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DEVELOPMENT OF ANALYTICAL PROCEDURES FOR COPROCESSING

SUMMARY

Coprocessing of coal with petroleum resid is a promising method for conversion of these low-grade materials to more easily refined liquids. As the supply of high quality petroleum diminishes and the use of lower grades of crudes increases, coprocessing could provide the means to convert the increasing amounts of resid to useful products and to initiate the utilization of coal for the production of distillate fuels.

This is the third quarterly technical report for a project designed to extend our understanding of coprocessing reactions. More specifically, this research is concerned with development of chemical analytical procedures needed to distinguish between materials and compound classes in the coprocessing products which are derived from the petroleum resid, the coal, or both. This project will provide new information on the structure of products derived from coprocessing and will aid in identification of the reaction mechanisms that affect conversion.

Carbon isotope ratios have been used to determine the relative contributions of coal and resid to various coprocessing fractions where the fractions were produced by distillation or solubility fractionation. In the current project, the carbon isotope technique will be utilized with chemical compound type fractionations which have been developed at NIPER. These comprehensive separation schemes have been extensively applied to petroleum but not to coprocessing products. These separation techniques will be used initially with coprocessing samples produced in-house with a 2-liter batch autoclave. Later in the project, these techniques will be applied to samples produced on process development units operated by other DOE contractors.

Materials selected for initial study were Maya >1000° F resid and Illinois #6 coal. Catalyst was introduced by aqueous impregnation of the coal with ammonium tetrathiomolybdate solution. Conditions for satisfactory conversion have been established and workup procedures have been developed. All runs at the selected loadings were completed this quarter.

INTRODUCTION

A number of separation and analytical characterization methods have been developed for petroleum and syncrude samples to provide information on composition. This information has been useful in selection of suitable refining processes for the crude material and for monitoring the reaction products. Coprocessing products contain materials derived from both petroleum and coal reactants. The composition will be affected by the conditions selected for the reaction and by the nature of the petroleum residue and coal that are converted in the processing procedure.

A series of coprocessing reaction runs have been carried out that differ only in the ratio of residue to coal in the reaction mix. The total amount of reactants, the level of catalyst added, and other reaction conditions were unchanged throughout the coprocessing reaction series. No attempt has been made to optimize the total yield or the amount of any fraction produced. However, the reactants and conditions are reasonably typical of single stage conversion methods and the products are expected to be representative of conventional products.

The objective of this project is development of analytical methods for determination of the contribution of residue or coal to specific species or narrowly limited compound classes. Separation and isolation of the components of the coprocessing products is based on distillation and preparative liquid chromatography procedures that have been developed at NIPER for studies of petroleum and syncrude materials. The determination of contribution of residue and coal to these fractions may be determined most directly by means of carbon isotope ratio values. In addition, products that are formed primarily from the residue or coal alone should be detected in amounts proportional to that specific reactant. The conversion of residue or the liquefaction of coal taken separately show some unique products as well as substantial amounts of similar materials. The products common to both processing methods are best evaluated by isotope ratio procedure. The detailed composition of the individual fractions will be determined by mass spectrometry and other characterization methods.

Coprocessing procedures have been shown to produce good yields of desirable products. However, there remain uncertainties on the mechanisms of the reactions and the origin of the products from the processing of petroleum residue and coal together. This project is intended to provide information on these questions, particularly the origin of products. This can aid in establishing the amount of products obtained from the residue and coal separately and in the choice of the reactants and operating conditions. In addition, the quality and refinability of the product components from the residue and coal separately can be controlled by the choice of these reactants as well as the coprocessing conditions.

The preparation of coprocessing products for this project and the preliminary workup through the distillations have been completed. These are described in detail in this report.

EXPERIMENTAL

1) Materials

The reactants used were a petroleum residue and coal used in other studies of coprocessing procedures (1). Maya crude residue boiling above 1000° F and Illinois No. 6 coal (Burning Star Mine) were used in all reactions. The petroleum residue was available in NIPER stocks from previous programs and the coal was obtained from the Advanced Coal Liquefaction Facility of Wilsonville, AL. Ammonium tetrathiomolybdate (Aldrich) was added to form the catalyst and dimethyl disulfide (Aldrich) added to insure complete sulfiding of the molybdenum.

In each coprocessing run 666.7 grams of combined residue and coal were used. The composition of the reaction mixtures were made up to contain 2, 20, 30, and 40 weight percent loading of coal. Each reaction mixture contained 1.81 grams of $(NH_4)_2MoS_4$, equivalent for 0.1 weight percent molybdenum on the total reaction mix basis. The molybdenum pre-catalyst was added by impregnating the coal in an aqueous solution. An excess of coal and $(NH_4)_2MoS_4$ were mixed in the proper ratio for the reactant mix. The slurry was partially dried in a porcelain pan on a hot plate at minimum setting. The mix was stirred often to avoid any overheating and the drying continued until the material was in a near-dry granular state. The drying was completed in a rotary vacuum evaporator at about 60° C and 100 torr vacuum. This procedure for impregnation of the coal with soluble catalyst agent is similar to that used in coal liquefaction studies (2,3). The residual moisture content of the impregnated coal was determined by weight loss on drying about 2 grams at 105° C for 30 minutes. When the reactants were loaded into the autoclave, 0.5 mL (0.52 g) of dimethyl disulfide was added.

2) Reaction Procedures

The coprocessing reaction was carried out in a 2-liter Hastalloy C autoclave (Autoclave Engineering). It utilized a magnetically coupled stirrer and was equipped with temperature and pressure monitors and a temperature controller. A stirrer impeller was constructed to provide narrow wall and bottom clearance in order to minimize sedimentation of solids. A second 2-liter autoclave was used as a high pressure hydrogen reservoir and was connected to the coprocessing reactor through a pressure regulator.

After the reactants were sealed in the autoclave the air was removed by repeated flushing with hydrogen. Hydrogen pressure was then raised to 1800 psi at room temperature. The autoclave was brought to the reaction temperature of 445° C under manual control in such manner as to avoid exceeding that temperature. The heating rate in this procedure was about 4° C/min. Some reaction occurred and hydrogen was consumed during this heating period. However, the start of the reaction period was taken as the time at which the temperature reached 445° C.

At the beginning of the reaction period the hydrogen pressure was substantially above 3000 psi. As hydrogen was consumed during the reaction, the pressure was prevented from falling below 3000 psi by addition of hydrogen from the second autoclave. The reaction temperature and pressure were maintained for a one hour reaction period. The hydrogen supply was then shut off and the heating terminated to end the reaction.

3) Coprocessing Product Work Up

After the reactor temperature had fallen to 20-30° C the first of the gas samples was collected in an evacuated 0.5-liter steel cylinder. The samples were analyzed by gas chromatography for hydrogen, the C_1 through C_7 hydrocarbons, carbon dioxide, and hydrogen sulfide. Gas from the autoclave was then metered through a wet test meter until the pressure had fallen to 300 psi, when the second gas sample was collected in another steel cylinder. Gas analysis was repeated and the two gas cylinders set aside for later work up to collect samples for carbon isotope ratio determination. The gas was again passed through the wet test meter and two more gas samples were collected at autoclave pressures of 75 and 3 psi. These two samples were collected in 40-mL glass flow through vessels placed in the line to the wet test meter. Gas analysis was repeated as before.

The total amount of gas liberated at the end of the coprocessing reaction was determined by combination of the metered quantities with that estimated from the PVT values of the two large gas samples. The mean composition of the gas was estimated by trapezoidal integration of the analytical composition of each component on the pressure coordinate, divided by initial pressure.

A pair of liquid cold traps were then attached to the autoclave vent valve, the first held at 0° C and the second at -80° C. The autoclave was heated to 75° C to promote vaporization of the condensate material. The autoclave was evacuated through the cold traps to a final pressure of about 100 torr. The material collected in the two cold traps was combined and stored in septum sealed vials under refrigeration.

The remaining liquid and solid contents of the autoclave were then transferred to a filter unit. This was a pressure filter (Fisher, Catalog No. 09-753-25G) of 1.5 liter capacity. A glass fiber filter membrane was used. The body of the filter unit was heated to about 80° C with electrical heating tape and the filtration carried out under a nitrogen pressure of 15-20 psi. The complete filtration required 2-3 hours and the last filtrate delivered was quite viscous and pitch-like. After filtration was completed, the wet solids remaining were dispersed in tetrahydrofuran (THF), agitated for about an hour to insure solution of soluble material, and filtered through Whatman No. 40 paper in a Buchner funnel. The THF soluble material was recovered by solvent stripping in a rotary vacuum evaporator. The washed solids were air dried to complete recovery of the coprocessing products.

4) Analytical Procedures

The filtrate liquids were distilled to produce suitable cuts for the separation procedures that are to follow. A Perkin-Elmer spinning band still was used to prepare cuts at initial boiling point (ibp)-175 and 175-350° C (corrected to atmospheric pressure). These distillation cuts were made at 100 torr and 1 torr respectively. The final cut to 538° C (1000° F) was made in a short path, high vacuum still that is used in the D-1160 method for crude oil analysis.

Simulated distillation of the filtrate and THF soluble fractions was carried out by a proposed ASTM crude oil method developed for high boiling samples.

The gas samples that had been collected from the autoclave in steel cylinders were processed in a scrubber and condensation train to collect components for carbon isotope analysis. Hydrogen sulfide was first removed in a scrubber containing copper acetate solution buffered to pH 5 with sodium acetate and acetic acid. Carbon dioxide was then collected in potassium hydroxide solution. The KOH solution was treated in advance with a small amount of $Ba(OH)_2$ solution to precipitate any carbonate impurity and then centrifuged to remove solids. Following the KOH scrubber was a silica gel drying tube and a pair of metal cold traps for collection of the light hydrocarbons. The first of the cold traps was open and the second contained activated carbon. Both were cooled with liquid nitrogen. The exit gas (hydrogen) was collected in a Tedlar gas bag and passage of the gas was continued until roughly 5-10 liters of sample had been processed as indicated by the volume in the gas bag. When the collection process was completed the cold traps were attached to vacuum manifold containing a gas sample cylinder and the gas transferred by heating the traps. The KOH solution was guarded against contact with air and the carbonate was precipitated by injection of $BaCl_2$ solution through a septum port. The precipitate was then washed with freshly boiled water introduced through the septum and the washings forced out under helium pressure through the sparger frit. This was continued until the washings were nearly neutral. The $BaCO_3$ was then transferred to a filter, washed and dried.

Elemental analysis for carbon, hydrogen, nitrogen, and sulfur was carried out on the filtrate, THF soluble, and dry solid samples. The coal was analyzed by the Commercial Testing & Engineering Co., South Holland, IL. Carbon isotope ratios were determined at the School of Geology and Geophysics, Energy Center, University of Oklahoma, Norman, OK.

RESULTS AND DISCUSSION

Table 1 shows the reaction composition used in each of the runs. In determining the amount of coal to be used in each run no allowance was made for the ash and moisture content. The ash and moisture contents of each impregnated coal preparation are included. The last row shows the combined weights of the residue and the moisture and ash free coal. Table 2 contains the detailed analysis of the Illinois No. 6 coal. The elemental composition of Maya residue >1000° F is shown in Table 3.

Table 1

Composition of Coprocessing Reactants, grams

	Run #8 2% Coal	Run #5 20% Coal	Run #7 30% Coal	Run #6 40% Coal
Residue reacted	653.3	533.3	466.7	400.0
Coal reacted	13.3	133.3	200.0	266.7
$(NH_4)_2MoS_4$	1.81	1.81	1.81	1.81
Coal ash	1.45	14.51	22.10	29.31
Coal moisture	0.38	3.88	2.94	5.23
Residue plus MAF coal	664.8	648.3	641.6	632.1

Table 2

COMMERCIAL TESTING & ENGINEERING CO.
GENERAL OFFICES: 1919 SOUTH HIGHLAND AVE., SUITE 210-B, LOMBARD, ILLINOIS 60148 • (312) 953-9300

Analysis Report No. 71-74012 **Page** 1 of 2

PROXIMATE ANALYSIS	**As Received**	**Dry Basis**
% Moisture	4.62	xxxxx
% Ash	10.69	11.21
% Volatile	37.68	39.51
% Fixed Carbon	47.01	49.28
	100.00	100.00
Btu/lb	11908	12485
% Sulfur	2.99	3.14
Alk. as Sodium Oxide	0.19	0.20

ULTIMATE ANALYSIS	**As Received**	**Dry Basis**
% Moisture	4.62	xxxxx
% Carbon	66.56	69.78
% Hydrogen	4.48	4.70
% Nitrogen	1.38	1.45
% Sulfur	2.99	3.14
% Ash	10.69	11.21
% Oxygen(diff)	9.28	9.72
	100.00	100.00

Analysis Report No. 71-74012 **Page** 2 of 2

ANALYSIS OF ASH	**WEIGHT %, IGNITED BASIS**
Silicon dioxide	46.94
Aluminum oxide	17.56
Titanium dioxide	0.87
Iron oxide	16.63
Calcium oxide	6.53
Magnesium oxide	0.93
Potassium oxide	1.91
Sodium oxide	0.56
Sulfur trioxide	6.51
Phosphorus pentoxide	0.19
Strontium oxide	0.02
Barium oxide	0.00
Manganese oxide	0.00
Undetermined	1.35
	100.00

Silica Value = 66.08
Base:Acid Ratio = 0.41
T_{250} Temperature = 2403 °F

Fouling Index = 0.23
Slagging Index = 1.29

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

W. Cox
Manager, South Holland Laboratory

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TIDEWATER AND GREAT LAKES PORTS, AND RIVER LOADING FACILITIES

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Table 3

Maya Crude Residue >1000° F, Elemental Composition

C	84.6
H	10.64
S	4.85
N	0.57

The yields of fractions obtained in work up of the coprocessing products are shown in Table 4. These values are calculated on the basis of moisture and ash free coal. However, the dry solids fractions will contain both the original ash and the MoS_2 catalyst. Therefore, the dry solids values are shown as the organic content excluding the calculated ash and catalyst.

Table 4

Yields of Coprocessing Products
Percentage of Residue and MAF Coal

	Run #8 2% Coal	Run #5 20% Coal	Run #7 30% Coal	Run #6 40% Coal
Methane	2.57	2.30	2.10	3.07
C_2-C_7	3.99	1.98	2.70	4.27
CO_2	0.04	0.13	0.26	0.62
H_2S	1.83	1.22	1.77	2.42
Condensate	10.29	3.42	7.59	3.15
Filtrate	66.52	65.42	68.73	65.67
THF Soluble	6.60	12.65	8.40	13.38
Dry Solids*	6.83	2.55	2.73	4.16
Total	98.67	89.67	94.28	96.74

* - Excluding ash and catalyst.

Figures 1 and 2 show the yield results of Table 1 in graphic form. The first figure shows the gas and condensate components while the second contains the major components. It is unlikely that trends in product yields can be established from this limited number of runs. Therefore, the plots simply show straight line traces connecting the four data points of each product type.

Figure 1

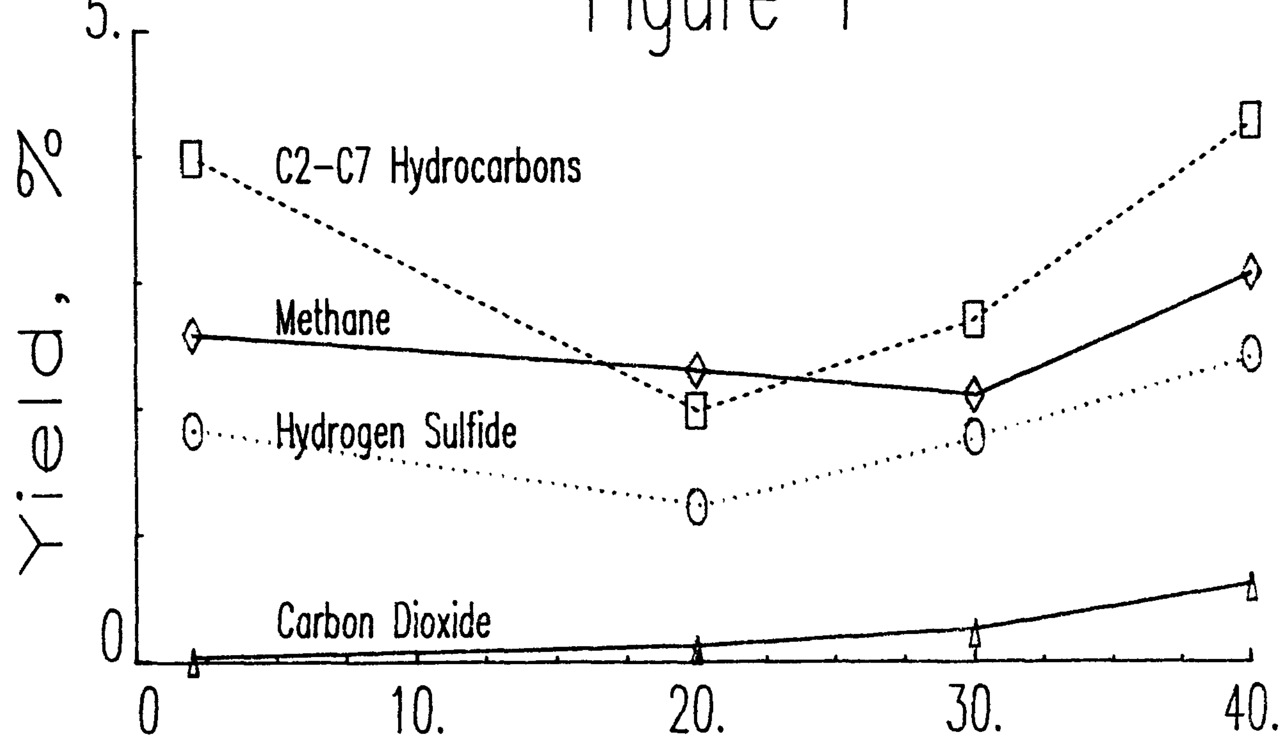
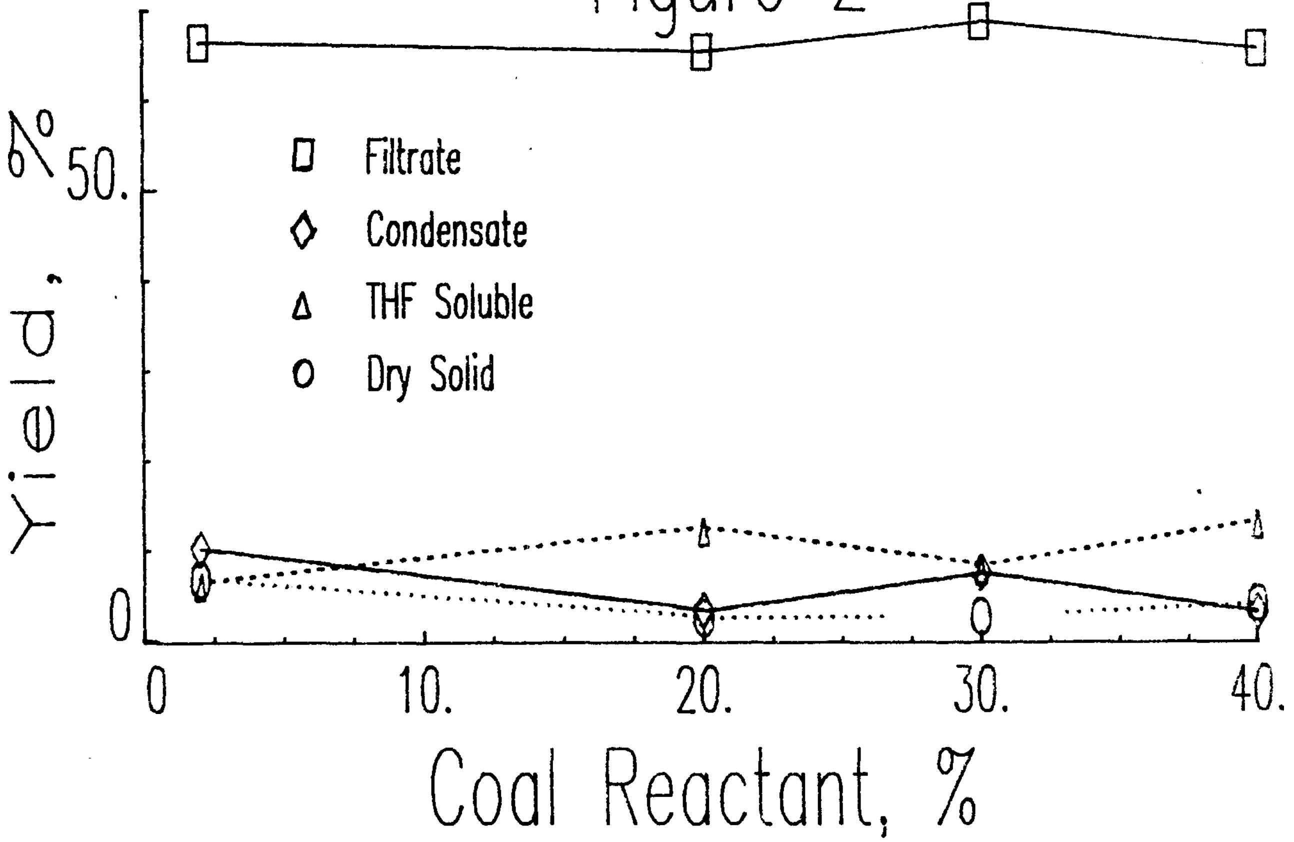


Figure 2



Figures 3-6 show the results of simulated distillation analysis in graphic form. In each case, the upper trace represents the filtrate product while the lower is the THF soluble material. While there is some difference in conversion to distillate below 1000° F among the samples, the plots show little difference in overall character. In every case the THF soluble product shows lack of material below C_9-C_{10}, probably because of vaporization loss in the solvent stripping operation. Also, all THF soluble products contain 1.5-2 percent tetrahydrofuran, showing the difficulty of removal of this solvent from high-boiling and residue materials. Table 5 shows the results in conversion to distillable material (below 1000° F). The first row shows the weighted mean percentage of <1000° F material for the filtrate and THF soluble products taken together and the second row the yields on reactant basis for the whole system including the gaseous hydrocarbons and condensate.

Table 5

Products Distilling Below 1000° F, Percentage

	Run #8 2% Coal	Run #5 20% Coal	Run #7 30% Coal	Run #6 40% Coal
Mean content in filtrate and THF soluble	83.0	79.5	77.6	75.1
Yield, all products <1000° F	77.5	69.8	72.2	69.9

The quantities of distillates obtained in the fractional and high vacuum distillations of the filtrate products are shown in Table 6. The THF soluble products were not included in this distillation procedure because of the unremovable content of tetrahydrofuran. It appeared that this THF might introduce errors in the the carbon isotope ratio determination that could not be estimated. The yield values of Table 4 and the distillation traces of Figures 3-6 show that reduction in material <1000° F caused by exclusion of THF soluble fractions is relatively small. A general shift to higher boiling products with increasing coal concentrations is apparent (table 6).

Figure 3

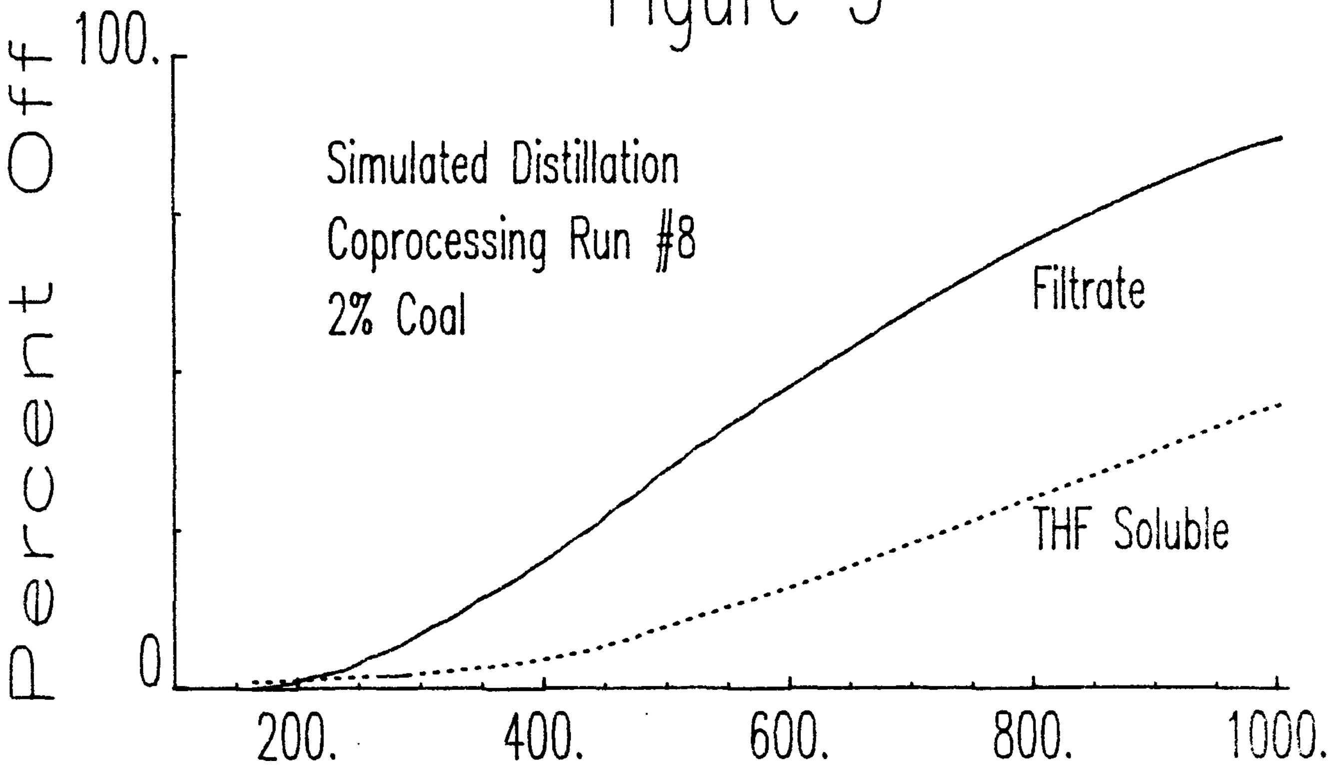


Figure 4

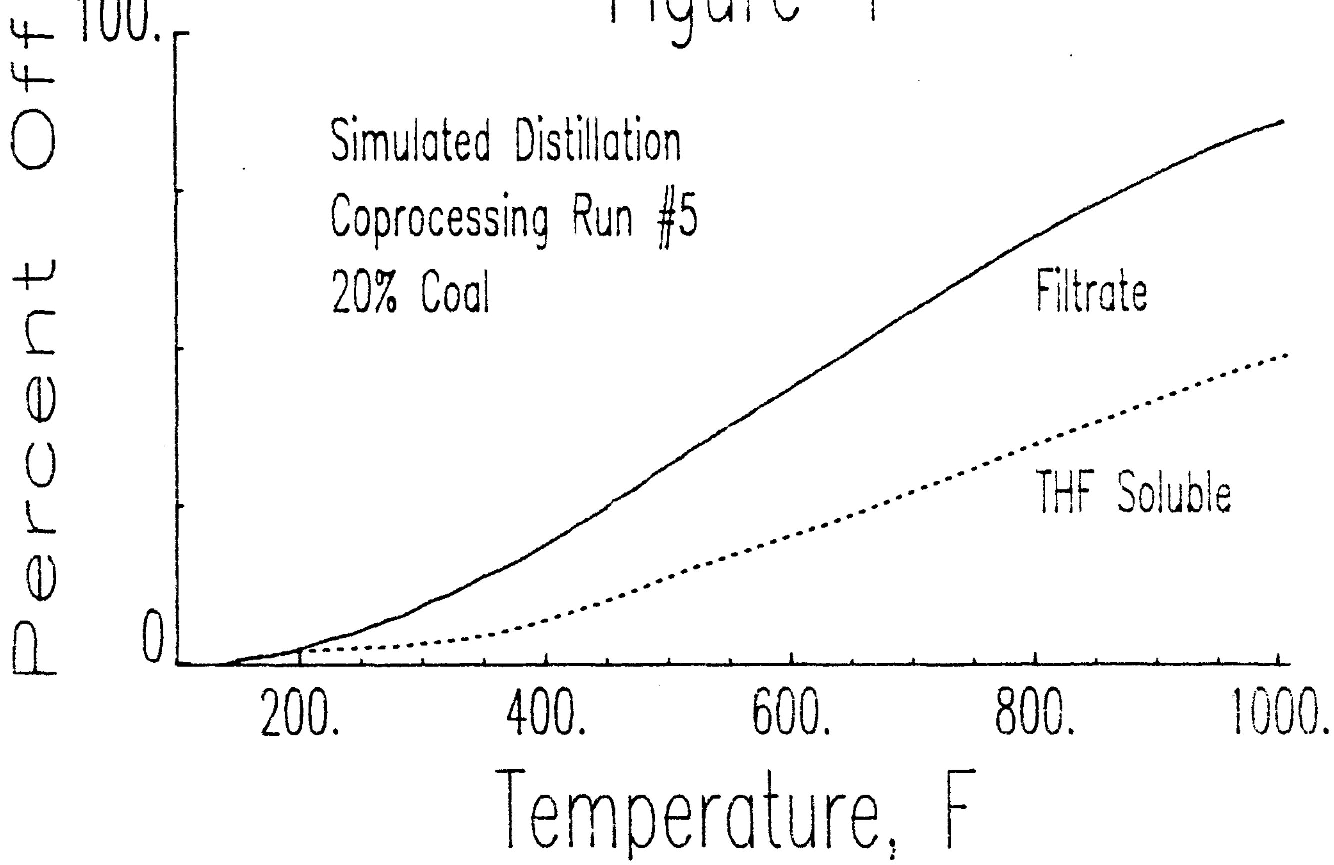


Figure 5

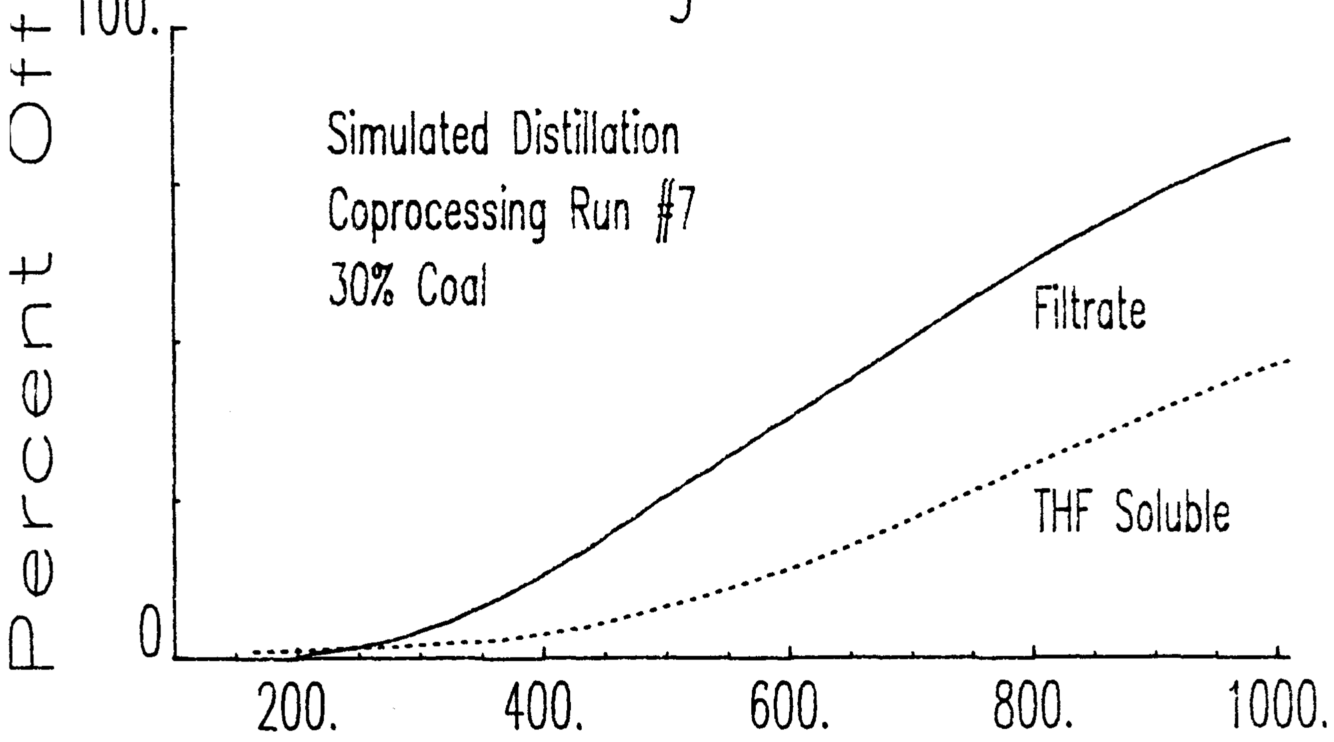


Figure 6

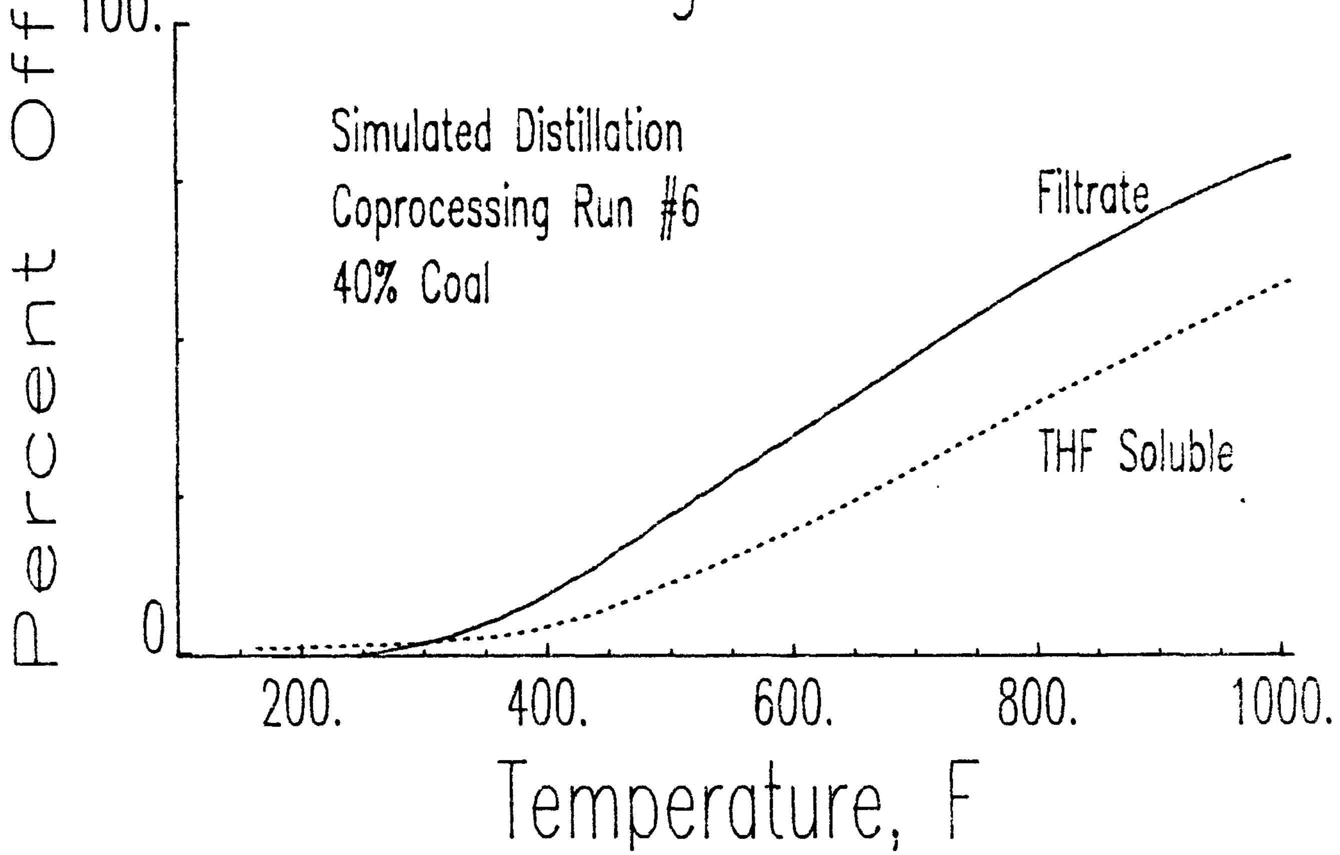


Table 6

Distillation Results from Filtrate Samples, Grams

	2% Coal 415.9 g		20% Coal 412.8 g		30% Coal 420.9 g		40% Coal 381.4 g	
Initial Charge	g	%*	g	%	g	%	g	%
Distillation Range								
IBP-175° C	57.9	14.2	56.6	14.0	41.0	9.9	20.5	5.5
175-350° C	157.3	38.6	145.9	36.0	141.8	36.7	137.2	36.7
350-538° C	111.6	27.3	105.1	25.9	131.2	26.9	100.3	26.9
Residue	81.4	19.9	97.9	24.1	99.1	30.9	115.4	30.9
Recovered	408.2 g		405.5 g		413.1 g		373.4 g	

*Normalized to 100%.

Elemental analyses for some of the fractions are shown in Table 7. The totals of the carbon, hydrogen, nitrogen, and sulfur for each sample are also shown. The difference of this total from 100 percent may be attributable to oxygen and ash. The last column shows the ratio of hydrogen to carbon on a molar basis for each sample.

Table 7

Coprocessing Fractions, Elemental Composition, Percentage

	C	H	N	S	Total	H/C
30% Coal Products						
Filtrate	85.22	10.64	0.608	1.67	98.14	1.498
THF Soluble	84.03	6.78	1.023	2.56	94.39	0.968
Dry Solids	33.18	1.78	0.660	6.52	42.14	0.644
40% Coal Products						
Filtrate	86.04	10.83	0.550	1.67	99.09	1.510
THF Soluble	82.24	7.08	1.024	2.40	92.74	1.033
Dry Solids	39.52	2.03	0.569	6.22	48.34	0.616

The results of carbon isotope ratio analysis are shown in Table 8 for the 20, 30, and 40 percent coal reactions. The ratio values ($\delta^{13}C$) for the Maya >1000° F residue and the Illinois No. 6 coal are included for reference. Estimates of $\delta^{13}C$ for the reaction mixes are based on the residue and coal values, the fractional amounts of residue and coal used, and the carbon analyses of 84.6 percent for the residue and 69.8 for the coal. All of the liquid and solid products have slightly less negative δ values than that calculated for the reaction mixes. The light hydrocarbons are substantially more negative, indicating depletion of ^{13}C to balance the enrichment in the liquid and solid products. The $\delta^{13}C$ values for CO_2 are nearly identical for the 20 and 30 percent coal products. This suggests that the CO_2 is formed from only one of the reactants. Table 3 and Figure 1 agree in indicating that CO_2 is formed predominantly from the coal. The CO_2 value differs significantly from the coal and reaction mix and may indicate that it is formed by mineral carbonate decomposition rather than decarboxylation of organic coal components.

Table 8

Carbon Isotope Ratios

	$\delta^{13}C$
Maya Residue >1000° F	-27.56
Illinois #6 Coal	-24.56

	Run #5 20% Coal	Run #7 30% Coal	Run #6 40% Coal
Reactant Mix*	-27.05	-26.79	-26.51
Filtrate	-26.17	-26.18	-26.00
THF Soluble	-26.85	-26.50	-26.05
Dry Solid	-26.38	-25.58	-25.70
Hydrocarbon Gas	-37.60	-34.31	nd
CO_2	-18.87	-18.88	nd

* - estimated
nd - not yet determined

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