5.0 LIQUEFACTION RESEARCH

5.1 Low-Rank Coal Direct Liquefaction

LOW-RANK COAL DIRECT LIQUEFACTION

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by

Melanie D. Hetland, Research Engineer
John R. Rindt, Research Supervisor

Energy and Environmental Research Center
University of North Dakota
P.O. Box 9018
Grand Forks, North Dakota 58202-9018

Task Contracting Officer's Representative: Mr. Michael J. Baird

for

U. S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236-0940

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LOW-RANK COAL DIRECT LIQUEFACTION

1.0 INTRODUCTION

Direct liquefaction is a process in which coal is converted to liquid products by adding hydrogen to coal that has been slurried in a solvent. The hydrogen addition takes place at elevated temperatures and pressures. The process was invented by Friedrich Bergius in 1913 and has remained relatively unchanged since its extensive use by Germany for the production of liquid fuels during World War II (1). Some improvements in conversion and product slate were noted when researchers in the United States substituted bituminous coal for the German brown coal. Attempts to use low-rank coals (LRCs) instead of bituminous coals have not been as successful. From the results of work performed earlier this decade, it is apparent that LRCs are very reactive (2). Current processing approaches work well with the less-reactive, higher-rank coals (HRCs), but when the LRCs are subjected to the optimum HRC processing conditions, they react too rapidly for the available hydrogen sources and result in a more retrograde product. On the surface, this may appear to be inconsistent with the accomplishments of the older German technology using LRCs. However, the older technology's conditions were so severe that even the retrograde products were eventually converted to distillate material. With the development of a less brute-force approach (i.e., everything developed since WWII), the subtleties of relative coal reactivity, particularly that shown between LRCs and HRCs, make it necessary to pay closer attention to the chemistry of the process.

Unfortunately, the reactions taking place during direct liquefaction are not fully understood. Due to their complexity, analyses of these chemical reactions have never led to universally accepted mechanisms, rate-determining step(s), critical reaction pathway(s), or reaction kinetics. Because very little is known about the actual reactions that occur during coal liquefaction, especially during the critical initial steps, improvements in product yield and/or quality are currently accomplished through largely empirical changes in the processing parameters and/or equipment. The current liquefaction approach assumes that the reactions occurring at the usually severe conditions provide the best way to convert coal to liquid products.

The apparent higher reactivity of LRCs offers a key to improved conversions and/or yield structures and/or lower processing severity. Changes utilizing this reactivity could improve the economic viability of the technology. Effective use of LRCs in direct liquefaction may require a fairly substantial change in the direct liquefaction process as it is currently known.

In an approach taken by the Reaction Engineering Group of the Energy and Environmental Research Center (EERC), the initial coal solubilization can be considered as reverse coalification and the subsequent upgrading as reforming or refining. Because of the high-severity conditions, single-stage liquefaction forces reverse coalification and refining to occur at the same time. The results of past efforts using this type of processing speak for themselves: this brute-force method produces a number of product streams, only one of which is the desired, value-added product. Mechanistically, it is somewhat easier to view these almost mutually exclusive processes as different, sequential steps. Staged liquefaction, as it currently exists (i.e., at least two reactors in series), is an attempt to best utilize the differences in preferred conditions for each step of a two-step method. Unfortunately, the processing parameters employed during both stages are usually so severe that the same type of high-temperature, high-pressure reactions occur (i.e., coalification), or at least compete, in both stages.

Dramatic improvements in the liquefaction process may be possible if the reactions involved are not required to compete against each other. Processing conditions must be changed, and the changes must be determined by an increased understanding of the reactions taking place. At the EERC, it is assumed that the structure of coal is comprised of physically and chemically tangled, highly cross-linked molecules. The molecular structures of premium distillate fuels, by comparison, are discrete molecules of similar size and chemical nature, having virtually no chemical or physical attachments. Using these two presumptions, it is possible to map potential mechanical and chemical mechanisms for the process of liquefaction.

The first step in liquefaction should be to "untangle" the coal structure, while the second step should be to "organize" the untangled pieces so that those of similar size and chemical nature are first separated from the remaining material and then stabilized to prevent back reactions. This simplistic, two-step mechanism will be used to develop a more effective scheme for coal liquefaction. It seems logical that, in order to prevent coalification reactions, "untangling" of the coal structure should take place at low-severity conditions.

Tailoring the processing parameters to the liquefaction reactions taking place, the EERC has developed a multistep direct liquefaction process specifically for LRCs consisting of pretreatment, solubilization, polishing, and hydrotreatment.

2.0 GOALS AND OBJECTIVES

Since 1986, the primary objective of the Low-Rank Coal Direct Liquefaction program has been to develop an LRC liquefaction process that results in increased levels of conversion to distillable liquids. The work effort to meet this objective has included:

- A preliminary mechanistic study of the retrograde reactions that occur as a function of typical liquefaction processing.
- Screening of various preconversion treatments.
- Development of a multistep process that results in virtually complete solubilization of the LRC in the solvent prior to hydrotreatment.
- An investigation of the effects of the use of hydrogen-donating solvents during liquefaction.
- Integration of all steps of the process.

3.0 RESULTS

As mentioned in Section 1.0, the EERC has developed a four-step liquefaction process consisting of:

- Step 1 - Pretreatment, which was investigated during FY89-90 and FY90-91.
- Step 2 - Solubilization.
- Step 3 - Polishing, which was investigated during FY88-89, Task K.
- Step 4 - Hydrotreatment.

Generic instructions for performance of these tests are given in the appendix.

This process was developed based, in part, upon earlier research (i.e., prior to 1986) performed at the EERC that showed that:

- Low-severity processing of lignites resulted in better conversion and yield structure than did the typically higher-severity single-stage liquefaction.
- Syngas is a more effective reductant than pure hydrogen gas.
- Hydrogen donor solvents are more effective than hydrogen gas for the hydrogenation of coal liquids.
- CO acts almost exclusively via the water/gas shift reaction.
- H_2S acts primarily as a hydrogen shuffler, typically from the gas phase to the liquid phase.

Knowledge of liquefaction reactions gained during a preliminary mechanistic study was also used in the development of the multistep process.

3.1 Preliminary Mechanistic Study of Liquefaction Reactions

Low- and high-rank coals are significantly different from each other. This is shown in Figure 1, which compares the ^{13}C nuclear magnetic resonance (NMR) spectra of a typical bituminous coal and a typical lignite. To aid in reading the NMR spectra contained in this report, Table 1 lists the locations of various functional groups on solid ^{13}C NMR spectra. Lignite contains considerably more phenolic, carboxyl, and methoxyl groups than the bituminous coal, which is comprised primarily of aliphatics and heavy aromatic groups. Due to these differences, the two probably do not react in the same manner during liquefaction processing.

To arrive at a better understanding of the reactions that occur during typical liquefaction of lignite, a preliminary mechanistic study was performed. Four batch tests were conducted. Three of the tests were performed at conditions designed to result in conversions of nominally 10%, 55%, and 95%. A test was also made at conditions selected intentionally to

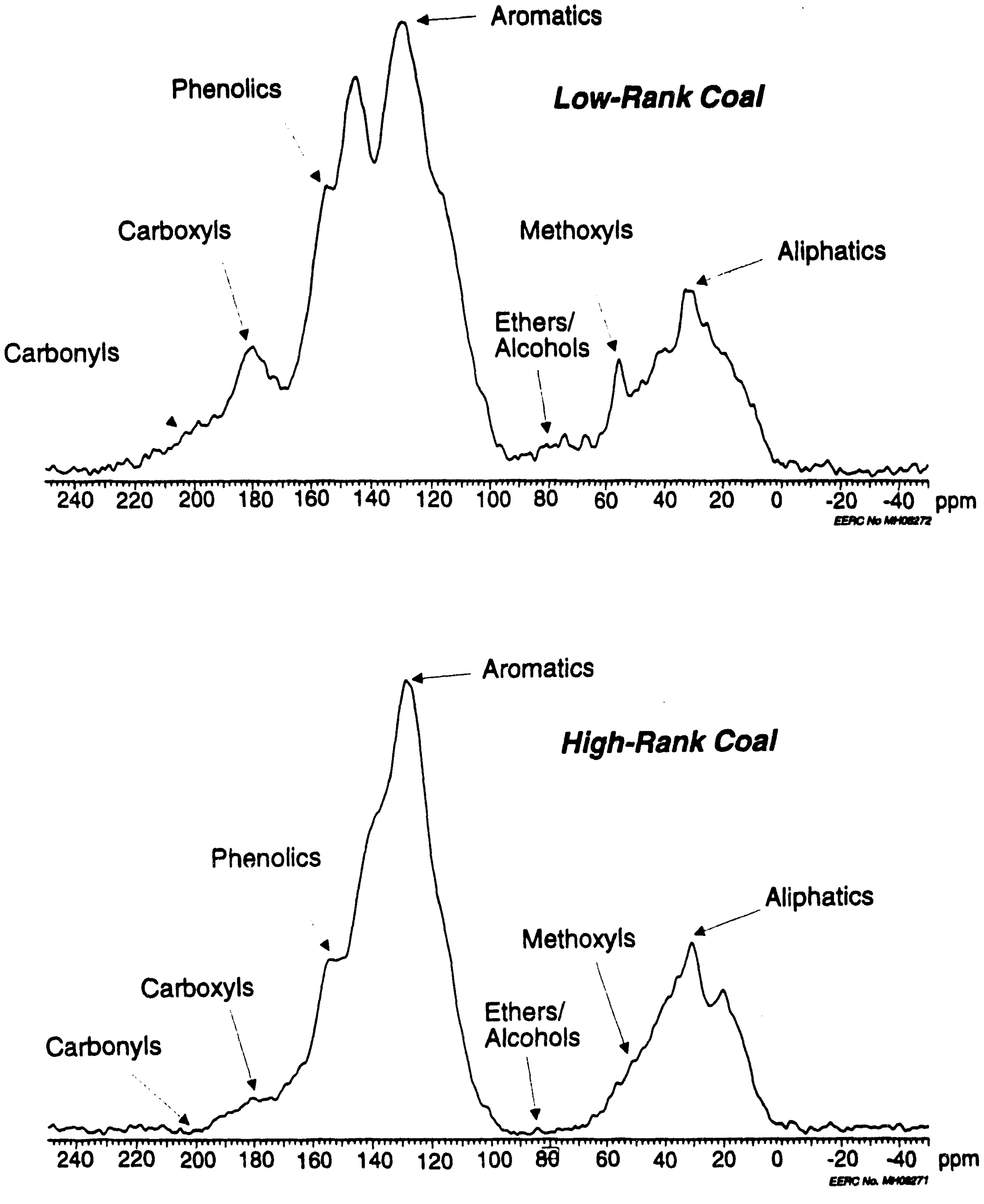

Figure 1. ^{13}C NMR spectra of typical low- and high-rank coals.

TABLE 1

Functional Group Locations on Solid ^{13}C NMR Spectra

Functional Group	Shift, ppm
Carbonyl	230-190
Carboxyl	190-170
Phenolic	170-148
Aromatic	
Alkyl Substituted	148-136
Unsubstituted	136-90
Ether/Alcohol	90-60
Methoxyl	60-50
Aliphatic	
-C-, -CH-	50-36
$-CH_2-$	36-24
Aromatic $-CH_3$	24-16
Alkyl $-CH_3$	16-0

result in the production of retrograded product at an intermediate level of conversion.

3.1.1 Comparison of Functional Group Reactivity During Liquefaction

The insoluble organic matter (IOM) remaining at the end of each reaction was analyzed in detail using ^{13}C NMR spectroscopy to provide a description of the reaction mechanisms as a function of conversion. Area-scaled spectra (i.e., all spectra were put on the same basis for comparison purposes) were constructed to provide information concerning the changes taking place in the coal functional groups during conversion. When the spectra are compared (as in Figure 2), it can be seen that the first functional groups to react were the ethers/alcohols, the methoxyl groups, most of the alkyl aliphatic groups, and some of the alkyl and unsubstituted aromatic groups. These reactions took place when the first 9% of the coal was converted. During the conversion of the next 51% of the coal (i.e., from 9% to 60% conversion), most of the carboxyl, phenolic, and aliphatic groups reacted. The carbonyl, alkyl aromatic, remaining ether/alcohol, and remaining methoxyl groups reacted during the time when 60% to 94% of the coal was converted. After 94% of the coal had been converted, the IOM which remained was primarily comprised of unsubstituted aromatic groups. The order of reaction of the functional groups is summarized in Table 2.

During the course of conversion of the coal, the liquid product yields reflect the large increase in phenolic products, and the gas product yields reflect the increased conversion of CH, CH_2, and CH_3 groups to hydrocarbon gases. This is seen in the water/gas shift-free product yields given in Table 3.

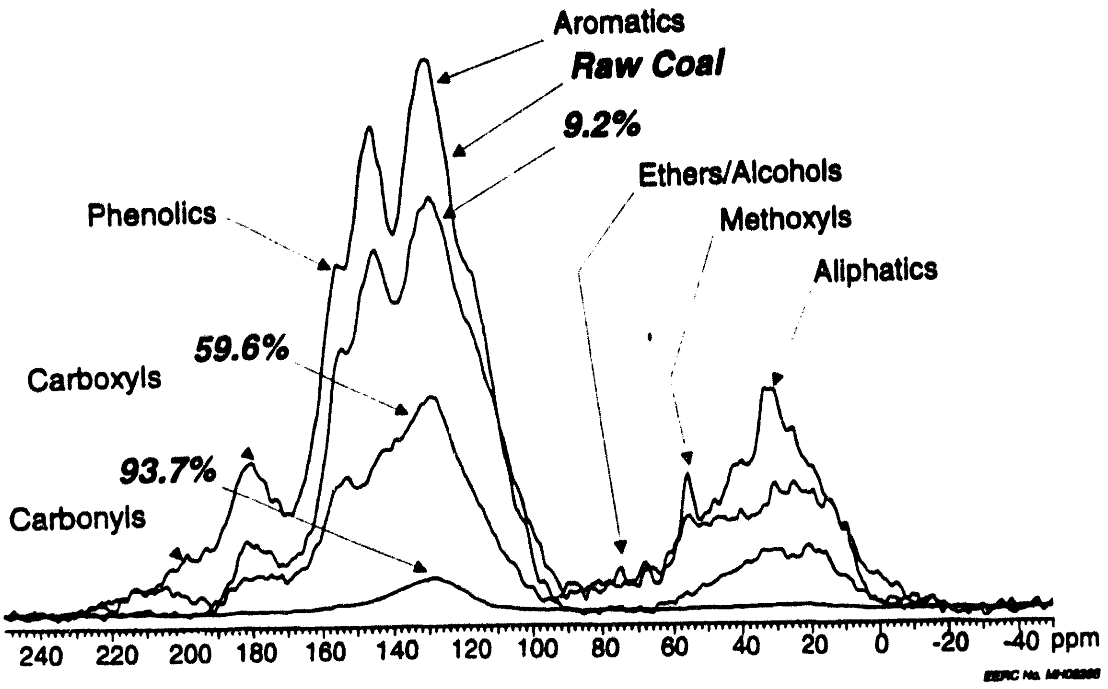

Figure 2. ^{13}C NMR spectra of IOM remaining after processing; values indicate conversion levels.

TABLE 2

Reaction of Functional Groups During Direct Liquefaction

0%-9.2% Conversion	9.2%-59.6% Conversion	59.6%-93.7% Conversion
Some ethers/alcohols	Carboxyls	Carbonyls
Methoxyls	Phenolics	Alkyl aromatics
Alkyl aliphatics	Aliphatics	Remaining ethers/alcohols
Some alkyl and unsubstituted aromatics		Remaining methoxyls

TABLE 3

Product Slates of the Mechanistic Studies Tests
on a Water/Gas Shift-Free Basis

Run No.	N469	N474	N468	N475[a]
Conversion, %	9.2	59.6	93.7	61.5
Avg. Temp., °C	201	303	354	444
Avg. Pressure, psig	1750	2505	3071	3570
Products[b]				
CO	0.00	0.00	0.00	2.09
H_2	0.04	0.43	1.06	-2.88
CO_2	4.38	18.86	9.92	16.47
C1-C3	0.25	0.52	1.36	4.31
H_2S	-5.89	-7.76	-5.29	2.61
Total Gas	2.26	22.80	38.61	22.60
H_2O	0.43	-10.02	-24.58	-11.90
Ash	0.85	0.60	-0.57	-0.11
IOM	91.38	40.20	6.29	38.49
Distillable Oils	-77.53	-47.41	-0.15	0.00
Soluble Resid	82.61	93.82	80.40	50.93
Total Liquid	97.74	77.20	61.39	77.40

[a] Products of this run were retrograded in nature.
[b] Values given as wt% of maf coal fed to the system, on a water/gas shift-free basis.

The greatest production of CO_2 was seen when most of the carboxyl and phenolic functional groups were released from the coal during the 9% to 60% range of conversion. The water/gas shift reaction was the most evident during the release of the aromatic functional groups toward the end of the conversion process. This can be seen in both the water consumption and CO_2 production given in Table 3. The majority of the hydrogenation takes place at this point in the processing as hydrogenation is virtually the only reaction in which the aromatics will take part.

The largest incorporation of H_2S occurred during the 9% to 60% conversion range, coinciding with the largest release of CO_2 and phenolics as well as the highest yield of total liquids. This may indicate a mechanistic link between the removal of the phenolic and carboxyl groups and the fact that sulfur apparently replaces the oxygen in many of the bonds.

3.1.2 Comparison of Retrograded and Nonretrograded Products

Two runs were performed at conditions which resulted in similar conversions of coal but different product yield structures. As Table 3 shows, the two tests took place via different mechanisms. The higher-temperature/higher-pressure test underwent substantially more cracking reactions than the less severe test, as seen in the production of hydrocarbon gases. The production of solubles was approximately the same for the two tests. A shift in carbon balance can be seen when the two tests are compared. Approximately twice as much of the carbon in the feed coal was present in the product gas of the more severe run as in the product gas of the less severe run. In other words, the carbon utilization efficiencies were grossly affected at the expense of the production of desirable liquids. Comparison of the ^{13}C NMR spectra of the IOM remaining after processing for both runs corroborates these data. As Figure 3 shows, the product of the more severe test consisted primarily of heavy aromatics, while the product of the less severe test retained more of the features of the original lignite.

3.2 Step 1 - Pretreatment

Low-severity pretreatments were screened to evaluate their impact on the direct liquefaction of Indian Head lignite. The rationale was that a completely solvent-soluble feed to the catalytic upgrading stage would not be as likely to undergo retrograde reactions as feed containing both the soluble fractions of converted coal and unconverted organic residue. If this were the case, it would result in a higher conversion of coal to desired liquid products than is usually obtained during direct liquefaction. As part of this solubilization process, it was hypothesized that pretreatment might reduce

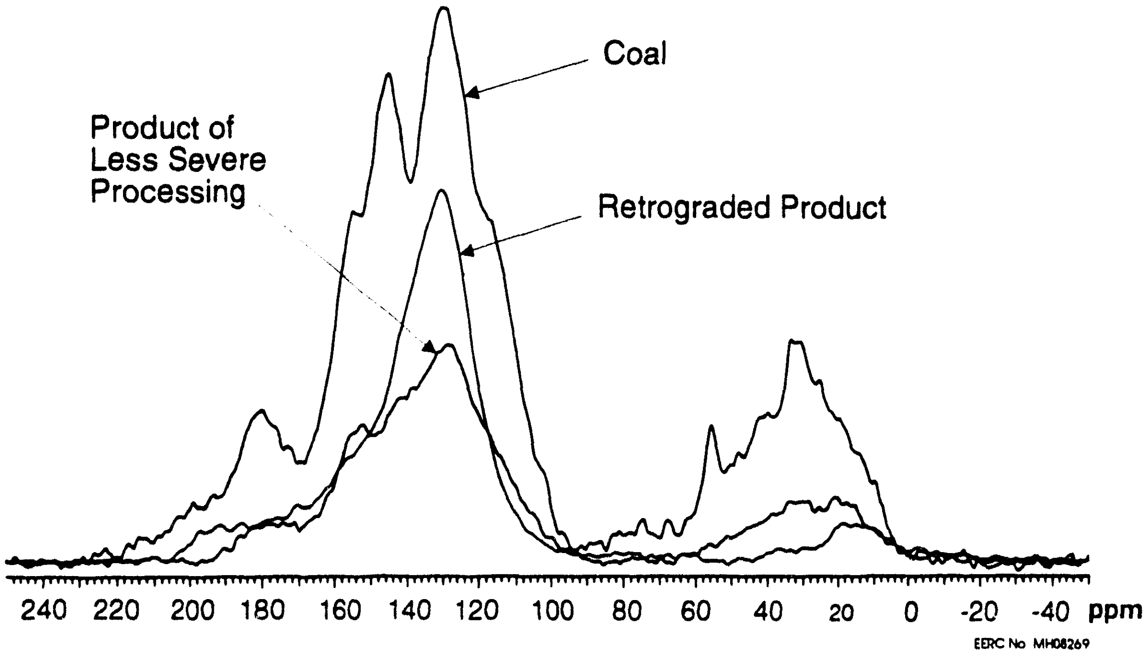

Figure 3. ^{13}C NMR spectra showing differences between retrograded and nonretrograded product.

retrograde behavior by placing hydrogen or radical capping agents in the correct location to facilitate "untangling" of the coal structure. **When used in this report, the term "pretreatment" refers to anything done to the coal prior to noticeable formation of soluble materials.**

Several preconversion treatment schemes were devised and screened for their effectiveness. An initial screening was carried out using the 20-cm^3 microreactor system. A second screening was performed using hydrogen-donating solvents in the batch autoclave system. The information gathered during these two screenings was combined, and the most promising schemes were tested further. Table 4 lists the pretreatment variables that were screened, and Table 5 presents the product slates (after solubilization) and molar hydrogen-to-carbon ratios of these tests.

As can be seen in Table 5, it appears that a 60-minute soak in HA061 (hydrogenated coal-derived anthracene oil) at 175°C in the presence of argon and H_2S enhances whichever reaction is taking place without substantially affecting the overall conversion. In the case of a pyrolysis-type reaction (N524), the use of pretreatment greatly increased the production of product gases and water while decreasing the production of soluble liquid products. In a liquefaction reaction such as N528, the use of pretreatment resulted in a decrease in the quantity of gaseous products and an increase in the production of soluble liquids. These trends can be clearly seen in Table 6, which places the yield structure of Runs N524 and N528 side by side with yield structures of the equivalent non-pretreated tests.

3.3 Step 2 - Solubilization

The purpose of this step is to solubilize as much of the coal as possible to enable more efficient hydrotreatment during a later step. **Hydrotreatment is not attempted during this step.** Tests were performed to study the effects of various hydrogen-donating solvents, gases, and pressures on the solubilization of the coal. A summary of these solubilization tests is presented in Table 7. The same matrix was performed again incorporating solvent-specific pretreatments. Additional data points were added at that time. Table 5 presented the results of the study incorporating pretreatment.

TABLE 4

Variables Screened During Pretreatment Studies

Solvent	Gas[a]	Additive[b]	Temperature
A04	H_2	Na	110°C
phenolic	CO	H_2S	175°C
tetralin	Ar	none	250°C
	none		
Reaction time = 60 min for all tests			

[a] 1000 psi gas charged.
[b] Additive = 5 wt% of maf coal fed to the system.

TABLE 5

Summary of Pretreatment/Solvation Tests using Hydrogen-Donating Solvents

	N501/N502	N503/N504	N505	N506	N507/N508	N509/N510	N511/N512	N513/N514
Matrix Point	1	2	3	4	5	6	7	8
Solvent	A04[a]+Tetralin/N501	A04/N503	A04	HA061[b]	HA061/N507	HA061/N509	HA061/N511	CA1[c]/N513
Additive	H_2S/None	None/None	None	None	H_2S/None	H_2S/None	H_2S/None	H_2S/None
Gas	Ar/CO	H_2/CO	H_2	H_2	Ar/CO	Ar/CO	CO/CO	CO/CO
Residence Time, min	60/60	60/60	20	20	60/60	60/60	60/60	60/60
Avg. Temp., °C	184/375	179/375	420	414	123/372	178/375	175/375	115/371
Max. Temp., °C	187/379	181/380	421	418	124/373	180/377	176/376	117/375
Avg. Pressure, psi	2230/3867	2100/3700	3734	3880	1730/3727	2141/3750	2075/3740	1864/3737
Max. Pressure, psi	2240/4000	2115/3865	3800	3905	1730/3875	2225/4000	2095/3825	1748/3780
Conversion, %	93.3	86.1	55.5	80.1	87.6	89.1	88.6	89.3
Products[d]								
CO	-50.73	-32.36	0.00	0.09	-32.34	-36.01	-34.61	-41.98
H_2	0.72	0.64	-1.87	-2.96	0.52	0.38	0.43	0.38
CO_2	93.75	65.63	21.58	17.55	73.31	77.62	62.24	70.94
C1-C3	0.92	0.65	10.21	8.32	0.49	0.79	0.75	0.76
H_2S	5.06	0.13	0.00	0.00	3.66	3.94	1.97	3.37
Total Gas	49.72	34.69	29.92	23.00	45.62	46.72	30.79	33.47
H_2O	-25.76	-23.62	2.15	0.39	-16.98	-38.13	-5.60	-21.73
Ash	-0.39	-0.10	-0.34	-1.26	-1.18	-1.49	-1.31	-1.04
IOM	6.70	13.95	44.51	19.90	12.40	10.88	11.45	10.74
THF Solubles	69.73	75.08	23.76	57.98	60.13	82.03	64.67	78.56
Total Liquid	50.28	65.31	70.08	77.00	54.38	53.28	69.21	66.53
Molar H:C, Feed	0.9827	0.7673	0.7646	0.8925	0.9003	0.8905	0.8933	1.0613
Molar H:C, After Pret.	0.8020	0.7796	--	--	0.9138	0.9138	0.9569	0.9614
Molar H:C, Product	0.8868	0.8517	0.7486	0.9018	0.9784	1.0576	0.9034	0.9964

[a] Coal-derived anthracene oil.

[b] Hydrotreated A04.

[c] Cresylic acid solvent.

[d] Values given as wt% of maf coal fed to the system; negative values indicate consumption; positive values indicate production.

TABLE 5 (continued)

Summary of Pretreatment/Solvation Tests using Hydrogen-Donating Solvents

	N519/N522	N519/N523	N519/N524	N525/N526	N525/N527	N525/N528	N525/N530	N549/N551
Matrix Point	9	10	11	12	13	14	15	16
Compares to[e]	N477	N483	N484	N487	N485	N486	N499	N476
Solvent	HA061/N519	HA061/N519[f]	HA061/N519[g]	HA061/N525	HA061/N525	HA061/N525	HA061/N525	A04/N549
Additive	H_2S/None	H_2S/None	H_2S/None	H_2S/None	H_2S/None	H_2S/None	H_2S/None	H_2S/None
Gas	Ar/None	Ar/None	Ar/None	Ar/Ar	Ar/H_2	Ar/CO	Ar/CO	Ar/Ar
Residence Time, min	60/60	60/60	60/60	60/60	60/60	60/60	60/60	60/60
Avg. Temp., °C	184/370	184/372	184/367	176/372	176/378	176/376	176/373	174/373
Max. Temp., °C	187/374	187/381	187/375	178/376	178/380	178/381	178/380	176/376
Avg. Pressure, psi	2106/600	2106/631	2106/953	2000/3581	2000/3352	2000/3434	2000/728	2100/4227
Max. Pressure, psi	2125/638	2125/663	2125/995	2000/3628	2000/3390	2000/3560	2000/745	2110/4260
Conversion, %	54.7	57.5	70.0	60.1	79.4	81.0	33.1	38.72
Products[d]								
CO	0.20	12.17	12.56	0.08	0.25	-54.25	-14.71	0.00
H_2	0.09	0.05	0.17	0.05	-2.71	1.01	0.90	0.05
CO_2	9.28	7.74	21.19	6.86	9.12	73.46	25.96	14.01
C1-C3	1.23	0.17	2.18	0.62	1.20	0.97	1.45	1.32
H_2S	5.69	0.19	2.56	3.61	2.93	2.90	1.26	3.72
Total Gas	16.48	20.32	38.65	11.22	10.78	24.09	14.85	19.10
H_2O	10.97	7.37	7.89	-2.23	14.48	-22.75	-40.31	8.69
Ash	0.01	0.14	0.29	-0.23	-0.64	-0.96	4.26	0.34
IOM	45.35	42.55	29.97	39.94	20.62	18.97	66.87	61.28
THF Solubles	27.28	29.61	23.20	51.30	54.76	80.65	54.33	10.59
Total Liquid	83.52	79.68	61.35	88.78	89.22	75.91	85.15	80.90
Molar H:C, Feed	0.8983	0.8983	0.8983	0.9098	0.9098	0.9098	0.9098	NA[h]
Molar H:C, After Pret.	0.8925	0.8933	0.9110	0.8562	0.8562	0.8562	0.8562	NA
Molar H:C, Product	0.8357	0.8359	0.8006	0.8259	0.8125	0.9724	0.8154	NA

[e] Tests performed during FY89-90 Task 2.

[f] 3 g HA061 added to preheated slurry before solubilization.

[g] 112.2 g HA061 added to pretreated slurry before solubilization.

[h] Elemental balance was not completed for this test.

TABLE 6

Comparison of Pretreated and Non-Pretreated Tests

	Pyrolysis		Liquefaction	
	Non-Pret. N484	Pretreated N519/N524	Non-Pret. N486	Pretreated N525/N528
Solvent	HA061	HA061/N519	HA061	HA061/N525
Additive	HA061	H_2S/None	--	H_2S/None
Gas	--	Ar/None	CO	Ar/CO
Residence Time, min	60	60/60	62	60/60
Avg. Temp., °C	371	184/372	373	176/376
Max. Temp., °C	375	187/381	376	178/381
Avg. Pressure, psi	1425	2106/631	3665	2000/3434
Max. Pressure, psi	1450	2125/663	3740	2000/3560
Conversion, %	67.9	57.5	87.7	81.0
Products:				
CO	0.26	12.17	-33.63	-54.25
H_2	0.02	0.05	0.41	1.01
CO_2	14.22	7.74	65.04	73.46
C1-C3	1.35	0.17	1.03	0.97
H_2S	0.00	0.19	0.06	2.90
Total Gas	15.85	20.32	32.91	24.09
H_2O	-1.17	7.37	-12.96	-22.75
Ash	-0.74	0.14	-0.81	-0.96
IOM	32.08	42.55	12.35	18.97
THF Solubles	53.99	29.61	68.50	80.65
Total Liquid	84.16	79.68	67.08	75.91

The fact that product quality is improved through the use of a hydrogen-donating solvent can be seen in the molar hydrogen-to-carbon ratios of the products of the tests. The molar H:C ratio for the tests using HA061 as the solvent was generally higher than the molar H:C ratio for the tests in which either A04 (coal-derived anthracene oil) or tetralin were used. In addition, increases in molar H:C ratios were noted for some of the tests in which HA061 was used as the solvent, most often when CO was present as the solubilization reductant. Increases in molar H:C ratios were not noted when A04 was the solvent. The highest product molar H:C ratio was produced when the solubilization processing conditions consisted of a temperature of 375°C, a pressure of 3500 psi, a residence time of 60 minutes, and the use of CO as the reductant.

TABLE 7

Summary of Solvation Tests using Hydrogen-Donating Solvents

	N476	N477	N480	N483	N484	N485	N486	N487	N497	N499
Solvent	A04	HA061	A04	HA061	HA061	HA061	HA061	HA061	A04	HA061
Additive	--[a]	--	Tetralin	HA061	HA061	--	--	--	Tetralin	--
Gas	--	--	--	--	--	H_2	CO	Ar	--	CO
Residence Time, min	60	60	60	60	60	60	62	60	60	60
Avg. Temp., °C	374	372	372	374	371	372	373	370	368	370
Max. Temp., °C	375	378	375	377	375	376	376	375	378	370
Avg. Pressure, psi	1429	1353	1496	1425	1425	3543	3665	3827	1111	512
Max. Pressure, psi	1525	1455	1581	1450	1450	3553	3740	3890	1180	512
Conversion, %	25.3	61.5	53.1	66.9	67.9	72.2	87.7	59.0	48.8	58.2
Products[b]										
CO	0.26	0.14	0.21	0.22	0.26	0.38	-33.63	1.72	0.61	33.42
H_2	0.45	0.02	0.01	0.02	0.02	0.19	0.41	0.03	0.03	0.08
CO_2	13.52	7.48	9.82	12.64	14.22	15.29	65.04	12.84	19.04	17.07
C1-C3	1.19	0.67	0.80	1.13	1.35	1.60	1.03	1.10	1.42	1.91
H_2S	0.20	0.00	0.00	0.02	0.00	0.09	0.06	0.00	0.07	0.00
Total Gas	15.62	8.31	10.84	14.03	15.85	17.55	32.91	15.69	21.17	52.48
H_2O	-4.77	-3.87	6.02	4.01	-1.17	1.87	-12.96	3.98	7.79	-5.53
Ash	0.53	-0.34	-0.05	-0.69	-0.74	-0.95	-0.81	-0.64	-0.90	-1.21
IOM	74.7	38.47	46.87	33.07	32.08	27.82	12.35	41.00	51.22	41.78
Solubles	13.93	57.45	36.31	49.57	53.99	53.71	68.50	39.97	20.72	12.47
Total Liquid	84.39	91.71	89.15	85.96	84.16	82.45	67.08	84.31	78.83	47.52
Feed H:C[c]	0.7627	0.8912	0.9587	0.8948	0.9133	0.9075	0.9121	0.9031	1.0221	0.8934
Product H:C[c]	0.6773	0.8922	0.8183	0.8500	0.8600	0.8885	0.9208	0.8558	0.8668	0.8701

[a] None used.

[b] Values given as wt% of maf coal fed to reactor. Negative values indicate a consumption; positive values indicate a production.

[c] Molar H-to-C ratio.

The data also indicated that:

- Nascent hydrogen from the water/gas shift reaction was more readily used than hydrogen gas.
- The use of H_2S improved solubilization.
- Merely heating the feed slurry did not improve solubilization.
- Solubilization of the coal could be improved through the use of specific, solvent-dependent pretreatments.

3.4 Step 3 - Polishing

The purpose of the polishing step is to complete the solubilization of the more intractable portions of the coal prior to hydrotreatment. The mechanistic study (discussed in Section 3.1) indicated that the coal-derived liquids were very phenolic in nature. Using the chemistry rule of "like dissolves like," this knowledge was incorporated into the design of the polishing step.

Two solubilization/polishing test sequences were performed. The run conditions are summarized in Table 8, while Table 9 presents the product slates of the tests. Table 9 shows that virtually all of the solvent used during the test was recovered during the processing. Conversion to THF solubles calculated for the tests was high: 96.4 wt% for the test with HA061 as the polishing-step additive and 101.6 wt% for the test with phenolic solvent as the polishing-step additive. The product slate indicates that minimal quantities of gas were produced during processing in either case, relative to the moisture- and ash-free (maf) coal fed to the system. In both combinations, about 90 wt% of the maf coal fed to the system was converted to soluble material, which was the desired product. The run performed with HA061 added during the polishing step resulted in a lighter product, in that the resulting soluble material consisted of both soluble resid and distillable oils. The product of the test in which phenolic solvent was added during the polishing step was comprised almost exclusively of soluble resid. Insoluble organic material was present in the product of the HA061 test, but was not detectable in the product of the phenolic solvent test.

The presence of excess H_2S in the product gas of the N443/444 run sequence in which HA061 was added in the polishing step indicates that not only was the sulfur incorporated from the H_2S completely removed, but some sulfur present in the feedstocks was also removed. In the phenolic solvent-added test, almost all of the sulfur incorporated into the coal structure during the processing sequence was removed.

3.5 Step 4 - Hydrotreatment

Steps 1-3 (pretreatment, solubilization, and polishing) were performed in an integrated fashion. The products were catalytically hydrotreated to demonstrate the maximum hydrotreatability of the solubilized slurry and to provide products that could be compared to the products of existing processes. The testing was performed using the "best" pretreatment and solubilization steps that had been evaluated during earlier work (see Sections 3.2 and 3.3).

TABLE 8

Summary of Polishing Step Tests

	Run No.	Temp. (C°)	Avg. Press. (psi)	Res. Time (min)	Reductant	Additive
Solubilization	N443	374	3373	60	CO	H_2S
Polishing	N444	430	3831	12	H_2	HA061
Solubilization	N447	374	3470	60	CO	H_2S
Polishing	N448	412	4092	19	H_2	POH

TABLE 9

Mass Balances and Product Slates of the Polishing Tests

	N443/N444	N447/N448
Additive[a]	HA061	POH
Material Balance, wt%	96.91	97.40
Solvent Recovery, wt%	102.36	100.30
Conversion to THF Solubles, wt%	96.44	101.56
Product Slate, wt% maf coal in[b]		
CO	-34.82	-36.12
H_2	-0.79	-0.64
CO_2	66.78	67.35
C1-C3	2.14	2.22
H_2S	2.53	-1.64
H_2O	-23.32	-16.90
Ash	-1.13	-2.56
IOM	4.91	-2.03
Distillable Oils	11.99	1.47
Soluble Resid	76.78	88.85

[a] Additive was added in an amount equal to approximately 25 wt% of the original pasting solvent.

[b] Positive values indicate production of the component; negative values indicate consumption.

Figure 4 shows the experimental matrix for the tests. As the figure shows, the testing was performed according to a tree diagram-type of matrix. Performing the tests in this manner, i.e, using the same feed slurry whenever possible, enabled direct comparisons to be made between the run sequences. Two Step 1 runs were performed at identical conditions to obtain sufficient pretreated slurry for the remaining processing. The pretreated slurries from these two runs, N553 and N554, were combined into a bulk sample. (All analyses were performed on the bulk sample rather than on the individual pretreated slurries.) Pretreated slurry was then solubilized in two batches, one at ~375°C (N555) and one at ~350°C (N556). The solubilized products of each of these Step 2 runs were polished (Step 3) at either 460°C (N558 and N557) or 435°C (N559 and N560) with a small amount of added cresylic acid. Each polished product was combined with a heavier vehicle solvent (hydrogenated anthracene oil) and distilled to remove a quantity of water and light, highly oxygenated solvent/coal-derived liquid equal to that added during the polishing step. Finally, each of the polished product slurries from Step 3 was hydrotreated in Step 4 (N562, N564, N563, and N566, respectively). The multistep run sequences are referred to in this report by the run numbers of their hydrotreatment steps. The specific run solvents, additives, and conditions for each step of the four run sequences are given in Table 10.

Testing was performed in the EERC's hot-charge, batch autoclave system. The 1-gallon autoclave was used when larger quantities were processed (i.e., during Steps 1 and 2 [pretreatment and solubilization]). The 1-liter autoclave was used for the polishing and catalytic upgrading (Steps 3 and 4). Karl Fischer water, ash, and tetrahydrofuran (THF) solubility analyses were performed on the feed and product slurries. Due to a lack of funding, elemental analyses were performed for only a few runs.

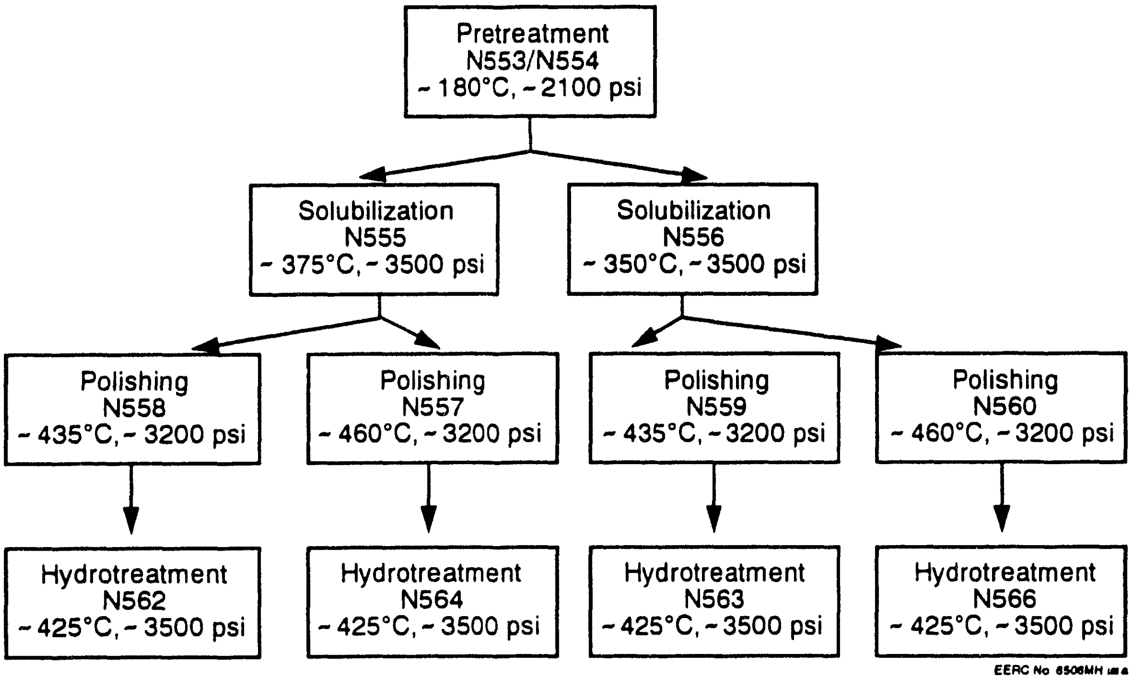

Figure 4. Experimental matrix for integrated run series.

TABLE 10

Conditions of Integrated Run Series

	N562	N563	N564	N565
Step 1 - Pretreatment				
Run No.	N553+N554	N553+N554	N553+N554	N553+N554
Solvent	HA061[a]	HA061	HA061	HA061
Additive	H_2S	H_2S	H_2S	H_2S
Gas	Ar	Ar	Ar	Ar
Avg. Temp., °C	179	179	179	179
Max. Temp., °C	184	184	184	184
Avg. Pressure, psi	2064	2064	2064	2064
Max. Pressure, psi	2100	2100	2100	2100
Residence Time, min	60	60	60	60
Step 2 - Solubilization				
Run No.	N555	N556	N555	N556
Feed	N553+N554	N553+N554	N553+N554	N553+N554
Additive	None	None	None	None
Gas	CO	CO	CO	CO
Avg. Temp., °C	375	353	375	353
Max. Temp., °C	385	354	385	354
Avg. Pressure, psi	3488	3460	3488	3460
Max. Pressure, psi	3600	3515	3600	3515
Residence Time, min	60	60	60	60
Step 3 - Polishing				
Run No.	N558	N559	N557	N560
Feed	N555	N556	N555	N556
Additive	CA1[b]	CA1	CA1	CA1
Gas	H_2	H_2	H_2	H_2
Avg. Temp., °C	435	433	458	461
Max. Temp., °C	437	435	461	465
Avg. Pressure, psi	3190	3363	3200	3439
Max. Pressure, psi	3226	3435	3275	3540
Residence Time, min	20	20	20	20
Step 4 - Hydrotreatment				
Run No.	N562	N563	N564	N566
Feed	N558	N559	N557	N560
Additive	Shell 424	Shell 424	Shell 424	Shell 424
Gas	H_2	H_2	H_2	H_2
Avg. Temp., °C	423	424	422	420
Max. Temp., °C	426	425	426	421
Avg. Pressure, psi	3459	3461	3525	3554
Max. Pressure, psi	3655	3635	3675	3675
Residence Time, min	180	180	180	180

[a] Hydrogenated coal-derived anthracene oil.
[b] Cresylic acid solvent.

Mass and material balances were performed for the run sequences based upon maf coal fed to the pretreatment step. Allowances were made for the removal of sample aliquots for analysis. Combining the analytical results and the material balances resulted in the calculation of product slates for the integrated run series. In other words, product slates were calculated for the entire four-step system based upon maf coal fed to the pretreatment step. These product slates are presented in Table 11.

Tables 12 and 13 summarize this information and organize it in a simplified manner to permit easier comparisons between run series. As seen in Table 12, comparison of solubilization (Step 2) at 350°C and at 375°C shows that higher-temperature solubilization ultimately resulted in less gas + water production (about 17 wt% compared to 34 wt%) and more total liquid product (about 70-80 wt% compared to 59 wt%) than solubilization at the lower temperature. More of the hydrotreated liquid product was in the form of premium distillate (66 wt% compared to 31-56 wt%) when the slurry had been solubilized at 375°C.

TABLE 11

Product Slates of Integrated Run Series[a]

Hydrotreatment Run No.	N562	N563	N564	N566
Solubilization Temp., °C	375	353	375	353
Polishing Temp., °C	435	433	458	461
Gas Out				
CO	-65.92	-36.92	-63.20	-36.44
H_2	-1.50	-0.93	-5.46	-2.64
CO_2	114.26	93.05	116.00	93.65
C1-C3	11.53	13.50	11.70	14.38
H_2S	1.48	0.58	0.92	0.42
H_2O	-42.57	-34.12	-42.27	-35.32
Total Gas + Water	17.27	35.16	17.68	34.04
Liquid Out				
Oxygenated Liquids	9.13	-0.13	2.49	17.77
Premium Distillate	66.04	56.35	67.08	31.46
Soluble Residuum	4.12	3.33	3.26	9.00
Total Liquids	79.29	59.55	72.83	58.23
Unconverted IOM	3.36	7.60	9.12	6.43
Total, All Products	99.93	102.31	99.64	98.70

[a] Product slates given include all steps (pretreatment, solubilization, polishing, and hydrotreatment) and are based upon percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

TABLE 12

Comparison of Effect of Solubilization and Polishing Temperatures on Final Hydrotreated Product Slate[a]

Hydrotreatment Run No.	N563	N566	N562	N564
Solubilization Step Temp., °C	353	353	375	375
Polishing Step Temp., °C	433	461	435	458
Gas + Water Yield	35.16	34.04	17.27	17.68
Liquid Yield				
Distillate	56.35	31.46	66.04	67.08
Soluble Resid	3.33	9.00	4.12	3.26
Oxygenates	-0.13	17.77	9.13	2.49
Total	59.55	58.23	79.29	72.83
Conversion, % maf coal fed to system	92.40	93.57	96.64	90.88

[a] Yields are given as percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

TABLE 13

Comparison of Gas Plus Water Production for Integrated Run Series[a]

Hydrotreatment Run No.	N563	N566	N562	N564
Solubilization Step Temp., °C	353	353	375	375
Polishing Step Temp., °C	433	461	435	458
Pretreatment	2.00	2.00	2.00	2.00
Solubilization	17.95	17.95	8.29	8.29
Polishing				
CO_2	4.77	5.42	2.55	4.50
C1-C3	6.77	7.62	2.91	2.75
Other	3.01	2.61	-0.21	0.15
Total Polishing	14.55	15.65	5.25	7.40
Hydrotreatment	0.66	-1.56	1.73	0.00

[a] Gas + water yields are given as the percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

When the polishing (Step 3) temperatures are compared, it can be seen that the higher-temperature polishing (~460°C) resulted in yields that were similar to those of the lower-temperature polishing (~435°C), but that the liquid product slates were very different. This is especially noticeable for N563 and N566, the run series with 353°C solubilization. The lower-temperature polishing step resulted in substantial differences in yields of distillate, soluble resid, and oxygenates. In this case, the higher polishing temperature seems to have cracked more of the coal-derived material, resulting in the production of far more oxygenates at the expense of distillate production. The higher polishing temperature also resulted in an increased production of soluble resid. The same differences were not as obvious for the N562 and N564 run series with 375°C solubilization. Slightly more distillate and soluble resid were produced when the higher polishing temperature was used, but far fewer oxygenates were produced. The highest overall conversions were produced when polishing was performed at the lower temperature. The higher polishing temperature seems to have retrograded some of the phenolic material, resulting in a conversion loss at the expense of the production of the oxygenates.

A comparison of the gas + water yields is presented in Table 13. As the table shows, 2.0 wt% of the maf coal fed to the system was removed during the pretreatment (Step 1) as gaseous products. Twice as much of the maf coal left the system as gas during both the solubilization and polishing steps (Steps 2 and 3, respectively) when the solubilization was performed at ~350°C. The gaseous product slates of the polishing step were very different for the run series performed at higher solubilization temperatures compared to those performed at lower solubilization temperatures. It appears that more CO_2 is produced at higher polishing temperatures, but that the hydrocarbon gas (C1-C3) yield is about the same.

The following conclusions could be drawn from the results of these studies:

- As part of the integrated run sequence, solubilization (Step 2) performed at 375°C produces higher yields of better-quality hydrotreated liquid products than solubilization performed at ~350°C.
- As part of the integrated run sequence, polishing (Step 3) performed at ~435°C results in desirable liquid product slates and high conversion levels without the retrograding that was noticed at the higher polishing temperature.
- Of the run sequences tested, it would appear that a run sequence incorporating a solubilization step at 375°C and a polishing step at 435°C (i.e., a run series similar to that of N562) would produce the greatest yield of high-quality, desirable products.

4.0 CONCLUSIONS

The positive results of the tests performed to date using the EERC's multistep LRC liquefaction process indicate that future work should be performed in two areas:

- The four-step sequence matrix should be performed using phenolic solvent rather than HA061.
- The range of effective hydrotreatment conditions should be determined.

After these two areas have been investigated, process optimization on a batch scale can begin, followed by one or more continuous demonstration runs.

5.0 REFERENCES

1. Committee on Production Technologies for Liquid Transportation Fuels, Energy Engineering Board, Commission on Engineering and Technical Systems, and National Research Council. 1990. *Fuels to Drive Our Future*. Washington, DC: National Academy Press.

2. Rindt, J.R. and S.J. Cisney. 1983. Low-Temperature Liquefaction of North Dakota Lignite. Presented at the Direct Coal Liquefaction Contractors' Review Conference, 16-17 November, Pittsburgh, PA.

APPENDIX A

GENERIC RUN INSTRUCTIONS

GENERIC RUN INSTRUCTIONS

Slurry (can be fed to any of the first three steps):
solvent-to-maf coal ratio = 3:1

If necessary, water is added to bring the water content to 30 wt% of the maf coal in the feed slurry

When used, additives = 5 wt% of the maf coal in the original feed slurry

Step 1 - Pretreatment Step

Slurry as mixed according to the instructions given above

Additive may be used according to the instructions given above

Gas is added in an amount equal to 10 gmoles gas/200 g maf coal in original feed slurry

Step 2 - Solubilization Step

Slurry as mixed according to the instructions given above **OR** pretreated slurry from pretreatment step

Additive may be used according to the instructions given above

Gas is added in an amount equal to 10 gmoles gas/200 g maf coal in original feed slurry

Step 3 - Polishing Step

Slurry as mixed according to the instructions given above (for a blank run) **OR** product slurry from solubilization step

Gas is added in an amount equal to 10 gmoles gas/200 g maf coal in original feed slurry

Interstep Distillation

Prior to distillation, vehicle solvent is added in a quantity equal to what is expected will be removed as overheads; i.e., equal to the cumulative quantity of oxygenated solvent added during any of the previous steps.

Distillation takes place at nominally 120°C and 4 psia.

Step 4 - Catalytic Hydrotreatment

Solubilized and/or polished slurry is used as the feed

Shell 424 catalyst is used in a weight ratio of 1 part catalyst to 2 parts maf coal in the original feed slurry

Hydrotreatment is performed at a constant gas pressure of 2500 psi. This pressure is maintained during heatup and hydrotreatment through the addition of gas.

Specific runs can be reproduced by following these instructions and performing the run using the gas, additive, and operating conditions listed in the table in the main body of this report.

6.0 GASIFICATION RESEARCH

6.1 Production of Hydrogen and By-Products from Coals

CATALYTIC GASIFICATION OF LOW-RANK COALS FOR HYDROGEN PRODUCTION

Final Technical Progress Report
for the Period April 1, 1986, to September 30, 1992

by

William B. Hauserman, PE
Senior Research Engineer

Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, North Dakota 58202-8213

Task Contracting Officer's Representative: Justin Beeson

for

U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880, MS C04
Morgantown, West Virginia 26507-0880

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CATALYTIC GASIFICATION OF LOW-RANK COALS FOR HYDROGEN PRODUCTION

1.0 INTRODUCTION AND SCOPE

This is a final summary report by the Energy and Environmental Research Center (EERC) for a six-year program exploring the effects of catalytically enhanced reactivity of coals to accelerate gasification rates for the production of hydrogen and methane. This project has consisted of bench-scale laboratory efforts; continuous pilot-scale process simulations; literature surveys; limited efforts dealing with solid, liquid, and gaseous coproducts; and subcontracted economic feasibility studies. Most of the technical highlights of this project are covered in the reports and papers cited in the bibliography.

2.0 PROJECT JUSTIFICATION

Since the mid-1970s, the United States has been in a state of apprehension over the next energy crisis and in eager anticipation of the next generation of energy supplies. While still unresolved, it appears reasonably certain that, for decades to come, the U.S. will, or should, rely increasingly on coal, simply because it is cheap and we have a lot of it. It is also apparent that somewhere within the shifting, multiple scenarios predicted, there is an expanded market for hydrogen as an end product or as an essential intermediate. This is summarized in Figure 1, showing the full array of potential markets for hydrogen from coal. Except for reforming natural gas, itself a valuable commodity, no other means of hydrogen production appears to be approaching economic competitiveness within several decades. Therefore, any medium-term policy of increased hydrogen production must depend upon coal.

The primary emphasis of this project has been on the effects of catalysis to accelerate reaction rates and increase yields, thus increasing gasifier throughput capacities and reducing capital costs. The fundamental measurement of steam-char reaction rates and initial screening of possible catalysts is by thermogravimetric analysis (TGA), which is established as a standard evaluation tool, is cost-effective, and has provided most of the useful data to date. More costly continuous process testing then serves to predict yields, compositions, and throughput capacities and to reveal specific equipment design problems to be solved in the course of process design for commercialization.

3.0 OBJECTIVES: ORIGINAL AND FINAL

As defined in annual research plans and in other reports throughout this project, its initial objectives, restated briefly, have been as follows:

- To determine optimum gasifier conditions and catalyst selections for production of either hydrogen, methane, condensable products, marketable char, or activated carbon.
- To develop empirical kinetic models to predict product yields under real-world conditions.

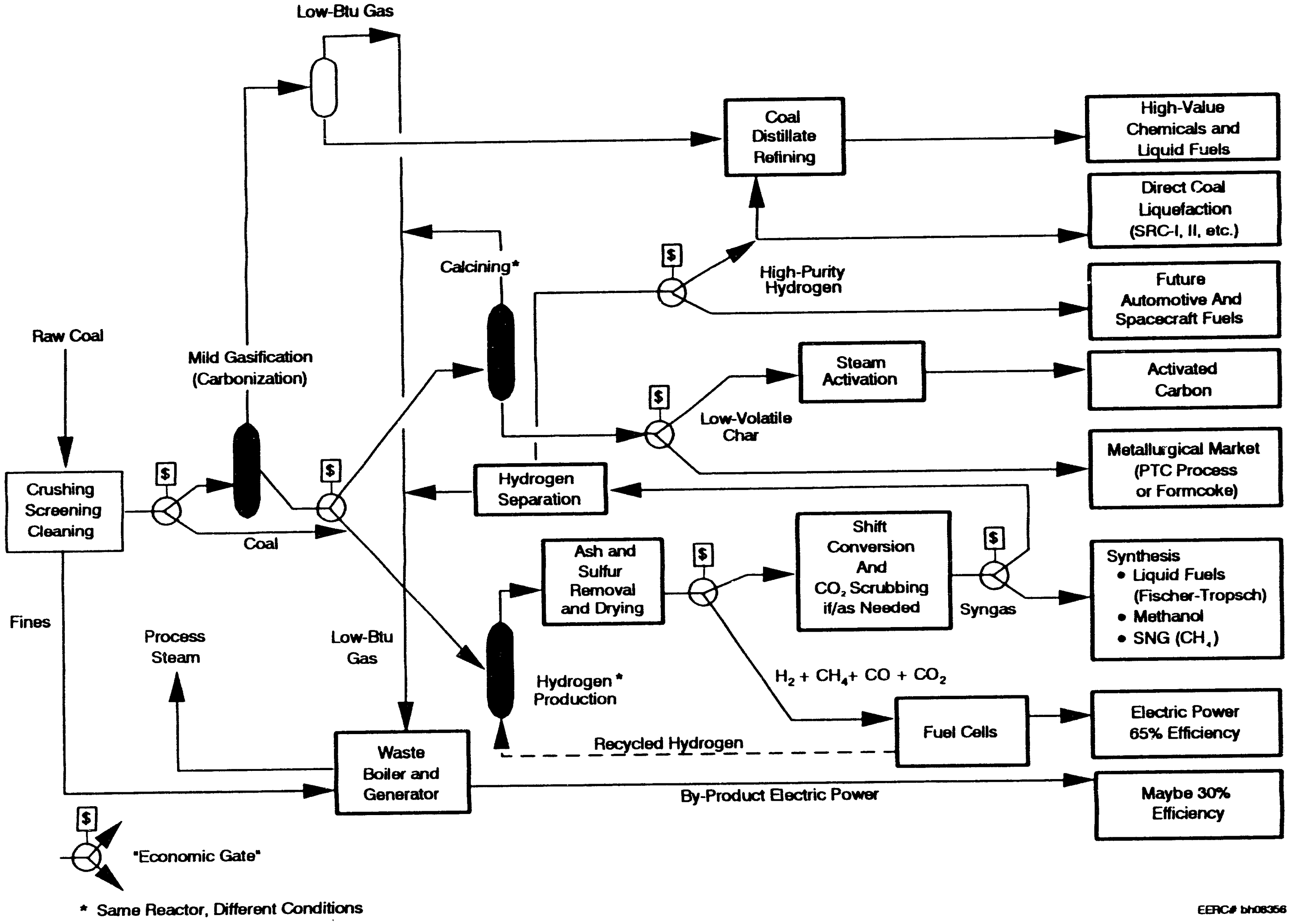

Figure 1. Markets for hydrogen from coal.

- To explore the potential for in-bed sulfur capture.
- To apply these objectives primarily to lignite and subbituminous coals.

During the course of the project, emphasis was expanded to cover hydrogen-methane mixtures, as the preferred feed to advanced fuel cells, which if combined with gasifiers in integrated designs may eventually achieve overall efficiencies approaching 60%. For this application, the project scope was expanded to include maximizing methane-hydrogen combinations from bituminous coals. These and future EERC efforts are being coordinated with Energy Research Corporation, a leader in the development of molten carbonate fuel cells.

In retrospect, exploring the original, broadly defined objectives has revealed considerable merit in more avenues of inquiry than could be covered by the time and funds available. In successive annual research plans, task objectives were adjusted to achieve balance between 1) generating more preliminary screening data, 2) demonstrating feasibility by continuous process testing, and 3) exploring peripheral areas, such as solid or liquid coproducts, catalyst recovery, and gas separation or enrichment, all within the severe limitations of time and funding and the priorities of related projects.

4.0 PROJECT HISTORY: ACCOMPLISHMENTS AND PROBLEMS

TGA analyses of a broad variety of coals and catalysts have been in progress throughout the project and are continuing under related projects. TGA tests have covered lignites, bituminous, and subbituminous coals, defining their intrinsic and catalyzed reactivities in the range of interest (600° to 800°C).

Peripheral studies included measurements of a specific surface area of coal and chars, as a physical factor critical to realization of the potential benefit of catalysis. The density of exposed active sites is proportional to the specific surface area, which changes during the course of gasification. A practical application of such knowledge is the production of activated carbon, by incomplete gasification under conditions to produce a char with maximum porosity and active site density. No pilot-scale tests were done in this area, although a literature survey of the state of the art in activated carbon production was produced.

Early in the project, a pilot-scale, atmospheric, continuous, fluidized-bed gasification system was designed and built. This pilot demonstration unit (PDU) had a feed capacity of 40 lb/hr injected by a screw feeder at the bottom of a refractory-lined vessel with a 6-inch inside diameter. As the mainstream of the project, extensive test matrices were carried out with two lignites and a subbituminous coal, at 700° to 800°C, in fluidized beds of limestone, silica, taconite, and coal alone. Added heterogeneous catalysts included trona, nahcolite (both common sodium-bearing minerals), and commercial K_2CO_3 and $CaCO_3$, for comparison with each other and with the coal's native or intrinsic reactivities. Over 50 successful, scheduled runs were accomplished, generating engineering data for potential design use.

Based on the best available set of PDU data, an economic feasibility study was done by Black and Veatch Engineers, to compare the profitability of plants producing high-purity hydrogen, methanol, or electricity by use of the product gas in a molten carbonate fuel cell. All cases assumed a subbituminous coal in a fluidized reactor bed of limestone as the catalyst.

An ongoing, parallel study by the EERC (experimental) and Fluor-Daniel Engineers, under subcontract to Energy Research Corporation, assumes an eastern bituminous coal, to produce hydrogen-methane mixtures for advanced fuel cells, which in turn may produce electricity at overall efficiencies approaching 60%. This study has also addressed the use of potassium-impregnated bituminous coal. It has, so far, produced a multioption engineering cost study by Fluor-Daniel, and continuing efforts are in progress.

Following completion of the above test matrix, the PDU was dismantled, rearranged, and integrated with an adjacent mild gasification process system, so that the hydrogen production PDU could, as an alternative function, serve as the calciner or second stage of the two-stage process to produce metallurgical char as well as gas and liquid products. The first-stage vessel was also designed to serve as either a carbonizer for mild gasification or as a pressurized fluid-bed combustion test unit. The modified process was also designed for operation at pressures up to 150 psig and included a test loop for the evaluation of hot-gas cleanup devices.

Following this renovation, a substantial amount of time and funding was required to bring the PDU to full operational status. Although the combined, two-stage process, funded under other projects, was never operated as such, the calciner stage was again used briefly in the hydrogen production PDU mode. Following several shakedown tests and minor modifications, mainly of instrumentation and downstream gas cleanup and scrubbing components, the system was restored to complete operability, yielding some data on operation with Wyodak coal in a limestone bed, but with no catalyst impregnation. At this point, escalating operating costs indicated serious limitations on the extent of useful data that might be expected from continued pilot operation on this scale.

To extract more useful data from the remaining project funding, scheduled runs were downscaled and carried out in a 1-lb/hr continuous process unit (CPU), producing the most recent conclusions of this report. This smaller unit was electrically heated and fed steam and nitrogen only, without combustion of any of the fuel for process heat, making it a less complete process simulation than the larger PDU. This system had a well-established history of operation in the mild gasification mode. Fed at the 1-lb/hr level, with the residence time limited by a bed overflow, carbon consumption was incomplete, allowing determination of effective reactivities.

While yield data based on small pilot tests are of dubious validity, gas compositions are a fair prediction of what a mechanically similar, commercial-scale version of the process should deliver. Table 1 compares inert-free product gas analyses from the most significant runs in this project with corresponding data from state-of-the-art gasifiers of other designs, all operating at far higher pressures than the near-atmospheric EERC tests and with no catalytic materials added. All three EERC data sets shown are for Wyodak subbituminous coal with a limestone bed only and no potassium

TABLE 1

Comparison of Normalized Product Gas Analyses

	EERC PDU		EERC CPU	State-of-the-Art Gasifiers			
				Lurgi	IGT	Destec	Texaco
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
% H_2	44.7	45.5	58.6	40.9	38.6	41.0	38.5
% CO	9.1	10.8	8.2	14.2	37.6	38.0	44.9
% CO_2	43.0	40.1	25.0	32.3	19.7	21.0	16.5
% CH_4	2.6	2.7	8.0	10.9	4.2	0.1	0.2
C_2+	0.5	0.8	0.3	1.6	--	--	--

(1) Early run, used as basis of Black and Veatch economic study.
(2) Final run of project, following renovation.
(3) Externally heated, no in-bed combustion.
(4) Great Plains Gasification Plant, Beulah, ND, fixed bed, large-scale commercial operation.
(5) Institute of Gas Technology, U-Gas Process, fluidized bed, pilot plant data, scheduled for commercialization.
(6) Dow Chemical Co., Plaquemine, LA, entrained bed, pilot plant data, process in commercial operation.
(7) Pilot plant data.

added. While overall yields, efficiencies, carbon conversion, and throughput capacities are optimized by proper process design for commercial-scale plants, Table 1 indicates that the simplest of process options covered by this study, a fluidized limestone bed with no potassium or other more effective catalyst added, is a promising source of high-hydrogen syngas for use in fuel cells or other hydrogen applications.

To augment TGA for feed-catalyst-condition screening, a new research tool, the integrated bench-scale gasifier (IBG) has completed preliminary shakedown testing and shows a good possibility of essentially replicating TGA data on a larger scale, of 200-300 grams, as compared with 20-50 milligrams for the TGA. Unlike the TGA, this unit can provide samples of residual ash or char and condensible liquid coproducts large enough for complete analysis and multiple or replicate gas samples. Extensive use of this unit is presently scheduled for two related projects.

All the conclusions, summarized below, favor impregnated potassium as the optimum catalyst. TGA data, however, indicate that sodium is roughly comparable, although it acts as a flux and causes agglomeration of char and ash. Sodium was rejected early in the project when pilot operations, on the PDU scale, feeding raw trona or nahcolite as the sodium source, revealed serious bed agglomeration or clinkering problems, which have also been reported for high-sodium coals in other fluid-bed gasifiers. While sodium in any form appears unacceptable for use in fluidized- or fixed-bed gasifiers, it is far cheaper than potassium. A worthy area of further research would, therefore, be development of a novel gasifier with a violent circulation pattern to break up agglomerates. This is also important because any leaching process to recover potassium from the ash will inevitably recover and accumulate sodium from the coal in the potassium recycle.

Among peripheral interests pursued during the project was limited, exploratory testing of the vortex venturi concept, to enrich product gases, concentrating hydrogen and rejecting carbon dioxide, by means of a super-cyclone achieving centrifugal force fields of 10,000 G to 20,000 G, with laminar flow and no moving parts. Cold simulation, using costly helium-argon mixtures in very short tests in the final working days of the project, indicated that significant separations are possible at modest pressure drops. No further work is planned at present. If any future tests are to be cost-effective, they must be far more extensive and be conducted on the site of a pressurized gasifier in continuous operation.

5.0 SALIENT CONCLUSIONS

The general, overriding conclusions from the TGA tests are as follows:

- Low-rank coals consistently show greater native or intrinsic reactivities than higher-rank coals.
- Reactivities, at the same temperature, may increase by up to two orders of magnitude, with the addition of certain catalysts.
- Heterogeneous or contact catalysis occurs when coal is simply mixed with granular catalytic materials, such as limestone, taconite, nahcolite, trona, or salts of potassium, calcium, or sodium. A durable heterogeneous catalyst may be a fluidized reactor bed of limestone or taconite.
- Homogeneous catalysis, which has proven consistently more effective than heterogeneous catalysis, occurs when the same catalytic elements in solution are chemically bonded to carboxylic active sites ($-COO^-$) on the coal's organic structure.
- Monovalent alkalies (K, Na) are far more effective than divalent alkali earths (Ca, Mg), when applied with the same degree of ionic mobility.
- Reactivity increases with catalyst addition up to a saturation point, at which all active sites are saturated, beyond which further addition of catalyst has no further effect.

The following are conclusions drawn from 1-lb/hr CPU tests and are generally confirmed by TGA results:

- Impregnation of Wyodak coal with potassium hydroxide, at a potassium to fixed carbon ratio of around 0.2 or greater, roughly doubles the gasification reaction rate in fluidized beds of limestone.
- Economically viable potassium impregnation will require an efficient leaching step for potassium recovery. Ash-leaching studies,

associated with these tests, using Wyodak coal, indicate that potassium recoveries well over 95% can be achieved.

- Depending on the coal and potassium impregnation level, the high catalyst levels may cause some agglomeration problems in fluidized beds, which may be obviated by a bed of some crushed rock, such as limestone or taconite, which will also contribute catalytic effects.

- In a fluidized bed of taconite, the reaction rate enhancement by potassium impregnation was substantially greater than in a limestone bed. This was not predictable from TGA measurements and is attributed to interaction between the potassium and reduced iron.

- Ash analyses and potassium balances for these tests indicated striking, consistent, but unexplained, differences as to how the potassium may be combined in beds of limestone, taconite, or coal ash alone. The mobility of potassium, and, hence, its catalytic effectiveness, appears to be substantially enhanced or limited by its reactions with mineral components in the bed or coal ash. Major differences can thus be expected in reactions between potassium or sodium catalysts and the ash of different coals, which will affect the ease of catalyst recovery.

- The CPU represents the barest minimum scale on which continuous process evaluation can be reliable. Any future tests limited to this scale should involve longer runs, multiple replications of material balance periods, and multiple samplings of all products to provide statistical credibility.

- In all gas samples, H_2S levels fell below the detectable analytical limit, precluding any observation of in-bed sulfur capture for the conditions studied. This is consistent with the use of low-sulfur (S = 0.63% maf) Wyodak coal.

- Results from these studies are inconclusive regarding the potential use of sodium as an economical alternative to potassium catalyst. Relatively large pilot-scale tests are needed to determine whether preimpregnation of sodium or potassium on feed coal, as homogeneous catalysts, will result in the agglomeration problems observed with heterogeneous trona and nahcolite earlier in this project. Because of the very small bed size, the 4-lb/hr unit is not suitable to study mechanical factors affecting bed fluidization.

- All the work reported here assumes fluidized-bed gasification. There is no *a priori* reason to doubt that the rate enhancement by catalysis could not also be achieved in a more traditional "fixed-bed" gasifiers, such as existing Lurgi, Wellman-Galusha, or Stoic designs.

6.0 RECOMMENDATIONS

Based on the above conclusions and experience gained during this project, the following specific recommendations are submitted for continued, near-future research efforts or as design assumptions for engineering economic studies:

- Feed coal impregnation with potassium, in any soluble form, is the recommended means of rate-enhancing catalysis, subject to site-specific economics of supply and effectiveness of recovery by ash leaching.
- Taconite should be further explored as a bed material for gasifier design, in combination with potassium impregnation, if a bed material is needed for thermal and mechanical stability.
- TGA and IBG tests to establish saturation levels, with potassium and sodium, should be done on any candidate coal for catalytic gasification.
- For any combination of coal and heterogeneous catalyst under serious consideration, tests should be done to establish the form of the catalyst and its leachability from the coal's ash at continuous equilibrium conditions.
- Sodium, as a heterogeneous catalyst, should be evaluated as an economical alternative to potassium, but in connection with efforts on novel gasifier designs that can tolerate or prevent agglomeration.
- Future test matrices should include high-sulfur coals in taconite beds to test sulfur-capture effects, as well as the effects of sulfidation on alkali catalysts.
- The application of catalytic rate enhancement to fixed-bed gasification should be explored.

Based on overall observations made in the course of this project, some less-specific recommendations for the future course of research in catalytic gasification appear justified.

For firm engineering design data and identification of operating problems, future efforts should be done on a pilot plant scale. Such a facility should be dedicated to the single purpose of hydrogen/methane production, on a budgetary scale big enough to ensure complete shakedown operation and extended runs of at least a week on each set of conditions considered, with several replications of all runs showing promise for commercial-scale designs. Any such demonstration project must include operation for a year or two, so that shakedown operation and the inevitable aborted runs and anomalous data sets do not consume major portions of a project budget.

As one such potential system, the EERC has on hand nearly all of the components of a slagging, fixed-bed gasifier that consumed up to 22 tons/day of lignite and subbituminous coals at 350 psig, until 1982. This unit could be reassembled and modified for use in an atmospheric fluidized-bed mode, with a probable capacity of 5 tons/day, based on the specific capacity of the more recent 40-lb/hr tests, using a limestone bed with no additional catalyst. This capacity could be substantially increased by operation at 350 psig and possibly further doubled by the use of potassium catalyst.

As an alternative approach to further, completely subsidized pilot operations, a small demonstration gasification project should be considered, integrated with a utility plant to reduce the capital and fixed operating costs of facilities and auxiliary systems. Such a system could achieve at least partial economic self-sufficiency. Once it is in operation, relatively inexpensive tasks would be to vary the bed material and impregnate weeklong runs of feed coal, with potassium or other catalysts. The first step along this route would consist of site-specific feasibility studies to establish the costs and benefits of such demonstration plants. Preliminary calculations suggest that the capital cost of such a demonstration facility, assuming an air-blown gasifier, could be reduced by possibly 40%, by using the marginal capacity of auxiliary components shared with the host power plant. Steam, cooling water, ash disposal, and feed handling and crushing would be services purchased from the host plant at variable cost, offset by sale to the utility of the product gas or electric power produced by a molten carbonate fuel cell. From an operability point of view, such a utility add-on demonstration unit should have a capacity of at least 40 tons per day. Depending on the financial structure of the project and the effectiveness of its integration with an existing electric utility, it is possible that such a partially subsidized operation could cost the funding agency no more than a fully subsidized, stand-alone pilot plant on the scale described above.

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6.2 Sulfur Forms in Coal

SULFUR FORMS IN COAL

Final Technical Progress Report
for the Period July 1, 1990, to June 30, 1992

by

Dr. Steven B. Hawthorne, Research Supervisor
Ronald C. Timpe, Research Associate
Dr. Peter K.K. Louie, Research Associate

Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, North Dakota 58202-8213

Task Contracting Officer's Representative: Dr. Jagdish Malhotra

for

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880, MS C04
Morgantown, West Virginia 26507-0880

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SULFUR FORMS IN COAL

1.0 BACKGROUND

A major problem facing the coal industry now and in the future is high sulfur levels in coal, leading to unacceptable atmospheric SO_2 concentrations and, in turn, resulting in environmental consequences from acid rain. Currently, three solutions to this problem are occasionally used. The first is the most obvious: that is, to stop using high-sulfur coal or dilute (blend) it with low-sulfur coal. This, however, is not easy when one considers that low-sulfur coal deposits are far from inexhaustible, and low-sulfur coals, especially low-sulfur bituminous coals, are becoming more difficult to find. Fuel switching from coal to natural gas or fuel oil is also considered a viable option (1). The second solution is postcombustion flue gas scrubbing with reagents to remove sulfur species. This is expensive, with less-than-excellent efficiency, and produces additional waste for disposal. Even so, the scrubbed generating capacity in this country is expected to increase by 43% over the next eight years (1). A third solution, that is, precombustion sulfur removal, is occasionally used. Physical cleaning—such as washing, froth flotation, selective agglomeration, magnetic separation, and solvent extraction—remove some pyrite and other inorganic sulfur forms. Chemical cleaning—such as acid washing and molten caustic leaching—remove some "organic" sulfur as well as inorganic sulfur. None of these methods remove the quantities necessary to reduce the sulfur in a medium- or high-sulfur coal to the desired level (1.2-lb S/MM Btu) in a manner that is feasible. In order to develop a successful method of removing sulfur from coal or char prior to combustion, the chemistry of removal must be elucidated. An improved method of chemical analysis of coal is the first step in that direction.

The accurate and precise analysis of a solid material, such as coal, requires that the analytical method utilize energy, solvent, or reagent that can effectively permeate the matrix and contact the element of interest. Physicochemical barriers preventing such contact have proven formidable when attempting sulfur analysis of solid coal by conventional technologies. Analysis of coal for sulfur by volatilization of sulfur moieties is limited by their volatilities and vapor transport through the matrix, and liquid extraction of those moieties is limited by conventional solubility and permeability. Chemical derivatization for ^{13}C nuclear magnetic resonance (NMR) spectroscopy is reagent transport limited, ^{33}S NMR is limited by absorption bandwidth, and x-ray techniques are limited to surface analysis by the inability to penetrate the solid more than a few angstroms. Given these drawbacks, a technique that would allow solvent penetration into the entire sample and dissolution of the sulfur species, with the ability to obtain those species intact in a form that can be identified and quantified by conventional analytical methods, would advance sulfur science immeasurably.

A method that might provide the desired improvement is supercritical fluid extraction (SFE). SFE as a separations method is superior to the other extraction methods, including Soxhlet extraction. Because of the relatively poor mass transfer in liquids, liquid solvent extractions are inherently slow. Compared to liquid solvents, supercritical fluids have several characteristics that make them attractive extraction solvents as well as media for selective reactions. First, supercritical fluids have solvent strengths similar to those of liquid solvents, but, in contrast to liquid solvents, they have lower viscosities (10^{-4} versus 10^{-3} N-sec/m^2) and higher solute diffusivities (10^{-4} versus 10^{-5} cm^2/sec), which greatly improve mass transfer and greatly reduce the time for quantitative extractions (and reactions) to be performed. Second, the polarity of a supercritical fluid changes with its density as described by several correlations (2-4), including the simple empirical correlation proposed by Giddings (5): $\delta = 1.25\ P_c^{1/2}(\rho/\rho_1)$, where δ is the Hildebrand solubility parameter, P_c is the critical pressure of the fluid, ρ is the density of the supercritical fluid, and ρ_1 is the density of the fluid in its liquid state. As shown by these correlations, the selectivity of a supercritical fluid for a target analyte can be optimized by simply controlling the extraction pressure (and, to a lesser extent, the temperature). Supercritical fluids are also available that have widely varying polarities ranging from low-polarity fluids (e.g., ethane) to moderately polar fluids (e.g., CO_2) to polar fluids (e.g., water), which, along with pressure and temperature control, gives the analyst an extremely wide range of extraction solvent polarities to perform selective extractions. Modifiers can be added to the fluid to change its polarity. Figure 1 is a schematic of SFE system for mixing fluids. Third, in contrast to popular belief, analytical-scale (not process-scale) SFEs are experimentally simple and inexpensive to perform, requiring small samples and resulting in minimal waste.

Preliminary investigations into utilizing supercritical CO_2 combined with pyrolysis to extract organic sulfur from an Indiana bituminous coal were very

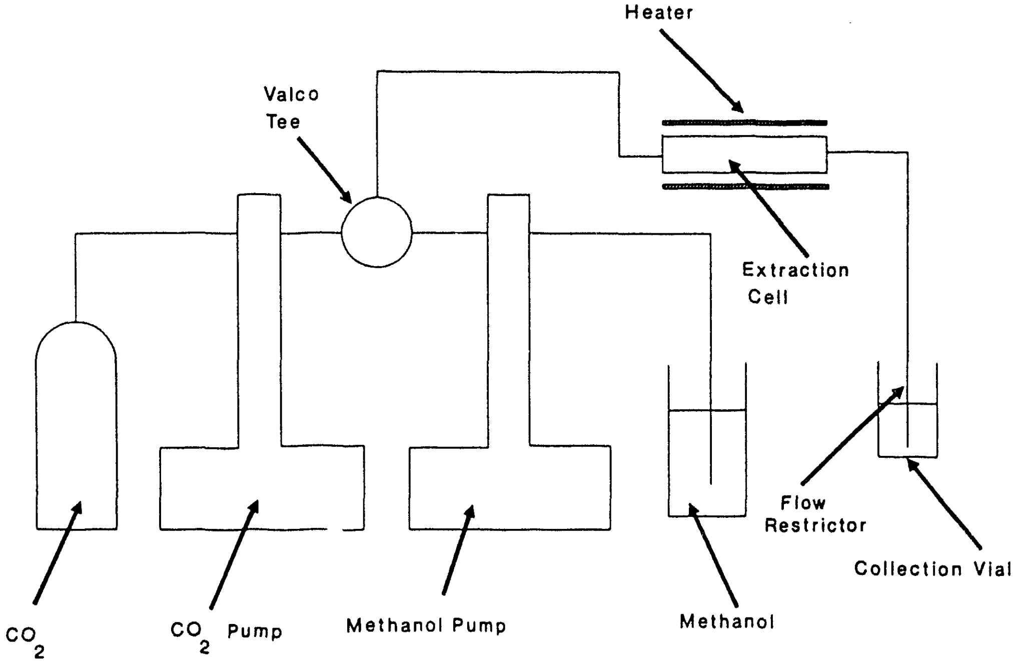


Figure 1. Schematic diagram of the SFE system for mixing and pumping binary fluids.

encouraging; i.e., this procedure reduced the organic sulfur content by ca. 50% and thus correlated well with the results of liquid solvent extractions. Unfortunately, while more than 50 organic sulfur compounds were identified in the supercritical CO_2 extract, these species could not quantitatively account for the extracted organic sulfur. Some evidence that the "missing" extracted organic sulfur compounds were quite volatile sulfur forms was obtained using a simple and reliable method, developed and validated in our laboratory, for directly coupling Thermogravimetric Analysis with mass spectrometry (TGA/MS).

Equipment capable of tolerating the rigors of SFE conditions at temperatures from ambient to 450°C was investigated as a means of extracting organic sulfur compounds. Cell heaters capable of the required range of temperatures and designed with safety in mind, but not commercially available, were built at the EERC. Sample cells were initially fabricated from stainless steel tubing and Swagelock and Parker fittings and found to be satisfactory when tested at the most rigorous of expected operating conditions. This past year, however, commercial cells made by Keystone™ were obtained that have proven to be a superior substitute for the home-built cells and are currently being used for the SFEs.

Several collection solvents were screened and toluene was selected on the basis of its superior collection efficiencies and gas chromatography (GC) characteristics.

Extraction with supercritical CO_2 at ca. 45°C and 400 atm was shown to be selective toward removal of elemental sulfur, primarily S_8. The extraction kinetics for removal of elemental sulfur were improved with $CHCl_2F$ (Freon 22) or CO_2/10% CH_3OH (CO_2 with methanol as a modifier), reducing extraction time to less than 20 minutes.

Good agreement of GC/MS data for the concentration of elemental sulfur in coal using two independent techniques (a selective triphenylphosphine reaction and selective SFE) was achieved early on in this project. The addition of the atomic emission detector (AED) and a Siever's sulfur-specific detector (SCD) provided a more convenient means of analyzing supercritical fluid extracts specifically for sulfur. Component separation by GC with detection and quantitation of sulfur species by AED minimizes the usual chromatographic complications caused by large numbers of components and coelution of compounds of interest with extraneous compounds.

Validation of the technique was initiated with preliminary spiking experiments involving S_8 on sand and glass beads. The results showed that extraction of elemental sulfur with SF CO_2 was reproducible.

2.0 GOALS AND OBJECTIVES

The overall objective of this project was to develop methodology to enable the rapid and accurate identification and quantitation of sulfur species in what is now referred to as the organic sulfur component of coal. To accomplish this, the following specific objectives must be met:

- To investigate and develop the use of SFE and pyrolysis/SFE (PYR/SFE) for the selective extraction of organic forms from coal.

- To identify and quantitate the individual sulfur organics recovered using SFE procedures.
- To investigate and develop the use of selective pyrolysis and/or chemical oxidation/reduction for the determination of organic sulfur forms in coal.
- To evaluate and incorporate other promising sulfur speciation techniques.

Coals

Heavily studied and well-characterized medium-sulfur coals were selected as the bases for this research program. Four coals from the Illinois Basin Coal Sample Program at the Illinois State Geological Survey were obtained: IBC-101, which served as the basis of the SFE methods development program; IBC-102, IBC-106, IBC-107, which served as the basis for mechanism studies involving sulfur form transformations as determined by stable sulfur isotope analysis; and IBC-109. Additional coals, an Alaskan subbituminous, a North Dakota lignite, and an Indiana bituminous, were analyzed in selected experiments. The analyses of these coals are shown in Table 1.

The sulfur analyses shown in Table 1 include results that accompanied the IBC samples; results obtained at the EERC with a LECO sulfur analyzer; and results obtained from an independent commercial laboratory, Minnesota Valley Testing Laboratory (MVTL). Table 2 contains the ASTM sulfur forms analyses results on the same coals. Although some of these values appeared in the

TABLE 1

Proximate and Sulfur Analyses of SFE Test Coals

Coal Samples: IBC-	101	102	106	107	109
Moisture	10.20	8.28	6.41	5.31	3.58
Volatile Matter	36.12	35.75	37.03	37.51	33.56
Fixed Carbon	44.69	50.90	48.82	46.01	54.34
Residue	9.01	5.08	7.72	11.19	8.55
Total Sulfur					
EERC[a]	4.13	3.35	3.53	3.54	1.13
IBCSP	4.36	3.30	3.77	3.72	1.13
MVTL[b]	4.44	3.27	3.68	3.59	1.00

Coal Samples:	Alaska	ND Lignite
Moisture	17.01	26.70
Volatile Matter	37.89	30.20
Fixed Carbon	40.21	36.38
Residue	4.88	6.75
Total Sulfur		
EERC	0.19	0.80
MVTL	0.14	0.87

[a] Total sulfur values determined by the EERC.
[b] Total sulfur values determined by MVTL laboratories, Inc., Bismarck, ND.

TABLE 2

Sulfur Forms Analyses of Coal Samples Used in This Work

IBC-	101	102	106	107	109	Alaska	ND Lignite
Sulfatic Sulfur							
A	0.05	0.06	0.01	0.26	0.00	--	--
B	0.67	1.17	0.73	0.37	0.05	0.02	0.18
C	0.07	0.16	0.11	0.29	--	--	--
Pyritic Sulfur							
A	1.22	2.26	1.86	0.48	0.50	--	--
B	0.53	0.61	0.72	0.42	0.54	0.01	0.17
C	1.09	1.66	1.50	0.51	--	--	--
Organic Sulfur							
A	3.08	0.98	1.90	2.98	0.63	--	--
B	3.24	1.48	2.24	2.80	0.41	0.10	0.52
C	1.09	1.58	2.29	2.76	--	--	--
Total Sulfur							
A	4.36	3.30	3.77	3.72	1.13	--	--
B	4.44	3.27	3.68	3.59	1.00	0.14	0.87
C	4.53	3.41	3.90	3.55	--	--	--
D	4.13	3.35	3.53	3.54	1.13	0.19	0.80

A Data after Illinois Basin Coal Sample Program.
B MVTL Laboratories, Inc., Bismarck, ND (12/9/91).
C MVTL Laboratories, Inc., Bismarck, ND (9/21/90).
D EERC.

previous reports, they are included here again for the convenience of the interested reader. Most of the work in this period was carried out with IBC-101, some with IBC-102, and only selected tests with the remainder of the coals.

3.0 RESULTS

3.1 GC/AED as a Sulfur-Specific Analytical Technique

The analysis of extracts from SFEs of coal required an analytical technique that has demonstrated reliability in terms of accuracy and precision. The reliability of the GC/MS is well-known and needs no further comment. The performance of the GC/AED and its application in sulfur species determination have been described by Sullivan and Quimby (6) and Tillota and others (7). Besides being accurate and precise, this analytical system requires a small sample size and generates minimal waste and, therefore, was the technique of choice for the analyses of SF extracts.

A typical chromatogram of coal extract analyzed by GC/AED with sulfur and carbon channels detected at 181 and 193 nanometers (nm), respectively, is given in Figure 2. The absence of a corresponding carbon peak with the

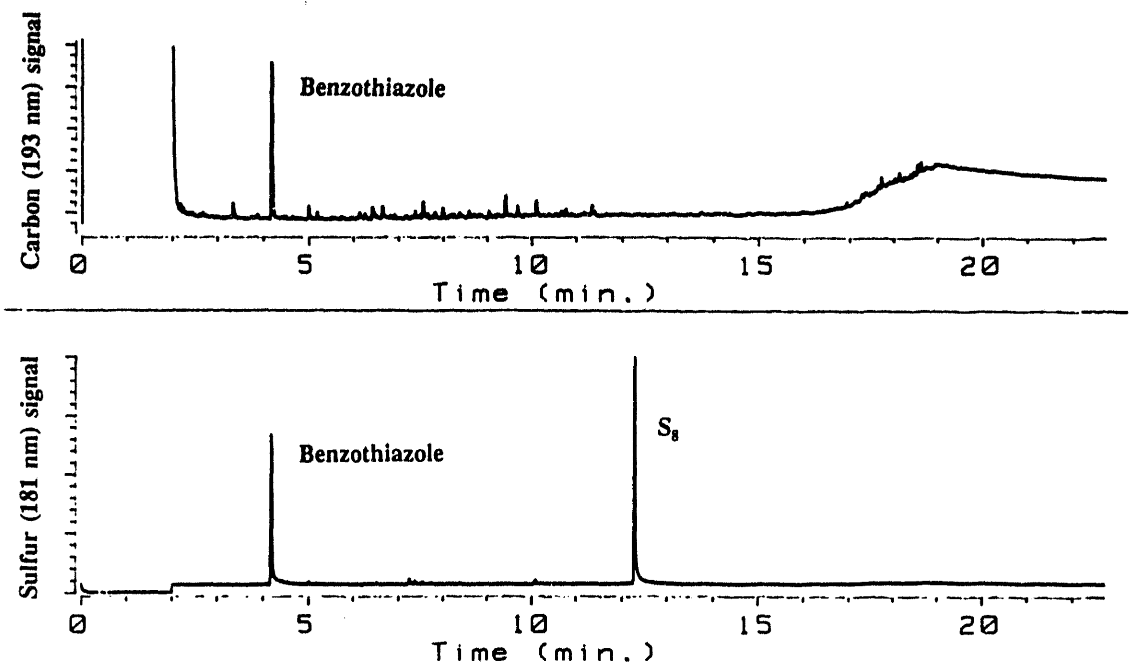


Figure 2. A typical GC/AED chromatogram of an SFE coal extract (IBC-101) showing the carbon (193 nm) and sulfur (181 nm) channels.

elemental sulfur detected indirectly confirmed, while GC/MS directly confirmed, the identity of the elemental sulfur peak. Elemental sulfur can be determined quantitatively by adding a known amount of internal standard, benzothiazole, to the coal extract prior to the GC/AED sulfur determination. Linear calibration curves of the GC/AED with elemental sulfur in toluene covering the concentration range between 10 to 1000 μg/mL were obtained. The correlation coefficient (R^2) of the calibration curve was 0.9992.

3.2 Efficiency of Extraction and Trapping of Elemental Sulfur

Elemental sulfur-spiked sea sand extractions and elemental sulfur extraction kinetics experiments reported earlier (8) indicated that elemental sulfur can be extracted and determined by using SFE followed by GC/AED analysis. Further investigation into aspects of removing elemental sulfur from the coal matrix was warranted in this suite of experiments in order to confirm that elemental sulfur can be extracted quantitatively from coal in its native form and no sulfur forms transformation occurred during the SFE step.

Elemental sulfur spike recovery experiments were performed with preextracted IBC-101 coal (-200 mesh) to assess the efficiencies of elemental sulfur removal and its subsequent trapping with toluene. Blank extractions of the preextracted coal matrix used in this spiking runs were carried out as a check, and no detectable amount of elemental sulfur was found.

Quadruplicate elemental spiking experiments were performed to determine the efficiency and reproducibility of the SFE and resulted in an average of 96% recoveries. The high percentage of elemental sulfur recoveries from these spiking experiments demonstrated that the SFE/GC/AED extract analysis technique is capable of quantitatively determining elemental sulfur from the coal matrix.

The sulfur extractions from preextracted coal also showed that elemental sulfur is not an artifact of the extraction process. It is unlikely that elemental sulfur was formed during the SFE since essentially all the spiked elemental sulfur was recovered and further blank extraction of the preextracted coal did not yield further elemental sulfur. Similarly, it is unlikely that additional sulfur is formed as the result of transformation of pyrite in coal to ferrous sulfide and elemental sulfur, since that reaction generally begins at 450° to 500°C (9), while the extractions were performed at only 110°C.

3.3 Elemental Sulfur in Illinois Bituminous Coals and Lignite Samples from Alaska and North Dakota

The method was further evaluated by extracting elemental sulfur from a suite of coal samples which included Beulah (North Dakota) and Alaskan lignite and IBC-101, IBC-102, IBC-106, IBC-107, and IBC-109 bituminous coals with SF 10% methanol/CO_2 at 110°C and 400 atm. The amounts of elemental sulfur in these selected coal samples determined by SFE/AED ranging from 2 to 3500 μg S_8/g(coal) are given in Table 3. Apart from the Alaskan lignite sample, the relative standard deviations (RSDs) associated with the elemental sulfur determinate are generally very good, demonstrating that SFE followed by GC/AED yields the precision necessary for an analytical method for extracting elemental sulfur from coal.

3.4 Interconversion of Sulfur Forms

Information regarding possible interconversion of sulfur forms is another important result of this study. With the sulfur forms data provided by the Illinois Basin Coal Sample Program (IBCSP) and analyses performed by MVTL Laboratories, Inc. (Table 2), together with the elemental sulfur values determined in a suite of coal samples (Table 3), some preliminary correlations relating sulfur forms in coal can be made.

3.5 Correlation Between Elemental Sulfur and Total Sulfur

Correlations were sought between weight percent elemental sulfur and weight percent total sulfur from data provided by IBCSP and MVTL for the suite of coals investigated. A similar comparison was done for Alaskan subbituminous and North Dakota lignite from data determined by MVTL. There were no apparent correlations between elemental sulfur and total sulfur in coal when using either the total sulfur results from either IBCSP or MVTL.

TABLE 3

Elemental Sulfur in a Suite of Coal Samples

Sample	$\mu g(S_8)/g(coal)^a$	%RSD
Alaska	2.0±0.3	13.9
Beulah	128±4	3.3
IBC-101	1100±60	5.7
IBC-102	3500±75	2.1
IBC-106	2000±32	1.6
IBC-107	490±23	4.6
IBC-109	26±1	5.0

[a] moisture-free basis

3.6 Correlation Between S_8 and Sulfatic Sulfur

No apparent correlation was found between elemental sulfur measured with SFE and the sulfatic sulfur value provided by IBCSP. However, the same elemental sulfur values correlate well with sulfatic sulfur value provided by MVTL. There are significant increases in sulfatic sulfur values of all the Illinois Basin Coal samples, as determined by MVTL, compared with values provided by the IBCSP. This is explained by coal sulfur oxidation that occurs during weathering and is consistent with one of the current coal sulfur oxidation mechanisms which suggests that sulfatic sulfur is one of the products formed when the pyritic sulfur in coal is oxidized. The magnitude of sulfatic sulfur increase is most noticeable with samples IBC-101, IBC-102, and IBC-106, where the weight percent increases are 0.62, 1.11, and 0.72 coal wt%, respectively.

3.7 Correlation Between Elemental Sulfur and Pyritic Sulfur

Elemental sulfur correlates well with pyritic sulfur values provided by IBCSP. The correlation between elemental sulfur and pyritic sulfur by using the MVTL values is not as good as the one using IBCSP values. Nevertheless, a nonlinear increase of elemental sulfur as a function of weight percent of pyritic sulfur in a coal pattern can be found in both correlation graphs. Apart from sample IBC-109, a noticeable reduction of pyritic sulfur values can be found with samples IBC-101, IBC-102, IBC-106, and IBC-107. This pyritic sulfur reduction not only is consistent with the current coal sulfur oxidation mechanisms, which suggests that pyritic sulfur is oxidized, the products being sulfatic and elemental sulfur, but also corresponds to the increase of sulfatic sulfur present in the coal samples as described above.

3.8 Correlation Between Elemental Sulfur and Organic Sulfur

There are no apparent correlations between elemental sulfur and the weight percent of organic sulfur of either the IBCSP or MVTL for the coal samples, suggesting that interconversion of organic to elemental sulfur is not a major pathway.

3.9 Correlation Between Pyritic and Sulfatic Sulfur

There is no obvious correlation shown between pyritic and sulfatic sulfur contents in a coal sample. However, the reduction of pyritic sulfur in a coal is accompanied by a corresponding increase in sulfatic sulfur. Samples IBC-101, IBC-106, and IBC-107 showed a reasonably linear correlation between the two sulfur forms. Samples IBC-102 and IBC-109, however, did not. The sulfatic sulfur value for sample IBC-102 appears to increase significantly more than the rest of the samples, while only a small increase in sulfatic sulfur value was found in sample IBC-109. The higher sulfatic value of sample IBC-102 may be explained by its high initial pyritic sulfur, some of which may have been already partially oxidized, though not completely, to sulfatic sulfur. The small increase seen in sample IBC-109 may be attributed to competition for oxygen between organic sulfur and pyritic sulfur resulting in loss of SO_x from the organic fraction rather than formation of sulfate.

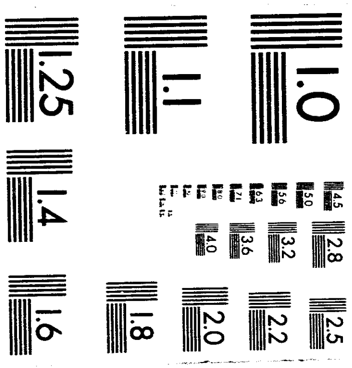
3.10 Effects of Coal Particle Size on SFE Kinetics

Particle-size distributions of coal sample IBC-101, ground to pass -60 mesh (250 μm), -100 mesh (149 μm), and -200 mesh (74 μm) for this study, were investigated by the Malvern particle-size test. The distribution pattern determined by the Malvern test appears to agree well with the expected pattern.

Coal samples IBC-101, IBC-102, IBC-106, IBC-107, Alaskan lignite, and North Dakota lignite were subjected to the Malvern particle-size test and found to have defined and consistent patterns.

Kinetics extractions of elemental sulfur from coal with 10% methanol/90% CO_2 at 110°C and 400 atm were performed with coal particle sizes ground to pass -60-, -100-, -200-mesh sizes. The cumulative amounts of S_8 extracted versus time normalized with elemental sulfur values obtained from five individual extractions on the three particle sizes (-60, -100, -200 mesh, ground under a stream of argon) of sample IBC-101 indicated that the two smallest coal particle sizes (-200 and -100) were slightly faster than the -60-mesh size. However, after 30 minutes of SFE, essentially all of the extractable elemental sulfur on the coal matrix was removed regardless of particle size. This suggests that the elemental sulfur extracted is likely to be at the surface of the coal particles. In addition, since no significant increase of elemental sulfur was extracted with the smallest coal particle size, the amount of elemental sulfur within the coal matrix is negligible.

Five individual 30-minute extractions of -200-, -100-, and -60-mesh IBC-101 by SFE with 10% methanol/CO_2 at 110°C and 400 atm were performed to determine the reproducibility of the SFE method to extract and quantify elemental sulfur. The RSDs of elemental sulfur determined in coal sample IBC-101 with particle sizes of -60, -100, and -200 mesh were 6.1, 3.4, and 5.7, respectively. There were essentially no significant differences in the amount of elemental sulfur extracted from the three particle sizes used, further demonstrating that the amount of elemental sulfur removal after 30 minutes of SFE is independent of coal particle size.


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3

5 of 5

3.11 Effect of High-Temperature Extraction on Acid-Extracted Coal

Supercritical fluid extraction (SFE) of organic sulfur from bituminous coal was studied using SF CO_2 to extract organic sulfur from a coal that had inorganic sulfur removed by the Riley method described above. Total sulfur analysis results of the acid-extracted residues before and after SFE are shown in Table 4. The sulfur extracted, calculated on acid-extracted coal basis, ranged from 38% to 47% in three experiments, indicating that the method enabled the removal of nearly one-third to one-half of the "true" organic sulfur. Periodic envelopes of true organosulfur compounds can be seen by overlaying the sulfur chromatograms. Individual compounds have not yet been identified.

TABLE 4

Effect of Supercritical CO_2 Extraction of Acid-Extracted IBC-101 at 450°C/400 atm

Sample	Sample Wt	Wt% Sulfur after SFE			
		As-Run	MF-Coal Basis	Removed	% Removed
EX-203	0.4683	1.77	1.28	1.12	46.8
EX-205	0.4673	2.01	1.45	0.95	39.5
EX-206	0.4471	2.08	1.50	0.90	37.6
		Wt% Sulfur Before SFE			
Raw Coal		4.36			
Acid-Extracted		2.40			

3.12 High-Temperature On-Line Extraction

On-line PYR/SFE/cryogenic trapping/GC with the mass spectrometer (MS) as a detector to analyze elemental sulfur-free IBC-101 reduced loss of sulfur compounds normally encountered in the solvent-trapping procedure, allowing the more volatile of the major gas chromatographable species to be identified. Total ion chromatograms showed all gas chromatographable components detected by the MS, resulting in many sulfur peaks buried under other organic compound peaks. AED chromatograms of non-sulfur-containing species were not seen on the sulfur chromatograms due to the different wavelengths monitored for each. Correlation of peaks in the sulfur chromatogram with those of the nonsulfur chromatogram showed which components are true organosulfur compounds. The AED information enables the sorting of peaks in the total ion chromatogram of the MS, which allows identification of individual sulfur compounds in the extract.

Sample IBC-101 bituminous coal was extracted with supercritical 10% methanol/CO_2 at 400 atm to remove elemental sulfur. Several fractions of the elemental sulfur-free IBC-101 were then extracted using the on-line method. Selected ion-current chromatograms showed the C_1-C_5 thiophenes, which make up a large portion of the volatile species.

Several additional sulfur compounds along with benzene, phenol, toluene, indan, indene, and other polynuclear aromatics, were also identified. Again the thiophenes were identified, but ethylene sulfide, benzo[b]thiophene, dibenzothiophene, and thianthrene were prominent in the chromatogram.

3.13 Effect of Chemical Reactants on SFE of Sulfur

Methods of removal of sulfur tested included SFEs of IBC-101 under mild pyrolysis conditions with and without the presence of chemical reagents. Dynamic extractions with supercritical CO_2 at 400 atm and 450°C in the absence of chemical reactant were successful in removing nearly 50 wt% of the sulfur from the coal, while supercritical 10% methanol/CO_2 extraction under the same conditions was successful in removing nearly 60 wt% of the sulfur from the coal. Supercritical fluid extractions (SFE) of IBC-101 containing 50 wt% added NaOH at the same conditions as above resulted in sulfur removals of slightly more than 50 wt% for each of the fluids. Dynamic SFE of 50 mg of IBC-101 spiked with 200 μL of 85% H_3PO_4 under the same conditions as the above resulted in >60 wt% sulfur reduction when extracted with 10% methanol/CO_2 and 85 wt% reduction of sulfur when extracted with CO_2. H_3PO_4 solubility in SF 10% methanol/CO_2 was greater than in SF CO_2, as evidenced by the amount of H_3PO_4 in the extract. Therefore, the residence time of the acid in the reaction cell during a dynamic extraction was significantly shorter in the 10% methanol/CO_2 extraction, allowing for shorter reaction time and accounting for reduced sulfur removal.

Extraction of coal with supercritical water has several attractive aspects. Included in the list of attractive features are the environmental acceptability of water, the polar nature (though not near the polarity of the liquid) of water as a SF with respect to other commonly used fluids, the variety of modifiers available for use with water, the specific heat capacity of SF water, and the cost of the water. At the test conditions of the initial supercritical water extraction of IBC-101, >50% by weight of the sulfur as measured on an absolute scale was extracted. Additional extractions and extraction strategies with SF water are planned.

3.14 Sample Preparation for Stable Sulfur Isotope Experiments and Background Information Related to This Work

The results of sulfur forms analyses shown in Table 2 indicate that sulfatic sulfur increases on prolonged (>6 months) exposure to air. The pathway followed by the sulfur seems to be by way of pyritic sulfur oxidation, as also indicated by Table 2. A method of investigating the pathway has been designed using a coal (IBC-107) that has a natural sulfur probe, i.e., unusually high levels of stable ^{34}S isotope, and is described below. The original coal and the residue of IBC-107 from the Riley acid extraction, with the high $^{34}S/^{32}S$, are excellent candidates for testing the potential for organic and pyritic sulfur conversion to elemental sulfur.

Coal IBC-107 was selected for stable sulfur isotope analysis because of the large isotopic difference of ~22 $^{\circ}/_{\circ\circ}$ between pyritic and organic sulfur (10). Because of this large isotopic difference, sulfur isotopic determination on the elemental sulfur obtained selectively by SFE may be applied to resolve the source of elemental sulfur in coal. Initially, two portions of ~4.5 g of IBC-107 (-200-mesh size) coal were extracted with SF 10%

methanol in CO_2 in a 10-mL Keystone extraction cell fitted with a stainless steel restrictor for 2 hours. An additional 15-minute extraction was performed during which no elemental sulfur was extracted as determined by GC/AED. The large coal sample sizes extracted were necessary in order to obtain a sufficient quantity (~4 mg) of elemental sulfur for isotopic determination. About half of the SF extracted coal was extracted with nitric acid (11) to collect the pyritic and sulfatic sulfur from the coal. Another portion of the SF extracted coal was extracted by the Canfield technique (12) to obtain the pyritic sulfur in coal. Stable sulfur isotope determinations were performed on the seven coal extracts and residues by an experienced research group headed by Professor Simon Bottrell in Leeds, UK, using an established procedure with stable sulfur isotope MS. In addition, total sulfur determination on all of the five solid residues were carried out. Data from the stable isotope determinations coupled with the total sulfur values of the five solid residues and original coal samples provided information regarding sulfur forms transformation mechanisms in the coal matrix which should lead back to the original source of elemental sulfur in coal. Table 5 shows the data obtained from the stable sulfur isotope analyses.

The analytical values for organic sulfur in the residues following Riley and Canfield extractions were identical within the precision of the isotope measurement. The analyses of the inorganic sulfur fraction collected during each of the extractions are not the same, but the difference is easily explained. Whereas the Canfield method liberates sulfur as H_2S exclusively from metallic sulfides, the Riley method oxidizes metallic sulfides to sulfates which cannot be separated from inherent sulfate. The Canfield method, then, gives what is expected to be a more accurate estimate of pyritic sulfur by measuring the isotope ratio in the liberated H_2S, while the inorganic sulfur in the Riley extract is determined from the total sulfate (sulfate and oxidized pyritic sulfur). In samples with low sulfate, the latter measurement fairly represents the pyritic sulfur, whereas in samples with high sulfate levels the sulfur in the Riley extract is interpreted as inorganic, but not exclusively pyritic sulfur.

Table 5 shows that the Riley acid extraction and the Canfield extraction separate the coal sulfur into fractions having nearly identical organic $^{34}S/^{32}S$ isotope ratios. The organic, pyritic, and total sulfur ratios compare favorably with those of other researchers (13). Interpretation of the data shown in Table 3 suggests that the elemental sulfur (PL-2) is related to the inorganic sulfur, but is inconclusive as to whether the relationship is exclusive; i.e., the argument can also be made that both inorganic <u>and</u> organic sulfur contribute to the formation of elemental sulfur.

To expand on the above findings, two additional coals, IBC-102 and IBC-106, were prepared for sulfur stable isotope analysis. The preparation included SFE to collect the elemental sulfur from the coal and Riley extraction to remove inorganic sulfur from the SF extracted residue. The Canfield extraction was carried out on the SF extracted residue at the Stable Isotope Laboratory. These samples, along with raw coal, were sent to the Stable Isotope Analysis group in Leeds, UK, for analysis.

TABLE 5

Sulfur Isotopic Composition of Fractions Obtained from IBC-107

Sample	Preparation	$\delta^{34}S°/_{oo\ CDT}$	Error (%)
PL-1	Parr bomb oxidation of total coal	+6.5	±0.2
PL-2	Parr bomb oxidation of S_8 in SF extract collected in toluene	+13.4	±0.2
PL-3x	Pyrite sulfur extracted from PL-3 by acidic chromous chloride. (Canfield method)	+26.4	±0.4
PL-3r	Organic S (residue from Canfield extraction) by Parr bomb oxidation	+1.6	±0.2
PL-4	Inorganic S in Riley* extract of PL-3	+12.1	±0.2
PL-5	Organic S (residue from Riley extraction) by Parr bomb oxidation	+1.5	±0.2

*Boiling 2N HNO_3 for 30 minutes.

3.15 Comparison of Forms of Sulfur Determined by Different Laboratories

Table 2 contains sulfur forms analysis results obtained from different laboratories. These values were obtained to represent the results of more conventional analyses in evaluating the SFE method and in the preliminary formulation of a mechanism to explain the occurrence of elemental sulfur in coal.

TABLE 6

Elemental Sulfur in Illinois Bituminous Coal Sample IBC-101

Extraction Method	Analytical Method	Sulfur, wt%	References
Soxhlet	GC/Hall Detector	0.07	Duran and others, 1985 (14)
SFE	GC/AED	0.11	This work
Batch/PCE[a]	GC/MS	0.23	Narayan and others, 1988 (16)
Soxhlet	GC/MS	0.10	Stock and Wolny, 1990 (15)
Soxhlet	HPLC/Spectroscopic	0.03	Buchanan and others, 1989 (17)
	Bacteriological	0.02	Schicho and others, 1988 (18)

[a] Perchloroethylene extraction.

3.16 Comparison of Elemental Sulfur Value Obtained by SFE and Other Existing Techniques

Elemental sulfur values of the IBC-101, -200-mesh size sample, together with the literature values, are given in Table 6 for comparison. There is good agreement of our data with Duran and others (14) and with Stock and Wolny (15). An original value of 1.54% elemental sulfur in the IBC-101 coal was provided by Narayan (16). However, further work performed by Narayan (15,16) has led to the realization that results from the wrong coal sample may have inadvertently been reported, and a revised value of 0.23% was subsequently reported by Stock and Wolny (15), although it is unclear to the authors of this paper as to how this number was determined.

4.0 CONCLUSIONS

Pyrolysis of medium- to high-sulfur bituminous coals under inert (argon) gas up to 800°C removes an amount of sulfur approximately equivalent to the pyritic sulfur in the coal. Similar results are obtained when heating the coal in reducing atmospheres, such as hydrogen gas or syngas (H_2/CO). The true organic sulfur is not easily removed by thermal means at ambient conditions. The ASTM sulfur forms method calls for direct measurement of total sulfur and sulfatic sulfur directly. However, the larger fractions of sulfur, i.e., pyritic and organic sulfur, are measured indirectly. Since the chemistries of reaction of these two fractions are substantially different, the design of a method for removal of sulfur from coal is very difficult if error is made in categorizing sulfur forms. ASTM organic sulfur consists of true organic, elemental sulfur, and other acid-insoluble sulfur species. Therefore, a forms method that directly measures additional classes of sulfur compounds is needed. Elemental sulfur can be determined by SFE using 10% methanol/CO_2 at 110°C and 400 atm and analysis by GC/AED. Sulfatic sulfur can be determined by a gravimetric method. Canfield acid extraction removes pyritic sulfur, allowing the determination of true organic sulfur by sulfur analysis of the Canfield residue. Direct analysis of Canfield extract gives pyritic sulfur. Water, at supercritical conditions, removed up to 85% of the sulfur when extracting coal spiked with H_3PO_4.

5.0 RECOMMENDATIONS

1. SFE techniques—such as the elemental sulfur method developed in this project—are rapid, reliable, and reproducible with a relative standard deviation (RSD) of ± 5%, and generate minimal waste. SFE with and without chemical reagents to differentiate and remove other sulfur forms, particularly organic, from coal should continue to be investigated.

2. Supercritical water has shown promise in removing sulfur from coal. Additional extractions of coal with SF water with and without reagents should be investigated.

3. Confirmation of forms analyses as they are developed is needed. Stable sulfur isotope analyses of fractions of IBC-101, IBC-102 and

IBC-106 should be completed to determine whether this technique has such potential.

4. Investigation of sulfate sulfur by HCl extractions under several conditions and comparison of ASTM sulfate value with that of Canfield extraction.

6.0 PRESENTATIONS AND PUBLICATIONS

Eckert-Tilotta, S.E.; Hawthorne, S.B.; Miller, D.J. "Comparison of Commercially Available Atomic Emission and Chemiluminescence Detectors for Sulfur-Selective Gas Chromatographic Detection," *J. Chrom.* **1992**, *591*, 313-323.

Timpe, R.C.; Louie, P.K.K.; Miller, D.J.; Hawthorne, S.B. "Determination of Organic Sulfur Species in Coal by Supercritical Fluid Extraction," Pittsburgh Coal Conference, Oct. 1991.

Louie, P.K.K.; Timpe, R.C.; Hawthorne, S.B.; Miller, D.J. "Determination of Elemental Sulfur in Coal by Supercritical Fluid Extraction (SFE) and Gas Chromatography with Atomic Emission Detection (GC/AED)," *Fuel*, in press.

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