6.0 GASIFICATION RESEARCH

6.1 Production of Hydrogen and By-Products from Coals

PRODUCTION OF HYDROGEN AND BY-PRODUCTS FROM COAL

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PRODUCTION OF HYDROGEN AND BY-PRODUCTS FROM COAL

1.0 INTRODUCTION

Coal gasification products consist of char solids, condensables, and gases. A flexible processing system that allows variation of products to meet market demand would substantially improve the marketability of coal. Such a processing system could integrate catalytic gasification and mild gasification (MG) of coal. Operating temperatures range from 500° to 800°C, at nominally atmospheric pressure. A hybrid system based on these two technologies should have the flexibility to optimize production of one, two, or all three of the products depending upon market demand.

A flexible system should have a single reactor capable of maximizing the yield of any product, depending on the markets. Fixed-bed gasification is limited by heat and mass transfer for the endothermic steam gasification reaction for hydrogen and syngas production. An entrained-bed system presents difficulties in maintaining sufficient solids residence times without extensive recycle. A fluidized-bed system offers excellent heat and mass transfer and significant flexibility of operating conditions with uniform temperature and solids distributions. The smaller particles in a fluidized-bed system result in less diffusional resistance than in a fixed-bed system, more efficient waste heat recovery, and smaller pressure drops. Tests at the University of North Dakota Energy and Environmental Research Center (EERC) have demonstrated that coal devolatilization, gasification, and ash removal can be done within a single vessel using a fluidized-bed system.

The two most important considerations for producing hydrogen from coal in a single reactor are to maintain operating conditions that favor the production of hydrogen and carbon dioxide over methane and carbon monoxide, and to obtain reaction rates that result in sufficient gasifier throughput. Optimization of the product gas hydrogen content requires steam gasification at 700° to 800°C and atmospheric pressure. Low-rank coals are the preferred feedstock because of lower mining cost and higher reactivity than higher-rank coals. Reactivity is higher because of higher concentrations of active sites, higher porosity, and a more uniform dispersion of alkali impurities that act as inherent catalysts. Reactivity can also be increased by increasing the temperature within the range that maximizes hydrogen production and with the addition of a catalyst. Although reactivity increases with temperature and catalyst addition, the hydrogen content of the product gas was shown by previous work to be relatively constant with those changes (1). Catalysis of a bituminous coal char with loadings of alkali carbonates similar to those of the low-rank coals also increased reactivity. However, catalyzed bituminous coal char was found to be five to six times less reactive than similarly catalyzed lignites. Operating the gasifier at pressure, as recommended in the preliminary economic assessment by Black and Veatch Engineers-Architects, would change the product distribution.

A high-hydrogen gas, from 45% to 50%, has been produced at EERC on a pilot scale with low-rank coals. Although the production of high-hydrogen gas from a single reactor has been demonstrated, further processing of the gas is required to remove contaminants: fine particulates and sulfur compounds (H_2S and COS), as well as other product gas constituents. Classification as a contaminant depends on the end-use application of the product gas.

Solid products of the MG process demonstrated at EERC have shown promise in areas not related to energy. One possible product is activated carbon, which is widely used in large quantities for removal of trace organics from secondary effluents. Sometimes more than 50% of the cost of wastewater treatment is attributed to the cost of makeup carbon. Activated carbon has also shown potential as a catalyst support (below 425°C).

Condensables produced by MG may be directly fired or blended with petroleum-derived fuels or solid coal. These fuels have potential uses in gas turbines, aviation jet engines, diesel engines, and as chemical precursors. These do not match existing specifications for No. 2 diesel fuel, but research has demonstrated that off-specification fuels can perform adequately in diesel engines and turbines. These products have characteristics not available from petroleum. For example, the aromatic nature of coal makes it a source of high-density fuel. Incorporating a primary separation scheme with the quench step to selectively remove certain desired fractions of condensables may provide an economic advantage in their further upgrading for chemical production.

Coal gasification at mild conditions of 500° to 800°C and atmospheric pressure has the potential to produce hydrogen, syngas, methanol, and other products, as well as a variety of by-products, including condensable liquids and low volatile-content char. In the temperature range of 500° to 700°C, hydrogen production proceeds quite slowly, while coal liquids (petroleum substitutes) and char (coke and activated carbon) are the predominate products. Production of hydrogen becomes technically feasible in the range of 700° to 800°C, where cracking of hydrocarbons and gasification of char carbon occur at an appreciable rate. The different product slates determine the difference between MG and hydrogen production.

2.0 GOALS AND OBJECTIVES

The objective of this research is to determine the optimum conditions for production of a gas stream enriched in hydrogen, and the preferred conditions for production of by-products. Technology previously developed at EERC which involves catalytic steam gasification of coal will be utilized. Development of gas cleanup and separation process schemes will be necessary for utilization of hydrogen produced for methanol synthesis and fuel for a closely coupled fuel cell. To better understand the catalytic steam gasification process, bench-scale work will be done to determine the kinetics of catalysis, identification of components of pyrolysis and coal-steam reaction streams, and feed coal characterization.

3.0 ACCOMPLISHMENTS

3.1 Hydrogen-From-Coal CPU

The fluidized-bed gasifier continuous process unit (CPU) used for production of hydrogen from low-rank coals has been incorporated into the 100 lb/hr MG process development unit (PDU). While the CPU can still function as it has in the past, it will also function as the calciner for the PDU. (See "Area 400" of the flowsheet that is Figure 1.) Shakedown of the carbonization portion of the PDU has begun. Piping and programming are not yet completed to allow operation of the CPU either autonomously or as the calciner of the PDU.

As part of the integration process, the level of automation of the CPU has been significantly increased. Data acquisition by computer has been expanded. Process parameters, such as oxygen and steam feed rates, will now be controlled by computer rather than by manual adjustment of controllers. Control of process parameters by computer will provide faster and more accurate responses, which should improve the operability of the CPU.

Incorporation of the CPU with the MG PDU will also allow the use of a broader range of controllable process parameters as future project needs for continuous hydrogen production are established. The moisture and/or volatile content of the coal fed to the CPU can now be controlled. Improved control of the natural gas fired preheater will allow its use as an additional source of heat.

The quench train for the CPU has been moved and expanded in capacity to permit continuous on-line operation. The cryogenic trap has been redesigned to increase the removal of condensable materials exiting the quench train. The expected increase in collection of condensable materials will increase the life of the gas meter measuring product gas flow and improve the material balance.

3.2 Catalyst Studies

Three coals were used to examine rank dependence on catalysis of the char-steam gasification reaction. Velva lignite, Wyodak subbituminous coal, and Indiana bituminous coal were chosen to represent the three coal ranks. The proximate and ultimate analyses of these coals are listed in Table 1.

3.2.1 Calcium Catalysis

Limestone has been shown to be effective in catalyzing the steam gasification of low-rank coal (2). The catalytic effect of the calcium rich mineral is noted with admixed coal and limestone, and when raw coal is gasified with limestone present as gasifier bed material. The mechanism by which the coal char-steam reaction is promoted with catalyst still needs clarification. The role of the calcium-associated anion, if any, in promoting the reaction is unknown and is part of this study. Four calcium compounds are being tested as part of this work. Natural limestone, primarily $CaCO_3$, was selected for the base case on the basis of results observed in the CPU. Calcium oxide, which is calcined calcium carbonate and reacts with water to

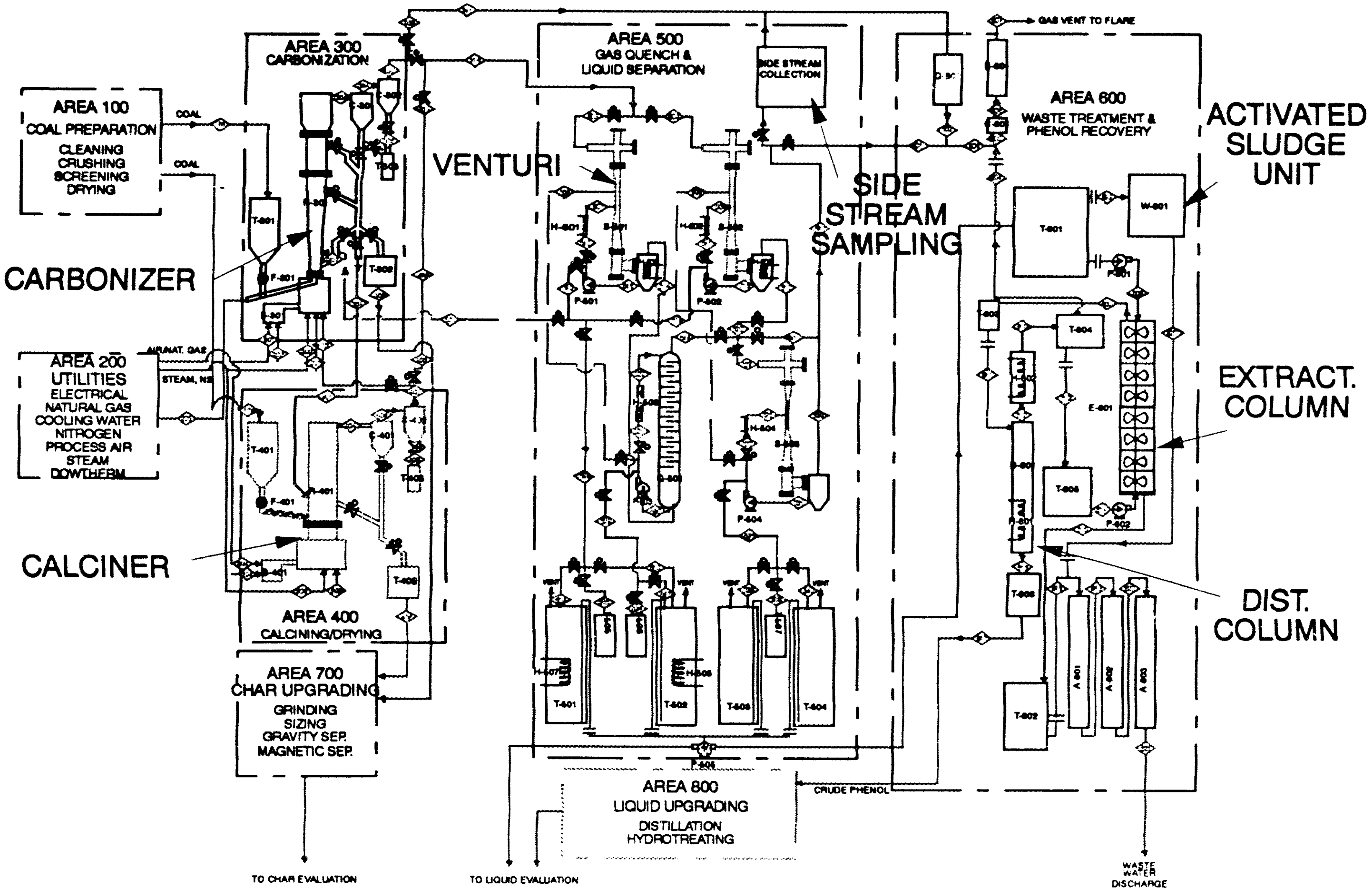

Figure 1. Flowsheet for EERC 100-lb/hr mild gasification process development unit (Area 400 -- hydrogen production CPU/mild gasification calciner).

TABLE 1

PROXIMATE AND ULTIMATE ANALYSES OF VELVA, WYODAK AND INDIANA COALS

	Velva	Wyodak	Indiana
Proximate Analysis, wt%			
Moisture	36.30	32.91	13.50
Volatile Matter, mf	47.36	44.74	41.25
Fixed Carbon, mf	45.70	46.21	46.31
Ash, mf	6.94	9.05	12.09
Ultimate Analysis, mf, wt%			
Hydrogen	4.31	4.89	5.16
Carbon	65.49	66.09	67.99
Nitrogen	0.97	0.99	1.32
Sulfur	0.22	0.39	4.86
Oxygen (Diff)	22.06	18.57	8.58

give $Ca(OH)_2$, was the second catalyst selected. Calcium sulfate, refractory at the conditions of the tests, was the third catalytic agent chosen. Calcium acetate, which initially is water soluble (thus facilitating its dispersion) and decomposes during the heat-up was the fourth catalyst to be tested.

Sodium and potassium, although excellent catalysts for the gasification reaction, were not included because the economics of using expensive potassium catalysts are unfavorable, and sodium causes agglomeration. Calcium oxide (CaO), calcium sulfate ($CaSO_4$), calcium acetate ($Ca(C_2H_3O_2)_2$), and limestone (primarily $CaCO_3$) were admixed with the coals in a coal-to-catalyst ratio of 90:10 by weight. This ratio resulted in 7.1 wt%, 2.8 wt%, 2.5 wt%, and 4.0 wt% calcium as catalyst with calcium oxide, calcium sulfate, calcium acetate and limestone, respectively. Additional tests were conducted with calcium oxide at a ratio of 96:4 (Ca = 2.8 wt%). Catalyzed char-steam gasification was carried out in an oxygen-free, argon-steam atmosphere at 973K, 1023K, and 1073K and ambient pressure on Thermogravimetric Analysis (TGA) equipment. Figures 2, 3, 4, and 5 indicate differences in the rate of Wyodak carbon gasification and in the effect of the catalysts at the various temperatures. Similar results were obtained for the Velva and Indiana char reactions.

Although calcium functions as the catalyst, it is apparent that the anion plays an important role in the catalysis as well. Calcium catalysis as a function of anion effects on coal char gasification was studied by focusing on the reactivities and surface chemistry of each of the coal chars. The reactions of the uncatalyzed and catalyzed chars with steam were carried out in the usual manner (1) and gave the results shown in Tables 2, 3, and 4. The tables show catalysts, reaction temperatures, reactivities (k), energies of

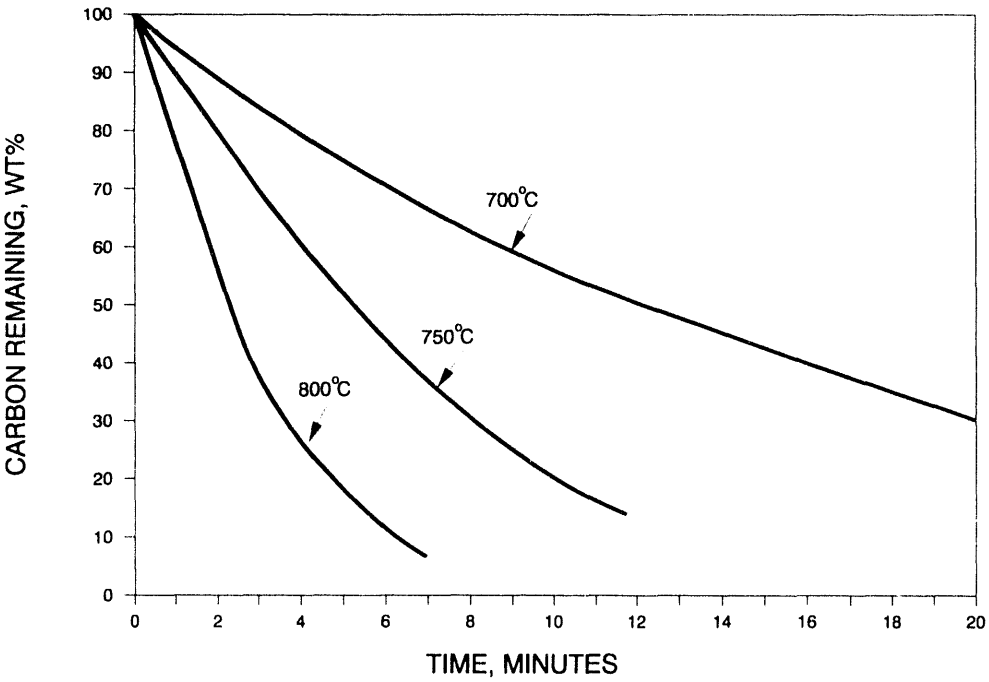

Figure 2. Wt% carbon remaining vs. time for the 10% wt calcium oxide-catalyzed Wyodak char-steam reaction at 700°, 750°, and 800°C.

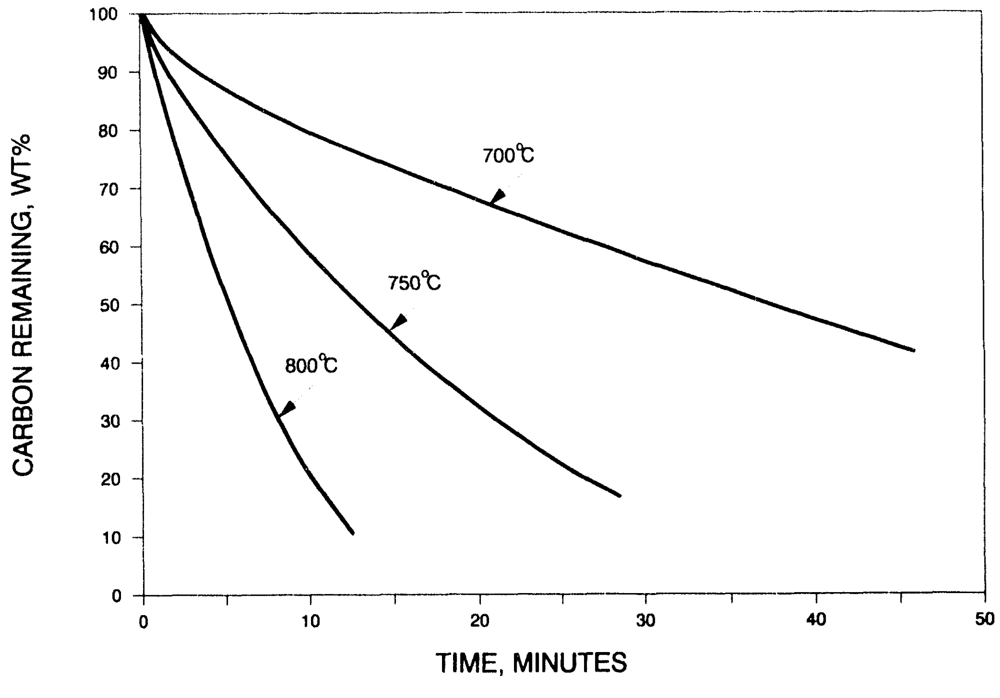

Figure 3. Wt% carbon remaining vs. time for the 10 wt% calcium sulfate-catalyzed Wyodak char-steam reaction at 700°, 750°, and 800°C.

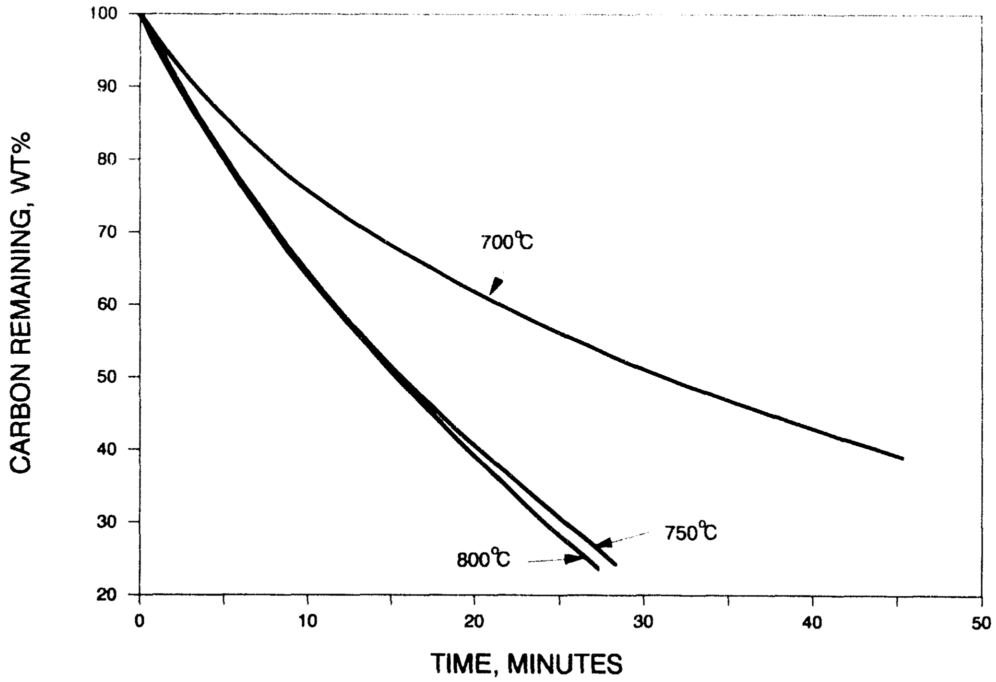

Figure 4. Wt% carbon remaining vs. time for the 10 wt% calcium carbonate (limestone) -catalyzed Wyodak char-steam reaction at 700°, 750°, and 800°C.

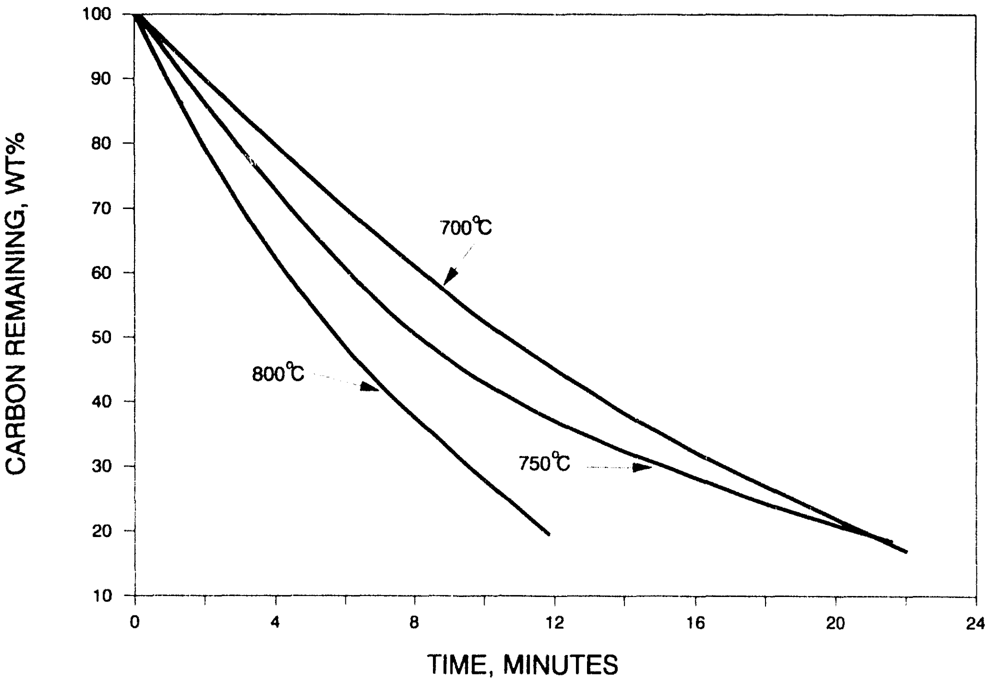

Figure 5. Wt% carbon remaining vs. time for the 10 wt% calcium acetate-catalyzed Wyodak char-steam reaction at 700°, 750°, and 800°C.

activation (E_a), and pre-exponential factors (A) for the reactions. E_a and A are calculated from the plot of ln k vs 1/T according to the Arrhenius relationship:

$$k = Ae^{-E_a/RT}$$

The reaction order for the uncatalyzed char-steam reaction at 1023K, the intermediate temperature, was calculated using the differential method (plot of Log (-dC/dt) vs. Log C), and was determined to be approximately first order for the low rank coals and second order for the bituminous coals used in this study. However, the kinetics of the catalyzed reactions were not necessarily of the same order as the uncatalyzed reactions. Thus, the reactivities shown in Tables 2, 3, and 4 were obtained from calculations based on order determined using the differential plot method from:

$$-\frac{dC}{dt} = kC^n$$

for order, n, with respect to carbon content, C, where k is the specific rate constant and t is the time in hours. The following are specific solutions of the above equation. The term C_0 denotes the original carbon concentration.

n	Rate Equation
0.5	$k = 2/t\ (C_0^{1/2} - C^{1/2})$
1	$k = (1/t)\ \ln\ ((C_0-C)\ /\ C)$
2	$k = (1/t)\ ((C_0-C)\ /\ (C(C_0-C)))$

Table 2 shows that the effective catalysis of the Velva lignite char-steam reaction occurs at a temperature >973K (700°C). The rate enhancement due to the calcium oxide is two to three times at each temperature while that of the calcium sulfate is only two times and occurs only at the highest temperature, indicating the effect of the composition of the additive on reactivity of the coal (3).

Table 3 shows the comparison of the reactivities of reactions carried out with the four catalysts with Wyodak coal. The average reactivity parameters (k) for each of the three temperatures with each of the four catalysts are shown. The apparent energies of activation and pre-exponential factors calculated from the Arrhenius plot of ln k vs 1/T are given, along with the correlation coefficients for the Arrhenius curve. Calcium acetate increased

TABLE 2

REACTIVITIES, ARRHENIUS ENERGIES OF ACTIVATION, AND PRE-EXPONENTIAL COEFFICIENTS FOR CALCIUM-CATALYZED VELVA CHAR-STEAM REACTIONS

	Reactivity, k (g/hr/g)				
	CaO		$CaSO_4$	Limestone	$Ca(Ac)_2$
Wt% Catalyst	10.0	4.0*	10.0	10.0	10.0
Wt% Calcium	7.1	2.8	2.9	4.0	2.5
Temp, K					
973	3.06	5.21	2.27	2.83	3.51
1023	9.20	10.60	4.93	8.66	7.51
1073	10.21	18.92	13.06	8.65	8.13
E_a, kcal/mol	25.38	25.78	36.86	29.33	17.05
A, hr^{-1}	8.22E6	5.45E6	4.03E8	1.03E7	2.69E4
r^2	0.91	1.00	1.00	0.88	0.92

* Based on one experiment at each temperature rather than two.

TABLE 3

REACTIVITIES, ARRHENIUS ENERGIES OF ACTIVATION, AND PRE-EXPONENTIAL COEFFICIENTS FOR RAW AND CALCIUM-CATALYZED WYODAK CHAR-STEAM REACTIONS

	Reactivity, k (g/hr/g)				
	Raw Coal	CaO	$CaSO_4$	Limestone	$Ca(Ac)_2$
Temp, K					
973	1.33	3.60	1.30	1.74	4.20
1023	3.28	7.92	3.04	3.33	6.18
1073	7.33	17.68	9.22	3.08	8.10
E_a, kcal/mol	35.45	33.00	40.50	12.10	13.70
A, hr^{-1}	1.20E8	9.20E7	1.53E9	1.03E3	4.99E3
r^2	0.91	1.00	1.00	0.88	0.92

TABLE 4

REACTIVITIES, ARRHENIUS ENERGIES OF ACTIVATION, AND PRE-EXPONENTIAL COEFFICIENTS FOR RAW AND CALCIUM-CATALYZED INDIANA STEAM GASIFICATION

	Reactivity, k (g/hr/g)				
	Raw Coal	CaO	$CaSO_4$	Limestone	$Ca(Ac)_2$
Temp, K					
973	0.18	0.21	0.17	0.18	0.36
1023	0.16	0.58	0.32	0.48	0.66
1073	0.31	1.26	1.17	1.17	1.53
E_a, kcal/mol	11.01	37.26	39.76	38.80	29.91
A, hr^{-1}	4.70E1	4.94E7	1.29E8	9.35E7	1.80E6

the reactivity two-fold at the lower two reaction temperatures but showed no effect at 1073K, which may or may not be principally due to diffusion limitations. Calcium oxide exhibited greater than two-fold enhancement of reaction rate at the two higher reaction temperatures, whereas calcium sulfate showed slight enhancement at the highest temperature only and limestone showed no catalysis for this suite of tests. The reactivities of the limestone-catalyzed reactions at the lower temperatures were nearly the same as those from the CPU, but differ at the highest temperature, reflecting operational differences between the two reactor types.

Table 4 shows that calcium sulfate, limestone and calcium oxide were ineffective as catalysts on Indiana char-steam reaction at 973K. The effective catalysis of this char-steam reaction occurs at a temperature >973K (700°C) for the three mentioned catalysts. The calcium sulfate doubled the rate of reaction over that of the raw coal, whereas the limestone tripled the rate and the calcium oxide nearly quadrupled it at 1023K. A four-fold increase in reactivity was noted for these three catalysts at 1073K. The calcium acetate, however, catalyzes the reaction over the entire temperature range. The reactivity is increased two times over that of the uncatalyzed reaction at the lower temperature, and five times at the higher temperature. In the temperature range 1023-1073K, the latter catalyst increases the reactivity by factors of four to five as compared with the increase of two to four times for the calcium sulfate and limestone catalyzed reactions.

Increased carbon reaction rate, however, is not the only consideration in the study of catalyzed reactions. Product quality and rate of production of hydrogen gas may also be affected by the added catalyst. Previous tests indicated that catalyst addition with a low-rank coal had the effect on liquid quality of altering proportions of liquid components such as benzene, phenol, catechol and related compounds, and therefore required further investigation (3).

3.2.2 Trona-Taconite Catalysis

A catalyst consisting of 20 wt% trona and 80% taconite was prepared by admixing the two components and heating to 800°C for 30 minutes. The agglomerated mass was crushed and mixed dry with the feed coal on a 90:10 coal-to-trona-taconite weight basis.

Gasification tests with the TGA were carried out on trona-taconite catalyzed Wyodak char-steam reactions. The results are shown in Table 5. The reaction order with respect to carbon was determined by the differential method to be first order in carbon at 1023K.

Gasification tests were also carried out on trona-taconite catalyzed Velva char-steam reactions. Again, the reaction order was determined by the differential method. The specific rate constants are shown for half, first, and second order along with the corresponding correlation coefficient for Log (-dC/dt) vs. Log C for each at all three temperatures. The results of this suite of experiments are shown in Table 6. Although the correlations are quite good for each of the orders, a comparison of r^2 clearly indicates that the reaction is not second order. Half order correlations are slightly better than first order correlations, indicating that the best estimate of order for trona-taconite catalyzed steam gasification of Velva lignite char is half order with respect to carbon.

3.3 Char Characterization

3.3.1 Surface Analysis

Wyodak subbituminous coal containing each of the four calcium compounds and carbonized at 1023K showed uniform dispersion of the calcium in only the char containing the calcium acetate. The calcium map of the surface of a char particle showed the calcium from calcium acetate to be dispersed uniformly over the entire surface. The other three calcium additives lacked uniform dispersion and were seen as discrete particles on the surface. The char containing the calcium acetate additive also showed signs of softening on the surface, whereas the others did not. This indicates the fluid disposition of the calcium acetate additive at elevated temperatures which contributes to the higher reactivity of the char in which it was present.

TABLE 5

REACTIVITIES, ARRHENIUS ENERGY OF ACTIVATION, AND PREEXPONENTIAL COEFFICIENT FOR TRONA-TACONITE CATALYZED WYODAK STEAM GASIFICATION

Temp, k	k, hr^{-1}
973	1.00
1023	3.33
1073	7.65
E_a,kcal/mole	42.09
A,hr^{-1}	3.00E9

TABLE 6

RATE CONSTANTS, CORRELATION COEFFICIENTS FOR DIFFERENTIAL PLOTS TO DETERMINE REACTION ORDER, ARRHENIUS ENERGY OF ACTIVATION, AND PREEXPONENTIAL COEFFICIENT FOR TRONA-TACONITE CATALYZED VELVA CHAR STEAM GASIFICATION

	1/2 Order		1st Order		2nd Order	
Temp, k	k*	r^2**	k	r^2	k	r^2
973	3.13	1.000	3.56	0.999	4.67	0.990
1023	7.22	0.887	8.46	0.994	11.84	0.972
1073	13.63	1.000	16.15	0.997	23.13	0.979
E^a,kcal/mole	30.56	0.999	31.42	0.997	33.25	0.996
A,hr^{-1}	2.34E7		4.16E7		1.41E8	

*k = Reactivity (rate constants)
**r^2 = Correlation Coefficient

X-ray diffraction (XRD) and scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS) of the trona-taconite catalyst was carried out on a ground (-60 mesh) sample. Spectra showed presence of quartz (SiO_2) as the major phase and magnetite (Fe_3O_4) as the only minor phase. No other crystalline minerals were detected by XRD. This was somewhat surprising in that no sodium-containing mineral was found even though there had been 20 wt% trona mixed with the taconite prior to heating to 800°C under argon to react the two minerals. Even more surprising was the failure of SEM-EDS to detect sodium. SEM photos are shown in Figure 6. Some evidence of sodium carbonate (trona) fluxing is seen. Although the measured temperature was below the vaporization point for sodium or its compounds, it appears that sodium was lost by that mechanism.

The order of the reaction with respect to carbon as determined from a plot of Log -dC/dt vs Log dC (Figure 7 shows an example of this method) was found to approximate unity for the Wyodak coal char-steam reaction (Table 7), whereas the reaction in the presence of limestone additive was found to be nearer 0.5. Tables 8, 9, 10, and 11 show the order and the reactivity, k, as calculated for first, one-half, and zeroth order limestone-catalyzed carbon

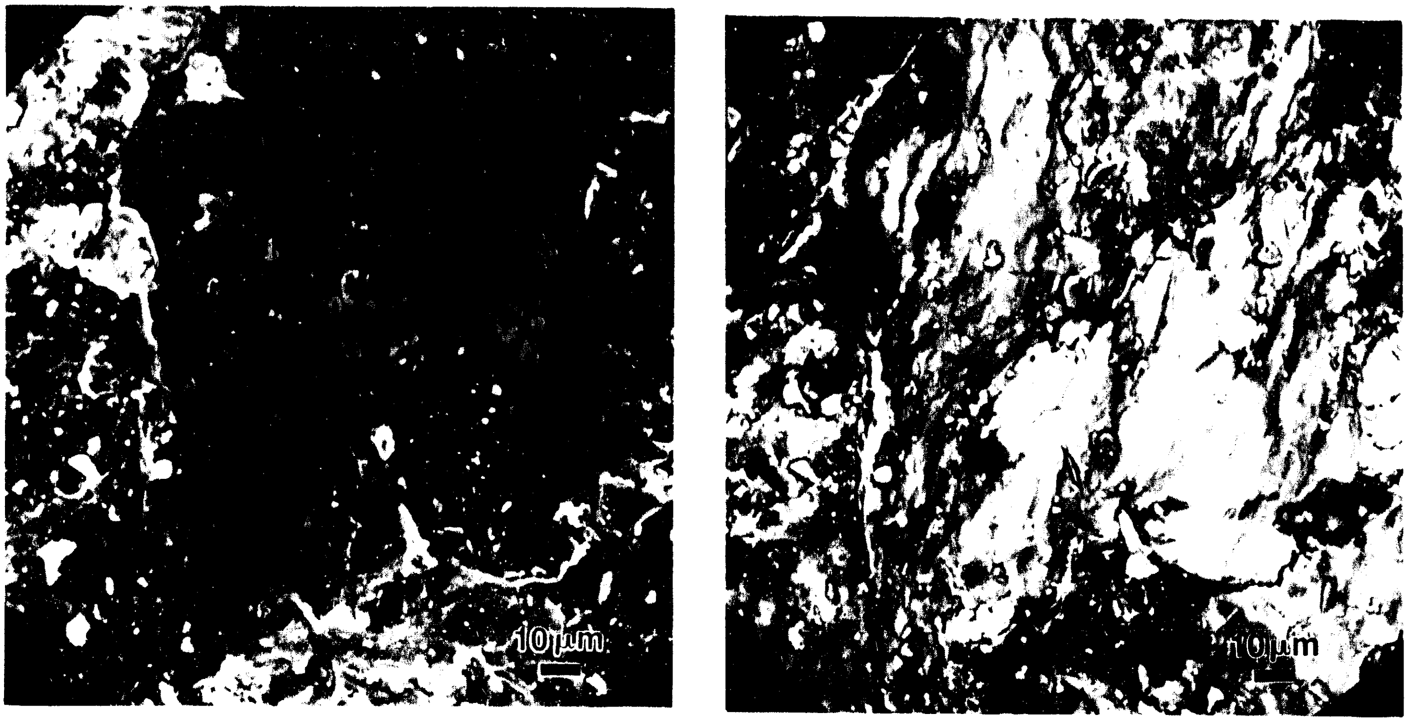

Figure 6. SEM photographs of sintered 20% torna:80% taconite.

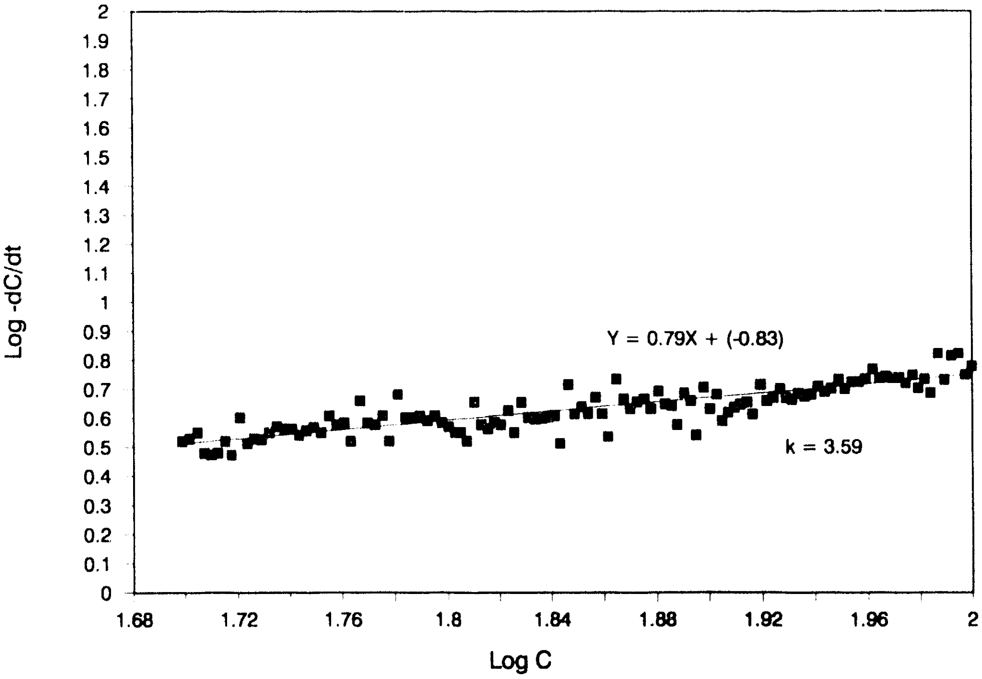

Figure 7. Steam gasification of Wyodak char.

TABLE 7

RATE CONSTANTS FOR 50% CONVERSION OF WYODAK CARBON AT 750°C.

	Run 1		Run 2	
Mesh Size	Order	Reactivity	Order	Reactivity
-60+100	1.04	3.30	0.80	3.23
-100+140	0.92	3.60	0.81	3.61
-140+200	0.97	4.16	0.94	3.98
-200+325	0.94	4.21	1.08	3.58
-325	0.79	3.76	0.91	3.76

TABLE 8

LIMESTONE CATALYZED WYODAK CHAR-STEAM REACTION, -60 X 100 MESH COAL

		Reactivity							
Temp, K	Order	1st Order	r^2	1/2 Order	r^2	0th Order	r^2	Calc	r^2
973	0.35	2.12	0.9959	1.80	0.9995	1.54	0.9992	1.72	0.9999
973	0.51	2.15	0.9968	1.82	0.9996	1.55	0.9983	1.83	0.9996
1023	0.72	4.71	0.9993	3.99	0.9992	3.40	0.9950	4.29	0.9997
1023	0.38	4.21	0.9965	3.58	0.9997	3.06	0.9989	3.45	0.9999
1073	0.79	7.96	0.9969	6.76	0.9987	5.79	0.9968	7.43	0.9981
1073	0.89	7.71	0.9989	6.56	0.9986	5.62	0.9946	7.49	0.9993

TABLE 9

LIMESTONE CATALYZED WYODAK CHAR-STEAM REACTION, -100 X +140 MESH COAL

		Reactivity					
Temp, K	Order	1st Order	r^2	1/2 Order	r^2	0th Order	r^2
973	1.04	2.04	0.99	2.20	0.98	1.86	0.27
973	0.74	2.20	0.69	1.37	1.00	1.17	1.00
1023	0.62	4.84	1.00	4.10	1.00	3.50	1.00
1023	0.99	3.93	1.00	3.31	1.00	2.81	0.99
1073	0.97	7.49	1.00	6.37	1.00	5.42	0.99
1073	1.15	9.79	1.00	8.25	1.00	7.00	0.99

TABLE 10

LIMESTONE CATALYZED WYODAK CHAR-STEAM REACTION, -140 X +200 MESH COAL

		Reactivity					
Temp, K	Order	1st Order	r^2	1/2 Order	r^2	0th Order	r^2
973	0.39	3.91	0.9959	3.33	0.9995	2.84	0.9992
973	0.23	3.70	0.9945	3.16	0.9990	2.71	0.9994
1023	0.32	7.70	0.9938	6.58	0.9983	5.66	0.9986
1023	0.16	11.50	0.9888	9.82	0.9964	8.47	0.9998
1023	0.14	9.16	0.9941	7.82	0.9989	6.70	0.9995
1073	0.18	24.92	0.9874	21.23	0.9957	18.35	0.9999
1073	0.44	22.55	0.9844	19.36	0.9935	17.01	0.9992

TABLE 11

LIMESTONE CATALYZED WYODAK CHAR-STEAM REACTION, -200 X +325 MESH COAL

		Reactivity					
Temp, K	Order	1st Order	r^2	1/2 Order	r^2	0th Order	r^2
973	0.41	4.08	0.9974	3.47	0.9998	2.95	0.9981
973	0.53	4.39	0.9971	3.72	0.9997	3.17	0.9984
1023	0.08	9.70	0.9929	8.25	0.9984	7.05	0.9997
1023	0.28	11.15	0.9957	9.47	0.9996	8.06	0.9993
1073	0.10	18.09	0.9948	15.44	0.9992	13.22	0.9991
1073	0.07	17.78	0.9906	15.16	0.9968	13.04	0.9990

reactions run in duplicate at each of three temperatures, 700, 750, 800°C. The correlation coefficient for each k value was determined from plots of the integrated form of:

$$-\frac{dC}{dt}-kC^{n}$$

where n is the order. In Table 8 the k values calculated at each temperature for each n were determined from the differential plot and are shown in the column indicated "Calc".

Total BET surface areas of the three coals with and without additives are shown in Figures 8, 9, and 10. Few correlations between total surface area and reactivity are evident. Catalysts, however, appear to produce different surface areas on a given coal at the same temperature.

3.3.2 Active Sites

Velva lignite and Wyodak subbituminous coal CO_2 active sites were measured on the TGA according to a method previously described (3). Similar effects, shown by parallel slopes in Figure 11, were shown for the coals with the $CaSO_4$ additive. However, there was significant difference between the chars in the presence of limestone (Fig. 12) and the calcined form of limestone, calcium oxide (Fig. 13). Figure 14 shows the relative numbers of carbon/active sites for the two coals with the three catalysts at each of the three temperatures.

3.4 Analysis of Vapor-Phase Volatile Products

An interface enabling products generated in a TGA to be introduced directly into the mass spectrometer (MS) was built. This will speed analyses and eliminate product loss or adulteration resulting from condensation and revolatilization. Figure 15 is a schematic of the interface.

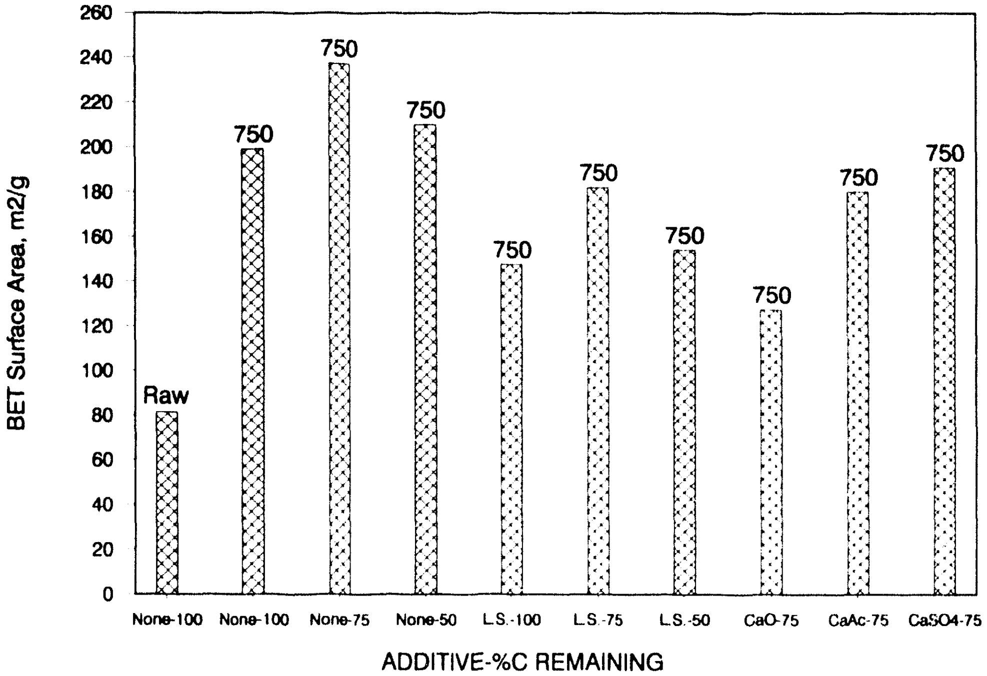

Figure 8. Effect of additive and temperature on surface area of Velva lignite.

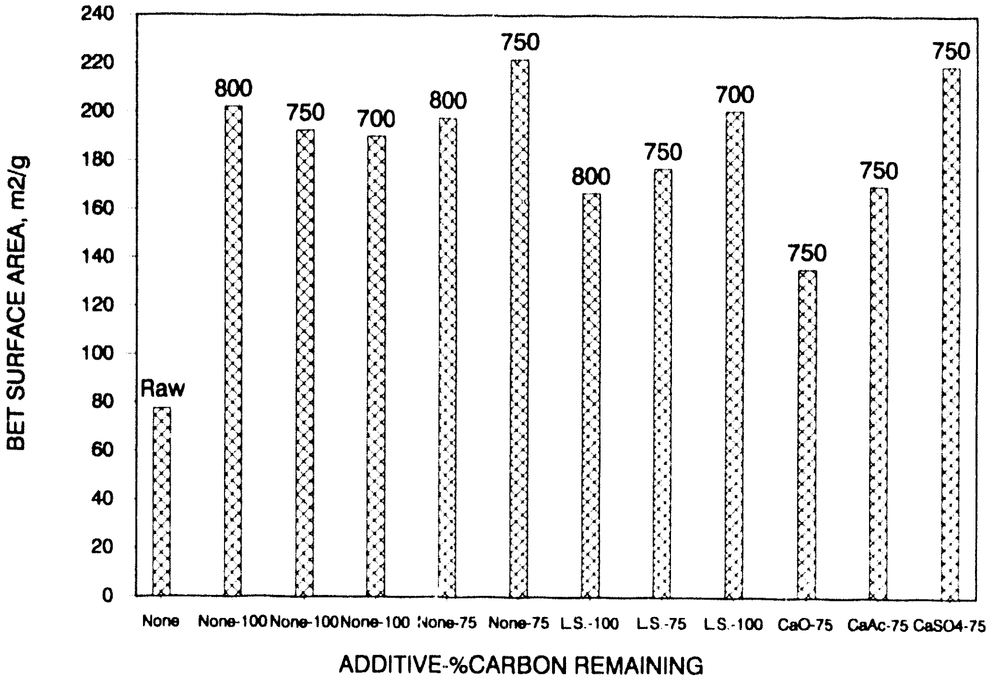

Figure 9. Effect of additive and temperature on surface area of Wyodak subbituminous coal.

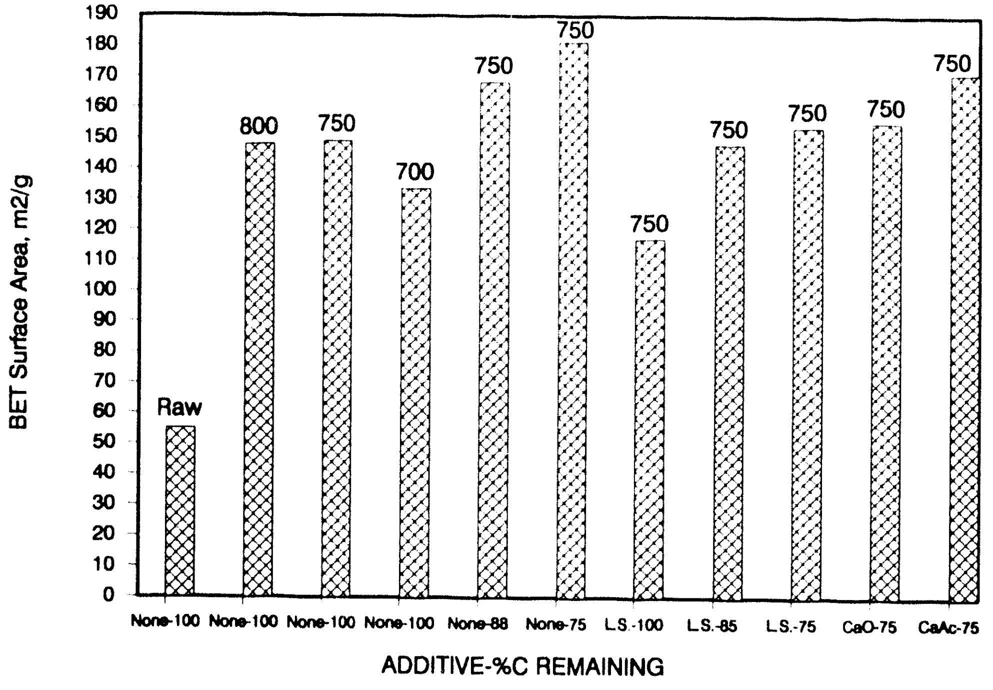

Figure 10. Effect of additive and temperature on surface area of Indiana bituminous coal.

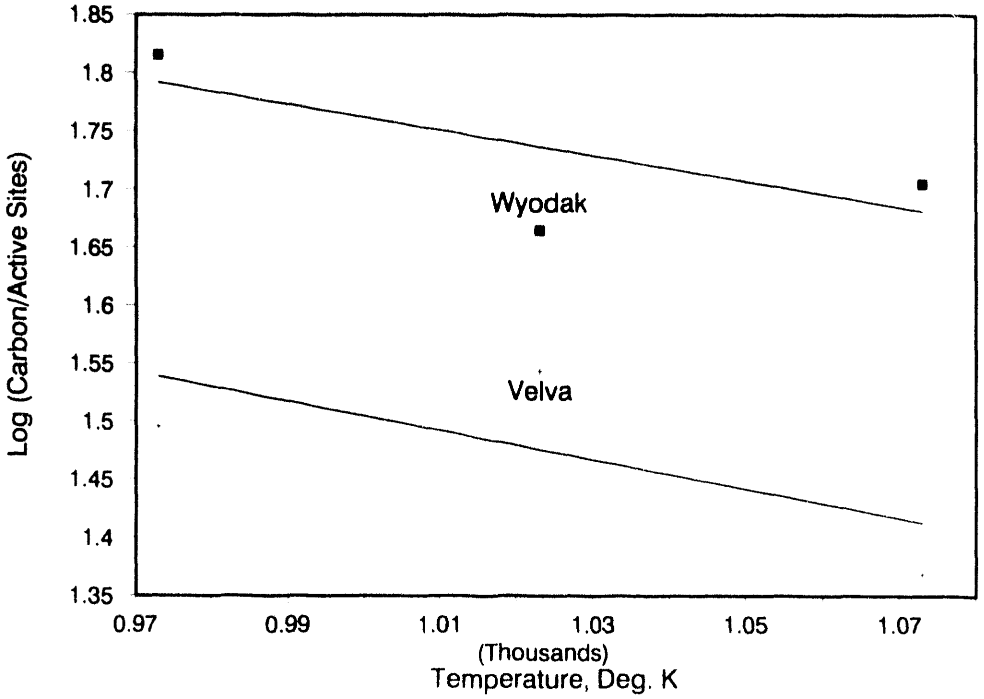

Figure 11. Log (carbon/active sites) vs. Temperature of Velva lignite and Wyodak subbituminous chars prepared at 973, 1023, and 1073K (700, 750, and 800°C).

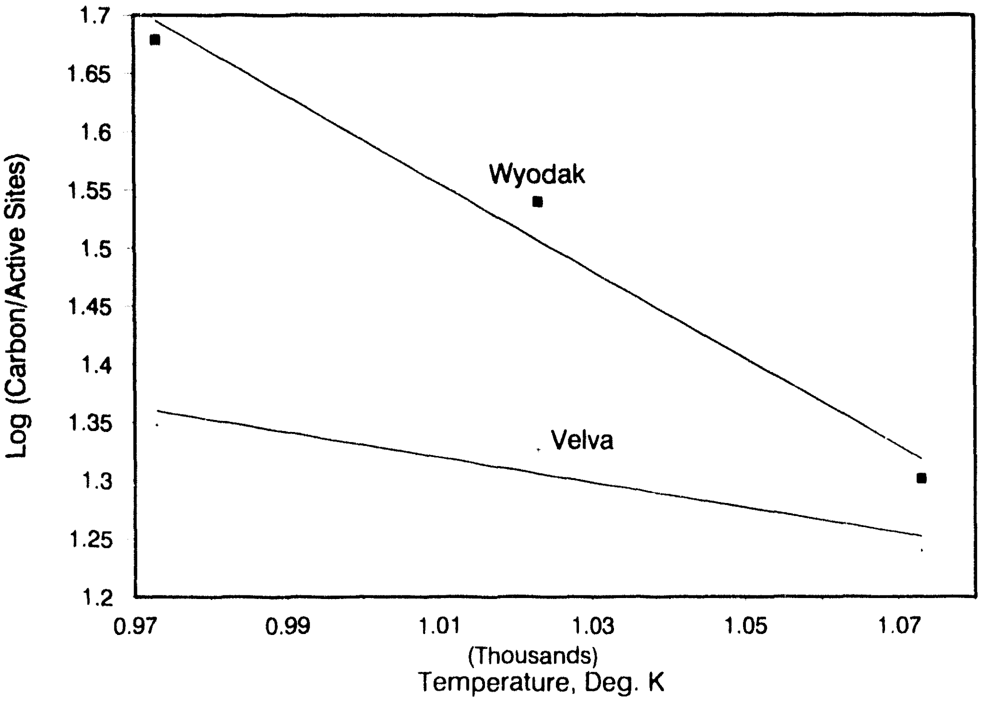

Figure 12. Log (carbon/active sites) vs. Temperature for Velva lignite and Wyodak subbituminous coal chars prepared at 973, 1023, and 1073k (700, 750 and 800°C) with limestone additive.

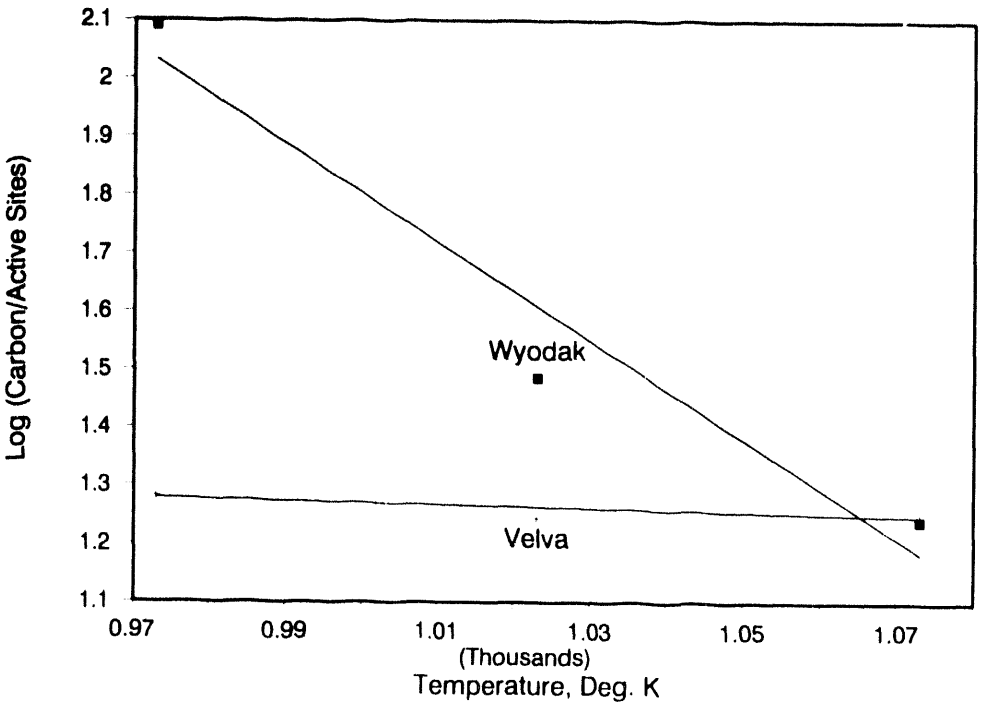

Figure 13. Log (carbon/active sites) vs. Temperature for Velva lignite and Wyodak subbituminous coal chars prepared at 973, 1023, and 1073K (700, 750 and 800°C) with calcium oxide additive.

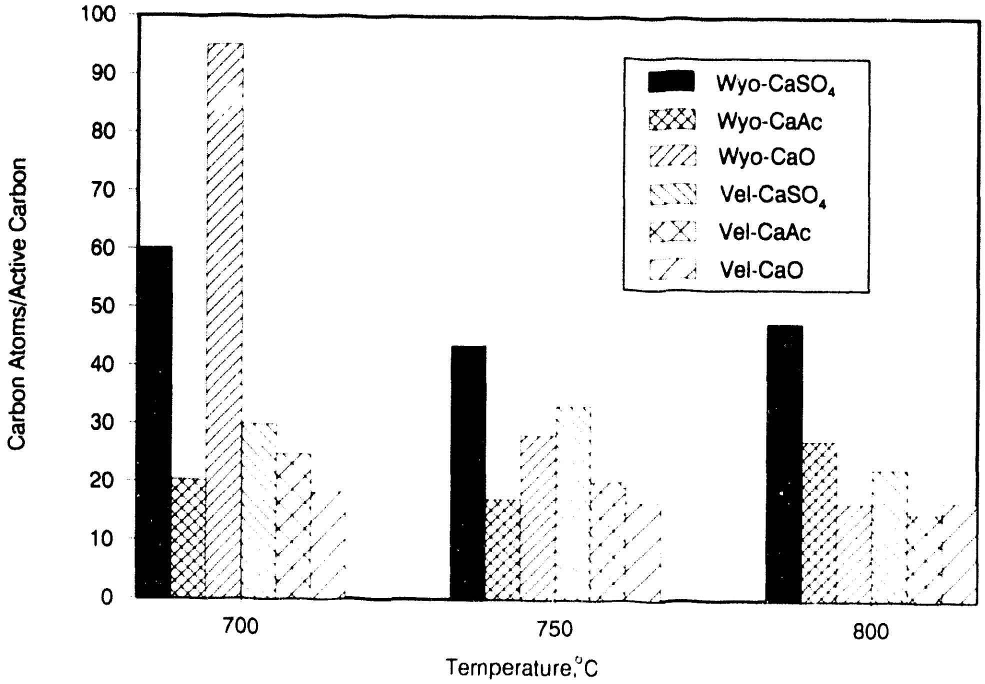

Figure 14. Carbon/active sites for Velva lignite and Wyodak subbituminous chars prepared from 10% calcium additive-raw coal mixture at 700, 750, and 800°C.

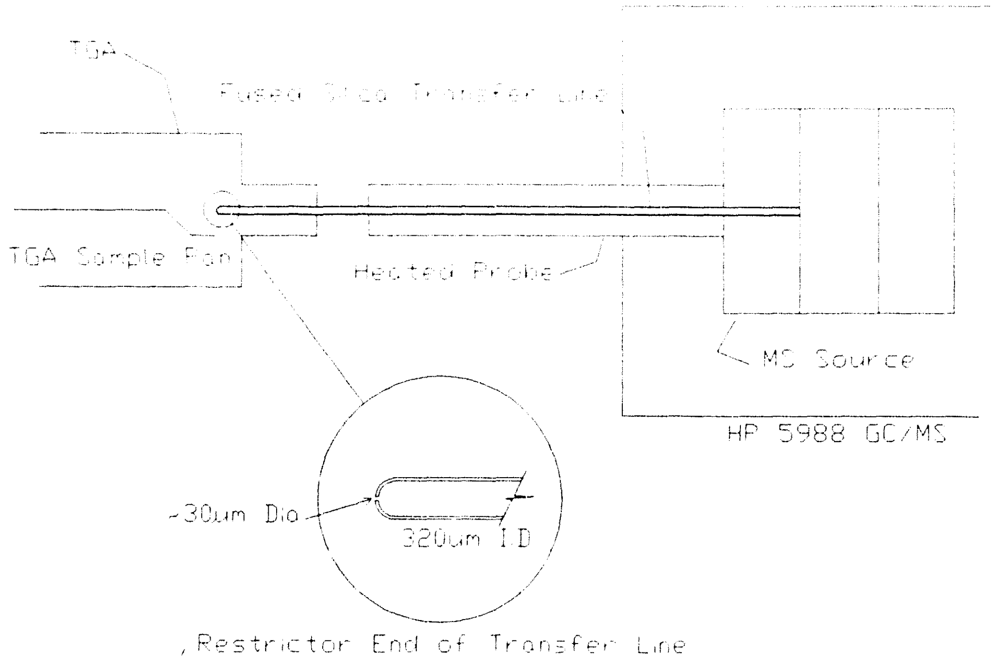

Figure 15. TGA/MS interface.

Several samples of coal and coal-catalyst mixtures were heated in the TGA and the products were "sipped" and analyzed by the MS. About one part in 101 of the sample of volatized material collected by the interface was introduced into the MS. Low voltage current (10 eV) was used to ionize the particles resulting in a spectrum that showed primarily molecular ions. Benzene, phenols, catechols, and small polynuclear aromatics predominated for the low rank coals.

3.5 Design of a Small Batch Gasifier

A laboratory-scale fluidized-bed reactor will be interfaced with a mass spectrometer to determine the effects of rapid heat up on the distribution of liquid products. The interface will allow identification of the major components of the pyrolysate directly as they are formed, without an intermediate condensation step. Information learned may make it possible to adjust the product slate (e.g. by catalytically hydrotreating the pyrolysate in the vapor phase utilizing the hydrogen in the product gas) to reduce downstream processing and meet changes in market demand. The design of the laboratory-scale reactor is illustrated in Figure 16.

Use of this device, when completed, will represent a process evaluation step intermediate between the small scale of TGA analysis and the larger scale of the CPU. The rapid heatup of the coal in the fluidized bed will more closely simulate the actual process conditions of larger scale operation.

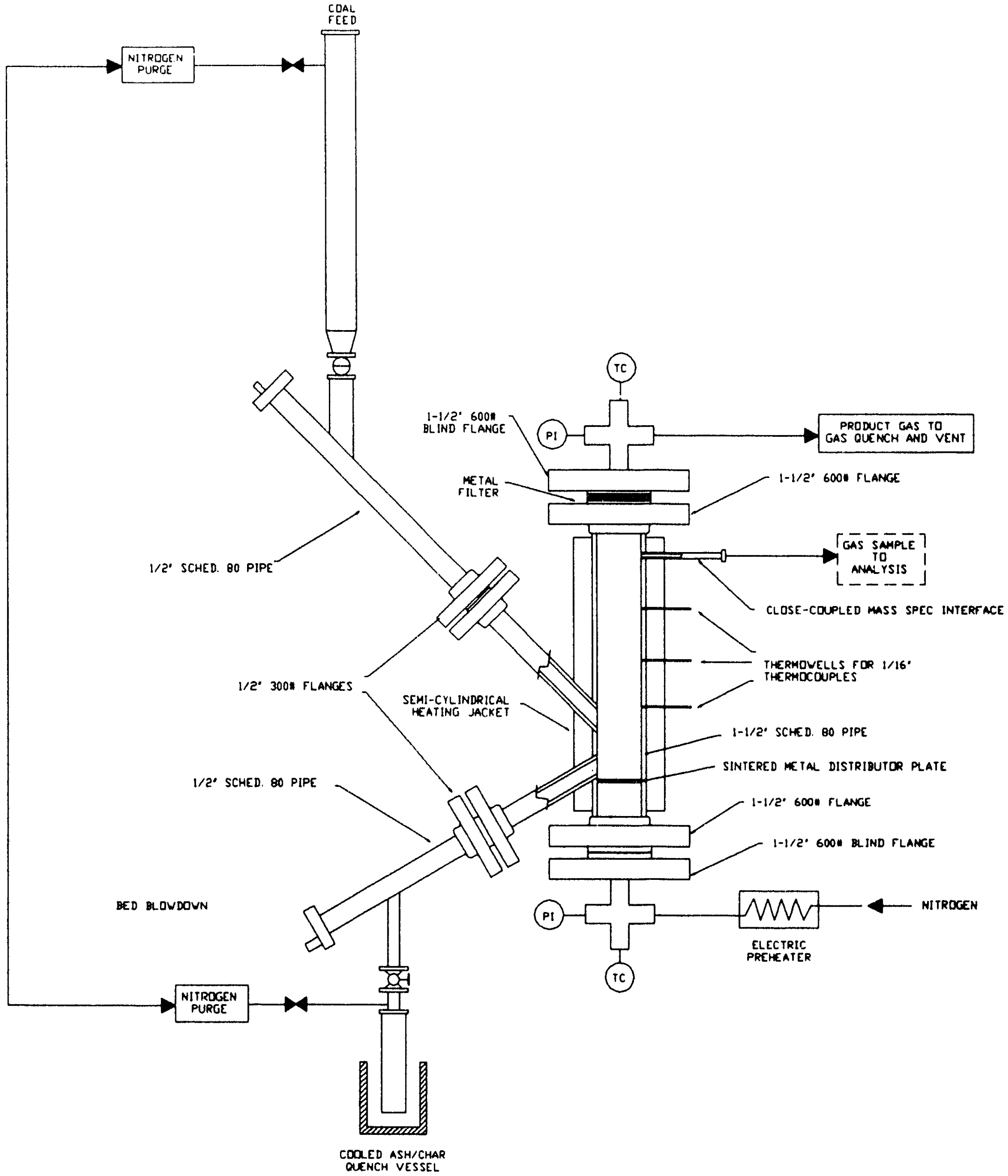

Figure 16. Schematic of laboratory-scale reactor.

3.6 Production of Activated Carbon from Coal

3.6.1 Literature Survey

Recent experimental efforts and marketing studies have been performed to assess the technical and economic feasibility of producing activated carbon (AC) from low-rank coals as an additional processing step in the emerging MG process presently under pilot-scale investigation at EERC. Normal operating conditions in MG are very similar to the conditions necessary for the activation of carbon. If integrated activation of carbon can be accomplished in a gasifier, it will contribute to the overall economic viability of the process.

Production of Activated Carbon

Currently, some MG operating conditions are expected to be suitable for the activation of carbon. To what extent the carbon will be activated and what surface areas and pore structures will be produced is not known. Both high- and low-rank coals are commonly used in the manufacture of AC. The steps of the MG process do not necessarily emulate, but are similar to, the procedures normally used to produce AC from those materials. These similarities offer the potential for production of AC by the MG process or a modification of it.

Typically, the source material is dried, pyrolyzed, and activated. Pyrolysis of the dried feed material produces a char by driving off most of the volatiles in the source material. The pyrolysis step is usually carried out at temperatures from 400° to 600°C in an inert atmosphere. If drying were to be done in the pyrolysis step, it would be virtually identical to the carbonization step of the MG process.

The activation step is implemented by either chemical or physical means. In the case of chemical activation, a compound such as ZnCl, H_3PO_4, KOH, K_2S or KCNS is added to the material to be carbonized. The added compound restricts the formation of decomposition products, or tars, which would cover existing pores during pyrolysis. In this way, a good AC can be produced in one operation. The activating compound is added in sufficient quantity to inhibit tar formation and removed by washing to expose the protected pore structure. The pore structure must already exist in the material being activated as it is not augmented by this method. (4)

Physical activation is really partial gasification. The activating agent is usually steam, carbon dioxide, or air (O_2). During the gasification process, tars blocking existing pores are removed. These pores are in turn deepened and enlarged. Increasing the duration of the activation step will result in greater enlargement of the pores, or burn off. In general, pores are categorized relative to diameter by the terms micropore (dia < 20 Å), mesopore (20 Å $<$ dia $<$ 500 Å) and macropores (dia 500 $>$ Å)]. As a result of reactivity and molecular dimensions, the diameter of effectively available pores increases from steam to air. Therefore, steam activation will best promote a well-developed micropore structure. Activation at 800° to 850°C with steam seems to be most effective (4,5,6).

The production of AC can be viewed as being between MG and hydrogen production. The goal of MG is to produce as much char as possible with a low volatile content. The hydrogen production process could consume all of the carbon. While production of AC with little loss of carbon is desirable, surface area is more important. Increase of surface area is effected by enlargement of pores by gasification of carbon forming the pores.

Little modification of the MG process would be needed to match the activation step. The second stage of the MG process is the calcination of the char. If not already present in the fluidization gas of the calciner, an activation agent could be added. Most probably, the residence time would be increased to improve the pore development. Required activation temperatures should be within the operating range of the calciner.

Activated carbons for special applications are often activated after the addition of an alkali metal compound. The char to be activated is impregnated by soaking in a water/alkali salt solution. After thorough rinsing to remove the excess, the char is then physically activated, usually with steam. The presence of the alkali compound enhances the reactivity of the gasification process. It also tends to promote the formation of high surface areas with a higher microporosity (4).

The effectiveness of an AC is derived from the surface area available for adsorption. Most of the surface area results from the pore structure. The pore size distribution is at least as important. A given molecule can enter a pore no smaller than a given diameter. The smaller the pore is relative to the adsorbed molecule, the more strongly that molecule will be held. The strongest adsorption occurs when the pore is barely large enough to admit the adsorbed molecule. The rate of adsorption and desorption may also be reduced as diffusion is limited. An AC with a high surface area will be relatively ineffective if a large portion of the pores are too small in diameter to accept the molecules to be adsorbed (7).

Activated carbons have found significant industrial use. Commercial applications include primarily decolorizing, gas/vapor separation, removal of heavy metal pollutants from wastewater and pharmaceutical applications. The application for which a particular AC is physically best suited will be determined by several factors. The more important are:

1. <u>Surface area</u>: Since adsorption is a surface phenomenon, surface area is a general measure of the ability of an AC to adsorb.

2. <u>Pore size distribution</u>: A characteristic of the pore structure which will have a significant effect on the rate of adsorption and desorption, and will dictate the application for which the AC would be best suited.

3. <u>Strength and abrasion resistance</u>: These characteristics will determine the type, i.e. fixed- versus fluidized-bed, and scale of allowable utilization methods. Abrasion resistance can be evaluated on a relative basis but can not be reliably known without observing actual degradation in the proposed application.

4. Mean particle diameter, shape factors, and uniformity: This is important in evaluating pressure drop through a bed.

5. Bulk density: This property will determine the volume requirements of a bed after the contact time requirements have been set.

The MG process as currently envisioned would be used to produce metallurgical coke from coal. With little modification of parameters, operating conditions can be changed to those intended to produce AC. Effective operating conditions listed in the literature apply to lab-scale tests. Because of the proprietary nature of commercial AC production systems, very little information is available on the effects of scaleup. Testing at proposed operating conditions will be necessary to determine actual results.

Characterization of Activated Carbon

One proposed structure for AC (8) consists of aromatic sheets and strips, often bent, resembling a mixture of wood shavings and crumpled paper, with variable gaps of molecular dimensions between them which are the micropores. The structure is highly disorganized and contains slit-shaped micropores.

The type of AC to be used is dependent upon the size of the molecules to be adsorbed by the carbon. The AC works best when the majority of the pores are just slightly larger that the molecules that are to be adsorbed. One way to determine the applicability of a particular AC is to perform an adsorption test, such as the BET test, or to determine the capacity for adsorption of phenol, methylene blue, benzene, tannin, molasses, iodine, or a number of other solutions. Measuring the adsorption capacity of the AC for materials having different molecular diameters gives an idea of the pore size distribution, which is helpful in determining if the AC will fit the intended application. Ultimately it is usually necessary to perform a test using the actual solution that is to be purified.

This indicates that more work could be done in the characterization of pore size distribution and surface area and in predicting the suitability of a particular AC based upon laboratory information.

The characterization of microporous AC requires information on both the physical and the chemical properties of the solids. Physically, the pore structure is of concern. The distribution of pore sizes plays an important role in the effectiveness of the AC in capturing the desired material from solution.

Most chemical reactions take place essentially on the edges of the graphitic sheets, where a variety of oxygen containing groups or other chemically active groups are found. The fraction of total surface occupied by edges is important in the selection of AC when chemical, rather than physical properties alone, are involved. Very little work has been done in the study of adsorption involving chemical sites. Knowledge of the distribution of these sites within the micropores is necessary to better understand adsorption phenomena.

Early approaches for evaluation of AC were basically focused on production parameters using adsorption of a particular material as a measure of activity. Work done by others such as Dubinin, Zaverina and Radushkevich, whose approach became known as the Theory for the Volume Filling of Micropores (TVFM) (8), and Brunaur, Emmett and Teller (BET Theory) (8) investigated the mathematical modeling of physical adsorption by AC. The TVFM approach applies to micropores while the BET approach applies to meso- and macropores so that the two approaches are complimentary.

Other modeling efforts were made by Manes (9), Suffet and McGuire (10), and Belfort (11,12). Their theories were developed primarily to understand the adsorption mechanisms of solutes from aqueous phases, rather than as predictors for the design of process parameters. Application of these models requires considerable insight and numerous parameters which may be difficult to obtain.

In an effort to provide a simple approach to predict the adsorption capacity of AC, Nirmalakhandan and Speece (13) developed a simplified application of Belfort's solvaphobic theory. This approach uses molecular descriptors, easy to calculate from the molecular structure of the adsorbates.

Absorbability data are routinely generated in the laboratory using isotherm studies on batch systems. Ideally, one should cover several orders of magnitude on the relative pressure scale in order to fully benefit from subsequent analysis of the data.

Some other analytical techniques, other than adsorption isotherms, include high-resolution transmission electron microscopy (HRTEM), dark-field micrographs, heat of wetting calorimetry, and immersion calorimetry.

Immersion calorimetry is used as a complementary technique for characterizing microporous AC. The enthalpy of immersion into organic liquids and into water can be related to either Dubinin's theory (TVFM) or to the Dubinin-Serpinski water adsorption isotherm. These complimentary techniques provide excellent assessment of microporosity below 80 to 100 Å.

The Market Outlook

A marketing survey done by J.E. Sinor (14) in 1988 shows that the total production of AC has fluctuated around 200 million pounds per year over the past ten years. The industry is currently operating at a capacity of between 70 and 90 percent. The Sinor study focused primarily on existing markets for AC and concluded that coal will never capture the entire market for AC, since the need for specific properties dictates the use of other materials from which these properties are more readily obtainable. Also, since the total U.S. market is only about 100,000 tons per year, it didn't meet the survey criteria for a char market of 1,000,000 tons per year. This criteria was based on the coal industry's assessment of the minimum coal sales necessary to open a new mine.

Recent marketing surveys (15,16) indicate that the areas of greatest growth for AC will be in water and air purification, gas adsorption, and gold recovery. Market growth in the range of 15 percent per year for the next three years is predicted (15). The price for AC is currently ranging from around 60 cents per pound to $1.25 per pound. The increase in demand is attributed to the increased public awareness in environmental pollution and to the pending Clean Air and Clean Water legislation. Most of the world's major producers are currently reactivating production plants shut down in the mid-seventies or are in the process of building new facilities in anticipation of the increased demand. Recent industry developments include:

* Calgon Carbon Corporation is restarting a production facility in Catlettsburg, Kentucky, with a capacity of 18 million pounds per year. This plant was scheduled to be in operation in January 1990. Calgon is also building a new plant in the Gulf Coast area with a capacity of 30 million pounds per year. This plant is scheduled to be in operation in late 1991.

* Atochem Inc., Ceca Division is expanding it's Pryor, Oklahoma, plant to add 5 million pounds per year to its capacity. Ceca is also planning a new 30 million pound per year facility to be in operation in three years. The site for this plant has not been decided yet. Atochem also expanded its plant in Parentis, France, to add 11 million pounds per year to its capacity.

* American Norit, a subsidiary of Norit NV of the Netherlands, is building a new 20 million pound per year plant in Marshall, Texas, which is scheduled to be in operation in late 1991. They are also planning to double the capacity of one of the three European plants.

* Sutcliffe Speakman PLC last year added 14 million pound per year capacity to its plant in Leigh U.K. They also commissioned a new 9 million pound per year rotary kiln (the world's largest) and have plans to double its capacity.

* The city of Cincinnati, Ohio, is currently building a new water treatment plant which is to be the largest user in the U.S. of AC at one site. The plant will be equipped with regeneration facilities capable of regenerating 80,000 pounds of spent AC per day. Currently, approximately 80 million pounds of spent AC are regenerated industry-wide each year.

Activated carbon is used in a wide variety of filtration applications as well as for storage of gases such as hydrogen and methane. Some of the more common uses are purification of drinking water, wastewater cleanup, sugar decolorization, and the removal of tastes and odors in the food processing industry. As people become more aware of environmental pollution, the number of uses for AC is expected to increase. AC is used heavily in environmental cleanup for the removal of synthetic organic chemicals such as pesticides and nonvolatile aromatics. Recent product developments include:

* The Westvaco Corporation has recently introduced a new adsorbent called Nuchar BX-7540 which is tailored to gas-phase uses such as solvent recovery, gas purification, and catalysis.

- Zimpro/Passavant Inc. has recently developed a new Powdered Activated Carbon Treatment (PACT) system that is used in wastewater cleanup. They have a trailer mounted version that can be rented for cleanup of landfill leachate and surface runoff sites.

- American Norit Company Inc. has recently introduced a new form of granular AC that is produced by extrusion of peat moss which is then charred. This process produces a product that is up to 100 times stronger than granular charcoal which means it is capable of withstanding the regeneration process with minimal makeup required. The reported surface area using the BET method is 1000 g/m^2.

Recent developments in the regeneration of AC also indicate the increase in demand.

- Atochem Inc., Ceca Div. has introduced its adsorbent Cecasorb in liquid- and gas-phase canisters which can be shipped to a regeneration plant when saturated. They're planning a new thermal regeneration plant to be in operation by the end of 1990. This plant will be located in Pryor, Oklahoma, and will have a capacity of 10 million pounds per year.

- Calgon Carbon Corporation currently operates four regeneration plants, two in the U.S. and two in Europe.

- Airco Gases in Murry Hill, New Jersey, has introduced a new regeneration process which uses heated nitrogen as a backflush agent. This reduces corrosion, extends bed life and eliminates the need to distill a solvent-water mixture to recover solvents, which reduces operating costs.

- Radiation Disposal Systems Inc. in Charlotte, North Carolina, has just introduced a new continuous process system called the Carbon Master Filter System.

- Zimpro/Passavant Inc. has developed new technology for separating regenerated carbon from ash.

Conclusions

Since the cost of the carbonaceous feedstock is only a small portion of the total cost in the production of activated carbon, the economic incentive to use lignite over other materials is small and the problem is exacerbated by the shipping costs of the raw material. As MG proceeds towards commercialization, it may be found that activated carbon can be produced as a by-product, with relatively minor capital investment beyond that already in place for production of metallurgical chars from low rank coals. In this case, it may be possible to produce by-product activated carbon less expensively than from an entire plant built specifically for that purpose. Any such favorable economics will probably prove very site-specific. It may prove economical to use the activated carbon produced for removal of contaminants from the wastewater that is generated on-site.

3.7 Primary Separation of Liquid By-Products

3.7.1 Literature Survey

Coal liquids are complex mixtures of water, phenolics, aromatics, nitrogen bases, sulfur-containing compounds, and fine particulates. The present state of coal liquid upgrading technology involves condensing these complex mixtures and reprocessing to upgrade. This literature search is the first step in a long-term development process to extend and improve on current coal liquid upgrading technology, such as that represented by the Great Plains Gasification Plant (GPGP) and various vendor-offered processes. The GPGP will soon be upgrading the crude phenol stream to cresylic acids. This stream, in addition to the rectisol naphtha and tar oil streams, was previously burned in the plant's boilers and superheaters to produce steam. The HRI Dynaphen Process, an extension of Hydrocarbon Research, Inc.'s commercially proven dyhrodealkylation (HDA) technology, can be used to upgrade coal liquids to benzene and phenol.

Numerous low severity pyrolysis processes have been economically unsuccessful in the past because it was assumed that the coal tar liquids could be sold for an attractive profit to pay for the operation of the plant. This was never realized in practice. Therefore, the success of a MG process will depend on obtaining a premium value for the char. However, the economic viability of the MG process will be enhanced by the production of high end-value liquid products requiring minimal upgrading. A reduction in the complexity and cost of liquid upgrading may be accomplished by incorporating a primary separation step with the primary condensation. In addition, it may be possible to adjust the product slate (e.g., by catalytically hydrotreating the pyrolysate in the vapor phase utilizing the hydrogen in the product gas) to reduce downstream processing and meet changes in market demand.

A complete and consistent set of physical property data for the liquids from MG is not available in the literature. The MG process is characterized by coal pyrolysis at temperatures less than 800°C (1472°F) and pressures less than 10 atm. The Morgantown Energy Technology Center (METC) has contracted with an independent laboratory with expertise in assaying petroleum products to establish standard and consistent data for one MG liquid. These data are necessary to: (1) make comparisons between liquids produced in various MG processes and petroleum and other liquid fuels, (2) evaluate the potential markets and upgrading techniques required for MG liquids, and (3) generate and validate models for evaluating various upgrading alternatives and predicting fuel performance characteristics based on physical and chemical properties. Data from early research are of limited use, since they were not obtained using standard techniques and thus are not presented on a consistent basis. Therefore, it was decided as a first step to focus the literature search on coal pyrolysis liquids from more recent investigations.

Appendix A contains additional data on the liquids from the Char Oil Energy Development (COED) process. These data are included because the EERC MG process is a simplification and improvement of the COED process. Appendix B contains additional references on the products from the low-temperature pyrolysis of coal.

CHARACTERISTICS OF PYROLYSIS LIQUIDS

The following analyses are commonly used to characterize MG liquids:

- elemental analysis for carbon, hydrogen, nitrogen, sulfur, and oxygen;
- water content;
- specific gravity;
- viscosity;
- heating value;
- atmospheric and vacuum distillation (ASTM D-86 and D-1160, respectively) and/or simulated distillation using gas chromatography (ASTM D-2887);
- aliphatics/aromatics ratio.

In addition to distillation and viscosity data, flash point, cloud point, water and sediment percent by volume, carbon residue, percent ash, percent sulfur, copper strip corrosion, and cetane number are commonly used to determine whether a liquid meets fuel specifications. Mass spectrometry, gas chromatography, and ^{13}C nuclear magnetic resonance are used to determine the compounds present in a particular MG liquid fraction.

The quality and quantity of MG liquids depend on coal type and process conditions. For example, high volatile bituminous coals give the highest liquid yields, while low-rank coals give much lower yields. The former tend to yield higher molecular weight species desired as pitch for anode production, and the latter yield lower molecular weight species with high phenolic content suitable as chemical intermediates (17). Temperature, pressure, reactor configuration, heating rate, and reaction atmosphere all affect the yield and composition of the liquid by-products.

Under rapid heating conditions in a fluidized-bed reactor, yields of heavier polynuclear aromatic hydrocarbons are greater than in a fixed-bed slow heating rate reactor. In a fixed-bed reactor, free radicals produced during pyrolysis may be hydrogenated in situ by donatable hydrogen. This increases the quality of the liquids (as defined by the H/C atomic ratio), but results in a lower yield. Additional cracking of the primary products often occurs in the fixed bed, producing lower molecular weight liquids. The higher H/C ratio of the fixed-bed liquids is due to the presence of a larger amount of hydroaromatic and naphthenic compounds and fewer polycyclic aromatic compounds. In this case, the pyrolysis products tend to bear little resemblance to the structures present in the parent coal (18).

The COED (Char Oil Energy Development) Process

The COED Process was developed from May 1965 to June 1975 under a series of contracts between FMC and the United States Government. The goal of the project was the development of an economic process for converting coal to gas, liquid, and solid products with a higher value tha the coal itself. Coals ranging in rank from lignite to high volatile A-bituminous were processed in the COED pilot plant.

The COED pilot plant consisted of a coal preparation system for pulverizing and partially drying coal, a staged fluidized-bed pyrolysis process operating at near atmospheric pressure, a pressurized rotary-drum precoat filter for removing solids from the pyrolysis oil, a fixed-bed catalytic hydrotreater, and oil recovery and hydrogen by-product gas handling facilities. Figure 17 is a flow diagram of the COED process. A four-stage process was used to overcome the agglomerating tendencies of the coal feed. Lignite and subbituminous coals could be processed in two stages, while bituminous coals required three or more stages. Typical operating temperatures for the four stages were 550, 850, 1050, and 1550°F, respectively. Originally the product recovery system consisted of a two-stage direct water quench, followed by one stage of indirect cooling. Late in 1972, an oil absorption tower was installed in parallel with the original aqueous quench system, so that either recovery method could be used. The purpose of installing the oil absorption tower was to recover product liquids in separate boiling ranges. Properties of the product liquids from bituminous coal runs with the oil scrubber (D-300) on-line are given in Table 12. Additional data for the COED process are given in Appendix A. Since the EERC MG PDU is a simplification and improvement of the COED process, these data should prove valuable.

The tar oil, crude phenol, and rectisol naphtha streams are the liquid by-product streams produced from the gasification of Beulah-Zap lignite at the GPGP. All three streams have been used to fire the plant's boilers and superheaters to produce steam. Plans are currently underway to upgrade the crude phenol stream to cresylic acids. A recent market assessment for the liquid by-products from the GPGP concluded that the optimum product slate for the plant is production of jet fuel from the tar oil stream and benzene and phenol from the rectisol naphtha and crude phenol streams (19).

Although the GPGP is not operated at MG conditions in the gasification zone (temperature and pressure less than or equal to 800°C and 10 atm, respectively), primary devolatilization occurs much higher in the bed at temperatures representative of "mild" gasification. Thus the data from the characterization of the liquid by-product streams from GPGP are valuable since it is anticipated that the liquids produced from lignite processed in the EERC MG PDU will have similar characteristics. Typical distillation data for the three streams are shown in Table 13.

The TOSCOAL Process

The TOSCOAL low temperature coal pyrolysis process is based on the TOSCO II oil shale retorting process, which began in the 1950s. Figure 18 is a schematic of the TOSCOAL Process (20). Coal is fed to a surge hopper and then dried and preheated with hot flue gas. If necessary, agglomerating coals may be treated in a fluidized bed with steam and air prior to processing. The preheated feed is contacted with heated ceramic balls in a pyrolysis drum. After leaving the pyrolysis drum at a temperature of 800-1000°F, the char product falls through a trammel screen, is cooled and sent to storage. The cooled ceramic balls pass over the trammel screen to a separate container and are returned to the ball heater by an elevator. The pyrolysis vapors are

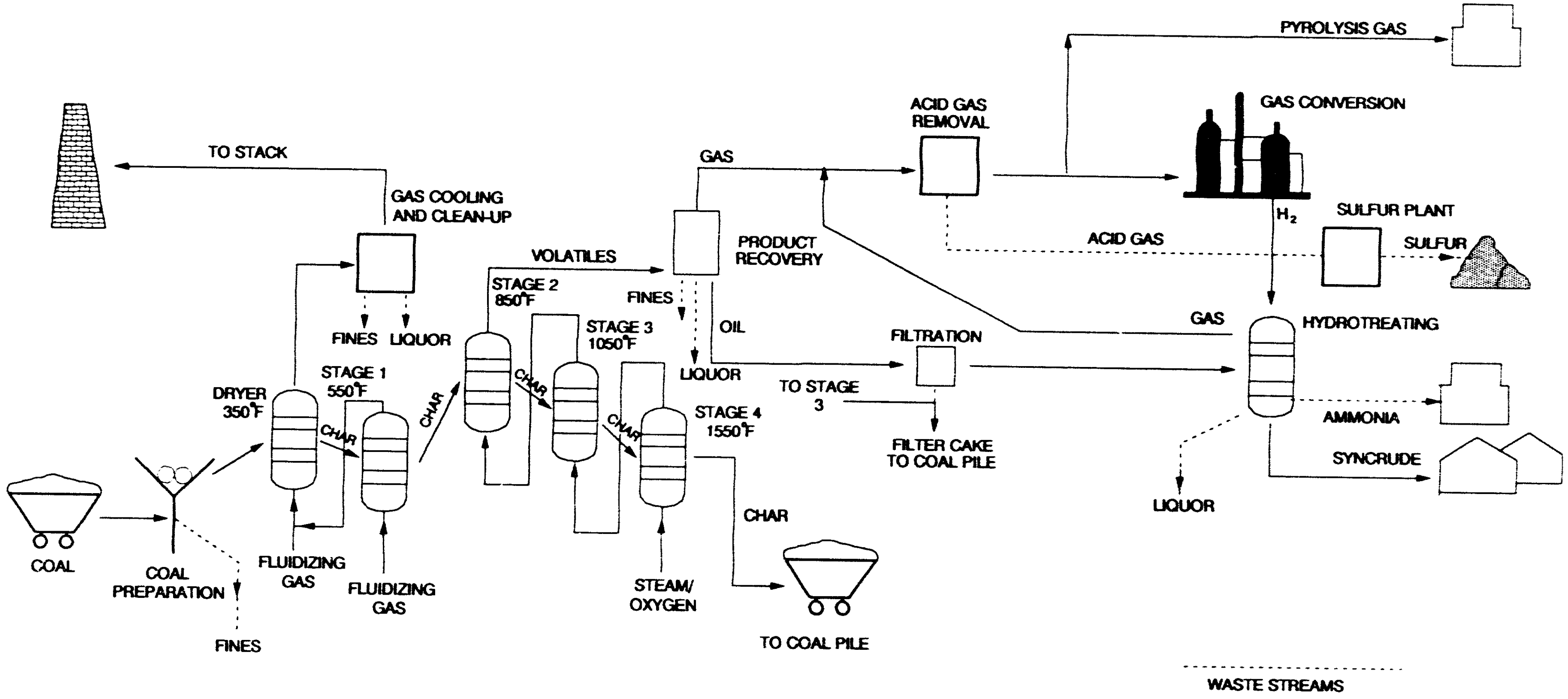

Figure 17. FMC COED process flow diagram, Great Plains Gasification Plant (GPGP).

TABLE 12

PROPERTIES OF OIL DERIVED FROM UTAH KING COAL COED RUN PDU-168B

	D-300 Bottoms		D-300 Top		Decanter	
Molecular Weight	390		280		240	
	Density		Density		Density	
	°F	g/cc	°F	g/cc	°F	g/cc
	356	0.89	189	0.97	140	0.86
	410	0.88	223	0.97	203	0.95
	428	0.82	298	1.03	219	0.96
	446	0.87			347	0.77
	464	0.92				

Distillation at 10 mm Hg, converted to atmospheric pressure using the "Esso Charts."

	D-300 Bottoms		D-300 Top		Decanter	
	10 mm(F)	760 mm(F)	10 mm(F)	760 mm(F)	10 mm(F)	760 mm(F)
IBP	300°	550°	236°	472°	160°	378°
1 ml	330	586	250	489	180	403
2	352	612	272	516	194	420
5	390	658	290	538	200	428
10	444	721	320	574	228	462
20	540	832	390	658	280	526
23	544*	836*				
30	436	712	330	586		
40	470	751	380	646		
50	504	791	434	709		
60	530	820	470	751		
70	560	855	510	797		
78	642*	947*				
80		566	861			
90		578	875*			

D-300 Bottom		D-300 Top		Decanter	
Temp. °F	Viscosity Centistokes	Temp. °F	Viscosity Centistokes	Temp. °F	Viscosity Centistokes
410	**	200	33.0	200	10.0
		220	25.0	220	6.5
		240	17.0	240	4.5
		260	11.0	260	3.5
		280	8.0	280	2.5
		300	6.0	300	2.0
		320	4.0	320	2.0
		340	3.0	340	1.5
		360	2.5	360	1.0
		380	1.5		

---

* Cracked

** D-300 bottom oil too stiff at 400°F for viscosity determination.

TABLE 13

TYPICAL ASTM-D86 DISTILLATION DATA FOR GPGP LIQUID BY-PRODUCTS

	Rectisol Naphtha	Crude Phenol	Tar Oil
Specific Gravity	0.825	1.072	1.014
Volume Percent Distilled	Temperature, °F		
	IBP= 100	210	210
10%	120	365	250
20%	140	380	360
30%	160	385	400
50%	180	395	440
70%	195	425	520
80%	215	470	640
90%	230	525	690
EP	270	570	

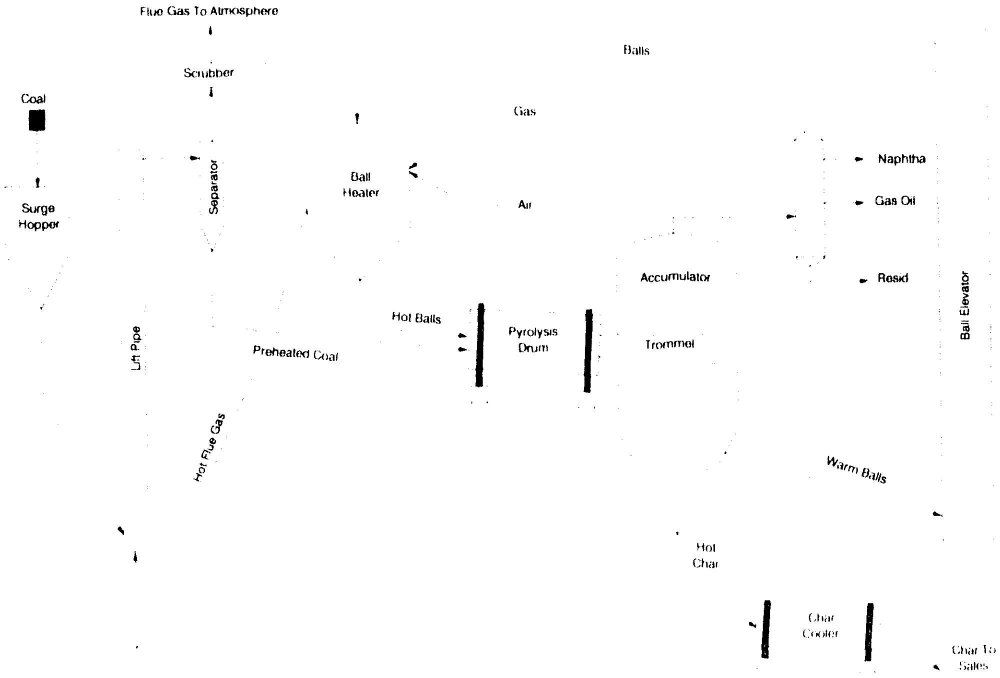

Figure 18. TOSOCAL process.

condensed and fractionated. The uncondensed gas, with a heating value of 500-1000 BTU/lb, may be used as a fuel for the ball heater. Properties of the product oil from TOSCOAL pilot plant runs with Wyodak subbituminous coal are given in Table 14.

LIQUID BY-PRODUCT MARKETS

Diesel Fuels and Fuel Additives

ASTM diesel fuel specifications are given in Table 15, along with specifications for a new diesel fuel which has been proposed by the Association of American Railroads (AAR) (21). The proposed new fuel, with a wider range of distillation temperature and viscosity and a lower minimum cetane rating than existing diesel fuels, may make it possible to use the fraction distillable below 700°F as blending stock, which accounts for over 90% of the total liquid.

Regulations modifying existing gasoline and diesel fuel compositions will be necessary to improve air quality and limit human exposure to critical hydrocarbons. Highly polluted areas such as Los Angeles may be required to use alternative fuels. Several Colorado cities, including Denver, require oxygenates in gasoline during the winter to reduce carbon monoxide emissions. Targets may include additional controls on gasoline volatility, limits on the amount of benzene in gasoline, and restrictions on undesirable hydrocarbons in both gasoline and diesel fuel. The concentration of aromatics in gasoline rose from 22% by volume in 1980 to the current level of 32% by volume in an effort to maintain octane quality in light of the phasedown of tetraethyl lead as an anti-knock agent (22). In addition to increasing the concentration of aromatics and isoparaffins, the lead phasedown has increased fuel volatility and decreased the concentration of l ane normal paraffins. Restrictions may be imposed to limit the concent f aromatics to 25 to 30 vol%. In addition, benzene concentration may ited to 0.5 to 1.0 vol% from the current level of 1-5 vol%.

Reduction of the aromatics in gasoline will be difficult to achieve, while maintaining fuel quality. Ethers are the only refinery component which can replace the octane quality lost when aromatics content is reduced. Methyl tertiary butyl ether (MTBE) is currently the most widely used additive to increase gasoline octane quality. It has been proposed that methyl aryl ethers produced from coal liquids would also be suitable as gasoline anti-knock additives. However, aryl ethers typically have higher boiling points and densities and lower octane blending values than alkyl ethers.

Military Jet Fuels

Jet fuels consist of four general types of hydrocarbons: paraffins, cycloparaffins or naphthenes, aromatics, and olefins. A typical fuel contains hundreds of different compounds. The proportions of hydrocarbon types are not directly controlled, although there are limitations on aromatics and olefins. Specifications for primary military jet fuels are given in Table 16. The navy fuel specification, JP-5, is identical to JP-8 except for a minimum flash point of 140°F for safety on aircraft carriers.

TABLE 14

PROPERTIES OF OIL FROM TOSCOAL PROCESS

Temperature	800°F	900°F	970°F
Run No.	C-8[1]	C-2	C-3
Distillation,[2]			
Vol% Recovered			
2.5	413°F	420°F	390°F
10.0	490	475	405
20.0	575	550	455
30.0	645	625	545
40.0	710	700	640
50.0	765	776	725
Viscosity, SUS[3]			
180°F	122	123	128
210°F	63	66	69
API Gravity	7.9	4.5	1.9
Pour Point (°F)	90	100	95
Heating Value (Btu/lb)	16,590	16,217	15,964

[1] Feed coal differed from that used in Runs C-2 and C-3.
[2] Combination of True Boiling Point (TBP) and D-1160 distillations.
[3] Saybolt Universal Seconds.

TABLE 15

ASTM DIESEL FUEL SPECIFICATIONS

Fuel Property				
Flash Point (°F), Min.	100	125	125	140
Cloud Point (°F), Max.	a	a	a	a
Water and Sediment (vol. %), Max.	0.05	0.05	0.05	0.05
Carbon Residue (% on 10% residuum), Max.	0.15	0.35	0.35	—
Ash (weight %), Max.	0.01	0.01	0.01	0.10
90% Distillation Temp. (°F)				
Minimum	---	540	---	---
Maximum	550	640	700	---
Saybolt Universal Viscosity at 100°F (sec)				
Minimum	---	32.6	29	45.0
Maximum	34.4	40.1	55	125.0
Sulfur (weight %), Max.	0.50	0.50	0.50	2.0
Copper Strip Corrosion, Max.	No. 3	No. 3	No. 3	---
Cetane Number, Min.	40	40	32	30

a To be set by fuel purchaser.

TABLE 16

PRIMARY MILITARY FUEL SPECIFICATIONS

	JP-4 (Jet B) MIL-T-5624L	JP-8 (Jet A-1) MIL-T-83133A
Specific Gravity, 60°F	0.751-0.805	0.775-0.840
Gravity, API at 60°F	45-47	37-51
Distillation, Max. °F		
10% Recovered	---	---
20% Recovered	293	401
50% Recovered	374	---
90% Recovered	473	---
Final Boiling Point	518	572
Freezing Point, °F	-72 (-58)	-54
Viscosity,		
Centistokes at -40°F, Max.	---	8.0
Aromatics, Vol% Max.	25.0 (20.0)	25.0 (20.0)
Olefins, Vol% Max.	5.0	5.0
Sulfur, Wt% Max.	0.40 (0.30)	0.40 (0.30)
Net Heat of Combustion,		
Btu/lb, Min.	184,400	18,400
Hydrogen Content, Wt%, Min.	13.6	13.6
Thermal Stability JFTOT		
Pressure Drop, mm Hg, Max.	25	25
Heater Deposit, Max.	3	3
Flash Point, °F, Min.	---	---
Vapor Pressure, Reid, psi	2-3	---

Coal liquids are unsuitable for use as jet fuels without hydroprocessing due to their high aromatics content, which causes smoking. Even a small percentage of naphthalenes causes problems. However, research with tar sand has shown that aromatic compounds can be converted to cycloparaffinic (naphthenic) compounds, which may be an excellent jet fuel.

The military (through various research contracts) has investigated the possibility of modifying jet fuel specifications to reduce fuel costs, while minimizing any effect on aircraft performance. This may be done by reducing the hydrogen requirement and increasing the aromatic content, thus reducing or eliminating the need for expensive hydrotreating of coal liquids. Allowing jet fuels to become more cyclic has the benefit of increasing the fuel density. Volumetric heating value increases with density, resulting in increased aircraft range and a lower freezing point. However, cyclic hydrocarbons have lower H/C ratios than their straight chain analogues, which results in increased flame radiation and soot formation. If the aromatics can be hydrogenated without cracking the naphthenic rings, coal/tar oil-derived liquids may be a preferred feedstock for the production of high density jet fuels.

Benzene and Phenol

Coke oven light oil was once an important source of benzene and BTX (benzene, toluene, xylene). However, the production of benzene from coke oven oil dropped precipitously between 1979 and 1982, from approximately 4% to less than 2% of total benzene production. The major sources of benzene and BTX are the catalytic reforming of petroleum naphtha, pyrolysis gasoline from the steam cracking of hydrocarbons to make ethylene and propylene, and hydrodealkylation of toluene. Other than gasoline, the largest markets for benzene and BTX are in the production of plastics and fibers. Major end uses for benzene include styrene for polystyrene production, cumene for phenol production, and cyclohexane for nylon production. Commercial grade benzene must have a minimum freezing point of 5.35°C, indicating a purity of 99.7%. Other specifications for commercial grades of benzene are given in Table 17 (19). Demand for benzene as an octane enhancer has increased due to the phaseout of leaded gasoline beginning 1986. In addition, the demand for benzene as a feedstock for the manufacture of petrochemicals has soared. These factors combined to push the price of benzene to approximately $1.50/gal in early 1987. The current selling price is $1.45/gal (23).

TABLE 17

BENZENE SPECIFICATIONS

Specification	Refined Benzene-535 (ASTM D2359-69)	Refined Benzene-485 Nitration-Grade (ASTM D835-71)	Industrial-Grade Benzene (ASTm D836-71)
Specific Gravity	0.8820-0.8869	0.8820-0.8860	0.875-0.886
Color (ASTM D1209)	No darker than 20 max. on the platinum cobalt scale		
Distillation Range	Not more than 1°C including 80.1°C	Not more than 1°C including 80.1°C	
Solidifying Point	5.35°C min.	4.85°C min.	
Acid Wash Color (ASTM D848)	No. 1 max.	No. 2 max.	
Acidity (ASTM D847)	Nil	No free acid	
Sulfur Compounds	Free of H_2S & SO_2	Free of H_2S & SO_2	
Thiophene	1 ppm max.		
Copper Corrosion (ASTM D849)	Copper strip shall not show discoloration.		
Nonaromatics (ASTM D236)	0.15% max.		

Coal was once the dominant source of phenol and other precursors for the production of resins and plastics. The crude phenol from coke ovens and coal gasification plants contains tar acids, tar bases (pyridines, picolines), neutral oil, organic acids, and pitch. Crude phenol contains phenol, cresols, xylenols, ethylphenols, and, in some cases, catechols and resorcinol. Currently, approximately 90% of phenol is synthesized from cumene. In the cumene process, cumene (produced by alkylating benzene with isopropylene) is oxidized with air to cumene hydroperoxide, which is converted by aqueous acid to phenol and acetone. Phenols are produced in the catalytic cracking of petroleum. The effluent from the cracker is washed with sodium hydroxide, primarily to remove mercaptans and organic sulfur compounds, and phenols and cresols are simultaneously extracted as the sodium salts. The caustic waste can be processed to recover phenols, cresols,and xylenols. Most synthetic phenol is sold at a purity of over 99.5% to control the properties of subsequent synthesis products. Typical specifications for phenol are given in Table 18. The selling price of phenol rose from $0.20/lb in 1986 to $0.45/lb in early 1987, with the current selling price at $0.41/lb (23).

The HRI Dynaphen process can be used to convert alkylphenols in coal liquids to benzene and phenol. A flow diagram of the Dynaphen process is shown in Figure 19. In the Dynaphen reactor, cresylic acids are dealkylated, and some dehydroxylation also occurs. Unconverted alkylphenols and toluene and xylene (the products of dehydroxylation) are recycled to the Dynaphen reactor, yielding benzene and phenol as the main products.

TABLE 18

PHENOL SPECIFICATIONS

Property	Specification	Test Method
Appearance	Crystalline Solid	Visual
Color of Melt, APHA	10 max.	ASTM D-1686
Color of NaOH Solution	1.5 max	ASTM D-1500
Freeze Point, °C	40.6 max	ASTTTM D-1493
Turbidity of Melt, APHA	1 max.	HC 390A-80
Iron, ppm	0.5 max.	WT-2
Water, wt%	0.07 max.	ASTM D-1631
Nonvolatile Residue, wt%	0.05 max.	ASTM D-1353
Impurities by GC, ppm		
a-methyl styrene	100 max.	
2-methylbenzyfluran	25 max.	
di-methylbenzyle alcohol	100 max.	
acetophenone	5 max	

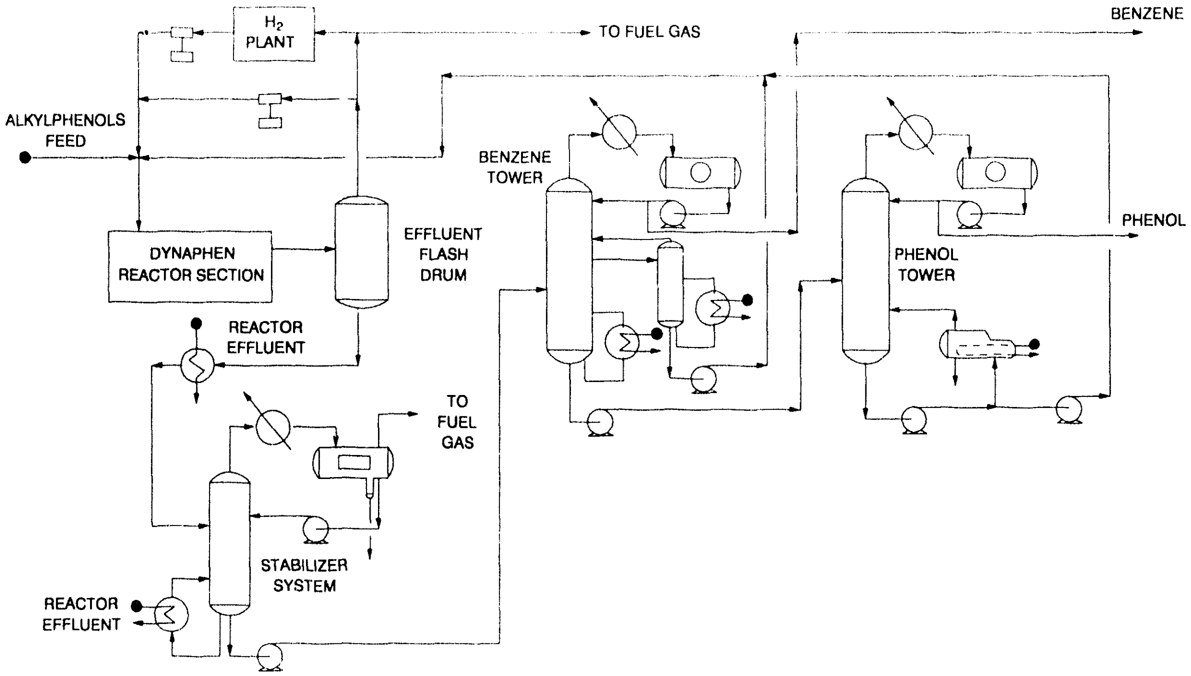

Figure 19. Dynaphen process.

CONCLUSIONS

Coal liquids have potential uses as military jet fuels, octane enhancers, blending stock for diesel fuels, pitch binders for coke briquetting, and intermediates for the production of valuable chemicals such as phenol and benzene. The challenge is to reduce the number of upgrading steps required. It is desirable to maximize production of the lighter components by gasification alone, without the consumption of hydrogen from the process. If, on the other hand, the demand and prices for these products are high enough, a separate gasification stage may be justified to produce the additional hydrogen needed. Coal liquids are complex mixtures of hundreds of compounds, and their composition is dependent on the coal used and conditions of pyrolysis (including temperature, reaction atmosphere, and reactor configuration). Therefore, it will be necessary to establish a program of bench- and pilot-scale research to identify the optimum primary separation and upgrading steps required to produce a slate of liquid products from a specific MG process capable of meeting changes in market demand.

3.8 Gas Cleanup and Separation

3.8.1 Design of a Versatile Test Area in CPU

In the scenario where the CPU would be closely coupled to a fuel cell, there are significant constraints on the concentrations of contaminants that can be tolerated. Among these constraints is the requirement that the fuel gas to the fuel cell should contain no more than 10 ppm of particles greater than 1 micron in diameter to limit fouling. This would be most efficiently achieved by reducing particulate levels without cooling the product gas from the CPU.

Several particulate removal systems are in various stages of development. Depending on availability, ceramic candles, sintered metal, high temperature fabric filters, and others will be tested. The vortex venturi described in the following section will be evaluated for its ability to remove fine particulates. To permit flexibility, a test area is being designed which should accommodate the filtration systems that will be tested. Figure 20 is a schematic of the hot gas cleanup test area.

In addition to operating the single gasifier vessel in a hydrogen production mode, the MG PDU is planned to have a fairly intensive operation schedule. Product gas from the CPU functioning as the calciner of the two-vessel PDU will be available for testing of hot gas cleanup devices also. Particulates produced during hydrogen production should by sufficiently similar to those produced by the CPU to permit shake down and preliminary evaluation of the particulate removal systems.

3.8.2 Vortex Venturi for Gas Separation

This device is similar to an ultra-high-G cyclone, originally developed with the intent of removing particulate from stack gases. The original research (24) demonstrated that 98.5% of particles having an average diameter of two microns were removed. Particles driven to the wall of a converging throat were captured and removed from the device in a film of water flowing down the throat. For a variety of reasons, the concept proved unfeasible as a stack gas scrubber and was abandoned, following granting of the patent, by its inventors and assignee.

Centrifugal forces in the converging throat were as high as 20,000 times the acceleration of gravity, which is comparable to those encountered in the gaseous diffusion process for uranium enrichment. The apparently laminar flow conditions in the throat, as indicated by the lack of reentrainment of water film or particulates, suggests that significant gas separation may be possible. The ratio of molecular weights of CO_2, CO or CH_4 to H_2 is orders of magnitude greater than that of ^{235}U to ^{238}U isotopes in the form of UF_6 vapor. A further possibility, within the scope of this program, is to use the same principle for hot particulate removal, which may be substantially more effective than by conventional cyclones.

A test unit has been built and is now ready for characterization tests. Initially, the effects of flow rates and the adjustable geometry on radial pressure gradients and differential pressures will be determined. This unit, shown schematically in Figure 21, is a simplified version of the device used by the original inventors (24) for laboratory confirmation of the claims subsequently cited in their patent. That experimental effort was assisted by W. B. Hauserman, presently Principal Investigator of this study. Presentation of further details of the device shown in Figure 21 and discussion of fundamental principles involved will be deferred pending a new invention disclosure, covering novel design features, not envisioned by the original inventors.

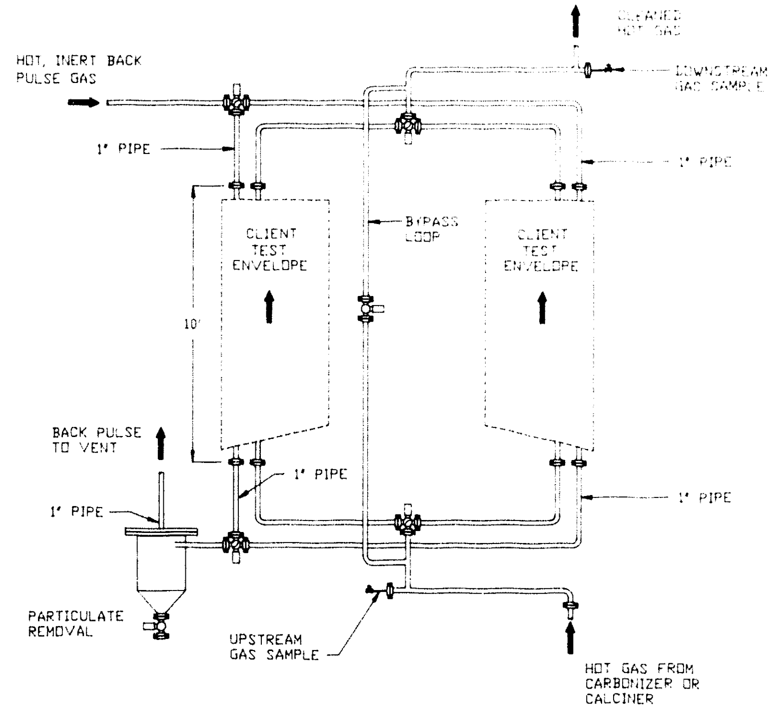

Figure 20. Schematic of hot-gas cleanup test area.

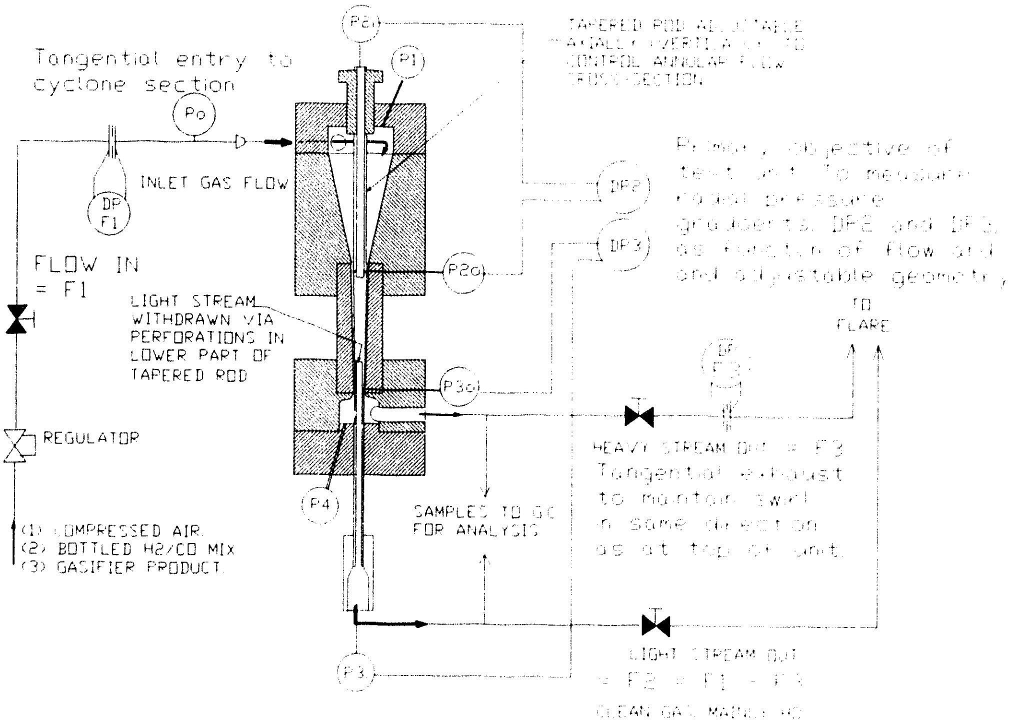

Figure 21. Schematic of Vortex Venturi.

4.0 PRESENTATIONS AND PUBLICATIONS

An abstract of a paper entitled "Characterization of Gasification Coal Char" was submitted for presentation at the Pittsburgh Coal Conference in September, 1990. The manuscript has been submitted.

5.0 REFERENCES

1. Sears, R.E.; Cisney, S.J.; Heidt, M.K.; Musich, M.A.; Timpe, R.C.; Willson, W.G. "Production of Hydrogen from Low-Rank Coals: Hydrogen-From-Coal Continuous Process Unit Testing"; Topical Report to DOE-METC; DOE-FE (Number unassigned at this time), USDOE, August 1989.

2. Timpe, R.C.; Sears, R.E.; Willson, W.G.; and Sondreal, E.A. "Hydrogen Production from Low-Rank Coals - Topical Report on Char Properties and Reactivity"; Topical Report to DOE-METC, DOE-FE (Number unassigned at this time), USDOE, May 1989.

3. Miller, D.J.; Hawthorne, S.B.; Timpe, R.C. Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. **1988**, 33, 2, 455-463.

4. Wigmans, T. "Industrial Aspects of Production and Use of Carbons"; Carbon **1989**, 27, 1.

5. Rist, L.P.; Harrison, D.P. "Surface Area and Pore Development During Lignite Activation"; Fuel **1985**, 64.

6. Klose, E.; Born, N. "Partial Gasification of Lignite Coke with Steam in a Rotary Kiln for Activated Carbon Production"; Fuel **1985**, 64.

7. "Process Design Manual for Carbon Adsorption"; U.S. Environmental Protection Agency, October, 1973.

8. Stoeckli, H.F. "Microporous Carbons and Their Characterization: The Present State of the Art"; Carbon **1990**, 28, 1, Great Britain, 1-6.

9. Manes, M. Activated Carbon Adsorption of Organics from Aqueous Phase; Suffet, I.H., McGuire, M.J., eds., Ann Arbor Sci. Pub.: Ann Arbor, MI, 1980; Vol. 1, Chap. 2, p 43-64.

10. Suffet, I.H.; McGuire, M.J. Activated Carbon Adsorption of Organics from Aqueous Phase; Suffet, I.H., McGuire, M.J., eds., Ann Arbor Sci. Pub.: Ann Arbor, MI, 1980; Vol. 1, Chap. 4, p 91-115.

11. Belfort, G.; Altshuler, G.L.; Thallam, K.K.; Feerick,C.P.; Woodfield, K.L.; AIChE J. **1984**, 30, 197-207.

12. Belfort, G.; Altshuler, G.L.; Thallam, K.K.; Feerick,C.P.; Woodfield, K.L.; Fundamentals of Adsorption; Myers, A.l., Belfort, G., eds., Proceedings of Engineering Foundation Conference; Bavaria, West Germany, 1984; Chap. 6, p 77-93.

13. Nirmalakhandan, N., Speece, R.E. "Adsorption from Aqueous Phase by Activated Carbon: A Simplified Application of the Solvaphobic Theory"; Environ. Sci. Technol. **1990**, 24, 4.

14. Sinor, J.E. "Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products"; Industrial Market Assessment of the Products of Mild Gasification; final report to METC on contract No. DE-AC21-87MC24267; University of North Dakota, Energy and Environmental Research Center; Grand Forks, ND, 1988.

15. "Activated Carbon: Industry Launches Expansion Round"; Chem. Marketing Reporter Dec. 25, **1989**, 7.

16. "New Zip in Activated Carbon"; Chem. Eng. Feb. **1990**, p 43.

17. Willson, W.G.; Ness, R.O.; Hendrikson, J.G.; Entzminger, J.A.; Jha, M.; Sinor, J.E. "Development of an Advanced, Continuous Process for the Production of CoProducts;" Literature Survey Results; January 1988; DOE Contract DE-AC21-87MC24267.

18. Khan, M.R. Fuel **1989**, 68, 12.

19. Sinor, J.E. "Production of Jet Fuels from Coal-Derived Liquids. Volume 1 Market Assessment for Liquid By-Products from the Great Plains Gasification Plant"; August 1987, Report No. AFWAL-TR-87-2042.

20. Atwood, M.T.; Schulman, B.L. "The TOSCOAL Process - Pyrolysis of Western Coals and Lignites for Char and Oil Production"; Division of Fuel Chemistry, 173rd ACS National Meeting; New Orleans, Louisiana, March 21-25, 1977.

21. Sinor, J.E. "Development of an Advanced, Continuous Process for the Production of Coproducts"; Final Report, January 1988; DE-AC21-87MC24267.

22. Unzelman, George H. :Reformulated Fuels - 1. Reformulated Gasolines Will Challenge Product-Quality Maintenance"; Oil and Gas Journal **1990**, 88, 15, 43-48.

23. Chemical Marketing Reporter February 26, **1990**.

24. Paul, D.G.; Berriman, L.P. "Particle Separation Apparatus"; U.S. Patent No. 4,279,627, July 21, 1981.

APPENDIX A

COED PILOT PLANT DATA

The data in this appendix are from COED report PCR-708. The COED pilot plant was also operated using lignite and subbituminous coals, however, no data on these runs were located. A water quench system was used in place of the oil scrubber for the majority of the runs, but no data on those runs were available. The EERC mild gasification PDU is a simplification and improvement on the COED process; therefore, it is expected that the liquids from the EERC PDU will possess qualities similar to those from the COED process.

COED Process (PCR-708)
ASTM Distillation Data for Oil from PDU Runs with Oil Scrubber, D-300

Run Number: PDU-163
Coal: Crown (Illinois #6)
Coal Type: Bituminous

Time Period[1], hr:	49 to 57	0 to 57	49 to 57
	D-300 Bottom	D-300 Top[2]	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	226	212	208
5	576	475	428
10	604	513	448
15	626	532	468
20	649	550	489
24	660		
25		568	513
30		586	540
35		601	561
40		615	586
45		628	608
50		640	626
55		651	642
60		662	662
65		673	673
70		684	687
72		684	
75			709

Temp., (°F)	Viscosity[3], centistokes	Temp., (°F)	Viscosity[2], centistokes	Temp., (°F)	Viscosity, centistokes
205	31,800	---	---	230	21.0
260	30,600			241	15.3
302	490			300	6.6
338	104			348	3.9
374	34			388	1.9

[1] Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

[2] No oil recovered fromtop section of D-300. Analysis represents material drained from column at end of run.

[3] All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-165

Coal: Peabody No. 10 (Illinois #6)

Coal Type: Bituminous

Time Period[1], hr:	32 to 40	0 to 40	32 to 40
	D-300 bottom	D-300 top[2]	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	250	210	208
5	507	214	428
10	595	450	444
15	608	484	459
17	617		
20		507	473
25		529	493
30		549	520
35		567	545
40		581	565
45		595	581
50		608	592
55		622	601
60		626	609
61		626	
65			617
70			624
75			631
80			635

Temp., (°F)	Viscosity[3], centistokes	Temp., (°F)	Viscosity[2], centistokes	Temp., (°F)	Viscosity, centistokes
310	11,000	200	105.0	200	70.0
315	6,000	220	45.0	220	35.0
320	3,500	240	23.0	240	16.0
330	1,750	260	12.0	260	9.5
340	850	280	7.5	280	6.0
350	400	300	5.5	300	4.0
		320	3.0	320	3.0
		340	2.0	340	2.0
		360	1.5	360	1.5

---

[1] Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

[2] No oil recovered fromtop section of D-300. Analysis represents material drained from column at end of run.

[3] All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-167A
Coal: Utah King
Coal Type: Bituminous
Time Period[1], hr:

	42 to 58	42 to 58	42 to 58
	D-300 Bottom	D-300 Top[2]	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	246	298	208
5	561	450	441
10	603	482	473
15	617	509	505
20	626	536	540
21	626		
25		562	565
30		585	590
35		606	612
40		626	628
45		644	640
50		658	649
55		669	655
60		679	664
65		685	667
69			667
70		694	
75		702	
80		707	
85		718	
88		720	

Temp., (°F)	Viscosity[3], centistokes	Temp., (°F)	Viscosity[2], centistokes	Temp., (°F)	Viscosity, centistokes
235	20,000	190	12.0	190	29.0
240	10,500	200	9.5	200	27.0
260	2,800	220	6.0	220	18.0
270	1,800	240	4.5	240	10.0
280	1,250	260	3.5	260	6.5
290	700	280	2.5	280	4.5
300	400	300	2.0	300	3.5
310	275	320	1.5	320	2.5
320	200	340	1.0	340	1.5
330	150	360	0.5-1.0	360	1.0
340	110				
350	80				
400	75				

[1] Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

[2] No oil recovered fromtop section of D-300. Analysis represents material drained from column at end of run.

[3] All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-167B
Coal: Utah King
Coal Type: Bituminous
Time Period[1], hr:

	29 to 37	29 to 37	29 to 37
	D-300 Bottom	D-300 Top	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	207	266	207
5	374	464	208
10	558	491	216
15	599	511	455
20	626	531	487
22	626		
25		550	512
30		568	555
35		585	581
40		599	608
45		612	621
50		624	637
55		635	646
60		642	655
65		648	660
70		653	664
75		637	666
80		658	
85		660	
89		664	

Temp., (°F)	Viscosity[3], centistokes	Temp., (°F)	Viscosity[2], centistokes	Temp., (°F)	Viscosity, centistokes
280	35,000	190	15.0	200	50.0
290	15,600	200	11.5	220	26.0
300	6,000	220	7.5	240	14.5
310	2,800	240	5.0	260	9.0
320	1,800	260	3.5	280	6.0
330	1,100	280	2.5	300	4.0
340	650	300	2.0	320	3.0
350	340	320	1.5	340	2.0
380	100	340	1.0	360	1.5
400	45	360	0.5-1.0		

[1] Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

[2] No oil recovered fromtop section of D-300. Analysis represents material drained from column at end of run.

[3] All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

APPENDIX B

BIBLIOGRAPHY

Birge, G.W.; Wolfson, D.E. "Carbonizing Properties of Westmoreland County, PA., Coals"; November 1957, USBM RI No. 5374.

Boley, C.C.; Fegley, M.M. "Design and Operations of Two Refractory-Lined, Internally Heated, Entrained-Flow Carbonizers"; January 1977; NTIS: GFERC/RI-77/1.

Bowling, K.McG.; Waters, P.L. Br. Chem. Eng. 1964, 13, 8, 1127.

Chao, K.C.; Greenkorn, R.A.; Lin, H.M.; Bienkowski, P.R.; Narayan, R. "Steam Pretreatment of Subbituminous Coal"; Purdue University: West Lafayette, Indiana, May 1986; prepared for EPRI Project RP2147-9.

Chemistry of Coal Utilization; Lowry, H.H. Ed.; John Wiley and Sons: New York, 1945; Vol. 1 and 2.

Chemistry of Coal Utilization, Second Supplementary Volume; Elliot, M.A. Ed.; John Wiley and Sons: New York, 1981.

Chemistry of Coal Utilization, Supplementary Volume; Lowry, H.H. Ed.; John Wiley and Sons: New York, 1963.

Dryden, I.G.C.; Sparham, G.A. BCURA Monthly Bulletin 1963, 27, 1.

Eccles, R.M.; DeVaux, G.R. Chemical Engineering Progress May 1981, 80-85.

Fallon, P.T.; Bhatt, B.; Steinberg, M. Fuel Process. Technol. 3; Elsevier Scientific Publishing Company, 1980, pp 155-168.

Fred, J.; Jackson, D.M.; Schmid, B.K. Chemical Engineering Progress May 1981, 86-91.

Friedman, S.; Hiteshue, R.W.; Schlesinger, M.D. U.S. Bureau of Mines, 1964, R.I. No. 6470.

Furimsky, E.; MacPhee, J.A.; Vancea, L.; Ciavaglia, L.A.; Nandi, B.N. "Effect of Oxidation on the Chemical Nature and Distribution of Temperature Pyrolysis Products from Bituminous Coal"; Fuel April 1983, 62, 397-400.

Gomez, M.; Goodman, J.B.; Parry, V.F. "Low-Temperature Tar from Fluidized Carbonizing Reactors"; February 1957, USBM RI No. 5302.

Gomez, M.; Landers, W.S.; Boyd, C.K. "Estimation of Low-Temperature Carbonization Product Yields-Utah Coal Fields"; 1967, USBM RI No. 6990.

Gomez, M.; Landers, W.S.; Schultz, J.L.; Sharkey Jr., A.G. "Distribution of Phenols in Low-Temperature Tar from Low-Rank Coals"; 1965, USBM RI No. 6586.

Goodman, J.B.; Gomez, M.; Parry, V.F. "Laboratory Carbonization Assay of Low-Rank Coals at Low, Medium, and High Temperatures"; January 1958, USBM RI No. 5383.

Graff, R.A.; Brandes, S.D. "Coal Liquefaction by Steam Pyrolysis"; The Clean Fuels Institute, The City College CUNY: New York, New York.

Hill, G.R.; Meuzelaar, H.L.C.; Heosterey, B.L. "Characterization of Coal Pyrolysis Liquids"; University of Utah, Salt Lake City, Utah, prepared for EPRI Project 2505-3, April 1987.

Howard, J.B.; Peters, W.A.; Serio, M.A. Final Research Report; EPRI, AP-1803, Research Project 986-5, April 1981.

Hydrocarbon Processing September 1976, 156.

Jones, J.F. et al. "Char Oil Energy Development, Final Report"; 8/18/71-6/30/75, VI, September 1975.

Karr, Jr. C.; Comberiati, C.R.; McCaskill, K.B.; Estep, P.A. "Influence of Continuous Carbonization Method, Temperature, and Carrier Gas on Amounts of Individual Pyrolysis Products from Subbituminous Coal"; 1966, USBM RI No. 6839.

Khan, M.R. Fuel Science and Technology International 1987, 5 (2) 185-231.

Knell, E.W. et al., "Flash Pyrolysis Coal Liquefaction Process Development"; Annual Report, January-December 1977; FE-72244-20.

Knell, E.W. et al., "Flash Pyrolysis Coal Liquifaction Process Development"; Annual Report, January-December 1977; FE-2244-20.

Mrochek, J.E.; Krishnan, R.P.; Graves, R.L. "Characterization and Upgrading of Coal Liquids Derived from Mild Gasification"; Oak Ridge National Laboratory, American Chemical Society Meeting, Miami Beach, Florida, September 10-15, 1989.

Ode, W.H.; Selvig, W.A. "Low Temperature Distillation Yields of Primary Tar and Light Oils from Coals of Various Ranks and Types"; March 1944, USBM RI No. 3748.

Parry, V.F.; Landers, W.S.; Wagner, E.O.; Goodman, J.B.; Lammers, G.C. "Drying and Carbonizing Fine Coal in Entrained and Fluidized State"; April 1953, USBM RI No. 4954.

Pelofsky, A.H. et al. "Short Residence Coal Hydropyrolysis"; Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. ACS Annual Meeting, August 1976.

Protopapas, T.E. Project Manager. Annotated Review and Classification of Char Producing Processes; Fuel and Mineral Resources, Inc.: Reston, Virginia, 1987.

Schmidt, L.D.; Elder, J.L.; Davis, J.D. Fuel 1940, 32, 548.

Schmidt, L.D.; Elder, J.L.; Davis, J.D. Fuel 1937, 16, 39.

Schroeder, W.C. "Hydrogenation of Coal"; U.S. Patent 2,030,297, 1962.

Sommers, H. VGB Kraftwerkstechnik 1974, 5, 360.

Sundaram, M.S.; Steinberg, M.; Fallon, P.T. Flash Hydropyrolysis of Coal for Conversion to Liquid and Gaseous Fuels; Brookhaven National Laboratory: Upton, New York, 1982; Summary Report No. DOE/METTC/82-48.

Suuberg, E.M.; Peters, W.A.; Howard, J.B. Advances in Chemistry Series, No. 183, Thermal Hydrocarbon Chemistry; Oblad, Alex. G; Davis, Hugbert G.; Eddinger, R. Tracy, Eds.; American Chemical Society; 1979; pp 239-257.

Suuberg, E.M.; Peters, W.A.; Howard, J.B. Fuel 1980, 59, 405.

Talwaker, A.T. A Topical Report on Coal Pyrolysis; DOE/MC/19316-1408.

Tao, J.; Jones, J.P. III Ind. Heating November 1982, 26-31.

Vick, G.K.; Epperly, W.R. Science July 1982, 287, 311-316.

Walters, J.G.; Ortuglio, C. "Analysis of Light Oils from Fluidized Carbonization"; 1966, USBM RI No. 6709.

Walters, J.G.; Ortuglio, C,; Glaenzer, J. "Yields and Analyses of Tars and Light Oils from Carbonization of U.S. Coals"; USBM Bulletin No. 643, 1967.

Willson, W.G.; Knudson, C.L.; Rindt, J.R.; Smith, E. "Feasibility of Producing Jet Fuel from GPGP By-Products"; Quarterly Technical Progress Report for November 26, 1986 - February 16, 1987, Contract No. DE-AC22-87PC90016.

6.2 Chemistry of Sulfur Removal in Mild Gas

SULFUR REMOVAL FROM COAL/MILD GASIFICATION CHAR

Annual Technical Project Report
for the Period July 1, 1989 through June 30, 1990

Including

the Quarterly Technical Progress Report
for the Period April through June 1990

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SULFUR REMOVAL FROM COAL/MILD GASIFICATION CHAR

1.0 INTRODUCTION

The objective of this research was to develop analytical methods for quantitating the sulfur forms in coal and char. Better analytical methods are needed to more accurately determine the chemistry of the sulfur contained in raw coal and char, to enable development of effective means for sulfur removal from coal--either during or before mild gasification char production. A primary goal of this work is to develop techniques for directly quantitating the pyritic and organic sulfur in coal and chars. Direct measurement techniques are needed, because in the American Society for Testing and Materials (ASTM) method for determining sulfur forms in coal, the pyritic sulfur content is calculated based on the amount of iron extracted from the coal using nitric acid, and the organic sulfur content is calculated to be the difference between the sum of the pyritic and sulfatic sulfur contents and the total sulfur content (1). For coals (and chars) with significant quantities of nitric acid-soluble iron in forms other than pyrite (such as pyrrhotite and iron oxides), the ASTM method may provide an inaccurate measurement of pyritic sulfur content, which would also result in an inaccurate measurement of organic sulfur content. It should be noted that the instructions published with the description of the ASTM sulfur forms analysis explicitly state that the method is not suitable for the analysis of coke.

The research is divided into two tasks: analytical methods development and char characterization. The analytical methods developed will be used (in addition to ASTM methods) to quantitate sulfur in chars produced in the 1-lb/hr continuous fluid-bed reactor (CFBR) at the University of North Dakota Energy and Environmental Research Center (EERC) as a means of evaluating in situ sulfur removal techniques for incorporation into the mild gasification process under development at EERC. Also analyzed were chars made in a thermogravimetric analysis (TGA) instrument.

2.0 CHAR PRODUCTION

Analytical methods development studies and char characterization studies were performed on Indiana No. 3 coal and chars produced from the coal using three reactors: the 1-lb/hr CFBR, the 30-lb/hr hydrogen production reactor, and a 30-gram capacity TGA instrument. The following chars were analyzed:

1. High sulfur-content char--produced under mild conditions that remove very little sulfur.
2. Low sulfur-content char--produced under conditions that significantly reduce total sulfur content.
3. Low pyritic sulfur-content char--produced at high temperature.
4. Char produced in the presence of ionic calcium--dolomite (calcium-magnesium carbonate)--under an atmosphere of 90% hydrogen/10% nitrogen (1).
5. Char produced under nitric oxide (NO).
6. Char produced from coal oxidized with iodine.

7. Char produced from coal solubilized with sodium hypochlorite (bleach).

To obtain Chars 1-3, a series of chars were produced in the CFBR under nitrogen, using varying temperatures and residence times. The chars were sent to AMAX Research & Development, Golden, Colorado, for ASTM sulfur forms and total sulfur analysis. Total sulfur analysis was also performed at EERC with a Leco sulfur analyzer. The results of the coal and char sulfur analyses are shown in Table 1. The actual feed coal for the CFBR was -60 x +200-mesh coal. Removal of the -200-mesh material from the initial -60-mesh feed coal was necessitated after an unsuccessful attempt to feed the -60-mesh coal. All chars were produced under nitrogen with no steam, using staged heating, which

TABLE 1

CFBR CHARS FOR ANALYTICAL METHODS DEVELOPMENT

		wt% Sulfur (moisture-free)				
		Total Sulfur		Sulfur Forms (AMAX)		
		EERC	AMAX	Pyr.	SO_4	Org.
Indiana No. 3 Coal						
-60 x +200 mesh (CFBR Feed Coal)		4.90	5.26	2.20	0.32	2.73
Chars						
Temp., °F (°C)	Residence Time					
1) 660° (350°)	25 min	5.13	5.62	2.45	0.29	2.88
2) 660° (350°)	2 hr	5.07	5.72	2.57	0.09	3.06
3) 750° (400°)	25 min	4.97	5.00	2.13	0.16	2.72
4) 750° (400°)	2 hr	4.86	5.02	2.11	0.11	2.80
5) 840° (450°)	25 min	4.75	5.03	2.16	0.15	2.72
6) 840° (450°)	2 hr	4.87	4.96	2.06	0.14	2.75
7) 930° (500°)	25 min	4.59	4.83	1.84	0.12	2.87
8) 1290° (700°)	25 min	3.82	4.25	0.54	0.06	3.65
9) 1290° (700°)	2 hr	4.07	NA[1]	NA	NA	NA
10) 1470° (800°)	6 hr[2]	NA	1.25	0.04	0.04	1.17
11) 1290° (700°)	25 min[3]	NA	2.80	0.41	0.04	2.15

[1] Not analyzed.
[2] Char 10 was made in the 30-lb/hr gasifier normally used for catalytic gasification.
[3] Char 11 was made with dolomite, which was added in an amount equivalent to 20% of the weight of 930°F (500°C) char fed to the reactor.

was performed as follows: Coal is reacted at 660°F (350°C) to yield char, which is then reacted at 750°F (400°C) to yield char, which is then reacted at 840°F (450°C), etc.

Based on the analytical results, the chars representative of the sulfur form and content requirements that define Chars 1-3 were selected for study in the development of sulfur analysis techniques. Char 1 was chosen as the high-sulfur content char, and Char 10 was chosen as both the low-sulfur content and the low-pyritic-sulfur content char. Char 8 was substituted for Char 10 in two of the analytical studies (Supercritical Carbon Dioxide Extraction and Perchloroethylene Soxhlet Extraction), since at the time of the studies, Char 10 was unavailable. Char 5 was also selected for analysis, since its 840°F (450°C) reaction temperature fell within the temperature range of observed agglomeration effects.

3.0 SUPERCRITICAL CARBON DIOXIDE EXTRACTION

Selected 400-mg coal and char samples were extracted sequentially with about 1.2 mL/min of supercritical CO_2 (400 atm of pressure) at 131°F (55°C) for 10 minutes, then at 840°F (450°C) for an additional 25 minutes (about 15 minutes of this time was required for heating to 840°F). The extracts were designated as the Low-Temperature Extract (collected over the first 10 minutes of extraction) and the High-Temperature Extract (collected over the remaining 25 minutes), respectively. The extracts were collected by bubbling the extracting CO_2 fluid through a vial containing benzene. Benzothiazole was then added as an internal standard, and the extracts were analyzed using gas chromatography/mass spectrometry (GC/MS) and GC/atomic emission detection (GC/AED). The recently acquired atomic emission detector can monitor individual compounds (as they elute from a GC column) for the presence of sulfur, carbon, hydrogen, nitrogen, and oxygen. Most importantly for this work, the AED can simultaneously monitor for the presence of carbon, nitrogen, and sulfur. The atomic emission data can be stored and used to quantitate (by weight percent) the amount of sulfur, nitrogen, and carbon in an extract, or in a specified simulated distillate fraction of the extract. This allows plotting a simulated distillation curve showing the weight percent of sulfur distilling over a specified temperature range.

Before the supercritical fluid extracts were analyzed, the ability of the AED to accurately quantitate organic sulfur on a weight-percent basis (regardless of how the sulfur was bound) was tested by analyzing 13 quantitative standards including alkylthiophenes, thiazole, thiocresol, mono- and di-sulfides, alkylthiols, and dibenzothiophene. On the basis of these analyses, it was determined that the GC/AED response per unit sulfur was the same (with a relative standard deviation of plus or minus 10%), regardless of how the sulfur was bound. Thus an average response factor can be used to quantitate the organic sulfur in each extract based on GC/AED analysis. The calibration for elemental sulfur (S_8) was not as successful; however, this is thought to be a chromatographic rather than an AED problem. The amounts of sulfur extracted from the coal and four chars are shown in Table 2 as micrograms of sulfur extracted per 400 milligrams of sample. Extractions were performed on three samples of -60-mesh Indiana No. 3 coal and two samples of each char.

TABLE 2

SUPERCRITICALLY EXTRACTED SULFUR

Sample		(μg S/400 mg Sample)					
		Extracted S 131°F (55°C)			Extracted S 840°F (450°C)		
		Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Indiana Coal		176	212	168	173	185	178
Char, Temp., °F (°C)	Residence Time						
660° (350°)	25 min	ND[1]	ND	NP[2]	215	207	NP
840° (450°)	25 min	ND	ND	NP	39	37	NP
1290° (700°)	25 min	ND	ND	NP	<1	<1	NP
660° (350°)	2 hr	ND	ND	NP	179	212	NP
750° (400°)	25 min	ND	ND	NP	117	126	NP

[1] Not detected (detection limit was <1 μg S/sample).
[2] Not performed.

With the exception of elemental sulfur, no sulfur species, and only traces of other organics, were found in the low-temperature extracts. The elemental sulfur was found primarily as S_8, with lesser amounts as S_6. None of the low-temperature extracts of the chars contained detectable amounts of any kind of sulfur. Approximately 150 significant sulfur organics were extracted from the chars (except the 1290°F (700°C) char) at 840°F (450°C). GC/MS analysis showed phenol- and catechol-related organics as major non-sulfur-containing species and alkyl thiophenes and alkyl benzothiophenes as the major sulfur-containing species (see Figures 1 and 2).

Table 3 shows the sulfur contents (determined using a Leco sulfur analyzer) of the coal and chars before and after extraction. The higher sulfur content of the extracted coal (compared to the unextracted coal) is due to the extraction of a significant amount of nonsulfur-containing organic material in addition to organic sulfur compounds. In order to compare the sulfur contents of the raw and extracted coal on an equal basis, the initial weight of coal can be adjusted by subtracting the weight of these other extractable organics, which results in a coal sulfur content, on an organic extract-free basis, of 6.53%. Similar calculations can be performed with the char sulfur data to show effective sulfur content reductions of about 1.5 percentage points for all of the chars except the 1290°F (700°C) char. The data for this char indicate that treatment at 1290°F (700°C) causes organic sulfur to be virtually inaccessible to the supercritical carbon dioxide.

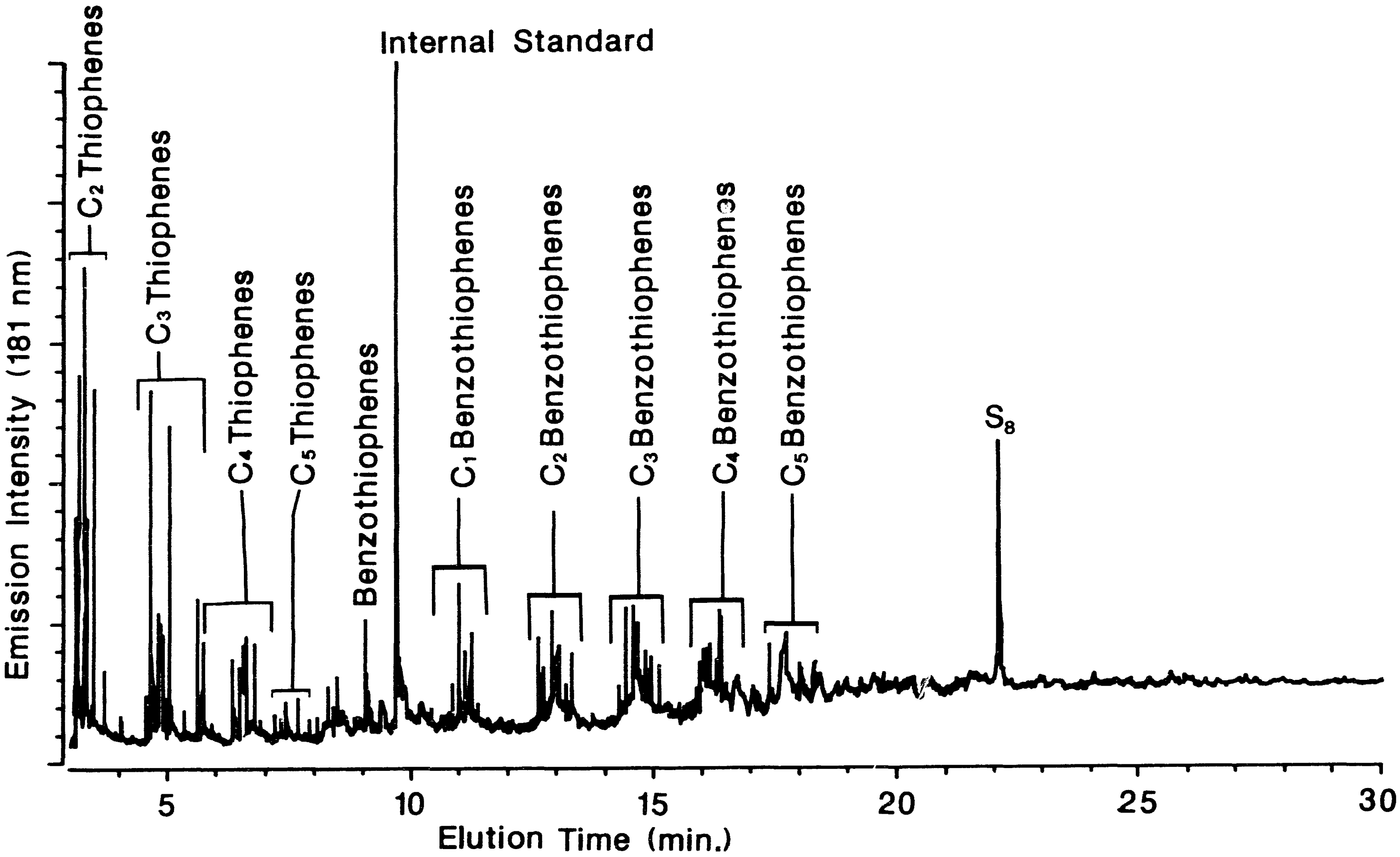

Figure 1. AED sulfur chromatogram showing sulfur-containing species extracted at 840°F (450°C) from 660°F (350°C) char using supercritical carbon dioxide. The vertical scale is the relative emission intensity at 181 nm.

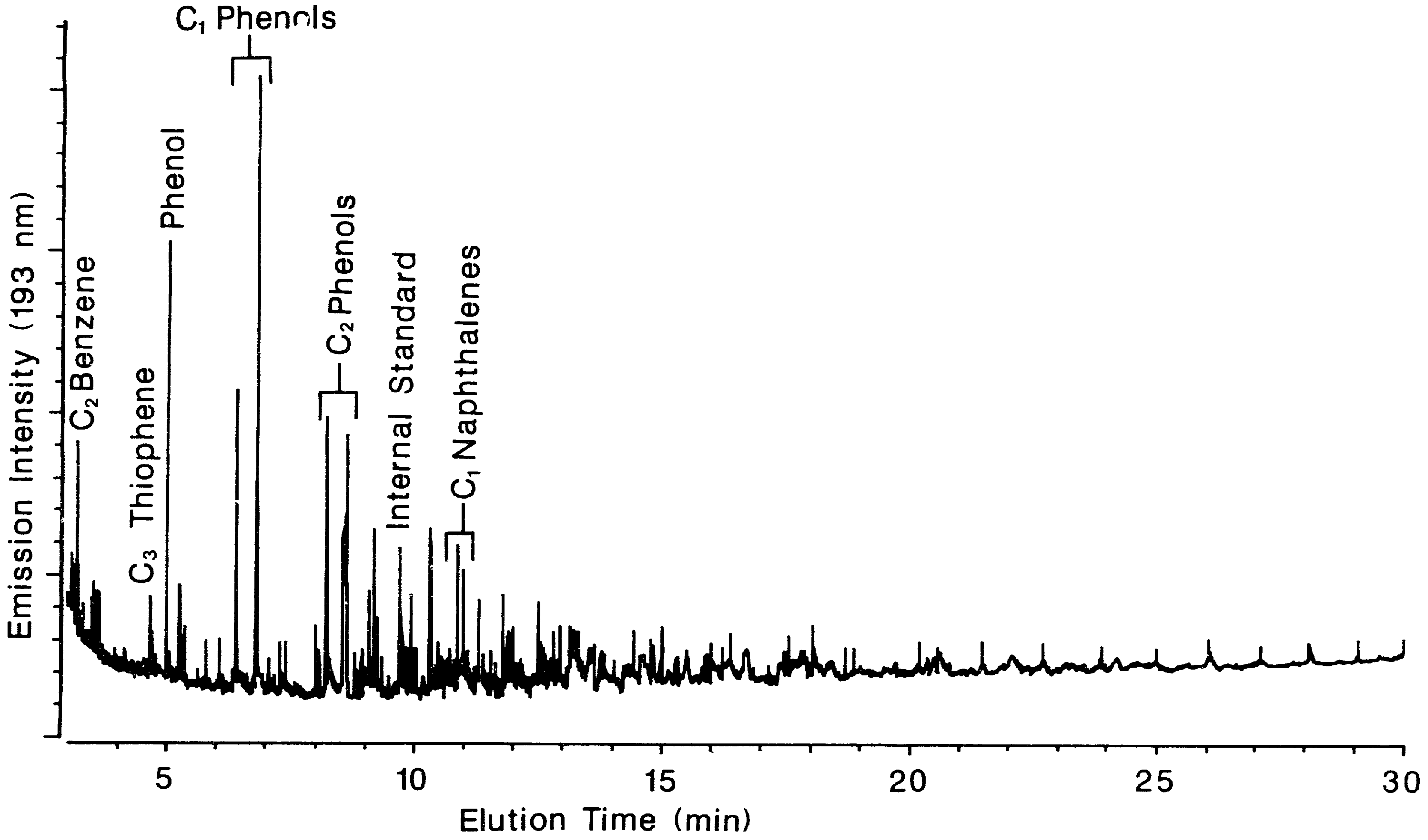

Figure 2. AED carbon chromatogram showing carbon- (as well as sulfur-) containing species extracted at 840°F (450°C) from 660°F (350°C) char, using supercritical carbon dioxide. Sulfur-containing species are detected when the AED monitors for carbon, since these species also contain carbon. The vertical scale is the relative emission intensity at 193 nm.

TABLE 3

SULFUR CONTENT OF SUPERCRITICAL CARBON DIOXIDE EXTRACTS[1]

		Sulfur Content (wt%)			
		Unextracted Samples	Extracted Samples (Duplicate Tests)		
Indiana Coal, MF		5.43	5.36	5.88	5.75
Char, Temp., °F (°C)	Residence Time				
660° (350°)	25 min	5.13	4.26	4.79	NP[2]
660° (350°)	2 hr	5.07	4.30	3.91	NP
750° (400°)	25 min	4.97	4.00	4.40	NP
840° (450°)	25 min	4.75	4.25	4.17	NP
1290° (700°)	25 min	3.82	3.85	3.74	NP

[1] Extraction at 131°F (55°C) for 10 min, then at 840°F (450°C) for 25 min.
[2] Not performed.

The data in Table 3 show that supercritical carbon dioxide extraction can lower measured sulfur content in chars by as much as 20%. This result could have significance if it could be proven that all or most of the sulfur extracted from the chars was organic. However, quantitation of the sulfur in the extracts using GC/MS and GC/AED did not yield sulfur extract weights equal to those calculated based on the Leco sulfur analyses of the chars before and after extraction. In most cases, GC quantitation accounted for only about 20% of the sulfur calculated to have been extracted. Possible explanations for this include:

1. A significant portion of the sulfur removed from the coal and chars is extracted as, or reacts during or after extraction to form, S_2, which, because of its high volatility, would be difficult to detect using the chromatographic techniques employed for this work.

2. A significant portion of the extracted sulfur is contained in gaseous molecules that are insoluble, or only marginally soluble, in the benzene used to trap the extracted sulfur compounds. However, such molecules would escape into the atmosphere and probably emit unpleasant odors--and none were noticed.

3. A significant portion of the extracted sulfur is contained in molecules too large (and/or nonvolatile) to elute through the GC column.

4.0 SOXHLET PERCHLOROETHYLENE EXTRACTION

A sample of -60 x +200-mesh Indiana No. 3 coal and four chars made from the coal were Soxhlet-extracted for 5 hours using perchloroethylene at 250°F (121°C) (2). All of the chars were made in the 1-lb/hr CFBR; three were made under nitrogen, and one was made under a mixture of hydrogen and nitrogen, in the presence of dolomite (dolomite was added to 930°F (500°C) char in an amount equal to 20 wt% of the char). The results of the extractions are shown in Table 4.

In Table 4, the column labeled "Total Wt% Extracted" refers to the percentage of the sample extracted, which includes both sulfur-containing and nonsulfur-containing species. The weight of this extracted material was subtracted from the total weight of each sample to calculate its moisture- and oil-free (MOF) sulfur content before extraction. The percentage of sulfur extracted was then obtained by comparing the MOF before-extraction sulfur content with the after-extraction sulfur content.

Comparison of the perchloroethylene extraction results with the results of the supercritical carbon dioxide extractions shows that both solvents removed similar amounts of sulfur from the coal and chars. Also, the two extraction techniques gave almost identical sulfur content reductions when performed on identical char samples, and neither solvent extracted a significant quantity of sulfur from the 1290°F (700°C) char.

TABLE 4

PERCHLOROETHYLENE EXTRACTIONS

	Total Wt% Extracted	Wt% Sulfur			% Sulfur Removed
		Before Ex.	Before Ex. (MOF[1])	After Ex.	
-60 x +200-mesh Indiana	17.93	4.82	5.87	4.46	24.02
660°F (350°C) Char	14.15	5.65	6.58	4.43	32.67
840°F (450°C) Char	17.13	4.62	5.57	4.10	26.39
1290°F (700°C) Char	0	3.74	3.74	3.69	1.30
1290°F (700°C) Char (with dolomite)	0	4.28	4.28	3.61	15.65

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[1] Moisture- and oil-free. Sulfur contents in this column were calculated based on the weight of coal remaining after subtracting the weight of the material extracted with perchloroethylene.

5.0 OTHER ORGANIC SULFUR ANALYSES

Two methods were studied for organic sulfur quantitation based on derivatization of the sulfur compounds. The first involved reacting coal and char with t-butylhypochlorite to selectively oxidize organic sulfur species to sulfoxides, which could then be quantitated using infrared (IR) spectroscopy. Although IR analysis indicated that the hypochlorite oxidized some of the carbon species in the coal, spectral subtraction techniques revealed no evidence of organic sulfur oxidation. The second method involved further derivatization of the t-butylhypochlorite-oxidized coal and char by treatment with trimethyloxonium tetrafluoroborate to convert any sulfoxides to methoxysulfonium salts. Unfortunately, solid-state carbon-13 nuclear magnetic resonance (NMR) analysis did not detect the presence of any methoxysulfonium salts in either the coal or char samples. Apparently, the t-butylhypochlorite was unable to react with the coal/char organic sulfur species under the conditions investigated.

6.0 INORGANIC ANALYSES

X-ray fluorescence (XRF) analysis is normally performed on the ash of a coal to determine the coal's mineral content, but the technique can also be applied (with varying degrees of accuracy) to raw coal. The quantitative accuracy of the technique when applied to coal usually depends primarily on the coal's carbon content: the higher the carbon content, the less accurate the analysis. According to XRF analysis of -60-mesh Indiana No. 3 coal, the moisture-free (MF) sulfur content of the coal is 3.5%. Leco sulfur analysis puts the coal's MF sulfur content at 5.1%, and XRF analysis of the ash of the coal gives an MF coal sulfur content of 4.1%.

X-ray diffraction (XRD) can be used to detect pyrite (FeS_2) and pyrrhotite (FeS_{1-x}) in ashes made from coal and char samples. Several factors influence the accuracy and ability of the instrument to detect these crystalline minerals. One factor is the quantity of the mineral compared to the quantity of amorphous material in a sample. If the quantity of amorphous material (which, in the case of most coal and char samples, is primarily carbon) is relatively high, the signal from the crystalline mineral will be obscured. For this reason, the coal or char sample is normally ashed to lower the ratio of carbon to mineral species. Several ashing methods can be employed, depending on which mineral species are to be analyzed. Two commonly used ashing procedures at EERC are high-temperature ashing and low-temperature ashing (3).

Whereas high-temperature ashing is performed when it is desired to simply remove carbon, low-temperature ashing is performed to both remove carbon and minimize the occurrence of thermally driven mineral transformations and sulfur vaporization. The effect of low-temperature ashing can be seen in Table 5, which is a comparison of selected elemental concentrations in oxygen-free low- and high-temperature ashes made from Indiana No. 3 coal, as determined using XRF analysis. The low-temperature ashes were analyzed using XRD, XRF, and SEMPC. CCSEM analysis was also performed on the coal and chars.

TABLE 5

COMPARISON OF LOW- AND HIGH-TEMPERATURE ASHES (XRF)

	-60-mesh Indiana No. 3 Low-temp. ash, wt%	-60 x +200-mesh Indiana No. 3 High-temp. ash, wt%
Silicon	25.7	35.8
Aluminum	13.5	19.3
Iron	28.1	33.4
Calcium	5.9	4.1
Magnesium	1.0	1.1
Potassium	1.0	2.5
Sulfur	22.3	2.5
Other	2.5	1.3

Another consideration when using XRD to quantitate sulfur-containing minerals is that a crystalline mineral that produces a large signal can mask the signal of another mineral that produces a smaller signal, or is present in a lower concentration. Also important is the degree of crystallinity, which is determined by several factors, including the purity of the crystal lattice and the type of lattice formation. Finally, preparation of the sample includes a grinding step, and improper grinding may affect quantitation of the XRD signal. If a certain mineral is, on the average, contained in larger particles than the average particle size of the sample, the larger signal from the larger-grained mineral may yield an artificially inflated concentration of the mineral. In light of these described considerations, it is important to note that sulfide minerals are reported to be massive and poorly crystallized (6).

For the purpose of this study, the quantities of pyrite and pyrrhotite in the 1290° and 1470°F (700° and 800°C) chars (as determined by the ASTM sulfur forms analysis) are assumed to be too low for detection by XRD. In regard to the coal and the lower temperature chars, XRD can be used to validate the presence of pyrite and pyrrhotite crystalline phases in these materials, but XRD cannot be used to validate the lack of these phases. The reason for this is that XRD only detects crystalline material. If a mineral has melted, either during the mild gasification reaction or during ashing of a product sample, it may exist in the sample as localized areas of amorphous material with the stoichiometric composition of the given mineral. If held above its melting temperature for a sufficient time, the melted mineral will assimilate into any liquid present. In the case of pyrite and pyrrhotite, if these minerals are melted and then quenched quickly, they will form an amorphous "glass" with the same stoichiometric composition as their crystalline counterparts. However, if the molten minerals are quenched slowly enough, they will undergo crystallization, which will allow their detection by XRD. In either case, assimilation of the iron and/or sulfur into the melt phase, or assimilation of other minerals into the pyrite and pyrrhotite crystalline phases, can cause the formation of impure, irregularly crystallized minerals, which cannot be accurately quantitated using XRD.

The scanning electron microscope point count (SEMPC) technique can detect the stoichiometric chemical composition of both the crystalline and amorphous phases of 245 3-square micrometer areas or "points" in a given sample. However, differentiation between crystalline and amorphous phases is performed by matching detected stoichiometric compositions with known crystalline stoichiometric compositions, rather than by a true crystallographic technique such as XRD. The advantage of SEMPC is that it can detect minerals which have melted.

Before being analyzed, SEMPC samples are ashed to reduce their carbon content, because in the presence of a large amount of carbonaceous material, mineral points are harder for the SEM beam to locate. In the analysis, the SEM beam is rastered across a polished cross section of the sample "plug" (which consists of sample grains embedded in hardened epoxy) until 245 mineral point compositions have been recorded. The SEMPC analysis is primarily suited for the detection of inorganic sulfur, since organically bound sulfur is normally oxidized and lost as vapor during the ashing process. Also, any organic sulfur molecules remaining after ashing are typically very finely sized, which makes them difficult to detect with the SEM. The inorganic sulfur content determined with the SEMPC analysis includes both the sulfatic and pyritic sulfur contents.

6.1 CCSEM Analysis

A sample of -60-mesh Indiana No. 3 coal was analyzed for mineral content using computer-controlled scanning electron microscopy (CCSEM). Details of the analytical procedure have been previously reported (5,6). A brief overview of the technique is provided here. The CCSEM analysis uses backscattered electron imaging (BEI) and energy-dispersive spectra (EDS) acquisition to detect minerals in coal and char.

A sample of ground coal or char is mixed with an epoxy and a "plug" is made. After hardening, the plug, which contains sample particles embedded in epoxy, is sliced, and the surface of the resulting cross section of the plug is polished. It is upon this polished cross-sectional surface that the CCSEM analysis is performed. Since mineral and ash particles appear brighter in BEI than the lower atomic number epoxy or coal matrix material, a distinction can be made between coal, epoxy, and mineral grains. Using software developed at EERC (5,6), the CCSEM electron beam is programmed to scan over the field of view to locate the bright inclusions that correspond to mineral or ash particles. On finding a particle, eight diameter-measurements are made of the particle, its center is located, and EDS from the particle are collected for 2 seconds. The system is set up to analyze for 12 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Ba, and Ti. The CCSEM software classifies the analyzed particles into categories based on size and composition. CCSEM analysis can provide quantitative data regarding the discrete mineral species and noncrystalline inorganic phases present in a coal or char.

A breakdown by mineral species of the total number of particles analyzed in a sample of -60-mesh Indiana No. 3 coal is given in Table 6. The definitions used to determine a particle's mineral/inorganic phase classification are listed in Table 7. These definitions are based on published compositions of known minerals and an extensive data base of mineral chemistries obtained by microprobe analyses performed at EERC (7,8). Because the SEM provides only elemental composition data and not crystallographic data, certain inorganic particle types that have compositions similar to a defined mineral may not have the same crystallographic properties as the mineral. Also, because no atomic number, absorbance, or fluorescence (ZAF) corrections are used in the CCSEM analyses, some mineral/inorganic phase definitions are relatively broad. In all cases, for a particle to be defined as a particular mineral/inorganic phase, the sum of its concentrations of the required constituent elements for the given mineral/inorganic phase classification must equal 80% or greater.

Composition of the coal mineral content, by weight percent of each mineral species or inorganic phase, is presented in Table 8. The amount of each mineral species or inorganic phase as a weight percentage of the raw coal is given in Table 9.

An inherent problem with using computer-controlled SEM (CCSEM) to determine sulfur content in coal is that quantitation (with the instrumentation and software presently employed at EERC) is ordinarily based on energy-dispersive spectra (EDS) emitted from analyzed particles. EDS for an analyzed particle can vary in intensity depending on the matrix surrounding the particle and the composition of any particles in close proximity. These interferences can result in significant quantitation errors. However, the technique is useful for determining whether certain mineral species are concentrated in specific particle-size ranges. CCSEM data obtained on the low-temperature ashes of the chars and coal showed no pattern of pyritic sulfur concentration as a function of particle size.

Table 10 compares inorganic sulfur contents (pyritic plus sulfatic sulfur) obtained using SEMPC data with inorganic sulfur contents obtained using the ASTM sulfur forms analysis. The table shows good agreement between the two analytical techniques for the Indiana coal and the chars produced at 660° and 840°F (350° and 450°C). However, the data for the 1290° and 1470°F (700° and 800°C) chars did not compare well.

Discrepancy between the values calculated using SEMPC point and bulk data is due to round-off errors made in calculating the bulk values. Table 11 shows data obtained by XRD analysis of low-temperature ashes made from the feed coal and the four chars.

As stated above, an inherent problem with using CCSEM to determine sulfur content in coal derives from the use of energy-dispersive spectra for quantitation. However, accurate sulfur quantitation may be possible using wavelength dispersive spectra SEM (WDS-SEM), since WDS are not subject to as severe a variation in intensity as EDS.

TABLE 6

DISCRETE MINERAL/INORGANIC PHASE PARTICLES IN INDIANA NO. 3 COAL

Mineral/Inorganic Phase	% of Total Particles Analyzed
Quartz	14.0
Aluminosilicate	13.8
Potassium-Aluminosilicate	7.4
Iron-Aluminosilicate	2.0
Iron Oxide	10.3
Calcite	3.5
Pyrite	23.0
Gypsum	2.4
Iron Sulfate/Pyrrhotite	11.0
Other	12.6
Number of Particles Analyzed	1719.0

TABLE 7

MINERAL/INORGANIC PHASE DEFINITIONS

Mineral/Inorganic Phase	% of Total X-Ray Counts Required
Quartz	$Al<5$, $Si\geq80$
Aluminosilicate	$K<5$, $Ca<5$, $Fe<5$, $Si>15$, $Al>15$, $Si+Al\geq80$
Potassium-Aluminosilicate	$K\geq Ca$, $K\geq Fe$, $K\geq5$, $Si\geq10$, $Al\geq10$, $K+Si+Al\geq80$
Iron-Aluminosilicate	$S<5$, $Fe>Ca$, $Fe>K$, $Fe>5$, $Si>10$, $Al>10$, $Fe+Al+Si\geq80$
Iron Oxide	$Si<10$, $S<5$, $Mg<5$, $Al<5$, $Fe\geq80$
Calcite	$S<10$, $Mg<5$, $Si<5$, $P<15$, $Ti<5$, $Ba<5$, $Ca>80$
Pyrite	$Ca\leq10$, $10\leq Fe<40$, $S\geq10$, $Fe+S\geq80$
Gypsum	$Ti+Ba<12$, $Si<10$, $S>20$, $Ca\geq20$, $Ca+S\geq80$
Iron Sulfate/Pyrrhotite	$10\leq S<40$, $Fe+S\geq80$

TABLE 8

COMPOSITION OF INDIANA NO. 3 COAL MINERAL CONTENT

Mineral/Inorganic Phase	Wt% of Mineral Content
Quartz	5.4
Aluminosilicate	8.6
Potassium-Aluminosilicate	5.3
Iron-Aluminosilicate	0.5
Iron Oxide	15.6
Calcite	3.4
Pyrite	37.0
Gypsum	2.6
Iron Sulfate/Pyrrhotite	14.4
Other	7.2

Note: Error margin is 15% of each wt% value

TABLE 9

MINERAL COMPOSITION OF INDIANA NO. 3 COAL

Mineral/Inorganic Phase	Wt% of Coal
Quartz	0.3
Aluminosilicate	0.5
Potassium-Aluminosilicate	0.3
Iron-Aluminosilicate	0.0
Iron Oxide	1.0
Calcite	0.2
Pyrite	2.3
Gypsum	0.2
Iron Sulfate/Pyrrhotite	0.9
Other Minerals	0.5
Total Minerals	6.2

Note: Error margin is 15% of each wt% value

TABLE 10

COMPARISON OF ASTM AND SEMPC INORGANIC SULFUR CONTENTS

	ASTM	SEMPC (point data)	SEMPC (bulk data)	XRFA
Indiana Coal	2.52	2.52	2.85	3.31
350°C Char	2.74	3.23	3.66	4.68
450°C Char	2.31	2.93	3.21	4.27
700°C Char	0.60	3.04 (3.46)[1]	3.67 (4.41)[1]	3.92
800°C Char	0.08	2.46	2.12	1.89

[1] Second analysis.

TABLE 11

XRD DATA

	Major Phases	Minor Phases	Note
Coal	Quartz, Pyrite	Kaolinite, Calcite	XRD agrees with SEMPC.
350°C Char	Quartz, Pyrite, Kaolinite	Calcite, Anhydrite	XRD agrees with SEMPC.
450°C Char	Quartz, Pyrite	Kaolinite	SEMPC shows pyrrhotite, XRD does not.
700°C Char	Quartz	Pyrrhotite	SEMPC shows pyrite (very small quantity), XRD does not.
800°C Char	Quartz	Anhydrite, Kaolinite	SEMPC shows both pyrite and pyrrhotite, XRD does not.

Note: Kaolinite, calcite, and anhydrite are artifacts of the low-temperature ashing process.

A proposed method for sulfur quantitation involves performing three sequential WDS-SEM scans across a specific area of the sample, which has been mounted in an epoxy plug, cross-sectioned, and polished. When the plug is cross-sectioned, particles contained in the plug are also cross-sectioned. This random slicing of particles theoretically allows SEM, which is a surface analysis technique, to be used for bulk analysis. However, since SEM is a surface analysis technique, the described method will need to be validated by other more widely accepted bulk quantitative analyses. The first SEM scan monitors for sulfur, the second for iron, and the third for calcium. Each scan traverses a straight line between identical starting and ending locations on the sample plug. The three scans are "superimposed" on each other to determine the occurrence of pyrite, calcium sulfate, and organic sulfur, using the following rationale: the simultaneous detection of iron and sulfur is indicative of pyrite, the simultaneous detection of calcium and sulfur is indicative of calcium sulfate, and the detection of sulfur without the simultaneous detection of either iron or calcium is indicative of organic sulfur. The successful development of this method would provide a means of directly quantitating the pyritic and organic sulfur contents in coal. Preliminary analyses were performed on Indiana coal, and standards were prepared using pyrite, calcium sulfate, and elemental sulfur ground to particle sizes similar to those found in the coal and chars. Unfortunately, a breakdown in the SEM computer system prohibited further evaluation of the method prior to the termination of the contract.

6.2 Oxidation of Coal with Iodine

Several coal samples were mixed with iodine in an attempt to oxidize organic sulfur. Iodine was mixed with coal in amounts equivalent to 5 and 20% of the weight of a coal sample. The mixtures were allowed to stand overnight and were then heated in the TGA instrument at various temperatures. Also, several tests were performed using steam as a reactant. The products were then analyzed for total sulfur content. The results (Table 12) show that iodine significantly affects sulfur content during mild gasification; however, the effect of iodine on organic sulfur was not determined because the samples produced were too small to allow the performance of sulfur forms analysis.

TABLE 12

IODINE OXIDATION OF INDIANA COAL

Sample	% added I_2	Reaction Temp, °F (°C)	Steam	Wt% Sulfur
Feed Coal[1]				4.81
Char 1	5	1020 (550)	No	2.97
Char 2	5	1470 (800)	No	3.22
Char 3	20	1290 (700)	Yes	2.04
Char 4	20	1290 (700)	No	1.47[2]
Char 5	20	1470 (800)	Yes	2.16
Char 6	20	1470 (800)	No	2.19
Char 7[3]	None	1290 (700)	Yes	2.88

[1] Moisture-free

[2] Value is artificially low due to residual iodine in the char (the sulfur analysis method is based on titration of oxidized sulfur with iodine)

[3] Included for comparison, this char was made with 25% added dolomite

6.3 The Effect of Nitric Oxide

Tests were conducted to determine whether nitric oxide would oxidize sulfur species found in Indiana No. 3 coal during char production. Chars were produced in the thermogravimetric analysis (TGA) instrument from 1/4-inch x 0-size coal under a mixture of 10% nitric oxide (NO) in argon. For comparison, chars were also produced under air and under pure argon. The effect of nitric oxide on total sulfur content is shown in Table 13. Values in the table were determined using a Leco sulfur analyzer. Samples produced from all tests were also sent to AMAX for total sulfur and sulfur forms analysis (using ASTM methods) and proximate analysis. The data in Table 13 show that the chars produced under the NO/argon mixture contain approximately 25 to 28% less sulfur than the moisture-free coal from which they were made. Comparison of the two 60-minute residence time chars--one made under argon and one made under the nitric oxide/argon mixture--shows that the nitric oxide effected the removal of about 17% more sulfur than was removed under argon only. The data also suggest that residence time may be more important in sulfur removal than temperature; however, more tests are needed to substantiate this. The effect of NO on sulfur removal will be truly significant if the sulfur forms data from AMAX indicate that the sulfur removed was primarily "organic." In addition to its apparent effect on sulfur content, the presence of NO also significantly reduced agglomeration during char production.

Nitric oxide data obtained using a newer sample of Indiana No. 3, ground to -60-mesh size, is listed in Table 14. Sulfur content reduction for this coal was approximately equal to the reduction achieved with the 1/4 x 0 coal under identical reaction conditions. Comparison of the two 1020°F (550°C), 60-minute residence time chars--one produced from the 1/4 x 0 coal and the other from the -60-mesh coal--shows that both chars contain about 27% less sulfur than the moisture-free coals from which they were produced. In addition to differing in particle size and sulfur content, the two coal

TABLE 13

EFFECT OF NITRIC OXIDE ON SULFUR REMOVAL -- 1/4 x 0 COAL
(10% NO/90% ARGON)

Coal/Char and Conditions	Sulfur (wt%)
Indiana Coal, washed, 1/4 x 0, moisture-free	4.09
Char - 1020°F (550°C), 60 min.	2.95
Char - 1020°F (550°C), 60 min., staged[1]	3.08
Char - 1470°F (800°C), 30 min., staged[2]	3.24
Char - 1020°F (550°C), 60 min. (under pure argon)	3.56

[1] Stages, 660°F (350°C) for 10 min., and 840°F (450°C) for 10 min.

[2] Stages, 660°F (350°C) for 10 min., 840°F (450°C) for 10 min., and 1020°F (550°C) for 10 min.

TABLE 14

EFFECT OF NITRIC OXIDE ON SULFUR REMOVAL -- -60-MESH COAL
(10% NO/90% ARGON)

Coal/Char and Conditions	Sulfur (wt%)
Indiana Coal, washed, -60-mesh, moisture-free	5.66
Char - 1470°F (800°C), 60 min. staged[1]	4.82
Char - 1020°F (550°C), 60 min.	4.17
Char - 1020°F (550°C), 30 min. staged[2]	4.11

[1] Stages, 660°F (350°C) for 10 min., 840°F (450°C) for 10 min., and 1020°F (550°C) for 10 min.

[2] Stages, 660°F (350°C) for 10 min., and 840°F (450°C) for 10 min.

samples also differ in moisture content. The 1/4 x 0 coal contains about 12% moisture, while the -60-mesh sample contains about 6% moisture. The consistency of the sulfur content reductions achieved under nitric oxide with the two coals indicates that comparing the experimental results obtained from the two coals is valid and lends credibility to the projection of experimental results for one coal based on actual performance data from the other coal.

6.4 Derivatization of Elemental Sulfur

A method for determining elemental sulfur in coal and char involves its derivatization with triphenylphosphine and subsequent quantitative analysis with gas chromatography (9). Triphenylphosphine reacts with elemental sulfur to form triphenylphosphine sulfide, but it will not react with organic sulfur species. In the procedure used, 1.0 gram of Indiana -60-mesh coal was placed in a Pierce HYPO vial. Next, 0.5 grams of triphenylphosphine and 1.0 mL of a gas chromatography internal standard (triphenylphosphate) were added, and the remainder of the vial was filled with chloroform. The vial was sealed with a teflon-lined septum and heated for 3 hours at 115°F (45°C). After cooling, the vial contents were filtered, and the filtrate was analyzed using gas chromatography. By calculating the mean of five analyses, the elemental sulfur content was determined to be 0.11 wt% of the as-received coal, with a relative standard deviation of 2.5%.

7.0 CONCLUSIONS

Although this research did not produce a definitive method for the quantitation of organic, pyritic, and sulfatic sulfur in coal and chars, several of the sulfur analysis methods tested appear worthy of further study. In the analysis of the feed coal and the 660 and 840°F (350 and 450°C) chars, the SEMPC (point data) method gave inorganic sulfur content values that were close to or slightly higher than the ASTM values. However, the SEMPC inorganic sulfur content values for the 1290 and 1470°F (700 and 800°C) chars were significantly higher than the ASTM values. The XRF and the SEMPC (bulk data) analyses gave inorganic sulfur content values that were significantly higher than the ASTM values for the feed coal and all of the chars. These three techniques share a common problem in that they all require ashing of a sample before the actual analysis. Even though low-temperature ashing minimizes mineral transformations and loss of material through volatilization, the ashing process is another unneeded variable in any sulfur analysis method.

Although the CCSEM technique does not require ashing prior to analysis, the technique did not yield a reasonable total sulfur or inorganic sulfur content value for any of the samples analyzed. The values determined were all significantly lower than the ASTM values, primarily because the CCSEM analysis is not able to accurately detect particles smaller than 1 micrometer in diameter; many pyrite grains are smaller than this. The SEM method based on the use of wavelength-dispersive spectra to detect sulfur, iron, and calcium appears to have promise and will probably be studied further.

Analytical methods based on derivatization of organic sulfur were unsuccessful due to nonreactivity of the organic sulfur-containing species with the derivatizing agents tested.

The analysis of supercritical carbon dioxide extracts from coal and char samples using GC/MS and GC/AED detected the presence of thiophenes and elemental sulfur, but the identified extracted sulfur species accounted for only a small percentage of the total sulfur-containing material (as determined by total sulfur analyses with a Leco sulfur analyzer). More work is needed to optimize extraction and chromatographic conditions. The analysis of perchloroethylene extracts yielded results similar to the supercritical extraction results--only a small percentage of the total sulfur-containing material was accounted for in the extracts.

Iodine appeared to be reactive with sulfur in coal and chars, but more analytical work is needed to determine which species the iodine reacts with, and how much iodine is needed to produce specific reactivity effects.

The method described for determining elemental sulfur contents in coal and chars appeared to be successful; however, the Indiana coal elemental sulfur content determined using the method was low (about 0.11%), and the char elemental sulfur contents were much lower, at about 0.001%.

8.0 REFERENCES

1. Ness, R.O.; Aulich, T.A. "Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products," Quarterly Technical Progress Report, April 1990, U.S. DOE, Contract No. DE-AC21-87MC24267.

2. Rose, K.D.; Francisco, M.A. "A Two-Step Chemistry for Highlighting Heteroatom Species in Petroleum Materials Using ^{13}C NMR Spectroscopy," J. of the American Chemical Society **1988**, 110, (2).

3. Falcone, S.K., "Ash and Slag Characterization," Final Report, June 1986, U.S. DOE, Contract No. FC21-83-FE60181.

4. Ribbe, P.H., ed., Sulfide Mineralogy--Vol. 1; Mineralogical Society of America, November 1974.

5. Benson, S.A.; Steadman, E.A. "Combustion Inorganic Transformations," Quarterly Technical Progress Report - September 1989; U.S. Department of Energy, Contract No. DE-FC21-86MC10637.

6. Zygarlicke, C.J., Benson, S.A. "Combustion Inorganic Transformations," Final Technical Report for the Period April 1, 1988 through June 30, 1989; U.S. Department of Energy, Contract No. DE-FC21-86MC10637.

7. Hurley, J.P. "A Pilot-Scale Study of the Formation of Ash During Pulverized Low-Rank Coal Combustion," Ph.D. Thesis, Pennsylvania State University Graduate School, Department of Materials Science and Engineering, 1990.

8. Jones, M.L.; Kalmanovitch, D.P.; Steadman, E.N.; Zygarlicke, C.J.; Benson, S.A. "Application of SEM Techniques to the Characterization of Coal and Coal Ash Products," First Symposium on Advances in Coal Spectroscopy; Salt Lake City, Utah, June 14-16, 1989.

9. Clark, P.D.; Lesage, K.L. "Quantitative Determination of Elemental Sulfur in Hydrocarbons, Soils, and Other Materials," J. of Chromatographic Science **1989**, 27.