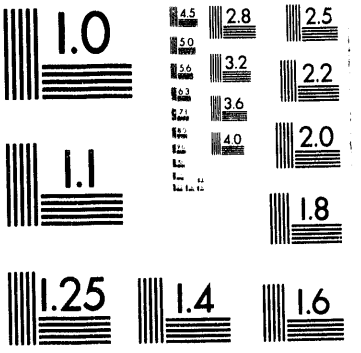
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1 of 1

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IMPROVED PERFORMANCE IN COPROCESSING THROUGH FUNDAMENTAL AND MECHANISTIC STUDIES IN HYDROGEN TRANSFER AND CATALYSIS

Contract No. DE-AC22-88PC88801

Quarterly Report

September 27, 1990 - December 26, 1990

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Submitted by

DEPARTMENT OF CHEMICAL ENGINEERING
AUBURN UNIVERSITY, ALABAMA

Dr. Christine W. Curtis, Principal Investigator

AB7/4Q90COAL.RPT

ACKNOWLEDGEMENTS

The experimental work of Ruth Owens, Honggon Kim, Michael Bedell, and Dr. Ke. Olson is sincerely appreciated. The technical assistance of Malcolm Clark, Christi Warnick, Robby Wilson, Evelyn Ellis, Wendy Slaten, Kamal Bouhadir, Franklin Bowers and Joseph Aderholdt is gratefully acknowledged.

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IMPROVED PERFORMANCE IN COPROCESSING THROUGH FUNDAMENTAL AND MECHANISTIC STUDIES IN HYDROGEN TRANSFER AND CATALYSIS

OBJECTIVE

To gain a fundamental understanding of the role and importance of hydrogen transfer reactions in thermal and catalytic coprocessing by examining possible hydrogen donation from cycloalkane/aromatic systems and by understanding the chemistry and enhanced reactivity of hydrotreated residuum, as well as by enriching petroleum solvent with potent new donors, nonaromatic hydoraromatics, thereby promoting hydrogen transfer reactions in coprocessing.

MAJOR TASKS AND THEIR OBJECTIVES

Task I. Elucidation of Hydrogen Transfer Reactions in Coprocessing

Objective. To attain a fundamental understanding of the hydrogen transfer reactions which occur during coprocessing and to elucidate their role and importance in achieving upgraded products.

Task II. Development of Potent Nonaromatic Hydroaromatic Hydrogen Donors for Coprocessing

Objective. To generate petroleum solvents enriched with nonaromatic hydroaromatics by metal or electrochemical reduction and to evaluate their reactivity and selectivity.

INTRODUCTION

Research continued this quarter on Subtask I.A., Hydrogen Transfer from Cycloalkanes, Subtask I.B.1., Pretreatment, Fractionation, and Reactivity of Petroleum Residua, Subtask II.A., Synthesis of Nonaromatic Hydroaromatics by Reduction with Metals and Electroreduction, and Subtask II.D., Chemistry and Reactivity of Nonaromatic Hydroaromatic Enriched Petroleum Solvents.

EXPERIMENTAL WORK

TASK I. ELUCIDATION OF HYDROGEN TRANSFER REACTIONS IN COPROCESSING

SUBTASK I.A. HYDROGEN TRANSFER FROM CYCLOALKANES

INTRODUCTION

The objective of Subtask I.A. is to investigate hydrogen transfer from cycloalkanes, such as those present in petroleum residua, to aromatics, such as those present in coal, during coprocessing. This quarter, hexahydroanthracene was reacted with a presulfided nickel-molybdenum catalyst in the synthesis of perhydroanthracene. Reactions were conducted using Illinois No. 6 coal, Maya Residuum, and the model compounds anthracene, pyrene, and perhydropyrene.

EXPERIMENTAL

Materials. The materials used this quarter included anthracene (ANTH), hexahydroanthracene (HHA), pyrene (PYR), perhydropyrene (PHPYR), biphenyl (BIP) as the internal standard for gas chromatography (GC) analysis, and tetrahydrofuran (THF) and toluene (TOL) as solvents. The ANTH, HHA, PYR, PHPYR, and BIP were all purchased from Aldrich Chemicals and had a purity of 99% or greater. The THF and TOL were Fisher certified.

Equipment. The equipment used for reactions consisted of a fluidized sand bath equipped with a horizontal agitation device, a volume determination device consisting of a series of gas sampling cylinders equipped with a pressure meter and corresponding transducer, and 3/4 inch stainless steel tubing bomb microreactors (TBMRs) with a length of 4.5 inches and a volume of approximately 20 cm^3. A Branson sonifier and Buchi rotary evaporator equipped with a Fisher high temperature bath were used in extracting coal products, and a Varian gas chromatograph

Model 3400 was employed for reaction product analysis.

Synthesis of Perhydroanthracene. The perhydroanthracene (PHA) needed for certain model compound reactions was synthesized, because it was unavailable through commercial sources. Because of the low yields of PHA when ANTH was used as the starting compound, HHA was used as the starting compound.

Procedure and Analysis for Perhydroanthracene Synthesis. The procedure used to synthesize PHA consisted of introducing one gram of HHA and one gram of presulfided nickel-molybdenum (NiMo) catalyst into a 20 cm^3 TBMR and charging with 1250 psig of hydrogen gas (H_2). The reactor was leak tested, submerged in a 380°C fluidized sandbath, and agitated horizontally for sixty minutes. At the end of the reaction, the TBMRs were quenched in a water bath, the pressure was released, and the products were extracted with THF. Products from the synthesis reactions were analyzed by the University Mass Spectrometry Facility. The instrumental conditions for product analysis by GC are shown in Table I.A.1.

Procedure and Analysis for Model Compound Reactions. Model compound reactions were conducted this quarter using varying ANTH/PHPYR weight ratios. A measured amount of each compound was introduced into a TBMR and then charged with 400 psig nitrogen. The reactor was leak tested, submerged in a fluidized sand bath at 430°C for sixty minutes, and agitated at a rate of 425 cpm. At the end of the reaction, the reactor was quenched in a water bath. The gas pressure in the bomb was released and measured using the volume determination apparatus designed and constructed by Mike Bedell, a chemical engineering graduate student at Auburn University. The products were recovered by extraction with THF. BIP, the internal standard for gas chromatography analysis, was added to the product vials. The products were

then analyzed by GC. The GC instrumental conditions for the ANTH and PHPYR reactions are shown in Table I.A.1.

Procedure and Analysis for Coal and Residuum Reactions. Residuum/aromatic, residuum/cycloalkane, residuum/aromatic/cycloalkane, coal/aromatic/cycloalkane, and coal/residuum/aromatic/cycloalkane reactions were performed this quarter. The aromatics used were ANTH and PYR, and the cycloalkane used was PHPYR. For all reactions, one gram of each component was introduced into a TBMR and then charged with 400 psig nitrogen. The reactor was leak tested, submerged in a fluidized sand bath at 430°C, and agitated at a rate of 425 cpm. At the end of the reaction, the reactor was quenched in a water bath. The gas pressure in the bomb was released and measured using the previously mentioned volume determination apparatus. The products were recovered by extraction with TOL and THF; the procedure is described in Appendix I.A.A. In order to determine the recovery of the model compounds used, BIP, the internal standard for GC analysis, was added to aliquots of the TOL and THF solubles, which were then analyzed by GC. The GC instrumental conditions used for the coal reactions are also shown in Table I.A.1.

RESULTS AND DISCUSSION

Mass spectrometry analysis confirmed that PHA was the major product from the synthesis reactions conducted this quarter. The synthesized PHA will be used in future model compound reactions.

Model compound reactions using different weight ratios of ANTH/PHPYR were continued this quarter. All reactions were duplicated and in some cases, triplicated. As with the other ANTH/PHPYR reactions, GC analysis revealed that DHA and PYR were formed. GC

analysis has also revealed small amounts of unknown products. Several samples are presently being analyzed by the University Mass Spectrometry Facility. The reactions conducted at the latter part of the quarter are presently being analyzed by GC. Tables I.A.2, I.A.3, I.A.4, and I.A.5 show the results of all the ANTH/PHPYR reaction products analyzed to date.

As can be seen from Tables I.A.2, I.A.3 and I.A.4, a definite relationship exists between the ANTH/PHPYR weight ratio and the amount of DHA and PYR produced. The conversion of ANTH to DHA was the greatest when the PHPYR, the hydrogen donor, was available in excess, whereas the conversion of PHPYR to PYR was the greatest when ANTH, the hydrogen acceptor, was available in excess. It was reported earlier that the most favorable condition for stoichiometric conversion would be at an ANTH/PHPYR weight ratio of 6.53/1.00. It was shown that the reactions with weight ratios of approximately 6.53/1.00 had ANTH and PHPYR conversions that were nearly equal. The data from reactions conducted this quarter indicates that the conversion of ANTH to DHA decreases at greater ANTH/PHPYR ratios while that of PHPYR to PYR increases. This seems probable because at greater ANTH/PHPYR ratios, ANTH, the hydrogen acceptor, is available in excess. Reaction time does not seem to have much effect on the reaction as indicated by the product conversions in Tables I.A.2, I.A.3, and I.A.4, and the hydrogen efficiencies in Table I.A.5. The product analysis from reactions conducted for 5, 15, and 30 minutes, as well as additional 90 and 180 minute reactions, should yield further information on the effect of reaction time and weight ratio. The results from these reactions will be reported later.

The results of the coal and residuum reactions conducted are shown in Table I.A.6. GC analysis of the reaction products revealed several unknown peaks which are presently being

analyzed by mass spectrometry. Reactions conducted with coal and residuum alone confirmed that these unknown peaks did not originate from the coal or residuum alone.

As with the model reactions, coal and residuum reactions in which both ANTH and PHPYR were used resulted in the formation of DHA and PYR. DHA was also formed in reactions in which ANTH but no PHPYR was used. Likewise, PYR was formed in reactions in which PHPYR but no ANTH was used. The overall conversion and the conversion to DHA and PYR was greater in those reactions in which both ANTH and PHPYR were used. There is some indication that there was higher conversion of ANTH and PHPYR to DHA and PYR in coal reactions than in residuum reactions when both ANTH and PHPYR were used. No products were formed in those coal and residuum reactions with PYR alone. Also, there was no indication that any products were formed in those reactions in which both PHYR and PYR were used. The overall conversion was better for the residuum reactions than for the coal reactions; this is most evident in the reactions with coal alone and residuum alone. In the coal/aromatic reactions, the overall conversion and the model compound recovery were low. Since the total recovery was high, there is the possibility that a portion of the aromatic was trapped in the IOM (insoluble organic matter). The addition of PHPYR to both residuum/aromatic and coal/aromatic reactions enhanced the overall conversion.

CONCLUSIONS

Mass spectrometry and GC analysis of the synthesis reaction products have confirmed that PHA was produced. Several reactions of interest will be conducted using the synthesized material.

This quarter reactions were conducted using varying ANTH/PHPYR weight ratios. Reaction times ranged from five minutes to three hours. All the results have not been analyzed yet, but definite trends are developing. As reported earlier, the reactant conversion is a function of weight ratios. Reaction time seems to have a much lesser effect.

Analysis of coal reaction products so far have indicated that the presence of PHPYR increases the overall conversion. Reactions in which ANTH and PHPYR were each reacted alone with coal or residuum had lower DHA and PYR yields than those reactions in which both ANTH and PHPYR were reacted. No products were formed in coal or residuum reactions with PYR alone or with PYR and PHPYR.

Table I.A.1
Instrumental Conditions for Product Analysis by GC

Gas Chromatograph	Varian 3400
Column	SGE HT-5 Al-clad
Split Ratio	50:1
Injector Temperature	340°C
Detector Temperature	350°C
Initial Column Temperature	80°C
Final Column Temperature	240°C
Temperature Programming	3°C/min

Table I.A.2
Recoveries and Conversions for Sixty Minute ANTH/PHPYR Reactions

Sample Number	Weight Ratio ANTH/PHPYR	Percent Recovery[1]		Percent Conversion[2,3]	
		ANTH	PHPYR	ANTH to DHA	PHPYR to PYR
212	0.140	76.0	88.2	12.84	0.26
177	0.166	71.1	81.0	13.32	0.34
175	0.167	77.5	87.6	13.40	0
143	0.170	77.7	88.6	12.24	0.12
213	0.208	64.1	75.6	10.76	0
141	0.245	84.9	97.5	11.00	0.22
142	0.254	85.7	97.5	9.54	0.16
214	0.315	64.6	77.6	9.40	0.68
215	0.326	64.0	72.1	11.69	0.50
96	0.501	55.9	76.2	10.08	1.21
95	0.510	78.8	98.6	6.87	1.19
124	0.547	78.7	115.7	6.96	1.18
123	0.555	59.0	97.0	7.86	1.08
88	1.010	72.2	85.7	6.35	2.76
91	1.030	84.6	86.7	5.14	1.61
90	1.054	83.0	78.4	5.98	1.94
125	1.914	64.8	96.0	4.71	2.86
98	2.018	67.0	84.3	3.93	3.40
97	2.023	63.6	81.9	3.30	2.91
126	2.100	88.8	92.3	4.32	3.02
240	3.011	68.3	82.7	7.13	3.34
139	3.560	91.0	100.2	3.86	2.04
241	4.006	80.4	92.2	6.27	0
140	4.264	81.1	88.2	3.38	1.50
242	4.538	82.5	99.9	6.59	4.16
161	4.989	90.0	95.7	5.81	6.29
257	5.022	75.0	84.3	6.68	6.30
144	5.892	92.7	106.9	5.32	5.66
176	5.938	88.2	95.8	5.43	8.83
178	6.004	101.8	115.8	6.17	8.77
160	6.201	66.8	93.5	6.87	6.53
237	6.360	79.3	80.3	6.45	9.17
259	6.544	90.4	97.2	5.01	7.70
238	8.162	87.0	85.0	6.25	12.08
260	9.252	87.9	87.5	4.24	7.18
239	9.975	98.2	80.9	5.40	13.71

[1] *Percent Recovery is defined as:*

$$(W_{initial} - W_{final}) \times 100/W_{initial}$$

[2] *Percent Conversion of ANTH to DHA is defined as:*

$$M_{DHA}\ produced \times 100/(M_{DHA}\ produced + M_{ANTH}\ recovered)$$

[3] *Percent Conversion of PHPYR to PYR is defined as:*

$$M_{PYR}\ produced \times 100/(M_{PYR}\ produced + M_{PHPYR}\ recovered)$$

where, M = moles, W = weight

Table I.A.3
Recoveries and Conversions for Ninety Minute ANTH/PHPYR Reactions

Sample Number	Weight Ratio ANTH/PHPYR	Percent Recovery[1]		Percent Conversion[2,3]	
		ANTH	PHPYR	ANTH to DHA	PHPYR to PYR
112	.523	95.4	96.9	6.53	1.61
111	.525	84.1	109.8	6.51	1.02
102	.530	75.4	84.5	7.87	2.13
99	1.016	83.8	102.4	4.98	2.32
127	1.017	62.8	85.0	4.73	2.86
101	1.027	80.7	96.2	5.47	2.20
128	1.057	95.5	91.2	7.10	2.18
100	1.931	65.0	97.7	6.72	3.01
109	2.020	104.3	76.9	3.33	3.38
110	2.057	84.2	71.2	4.32	3.53
258	4.493	57.2	61.3	8.82	10.07
261	4.527	60.8	72.1	5.26	5.46

[1]Percent Recovery is defined as:

$$(W_{initial} - W_{final}) \times 100/W_{initial}$$

[2]Percent Conversion of ANTH to DHA is defined as:

$$M_{DHA} \text{ produced} \times 100/(M_{DHA} \text{ produced} + M_{ANTH} \text{ recovered})$$

[3]Percent Conversion of PHPYR to PYR is defined as:

$$M_{PYR} \text{ produced} \times 100/(M_{PYR} \text{ produced} + M_{PHPYR} \text{ recovered})$$

where, M = moles, W = weight

Table I.A.4
Recoveries and Conversions for Three Hour ANTH/PHPYR Reactions

Sample Number	Weight Ratio ANTH/PHPYR	Percent Recovery[1]		Percent Conversion[2,3]	
		ANTH	PHPYR	ANTH to DHA	PHPYR to PYR
231	0.509	72.1	80.6	10.44	1.91
233	2.078	76.6	88.9	3.69	6.25
262	6.520	83.9	76.3	5.36	9.51
281	7.537	76.5	60.0	8.62	23.50
280	8.520	81.6	78.3	7.03	16.11

[1]Percent Recovery is defined as:

$$(W_{initial} - W_{final}) \times 100/W_{initial}$$

[2]Percent Conversion of ANTH to DHA is defined as:

$$M_{DHA} \text{ produced} \times 100/(M_{DHA} \text{ produced} + M_{ANTH} \text{ recovered})$$

[3]Percent Conversion of PHPYR to PYR is defined as:

$$M_{PYR} \text{ produced} \times 100/(M_{PYR} \text{ produced} + M_{PHPYR} \text{ recovered})$$

where, M = moles, W = weight

Table I.A.5
Hydrogen Efficiencies and ANTH/PHPYR Weight Ratios

Sample Number	Weight Ratio	[1]Hydrogen Efficiency (%)	Reaction Time (min)
96	0.501	45.9	60
95	0.510	38.1	60
123	0.547	40.3	60
124	0.555	35.7	60
88	1.010	31.2	60
91	1.030	51.1	60
90	1.054	55.0	60
125	1.914	33.2	60
98	2.018	28.5	60
97	2.023	27.4	60
126	2.100	44.9	60
240	3.011	84.5	60
139	3.560	95.6	60
242	4.538	93.3	60
161	4.989	66.0	60
257	5.022	72.7	60
144	5.892	73.4	60
176	5.938	49.7	60
178	6.004	55.3	60
160	6.201	71.6	60
237	6.360	65.6	60
259	6.544	59.0	60
238	8.162	62.0	60
260	9.252	81.5	60
239	9.975	66.7	60
112	0.523	33.6	90
111	0.525	41.7	90
102	0.530	28.4	90
99	1.016	28.1	90
127	1.017	19.4	90
101	1.027	33.9	90
128	1.057	35.3	90
100	1.931	45.6	90
109	2.020	41.3	90
110	2.057	46.0	90
258	4.493	55.4	90
261	4.527	56.1	90
231	0.509	41.7	180
233	2.078	21.2	180
262	6.520	59.1	180
281	7.537	45.2	180
280	8.520	53.5	180

[1]Hydrogen efficiency = (H_2 accepted/H_2 donated) x 100%

Table I.A.6
Reactant Recoveries and Product Yields for Coal and Residuum Reactions

Sample Number	Reactants	Total Recovery %	Asphaltenes %	Preasphaltenes %	IOM	Reactant Recovery %			Product Yield %		Overall Conversion
						PHPYR	ANTH	PYR	DHA	PYR	
145	Coal/PHPYR	85.1	71.3	15.3	13.4	78.4				12.6	86.6
146	Coal/PHPYR	86.3	67.2	16.7	16.0	90.2				7.8	84.0
162	Coal/ANTH	95.8	49.1	11.4	39.6		59.8		6.5		60.4
188	Coal/ANTH	105.1	43.7	14.6	41.6		50.9		8.0		58.4
163	Coal/PYR	98.9	55.6	11.6	32.8			69.3			67.2
189	Coal/PYR	96.8	52.5	16.6	30.8			61.0			67.2
190	Coal/ANTH/PHPYR	97.4	80.7	7.0	12.4	66.9	35.0		22.8	14.9	87.6
221	Coal/ANTH/PHPYR	87.8	78.3	8.7	13.0	65.1	31.1		28.4	15.8	87.0
191	Coal/PYR/PHPYR	89.2	81.6	7.3	11.1	88.1		96.3			88.9
220	Coal/PYR/PHPYR	90.8	84.2	6.1	9.7	114.8		66.8			90.3
223	Resid/PYR	89.2	83.1	9.4	7.5			47.8			92.5
225	Resid/PYR	93.6	75.9	15.7	8.4			75.0			91.6
246	Resid/ANTH	84.1	78.9	9.2	12.0		69.4		9.7		88.0
243	Resid/PHPYR	81.4	92.5	6.2	1.3	85.9				5.6	98.7
247	Resid/ANTH/PHPYR	85.8	99.0	0.0	1.0	83.1	48.2		22.8	9.3	99.0
248	Resid/ANTH/PHPYR	87.6	96.1	3.0	0.9	91.1	56.1		20.8	10.4	99.1
245	Resid/PYR/PHPYR	92.7	95.3	3.8	0.9	99.1		89.6			99.1
266	Coal	99.3	2.0	26.1	71.8						28.2
267	Coal	96.3	4.9	27.1	68.0						32.0
268	Resid	57.1	62.7	10.3	27.0						73.0
269	Resid	92.8	43.8	35.2	21.0						79.0

SUBTASK I.B. PRETREATMENT OF PETROLEUM RESIDUA FOR ENHANCED HYDROGEN TRANSFER

SUBTASK I.B.1. PRETREATMENT, FRACTIONATION AND REACTIVITY OF PETROLEUM RESIDUA

INTRODUCTION

This quarter size exclusion chromatography (SEC) was used to examine molecular size changes in coprocessing products prepared thermally and catalytically with different metal species in a previous experiment. Using the SEC technique, molecular size distributions of oil, asphaltenes and preasphaltenes from each coprocessing reaction of Maya residuum and Illinois No. 6 coal were compared with each other and also with those obtained under different reaction conditions. In another experiment, X-ray diffraction analysis of a powdered molydenum (Mo) species generated *in situ* from a reaction of Mo naphthenate (MoNaph) with excess sulfur was conducted to determine the structure of the *in situ* generated Mo compound.

EXPERIMENTAL

Size Exclusion Chromatographic Analysis. Size exclusion chromatography was performed to compare the different molecular size distributions in various fractions extracted from thermal and catalytic coprocessing products. The liquid chromatograph used was equipped with a Waters 590 programmable HPLC pump, a Waters 484 ultraviolet (UV) absorbance detector, and four size exclusion columns connected in series, which were composed of one each 500 Å and 100 Å porosity Ultrastyragel columns (Waters), and one each 100 Å and 50 Å porosity 5μ-Phenogel columns (Phenomenex); each column was 30 cm in length and had a 0.74 mm inside diameter.

Oil, asphaltenes and preasphaltenes from coprocessing reactions with Maya (6g) and Illinois No. 6 coal (3g) were prepared in previous experiments under the following different

conditions: a mixture of Maya residuum and coal without reaction, thermal reactions and catalytic reactions with MoNaph, nickel naphthenate (NiNaph), vanadium naphthenate (VNaph), and nickel-molydenum on alumina (NiMo/Alumina). Each fraction extracted from coprocessing products was dissolved in tetrahydrofuran (THF). The oil and preasphaltene fractions were diluted to 0.1 wt% for SEC analysis; however, the asphaltene fractions required dilution to 0.05 wt% for SEC analysis. Each sample solution was filtered using a Micron 0.2 μm polytetrafluoroethylene (PTFE) laminated membrane, and 25 μL of the filtered solution was injected into the SEC columns. Size separation was performed using the SEC columns at 50°C in THF at a 1 mL/min flow rate. The eluting fractions were detected using a UV detector at 254 nm fixed wavelength.

X-Ray Diffraction of *In Situ* Generated Mo Sulfide. Molybdenum-sulfur catalyst species were prepared *in situ* using tubing bomb microreactors (TBMRs) charged with 15 g n-hexadecane, 0.75 g Mo naphthenate paste, and 0.09 g elemental sulfur (three times the stoichiometric amount of sulfur required to form MoS_2) under a hydrogen (H_2) atmosphere (1250 psig at ambient temperature). Two different conditions, (1) 380°C for 30 minutes using a copper sealant for sealing the TBMR, and (2) 400°C for 1 hour without using a copper sealant were used to prepare the molybdenum-sulfur catalyst. After the reaction, black precipitates were recovered and washed with 20 mL tetrahydrofuran (THF) three times a day for three weeks. After THF washing, the solids were dried using a dry nitrogen gas purge. Structures of these *in situ* generated Mo samples were characterized using two different X-ray spectrometers. A Rigaku DMAXB X-ray spectrometer operated at a scanning rate of 1° 2θ/min was used to characterize the sample prepared using condition (1). A Philips X-Ray Spectrometer operated at a scanning

rate of 2° 2θ/min equipped with XRG 3100 X-ray generator was used to characterize sample (2). A commercial molybdenum sulfice (MoS_2) powder (Alfa Chemical) was also characterized and used as a reference material.

RESULTS AND DISCUSSION

Size Exclusion Chromatographic Analysis of Coprocessing Products. Size exclusion chromatography was used to observe size changes in the products of coprocessing reactions with Maya residuum and Illinois No. 6 coal under different reaction conditions. Molecular size distributions in the oil, asphaltene, and preasphaltene fractions from each coprocessing reaction were compared with each other and also with those obtained under different reaction conditions. A properly selected UV wavelength for the detector produced a proportional response for the different compounds during quantitative analysis. A fixed wavelength of 254 nm, commonly used in asphalt and coal studies, was used. To reduce the possible self-assembling effect of the molecules, which may occur at low temperature in the carrying solvent (THF), the SEC column was operated at 50°C, which is lower than the boiling point of THF. The intensity curve (corresponding to the UV absorbance) of the eluting fraction was smoothed to reduce noise. The starting and ending times of elution, the maximum eluting position, and the shape and broadness of the size distribution for each sample were compared.

First, the column was calibrated and its resolution was determined by analyzing the position and the shape of peaks from polystyrene standard samples of different molecular weights, and from aromatic chemicals, such as naphthalene, anthracene, and pyrene (Table I.B.1.1). As shown in Figure I.B.1.1, the column separated different size molecules.

Second, the molecular size distributions of the oil, asphaltene and preasphaltene fractions

of each coprocessing reaction were determined. Figure I.B.1.2 shows an example of the molecular size distribution in three different fractions from the Illinois No. 6 coal-Maya residuum coprocessing reaction with NiNaph. The maximum peak elution times for the extracted fractions were in the order, preasphaltenes < asphaltenes < oil. In addition, compared to the oil and the asphaltenes peak, the preasphaltenes peak showed a steep ascending slope, possibly indicating that the preasphaltenes contained a greater portion of large size molecules than the other fractions.

The molecular size distribution of each fraction produced under different conditions was compared (Figure I.B.1.3, I.B.1.4 and I.B.1.5). Compared to the oil and asphaltene fractions of the original coal-Maya coprocessing reaction, the same fractions from thermal and catalytic coprocessing products showed broader molecular size distributions. These broad distributions, both in the large molecular size range and in the small molecular size range, indicated that the coprocessing reactions produced smaller sized products by hydrocracking, and perhaps, some larger sized products by recombination of several molecules. Regardless of the different reaction conditions, each fraction of oil, asphaltenes and preasphaltenes for the thermal and catalytic reactions showed a similar molecular size distribution. Preasphaltenes possessed more large molecules, and hence, showed earlier elution of the maximum peak position than asphaltenes. Asphaltenes possessed more large molecules than oil. The oil fractions showed a more symmetrically shaped distribution than the asphaltene and preasphaltene fractions.

To quantitatively compare the molecular size distribution of each product, the SEC curve was sliced into several regions as shown in Figure I.B.1.6, and the area of each slice was calculated. The area of each slice is not directly proportional to the amount of compounds

eluting in a region because of differences in UV response to different compounds. For example, alkanes show nearly negligible response regardless of their molecular size; however, aromatic compounds show high intensity responses even though they are small in size or few in number. Because aromatic compounds are the major components in coal-residuum coprocessing, the area of each slice was assumed to be proportional to the concentration of the components in that area and was used directly for comparison of molecular size distributions.

Two sets of experiments were compared separately because an appreciable change of the SEC operating pressure was found in two experimental sets conducted at different times. The increase of the operating pressure by about 200 psi may have occurred because of a gradual column plugging (mainly in the 50 Å pore size column) by large molecules in the samples. The initial elution time, the peak width, and the area of each slice were compared for each case (Table I.B.1.2 and I.B.1.3). In the comparison of oil fractions, the VNaph catalyst was the most active for producing more small molecular components and fewer large molecular components for the different reactions shown. In the asphaltene fraction, the fractions produced by Ni and V catalysts contained more small molecular components than did the other cases. However, overall differences in size distributions of all three fractions obtained from different coprocessing reactions were not observed. In general, the asphaltene fractions of all coprocessing reactions showed the most appreciable change in peak shape, peak width and area distribution from those of the reactant (original). This indicated that the coprocessing reactions produced a broad range of small and large size toluene-soluble aromatic compounds from coal.

The difference in each molecular size distribution was interpreted using the terms defined in Figure I.B.1.7. The area ratio of A_S/A_L (A_S: an area for the components smaller than the

polystyrene of molecular weight 800; A_L: an area for the components larger than the polystyrene 800) indicated the relative amount of small components produced. The ratio of peak widths, D_s/D_l (D_s: a peak width between a point on the descending curve and the mean retention time, MRT, at the maximum peak position, D_l: a peak width between MRT and a point on the ascending curve) represented both the relative amount of small components to large components produced and the peak shape. Compared to the reactant, the oil fraction from coprocessing reactions produced appreciable amounts of small components with the possible exception of MoNaph (Table I.B.1.4, I.B.1.5). When the asphaltene fractions are compared, Ni and V catalysts produced appreciable amounts of small components smaller than the polystyrene 800. In the preasphaltene comparison, most coprocessing reactions produced less A_S/A_L than the reactant, indicating that coprocessing converted coal to small size molecules which were soluble in THF, but were larger than the polystyrene 800 in size.

Even though there were appreciable differences in the molecular size distributions of the different fractions from each coprocessing reaction, the differences found among the same fractions from different reactions were only slight under the present SEC conditions. During a recent experiment, the performance of the SEC instrumentation appeared to be improved by refinement of certain operating conditions and by the selection and combination of SEC columns, enhancing the system resolution for molecules of different sizes. Next quarter, comparisons among the molecular size distributions for each fraction of differently prepared coprocessing products (coal-Maya) will be made again using optimized SEC operating conditions. Pure Maya residuum and the THF-solubles from Maya residuum pretreated with different catalysts will also be analyzed.

X-Ray Diffraction of *In Situ* Generated Mo Sulfide. The sample (1) of *in situ* generated Mo sulfide, which was recovered from the reaction at 380°C for 30 minutes using a copper sealant for the TBMR, showed an X-ray powder diffraction pattern with several broad peaks and many sharp peaks. By matching the line positions with X-ray powder diffraction files (1,2), the major sharp peaks appeared to represent an impurity, $CuSO_4.5H_2O$, which was produced *in situ* from the copper sealant for the TBMR and the added sulfur. After the subtraction of impurity peaks, only broad peaks remained for the X-ray pattern shown in Table I.B.1.6.

Sample (2), which was prepared at a higher reaction temperature for a longer time without a copper sealant, also showed a very similar X-ray powder pattern to sample (1), but without the sharp peaks for $CuSO_4.5H_2O$. By comparing the X-ray diffraction pattern for sample (2) to the X-ray diffraction pattern of the commercial MoS_2, which was most likely MoS_2-$2H_1$, and the X-ray powder diffraction file, the line positions of the broad peaks indicated that MoS_2-3R was the most plausible structure for the *in situ* generated Mo-sulfur compound.

Even though the X-ray powder diffraction patterns of the *in situ* generated Mo sulfide were not as sharp and conclusive as the commercial MoS_2, two different X-ray spectrometers produced the same diffraction patterns for the differently prepared Mo samples. The low intensity, broad XRD peaks observed for the *in situ* generated molybdenum species are thought to be due to the presence of microcrystalline MoS_2 which had limited opportunity to grow larger because of the short, high temperature reaction conditions used. The low intensity of the peaks for the *in situ* generated species is also thought to be associated with the formation of microcrystalline MoS_2; microcrystals do not contain sufficient numbers of crystalline layers to produce diffraction patterns having intense peaks. These results may indicate that a

microcrystalline form of MoS_2, having both a large unit surface area and a high mobility resulting in high catalytic activity, is produced during the *in situ* reaction of molybdenum naphthenate with excess sulfur.

SEC Analysis of Coprocessing Products. Even though the analysis of the coprocessing products using SEC showed some differences for different reaction conditions, the large differences expected for coprocessing reaction conditions which previously produced large differences in product quantity and quality were not observed using SEC to date. As mentioned previously, further optimization of the SEC instrumentation will be performed to improve the resolution, so that overlap between fractions is minimized or eliminated completely. The SEC analysis showed consistent differences in the molecular size distributions for oil, asphaltene and preasphaltene fractions regardless of the reaction condition. Because the same quantities of different components show different UV responses, the absolute amount of components for a specific molecular size produced from coprocessing reactions could not be determined exactly. In order to understand the activity and selectivity of different catalysts for coprocessing, further refinement of the SEC technique and the development and application of new analytical methods, which can measure the amount of heteroatoms, aromatic components, and upgraded coal molecules of a specific size or weight, is required.

X-Ray Diffraction of Molybdenum Sulfide. The Mo species generated *in situ* under different reaction conditions showed the same X-ray powder diffraction patterns. Even though the diffraction peaks were broad, the peak positions and the ratios of their intensities showed that MoS_2-3R was a plausible structure for the *in situ* generated Mo sulfide. The broad peaks in the X-ray diffraction suggested that the *in situ* generated Mo sulfide consisted of very small crystals

which were not well-grown during the reaction period and smaller than the optimal crystal size for X-ray diffraction analysis. This hypothesis is consistent with former results for the *in situ* generated Mo sulfide, which had a larger unit surface area and a higher catalytic activity for hydrogenation of model compounds than the MoS_2 prepared by precipitation methods (3,4).

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Table I.B.1.1. Retention Time and Peak Width of Reference Samples in Size Exclusion Chromatography (SEC)[a]

Polystyrene or Aromatics	Molecular Weight (Mw)	Molecular Weight Distribution (Mw/Mn)	Approx. Mean Retention Time, sec.	Approx. Initial Elution Time, sec.	Approx. Peak Width[b], sec.
Polystyrene (PS)					
PS-A	111,000	≤ 1.00	1220	1175	164
PS-B	33,000	≤ 0.92	1253	1199	178
PS-C	20,800	≤ 1.03	1276	1224	178
PS-D	4,000	≤ 1.29	1409	1343	242
PS-E	2,100	≤ 1.08	1442	1356	254
PS-F	1,574	≤ 1.06	1530	1430	265
PS-G	1,152	≤ 1.07	1569	1473	277
PS-H	800	≤ 1.20	1671	1578	288
PS-I	568	≤ 1.13	1717	1570	461
Pyrene	202	-	2378	2330	220
Anthracene	178	-	2312	2240	455
Naphthalene	128	-	2366	2314	202

a Samples were dissolved in tetrahydrofuran at the levels of 0.1 wt% of polystyrene and 0.02 wt% of aromatics. Each sample was analyzed under the following HP-GPC condition: Styragel size exclusion columns in series (500-100-100-50 Å), 50°C column temperature, 1 ml/min flow rate of a carrier (tetrahydrofuran), and UV detection with a fixed wave length at 254 nm.

b Peak width between the points where the intensities of UV absorption at the ascending and descending curves were 20 % of the intensity at the maximum peak position (mean retention time).

Table I.B.1.2. Comparison of Molecular Size Distribution of Coprocessing Products - Set A

Reaction Condition and Product[a]	Initial Elution Time[b] (min)	Peak Width[b] (min)	Molecular Size Distribution, area %			
			Slice 1-3	Slice 4-6	Slice 7-9	Slice 10-12
Oil						
Reactant	22.0	14.5	17.4	56.2	23.8	2.6
Thermal	23.2	16.8	6.3	45.7	32.9	15.1
MoNaph	22.7	17.1	11.2	48.2	28.7	11.9
NiNaph	22.6	18.0	8.8	44.2	31.8	15.2
VNaph	22.9	17.8	6.3	41.3	34.5	17.9
$NiMo/Al_2O_3$	22.9	17.6	7.1	44.1	33.5	15.3
Asphaltenes						
Reactant	20.6	13.6	53.1	36.5	10.4	0.0
Thermal	21.8	15.4	31.1	43.6	21.5	3.8
MoNaph	21.8	15.5	30.6	44.4	21.0	4.0
NiNaph	21.5	18.3	19.2	42.4	29.5	8.9
VNaph	21.4	18.1	21.5	43.0	27.5	8.0
$NiMo/Al_2O_3$	21.4	17.7	22.8	43.5	26.6	7.1
Preasphaltenes						
Thermal	20.6	22.6	21.9	31.0	23.3	23.8
MoNaph	20.9	20.3	31.6	35.9	19.4	13.1
NiNaph	21.1	17.4	33.0	41.4	19.6	6.0
VNaph	20.6	20.3	28.4	38.4	22.8	10.4
$NiMo/Al_2O_3$	20.9	18.7	28.5	40.9	22.3	8.3

a Reactant (mixture of Maya and Illinois no. 6 coal), Thermal (products from thermal coprocessing), MoNaph, NiNaph and VNaph (products from catalytic coprocessing with naphthenate of Mo, Ni and V).

b Peak width between the points where the intensities of UV absorption at both the ascending and descending curves were 10 % of the intensity at the maximum peak position (mean retention time). Initial elution time at the point where the UV intensity was 10 % of that at the mean retention time.

Table I.B.1.3. Comparison of Molecular Size Distribution of Coprocessing Products - Set B

Reaction Condition and Product[a]	Initial Elution Time[b] (min)	Peak Width[b] (min)	Molecular Size Distribution, area %			
			Slice 1-3	Slice 4-6	Slice 7-9	Slice 10-12
Oil						
Reactant	22.1	14.4	16.5	57.3	23.9	2.3
Thermal	23.0	18.2	6.1	42.3	33.1	18.5
MoNaph	22.6	18.2	8.0	42.4	33.0	16.6
NiNaph	22.7	17.8	8.6	44.4	31.9	15.1
VNaph	23.2	17.7	4.8	40.2	35.7	19.3
$NiMo/Al_2O_3$	22.8	17.5	7.1	43.4	33.7	15.8
Asphaltenes						
Reactant	20.5	13.6	50.8	38.0	11.2	0.0
Thermal	20.8	18.8	29.4	41.2	22.3	7.1
MoNaph	21.4	18.5	24.9	44.8	22.6	7.7
NiNaph	21.3	18.7	20.9	42.5	27.8	8.8
VNaph	21.5	17.8	21.4	43.1	27.3	8.2
$NiMo/Al_2O_3$	21.6	18.4	18.7	43.4	28.6	9.3
Preasphaltenes						
Thermal	20.2	19.5	35.3	32.8	21.1	10.8
MoNaph	20.5	18.1	33.5	40.3	18.8	7.4
NiNaph	20.5	18.4	35.2	39.8	19.1	5.9
VNaph	20.7	19.0	30.6	38.1	22.6	8.6
$NiMo/Al_2O_3$	20.6	17.8	34.6	40.5	19.2	5.7

[a] Reactant (mixture of Maya and Illinois no. 6 coal), Thermal (products from thermal coprocessing), MoNaph, NiNaph and VNaph (products from catalytic coprocessing with naphthenate of Mo, Ni and V).

[b] Peak width between the points where the intensities of UV absorption at both the ascending and descending curves were 10 % of the intensity at the maximum peak position (mean retention time). Initial elution time at the point where the UV intensity was 10 % of that at the mean retention time.

Table I.B.1.4. Comparison of Size Exclusion Chromatographic Analysis of Coprocessing Products - Set A

Reaction Condition and Product Fractions[a]	Mean Retention Time (min)	Area Ratio of A_S/A_L[b]	20 % Cut[c]			66.7 % Cut[c]		
			Initial Elution Time (min)	Peak Width (min)	Width Ratio of D_s/D_l[d]	Initial Elution Time (min)	Peak Width (min)	Width Ratio of D_s/D_l[d]
Oil								
Reactant	27.4	0.97	22.5	11.8	1.42	24.4	5.8	0.89
Thermal	28.2	2.26	23.6	15.5	2.42	25.4	6.8	1.43
MoNaph	27.0	1.58	23.1	15.3	2.93	24.7	6.2	1.71
NiNaph	27.9	2.05	23.1	16.0	2.30	25.1	7.3	1.54
VNaph	28.5	2.62	23.5	15.9	2.19	25.5	8.0	1.68
$NiMo/Al_2O_3$	28.2	2.24	23.4	15.6	2.25	25.4	7.2	1.54
Asphaltenes								
Reactant	23.1	0.27	20.9	10.1	3.65	21.7	3.9	1.73
Thermal	24.0	0.70	22.0	12.9	5.40	22.8	4.9	2.97
MoNaph	24.1	0.71	22.0	12.5	5.22	22.9	4.7	3.21
NiNaph	27.5	1.32	21.8	15.7	1.76	23.1	9.5	1.17
VNaph	26.0	1.14	21.8	15.3	2.65	23.0	9.0	1.98
$NiMo/Al_2O_3$	25.9	1.07	21.7	15.1	2.55	22.8	9.2	1.86
Preasphaltenes								
Thermal	23.8	1.32	21.1	19.6	6.17	22.2	10.5	5.48
MoNaph	23.5	0.83	21.0	16.7	5.62	22.3	5.5	3.33
NiNaph	24.1	0.68	21.4	13.5	3.97	22.5	5.7	2.49
VNaph	23.6	0.93	21.0	16.8	5.54	22.2	8.1	4.99
$NiMo/Al_2O_3$	24.0	0.86	21.2	15.7	4.61	22.4	7.5	3.75

[a] Reactant (mixture of Maya and Illinois no. 6 coal), Thermal (products from thermal coprocessing), MoNaph, NiNaph and VNaph (products from catalytic coprocessing with naphthenate of Mo, Ni and V).

[b] Ratio of the area for small size components eluted before 1670 seconds (A_S) to that for large size components eluted after 1670 seconds (A_L). The areas were counted between 10 % cut points[c] and 1670 seconds.

[c] Peak width between the points where the intensities of UV absorption at both the ascending and descending curves were 10, 20 or 66.7 % of the intensity at the maximum peak position (mean retention time).

[d] Ratio of the molecular size distribution for small size components (D_s) eluted before the mean retention time (MRT) to that for large size components (D_l) eluted after MRT.

Table I.B.1.5. Comparison of Size Exclusion Chromatographic Analysis of Coprocessing Products - Set B

Reaction Condition and Product Fractions[a]	Mean Retention Time (min)	Area Ratio of A_S/A_L[b]	20 % Cut[c]			66.7 % Cut[c]		
			Initial Elution Time (min)	Peak Width (min)	Width Ratio of D_s/D_l[d]	Initial Elution Time (min)	Peak Width (min)	Width Ratio of D_s/D_l[d]
Oil								
Reactant	27.2	0.98	22.6	11.6	1.56	24.5	5.7	1.10
Thermal	28.1	2.54	23.5	16.6	2.60	25.5	7.3	1.79
MoNaph	28.2	2.03	23.2	16.0	2.20	25.0	7.2	1.29
NiNaph	27.7	2.01	23.2	15.8	2.50	25.0	7.3	1.71
VNaph	29.2	2.95	23.8	15.8	1.91	25.8	8.1	1.34
$NiMo/Al_2O_3$	28.4	2.28	23.4	15.7	2.13	25.3	7.7	1.48
Asphaltenes								
Reactant	23.1	0.30	20.9	10.7	3.86	21.6	4.4	2.09
Thermal	25.0	0.83	21.0	15.2	2.85	22.2	8.2	1.91
MoNaph	24.7	0.91	21.7	13.9	3.69	22.9	7.4	3.10
NiNaph	27.8	1.21	21.7	15.5	1.56	23.0	9.3	0.92
VNaph	25.8	1.13	21.8	15.2	2.84	23.0	8.7	2.18
$NiMo/Al_2O_3$	27.5	1.30	22.0	15.4	1.80	23.3	8.9	1.13
Preasphaltenes								
Thermal	23.0	0.80	20.5	17.3	5.79	21.5	6.2	3.02
MoNaph	23.7	0.68	21.0	15.6	4.85	22.4	5.9	3.49
NiNaph	23.6	0.65	20.8	14.6	4.14	21.9	6.6	2.88
VNaph	23.7	0.85	21.0	15.9	4.75	22.1	7.5	3.59
$NiMo/Al_2O_3$	23.7	0.65	21.0	13.9	4.34	22.1	6.4	3.03

[a] Reactant (mixture of Maya and Illinois no. 6 coal), Thermal (products from thermal coprocessing), MoNaph, NiNaph and VNaph (products from catalytic coprocessing with naphthenate of Mo, Ni and V).

[b] Ratio of the area for small size components eluted before 1670 seconds (A_S) to that for large size components eluted after 1670 seconds (A_L). The areas were counted between 10 % cut points[c] and 1670 seconds.

[c] Peak width between the points where the intensities of UV absorption at both the ascending and descending curves were 10, 20 or 66.7 % of the intensity at the maximum peak position (mean retention time).

[d] Ratio of the molecular size distribution for small size components (D_s) eluted before the mean retention time (MRT) to that for large size components (D_l) eluted after MRT.

Table I.B.1.6. X-Ray Powder Diffraction Data for Molybdenum Sulfide and Copper Sulfate

Mo Sulfide Sample[a]		Molybdenite $2H_1$				Molybdenite 3R		$CuSO_4 \cdot 5H_2O$[e]	
d(Å)	I/Io[b]	d(Å)	I/Io[c]	d(Å)	I/Io[d]	d(Å)	I/Io[c]	d(Å)	I/Io
7.69	23	6.145	100	6.146	100	6.145	100	10.4	5
6.80	20	2.742	6	3.072	2	2.712	23	5.73	35
6.55	20*	2.676	32	2.742	8	2.628	21	5.68	20
6.32	20	2.504	12	2.676	43	2.356	27	5.48	55
5.71	39	2.279	43	2.504	16	2.200	27	5.21	9
5.48	45	2.046	14	2.279	61	2.048	4	5.15	25
5.21	33	1.830	16	2.048	6	1.899	14	4.84	10
4.72	100	1.641	2	2.046	17	1.764	8	4.73	100
4.65	31	1.583	10	1.830	26	1.583	10	4.66	20
3.99	58	1.536	4	1.641	3	1.523	10	4.28	13
3.70	56	1.533	8	1.583	17	1.533	8	4.00	11
3.54	25	1.479	3	1.536	5	1.530	6	3.99	60
3.46	32			1.533	11	1.430	2	3.71	85
3.30	42			1.479	6			3.54	20
3.25	31							3.45	17
3.04	24							3.83	34
2.83	34							3.30	60
2.75	60							3.26	20
2.73	45							3.18	17
2.71	35							3.06	15
2.70	44							3.05	30
2.68	38*							2.90	11
2.66	66							2.82	40
2.64	32							2.79	20
2.63	33							2.75	50
2.61	30							2.72	15
2.59	45							2.66	40
2.56	33								
2.55	30								
2.42	22								

[a] Mo sample was generated *in situ* from a hydrogenation reaction of Indole with Mo naphthenate and excess sulfur (with a Cu sealant).

[b] Relative intensity

[c] Calculated pattern using a peak height (1,2)

[d] Calculated pattern using an integrated area (1,2)

[e] X-ray pattern data (1,2)

* Maximum peak position of major broad peaks: d = 6.6, 2.67, 2.3, 2.025, 1.567

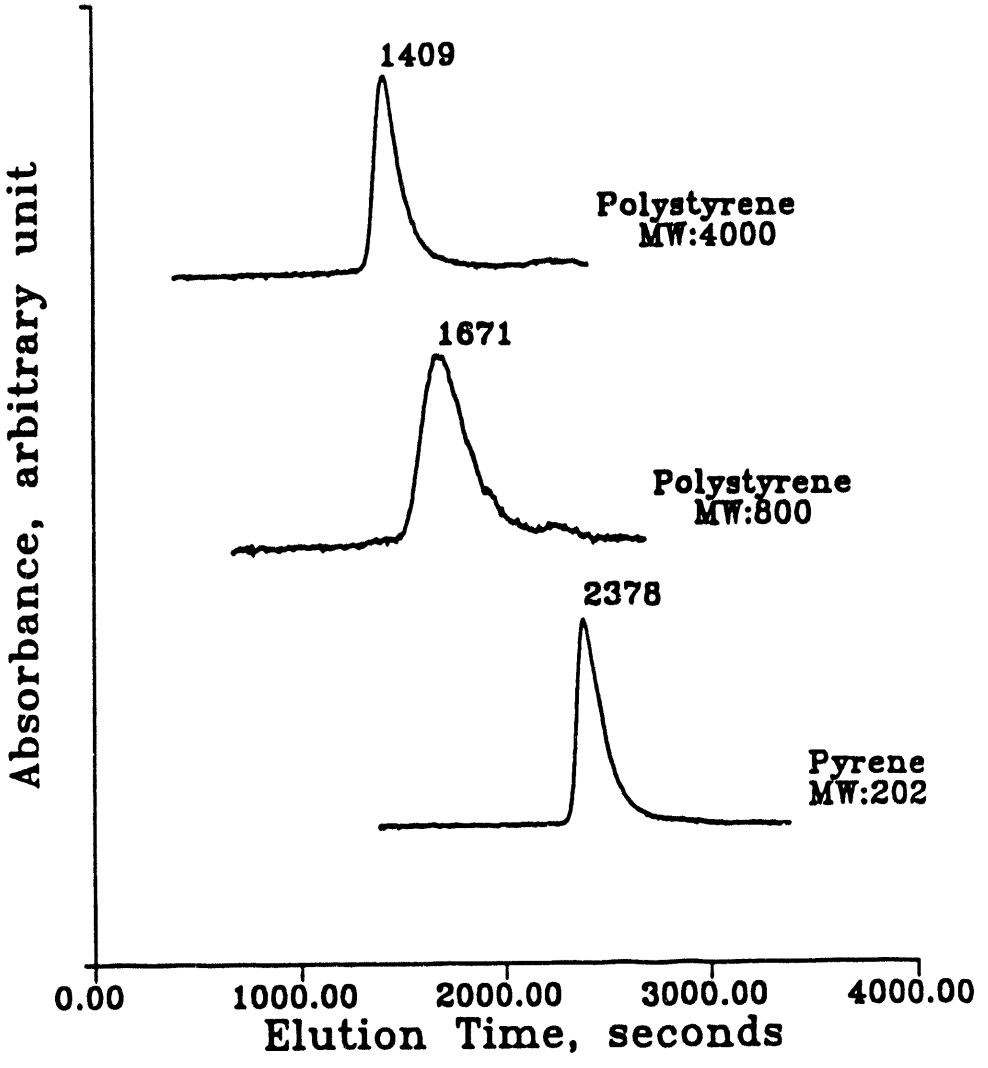

Figure I.B.1.1. Size Exclusion Chromatogram of Different Molecular Weight Compounds

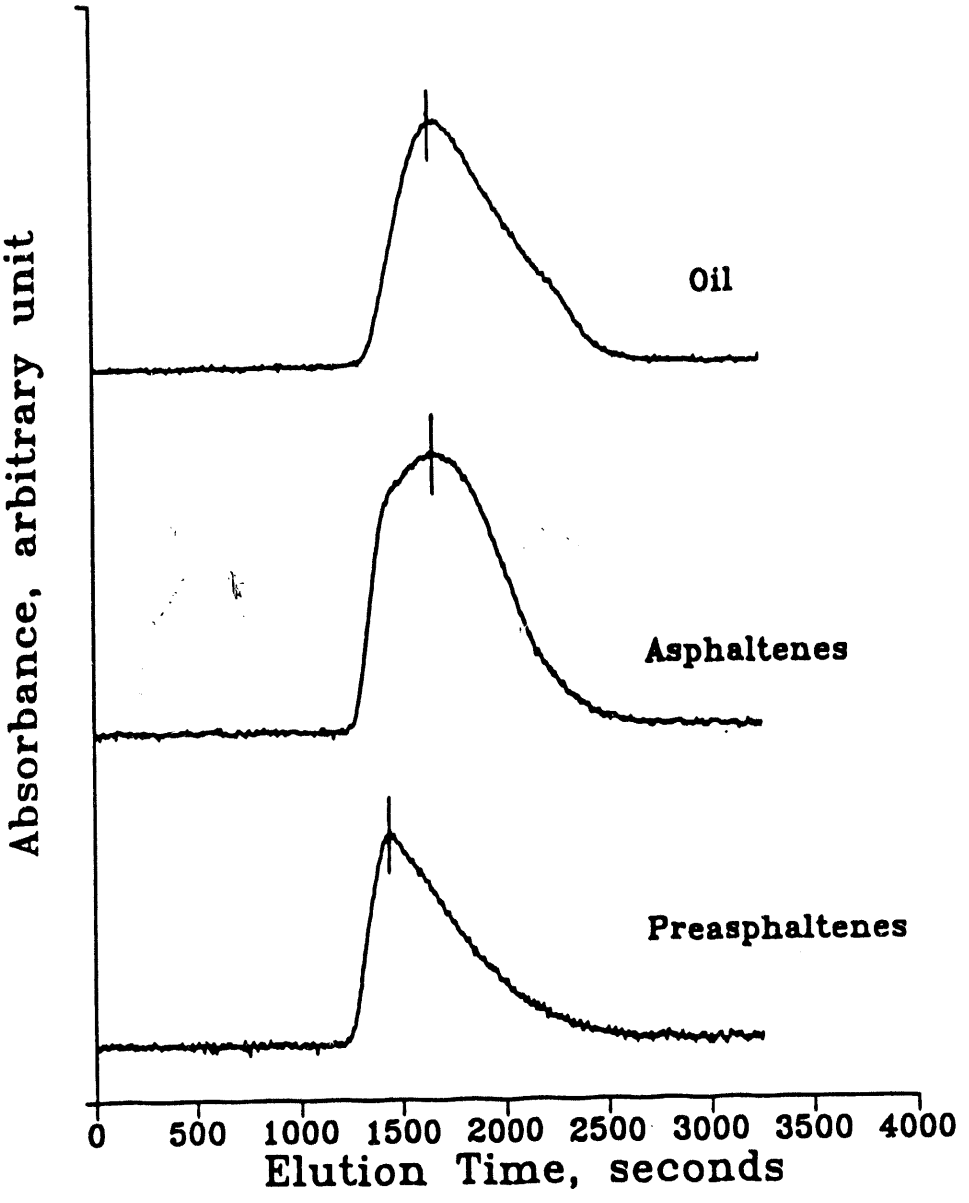

Figure I.B.1.2. Molecular Size Distribution of Oil, Asphaltene, and Preasphaltene Fractions from Coal-Maya Coprocessing Reactions with Nickel Naphthenate

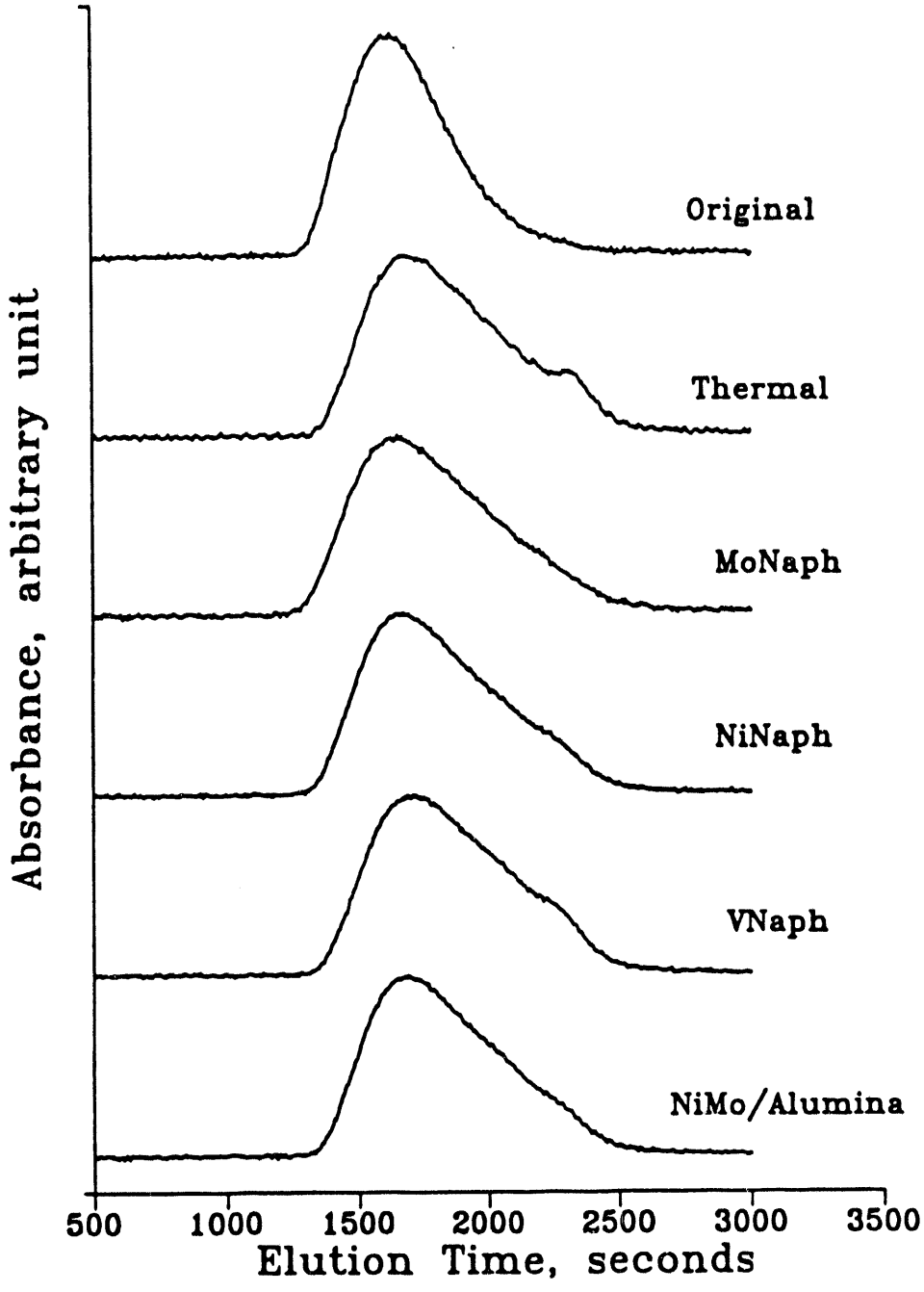

Figure I.B.1.3. Comparison of Molecular Size Distributions of Oil Fractions from Different Coprocessing Reactions

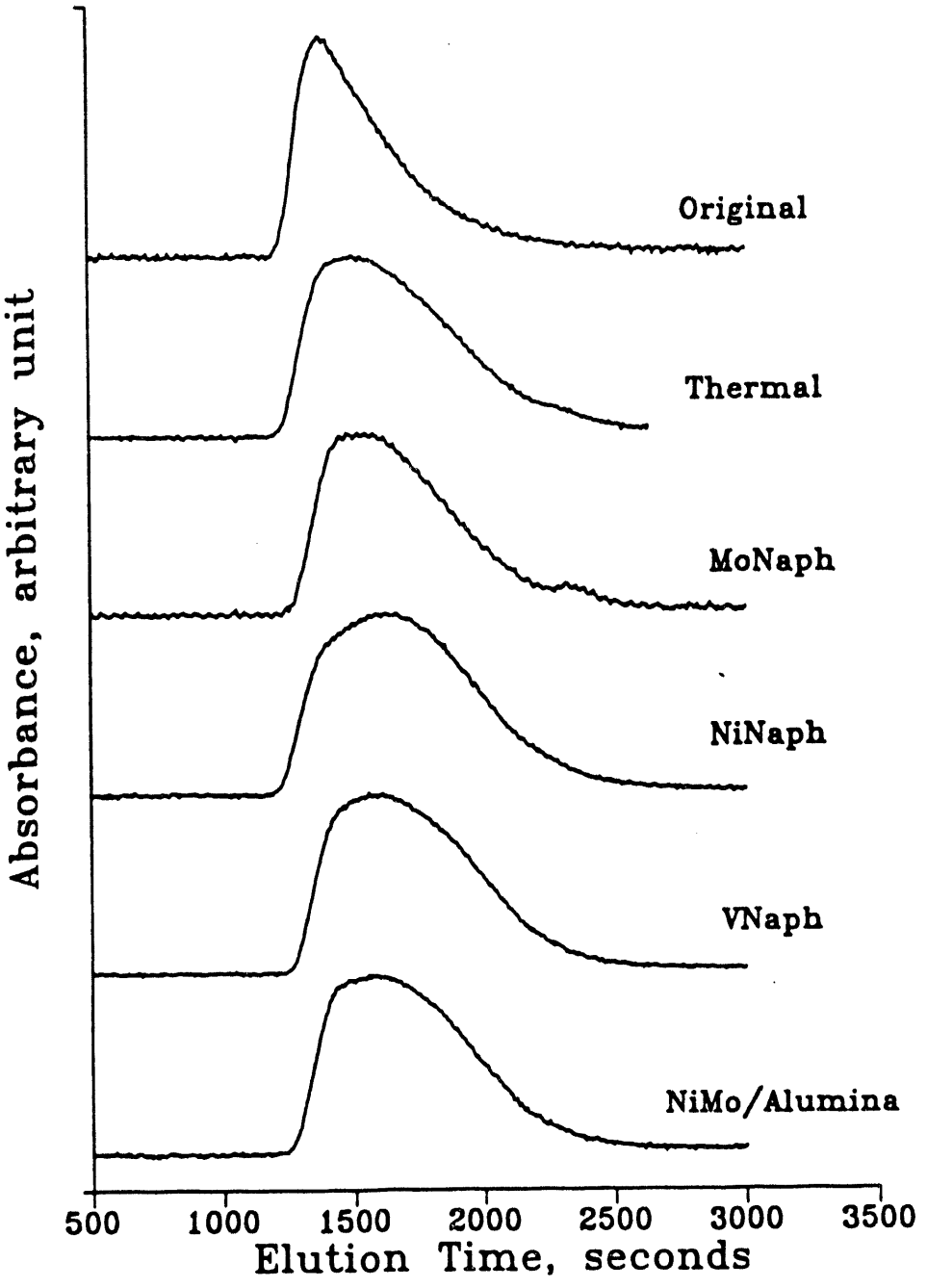

Figure I.B.1.4. Comparison of Molecular Size Distributions of Asphaltene Fractions from Different Coprocessing Reactions

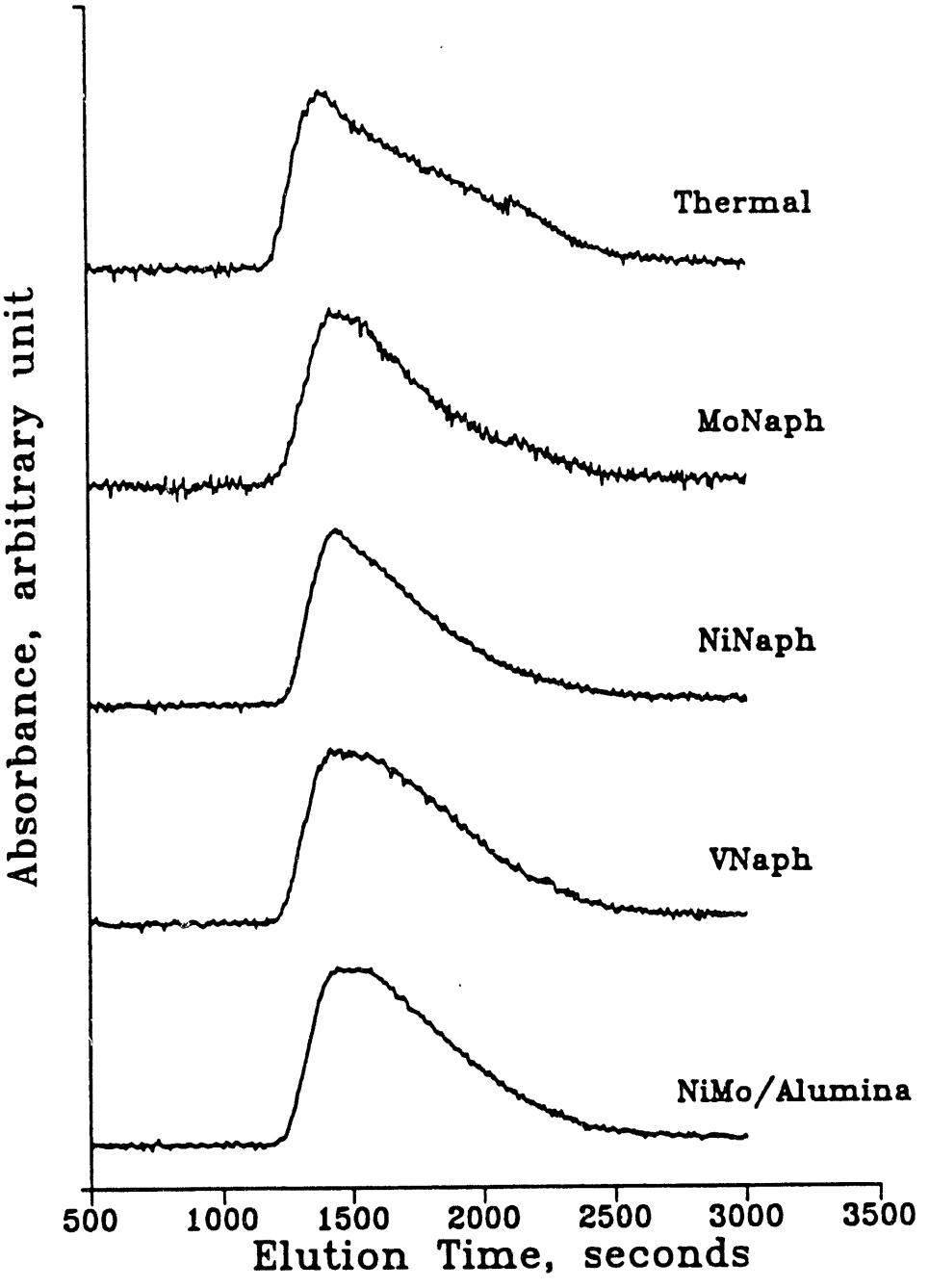

Figure I.B.1.5. Comparison of Molecular Size Distributions of Preasphaltene Fractions from Different Coprocessing Reactions

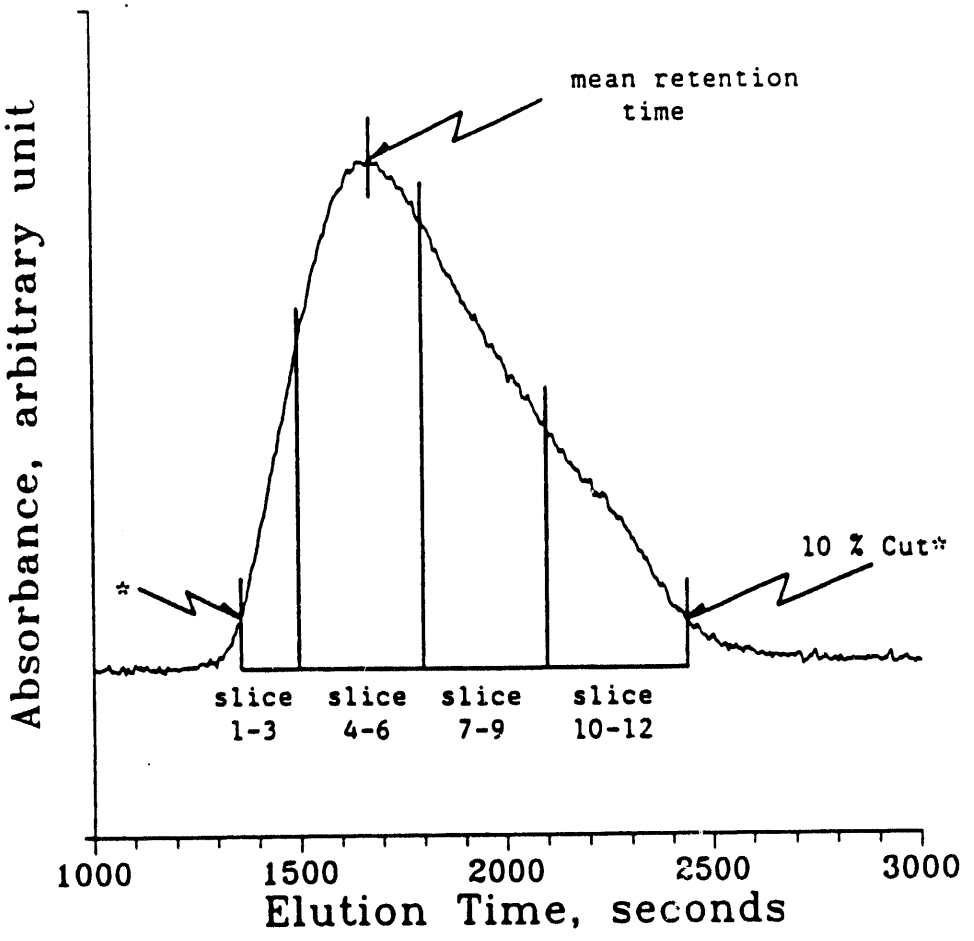

Figure I.B.1.6. SEC Curve Slicing for Quantitative Analysis Example

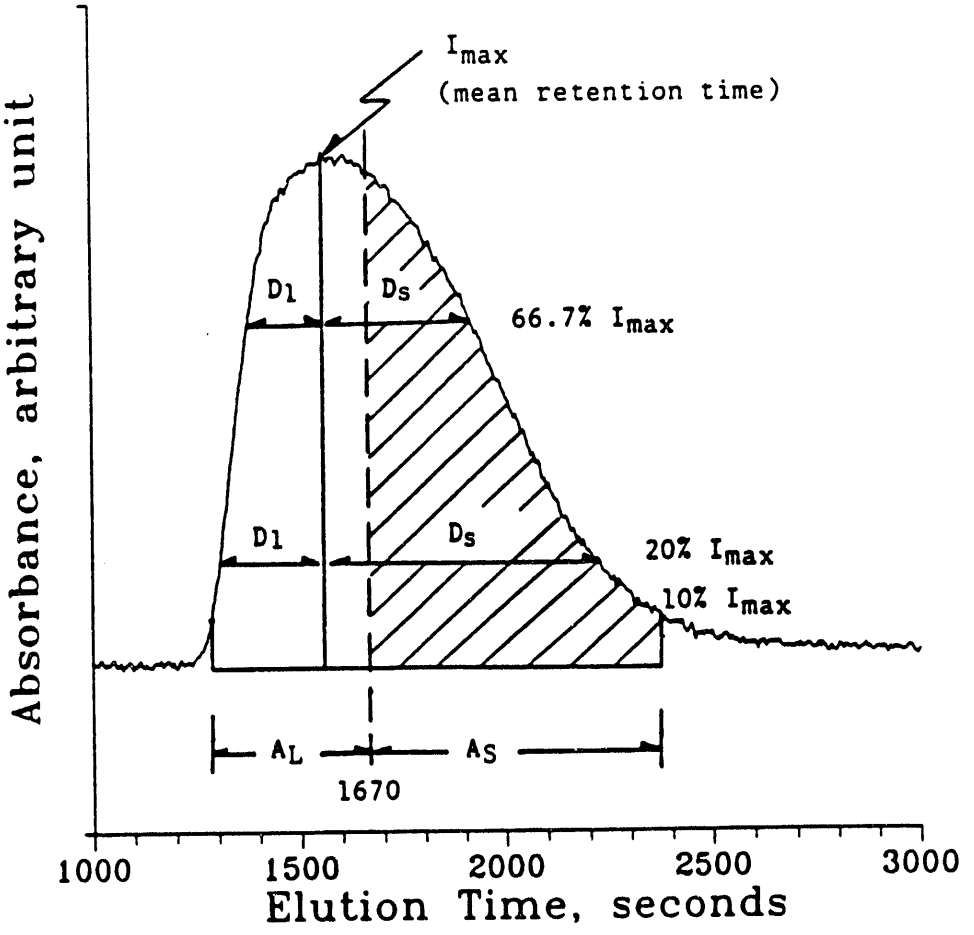

Figure I.B.1.7. Terms for Size Exclusion Chromatography Analysis

TASK II. DEVELOPMENT OF POTENT NONAROMATIC HYDROAROMATIC DONORS FOR COPROCESSING

SUBTASK II.A. SYNTHESIS OF NONAROMATIC HYDROMATICS

INTRODUCTION

The objective of this subtask is to synthesize high yield and essentially pure nonaromatic hydroaromatic compounds from their aromatic analogues by reduction with metals and/or electroreduction. Once successful methods have been developed using aromatic model compounds for the synthesis of nonaromatic hydroaromatics, their syntheses will be performed in real solvent materials such as atmospheric (or vacuum) residua and FCC Bottoms (Subtask II.C.). Because of the continued availability of sufficient manpower, research continued this quarter on the synthesis of nonaromatic hydroaromatic compounds both by Birch reduction with metals and by electroreduction methods.

EXPERIMENTAL

During the quarter, the modified Birch synthesis which involved the reduction of the aromatic compound, naphthalene, to form the nonaromatic hydroaromatic compound, isotetralin, was repeated using high purity chemicals (ethanol (HPLC grade) used during the actual synthesis of isotetralin, and methanol (Fisher Optima) used during the recrystallization of isotetralin) to enhance the purity of the isotetralin produced, and also to extend the time allowed for recrystallization of isotetralin from 24 hours to 72 hours to maximize the synthesis yield. The delivery funnel, designed and constructed last quarter for use in the Birch synthesis of isotetralin for the safe, convenient delivery of sodium metal spheres (3mm to 8 mm diameter), was tested and modified to incorporate improved construction materials. A new two-stage trap was also designed and constructed; an improved potassium hydroxide drying tube and a mineral oil filled

bubbler were incorporated into the trap design for safety and convenience reasons. The first extraction with ethyl ether and recrystallization from methanol resulted in a 50 percent yield of isotetralin (approximately 100 g) at a purity of 97.2 percent (determined by gas chromatographic analysis) with naphthalene as the major impurity. A second extraction produced another 50 g of isotetralin at a purity of 93.7 percent, for an overall synthesis yield of 80 percent. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of the synthesized isotetralin was in good agreement with previous ^{1}H-NMR spectra obtained for isotetralin. The results obtained from the analysis by mass spectrometry of the isotetralin synthesized this quarter will be reported next quarter.

Research was also initiated this quarter to determine the feasibility of using the modified Birch synthesis to chemically reduce the aromatic compounds found in Maya petroleum residuum to nonaromatic hydroaromatic compounds, thereby enhancing the effacacy of Maya residuum as a hydrogen donor in coal coprocessing. Ethyl ether, the solvent employed for aromatic compounds in the modified Birch synthesis, was a poor solvent for Maya residuum; however, Maya residuum had a suitable solubility (approximately 42 g/L) in tetrahydrofuran (THF), a cyclic ether. Addition of ethanol, the hydrogen source in the modified Birch synthesis, had no adverse effect on the solubility of Maya residuum in THF. Therefore, THF will be substituted for ethyl ether in the modified Birch synthesis procedure during the chemical reduction of Maya residuum.

Additional difficulties were encountered during the quarter with the constant temperature bath to be used to control the temperature of the electrochemical cell during the electroreduction of aromatic compounds to their nonaromatic hydroaromatic analogues. After all electronic

components were replaced, and the orientation of the thermoregulator was optimized in the bath, excessive switching of the mechanical relay employed in the control circuit caused it to overheat and fail. After the excessive switching problem was solved by vibrational isolation of the thermoregulator from the constant temperature bath stirrer motor, the decision was made, for reasons of safety and durability, to order a sealed, solid state relay to replace the mechanical relay used in the control circuit of the constant temperature bath.

FUTURE WORK

During the next quarter, research efforts will be directed to conversion of aromatic compounds present in Maya residuum to their nonaromatic hydroaromatic analogues by modified Birch reduction. The activity of the Maya residuum pretreated by Birch reduction will be evaluated in Subtask I.B.1. If all difficulties associated with the constant temperature bath are overcome, and no other major problems arise, the synthesis of nonaromatic hydroaromatic compounds by electroreduction will be performed next quarter, and the purity and yield of nonaromatic hydroaromatic compounds produced will be determined.

SUBTASK II.D. CHEMISTRY AND REACTIVITY OF NONAROMATIC HYDROAROMATIC ENRICHED PETROLEUM SOLVENTS

INTRODUCTION

Research this quarter consisted of the completion of the coprocessing reactions with Maya residuum and the Argonne Premium Coals. The coals, and their ranks are presented in Table II.D.1.

Analysis by gas chromatography (GC) of the reaction products was performed to determine the effects the coprocessing reactions had on model compounds. The GC analyses have been completed for five of the reacted coals, and is on-going for the remaining coals. The results will be detailed in a future monthly and quarterly report when all 8 coals have been analyzed.

EXPERIMENTAL

The reactions of both cyclic olefins, isotetralin (ISO) and hexahydroanthracene (HHA), and three conventional hydroaromatic donor compounds with Maya residuum and one of the Argonne Premium coals were performed. For these studies, the following reaction conditions were employed: 30 minute reaction time; 1250 psig hydrogen atmosphere at ambient conditions; 380°C reaction temperature; 2.0 g coal; 4.0 g total solvent mixture including 0.5 wt % donable hydrogen of the model compound with the balance being Maya residuum; 700 cpm vertical agitation rate in a stainless steel tubing bomb microreactor with a volume of approximately 50 cm^3.

RESULTS AND DISCUSSION

Table II.D.2 presents a summary of the results obtained for coal conversion to tetrahydrofuran (THF) solubles for the Argonne Premium coals with Maya residuum. Also

included, for comparative purposes, are the reactions previously performed with Western Kentucky No. 9 coal.

Some conclusions that can be made based upon the data presented in Table II.D.2 are as follows. First, some coals are inherently more reactive; i.e. some have greater conversion to THF solubles than others. In comparing the reaction of the different coals with no hydrogen donor compound added, the reactivity ranking of the coals with Maya residuum would be as follows: Illinois No. 6 > Pittsburgh No. 8 > Western Kentucky No. 9 and Blind Canyon > Upper Freeport and Beulah-Zap > Wyodak-Anderson and Lewiston-Stockton > > > Pocahontas No.3. These rankings get less defined when different hydrogen donor compounds are added to the reaction system. The order of the more moderately reactive coals, e.g. Upper Freeport, Beulah-Zap, Lewiston-Stockton, and Wyodak-Anderson varies depending upon the model donor that is present. With DHA (1.2 g resid), DHA (3.0 g resid), and HHA, those hydrogen donor compounds producing the highest coal conversion to THF solubles, Western Kentucky No. 9 coal was the most reactive. By comparison, Illinois No. 6 was the more reactive coal with OHA, ISO, and TET. In general, Illinois No. 6, Western Kentucky No. 9, and Pittsburgh No. 8 are all reactive coals; in the current reaction system, regardless of the compounds present, Pocahontas No. 3 coal is extremely unreactive.

In the present reaction system, independent of the particular coal that was present, (1) DHA with 1.2 g Maya residuum always gave the highest coal conversion to THF solubles, (2) DHA with 3.0 g Maya residuum always produced less coal conversion than when only 1.2 g residuum was present, all other things being equivalent, (3) the cyclic olefin, HHA, always gave higher conversion than its conventional hydroaromatic hydrogen donor analogue, OHA, (4) HHA

usually gave either greater coal conversion or nearly equivalent conversion compared to its analogue, DHA, in the presence of 3.0 g Maya residuum with the exceptions of Lewiston-Stockton, Blind Canyon, and Beulah-Zap coals, (5) the cyclic olefin, ISO, always produced higher coal conversion to THF solubles than did its conventional hydrogen donor analogue, TET, (6) the cyclic olefin, ISO, generally produced either greater coal conversion or nearly equivalent conversion compared to the conventional hydroaromatic hydrogen donor, OHA, with the exceptions of Upper Freeport and Blind Canyon coals, and 7) the conventional hydrogen donor compound, TET, produced little or no additional coal conversion over that which was produced by the coal alone. For Upper Freeport, Lewiston-Stockton, Blind Canyon, and Beulah-Zap coals, TET actually produced less coal conversion to THF solubles than was obtained with Maya residuum and the coals reacted with no added hydrogen donors.

FUTURE WORK

Work next quarter will consist of the completion of the gas chromatographic analysis of the remaining reaction samples. Also, a selection procedure for different residua will be determined in order to begin reacting a slate of residua with Pittsburgh No. 8 coal under equivalent conditions. This will be performed to attempt to determine the effect that different residua have on coal conversion. The residua slated to be tested may include Yates, Alaskan North Slope, Arabian Heavy, Cobinda Takula, Duri, Gollfaks, and South Louisiana residua. A selection of 4-5 properly chosen residua will be reacted with Pittsburgh No. 8 coal.

Table II.D.1
Coals Reacted with Maya Residuum

Coal Seam	Rank
Upper Freeport	Med. Vol. Bit.
Wyodak-Anderson	Sobbituminous
Illinois No. 6	High Vol. Bit.
Pittsburgh No. 8	High Vol. Bit.
Pocahontas No. 3	Low Vol. Bit
Blind Canyon	High Vol. Bit.
Lewiston-Stockton	High Vol. Bit.
Beulah-Zap	Lignite

Table II.D.2
Coal Conversion Results for Model Donors[1] and Maya Residuum with Kentucky No. 9 and Argonne Premium Coals

Coal	DHA (1.2)	DHA (3.0)	HHA	OHA	ISO	TET	None
Western Kentucky No. 9	73.6(0.7)[2]	65.0 (1.6)	65.9 (0.7)	45.4 (1.0)	44.8 (0.3)	31.7 (2.6)	24.3 (3.3)
Illinois No. 6	71.8 (0.3)	56.6 (0.3)	62.7 (1.7)	52.4 (0.4)	58.9 (2.4)	55.5 (0.5)	51.3 (2.4)
Upper Freeport	48.3 (0.5)	36.4 (2.1)	35.3 (0.1)	23.7 (2.9)	16.5 (3.4)	9.6 (0.2)	14.0 (1.6)
Pocahontas No. 3	N/A	N/A	-2.1 (0.4)	N/A	N/A	N/A	N/A
Pittsburgh No. 8	62.9 (0.2)	55.3 (1.3)	55.0 (1.1)	43.3 (0.8)	41.5 (0.6)	32.3 (1.6)	32.2 (1.5)
Lewiston-Stockton	38.0 (4.2)	36.0 (0.4)	25.3 (0.4)	19.8 (1.0)	20.6 (1.5)	9.8 (1.2)	10.0 (0.2)
Blind Canyon	66.5 (3.8)	59.8 (1.9)	53.3 (1.2)	39.1 (2.8)	35.4 (0.1)	16.4 (1.2)	24.1 (3.2)
Wyodak-Anderson	53.8 (2.0)	39.6 (1.1)	37.9 (1.8)	20.3 (2.7)	18.1 (3.0)	13.5 (1.5)	8.7 (1.7)
Beulah-Zap	44.0 (0.8)	29.0 (0.3)	20.5 (1.3)	15.2 (1.5)	15.4 (1.3)	5.5 (1.0)	11.1 (1.4)

[1]DHA (1.2) = dihydroanthracene (1.2 g Maya residuum); DHA (3.0) = dihydroanthracene (3.0 g Maya residuum); HHA = hexahydroanthracene; OHA = octahydroanthracene; ISO = isotetralin; TET = tetralin

[2]The percent coal conversion is followed by the standard deviation in percent in parentheses.

Appendix I.A.A

Procedure for Extraction of Toluene and Tetrahydrofuran Solubles

In order to recover the TOL and THF solubles in the coal reaction products, the following procedure was employed:

After the TBMR pressure had been released, the TBMR was placed in an ultrasonic bath, and the reaction products were rinsed into a 250 mL beaker with 50 milliliters of TOL. The contents of the beaker were then placed in a sonicator chamber for four minutes, after which the contents were poured into a 250 mL centrifuge bottle. This procedure was repeated three times until the volume in the centrifuge bottle was approximately 150 milliliters. The contents of the bottle were then centrifuged for ten minutes and carefully decanted into a 500 mL flat bottomed boiling flask. The entire procedure was repeated two more times until the volume of the boiling flask was approximately 450 milliliters. The boiling flask was then placed on a rotary evaporator and the TOL was evaporated. The remaining contents of the boiling flask were that portion of the products which were TOL soluble. The procedure used for the extraction of THF solubles was the same except that THF was used as the solvent. The same centrifuge bottle was used for extracting both TOL and THF solubles. At the end of the extractions, the reaction products which remained in the centrifuge bottle were the insoluble organic matter (IOM), which were soluble in neither TOL nor THF.

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