot of the total sulfur content with time was made (Figure 2). The plot indicated two independent first-order reactions with greatly different rate constants. This is in agreement with the findings of Gates, et al. (7) and Pitts (3). A procedure similar to that of Pitts (3) was used to describe the hydrodesulfurization kinetics. The rate expression is given below:

$$S_{\text{Total}} = S_{10} \text{ EXP } [-K_{10} \text{ EXP } (-\Delta E_1/RT) t] + S_{20} \text{ EXP } [-K_{20} \text{ EXP } (-\Delta E_2/RT) t]$$

The empirical parameters S_{10} , S_{20} , K_{10} , K_{20} , ΔE_1 , and ΔE_2 were determined by a numerical search routine. Figure 3 compares the theoretical curves with the experimental data and represents a satisfactory curve fit.

The amount of hydrogen gas present in the reactor was plotted against reaction time on a semi-logarithmic scale (Figure 4). This plot gave a straight line indicating a first-order rate expression. Pitts (3) also suggested a first-order rate expression for hydrogen consumption. A procedure similar to that of Pitts (3) was used. The hydrogen consumption rate expression is given by:

$$\frac{H}{H_{go}} = \text{EXP } [-K_o \text{ EXP } (-\Delta E/RT) t]$$

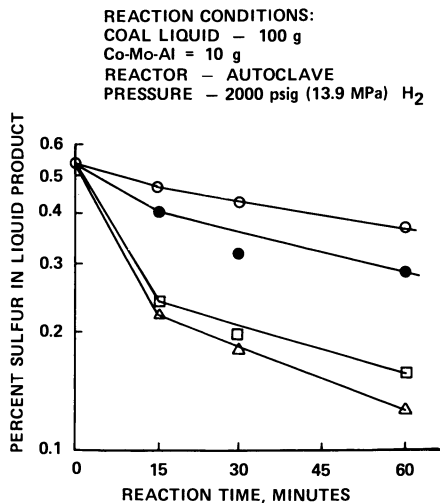


Figure 2. Semilog plot of total sulfur (%) vs. time for hydrotreating reaction in the presence of Co-Mo-Al: (○) 360° C, (●) 385° C, (□) 410° C, (△) 435° C

REACTION CONDITIONS: SEE FIGURE 2

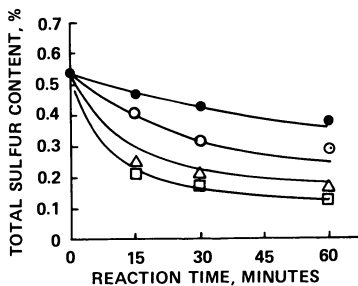


Figure 3. Effect of hydrotreating reaction time on total sulfur content: (—) theoretical curve, (●) 360° C, (○) 385° C, (△) 410° C, (□) 435° C

REACTION CONDITIONS: SEE FIGURE 2
 H_g = AMOUNT OF HYDROGEN (g) IN THE REACTOR AT ANY TIME
 H_{g0} = AMOUNT OF HYDROGEN (g) INITIALLY CHARGED TO THE REACTOR

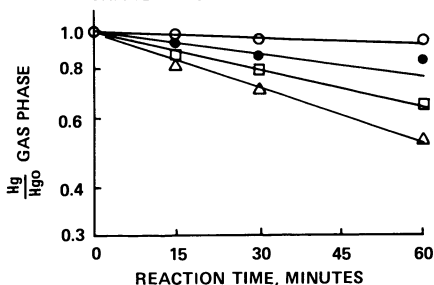


Figure 4. Semilog plot of H_g/H_{g0} vs. time for hydrotreating reaction in the presence of Co-Mo-Al: (—) theoretical curve, (○) 360° C, (●) 385° C, (□) 410° C, (△) 435° C

A numerical search routine was applied to determine the value of K_0 and ΔE . Figure 4 compares the theoretical curve with the experimental data and represents a satisfactory curve fit. The total sulfur content and SRC sulfur content for hydrotreated product were plotted (Figure 5), and a linear relationship was shown to exist between them.

The rate expression for hydrodesulfurization and hydrogenation described above were used to compute selectivity. The optimum process conditions for different SRC sulfur contents (specifically, 0.6, 0.5, and 0.4 percent) were determined. The optimization procedure used is illustrated below for a specified SRC content of 0.5% or a total sulfur content of 0.23% (see Figure 5).

The variation of the calculated total sulfur values versus reaction time and reaction temperature was plotted (Figure 6). A dashed line was drawn at a total sulfur level of 0.23 percent; the region above this line was labelled as being infeasible, because, for a total sulfur content higher than 0.23 percent, the SRC content was more than 0.5 percent. So, the feasible region of search was that below the dashed line. The computed values of selectivity were plotted versus the reaction time and the temperature (Figure 7).

The maximum selectivity for each temperature was found to be located on the dashed curve shown in Figure 7, that is, at the boundary. The maximum selectivity values for each temperature were compared (Table V). The highest temperature and the shortest reaction time used gave the maximum selectivity. The conversion of SRC to oil with reaction time and temperature were plotted also for comparison purposes (Figure 8). As shown in Table V, the highest temperature and the shortest reaction time resulted in the lowest amount of conversion of SRC to oil. Similar analyses were performed for different SRC sulfur contents, and for each case, the highest temperature and the shortest reaction time gave the maximum selectivity and the lowest SRC conversion. A summary of the optimum reaction conditions obtained for different sulfur levels is given in Table VI.

The optimization study discussed above suggests the use of a high temperature and a short-reaction time. Because of the heat-up and cool-down time limitations of the autoclaves used, this study was limited to reaction temperatures $\leq 435^\circ\text{C}$. Verification studies at higher temperatures ($>435^\circ\text{C}$) are required. The present study should be supported by complementary catalyst aging studies to determine the maximum temperature limit below which severe deactivation and aging does not occur.

Figure 5. Relationship between hydro-treated total sulfur content (%) and SRC sulfur content (%)

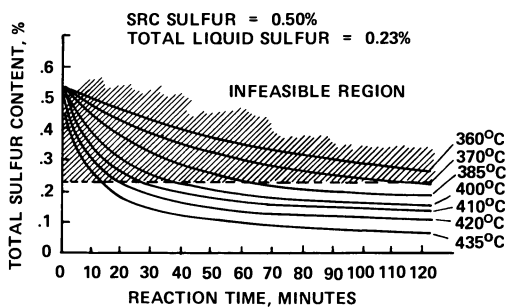
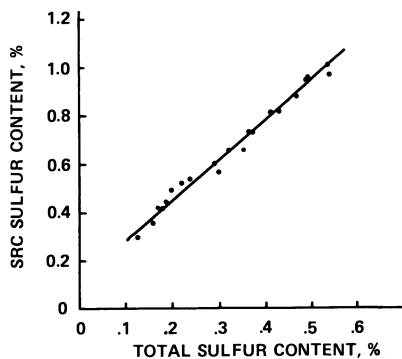


Figure 6. Variation of total sulfur content with reaction time and temperature for hydrotreating reaction

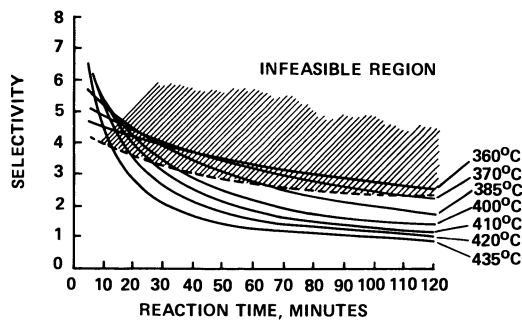


Figure 7. Variation of selectivity with reaction time and temperature for hydro-treating reaction

Table V

Maximum Selectivity at Different Reaction Conditions Meeting 0.5% SRC Sulfur Content

Temp., °C	Time, Min.	Se	Deviation in Se, %	SRC Conversion, % (Estimated from Fig. 8)
370	114	2.50	6.3	>20.0
385	62	2.80	7.5	>20.0
400	38	3.20	7.2	--
410	27	3.50	7.2	20.5
420	20	3.70	7.0	--
435	13	3.85	7.3	19.5

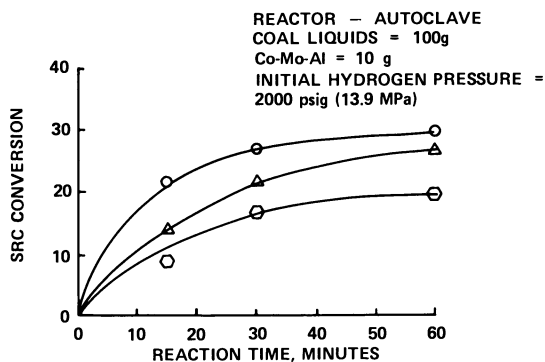


Figure 8. Conversion of SRC with hydrotreating reaction time and temperature: (O) 435° C, (Δ) 410° C, () 360° C

Table VI

Summary of Operating Conditions for
 Various Maximum SRC Sulfur Contents

<u>SRC Sulfur,</u> <u>%</u>	<u>Total</u> <u>Sulfur, %</u>	<u>Temperature,</u> <u>°C</u>	<u>Time,</u> <u>Min.</u>	<u>Se</u>
0.6	0.29	435	7	5.40
0.5	0.23	435	13	3.85
0.4	0.17	435	21	2.80

Conclusions

The proposed NSPS can be met by hydrotreating the coal liquids obtained by filtering the product from the coal dissolution stage. The desulfurization kinetics can be presented by two parallel first-order rate expression, and hydrogen consumption kinetics can be presented by a first-order rate expression. A linear relationship exists between total sulfur content and SRC sulfur content of the hydrotreated product. For the Western Kentucky bituminous #9/14 coal studied here, the maximum selectivity and lowest SRC conversion to oil for a fixed SRC sulfur content are obtained using the highest reaction temperature (435°C) and the shortest reaction time (~7 min.).

Acknowledgements

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A Comparison of the Hydrodesulfurization and Hydrodenitrogenation Activities of Monolith Alumina Impregnated with Cobalt and Molybdenum and a Commercial Catalyst

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In the wake of precarious supplies of petroleum, the need to turn to the abundant reserves of coal as an energy base can hardly be overemphasized. However, to accomplish the objective of using coal extensively, much research effort in the field of converting coal to environmentally clean and convenient fuel is required. The work presented here is so directed and is a part of the research program, at Oklahoma State University, which has the goal of tailoring catalysts for upgrading of liquids derived from coal.

In this study, a novel Monolith alumina structure was of interest as a base (or a carrier) material for Co-Mo-Alumina catalysts. The specific interest centered around assessing the suitability of the catalyst prepared by impregnating the novel alumina support with Co and Mo for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of a relatively high boiling stock. The Monolith catalyst was also tested on a low boiling coal-derived liquid.

Objective

The objective of this work was to study the activity of the Monolith catalyst for removing sulfur and nitrogen from a Synthoil process liquid (heavy stock) and Raw Anthracene Oil (light feedstock), and to make a preliminary assessment of the advantages and/or disadvantages of the Monolith catalyst over a commercial catalyst used in the petroleum industry.

Materials

Feedstocks. The Raw Anthracene Oil was obtained from the Reilly Tar and Chemical Corporation, and the Synthoil liquid from the Pittsburgh Energy Research Center. The properties of these two liquids are given in Table I. The feedstocks were used as received from suppliers without pretreatment. As is clear

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TABLE I
 PROPERTIES OF THE FEEDSTOCKS

	RAW ANTHRACENE OIL	SYNTHOIL LIQUID
	<u>Wt. %</u>	<u>Wt. %</u>
Carbon	90.3	80.5
Hydrogen	5.57	7.72
Sulfur	0.47	1.02
Nitrogen	1.035	1.19
Oxygen	2.625	--
Ash	Nil	3.4
API Gravity	-7	-8.5
<u>Volume Distilled, Percent</u>	<u>BOILING RANGE Vapor Temperature, C(F) at 50 mm Hg.</u>	
10	139 (282)	170 (339)
20	169 (337)	212 (413)
30	186 (367)	260 (500)
40	203 (397)	--
50	215 (419)	--
60	227 (441)	--
70	240 (465)	--
80	256 (493)	--
90	279 (534)	--

from the boiling point ranges of the two liquids, Synthoil is high boiling as compared to the Raw Anthracene Oil. Moreover, the sulfur and ash contents of Synthoil liquid are relatively higher.

Catalysts. The properties of the two catalysts used in this study are given in Table II. The Monolith catalyst was prepared in the laboratory at OSU by impregnating Co and Mo on the Monolith alumina support received from the Corning Glass Company. The Nalco 474 catalyst was received from the Nalco Chemical Company and is a commercial preparation used as a reference catalyst in this study.

Figure 1 shows the pore size distribution of the two catalysts as determined from the mercury porosimeter data. The most frequent pore radius of the Monolith catalyst is 80°A as compared to 33°A of the Nalco 474 catalyst. On the other hand, the surface area of the Monolith catalyst is 92.0 m²/gm as compared to 240 m²/gm of the Nalco 474 catalyst. The chemical compositions of the two catalysts also differ as shown in Table II.

Figure 2 shows the shape and size of the Monolith alumina supports. These are in the form of cylindrical segments of about 2.54 cm in length and about 1.0 cm in diameter. These have longitudinal and parallel channels along their length. The size, shape and thickness of the walls of the channels are also shown in Figure 2. The Monolith structure has about 60 to 80 percent of its cross-sectional area open. Therefore, a bed of regularly stacked Monoliths would offer significantly less pressure drop than that encountered in conventional packed beds. This has been observed by Satterfield and Ozel (1) for a water-air system. Some of the other potential advantages listed are:

- (1) Where intraparticle diffusion appreciably affects the rate of the reaction, reduction in catalyst particle size would be necessary to increase the effectiveness factor and hence conversion. But this may not be possible due to the pressure drop limitations in conventional packed beds. In such situations, the use of Monoliths would provide the advantage of higher effectiveness factor.
- (2) When processing coal derived liquids which contain fine solid particles, the possibility of bed plugging may be minimized.
- (3) The flow of the liquid through regular channels would provide better gas-liquid contact, liquid distribution and wetting of the catalyst.
- (4) The compressive strength of Monoliths would be much higher than the catalyst particles generally used in packed. Therefore, the use of Monoliths would enable deep beds to be constructed without using intermediate supports and gas-liquid distributors.

TABLE II
 PROPERTIES OF THE CATALYSTS

	MONOLITH	NALCOMO 474
	<u>Wt. %</u>	<u>Wt. %</u>
CoO	3.37	3.5
MoO ₃	7.25	12.5
Na ₂ O	--	0.08
Fe	--	0.03
SiO ₂	--	1.5
Support	Alumina	Alumina
Surface Area, m ² /gram	92	240
Pore Volume, cc/gram	0.55	0.46
Most Frequent Pore Radius, °A	80	33
Structure	Open Monolith	Extrudate (8-10 mesh)

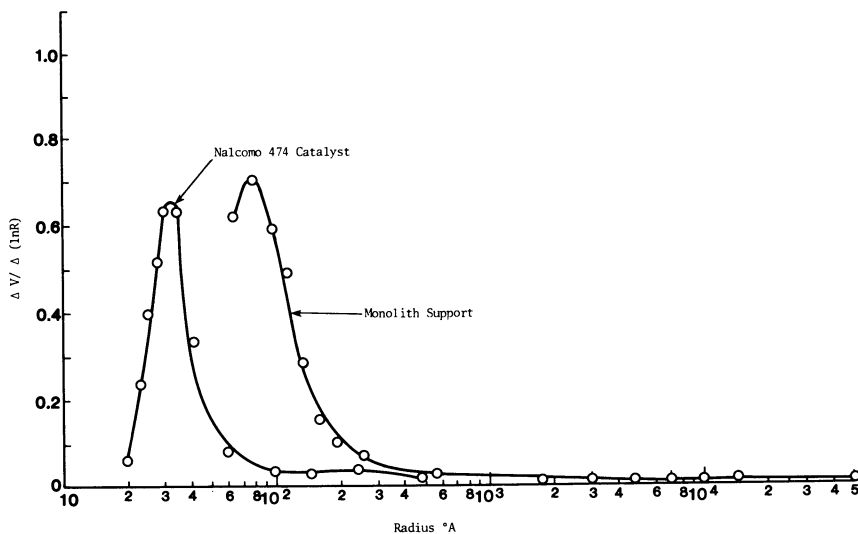


Figure 1. Pore size distribution of the catalysts

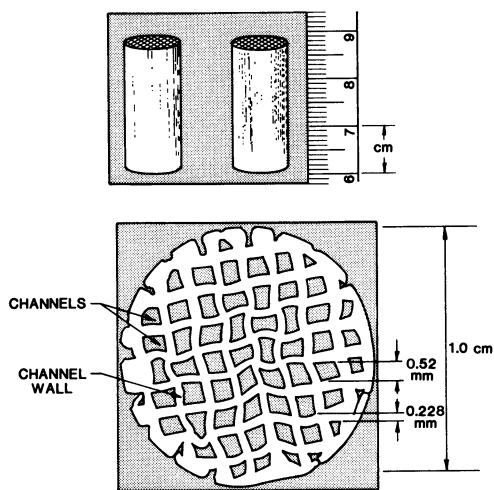


Figure 2. Monolith alumina structure: top, Monolith alumina segments; bottom, cross section of a monolith alumina segment

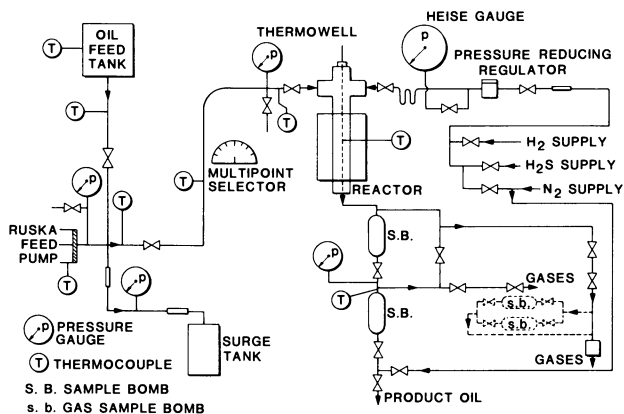


Figure 3. Reactor system

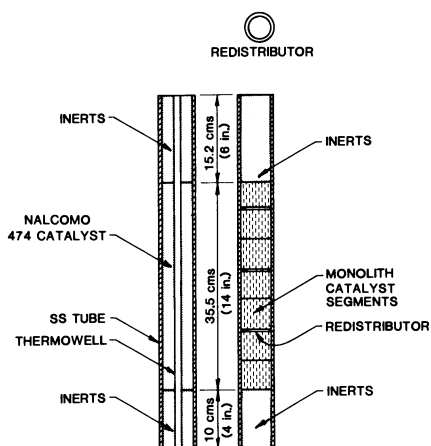


Figure 4. Cross sections of the reactors packed with Nalco 474 and Monolith catalysts

All of the above advantages stem from the special geometry of the Monoliths as compared to that of the usual catalyst particles.

Experimental Setup and Procedure

Reactor System. A trickle bed reactor system was employed in this study - schematic in Figure 3. The reactor was a 12.7 mm O.D. stainless steel tube packed with the catalyst. The catalyst bed height was 35.5 cm. When using Monolith catalysts, redistributors were put at intervals of 10.16 cm each to ensure that the liquid passes through the channels. Figure 4 shows cross-section of the reactor packed with the Monolith and Nalcomo 474 catalysts. The latter catalyst was used in the form of 8-10 mesh (2mm) size extrudate particles.

The reactor was heated by resistance wires wound in massive aluminum blocks placed around the reactor. The reactor temperature was measured at every inch of the catalyst height by traversing a thermocouple in a thermowell placed along the reactor bed. The reactor was operated at nearly isothermal conditions (1.5°C° radial differences).

Method of Operation. The catalyst was activated in the reactor by first calcining at 232.2 C (450 F) and then sulfiding with a mixture of 5.14 volume percent H₂S in H₂. The reactor was then brought to the operating conditions and the flow of hydrogen and oil started. After about 32 hours of operation for catalyst stabilization, representative product oil samples were taken at specified reactor conditions. The product oil samples were analyzed for sulfur and nitrogen contents with the help of a Leco Model 634-700 automatic sulfur analyzer and Perkin Elmer Model 240 elemental analyzer, respectively.

Results

Figures 5 and 6 show the results of this study along with the results of Sooter (2) and Satchell (3) who conducted similar studies using the same experimental set up but with Nalcomo 474 catalyst and Raw Anthracene Oil. The graphs presented here are either sulfur or nitrogen weight percent in the product oil from the reactor vs the volume hourly space time. Of course, low sulfur or nitrogen in the product oil would correspond to higher activity of the catalyst.

The results with each feedstock and catalyst were obtained over a single reactor experimental run lasting 105-132 hours. In each reactor experimental run, the start up reactor conditions were repeated at the end to check for loss, if any, of the catalyst activity. No significant decrease in catalyst activity was observed over the conditions studied.

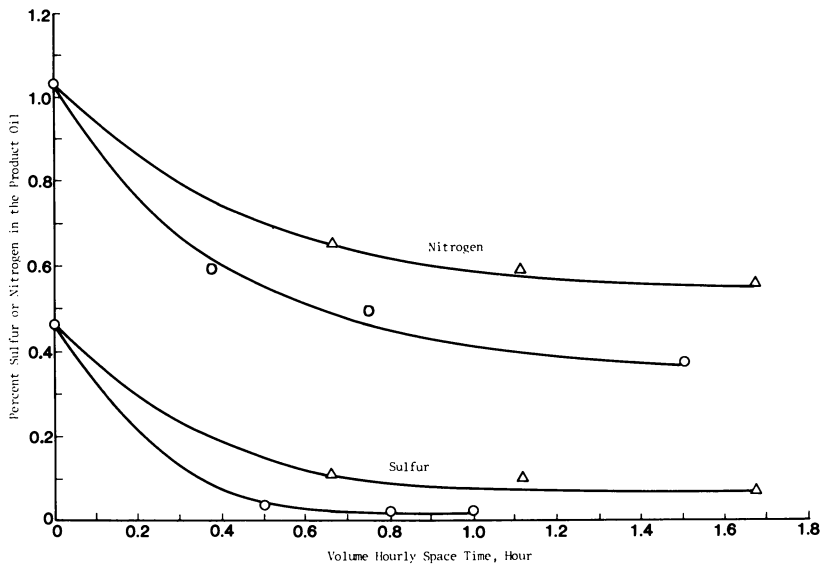


Figure 5. HDS and HDN responses to the changes in the volume hourly space time, raw anthracene oil, 1500 psig, 371° C (700° F): (Δ) Monolith catalyst, (\circ) Nalcomo 474 catalyst

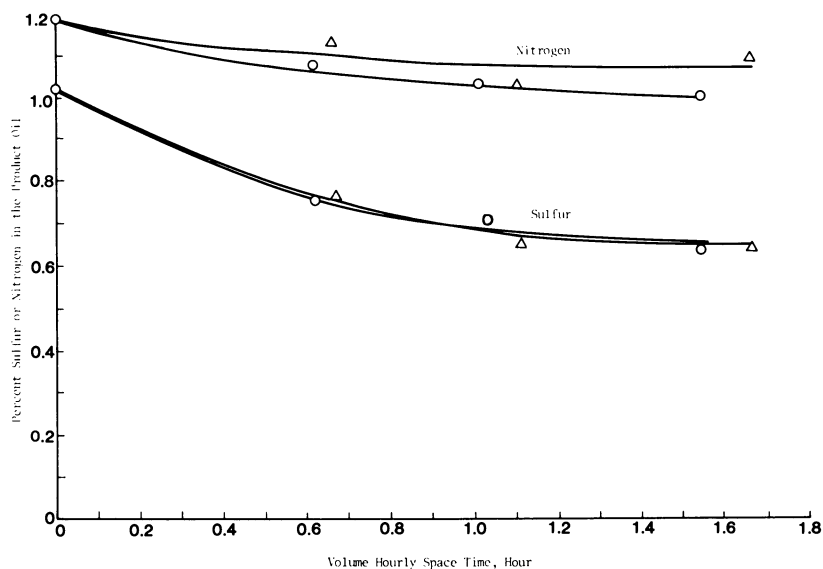


Figure 6. HDS and HDN responses to the change in the volume hourly space time, synhoil liquid, 1500 psig, 371° C (700° F): (Δ) Monolith catalyst, (\circ) Nalcomo 474 catalyst

The precision of sulfur and nitrogen analyses was determined by multiple analysis of Raw Anthracene Oil and Synthoil liquid. The results of sulfur analysis of Raw Anthracene Oil were found to be precise within $\pm 0.25\%$. But the precision of other results was within $\pm 5.0\%$.

Discussion

Figures 7 and 8 show the comparison of the two catalysts on a weight hourly space time (WHST) basis. The reactor operating conditions were 371C (700F) and 1500 psig. The studies of Sooter (2) and Satchell (3) were, however, conducted at 1000 psig. But this difference is not significant as far as comparison of the two catalysts is concerned, because the two studies revealed that pressure beyond 1000 psig had marginal effect on the activities of Nalcom 474 catalyst with the Raw Anthracene Oil as the feedstock. Same was the case when Monolith catalyst was used.

Figures 5 and 7 indicate that on the volume and weight bases, the activity of the monolith catalyst when tested on Raw Anthracene Oil was less than that of Nalcom 474 catalyst. On the other hand, Figures 6 and 8 show that when tested on Synthoil liquid, the desulfurization activities of the two catalysts were approximately the same on a volume basis, whereas on a weight basis, the Monolith catalyst was more effective. The denitrogenation activity of Nalcom 474 was somewhat better even on this feedstock.

Since the surface areas of the two catalysts differed widely, a comparison of activities of the two catalysts on unit surface area basis was made. Figures 9 and 10 represent such a comparison. The abscissa of these graphs is S/Q , where S is the total surface area of the catalyst in the reactor and Q is the volumetric flow rate of oil. S/Q or S/W are quite akin to volume hourly or weight hourly space times. Figure 9 shows that as far as the desulfurization of lighter stock such as Raw Anthracene Oil is concerned, the unit surface activity of the two catalysts is almost the same. But the surface activity towards denitrogenation is higher for the Monolith catalyst than for the Nalcom 474 catalyst.

Figure 10 shows the comparison of the surface activities of the two catalysts on the heavier feedstock, Synthoil liquid. In this case the unit surface area activity of the Monolith catalyst is greater than that of the Nalcom 474 catalyst. This behavior is different from that observed on the Raw Anthracene Oil, and as further discussion will show, this difference in the superiorities of the Monolith catalyst on the two feedstocks throws light on some interesting observations of this study.

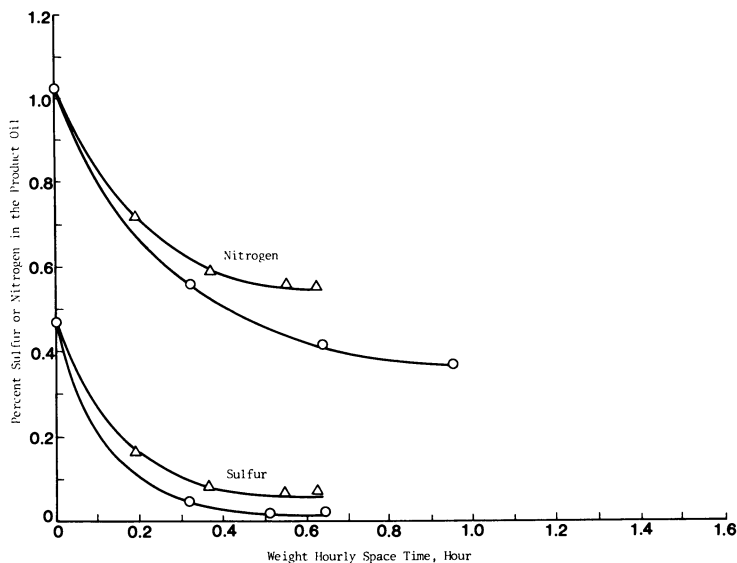


Figure 7. HDS and HDN responses to the change in the weight hourly space time, raw anthracene oil, 1500 psig, 371° C (700° F): (○) Monolith catalyst, (△) Nalcomo 474 catalyst

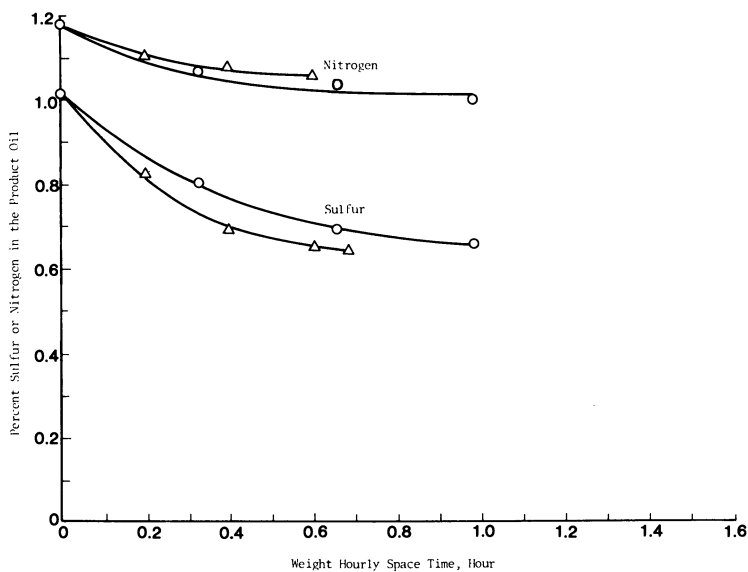


Figure 8. HDS and HDN responses to changes in the weight hourly space time, synthoil liquid, 1500 psig, 371° C (700° F): (△) Monolith catalyst, (○) Nalcomo 474 catalyst

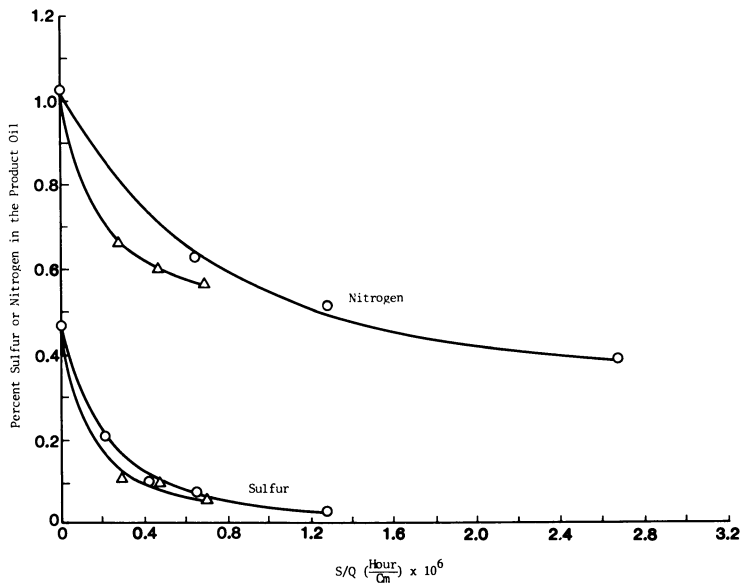


Figure 9. HDS and HDN responses to the change in surface area/volumetric flow rate of oil, raw anthracene oil, 1500 psig, 371° C (700° F): (Δ) Monolith catalyst, (\circ) Nalcomo 474 catalyst

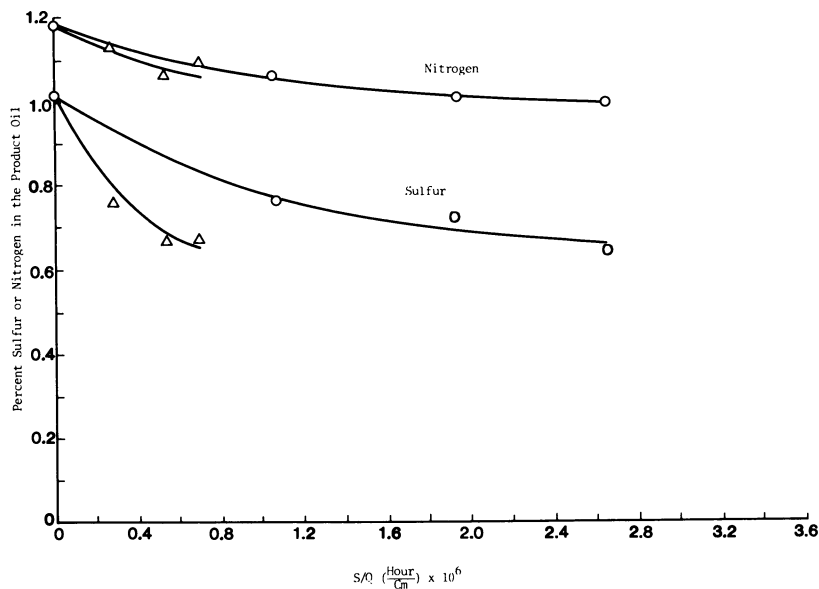


Figure 10. HDS and HDN responses to the change in surface area/volumetric flow rate of oil, synthoil liquid, 1500 psig, 371° C (700° F): (Δ) Monolith catalyst, (\circ) Nalcomo 474 catalyst

To have a quantitative idea of the higher unit surface area activity of the Monolith catalyst, rate constants based on surface area were considered essential to know. To accomplish this, the global reaction kinetics of desulfurization and denitrogenation were determined. For the desulfurization the following three kinetic models, as suggested in the literature, were tested to determine which best represented the data of this study.

(1) Second order; $\frac{1}{C_A} = kt + \frac{1}{C_{A0}}$

- (2) Combination of two first order reactions; one for the lighter and the other for the heavier fractions of the stock

$$\frac{C_A}{C_{A0}} = \alpha e^{-k_1 t} + (1 - \alpha) e^{-k_2 t}$$

where α is the fraction of light or heavy component in the feed.

(3) First order; $\frac{C_A}{C_{A0}} = e^{-kt}$

The second model was discarded because the value of the rate constant k_2 found by non-linear regression of the data was approximately zero which was not considered reasonable on a physical basis. Of the other two models, the second order rate expression was found to fit the data better. For denitrogenation only the first and second order models were examined, and in this case also, the latter model was found to represent the data better.

Table III presents the values of the second order rate constants for the HDS and HDN data. The values of the rate constants for HDS and HDN of Raw Anthracene Oil using Nalcom 474 catalyst were obtained by applying the same non-linear regression analysis technique to the data of Sooter (2) and Satchell (3). The comparison of the rate constants leads one to the same conclusions as shown by Figures 5 and 6.

The rate constant based on surface area, k_s , was calculated from the volumetric rate constants as given in Table III, by using the following equation

$$k_s = k \frac{V}{S}$$

TABLE III
SECOND ORDER RATE CONSTANTS (VOLUMETRIC)

$$k, \frac{\text{Cm}^3}{(\text{Gm.})(\text{Hour})}$$

	Raw Anthracene Oil		Synthoill Liquid	
	Monolith Catalyst	Nalcomo 474 Catalyst	Monolith Catalyst	Nalcomo 474 Catalyst
Desulfurization	8.68	48.8 ^a	0.427	0.431
Denitrogenation	0.724	1.4 ^b	0.084	0.134

^aObtained by the non-linear regression of Sooter's data (2)

^bObtained by the non-linear regression of Satchell's data (3).

where

k = volumetric rate constant, $\frac{\text{cm}^3}{(\text{hour})(\text{gm.})}$

V_r = volume of the reactor, cm^3

S = total surface area of the catalyst, cm^2

The values of k_s calculated for the various values of k are given in Table IV. In the case of Synthoil liquid, the observed surface area rate constants for desulfurization as well as denitrogenation are three to four times higher for the Monolith catalyst than those for the Nalcomo 474 catalyst. This further confirms that the observed surface activity of the Monolith catalyst for treating heavier liquids is much higher than the commercial Nalcomo 474 catalyst. However, in the case of Raw Anthracene Oil, the observed surface area rate constants for desulfurization are about the same for both catalysts and hence they have the same observed surface activity for this lighter feedstock. But the denitrogenation rate constant even on this liquid is higher for the Monolith catalyst than for the Nalcomo 474 catalyst. Thus, the Monolith catalyst seems to have potential superiority over the commercial catalyst used in this study, especially for treating high boiling stocks.

Reasons for the Higher Observed Unit Surface Area Activity of the Monolith Catalyst. There can be three main reasons:

- (1) Intrinsic activity of the Monolith catalyst was higher than that of the Nalcomo 474 catalyst.
- (2) Fluid dynamic effects in the reactor when Nalcomo 474 catalyst was used did not provide efficient solid-liquid contacting.
- (3) There were severe diffusional limitations in the case of Nalcomo 474 catalyst which had a pore radius of 33°A due to which its surface area utilization was low as compared to surface area utilization in the case of the Monolith catalyst which had a pore radius of 80°A .

If one considers that the Monolith catalyst was intrinsically more active than the Nalcomo 474 catalyst then the observed superiority of the Monolith catalyst should be essentially the same, or at least be comparable, when tested on two different feeds. But as explained earlier the observed surface activities of the two catalysts for HDS are almost equal in the case of Raw Anthracene Oil, while, on Synthoil liquid the observed surface activity of the Monolith is about four times that of the Nalcomo 474 catalyst. Therefore, there is some basis to

TABLE IV

SURFACE AREA RATE CONSTANTS, $k_s \frac{(\text{Cm})^4}{(\text{Gm.}) (\text{Hour})}$

	Raw Anthracene Oil	Synthoil Liquid
	Monolith Catalyst	Monolith Catalyst
	Nalcomo 474 Catalyst	Nalcomo 474 Catalyst
Desulfurization	2282	108
	2400 ^a	25
Denitrogenation	190	24
	81 ^b	8.5

^a Corresponds to the volumetric rate constant obtained using Sooter's data (2).

^b Corresponds to the volumetric rate constant obtained using Satchell's data (3).

believe that the Monolith catalyst used in this study was not intrinsically more active than the Nalcom 474 catalyst as far as the HDS was concerned.

In previous studies, Sooter (2) and Satchell (3) observed that reducing the particle size of the Nalcom 474 catalyst from 8-10 mesh to 40-48 mesh did not have any significant effect on the desulfurization and denitrogenation of Raw Anthracene Oil under similar experimental conditions as employed in this study. This suggests that the fluid distribution and hence the fluid dynamic effects, were not important in the trickle bed reactors as operated for this work. If these effects were important then the reduction in particle size should increase conversion of the HDS and HDN by improving fluid distribution and reducing the intraparticle diffusion resistances.

Under the likelihood that the first two reasons do not explain the results of this study or are not important in the present context, intraparticle diffusion limitations appear to be responsible for differentiating the activities of the two catalysts. Table I shows that the Synthoil liquid is a high boiling liquid as compared to Raw Anthracene Oil. This means that the molecules that constitute Synthoil liquid are larger on the average than the molecules that constitute the Raw Anthracene Oil. Therefore the smaller pore radius, 33 μ A, of the Nalcom 474 catalyst and its longer diffusion path, which is the radius of the catalyst particle (about 1 mm) would offer higher intraparticle diffusion resistance to Synthoil molecules than to the Raw Anthracene Oil molecules. This would severely limit surface area utilization of Nalcom 474 on Synthoil liquid but not as much on Raw Anthracene Oil. Therefore observed unit surface area activity of Nalcom 474 catalyst on Synthoil would be lowered appreciably as compared to the lowering of the activity of the same catalyst on Raw Anthracene Oil. On the other hand, pores of the Monolith catalyst are approximately two and a half times larger than the pores of the Nalcom 474 catalyst. The diffusion path is only 0.114 mm, half the thickness of the channel wall. This is 1/9 times the diffusion path length of the Nalcom 474 catalyst. Thus the Monolith catalyst would offer much less diffusion resistance to Synthoil molecules than that offered by the Nalcom 474 catalyst. Therefore, the percent surface area utilization of the Monolith catalyst would be much higher than the percent surface area utilization of the Nalcom 474 catalyst. But the larger pore size and smaller diffusion length of the Monolith catalyst could not have any advantage when a lighter feedstock, Raw Anthracene Oil, is processed. Recall that Sooter (2) and Satchell (3) showed that this feedstock does not have significant diffusion problems with the Nalcom 474 catalyst.

Thus intraparticle diffusion was likely responsible for showing higher activity, on unit surface area basis, of the Monolith catalyst when processing the Synthoil liquid.

To have a quantitative idea of the problem of intraparticle diffusion, effectiveness factors for the two catalysts were calculated from the observed second order rate constants (based on surface area) using the "triangle method" suggested by Saterfield (4). The effectiveness factors for Monolith and Nalcom 474 catalysts on Synthoil liquid at 371°C (700 F) were calculated to be 0.94 and 0.216, respectively. In applying the relationship between the "Thiele Modulus," ϕ , and the "effectiveness factor," η , the following simplifying assumptions were made:

- (1) The shape of the catalysts does not appreciably affect the effectiveness factor. Emig and Holfman (5) have shown that the greatest difference between the effectiveness factors of such diverse shapes as sphere and infinite plate remain within 10%. Therefore, if effectiveness factor is known for one catalyst shape, it can be used for other forms with slight error.
- (2) The average pore radius of a catalyst particle is the average of the dominant pore radii as observed from the frequency plot of the catalyst.
- (3) If intrinsic activities of two catalysts are equal on one feedstock, they would be equal on another feedstock also.
- (4) The diffusion of the sulfur molecules in the pores of the catalyst would be assumed to be mainly influenced by molecular diffusion. This type of diffusion generally occurs in the liquid phase. Since the same liquid was used in both the cases, the coefficient of diffusion would be assumed to be the same.

The effectiveness factors calculated in this study are under the experimental conditions utilized in this study and give an idea of the magnitude of pore diffusion problem in the case of the Nalcom 474 catalyst when Synthoil liquid is processed. On the other hand, the Monolith catalyst shows promise in this regard and warrants further investigation regarding its activity under different compositions of the catalyst and different reactor operating conditions.

Abstract

The hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities of two Co-Mo-alumina catalysts were tested on two coal derived liquids using a trickle bed reactor system. The two liquids used were; Synthoil liquid (high-boiling stock) and Raw Anthracene Oil (low-boiling stock). One of the two catalysts was prepared in the laboratory at Oklahoma State University by

impregnating Co and Mo on the Monolith alumina supports received from the Corning Glass Company. The other catalyst used was Nalcom 474 (a commercial preparation) received from Nalco Chemical Company (now Katalco).

The results of this study indicated that at the reactor operating conditions of 371 C and 1500 psig, the observed HDS activity based on unit surface area was higher for the Monolith catalyst as compared to the Nalcom 474 catalyst when processing the heavier feedstock, Synthoil liquid. But HDS activity was about the same when processing the lighter feedstock, Raw Anthracene Oil. Since the average pore radius and the intraparticle diffusion length of the Monolith catalyst were 80°A and 0.114 mm versus 33°A and 1 mm of the Nalcom 474 catalyst, the intraparticle diffusion was considered to be responsible for the lower observed activity of the Nalcom 474 catalyst on the heavier feedstock. From the observed rates of reaction, the effectiveness factors for the Monolith and Nalcom 474 catalysts were found to be 0.94 and 0.216 respectively for the HDS of Synthoil.

Acknowledgments

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The Thermal Cracking of Coal-Derived Materials

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Many of the feedstocks for the chemical industry, especially aromatic hydrocarbons, were originally obtained as by-products from the carbonization of coal. (1,2) However, nowadays, most of these chemical feedstocks are derived from petroleum. Nevertheless, it is probable that, within the next few decades, the shortage of world reserves of petroleum will mean that BTX will once again have to be produced from coal, as will ethylene. It is, therefore, appropriate to examine ways in which these materials can be produced from coal; the present investigation was designed to study the formation of BTX and ethylene by the thermal cracking of coal-derived materials from the NCB coal liquefaction/hydrogenation processes. (3)

Experimental

Feedstocks - The vapors from the carbonization of a bituminous, low-rank coal, an anthracene oil, and a coal extract in anthracene oil were diluted with nitrogen and cracked; their product yields were compared with those from the cracking of a partially hydrogenated anthracene oil and coal extracts hydrogenated to various extents. The coal was Linby (National Coal

Board, Coal Rank Code 802), and the extract was prepared by digestion at 673°K and 8 bar in anthracene oil, filtration to remove mineral matter and dissolved coal, followed by distillation under reduced pressure until the extract contained about 70% coal. The two coal extract hydrogenates were prepared by catalytically reducing a dilute extract from Annesley (NCB, CRC 702) coal in a trickle bed reactor and fractionating the product. The fractions were further reduced in a vapor phase reactor to give two highly hydrogenated liquids.

Four model compounds, n-undecane, tetralin, cis/trans decalin and mesitylene, and a natural gas condensate from the North Sea were also cracked. Analyses and the reference code key of the coal-based feedstocks and the gas condensate are given in Table 1. Paraffin, naphthene, and aromatic-type analyses were calculated from gas chromatographic analyses of the partially hydrogenated anthracene oil and gas condensate; whereas, mass spectrometric analysis was performed on the two coal extract hydrogenates and their further hydrogenated products.

Apparatus and Procedure - The experiments with the solid feedstocks and the initial experiments on liquid samples were carried out in the apparatus shown in Figure 1A. The vapors from a stainless steel, stirred-bed carbonizer/vaporizer at 873°K were cracked at atmospheric pressure in a tube reactor heated in a platinum-wound furnace. The reactor was 30 mm ID and had a 100 mm long hot zone within 20°K of the maximum reactor temperature. Solid feedstocks were introduced at about 1 g min.⁻¹ from a vibratory table through a water-cooled port. Liquids were injected at the same point from a mechanically driven syringe at 0.1-0.8 ml min.⁻¹. The amount fed was determined by weighing the feeders.

Liquid products were collected in two glass traps at 258°K and in a glass wool filter. The gas was measured in a dry gas meter and sampled over mercury into glass bottles. The reactor and collection train were weighed and the liquids removed with a known amount of chloroform. The effects of vapor residence time and cracking temperature on the product yields from each feedstock were investigated. The effects of variables such as reactor surface, type and area, feedstock vapor concentration, and the addition of steam was also tested over a limited range of conditions with a hydrogenated coal extract. Gaseous and liquid products were analyzed by chromatography.

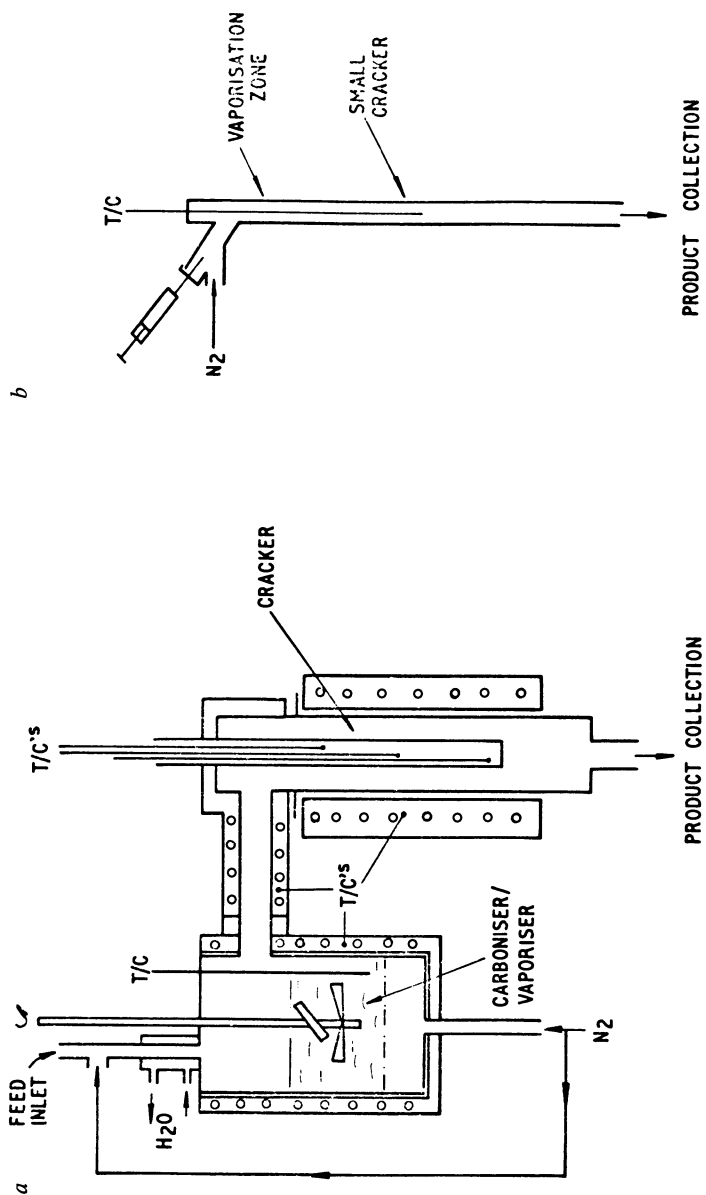


Figure 1. Thermal cracking apparatus: a, carbonizer/vaporizer/cracker; b, small vaporizer/cracker

Table 1 Analyses of Feedstocks

SOLID FEEDSTOCKS	KEY	SIZE, μm	PROXIMATE ANALYSIS, % W/W			ULTIMATE ANALYSIS, % W/W d.a.f.						H/C ATOMIC RATIO
			MOISTURE, a.d.	ASH, a.d.	V.M., d.a.f.	C	H	O	N	S		
Linby coal	A	210 to 350	8.3	6.0	39.1	82.4	5.3	9.0	1.95	1.00	0.77	
Anthracene oil extract of Linby coal	B	210 to 350	0.3	0.3	50.5	88.7	4.8	3.8	1.90	0.55	0.65	
LIQUID FEEDSTOCKS			HYDROCARBON ANALYSIS, % W/W									
		DISTILLATION RANGE, K	PARAFFINS	NAPHTHENES	AROMATICS + HYDROAROMATICS							
Anthracene oil	C	573 to 673	N.D.	N.D.	N.D.	90.6	6.9	1.9	0.6	0.55	0.91	
Partially hydrogenated anthracene oil	C1	IBP to 503	1.7	20.7	64.4	88.2	10.7	0.5	0.4	<0.1	1.46	
Hydrogenated coal extracts	D	443 to 523	0	28.5	71.5	89.4	10.1	0.7	0.25	0.1	1.36	
	E	523 to 573	0	23.7	76.2	89.6	9.4	N.D.	N.D.	N.D.	1.26	
Further hydrogenated coal extracts	D1	443 to 523	0	95.5	2.2	86.4	13.2	0.5	<0.1	<0.1	1.83	
	E1	473 to 573	0	90.7	6.9	86.9	13.0	N.D.	N.D.	N.D.	1.78	
Gas condensate	F	IBP to 623	56.0	11.9	14.0	85.1	14.4	<0.2	<0.1	<0.1	2.03	

N.D. = Not Determined

Later, experiments with the hydrogenated feedstocks, which were completely vaporizable, were performed by injecting the liquids into the top of the smaller reactor (9 mm ID) shown in Figure 1B. The liquid feed rate was only a tenth of that required for the larger apparatus; the furnace and collection systems were similar. Comparative tests with *cis/trans* decaline and hydrogenated anthracene oil showed that the smaller reactor gave marginally high BTX and ethylene yields than the larger reactor.

Results

The Effect of Surface, Reactant Concentration, and Diluent - Results from the cracking of a hydrogenated coal extract similar to (D) in the larger reactor with and without copper or stainless steel packing, which increased the surface area about threefold while decreasing the reactor volume by only 10%, showed that neither copper nor stainless steel significantly affected the yields of BTX and ethylene. An eight-fold reduction in the concentration of the feedstock vapor (at constant vapor residence time) also had no significant effect. Replacement of part of the diluent nitrogen to give a 70% steam plus 30% nitrogen mixture had a negligible effect on the yields of BTX and ethylene, although xylenes were favored at the expense of benzene.

Unhydrogenated Coal-Derived Materials - Preliminary experiments on cracking the vapor from coal extract (B) at 1133°K for 0.7-8 s showed that the BTX yield peaked at 2 s; whereas, ethylene was favored by shorter residence times. Figure 2 shows the effect of cracking temperature at 2 s vapor residence time on the yields of BTX, benzene, and ethylene from Linby coal (A), coal extract (B), and anthracene oil (C). Yields of BTX and benzene peaked at about 1273°K; whereas, the maximum ethylene yields were obtained at about 1100°K. The mass balances and yields of the gaseous and liquid products at one condition, 1273°K for 2 s, are given in Table 2.

The yields of BTX and ethylene are low, less than 3.5% BTX and 1.5% ethylene: the highest yields were from Linby coal. Although the BTX yields are greater than the 1% from conventional, high temperature coal carbonization (2), they are only a fraction of those obtainable from petroleum feedstocks. (4)

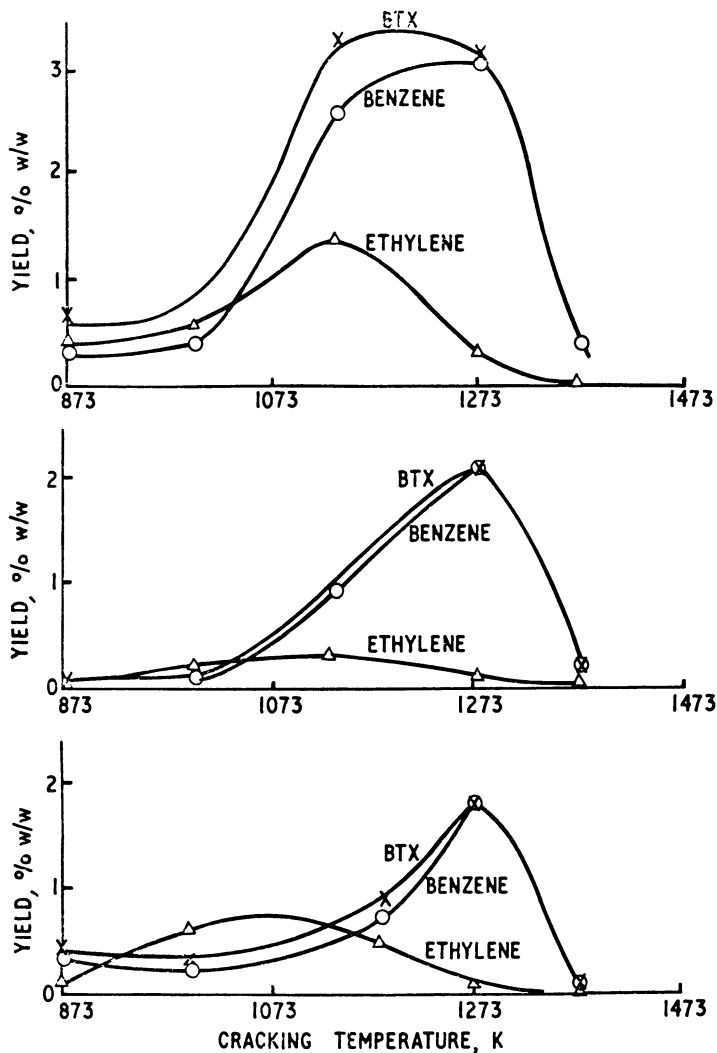


Figure 2. Effect of cracking temperature on yields from unhydrogenated coal-derived materials: top, Linby coal; middle, anthracene oil extract of Linby coal; bottom, anthracene oil; carbonizer temperature, 873 K; vapor residence time, 2 s; nitrogen diluent

Hydrogenated Coal-Derived Materials - The yields from the partially hydrogenated anthracene oil (C1), two coal extract hydrogenates (D and E), and their further hydrogenated products (D1 and E1) when cracked at 1133°K, which favored ethylene formation, are listed in Table 2, together with the yields from the gas condensate at 1158°K. The BTX benzene and ethylene yields from the two further hydrogenated materials (D1 and E1) are plotted against cracking temperature in Figure 3.

Table 2 shows that the parent hydrogenates (D and E) gave relatively low yields of BTX and ethylene (<10%); whereas, considerable yields of polynuclear aromatics such as naphthalene, methyl naphthalenes, acenaphthylene, fluorene, anthracene, and phenanthrene were obtained. In contrast, the further hydrogenated materials (D1 and E1) gave high yields of BTX and ethylene (<20%) and relatively low yields of polynuclear aromatics. The highest yields of BTX, 27% at 1083°K for 1 s and at 1108°K for 0.4 s, and of ethylene, 24% at 1158°K for 0.4 s, were both obtained from D1. The curves in Figure 3 for a vapor residence time of 0.4 s show broad maxima in BTX and ethylene yields; similar maxima were obtained at 1 s and 2 s but at slightly lower cracking temperatures.

The yields from the partially hydrogenated anthracene oil (C1), also given in Table 2, are relatively low, little more than 10% BTX and ethylene being obtained.

Natural Gas Condensate - To compare the yields from coal-derived materials with those from a petroleum material, a full range, North Seal gas condensate (F) was cracked at 1158°K for 0.4 s. Its analysis is given in Table 1, and the yields obtained are listed in Table 2. More ethylene (30%) but less BTX (16%) were produced than from the highly hydrogenated coal materials.

Model Compounds - Four model compounds (mesitylene for aromatics, tetralin for hydroaromatics, decalin for naphthenes, and n-undecane for paraffins) were cracked singly and as mixtures at 1133°K for 1 s. The yields of BTX, ethylene, butadiene, and methane are shown as a bar chart in Figure 4. Decalin gave the highest BTX yield, 25%, compared with less than 7% from n-undecane. Mesitylene gave only 8% BTX. Tetralin produced the least BTX, 3%, its major products being polynuclear aromatics. n-Undecane gave 37% ethylene compared to 20% from decalin, 3% from tetralin, and 0.2% from

Table 2 Yields (% w/w) from Cracking

Cracking Temperature, K	1273			
Vapour Residence Time, s	2.0			1.0
Feedstock	Linby coal*	Anthracene Oil Extract of Linby coal*	Anthracene oil	Partially hydrogenated anthracene oil
	A	B	C	C1
<u>Product</u>				
Benzene	3.1	1.8	2.1	6.6
Toluene	0.1	<0.1	<0.1	2.7
Xylenes	<0.1	<0.1	<0.1	1.3
Total BTX	3.2	1.6	2.1	10.6
CH ₄	4.3	2.6	2.7	8.2
C ₂ H ₆	0.2	<0.1	<0.1	0.8
C ₂ H ₄	0.3	0.1	0.09	10.8
C ₂ H ₂	N.D.	N.D.	N.D.	0.3
C ₃ -C ₄ sats.	0.4	0.1	<0.1	<0.1
C ₃ -C ₄ unsats.	<0.1	<0.1	<0.1	1.8
H ₂	1.3	1.0	1.3	1.2
CO	7.8	1.7	1.6	0
CO ₂	3.8	0.4	0.4	0
Indene	<0.01	<0.01	<0.01	1.3
Naphthalene	0.3	0.2	1.4	19.5
Methyl Naphthalene	<0.01	<0.01	<0.01	3.1
Diphenyl	0.03	0.01	<0.01	1.1
Acenaphthylene	0.08	0.06	0.07	1.8
Fluorene	0.01	<0.01	0.07	0.5
Anthracene and Phenanthrene	0.2	0.2	1.7	1.4
Fluoranthene	0.06	0.2	0.4	<0.01
Pyrene	0.06	0.2	0.4	0.5
<u>Mass Balance</u>				
Gas	21	13	8	28
Liquid/Tar	17	15	56	46
Solid	61	72	23	10
Total	99	100	87	84

* Carbonisation temperature 873 K

Coal-Derived Feedstocks and a Gas Condensate

1133				1158
0.4				
Hydrogenated coal extract D	Hydrogenated coal extract E	Further hydrogenated coal extract D1	Further hydrogenated coal extract E1	Gas condensate F
3.5	2.5	17.1	13.6	11.9
1.9	1.3	5.3	5.1	2.5
1.7	1.1	3.0	2.8	1.7
7.1	4.9	25.4	21.4	16.1
6.4	5.5	12.0	10.8	13.4
1.0	0.8	1.5	1.7	1.7
9.1	7.6	23.1	21.5	30.3
0.1	0.1	0.4	0.3	0.7
0.05	0.05	0.1	0.1	0.2
3.4	2.7	7.9	10.6	11.2
1.1	0.9	1.3	1.2	1.0
0	0	0	0	0
0	0	0	0	0
3.4	2.2	1.9	1.8	0.8
23.5	15.6	4.6	5.3	2.0
7.9	8.6	1.3	2.5	0.6
3.3	4.1	0.4	0.3	0.3
3.9	5.1	0.9	1.3	0.4
0.5	2.2	0.3	0.3	0.2
0.4	6.0	0.9	0.2	0.2
0.3	0.2	< 0.01	0.1	< 0.01
0.3	0.3	< 0.01	0.4	< 0.01
24	20	58	57	70
69	82	29	31	13
10	5	11	5	11
103	107	98	93	94

N.D. Not Determined

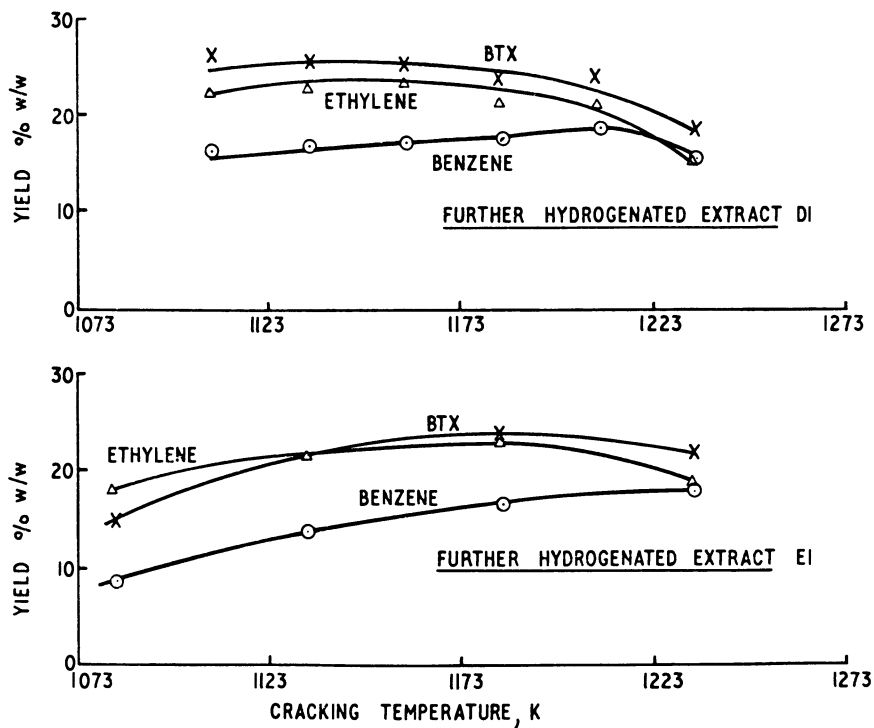


Figure 3. Effect of cracking temperature on yields from further hydrogenated extracts D1 (top) and E1 (bottom): (X) BTX, (Δ) ethylene, (\odot) benzene; vapor residence time, 0.4 s; nitrogen diluent

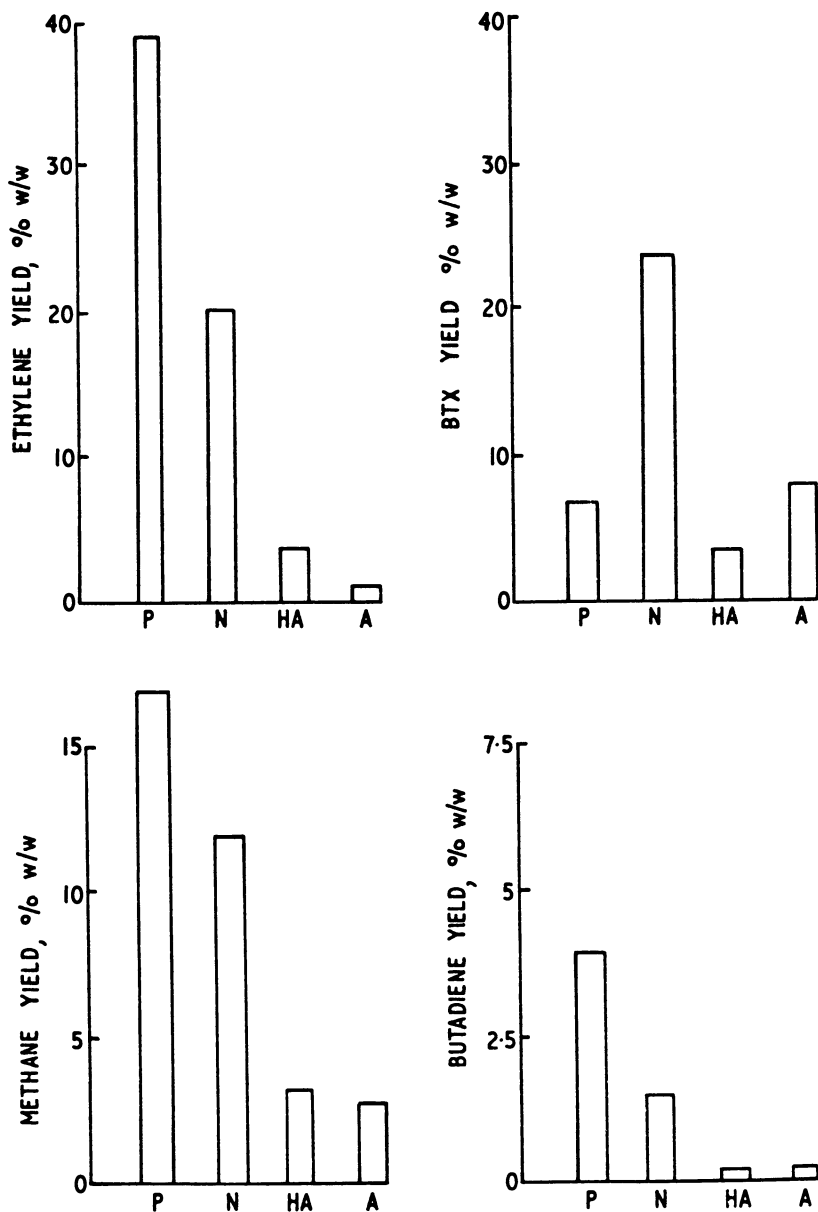


Figure 4. Variation of yields with hydrocarbon type: P = paraffin (n-undecane), N = naphthalene (cis/trans decalin), HA = hydroaromatic (tetralin), A = aromatic (mesitylene); cracking temperature, 1133 K; vapor residence time, 1 s

mesitylene. Six binary, four ternary, and the quaternary mixtures of the four compounds were cracked, and the observed product yields were within +2% of the values calculated from the constituents' yields.

Discussion

The low yields of BTX and ethylene from the unhydrogenated feedstocks reflect the stability of the condensed aromatic structures which constitute much of their volatiles and confirm the findings of a literature review. (5) It is interesting that the coal extract (B), which contained 70% coal, yielded even less BTX and ethylene than the coal itself; this is probably due to elimination of reactive constituents and cross-linking during digestion/extraction of the coal.

Yields of BTX and ethylene increased with increasing extent of hydrogenation of coal extract, as indicated by the H/C ratios listed in Table 1. This was reflected in their naphthene contents, which were in the order D1 > E1 > D > E, and confirms the finding (6) that polynuclear aromatic hydrocarbons need to be fully hydrogenated to the naphthenic structure to maximize their conversion to BTX and ethylene. Concomitantly, the yields of tar and polynuclear aromatics decreased with decrease in the (hydroaromatic plus aromatic) content of the feedstock, suggesting that the higher aromatics result from the dehydrogenation of hydroaromatics to the parent aromatics and from the survival of those aromatic hydrocarbons already present. 34% of C₂-C₄ gaseous hydrocarbons (C₂H₆, C₂H₄, C₃-C₄ unsaturates and saturates) were obtained from E1 at 1133°K for 0.4 s (up to 17% C₃-C₄ unsaturates were obtained at a lower cracking temperature of 1083°K). The sum of BTX plus valuable gaseous hydrocarbons amounted to 55% at 1133°K, 60% at lower temperatures.

Some acetylene and polyacetylenes, which are undesirable, explosive by-products, were also formed. The amount increased with the severity of cracking but was only 2.5% of the maximum ethylene yield; this value is about that found in the industrial cracking of petroleum naphtha to ethylene. (7,8)

Cracking temperature and vapor residence time were the most important parameters controlling the cracking reactions. Within the range of conditions tested, other variables such as type and area of cracking surface, the vapor concentration of the feedstock and presence of steam made little difference to the yields of BTX and ethylene. Steam is used as a diluent and

carrier in industrial ethylene crackers, where it reduces carbon laydown in the reactors. (9)

The aromatic and hydroaromatic components of coal-derived feedstocks are potential sources of carbon laydown, and steam would be needed to reduce reactor fouling.

The high ethylene and moderate BTX yields from the gas condensate are commensurate with its 56% paraffin and 12% naphthene content. (See Table 1.) This was confirmed by the 37% ethylene and 7% BTX obtained from the model paraffin, n-undecane. (See Figure 4.)

The model compound studies confirmed that the molecular structure of the hydrogenated coal extract is of paramount importance in determining the product pattern: hydroaromatics dehydrogenate to aromatics, which either survive or polymerize to tars and, eventually, to carbon; naphthenes crack principally to BTX and ethylene; aliphatics mainly give small unsaturates such as ethylene and butadiene. The abnormally low yield of BTX from mesitylene is attributed to its high symmetry and thermal stability.

Conclusions

The results from the thermal cracking of unhydrogenated and hydrogenated coal-derived materials, a gas condensate, and model compounds led to the conclusions that:

1. Only low (<3.5%) BTX and ethylene yields were obtained by cracking the vapors from a bituminous coal, an anthracene oil, and the anthracene oil extract of the coal.
2. The BTX and ethylene yields increased with increasing extent of hydrogenation of the extract (which increased the naphthene content); tar was mainly derived from the aromatic and hydroaromatic components.
3. About 27% BTX and 24% ethylene were obtained from the highly hydrogenated coal extract; in comparison, a paraffinic North Sea gas condensate gave 16% BTX and 30% ethylene.
4. The product yields from mixtures of model compounds were predicted to within +2% from those of the constituents.

Acknowledgment

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Abstract

Up to 27% benzene, toluene, xylenes (BTX), and 24% ethylene were obtained by cracking a highly hydrogenated coal extract, compared to less than 4% of each from unhydrogenated coal, coal extract, and anthracene oil. The importance of naphthenes as BTX and ethylene precursors was confirmed.

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Liquid Sulfur Dioxide as an Agent for Upgrading Coal Liquid

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One approach to the processing of coal-derived liquid is to utilize advanced petroleum refining technology. The physical and chemical characteristics of coal liquid currently produced by pilot plants differ from those of petroleum crude. Although various coals may appear different, there is a striking similarity in the nature of major chemical species present in the coal liquids from different sources. Analytical data (1-8) on various coal liquids and various distillation cuts show that coal liquids are composed of bulk species such as straight chain hydrocarbons, 'asphaltenes', (the term 'asphaltene' is used for the coal liquid fraction which is nonvolatile but soluble in tetrahydrofuran and SO_2 currently), one or two ring alkylated aromatics (alkylated benzenes, indans and naphthalenes), and phenols (alkylated phenols, indanols and naphthols). Straight chain hydrocarbons include slightly branched hydrocarbons such as pristane and phytane and long chain monoolefins. The concept of using sulfur dioxide for refining coal liquid is very attractive due to the fact that sulfur is going to be one of the large byproducts of any coal conversion technology. Liquid sulfur dioxide is a very good solvent for most of the bulk species in any coal liquid, except for saturated hydrocarbons. Coal liquefaction technology is costly due to several factors including consumption of large quantities of hydrogen to liquefy coal. The recovery of saturated hydrocarbon, the hydrogen rich fraction, from the coal liquid has important economic interest.

Experimental

Since liquid sulfur dioxide boils at -10.2°C the extraction can be conducted at atmospheric conditions. The liquid sulfur dioxide is obtained by cooling the gas from the cylinder using a Dry Ice acetone bath. When a coal liquid (usually in a waxy state) is treated with liquid sulfur dioxide, the insolubles remain with the minerals and the coal fragments as a solid residue. The SO_2 -solubles are separated from the insolubles by filtration. The filtrate is

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degassed to remove SO₂ from the SO₂ solubles. The hydrocarbons in the SO₂-insoluble residue are separated from the mineral and coal fragments by Soxhlet extraction with tetrahydrofuran (THF - additive free). Both SO₂-solubles and the THF extract of SO₂-insolubles were separated by gel permeation chromatography (GPC). The details of the GPC separation technique is published elsewhere (7). The GPC system uses four 100 Å μ Styragel columns (total length: 120 cm.) and THF (dry, additive free) as the liquid mobile phase. Two hundred μ l of 50% THF solutions of the SO₂-solubles were separated into four fractions by GPC. Since the preliminary tests revealed that the THF extract of the SO₂ insolubles is mostly saturated hydrocarbons and other major bulk species are absent, the GPC did not play a significant role in the separation except to remove the gas chromatographic nonvolatiles from the sample, as they belong to larger linear molecular size. The GPC fractions 1 and 2 of the SO₂-solubles are gc-nonvolatiles and they cannot be analyzed by gas chromatography - mass spectrometry (GC-MS). All other fractions were analyzed by GC-MS. Proton nuclear magnetic resonance (nmr) and infra-red (ir) are used for analyzing nonvolatiles. The elemental composition and BTU values are determined by the Center for Trace Characterization of Texas A&M University and by the Galbraith Laboratories, Knoxville, Tenn.

Results and Discussion

Liquid sulfur dioxide was used to separate two coal liquids produced from West Virginia subbituminous coal and North Dakota lignite. The samples were obtained from the pilot plant at the Pittsburgh Energy Technology Center where the solvent refined coal (SRC) process was used for the liquefaction. Since the liquid sulfur dioxide separation of saturated hydrocarbons from the coal liquid worked equally well for both coal liquids, only the separation of the SRC from West Virginia subbituminous coal is discussed in detail for the analytical evaluation of the SO₂ separation. Figure 1 is the GPC of SRC from the subbituminous coal. The components of the coal liquid are separated in the order of decreasing linear molecular size. (GPC is used for molecular weight determinations as well as for molecular size determinations. Our unpublished GPC data on a number of compounds such as normal alkanes, amines, alcohols, multi-ring aromatics and etc. shows that the retention volume is a function of the length of the molecule rather than molecular volume or any other molecular size parameter. Therefore, the authors think that it is quite appropriate to say that GPC separations are on the basis of linear molecular size rather than just molecular size.) For analytical convenience the effluents from the GPC were collected as four fractions. Fraction 1 is composed of high molecular weight species which are nonvolatiles for gc separation. Fraction 2 is composed of saturated hydrocarbons, which could be separated and identified by GC-MS and 'asphaltenes', a mixture of high molecular weight

species which have linear molecular sizes comparable to straight chain alkanes in the range $n\text{-C}_{14}\text{H}_{38}$ to $n\text{-C}_{44}\text{H}_{90}$. Vacuum distillation separates the nonvolatile asphaltenes from the volatile alkanes. Fraction 3 is composed mostly of phenols which have an 'effective linear molecular size' of normal alkanes ranging from C_7H_{16} to $\text{C}_{13}\text{H}_{28}$. Each molecule of phenol has a tendency to hydrogen bond with one molecule of THF which results in an increase in effective linear molecular size by 3 to 4 linear carbon units (propane to butane size). Fraction 4 consists mostly of aromatics. In a nonhydrogen bonding system such as toluene both phenols and aromatics will have similar molecular sizes. Hence, they could not be separated by GPC using toluene as the mobile liquid phase.

Figure 2 is the GPC of SO_2 -solubles of SRC from subbituminous coal. As in the case of the sample in Figure 1, the GPC effluent was collected as four fractions. After SO_2 extraction, the GPC areas of fraction 1 and 2 have decreased and the analysis of fraction 2 of the SO_2 -solubles does not show the presence of any alkanes. Elemental analysis of fraction 2 following the evaporation of all the THF shows the following composition

C	H	S	N	O
83.79%	7.39%	3.96%	1.64%	3.22% (by diff.)

The proton nmr spectrum of fraction 2 of the SO_2 -solubles resembles that of asphaltenes as reported by other workers (1). The elemental composition and the GPC size distribution agrees with the values published for coal derived asphaltenes (1,3). Fractions 3 and 4 of the SO_2 -solubles were separated and identified by GC-MS (see Figures 4 and 5). These fractions contain only a small amount of alkanes. The components are listed in Tables I and II.

Figure 3 shows the GPC of the THF extract of the SO_2 -insolubles. The GC-MS of the THF extract is shown in figure 6 and the components are listed in Table III. The THF extract is free of any phenols or aromatics and contains only straight chain hydrocarbons showing the insolubility of straight chain hydrocarbons, as well as branched saturated hydrocarbons in liquid SO_2 even after stirring the sample in SO_2 for several hours.

When solvent refined lignite (SRL) produced from North Dakota lignite was treated with liquid sulfur dioxide, the bulk of the coal liquid dissolved except for the saturated hydrocarbons and the mineral rich residue. The SO_2 -soluble part did not contain any saturated hydrocarbons. The THF extract of the insolubles was mostly alkanes ranging from n -dodecane ($\text{C}_{12}\text{H}_{26}$) to n -tetra-tetrancontane ($\text{C}_{44}\text{H}_{90}$).

Table IV lists the elemental composition and the BTU value of various fractions. The SO_2 solubles are virtually free of mineral matter and have a higher BTU content than the starting material. The deoxygenation of SO_2 solubles could raise the BTU level to that of petroleum crude. The THF extracts of the SO_2 -

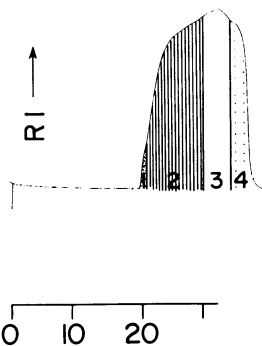


Figure 1. GPC separation of SRC from West Virginia subbituminous coal. The GPC system consisted of four 100 Å μ Styragel columns and the THF flow rate of 1 mL/min.

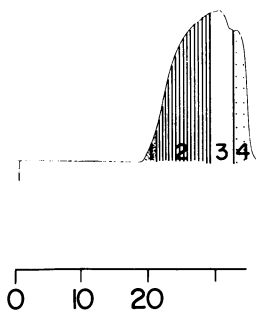


Figure 2. GPC separation of SO_2 -solubles of SRC from West Virginia subbituminous coal. Fraction 3 and 4 are identified by GC-MS (see Figures 4 and 5, Tables I and II).

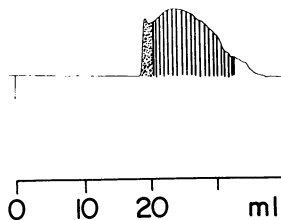


Figure 3. GPC of the THF extract of SO_2 -insolubles of SRC from West Virginia subbituminous coal. See Figure 6 for the GC-MS of the extract and Table III for the identification of the components.

Table I. Phenolic Fraction (GPC Fraction
#3 From SO₂ - Solubles)

<u>Retention Time</u>	<u>Compound</u>
4.5	Phenol
6.7	O-Cresol
7.7	p-Cresol + m-Cresol
9.9	C ₂ -Alkylphenol
11.0	C ₂ -Alkylphenol
11.6	C ₂ -Alkylphenol
12.1	C ₂ -Alkylphenol
13.0	C ₃ -Alkylphenol
13.5	C ₃ -Alkylphenol
14.1	C ₃ -Alkylphenol
14.6	C ₃ -Alkylphenol
15.5	C ₃ -Alkylphenol
16.2	C ₃ -Alkylphenol
16.7	C ₃ -Alkylphenol
17.3	C ₃ -Alkylphenol
18.0	C ₃ -Alkylphenol
18.5	C ₄ -Alkylphenol + Dodecane (trace)
19.3	C ₄ -Alkylphenol
19.6	C ₄ -Alkylphenol
20.5	C ₄ -Alkylphenol
21.7	C ₄ -Alkylphenol
22.3	C ₅ -Alkylphenol + Methyl Indanol
23.2	C ₅ -Alkylphenol + Methyl Indanol
24.3	C ₅ -Alkylphenol + n C ₁₃ H ₂₈ + Methyl Indanol
24.8	Methyl Indanol
25.7	C ₅ -Alkylphenol
26.2	C ₅ -Alkylphenol
26.6	C ₅ -Alkylphenol
27.1	C ₅ -Alkylphenol
27.7	C ₂ -Indanol + C ₅ -Alkylphenol
28.3	C ₅ -Alkylphenol +
29.1	Dimethyl Indanol
30.2	C ₆ -Alkylphenol + nC ₁₄ H ₃₀ (trace)
31.7	C ₂ -Alkylindanol + C ₆ Alkylphenol
32.6	C ₂ -Alkylindanol + C ₆ Alkylphenol
33.7	C ₆ -Alkylphenol + C ₂ Alkyl Naphthol
34.4	C ₆ -Alkylphenol + C ₂ Alkyl Naphthol
36.0	C ₃ -Alkylindanol
36.5	C ₃ -Alkylindanol
37.2	C ₃ -Alkylindanol
38.2	C ₁ -Alkyl naphthol + C ₃ Alkylindanol

Table II. Aromatic Fraction
(GPC fraction #4 From SO₂ - Solubles)

<u>Retention Time (min.)</u>	<u>Compound</u>
3.6	Phenol
4.6	C ₃ -Alkylbenzene
5.4	o-Cresol
6.2	p-Cresol
7.3	m-Cresol
8.0	C ₂ -Alkylphenol
8.8	C ₂ -Alkylphenol
9.4	C ₂ -Alkylphenol
9.9	C ₂ -Alkylphenol + Methyl Indan +
10.3	Methyl Indan
11.2	C ₁ -Alkylindan
12.1	Naphthalene
12.8	C ₂ -Alkyl Indan
13.4	C ₂ -Alkylindan
14.5	C ₂ -Alkylindan
15.5	C ₂ -Alkylindan
16.3	C ₂ -Alkylindan
17.0	C ₂ -Alkylindan
17.1	C ₁ -Alkyl-naphthalene
18.3	C ₃ -Alkylindan + C ₁ -Alkyl-naphthalene
18.9	C ₁ -Alkyl-naphthalene + C ₃ -Alkylindan
19.5	C ₃ -Alkylindan
20.2	C ₃ -Alkylindan
21.5	C ₄ -Alkylindan
22.6	C ₄ -Alkylindan
23.4	C ₄ -Alkylindan
24.2	C ₂ -Alkyl-naphthalene + C ₄ -Alkylindane
24.6	C ₄ -Alkylindane + C ₂ -Alkyl-naphthalene
25.0	C ₄ -Alkylindane + C ₂ -Alkyl-naphthalene
25.5	C ₄ -Alkylindane + C ₂ -Alkyl-naphthalene
26.7	C ₂ -Alkyl-naphthalene
27.5	C ₂ -Alkyl-naphthalene
28.1	C ₅ -Alkylindan
28.7	C ₃ -Alkyl-naphthalene
30.0	C ₃ -Alkyl-naphthalene
31.7	C ₃ -Alkyl-naphthalene

Table III. Hydrocarbon Chains Separated
from THF Extract of SO₂ - Insolubles

<u>Retention Time (min.)</u>	<u>Compound</u>
12.9	Tridecane
13.6	Tetradecane
15.4	C ₁₄ H ₃₀
16.7	Pentadecane
19.7	Hexadecane
21.0	C ₁₆ H ₃₄
22.7	Heptadecane + Pristine
25.6	Octadecane
28.4	Nonadecane
31.0	Eiconsane
33.4	Heneicosane
35.9	Docosane
38.2	Tricosane
40.4	Tetracosane
42.6	Pentacosane
44.7	Hexacosane
46.7	Heptacosane

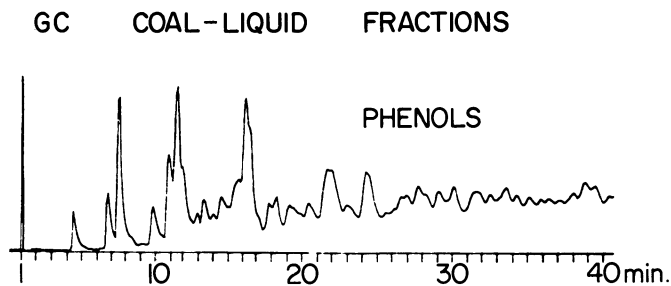


Figure 4. Total ion gas chromatogram of GPC fraction 3 of SO_2 -solubles (Figure 2). Columns 5% Dexsil 300 on 100/120 Chromosorb H-WP, 1/8 in o.d. \times 8 ft, carrier gas: 20 mL helium/min, temperature program: 80° - 270° C at 2° /min for 40 min followed by 4° /min. See Table I for peak identification.

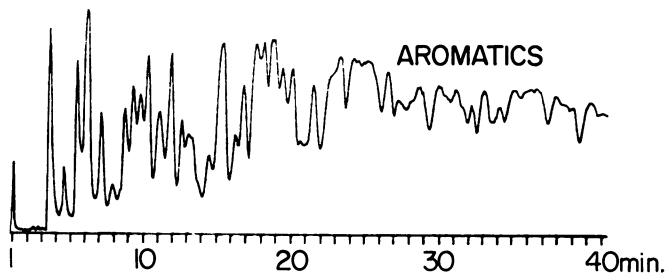


Figure 5. Total ion gas chromatogram of GPC fraction 4 of SO_2 -solubles (Figure 2). Same GC conditions as in Figure 4. See Table II for peak identification.

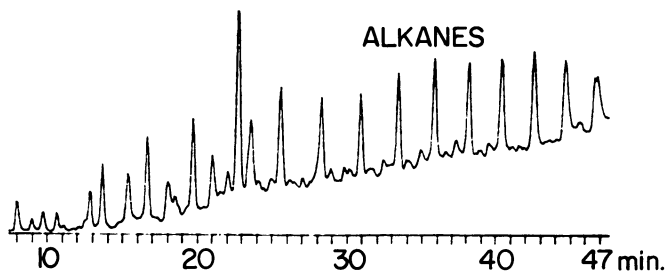


Figure 6. Total ion gas chromatogram of the THF extract of SO_2 -insoluble of SRC from West Virginia subbituminous coal. GC conditions were same as in Figure 4 except the temperature program of 80° to 270° C at 4° /min. See Table III for peak identification.

Table IV Ultimate Analysis of Coal Liquids
and the fractions separated by liquid sulfur dioxide

Sample	% of Total	% Ash	% C	% H	% N	% O	% S Total	% S Organic	% S Sulfate	% S Pyrite	Btu/lb
SRC	100	1.40	86.70	7.39	1.32	3.41	0.73	NA	NA	NA	16840
SRC 1	83.5	0.08	84.48	7.81	1.13	5.05	1.12	0.90	0.22	0.00	16080
SRC 2	8.5	0.25	86.31	7.29	1.30	3.30	0.86	0.08	0.02	0.76	16677
SRC 3	8	15.97	68.59	4.06	1.86	14.14	3.38	2.68	0.40	0.30	11676
SRL	100	3.86	85.10	6.40	1.17	5.02	0.33	NA	NA	NA	15800
SRL 1	72	0.11	86.47	7.14	1.21	4.63	0.49	0.33	0.16	0.00	16402
SRL 2	9	0.13	79.31	7.91	0.92	9.55	0.53	0.00	0.13	0.32	15719
SRL 3	19	16.82	70.41	3.83	1.51	13.20	2.39	1.33	0.50	0.56	11839

Legend: SRC, coal liquid from West Virginia coal; SRL, coal liquid for North Dakota lignite; 1, soluble in SO₂, 2 insoluble in SO₂, soluble in THF; 3, insoluble in SO₂ and THF. NA, not available.

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insolubles contain both volatiles and nonvolatiles. The volatiles are identified by GC-MS as long chain saturated hydrocarbons. From the elemental composition data it could be deduced that the nonvolatiles consist of low hydrogen containing species with a fair amount of oxygen. Since most of the experimental work was done on a small sample under atmospheric conditions, the higher sulfur content of the fractions could be due to the incorporation of SO₂, perhaps in its oxidized form as sulfates. In a large scale process such incorporation could be minimized.

Liquid sulfur dioxide was used to separate the liquefaction products from Texas lignite when Tetralin had been used as the hydrogen donor solvent. The large excess of Tetralin present with the lignite liquefaction products did not interfere with the liquid sulfur dioxide separation procedure. The chemical composition of the fractions were similar to that of SRC and SRL.

Most coal liquids are composed of similar major chemical species, which may differ in exact composition. Liquid sulfur dioxide can be used to extract all the aromatic species of the coal liquid, free of saturated hydrocarbons and ash precursors. After removing the SO₂ by degassing, distillation under reduced pressure can yield all the phenols and aromatic from the SO₂-solubles of the coal liquid. The residue, which is similar to GPC - fraction 2 of the SO₂-solubles, can be called coal asphaltenes. The average molecular size of coal asphaltenes (linear molecular size is more precise since it is derived from GPC data) is smaller than that of petroleum derived asphaltenes.

Acknowledgements

We acknowledge the financial support of the Texas Engineering Experiment Station, Department of Chemical Engineering, the Texas A&M University Center for Energy and Mineral Resources, Dow Chemical Co., The Alcoa Foundation, Pittsburgh, PA. and the Gulf Oil Co. Mrs. Argentina Vindiola assisted in the collection of some of the data.

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Refining of Coal-Derived Syncrudes

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In order to increase the supply of liquids fuels, DOE has embarked on an ambitious program to develop and commercialize direct hydro-liquefaction processes. These liquids will be used to replace our dwindling supply of domestic petroleum. The initial marketing strategy calls for the utilization of the first coal derived liquids as boiler fuels. Use of these liquids as low sulfur fuel oil has substantial merit because it directly displaces imported oil in a market area which can easily absorb the output of the initial commercial ventures. While it is recognized that the byproduct naphtha will be refined to gasoline, this overall approach decouples to a significant extent the engineering scale-up and process development of the liquefaction technology from the downstream product upgrading optimization.

Although the first major use of coal liquids will be as boiler fuels, it is clear that in order to make the largest impact on the U.S. liquid fuel demand, products from direct liquefaction have to be upgraded to quality liquid fuels for both transportation and home heating oil uses. The products coming from the all-distillate coal liquefaction processes such as H-Coal Syncrude, SRC-II and Donor Solvent, along with shale oil production will be candidates for use as refinery feedstock. It is, therefore, a matter of considerable interest to examine the outlook for the refining of syncrudes. In support of this effort, DOE is funding a number of small scale studies in upgrading refining. The objectives of this program are:

- To define the capabilities of state of the art petroleum processing for syncrude upgrading
- To develop new refining methods specifically tailored towards syncrudes
- To determine the relationship between syncrude refining and product toxicity.

State of the Art Assessment

It is generally recognized that the best refining strategy involves the use of each potential feedstock and fraction in a way

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Table I. Comparison of Hydrogen Contents

FEEDS	
—PETROLEUM	11 to 14.5%
—SHALE OIL	11 to 12.0%
—COAL SYNCRUDE	9 to 10.0%
PRODUCTS	
—BOILER FUEL	9.0 to 12.0%
—HIGH OCTANE GASOLINE	11.0 to 11.5%
—NO. 2 FUEL OIL	12.0 to 14.0%
—JET FUEL	13.5 to 14.0%

Table II. Boiling Range of Typical Petroleum (Arabian Lift Blend), Coal Syncrude, and Shale Oil

	<u>PETROLEUM</u>	<u>COAL SYNCRUDE</u>	<u>SHALE OIL</u>
<u>NAPHTHA</u> (C₅–400°F)			
VOL. %	25	15–35	4
<u>ATM GAS OIL</u> (400–650°F)			
VOL. %	25	40–60	25
<u>VACUUM GAS OIL</u> (650–1000°F)			
VOL. %	30	10–20	68
<u>VACUUM RESIDUE</u> (1000°F +)			
VOL. %	20	0	3

in which it can most easily and efficiently be tailored to meet the market use. This is equivalent to the view that the most economic refining scheme is found by following the path of least resistance from feed to product. Table I examines the hydrogen content of typical feeds and products. The coal syncrude is a low hydrogen content liquid that is close to the hydrogen level found in a highly aromatic high octane gasoline. Indeed, the similarity in the hydrocarbon structure present in both good unleaded gasoline and in distillate coal liquids is a key factor for developing a syncrude utilization strategy. Also, the hydrogen content of petroleum and shale oil in comparison to the hydrogen contents of No. 2 fuel oil, jet fuel and diesel fuel is of prime importance. The diesel and jet fuel require much higher levels of hydrogen to meet specifications. Consequently, it appears reasonable to assume that coal liquids will be best suited for the gasoline market, while petroleum can most easily be converted to desirable, more paraffinic middle distillates.

In Table II, the boiling ranges of petroleum and the two major syncrudes are shown. The very high naphtha yield and the absence of residue in coal derived syncrudes are significant. Also, it should be noted that shale oil is predominantly in the middle distillate boiling range with low residue and naphtha content. The absence of resid in coal liquids results from the severe hydrogenation conditions imposed in the coal liquefaction processes and the use of the remaining residue for hydrogen production. For shale oil, the retorting process destroys most the residual materials leaving a syncrude that is mainly a distillate.

Table III shows elemental composition of typical sour petroleum, coal syncrudes or shale oils. Compared with typical sour petroleum, the coal syncrude is lower in sulfur content but significantly higher in nitrogen. Compared with shale oil, coal syncrude is lower boiling and contains only about one half the nitrogen. A major difference between the two liquids is the highly aromatic structure of coal liquids and the absence of long paraffinic structures. Shale oil is more aromatic than petroleum but significantly less aromatic than coal liquids. This is mirrored by the hydrogen contents which were shown in Table I. In determining an optimum strategy, the end use requirement of the market place must be satisfied. A key requirement is fuel stability. High value fuels have very stringent requirements. This results in the need for 99% removal of nitrogen and oxygen. All gasolines produced by reforming meet this criterion. Also, a substantial net yield of hydrogen results from naphtha pretreating and reforming. Stable mid-distillates from shale oil are high enough in hydrogen content to produce quality jet fuel. However, stable coal derived mid-distillates are lower in hydrogen and higher in aromatics. Consequently, they will probably be used as fuel oil. Figure 1 shows the boiling range for three different coal derived liquids. These three liquids cover the boiling range that is usually achieved by the syncrude coal liquefaction pro-

Table III. Heteroatom Content of Typical Petroleum (Arabian Lift Blend), Coal Syncrude, and Shale Oil

	<u>PETROLEUM</u>	<u>COAL SYNCRUDE</u>	<u>SHALE OIL</u>
<u>NAPHTHA</u> (C₅-400°F)			
%S	0.3	0.1-0.2	0.9
%N	-	0.2-0.8	1.6
<u>ATM GAS OIL</u> (400-650°F)			
%S	1.4	~0.2	0.7
%N	.01	0.4-1.0	1.6
<u>VACUUM GAS OIL</u> (650-1000°F)			
%S	3.0	0.4-0.7	0.7
%N	.07	1.0-1.5	2.2
<u>VACUUM RESIDUE</u> (1000°F+)			
%S	5.0	-	0.8
%N	0.3	-	2.3

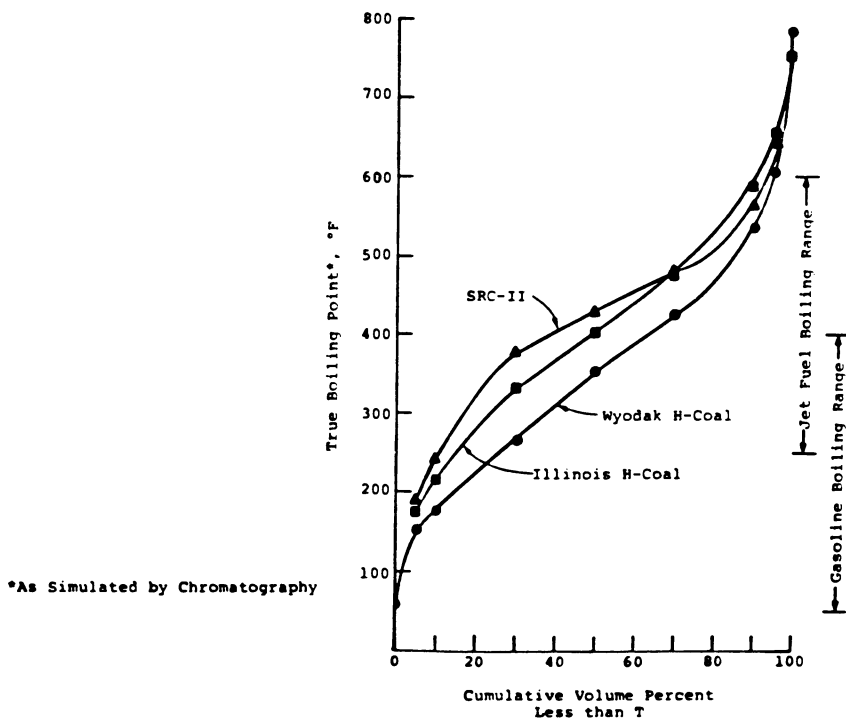


Figure 1. Simulated true boiling point distillations for SRC-II, Illinois H-coal, and Wyodak H-coal whole process products

cesses. The SRC-II is derived from a run on Pitt Seam Coal and shows a higher boiling range than the H-Coal products. The Illinois No. 6 H-Coal liquid is intermediate, with the Wyodak H-Coal liquid being the lightest of the materials. The Wyodak liquid contains the most hydrogen and least nitrogen while the SRC-II contains the least hydrogen and the most nitrogen.

Conventional Refining Processes Applied to Coal Liquids

In order to fulfill the objective of assessing state of the art petroleum refining for syncrudes, UOP and Chevron have both been performing bench scale refining studies on coal liquids. UOP has evaluated H-Coal, EDS and SRC-II liquids in naphtha hydrotreating and reforming, mid-distillate hydrotreating, fluid catalytic cracking (FCC) and hydrocracking. Figure 2 shows data for the reforming of hydrotreated naphtha. The Illinois No. 6 H-Coal derived naphtha cut was hydrotreated with the addition of 480 standard cubic feet per barrel of hydrogen and then reformed to octanes ranging from 94 to 102 clear. As shown in Figure 2, the C₅+ volume ranges between 88 and 92.5% while the hydrogen produced by the reformer ranges between 1250 and 1750 standard cubic feet per barrel. This gives a net yield of between 800 to 1250 standard cubic feet per barrel. Figure 3 shows similar data for SRC-II naphtha derived from Illinois No.6 coal. In this case, the octane ranged between 88 and 100 and achieved a C₅+ yield of 86 to 93 volume percent. The reformer produced between 1200 and 1550 standard cubic feet per barrel of hydrogen. Upgrading of this naphtha to a quality acceptable as reformer feedstock required 560 standard cubic feet per barrel which results in a net hydrogen production from the reforming operation of between 650 and 1000 standard cubic feet per barrel. Consequently, in a coal liquid refining scheme, the naphtha reformer can be a key item because it will provide a source of valuable hydrogen.

UOP has also done a significant amount of work on the evaluation of the Fluid Catalytic Cracking Unit. Figure 4 shows the H-Coal derived mid-distillate. The raw coal derived mid-distillate was hydrotreated so that the feed hydrogen content was varied between 9 and 13%. As the hydrogen content increases, both conversion and gasoline yield increases while the carbon yield decreases. Figure 5 shows similar data for an EDS process derived feedstock and a West Coast refinery feedstock. The West Coast feedstock was used as a comparison because California crudes contain significant amounts of nitrogen. Again, as the hydrogen content is increased, carbon yield decreases and conversion and gasoline yield increases. A detailed analysis of this data indicates that the optimum hydrogen treatment level exists at about 11.5 to 12% hydrogen. This seems to be the most economical way to produce high octane gasoline from coal derived distillates in an existing complex refinery.

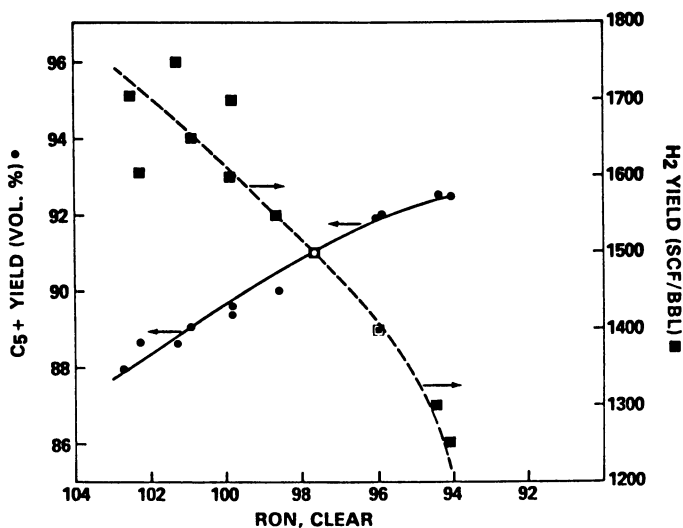


Figure 2. Hydrogen and liquid yield vs. octane for upgraded H-coal naphtha

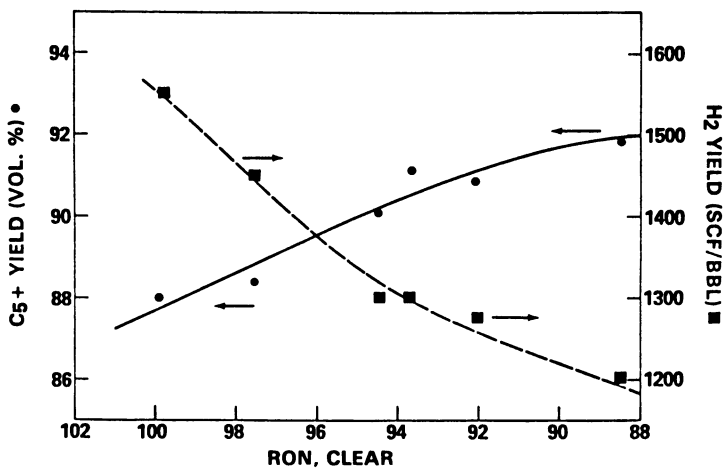


Figure 3. Hydrogen and liquid yield vs. octane for upgraded SRC-II naphtha

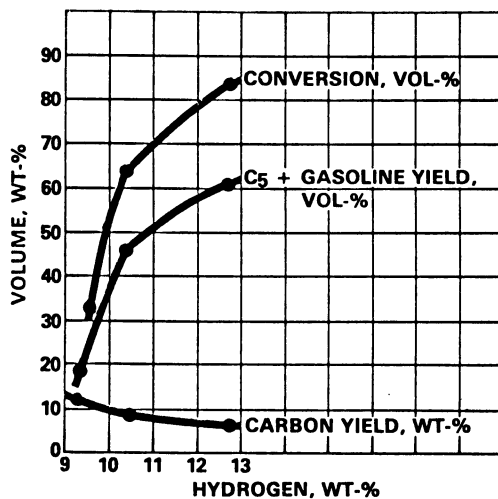


Figure 4. Effect of hydrogen content of coal liquids on response to fluid catalytic cracking

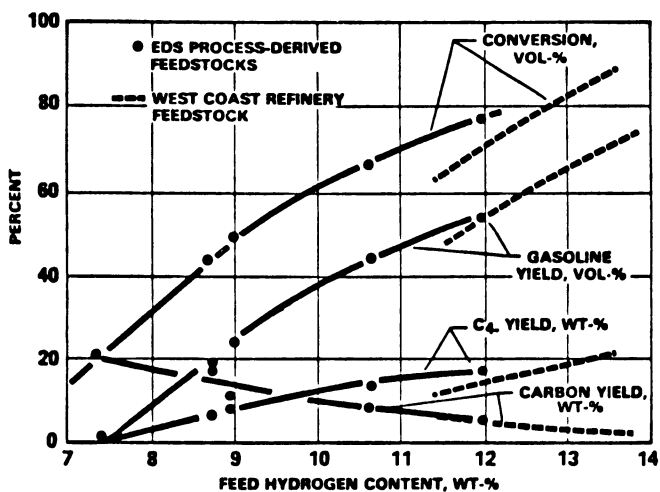


Figure 5. Effect of feedstock hydrogen content on response to fluid catalytic cracking

Previously, Chevron has published a detailed study of the refining of Paraho shale oil. They recently completed a similar study for SRC-II. This should be available for publication in May of 1980. Some of the data from the SRC-II study are shown in Figure 6. This compares the nitrogen level with the amount of hydrogen consumed during a high pressure hydro-treatment. Significantly less hydrogen is consumed by the coal liquid to achieve a given product nitrogen level. Further, at a fixed product nitrogen level the SRC-II product has a substantially lower boiling range than the shale oil. This is due to its higher initial naphtha content. Figure 7 shows the effect of hydrotreating severity and coal source on the aromatic content of the whole liquid product. In this figure, data for Wyodak H-Coal, Illinois No. 6 H-Coal and Pitt Seam SRC-II is plotted as hydrogen consumption verses aromatics content in the whole liquid product. Because of the lower boiling range and aromatic content of the Wyodak H-Coal, it requires substantially less hydrogen and a lower processing severity to achieve the same level of aromatics as Illinois derived H-Coal or the Pitt Seam SRC-II. Particular attention should be paid to Figure 7 because it indicates that the prime factors in determining how to refine the coal derived liquid are the boiling range and the elemental composition of the liquid. The data from UOP and Chevron strongly indicate that, based on inspections of the coal liquid, a very good process design and cost estimate can be made for refining this material without any knowledge of the coal source or the liquefaction process used.

Refining Process Schemes

The process data can now be translated into refinery processing configurations. Figure 8 is a schematic diagram of a typical sour crude refinery. While we realize that there is no such thing as a typical refinery, and many American refineries are not sour crude refineries, this figure represents what we believe to be a reasonable approximation of the type of refinery that will be operating in the United States in 1990. It will include a naphtha pretreater, a high severity reformer and a hydrotreater for production of diesel fuel and middle distillates from more sour crudes than are currently being used. Also, a hydrotreater will precede the fluid catalytic cracking unit. The UOP data shows conclusively that, if the feedstock from the coal liquid is hydrotreated to approximately 12 percent hydrogen, it can be an acceptable FCC feed. The refinery in Figure 8 can be modified to accept syncrude by the addition of large syncrude hydrotreater, Figure 9. The treated syncrude can be mixed with petroleum feedstock and run through the refinery with only a minor amount of additional change. The severity of the syncrude hydrotreater would be tailored to match the severity of the existing or revamped hydrotreaters within

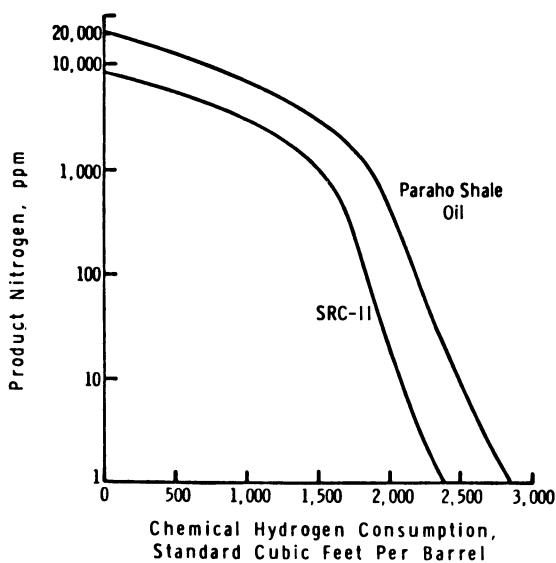


Figure 6. Product nitrogen vs. hydrogen consumption

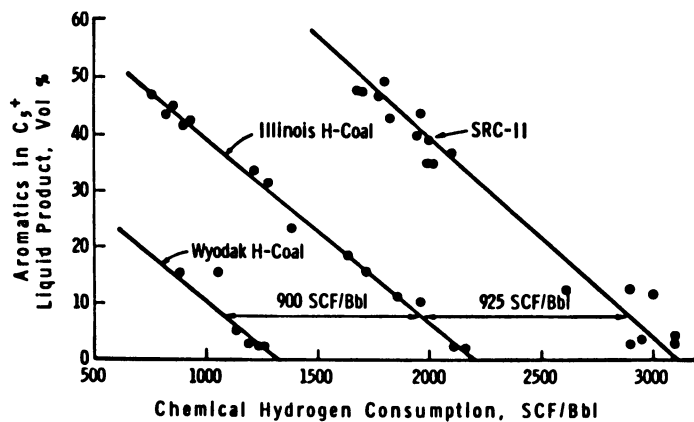


Figure 7. Product aromatic content vs. hydrogen consumption for Illinois H-coal, Wyodak H-coal, and SRC-II syncrudes

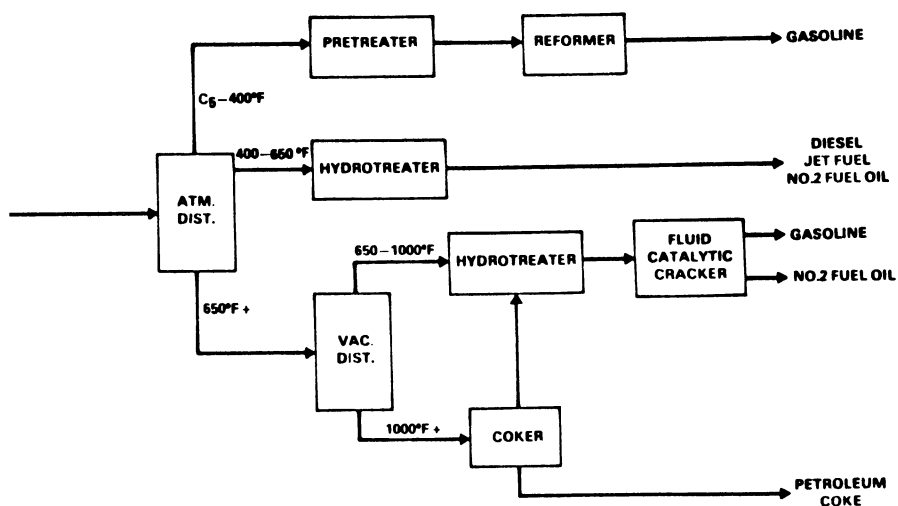


Figure 8. Typical American sour crude refinery

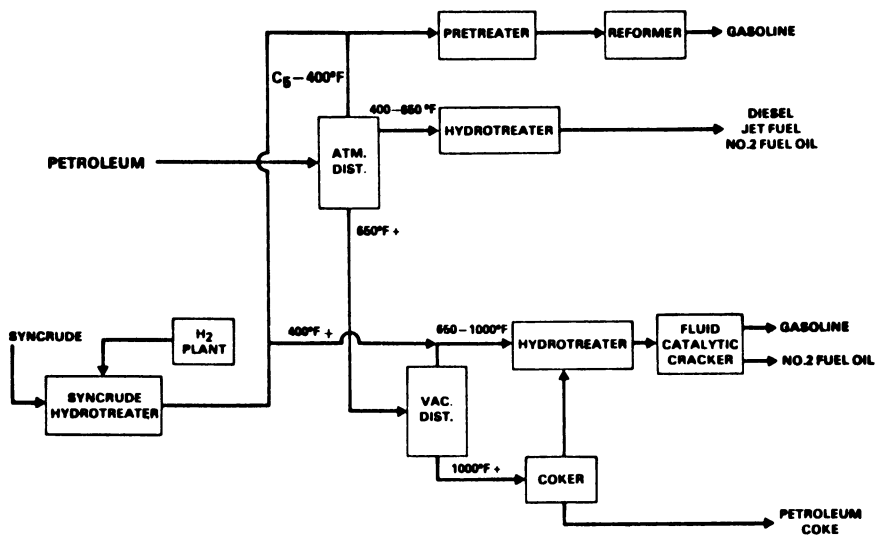


Figure 9. Refinery with coal syncrude addition

the existing refinery. The limiting factor would be the amount of nitrogen in the FCC feed or the severity required in the syncrude hydrotreater to be sure that the existing reformer pretreater could achieve a nitrogen level low enough for the reformer feedstock.

The syncrude hydrotreater does not necessarily have to be located at the refinery and it is feasible that this very large, high H_2 consumption unit could be part of the coal liquefaction facility. Because of the aromatic nature of coal liquids, production of quality mid-distillates will require a substantial consumption of hydrogen at a significant economic cost. The scheme in Figure 10 attempts to maximize the amount of gasoline by feeding all the naphtha to a pretreater and reformer and by feeding the FCC unit with a light 450°F+ material. This will require a revision to existing FCC units, but the scheme is the simplest way to achieve a maximum yield of gasoline from a coal liquid.

Economic Assessment

UOP is performing a economic analysis based on the refining data developed by UOP Process Research division. In one case the cost of refining an Arabian blend versus H-Coal syncrude is being compared to a grassroots refinery. A blend of 65 percent light and 35 percent heavy was chosen because this could be considered to be the "swing" crude for American refineries. The crude analysis for H-Coal liquids was carefully selected based on a study by Mobil Research Corporation of an analysis of H-Coal syncrude liquids that was performed under contract EF-77-01-2676. UOP is also working on an SRC-II case for the grassroots refinery along with blend cases for an existing refinery. In the blend situation, 5, 10, and 30 percent coal liquids are being added to an existing refinery sour crude feed in the year 1990.

In doing the grassroots case, a range of gasoline to distillate ratios between 0.7 and 2.0 were evaluated and the refinery was constrained to produce heating oil and gasoline with no high sulfur products allowed. This restriction eliminates the production of high sulfur fuel from the petroleum refinery, a significant handicap to the petroleum case. Because of the constantly changing price structure in today's market, the analysis was performed by choosing a reasonable set of product values at the time of the study and then the value of the feedstock was calculated for a given set of economic parameters, Figure 11. Numerous schemes were evaluated and optimized and the analysis indicates that, for a gasoline to distillate ratio of one, the hydrotreating scheme with no conversion operation is the favored case. For gasoline to distillate ratios above 1.5, a reforming/hydrocracking scheme would be the preferred mode of operation. Also, the FCC scheme for the coal liquid is significantly less favorable than the hydrocracking for this grassroots

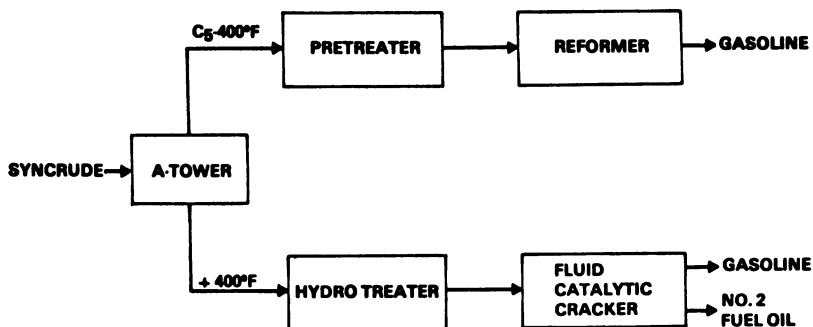


Figure 10. Refinery for coal syncrudes

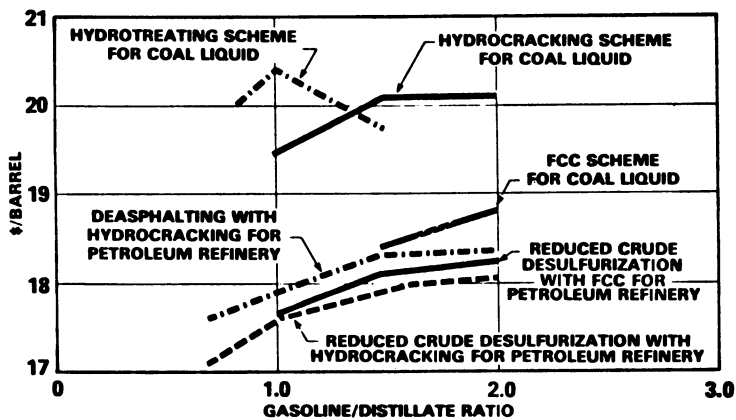


Figure 11. Economic comparison for petroleum vs. coal liquid refinery

case. Again, because the production of high sulfur fuel oil is not allowed and because we did not require the coal liquid refinery to produce diesel or jet fuel, the value of the coal liquid turns out to be higher than the value of the petroleum feedstock. If the refinery had been required to produce these higher hydrogen content products, much more severe hydrotreating would have been required and the value of the coal liquid feedstock would have been reduced.

UOP and Chevron have both produced numerous reports which are detailed in the list of references. These contain a substantial amount of data for the refining of coal liquids and shale oil. From this work we have concluded that:

- Syncrudes can be refined by conventional methods; high severities are needed but they are in the range of conventional technology
- Coal liquids require less severe hydrotreatments than shale oil due to the lower nitrogen content.
- Products can be substituted for petroleum based products once sufficient hetroatoms are removed to assure the materials will meet the conventional stability specifications
- High octane gasoline and fuel oil is cheaper to produce than diesel or jet fuel. This is because of high octane gasoline can be produced with a lower hydrogen content than quality diesel or jet fuel. However, an attempt to produce only gasoline results in higher costs due to the high and unselective use of hydrogen at very high severities.

New Refining Research

DOE has also engaged in a limited program to develop new methods for refining syncrudes. One of the major projects in this area is a catalyst development program now going on at Filtrol. Filtrol is evaluating new and optimized catalysts for hydrotreating, hydrocracking and FCC of coal derived liquids. One of the prime objectives of this project is to develop an FCC catalyst ideally suited for refining of a 450°F+ coal distillate. They are also evaluating some unique exchanged and substituted zeolites and synthetic montmorillonite mica (SMM) components in hydrocracking and FCC applications.

Suntech is looking at the benefits that can be derived in the processing of syncrudes by combining extraction operations with hydrotreatment. A significant development in this study has been the discovery that the extraction of coal derived naphtha to remove the oxygen components (phenols and creosols) results in substantial improvements in the kinetics for denitrogenation. If this extraction can be done at high selectivity, the oxygen containing material could then be reacted with a low molecular weight olefin to produce a high octane blending component. This

is analogous to the reaction currently being used of methanol with higher molecular weight olefins to produce oxygenated high octane blending components (TAME and MTBE).

Toxicity Evaluations

An equally important part of the refining activities of DOE is to determine the effect of refining severity on end use performance and the toxicity of the products. There have been numerous articles discussing the potentially carcinogenic nature of coal liquids. It is fairly well accepted that severe refining will reduce the toxicity of coal liquids to that comparable to similar petroleum derived liquids. The question to be answered is: What is the optimum level of refining severity? It is equally important to determine the relationship between end use performance and refining severity. The goal is to determine how severely one has to hydrotreat a coal liquid to assure that the products have no detrimental effects on either the end use equipment or on the environment via combustion emissions. Initial data developed by Chevron indicates some of the types of information that have to be quantified. Figure 12 shows the aromatic concentration as a function of hydrogen consumption. Data for both M-M (ICR-113) and M-W (ICR-106) on microporous supports are shown. Also, shown earlier was nitrogen concentration as a function of hydrogen consumption. These can give biologists some indication of carcinogenic potential. In terms of end use application, Figure 13 shows the effect of aromatic concentration on the smoke point for various SRC-II mid-distillates boiling ranges, while Figure 14 shows the effect of aromatic content on the cetane number for SRC-II liquids. An important factor is that coal derived No. 2 oil refined at low severity will meet every specification but the API gravity. If this fuel oil is hydrotreated sufficiently to increase the gravity to the current specification, the aromatics concentration is decreased enough that one has a suitable cetane index for a diesel fuel or suitable smoke point for a jet fuel. This would indicate that, to use the coal liquids in an optimum fashion with a minimum amount of hydrogen consumption, a lowering of the API gravity specification would be required. This would not have detrimental effects on the end user, providing the gravity specification is high enough to assure the soot formulation in combustion applications would not be a problem, or that the liquid would not be any more toxic than No. 2 fuel oil derived from petroleum.

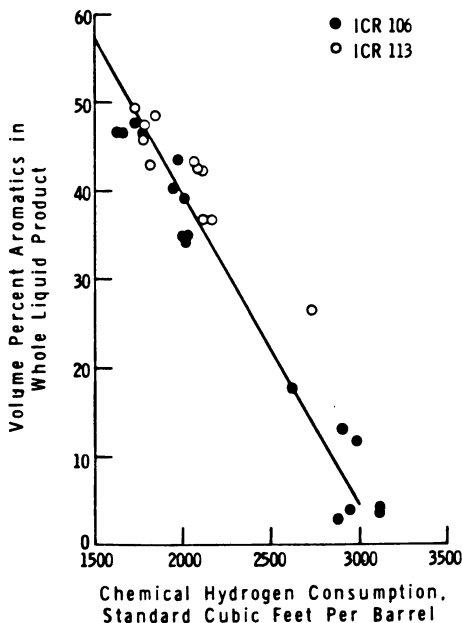


Figure 12. Product aromatic content vs. hydrogen consumption hydrotreating whole SRC-II oil at various severities; group type calculated from GC or MS of individual fractions

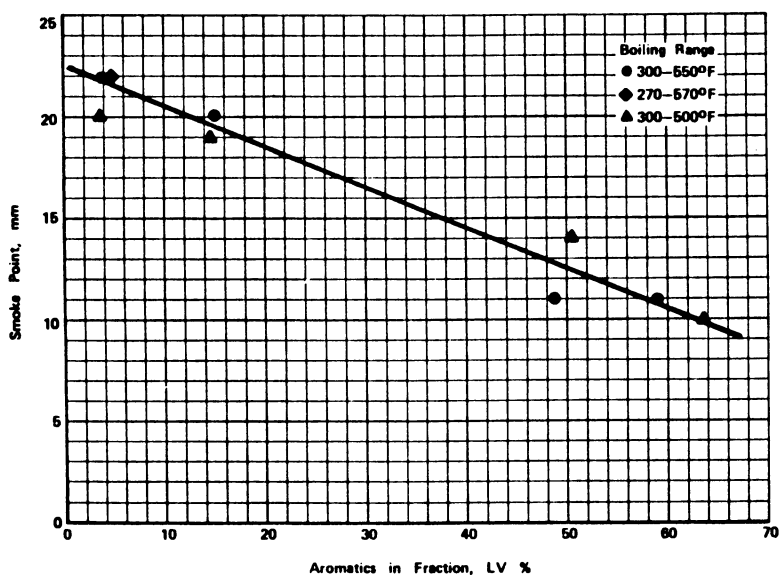


Figure 13. Effect of aromatics on smoke point hydrotreating of SRC-II with ICR 106

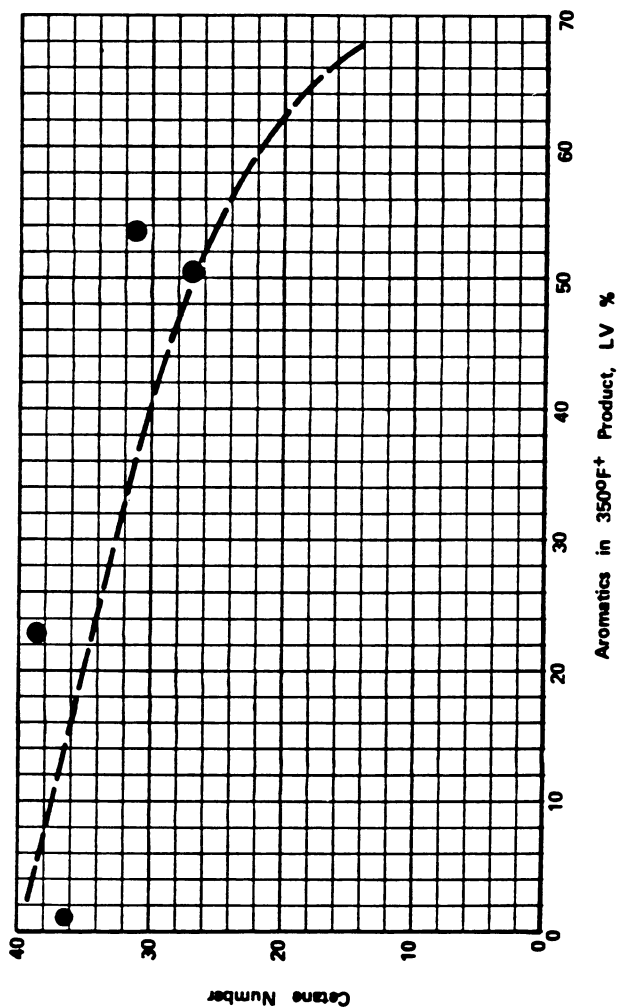


Figure 14. Effect of aromatics on cetane number of 350° C+ product hydrotreating of SRC-11 with ICR 106

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RECEIVED January 13, 1981.

INDEX

- A**
- Acenaphthene59, 62, 66, 69
 hydrogenation of 68*f*
 Acenaphthenols 44
 Acenaphthylene 231
 Acetylene 236
 Acid(s)
 in anthracene oil, oxygen-containing 46*t*
 and coal liquid oxygen, total 28*f*
 fractions 27
 from anthracene oil, homologs in
 -base separation, from14*t*-15*t*
 composition of anthracene oil44-48
 Acridine56, 58
 hydrogenitrogenation of 57*f*
 Activation, metabolic 149
 Adsorption
 chromatographic fractions10-11, 27
 chromatographic separations of
 distillates 10
 chromatography, fractions from .14*t*-15*t*
 Aging run, West Kentucky SCT SRC 187*f*
 Alkyl carbon number, hydro-
 deoxygenation and 47
 Ames assay149, 150*t*
 Analysis scheme for distillates 5*f*
 Anthracene29, 231
 oil 229
 composition of39-73
 raw 208*t*
 separation data for 43*t*
 Anthracite coals 30
 API gravity83, 122, 264
 Aromatic(s)
 and cetane number 266*f*
 fraction 244
 hydrotreating severity and product
 and smoke point265*f*
 Asphaltene(s) 239
 content, ring number and 25*t*
 Attapulgas clay 41
 Azaanthracenes 55
 in base fraction 56*t*
 1-Azaanthracene 58
 Azaaromatics 55
 hydrogenation/hydrogenolysis of .. 52
- B**
- Azafluorenes49, 55
 Azaoaromatics 49
 Azaphenanthrene(s) 55
 in base fraction 56*t*
 1-Azaphenanthrene 58
- C**
- Base fraction(s) 27
 analysis of 42
 composition of anthracene oil49-59
 Bases and nitrogen content 28*f*
 Benzene(s) 229
 alkylated 239
 Benzocarbazoles 48
 Benzonaphthenofurans 59
 Bicyclonane 122
 Biological test of SRC-II coal
 liquid145-152
 Biphenyl59, 62, 66, 69
 hydrogenation of 68*f*
 Bituminous coal 30
 Pittsburgh 1
 Boiler fuels 251
 SCT SRC to low sulfur175-190
 Boiling point distillation for
 syncrudes
 Illinois H-coal 119*f*
 SRC-II 119*f*
 Wyodak H-coal 119*f*
 Boiling range, solvent167-169
 Butadiene231, 237
 2-Butylnaphthalene 66
 6-Butyltetraline 66
- C**
- Co-Mo
 catalyst(s)7, 29, 156
 -alumina40, 192, 195
 California gas oils 118
 Carbazole(s)48, 70
 Carcinogenesis and mutagenicity 149
 Carbon bond(s)
 -carbon hydrogenolysis 66
 -carbon, hydrogenation of 58
 -nitrogen, hydrogenation of 58

- Carbonization vapors 225
 Carbonizer/vaporizer/cracker 227f
 Catalyst(s)
 activity159-162, 167
 bed, expanded 156
 Co-Mo156
 -alumina40, 207-224
 deactivation 182
 loading and hydro-
 treating194t, 195, 197t
 loading and selectivity 196f
 Ni-Mo-alumina147, 176
 properties179t, 210t
 used 182t
 surface activity 220
 Catalytic
 activity176-177, 182
 cracking88, 93
 fluid93, 97f, 255, 258
 feedstock hydrogen content
 and 257f
 hydroprocessing 176
 CCR reduction activity(ies)177,181f
 Cetane
 index 264
 number, aromatics and 266f
 test 122
 Characterization of distillate
 fractions 10
 Characterization scheme for
 distillates 6f
 Chloride in synfuels 118
 Chromatographic
 preparation 41
 separation of anthracene oil41-42
 separation of distillates 3-7
 adsorption 10
 Chromia-alumina hydrotreating of
 phenanthrene 66
 Cloud points 128
 Coal
 extract, short contact time (SCT) .. 158
 liquids, properties of 9t
 rank
 and liquids composition30-32
 ring content and33f, 34f
 total saturates and 31f
 Coke depositions 182
 Colstrip liquids 32
 Combustion emissions 264
 Composition
 of anthracene oil39-73
 coal rank and coal liquids 1-37
 and hydrotreating severity147-149
 Condensate, natural gas226, 231
 Conversion and hydroprocessing
 severity 183f
 Cost estimates of SRC-II100, 109
 Cost summary, SRC-II 110t
 Cracking
 catalytic88, 93
 fluid93, 97f, 255, 258
 hydrogen content and 257f
 hydrocarbon 29
 ring-opening 29
 temperature 236
 and yields230f, 234f
 thermal225-238
 Crosslinking during digestion/
 extraction 236
 Cyclohexylbenzene 69
- D**
- Deactivation, catalyst159, 182
 Deactivation equation185, 189
 Decahydroquinoline 53
 Decalin 226
 Decaline 231
 Denitrogenation167, 169, 170f
 activities 180f
 and equivalent time 168f
 Deoxygenation activities 180f
 Deoxygenation, phenol44-46
 Design variables for fixed-bed reactor 188f
 Desulfurization 192
 activities 178f
 catalysts176-177
 Diaromatic concentrate from coal
 liquids18f-19t
 Dibenzofurans 59
 Dibenzothiophene(s)59, 69
 hydrodesulfurization of 68f
 Diesel fuel86, 133
 preparation of122, 128
 Diffusion, intraparticle 209
 Digestion/extraction, crosslinking
 during 236
 Dihydroacridines 58
 Dihydrophenanthrene 66
 Dihydroxyrenols 44
 Dinaphthenes 122
 Dinitrogen compounds 52
 Distillate(s)
 conversion to164, 167
 fractions characterization 10
 fractions separation 10
 H-coal 116
 hydrocarbons, composition of 13t
 scheme for
 analysis 5f
 characterization 6f
 separation 5f
 Distillation(s)
 coal liquids 3
 cuts 239
 fractions 12t
 of liquid feed 148t

Distillation(s) (*continued*)

residue	76
scheme for coal liquids	4f
syncrude, boiling point	
for Illinois H-coal	119f
for SRC-II	119f
for Wyodak H-coal	119f
of upgraded coal liquids	7-10
<i>n</i> -Dodecane	241

E

Ebullated bed reactors	185
Electron-impact mass spectra for	
adsorption concentrates	24t
Electron-impact mass spectroscopy ...	42
Equivalent time, denitrogenation	
and	168f
2-Ethylbenzylamine	55
2-Ethylbiphenyl	66
Ethylene	229, 231, 237
Extinction recycle hydrocracking	88

F

Feed for hydrocracker	90t, 91t, 92t
Feed properties	161t
SCT coal extracts	160t
SRC-I coal extracts	160t
Feedstock(s)	
balance(s)	100
SRC-II	104t
hydrogen content and fluid	
catalytic cracking	257f
hydrogenated	229
petroleum	258
refinery	251, 255
reformer	255
Field ionization mass spectra for	
adsorption concentrates	24t
Field-ionization mass spectroscopy ...	42
Fixed-bed reactor, design	
variables for	188f
Fluid catalytic cracking ...93, 97f, 255, 258	
hydrogen content and	257f
feedstock	257f
Fluoranthene	62
Fluorene	62, 231
Fluorenols	44
Fouling during hydrotreatment	134f
Fractions from acid-base separa-	
tions	14t-15t
Fractions from adsorption chroma-	
tography	14t-15t
Fuel oil(s) from syncrude	122
Illinois H-coal	125t
SRC-II	125t
Wyodak H-coal	125t
Furan	59

G

Gas oils, California	118
Gasoline	
blending	100
high octane	255
motor	93
Gel-permeation chromatography	7, 240
Gradient elution chromatography 177, 182t	
Gum content	133

H

H-coal refinery plans	120
H-coal syncrudes	115-144
Heat of combustion, gravimetric	83
Heating fuel(s)	
preparation of	128-133
Heating oil, SRC-II	86
Hexahydroacridines	58
Hexahydrophenanthrene	62
High severity hydrotreating	95f, 121f
Homologs in fraction(s)	
acid	44, 45f
from anthracene oil	48t
base	50t
neutral	63t-65t
-nitrogen from anthracene oil ...	48t
Hydrocarbon(s)	
cracking	29
fractions, analysis of	42
hydroaromatic	70
from tetrahydrofuran extract	245t
Hydrocracker, feed for	90t-92t
Hydrocracking	93, 98f, 255
extinction recycle	88
Hydrodenitrogenation (of)	
acridine	57f
activities	207-244
intermediates	52
isoquinoline	54f
quinoline	54f
Hydrodeoxygenation and alkyl	
carbon number	47
Hydrodesulfurization	
activities	207-224
of dibenzothiophene	68f
kinetics	199
of thiophene	70
Hydrofining of hydrotreated naphtha	87t
Hydrogen	
consumption and	182, 199, 258, 264
processing severity	78
product	
aromatics	84f, 137f, 259f, 265f
nitrogen	81f, 78, 259f
sulfur in	184f
content	253
and fluid catalytic cracking	257f

- Hydrogen (*continued*)
 partial pressure and selectivity ..197-199
 production 255
 Hydrogenated feedstocks 229
 Hydrogenation 192
 of acenaphthene 68f
 batch 2
 of biphenyl 68f
 /hydrogenolysis of azaaromatics ... 52
 /hydrogenolysis of phenanthrene .. 68f
 of hydrotreated SRC-II 89t
 jet fuel 88
 mechanisms56, 57f
 ring(s) 58
 polyaromatic 27
 Hydrogenolysis, carbon-carbon bond 66
 Hydrogenolysis, structure-reactivity
 relationships for 53
 Hydroliquefaction176, 182
 Hydroprocessing severity, conversion
 and 183f
 Hydrotreated H-coal syncrudes,
 stability of133-136
 Hydrotreated SRC-II, processing of ..86-88
 Hydrotreater, syncrude258-261
 Hydrotreating97f, 98f
 conditions 146t
 anthracene oil 40
 liquid product in 194t
 naphtha 255
 of phenanthrene, chromia-alumina.. 66
 reproducibility of 198t
 of rerun Illinois H-coal136-139
 severity
 composition and147-149
 high95f, 121f
 intermediate 96f
 moderate 99f
 and product aromatics 258
 of SRC-I191-205
 time and sulfur content 200f
 Hydrotreatment of SRC-II coal
 liquid145-152
 Hydrotreatment, fouling during 134f
 Hydroxyazanaphthalenes 48
 Hydroxyazaphenanthrenes/anthra-
 cenes 48
- I**
- ICR 10678, 79t, 82t, 85t, 89t, 91t, 120
 processability of coal-derived
 syncrudes 137f
 ICR 11378, 80t, 87t, 120, 128
 Illinois
 H-coal, hydrotreating of rerun136-139
 H-coal syncrude(s)120, 124t, 128
 boiling point distillations for 119f
 fuel oils from 125t
- Illinois (*continued*)
 H-coal syncrude(s) (*continued*)
 heating fuel from130t, 132t
 hydrotreated products from 123t
 naphthas from126t, 131t
 liquid(s)11, 29
 No. 6 coal(s)3, 7, 116
 No. 6 H-coal 258
 liquid 255
 Indane 62
 Indanols 44
 alkylated 239
 Indans, alkylated 239
 Indoles48, 55
 Intermediate severity hydrotreating .. 96f
 Intraparticle diffusion222-223
 Ion gas chromatogram, total 246f
 Iron depositions 182
 Isoquinoline 52
 hydrodenitrogenation of 54f
- J**
- Jet fuel93, 133, 253, 264
 hydrogenation 88
 preparation of120-122
 SRC-II83, 86
- K**
- Kerosene 93
 fraction 83
 Kinetics, hydrodesulfurization 199
 Kinetics, surface 221t
- L**
- LC-fining process 157f
 LC-fining of SRC-I153-173
 Light recycle oil 193
 Lignite 1
 extract 2
 liquids11, 32
 North Dakota 240
 Texas 248
 Linby coal 229
 Liquefaction, two-step 155f
 Liquid(s)
 Pittsburgh 11
 product in hydrotreating 194t
 properties, SRC-II79t, 80t, 85t
 Wyodak 11
- M**
- Mass
 spectra for adsorption concentrates,
 field ionization 24t
 spectra for adsorption concen-
 trates, electron-impact 24t

- Mass (*continued*)
 spectroscopy, electron-impact 42
 spectroscopy, field-ionization 42
 Mesitylene226, 231, 237
 Meta anthracite coals 30
 Metabolic activation 149
 Methane 231
 2-(2-Methylcyclohexyl) aniline 58
 Methylnaphthalene(s)59, 231
 Methylcyclopentane 122
 2-(2-Methylphenyl) ethylamine 55
 Microscopy, scanning electron185, 186f
 Moderate severity hydrotreating 99f
 Monaromatic concentrates from coal
 liquids 17t
 Monolith alumina structure 211f
 Monolith alumina supports 209
 Mutagenicity and carcinogenesis 149
- N**
- Ni-Mo Catalyst7, 29, 156
 -alumina147, 176
 Naphtha(s)93, 122, 251
 H-coal 116
 hydrotreating86-88, 255
 product, SRC-II78, 83
 properties, hydrotreating 82t
 syncrude
 from Illinois H-coal126t, 131t
 from SRC-II126t, 131t
 from Wyodak H-coal126t, 131t
 yield 253
 Naphthalene(s)59, 62, 231
 alkylated 239
 Naphthalenols 44
 Naphthene(s)226, 237
 Naphthols, alkylated 239
 Natural gas condensate226, 231
 Neutral fraction, composition of
 anthracene oil59-69
 Neutral fraction, homologs in60, 61t
 Neutral-nitrogen fractions from
 anthracene oil 48t
 Nitrogen content
 bases and 28f
 of Pittsburgh liquid 11
 polyaromatic-polar and 26f
 Normalizing procedure 167
 North Dakota lignite 240
 North Seal gas condensate 231
 Nuclear magnetic resonance 240
- O**
- Octahydroacridine 58
 Octahydroindenes 122
 Octahydropentalene 122
 Octahydrophenanthrene 66
 Octane, yield and 256f
 Oxygen-containing acids in anthra-
 cene oil 46t
 Oxygen, total acids and coal liquid 28f
- P**
- Paraffin 226
 Paraho shale oil75, 258
 Perhydroacridine 58
 Petroleum
 boiling range of 252t
 feedstock 258
 heteroatom content of 254t
 Phenanthrene29, 59, 62, 231
 chromia-alumina hydrotreating of .. 66
 hydrogenation/hydrogenolysis of .. 68f
 Phenanthrenols/anthracenols 44
 Phenol(s) 44
 alkylated 239
 in anthracene oil 47t
 deoxygenation44-46
 Phenolic fraction 243t
 3-Phenylpropylamine 53
 Phenylpyridines 55
 Phytane 239
 Pilot plant90t-92t
 Pitt Seam SRC-II 258
 Pittsburgh bituminous coal 1
 Pittsburgh liquid(s) 11
 nitrogen content of 11
 Polyacetylenes 236
 Polyaromatic
 -polar (PAP) concentrates from
 coal liquids20t-23t
 -polar content(s) 30
 distillate 11
 and nitrogen 26f
 rings, hydrogenation of 27
 Pore size distribution 211f
 catalyst 209
 and catalytic activity 177
 Pressure and catalyst deactivation 162
 Pristine 239
 Process variable space, optimiza-
 tion191-205
 Processability of coal-derived syn-
 crudes over IRC 106 137f
 Processing severity and hydrogen
 consumption 78
 Product aromatic and hydrogen con-
 sumption84f, 137f, 259f, 265f
 Product nitrogen and hydrogen con-
 sumption78, 81f, 259f
 Pyrene 62
 Pyrenols/fluoranthenols 44
 Pyridine extracts of coals 2
 Pyridine nucleus 70
 Pyrrole nucleus 70

- Q**
- Quinoline(s)52, 55, 70
 hydrodenitrogenation of 54f
- R**
- Rank and coal liquids composition,
 coal 1-37
- Reaction time and temperature and
 selectivity199-201, 203f
- Reactor
 design variables for fixed-bed 188f
 ebullated bed 185
 pressure and conversion 154
 pressure and space velocity162-164
 trickle bed213, 226
- Refinery
 for/with coal syncrude(s) 262f
 addition 260f
 economics 262f
 process261-263
 feedstock251, 255
 fuel 136
 plans93, 100
 H-coal 120
 processing 258
 sour crude 260f
- Refining of coal derived syncrudes 251-267
 Refining research263-264
- Reformer feedstock93, 255
- Residence time, vapor 236
- Residence time and yield 229
- Residuum content and ring number .. 25t
- Ring
 content and coal rank33f, 34f
 content and reaction time 33f
 distributions of saturate concen-
 trates 16t
 hydrogenation 58
 number
 and asphaltene content 25t
 distributions 25t
 in coal liquids27-29
 and residuum content 25t
 -opening cracking 29
- S**
- Salmonella typhimurium* mutagenicity 149
- Saturate concentrates, ring distri-
 butions 16t
- Saturate(s), total
 and coal rank 31f
 content 30
 and reaction time 31f
- Scanning electron microscopy185, 186f
- SCT (*see* Short contact time)
- Selectivity
 and catalyst loading196f, 197
- Selectivity (*continued*)
 and reaction conditions 203t
 and reaction time and temperature 203f
- Semianthracite coals 30
- Separation(s)
 anthracene oil, chromatographic 43t
 data for anthracene oil 43t
 of distillate(s)
 chromatographic 3-7
 adsorption 10
 fractions 10
 scheme for 5f
 fraction from acid-base14t-15t
- Severities, characterization of 94f
- Shale oil 253
 boiling range of 252t
 heteroatom content of 254t
 Paraho 258
- Short contact time (SCT)
 coal extract(s) 158
 feed properties 160t
 SRC, aging run, West Kentucky 187f
 SRC to low sulfur boiler fuels ...175-190
- Smoke point83, 133, 264
 and aromatics 265f
- Solvent blend, West Kentucky/SRC .. 175
- Solvent boiling range167-169
- Space velocity and conversion154, 163f
- Space velocity and reactor pressure 162-164
- Specific gravity 147
- SRC-I 76
 coal extracts, feed properties 160t
 hydrotreating of 191
 LS-fining of153-173
- SRC-II255, 258
 coal liquid, hydrotreatment bio-
 logical test of145-152
 naphtha 255
 Pitt Seam 258
 process product 77t
 syncrude(s)75-113, 120, 124t, 128
 boiling point distillations for 119f
 fuel oils from 125t
 heating fuel from130t, 132t
 hydrotreated products from 123t
 naphthas from126t, 131t
- Stability of hydrotreated H-coal
 syncrudes133-136
- Structure-reactivity relationships
 for hydrogenolysis 53
- Subbituminous coal, Utah 1
- Subbituminous coal, West Virginia 240
- GPC of SRC from 242f
- Sulfur
 content, hydrotreating time and 200f
 dioxide for upgrading coal
 liquid, liquid239-249
 in product, hydrogen consumption
 and 184f

- Surface
 activity, catalyst 220
 area and catalytic activity 177
 kinetics 221*t*
- Syncrude(s)
 coal
 addition, refinery with 260*f*
 boiling range of 252*t*
 heteroatom content of 254*t*
 refinery for 262*f*
 H-coal 115-144
 hydrotreater 258-261
 properties 116-118
 refining of coal derived 251-267
 SRC-II 75-113
 Synthoil liquid 208*t*
- T**
- Tetrahydroacenaphthene 66, 69
 Tetrahydroacridine 58
 Tetrahydrofuran 240
 extract, hydrocarbons from 245*t*
 Tetrahydrophenanthrene 66
 Tetrahydroquinolines 53
 Tetralin 226, 248
 nucleus 2
 Tetraline 231
n-Tetratetracontane 241
 Texas lignite 248
- Thermal
 baseline 169-171
 cracking 225-238
 stability 133
 specification 83
- Thiophene(s) 59
 hydrodesulfurization of 70
- Total
 acids and coal liquid oxygen 28*f*
 ion gas chromatogram 246*f*
- Toxicity evaluations 264
 Trickle bed reactor 213, 226
- U**
- n*-Undecane 226, 231
 Utah subbituminous coal 1
- V**
- Vapor residence time 236
 Vaporizer/cracker 227*f*
- W**
- Weight percent of coals 8*t*
 West Kentucky coal 191, 193
 SCT SRC, aging run 187*f*
 /SRC solvent blend 175
 West Virginia subbituminous coal 116, 240
 GPC of STC from 242*f*
- Wyodak
 coal 3, 7, 116
 H-coal 258
 liquid 255
 syncrude 124*t*, 128, 133
 boiling point distillations for .. 119*f*
 fuel oils from 125*t*
 heating fuel from 130*t*, 132*t*
 hydrotreated products from 123*t*
 naphthas from 126*t*, 131*t*
 liquids 11, 29
 syncrude 122
- Y**
- Yield(s)
 and cracking temperature 230*f*, 234*f*
 and octane 256*f*
 and residence time 229
 SRC-II hydrotreating 79*t*, 80*t*, 85*t*