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THE CHARACTERISTICS OF AMERICAN COALS IN RELATION TO THEIR
CONVERSION INTO CLEAN ENERGY FUELS

Quarterly Technical Progress Report, April-June 1979

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U. S. DEPARTMENT OF ENERGY

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W. Spackman, A. Davis, P.L. Walker, H.L. Lovell,
F.J. Vastola, P.H. Given, N.H. Suhr and R.G. Jenkins

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ABSTRACT

Three channel samples of coal were collected from Pennsylvania during the quarter.

In a comparison of some properties of three whole coals and vitrinite concentrates picked from these coals, it was found that the vitrinite concentrates have higher vitrinite reflectance values and display greater degrees of fluidity on testing in a Gieseler plastometer.

A total of 92 coal samples and 201 printouts of coal data were provided on request to the coal research community.

In Task 7 experiments were conducted that showed how the size and relative reflectance of coal components can affect a reflectogram generated by automated reflectance microscopy. These phenomena must be taken into consideration into quantitative interpretations of those reflectograms.

Under Task 23 an investigation into the maximum potential weight loss, ΔW_{∞} , in the isothermal furnace was performed. For Texas lignite PSOC-412, ΔW_{∞} was not measurable directly by recycling the char through the furnace. The increased isothermal residence time due to recycling is apparently not of the order required for the completion of pyrolysis. The maximum potential weight loss can be calculated, however, from the empirical linear relationship between weight loss in the isothermal furnace and the change in proximate volatile matter between the original coal and char. For the Texas lignite ΔW_{∞} is 66% of the original dry, ash-free coal. This is a factor of 1.3 enhancement over the proximate volatile matter. ΔW_{∞} is essentially temperature independent over the range 700 to 1000°C and particle size independent over the range 40 to 200 microns.

The study is continuing into the effects of low temperature oxidation on reducing the agglomerating properties of caking coals. Increases in oxidation temperature are shown to increase the effectiveness of oxygen in destroying plastic properties. Controlled studies indicate that additions of small amounts of oxygen (1-2% by wt) bring about drastic reductions in swelling properties. Oxidation may be considered a surface phenomenon and it is shown here that the plastic properties of oxidized coals are partially restored by grinding to expose new surface. Finally, water vapor is shown to have an enhancing effect on room-temperature oxidation of coal. In the same task, small angle x-ray scattering (SAXS) techniques are being evaluated as a method for determining size distributions of heterogeneities in coal chars. To test the applicability of the procedures, SAXS data have been generated from a well characterized glassy carbon (Tokai GC-30) and Saran chars prepared at different heat treatment temperatures (1100, 1300, 1500°C). Results indicate that these approaches hold much promise for characterizing the porous structure of microporous carbons. These procedures are being extended and applied to samples of the heat-treated demineralized coals. Results are shown for chars from two coals (PSOC-379 and PSOC-420) (Task 27, Facet IV-B).

Experimental conditions for Saran char burn-off have been chosen. Burn-off plots for two different particle sizes using the gas chromatograph tube furnace system have been constructed. Active surface area (ASA) measurements on a 20.1% burn-off Saran char have been made (Task 28).

The determination of the carboxyl group content of the three American lignites chosen has been completed. The results are included in this report. Also, the exchanged coal was back-exchanged with perchloric acid. The barium released was analyzed by emission spectrometry and compared to the value found by the original barium acetate treatment. The results show good agreement.

Work was also undertaken to analyze the carboxylic salts. The cations were exchanged by treatment with 1 N ammonium acetate. The results for PSOC-833 (a Montana lignite) are included in this report. They show that magnesium and calcium are the principal cations and that approximately 60% of the carboxyl groups are associated with cations. Reactivity of char samples prepared at 800°C from a lignite containing equivalent amounts of exchangeable Na, K, Ca, Mg and Fe ions has been measured in 1 atm CO₂ at 760°C and in 1 atm H₂ at 790°C. Exchangeable cations increase the reactivity of the char produced, but the extent of the increase is markedly dependent upon the nature of the exchangeable cation (Task 30).

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OBJECTIVE AND SCOPE OF WORK

The primary objective of the overall program is to achieve the capability of predicting, from a knowledge of coal composition, the behavior of a coal in pre-conversion processing, coal gasification and coal liquefaction processes.

It is reasonable to ask if this goal is in fact attainable, recognizing the heterogeneity of coal seams. Clearly, it is not if one concerns oneself simply with the rank of the coal seam and its aggregate chemistry. A high volatile B coal from Indiana need not react to processing in the same manner as a high volatile B coal from Utah, even though their "chemistries" may be very similar. In contrast, a coal lithotype of a specific kind, at a given level of rank, can be expected to behave consistently, whether it derives from Alabama or Pennsylvania. Hence, the goal may very well be attainable if, as in the case of coal carbonization, we concern ourselves with the reacting entities and the properties of the important lithotypes.

The goal is to attain the same high level of predictive accuracy that is now found in the area of coal carbonization, where Penn State's collaborative work with the steel industry proved highly successful. To achieve this goal Penn State has devised an integrated program in which the success of the research is highly dependent on the effective operation of ALL of the program's Facets and Sub-facets which are as follows:

Facet I: Characterization of the Nation's Coal Resources
I-A: Sample Collection and Seam Characterization
I-B: Coal Characterization
I-C: Sample Bank Operation, Maintenance and Development
I-D: Penn State-DOE Coal Data Base

Facet II: Coal Beneficiation and Pre-Use Processing

Facet IV: Significance of Coal Characteristics in Gasification Processes
IV-A: Reactor Development and Operation
IV-B: Cokes and Chars
IV-D: Reactivity of Coal Chars
IV-E: Catalysis Research
IV-F: Differential Scanning Calorimetry

Facet V: Coal Combustion Research
V-A: Combustion of Chars and Low Volatile Fuels
V-B: Combustion of Coal-Oil Emulsions

THE CHARACTERISTICS OF AMERICAN COALS IN RELATION TO
THEIR CONVERSION INTO CLEAN ENERGY FUELS

Task Descriptions

<u>FACET I-A</u>	<u>Sample Collection and Seam Characterization</u>
Task 1	Sampling Survey
Task 2	Sampling Plan
Task 3	Sampling
<u>FACET I-B</u>	<u>Coal Characterization</u>
Task 5	Characteristics and Use Potential of U. S. Coal Seams
Task 6	Characterization of Other DOE Contractor Samples
Task 7	Automation of Microscopic Analytical Methods
<u>FACET I-C</u>	<u>Sample Bank Operation, Maintenance and Development</u>
Task 8	Maintenance of Coal Sample Bank
Tasks 9-14	Provision of Samples and Data to Penn State and Other Investigators
<u>FACET I-D</u>	<u>Penn State/DOE Coal Data Base</u>
Task 15	Computerization of Data
Task 16	Evaluation of the Data Base
Task 17	Structuring and Utilization of the Data Base
<u>FACET II</u>	<u>Coal Beneficiation and Pre-Use Processing</u>
Task 18	Washability Characterization
Task 19	Physical Properties of Coal Lithotypes
Task 20	Techniques for Fractionation
Task 21	Beneficiation of Conversion Feedstocks
Task 22	Evaluation of Dry Flo Separator
<u>FACET IV-A</u>	<u>Reactor Development and Operation</u>
Task 23	Operation of Isothermal Furnace
Task 24	Pyrolysis of Coal Lithotypes
Task 25	Operation of Pressurized Isothermal Reactor
Task 26	Coal Reactivity
<u>FACET IV-B</u>	<u>Cokes and Chars</u>
Task 27	Effect of Variables on Char Structures
Task 28	Effect of Char Structures on Reactivities
Task 29	Catalytic Effect of Minerals in Gasification
Task 30	Effect of Catalytic Cations on Gasification
<u>FACET IV-F</u>	<u>Differential Scanning Calorimetry</u>
Task 31	DSC in Evaluating Coals for Conversion
<u>FACET V-A</u>	<u>Combustion of Chars and Low Volatile Fuels</u>
Task 32	Flame Ball Combustion Model
Task 33	Plane Flame Furnace
<u>FACET V-B</u>	<u>Combustion of Coal - Oil Emulsions</u>
Task 34	Combustion of Coal - Oil Emulsions
<u>FACET VI</u>	<u>Project Planning, Management and Administration</u>
Task 35	Administrative Plan and Program
Task 36	Cooperation and Collaboration with Other Agencies
Task 37	Communication of Research Results

SUMMARY OF PROGRESS TO DATE

Table 1 summarizes the status of coal characterization and the Penn State Coal Data Base. A comparison has been made of the chemical, reflectance and fluid characteristics of 3 whole coals and vitrinite concentrates prepared from those coals (Task 5).

Two experiments have been performed to test the influence of particle size and relative reflectance of coal components on reflectograms generated by automated reflectance microscopy under Task 7.

In Task 23 of Facet IV-A, laminar flow isothermal pyrolysis furnace has been constructed and used to study the kinetics of lignite pyrolysis in nitrogen between 700 and 1000°C. The maximum operating temperature of the furnace has recently been raised to 1350°C. Interpretation of, and errors associated with data from the isothermal furnace have been thoroughly investigated. Texas lignite, PSOC-412 has been characterized extensively with respect to the kinetics of pyrolysis and its behavior compared with that during the proximate volatile matter test in the ASTM proximate analysis. This has led to an understanding of the important parameters affecting lignite pyrolysis.

Under Task 27 of Facet IV-B, a DuPont 942-TMA dilatometer has been shown to be a valuable quantitative tool for the characterization of selected swelling and softening parameters of caking coals. Six coal channel samples and their corresponding lithotypes were analyzed using the dilatometer technique developed in this work. Nineteen samples were studied in all. Results show that swelling passes through a maximum for coals of 84-85% carbon content. Combined Thermogravimetric (TGA) and Thermomechanical (TMA) studies have been used to quantify the effects of preoxidation on the caking parameters of selected coals. Additions of small amounts of oxygen (1-2% by wt) bring about drastic reductions in dilation and a steady increase in dilation temperature. Experiments were conducted to see what effect preoxidation temperature has on reducing plastic properties. Increases in oxidation temperature were shown to increase the effectiveness of oxygen in destroying plasticity. A particle size study was also carried out. This shows that the plastic properties of an oxidized coal can be partially restored upon grinding. Finally, a weathering study was completed which indicates that moisture has an enhancing effect on room temperature oxidation of coal. In all, over 600 dilatometer experiments have been conducted. Work on this project is complete and no future work is planned at this time. A special report on the work is being prepared. In the same task, small angle x-ray scattering (SAXS) data from a glassy carbon (Tokai GC-30) and Saran chars prepared at different heat treatment temperature (1100, 1300, 1500°C) have undergone manipulation to obtain various structural parameters and distributions. Surface areas of Saran chars, determined by SAXS, have been compared to values obtained from CO₂ adsorption at 298°K. Samples of three heat treated demineralized coals (PSOC-379 - Pennsylvania anthracite, PSOC-420 - Texas subbit., PSOC-620 - Texas lignite) have been prepared and subjected to SAXS examination.

Table 1. Penn State/DOE Coal Data Bank Status

Data Category	Data Elements Per Data Category	Previous OCR/ERDA Contract (OCR 14-01-001-390; ERDA E(49-18)-390)	Current ERDA/DOE Contract (DOE EX-76-C-01-2030)	Total	Current Contract Goal
Seam & Mine Information	66	300	836	1136	1300
Proximate	6	291	595	886	1300
Ultimate	7	284	590	874	1300
Equilibrium Moisture	1	18	427	445	1300
Sulfur Forms	4	288	596	884	1300
Maceral Analyses	43	300	596	898	1300
Reflectance Analyses	67	284	575	859	1300
Free Swelling Indices	1	161	567	747	1300
Gray-King Coke Types	1	88	535	623	1300
Plastometer	6	25	11	36	150
Hardgrove Grindability	1	238	560	798	1300
Vickers Hardness	1	196	175	371	1300
Ash Fusion	8	0	506	506	1300
Low Temperature Ash	3	57			1300
Ash Analysis Related Data	1	57			1300
Major and Minor Elements	10	57	625	682	1300
Trace Elements	34	57	1086	1143	1300
Mercury	1	0	191	191	1300
Uranium	1	0	609	609	1300
Mineralogical	35	57	75	132	1300
Calculated Compositional Values	225	300	595	895	1300
Analysis Log	18	300	836	1136	1300
Other Categories	52	269	40	309	630
Total: 33 Data Categories		592 Data Elements			

Under Task 28, work was initiated to explore a possible correlation between the active surface area of a char and its reactivity during gasification. The effect of bed height and particle size on reactivity of a Saran char in a TGA system was studied. In this report initial data from both the gas chromatograph-tube furnace system and the mass spectrometer (MS) are presented.

In work performed under Task 29, a method of qualitative and quantitative analysis of the major minerals in lignites has been outlined. PSOC-623 (a Texas lignite) has been analyzed by this method, and the quantitative analysis of a North Dakota and a Montana lignite is being pursued. A method for the quantitative determination of the carboxyl group content of lignites has been defined as part of Task 30. The results for the three lignites chosen are presented in this report. The carboxyl content was determined by both the hydrogen released when the coal is exchanged with barium acetate and by the barium released when the exchanged coal is treated with acid. Finally, the carboxylic salts of PSOC-833 (a Montana lignite) have been analyzed. This was accomplished by treating the raw coal with 1 N ammonium acetate and by analyzing the exchanged cations using emission spectrometry. The technique and results are discussed in detail in this report. The effect of Ca-exchange on the subsequent reactivity of lignite chars to the hydrogasification reaction have been investigated in this task. Also, the reactivity in air at 300°C of chars produced at 800°C from a lignite containing equivalent amounts of different exchangeable cations has been measured. In this report we describe the influence of such cation additions on reactivity in CO₂ and H₂. The presence of cations generally enhances reactivity of the char produced, but the extent of the increase is markedly dependent upon the nature of the exchangeable cation.

A list of Technical Reports produced as a result of this contract, and available from TIC, Oak Ridge, is given in Table 2. The following Technical Reports are in preparation and will be available in August, 1979.

FE-2030-TR16	An Automated Microscopical Method for the Characterization of Pyrite in Coal--
K.W. Kuehn and A. Davis
FE-2030-TR17	Kinetics of Lignite Pyrolysis in Fixed Bed and Enhanced Flow Reactors--
A.W. Scaroni and P.L. Walker

This quarterly report is the last to be submitted under the present contract.

LEGEND

SCHEDULED

PROGRESS

SCHEDULE EXTENSION

EARLY START

PROJECT PLAN AND PROGRESS REPORT

Quarter Ending June 30, 1979

FACET I-A: SAMPLE COLLECTION AND SEAM CHARACTERIZATION

COAL SAMPLING (TASK 3)

Three samples of coal (PSOC-1141, -1142, and -1143) were collected from three Pennsylvania mines in Jefferson and Armstrong Counties during this quarter.

FACET I-B: COAL CHARACTERIZATION

COAL CHARACTERIZATION (TASK 5)

Maceral Analyses were completed on 22 PSOC samples along with 23 reflectance analyses and one fluorescence analysis in blue light. In addition, Hardgrove grindabilities were determined for 64 coals, FSI on 89 coals and Gray-King Coke analyses on 89 coals. Other analyses have been performed as reflected in the table showing the status of the coal data bank.

The Plastic Properties of Coals and Their Influence in Conversion Processes

As part of Task 5 we are continuing to study the thermoplastic behavior of coals using the Gieseler plastometer. During this quarter three freshly collected, well preserved coal samples were studied. In addition, vitrinite concentrates from vitrain bands were hand picked from a sample procured at each sample site. These were also studied in detail.

Experimental

The coal samples selected for this study were collected from the Lower Kittanning seam in Pennsylvania. This seam is of interest because it displays a considerable lateral variation of rank (medium volatile to high volatile C bituminous).

Three coal channel samples, PSOC-1141, -1142, and 1143 were taken from different lateral locations in the Lower Kittanning seam. Vitrinite concentrates were hand picked from subsamples taken at each sample location. Petrographic analysis of the concentrates shows them to contain more than 97% vitrinite.

The thermoplastic behavior of the samples was characterized using the Gieseler plastometer (Table 3). Additional characterization of the samples was performed, including proximate and ultimate analyses and petrographic analysis. Some of the results of these analyses are reported in Table 4.

A comparison of the fluidity and reflectance values between the coal samples and the vitrinite concentrates is given in Figure 1. The vitrinite concentrates consistently displayed a higher degree of fluidity and reflectance. Several authors have noted the tendency for vitrinite occurring in relatively thick vitrain bands to have higher reflectance than that which occurs in the fine-grained attrital matrix. In fact, microscopic examination of the concentrates prepared for this study shows that they are typical of this kind of vitrinite, which has been called pseudovitrinite¹ but which is more appropriately termed telocollinite, homocollinite or band vitrinite.

Table 3. Gieseler fluidity for the Lower Kittanning seam samples

	Max Fluidity (ddpm)	T°C Max Fluidity	T°C On set of Fluidity	T°C Temp of Resolidifi- cation	T°C Temp Range
PSOC-1141	2,195	449	407	484	77
Vitrinite Concentrate	3,108	453	403	491	88
PSOC-1142	8,951	442	395	482	87
Vitrinite Concentrate	15,292	443	391	482	91
PSOC-1143	16,634	440	382	477	95
Vitrinite Concentrate	24,674	440	386	481	95

Table 4. Results of some characterization tests on the Lower Kittanning coal samples and vitrinite concentrates

	Carbon	Hydrogen	Nitrogen	Oxygen	Chlorine	Vol. Matter	Fixed Carbon	Mean Max R ₀ , %
PSOC-1141	86.80	5.69	1.53	6.15	.11	34.53	65.47	1.019
Vitrinite Concentrate	86.44	5.59	1.42	6.20	.15	32.90	67.10	1.042
PSOC-1142	85.65	5.73	1.61	6.48	.21	37.55	62.45	0.881
Vitrinite Concentrate	85.10	5.53	1.48	6.92	.15	36.85	63.15	0.908
PSOC-1143	84.68	6.05	1.59	5.66	.21	40.78	59.22	0.778
Vitrinite Concentrate	84.81	6.02	1.56	6.81	.18	39.80	60.20	0.826

Figure 1. COMPARISON OF GIESELER FLUIDITY AND REFLECTANCE BETWEEN COAL SAMPLES AND CORRESPONDING VITRINITE CONCENTRATES

Benedict et al.¹ have suggested that "pseudovitrinite" was produced by low-temperature oxidation during the biochemical stage of coalification. Coals containing appreciable quantities of "pseudovitrinite" exhibit anomalous chemical properties which appear to be quite similar to properties produced by oxidation in the laboratory study by Benedict and Berry². Further, "pseudovitrinite" apparently does not behave like other vitrinite during the coking process but more like the semi-inert and inert macerals. Based on the above observations, one might expect the coal samples to exhibit a higher degree of fluidity because they contain a much smaller proportion of telocollinite ("pseudovitrinite"). The lower fluidity fluid values obtained for the coal samples, however, are probably due to the diluent effects of the mineral matter and inert macerals in the coal.

The chemical analyses (Table 4) show that the vitrinite concentrates consistently had a higher oxygen (by difference) contents and a lower hydrogen and nitrogen contents than the corresponding coals.

Preliminary results suggest that differences exist between the chemical and thermoplastic properties of coal and vitrinite concentrates prepared from the coal. Continuation of this research using additional samples is planned. Further, the influence of these variations on liquefaction behavior will be studied.

RAPID SCAN AUTOMATED REFLECTANCE MICROSCOPE SYSTEM (TASK 7)

Work under Task 7 has been directed toward examining the influence of particle size on reflectogram resolution. Coal macerals, in a sample briquette vary in size from submicron particles to the particle top size in the briquette (850 μm). The interaction between the 2.5 μm x 2.5 μm sampling spot and the maceral perimeter (interface) is directly related to maceral size. The ratio of interface reflectance readings to unique phase readings increases substantially for smaller sized particles. Consequentially the reflectance population for the smaller macerals will be more distorted and diffuse.

In order to examine these effects two experiments were devised to model a binary system. In both experiments the proportions of the two phases (epoxy resin binder and glass) were kept constant and size or relative reflectance was varied. In the first experiment the sizes of the two components were varied from 800 μm to 25 μm . The results, shown in Figure 2, indicate that the interface reflectance readings are dispersed randomly between the two phases with the frequency increasing as the particle size decreases. The figure also shows that with decreasing particle size the lower reflecting population is distorted more readily than the higher reflecting population.

This effect is related to the relative contribution of the two phases to the "average" reflectance value recorded for an interface reading. The low reflecting material's contribution to the recorded value is not in proportion to its area distribution in the interface sensing spot. It will be necessary to account for these "misplaced" reflectance readings, in quantitative reflectogram analysis, especially for fine-grained components.

Figure 2. THE EFFECT OF DECREASING PARTICLE SIZE ON A TWO-COMPONENT SYSTEM

The second experiment was designed to evaluate whether or not distortions of this type altered the mode of the individual reflectance distributions. Figure 3 shows three binary profiles in which size and volume were held constant and the relative reflectance of the higher reflecting component was varied (three glasses of known reflectances were used, viz. 0.533%, 1.006% and 1.815%). The modal value of the second component (glass) remains constant, despite changes in the reflectance difference between the two populations. However, as the second component is shifted up in reflectance the mode of the first component (epoxy resin binder) is also shifted slightly up scale.

These results indicate that increased amounts of low reflecting material will not affect the mode of the vitrinite peak on a reflectogram. A quantitative vitrinite reflectance value derived from the reflectogram will therefore be independent of increasing liptinite content. However, if the vitrinite is finely intermixed with high reflecting inert macerals, some deviation might be recorded.

Previous quarterly reports have referred to the use of the Rapid Scan system for estimating pyrite chord size distributions in coals. A report (FE-2030-TR16) entitled "An Automated Method for the Characterization of Pyrite in Coal" has been completed and will be published in August.

Figure 3. THE EFFECT OF INTERFACE REFLECTANCE READINGS ON A TWO-COMPONENT SYSTEM OF INCREASING REFLECTANCE

FACET I-C: SAMPLE BANK OPERATION, MAINTENANCE AND DEVELOPMENT

SERVICE TO OTHER AGENCIES (TASKS 8-14)

A total of 92 coal samples, ranging in amount from 50 grams to 35 pounds, were supplied to other agencies engaged in coal research throughout the country. In addition, printouts of analytical data for 201 coals plus 3 selected sort lists of all the coals in the data base were supplied to other agencies.

The agencies requesting these data included: Standard Oil of Indiana, Iowa State University, Frontier Technology Associates, The University of Missouri, Aerospace Corporation, U.S. Naval Research Laboratory, Amoco Products Company, Amoco Research Center, Cogas Development Company, Calgon Corporation, Kentucky Center for Energy Research, Shell Development Company, Research Triangle Institute, Brookhaven National Laboratories, Southwestern Research Institute, South Dakota School of Mines, and Gulf Research and Development Company.

During this period, the storage racks were installed in the new Coal Sample Bank facility and transfer of the coal samples from the temporary storage areas was well underway. An inventory of the coals in stock along with quantity and location of each is being made as the samples are transferred to the new facility.

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

OPERATION OF ISOTHERMAL FURNACE (TASK 23)

Maximum Operating Temperature of the Isothermal Furnace

The recent installation of a second preheater on the secondary nitrogen stream has increased the maximum operating temperature from 1000°C to 1350°C. Previous restrictions on the upper temperature were caused by a lack of heat transfer surface. This is overcome by the addition of a second preheater in series with the existing one.

Maximum Potential Weight Loss Under Isothermal Furnace Conditions

An important parameter required to model the kinetics of the overall pyrolysis process is the maximum potential weight loss, ΔW_{∞} , in the isothermal furnace. In addition, this parameter has practical significance to pulverized coal combustors and gasifiers in which it is advantageous to maximize the yield of volatiles. Unfortunately, ΔW_{∞} is not measurable directly by a single pass of coal through the isothermal furnace due to insufficient residence time. Recycling the char through the furnace to extend residence times is potentially a viable technique for achieving maximum weight loss.

Recycle data for 70 x 100 mesh PSOC-412 is given in Figure 4. Data are for isothermal pyrolysis in nitrogen at 950°C. Cumulative residence times include only the initial heat-up period of 0.058 sec, with subsequent heat-up times during recycles subtracted out. Residence times, therefore, represent initial heating followed by isothermal pyrolysis. It is apparent from Figure 4 that on a time scale of seconds, significant weight loss by pyrolysis ceases after one recycle. The maximum measured weight loss is 49% of the dry-ash-free (daf) coal, slightly less than the proximate volatile matter of 51% of the daf coal. The proximate test is also conducted at 950°C. Proximate volatile matter tests on the recycle chars, however, reveal that they still contain some residual volatiles. This is also illustrated in Figure 4. The implication is that a residence time of 1.7 sec in the isothermal furnace (compared with 7 min in the proximate test) is insufficient to allow complete pyrolysis.

An alternative is to calculate ΔW_{∞} based on a standard property which changes regularly with weight loss in the isothermal furnace. Change in proximate volatile matter between the original daf coal and char is one property which correlates well with weight loss. The relationship is linear and is relatively independent of particle size over the range 40 to 200 microns (Figure 5) and temperature over the range 700 to 1000°C (Figure 6). The derived relationship is

$$\Delta W = 1.30 \Delta V$$

where ΔW = weight loss in isothermal furnace, % daf coal

ΔV = change in proximate volatile matter between coal and char, % daf coal

Figure 4. EFFECT OF CHAR RECYCLING ON WEIGHT LOSS IN THE ISOTHERMAL FURNACE FOR 70 x 100 MESH LIGNITE AT 950°C

Figure 5. VARIATION OF WEIGHT LOSS IN ISOTHERMAL FURNACE AT 1,000°C WITH CHANGE IN PROXIMATE VOLATILE MATTER BETWEEN COAL AND CHAR

Figure 6. VARIATION OF WEIGHT LOSS IN ISOTHERMAL FURNACE WITH CHANGE IN PROXIMATE VOLATILE MATTER BETWEEN COAL AND CHAR FOR 140 x 200 MESH SIZE FRACTION

The maximum potential weight loss is obtained from the linear relationship when there is no proximate volatile matter remaining in the char. For PSOC-412 lignite ΔW_{∞} is 66% of the daf coal.

FACET IV-B: COKES AND CHARS

EFFECT OF VARIABLES ON CHAR STRUCTURE (TASK 27)

Preoxidation of Caking Coals to Diminish Their Softening and Swelling

Combined Thermogravimetric (TGA) and Thermomechanical (TMA) studies have been used to quantify the effects of preoxidation on the caking parameters of selected coals. This work was completed this quarter.

The first step in these oxidation studies was to determine what effect the temperature of preoxidation has on altering plastic properties. Samples of 200 x 250 mesh PSOC-1099 were oxidized to a set level (0.50% by wt) at several temperatures (75°C, 100°C, 125°C, 150°C, 175°C, and 200°C). Table 5 shows that as the temperature of oxidation rises the reduction in plastic behavior becomes more marked. This oxidation temperature dependence is not surprising. Oxidation kinetic studies (ERDA Progress Report July - Sept., 1977) have shown significant gasification at 200°C. Gasification brings about a loss in carbon and hydrogen and leads to artificially low oxidation levels. All further oxidation work was conducted at 125°C. This temperature provided reasonable preoxidation times with undetectable gasification.

Controlled oxidation studies were carried out and the dilation then measured. Some of these data for the oxidation of PSOC-1099 (hvAb coal) has been presented in a previous report (DOE Quarterly Technical Progress Report FE-2030-14, Oct. - Dec., 1978). Since that time more data have been collected which have led to some new observations. These data can be found in Table 6 and in Figures 7 through 9.

Figure 7 shows the dramatic effect that preoxidation has upon the swelling and softening parameters of PSOC-1099. Additions of small amounts of oxygen bring about a drastic reduction in dilation values and a steady increase in dilation temperatures.

A more detailed picture of oxidation effects can be seen in Figure 8. Initially, addition of oxygen (< 0.1%) causes an increase in dilation. At first, these results were thought to be inconsistent; however, Loison et al.³ reports that several investigators have observed similar behavior for certain coals. Also, this same behavior was observed for another hvAb coal (PSOC-1103). See Table 7.

Further oxidation (> 0.10%) brings about a sharp, almost linear, decrease in dialtion values until approximately 1.5% oxygen has been added. Above this level dilation changes become less sensitive to oxidation until 2.0% oxygen addition at which level all dilation has been destroyed.

Oxidation studies were also carried out on a higher rank, 1vb bituminous coal (PSOC-1133). This coal exhibits high swelling much like PSOC-1099. The dilation data can be found in Table 8 and Figure 10. The initial dilation increase observed for the two hvAb coals does not occur in the case of PSOC-1113. Loss of dilation begins immediately

Table 5. Effect of oxidation temperature on subsequent expansion of PSOC-1099 during heating

Oxidation Temp., °C	Oxygen Added, %	Total Volume Expansion, %
---	0	805 ± 24
200	0.51	174 ± 40
175	0.53	313 ± 14
150	0.50	392 ± 26
125	0.50	479 ± 16
100	0.50	505 ± 30
75	0.49	550 ± 30

Table 6. Effect of oxidative level on subsequent behavior of PSOC-1099 upon heating

Wt. Gain, %	Volume Contraction, %	Volume Expansion, %	Total Volume Expansion, %	Softening Temperature T_s , °C	Dilation Temperature T_D , °C	Resolidification Temperature T_R , °C
Fresh Coal	41 ± 11	703 ± 17	744 ± 18	362 ± 7	475 ± 2	559 ± 3
Stored 80 days Under N_2	50 ± 3	755 ± 22	805 ± 24	362 ± 7	475 ± 2	559 ± 3
0.10	50 ± 2	728 ± 25	777 ± 28	351 ± 7	473 ± 2	555 ± 2
0.24	45 ± 5	650 ± 3	595 ± 8	356 ± 6	479 ± 2	555 ± 4
0.33	43 ± 6	552 ± 29	595 ± 27	358 ± 3	483 ± 3	554 ± 4
0.50	45 ± 3	435 ± 17	479 ± 16	362 ± 6	487 ± 8	557 ± 5
0.72	44 ± 6	269 ± 15	313 ± 14	337 ± 25	484 ± 4	550 ± 3
0.75	39 ± 3	229 ± 29	268 ± 29	351 ± 2	494 ± 1	546 ± 4
0.99	40 ± 4	144 ± 16	183 ± 12	349 ± 10	491 ± 3	543 ± 4
1.31	37 ± 6	49 ± 8	86 ± 10	348 ± 15	492 ± 3	---
1.48	38 ± 5	-8 ± 10	30 ± 8	343 ± 18	514 ± 2	---
1.99	48 ± 4	-48 ± 4	NONE	279 ± 8	---	---
2.74	30 ± 2	-30 ± 2	NONE	261 ± 5	---	---

Figure 7. TMA OXIDATION DATA
PSOC - 1099 (hvAb)

**Figure 8. PERCENT VOLUME EXPANSION VS OXYGEN UPTAKE
PSOC - 1099**

Figure 9. DILATION TEMPERATURE T_D VS OXYGEN UPTAKE
PSOC - 1099

Figure 10. % VOLUME EXPANSION VS % OXYGEN ADDED
PSOC - 1133 (lvb)

Table 7. Effect of the initial stages of oxidation on subsequent behavior of PSOC-1103 upon heating

Wt. Gain, %	Volume Contraction, %	Volume Expansion, %	Total Volume Expansion, %	Softening Temperature T_s , °C	Dilation Temperature T_D , °C	Resolidification Temperature T_R , °C
Fresh Coal	45 ± 4	577 ± 50	261 ± 39	339 ± 2	470 ± 3	549 ± 4
Stored 119 days Under N_2	52 ± 5	616 ± 39	669 ± 41	355 ± 7	472 ± 2	549 ± 2
0.05	52 ± 5	650 ± 51	703 ± 51	345 ± 2	472 ± 1	548 ± 3
0.10	54 ± 3	587 ± 75	641 ± 76	347 ± 3	474 ± 2	548 ± 2

Table 8. Effect of oxidation level on subsequent behavior of PSOC-1133 upon heating

Wt. Gain, %	Volume Contraction, %	Volume Expansion, %	Total Dilation Volume, %	Softening Temperature T_S , °C	Dilation Temperature T_D , °C	Resolidification Temperature T_R , °C
0.00	41 ± 3	473 ± 29	514 ± 29	396 ± 5	531 ± 1	586 ± 7
0.10	40 ± 3	343 ± 15	381 ± 17	466 ± 2	525 ± 2	583 ± 4
0.25	35 ± 4	256 ± 17	292 ± 16	461 ± 5	531 ± 2	585 ± 3
0.43	35 ± 4	99 ± 31	134 ± 34	470 ± 4	541 ± 3	---
0.56	32 ± 4	14 ± 8	47 ± 11	462 ± 20	548 ± 2	---
0.75	35 ± 6	---	---	467 ± 15	---	---
1.00	27 ± 2	---	---	474 ± 6	---	---

upon oxidation. This coal is much more sensitive to oxidation. All dilation has been removed with less than 1% oxygen addition.

The difference in behavior between the lvb coal and the hvAb coals is believed to be due to the large difference in fluidity between these samples. Maximum Gieseler fluidities measured for the fresh coal samples were:

PSOC-1099	hvAb coal	14,681 DDPM
PSOC-1103	hvAb coal	29,944 DDPM
PSOC-1133	lvb coal	58 DDPM

Weathering studies (see Task 5, previous Quarterly Technical Progress Reports) have shown that the Gieseler fluidity drops very rapidly during the first two weeks of weathering (PSOC-1099). The amount of oxygen chemisorbed in this time frame is certainly less than 0.1% (see weathering study data below). This decrease in fluidity of the plastic coal mass could lead to the observed increase in dilation. Lower fluidity increases the resistance to escape of volatile gases. That is, the volatile pyrolysis products will require a longer time to escape from the less fluid (more "viscous") material. The increased residence time of the gases in the plastic mass may well lead to an increase in internal gas pressure and a subsequent increase in swelling.

This increase in swelling does not go on indefinitely. Figure 9 shows that as the coal is oxidized and fluidity is decreased the dilation temperature T_D rises steadily. An increase in T_D corresponds to a decrease in the amount of volatile gases available for swelling. As T_D rises more pyrolysis gases escape before swelling begins and this brings about a decrease in dilation.

An increase in swelling is not observed for the lvb coal because the fluidity is very low for the original coal. Initial oxidation cannot bring about the rapid decline in fluidity observed in the hvAb coals.

Kinetic studies (ERDA Quarterly Technical Progress Report FE-2030-9) have shown that oxidation is a surface phenomenon and suggest that low temperature oxidation is controlled by diffusion through the coal particles. Van Krevelen⁴ shows the formation of oxidation rims on coal particles and Carpenter and Giddings⁵ discuss the diffusion limitations of low temperature oxidation. With this in mind, one might expect to find a higher concentration of oxygen groups at the outer edges of the coal particle. A study was conducted to test this hypothesis. Several 40 x 60 mesh samples (PSOC-1099) were oxidized to various levels. These samples were split and one half of each sample was ground to pass a 200 mesh sieve. The oxidized samples, both 40 x 60 mesh and minus 20 mesh, were then tested in the dilatometer. The results of this work can be found in Table 9. Figure 11 is a plot of dilation values normalized for dilation of the raw unoxidized samples. The figure shows the partial restoration of dilation upon grinding to expose new surface. These results support the idea of formation of oxidation rims on the coal particles. Since agglomeration and swelling appear to be partially

Table 9. Effect of oxidation level and grinding on a subsequent behavior of PSOC-1099 upon heating

Oxygen Added, %	Volume Contraction, %	Volume Expansion, %	Total Dilation Volume, %	Softening Temperature T_s , °C	Dilation Temperature T_D , °C	Resolidification Temperature T_R , °C
<u>Oxidation</u>						
0.00	7 ± 3	591 ± 20	598 ± 18	357 ± 4	467 ± 1	558 ± 4
0.25		516 ± 33	516 ± 33	360 ± 4	475 ± 2	559 ± 3
0.48		304 ± 34	304 ± 34	364 ± 8	486 ± 3	555 ± 4
0.79		99 ± 12	99 ± 12	373 ± 11	503 ± 4	543 ± 5
1.00		51 ± 11	52 ± 11	372 ± 6	509 ± 3	547 ± 4
<u>Oxidation and Grinding</u>						
0.00	44 ± 3	742 ± 13	785 ± 13	365 ± 5	471 ± 2	558 ± 1
0.25	49 ± 8	692 ± 42	740 ± 50	364 ± 5	476 ± 1	558 ± 2
0.50	36 ± 5	439 ± 50	474 ± 51	359 ± 5	479 ± 2	552 ± 6
0.78	32 ± 3	199 ± 26	232 ± 24	372 ± 5	493 ± 1	554 ± 3
0.99	35 ± 2	108 ± 15	142 ± 15	364 ± 5	493 ± 3	543 ± 4

restored upon grinding of an oxidized coal, one must be wary when processing coals to be used in a gasifier or combustion unit. However, consideration has to be given to the effect of varying the particle size on the resulting dilation.

The final facet of this work involved a weathering study designed to look at room temperature oxidation and to investigate the effects of moisture on the oxidation rate. The coal used in this study was PSOC-1099. A 200 x 250 mesh coal sample was placed in a desiccator in dry air and tested periodically. Another sample was placed in a second desiccator in a humid atmosphere (88% humidity, produced using a $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ saturated solution at 25°C) and was also tested periodically. The results of this study can be found in Table 10 and may be compared to the data in Table 6. As one can see exposure to dry air has much less effect on subsequent volume expansion of PSOC-1099 upon heating than does exposure to wet air. This suggests that water is interacting with oxygen groups on the coal surface. One might expect this kind of interaction to bring about an increase in the number of acid hydroxyl groups on the coal surface. These results lend some support to the theory that condensation reactions between acid hydroxyl groups lead to crosslinking and a subsequent loss in plastic properties.

Characterization of Heat-Treated Coals by Small Angle X-Ray Scattering

The major objective of this project is to characterize the porous nature of chars and cokes by small angle x-ray scattering (SAXS). The advantage of SAXS over methods which involve fluid penetration for these types have been described and demonstrated in previous quarterly reports. A method has been developed to describe the pore structure of micro-porous carbonaceous solids in terms of size distributions and characteristic averaged structural parameters. In this study a general computer program developed by Vonk is being used to manipulate all SAXS data. To test the applicability of the procedures, SAXS data of well characterized carbon chars have been examined. In the last Quarterly Technical Progress Report FE-2030-15, we described the size parameters and distributions computed from these procedures and reported results obtained from heat-treated Saran chars (1100, 1300, 1500°C). During this quarter the method has been applied to demineralized coal chars of different rank.

SAXS parameters obtained for demineralized coal chars of PSOC-379 (Pennsylvania semianthracite) and PSOC-420 (Texas subbituminous C) are listed in Table 11 and 12 respectively. In previous reports we have described how averaged structural parameters are calculated from measured intensity function $[J(h)]$, a number-diameter distribution $[f_N(D)]$ and a chord-distribution in function $[g(\ell)]$. It will be recalled that for the Saran chars, the results showed that structural parameters obtained from different functions are quite close.

Table 11 lists the values obtained for the averaged SAXS parameter for demineralized coal chars (1000, 1300, 1500°C) from PSOC-379

Table 10. Effect of weathering on subsequent behavior of PSOC-1099 upon heating

Weathering Time, Days	Volume Contraction, %	Volume Expansion, %	Total Dilation Volume, %	Softening Temperature T_s , °C	Dilation Temperature T_D , °C	Resolidification Temperature T_R , °C
<u>Dry Air</u>						
0	47 ± 11	703 ± 17	744 ± 18	362 ± 7	475 ± 2	559 ± 3
13	47 ± 4	769 ± 15	817 ± 13	354 ± 3	472 ± 1	559 ± 2
25	50 ± 5	754 ± 19	804 ± 24	357 ± 3	477 ± 1	557 ± 2
44	48 ± 4	748 ± 15	796 ± 16	360 ± 3	477 ± 2	556 ± 2
65	50 ± 3	746 ± 41	796 ± 43	353 ± 6	482 ± 4	561 ± 2
94	48 ± 6	709 ± 56	758 ± 60	359 ± 6	479 ± 3	558 ± 1
<u>Moist Air</u>						
13	49 ± 3	759 ± 33	808 ± 33	358 ± 3	477 ± 1	557 ± 4
25	48 ± 5	695 ± 38	743 ± 38	358 ± 4	479 ± 4	555 ± 1
44	48 ± 3	673 ± 41	721 ± 40	359 ± 5	480 ± 3	556 ± 2
65	47 ± 4	651 ± 47	697 ± 49	361 ± 6	483 ± 5	560 ± 3
94	47 ± 5	577 ± 26	624 ± 26	357 ± 2	483 ± 2	556 ± 5

(semianthracite). It can be seen that the values obtained by the different procedures do show more variation than those obtained for the Saran chars. However, definite trends can be observed. Firstly, as heat-treatment temperature is increased there is comparatively little change in those parameters which describe "average pore size" (R_g , λ_c and λ_{pore}). This observation is to some degree confirmed by plots of the pore volume distribution function [$f_v(D)$] shown in Figure 12. Examination of these plots reveal that as heat-treatment temperature increases, the maxima of the curves remain essentially at the same position. However, the distribution obtained for the 1300°C and 1500°C samples are much broader and indicate the development of a bimodal (and possibly trimodal for 1500°C) distribution of pore volumes. These data exemplify the need to look at distributions in addition to averaged parameters.

The parameter λ_{solid} also shows an interesting trend. As heat treatment increases the λ_{solid} (a characteristic dimension of the solid matter between pore walls) increases significantly in magnitude. It is suggested that this observation indicates an improvement in order of the carbonaceous material. Surface area values from SAXS show a decrease with increasing heat-treatment temperature. Although not complete, preliminary surface area data from CO₂ adsorption measurements are much smaller, indicating that CO₂ is being excluded from the pore systems because of molecular sieving.

Examination of the SAXS parameters listed in Table 12, for the 1000°C and 1300°C chars of demineralized PSOC-420 (Texas, subbituminous C) reveals again that heat-treatment temperature has little effect on the average size of pores. Figure 13 shows again that increasing heat-treatment does cause a broadening of the volume distribution and the development of bimodality.

In terms of the parameter λ_{solid} , one notes that in this case, increasing heat treatment temperature (in this range) has little effect on development of order in the carbonaceous matrix. However, it is significant that values of λ_{solid} for the subbituminous coal chars are much smaller than those obtained for the anthracite coal chars (Table 11). These data reflect the relative disorder in the chars from lower rank coals.

SAXS surface area data (Table 12) for the PSOC-420 chars are essentially constant. It would appear that the two chars for PSOC-420 are very similar structurally. Samples of heat-treated lignites (PSOC-623) will be subjected to examination by SAXS in the near future. Surface area data for CO₂ adsorption will be completed.

Table 11. SAXS Parameters for Heat-Treated Coal Chars
PSOC-379 (semianthracite)

Parameters	1000°C			1300°C			1500°C		
	J(h)	From $f_N(D)$	$g(\ell)$	J(h)	From $f_N(D)$	$g(\ell)$	J(h)	From $f_N(D)$	$g(\ell)$
R_g , Å	8.3	6.1	6.6	9.9	9.6	11.0	10.9	12.1	15.0
ℓ_p , Å	7.3	6.1	6.0	8.3	7.2	7.2	9.4	8.1	8.1
ℓ_c , Å	10.6	9.1	9.2	11.8	11.6	11.6	13.3	13.7	13.5
ℓ_{pore} , Å	9.4	7.9	7.8	10.2	8.9	8.8	9.2	7.9	7.9
ℓ_{solid} , Å	32.3	26.9	26.7	43.7	37.9	38.1	55.7	48.1	48.0
S_p (m ² /g)	653	784	789	482	552	555	379	438	439

Table 12. SAXS Parameters for Heat-Treated Coal Chars
PSOC-420 (subC)

Parameters	1000°C			1300°C		
	J(h)	From $f_N(D)$	g(ℓ)	J(h)	From $f_N(D)$	g(ℓ)
R_g , A	7.5	6.5	6.8	8.1	8.6	9.2
ℓ_p , A	7.6	6.4	6.4	7.9	6.9	6.8
ℓ_c , A	10.1	9.6	9.6	12.1	10.7	10.6
ℓ_{pore} , A	11.0	9.2	9.2	11.7	10.2	10.0
ℓ_{solid} , A	23.5	nc	nc	24.1	nc	nc
S_p (m ² /g)	843	1001	1001	876	1001	1016

nc = not completed

Figure 11. NORMALIZED EXPANSION VS PERCENT OXYGEN ADDED

Figure 12. PORE VOLUME DISTRIBUTION FUNCTIONS FOR COAL CHARs PREPARED FROM PSOC-379 (SEMIANTHRACITE)

Figure 13. PORE VOLUME DISTRIBUTION FUNCTIONS FOR COAL CHARs PREPARED FROM PSOC-420 (SUB C)

RELATION OF CHAR STRUCTURE TO CHAR REACTIVITIES (TASK 28)

Relation of Active Surface Areas of Chars to Their Reactivity

The gas chromatograph tube furnace system discussed in previous reports has been used in the preparation of burn-off (BO) curves for Saran char. Briefly, the Saran char samples (~ 1.7 gm) were placed in a ceramic boat (105 x 45 mm), and the boat was sealed in the tube furnace. The furnace tube was purged overnight with N_2 (pre-purified, passed over Cu turnings, and through a Drierite column). The furnace was then heated to $\sim 950^\circ C$ for 4 hr and then cooled to $375^\circ C$. Following this, the furnace tube was sealed and evacuated slowly through a capillary. The tube was then brought to atmospheric pressure through the capillary tube with air, and flow begun (25-55 cc/min). The products of the reaction were analyzed periodically with the GC. Data were analyzed and BO plots constructed. Figure 14 gives the BO curves for a 70 x 100 and a 200 x 400 mesh Saran char.

While Saran char BO plots usually show a narrow range of slowly increasing rate of burn-off for early gasification times, these curves do not. Jenkins, et al.⁶ have suggested that after about 10-20% burn-off for microporous coal chars, this induction period should be eliminated. The Saran chars were reported in the last report to lose $\sim 10\%$ of their weight upon heat treatment to $950^\circ C$; this could account for the absence of the induction period.

The center regions of the curves in Figure 14 are not in good agreement. This difference in the curves cannot be a diffusional effect since the larger particles have the higher reactivity. Some evidence of particle "blow out" from the boat was found for the 200 x 400 mesh char; this may account for the difference.

The curves are in good agreement in the final stages of burn-off but appear to be leveling off after a loss of about 85% of the initial weight. This "lost" 15% of the initial weight is thought to be due to the difference between the weights of the sample and the time of weighing and at the time the burn-off is begun and errors involved in analyzing the product gases. During the coming quarter work will be continued to explain quantitatively this difference. Also burn-off studies showing particle size and bed height independence will be conducted.

The use of the mass spectrometer (MS) system to measure active surface area (ASA) of carbons is not a new technique in this laboratory.⁷ Briefly, the char sample (0.07 gm) was placed in a quartz boat, a quartz wool plug placed over it and it was sealed in the reactor. The system was evacuated and then heated to $375^\circ C$ and then to $950^\circ C$, or heated directly to $950^\circ C$, and held for 4 hr. In either case the products of the decomposition of surface complexes (CO and CO_2) were analyzed. (The CO_2 was frozen out in a liquid N_2 trap to prevent reaction with the sample at high temperatures). The sample was then cooled to $100^\circ C$

Figure 14. BURN-OFF CURVES FOR SARAN CHAR AT 375°C

and the system evacuated. Oxygen (0.5 torr) was then introduced and left in contact with the sample for 24 hr following which the sample was evacuated and the products of the decomposition of surface complexes were measured as before.

Table 13 gives the data for two samples of a Saran char burned off to 20.1%. In the case of sample 1, the sample was heated, first to 375°C and then to 950°C. Sample 2 was heated directly to 950°C. In all cases the CO and CO₂ were collected and analyzed. The amounts of CO and CO₂ were converted to the equivalent area of carbon surface which they occupied, as discussed in previous reports. The amounts of CO and CO₂ decomposed between ambient and 375°C were taken as an approximate measurement of the ASA unoccupied during reaction at 375°C (UASA). The amounts of CO and CO₂ decomposed between 375 and 950°C were taken to correspond to the ASA occupied during the reaction (OASA), while the total amounts of CO and CO₂ desorbed up to 950°C were taken as a measure of total ASA (TASA), during reaction.

TASA measurements, by Laine's method⁷, were made of samples 1 and 2 at 100°C and 0.05 torr O₂, as described above. The samples were again cooled to 100°C following the desorption step, and the measurements repeated. These data are given in Table 14. During the coming quarter further runs will be conducted on this system to explore ASA as a function of temperature. Furthermore, studies on Saran char samples prepared at different levels of carbon burn-off in the tube furnace will be continued.

Table 13. ASA of 20.1% BO Saran Char 375°C - 1 ATM Air Adsorption*

Sample	375°C			950°C			
	P _{CO}	P _{CO₂}	UASA	P _{CO}	P _{CO₂}	OASA	TASA
1	18.3	27.0	37.3	367	27	329	366
2	----	----	----	402	65		371

Table 14. ASA of 20.1% BO Saran Char 100°C - 0.5 torr O₂ Adsorption*

Sample	Run 1			Run 2		
	P _{CO}	P _{CO₂}	ASA	P _{CO}	P _{CO₂}	ASA
1	12.4	3.6	13.3	12.7	2.8	12.9
2	18.0	3.7	14.4	15.8	3.1	15.1

*P_{CO} and P_{CO₂} are given in millitorr pressure (no correction for sample size or reactor volume). ASA's are given in m²/gm.

EFFECT OF CATION EXCHANGE AND METAL ADDITION ON CHAR REACTIVITY (TASK 30)

Carboxyl Groups and Exchangeable Cations in Lignitic Coals

The carboxyl content of the three lignites chosen was determined. The procedure used was outlined in a previous report. Results for this analysis can be seen in Table 15. The values shown here are the average of 6-8 runs along with the value for one standard deviation.

A check on the carboxyl contents was also performed. This entails back-exchanging the barium put on the carboxyl groups by treatment with barium acetate. The first step of the procedure is to wash the coal with 1 N sodium acetate (pH = 8.25) under flowing nitrogen. Washing must be carried out with care to ensure the removal of excess barium acetate without exchange or hydrolysis of the barium on the carboxyl groups. The washed coal (approximately 0.625 g) is then transferred to a beaker and 50 ml of 0.2 N perchloric acid is added. This mixture is then covered and brought to a boil. It is then stirred for 20 min. The mixture is then filtered and washed with distilled water and the filtrate diluted to 100 ml. The barium content of the solution is then determined by emission spectrometry.

The results of this analysis can be seen in Table 16. The data presented are from a representative run where the carboxyl group content as measured by the barium released is calculated by assuming that two carboxyl groups are associated with each barium ion. The close agreement of these results supports this hypothesis.

Work was also started on the determination of the cations exchanged on the carboxyl groups in the raw coal. For this determination about 0.5 g of coal is exchanged with 50 ml of 1 N ammonium acetate (pH = 7.0-7.2). The solution is stirred for three-hour periods after which the coal is filtered and the filtrate diluted with 5 ml of glacial acetic acid and distilled water to 100 ml. Fresh ammonium acetate is then added and the stirring repeated. This was carried out for five 3-hr periods, followed by mixing overnight and subsequently one more 3-hr period. The results of this work for PSOC-833 (a Montana lignite) can be seen in Table 7.

The total milliequivalents of carboxylic salts for PSOC-833 is 1.81 ± 0.06 mequiv/g dmmf. This compares to 3.00 ± 0.06 mequiv/g dmmf for the total carboxyl group content. Thus, about 60% of the groups have an associated cation, which is what one would expect since the pH of the formation of coal is considerably less than that for complete exchange of the carboxyl groups. Schafer⁸ found a linear relationship between the carboxyl content and pH of exchange. Assuming this is true, the coal must have been exposed to water of about pH = 5 which is within the limits of the environment that is normally associated with coal deposits.

The results also show that almost all of the carboxylates are composed of either magnesium or calcium. Barium, strontium, sodium and potassium are present in relatively small amounts.

Table 15. Carboxyl Group Analysis

Lignite	State	Carboxyl Content via titration Mequiv/g dmmf
PSOC-623	Texas	2.11 ± 0.08
PSOC-833	Montana	3.00 ± 0.07
PSOC-246	North Dakota	3.13 ± 0.05

Table 16. Comparison of Two Techniques to Measure Carboxyl Content

Lignite	State	Mequiv/g dmmf	
		Titration	Barium Released
PSOC-623	Texas	2.15	2.22
PSOC-833	Montana	3.07	3.07
PSOC-246	North Dakota	3.18	3.24

Table 17. Carboxylic Salts in Montana Lignite

Concentration 10 ⁻⁶ moles/g dmmf					
Mg	Ca	Sr	K	Na	Ba
271.9	585.2	4.25	14.99	41.08	8.46
total = 1.81 ± 0.06 mequiv/g dmmf					

Effect of Cation Addition on Char Gasification

During this quarter, we have studied the reactivities in CO_2 at 760°C and in H_2 at 790°C of chars produced at 800°C from a lignite containing equivalent amounts of different exchangeable cations. A DuPont 951 TGA balance in conjunction with a 990 Thermal Analyzer were used to monitor weight changes during the char- CO_2 and char- H_2 gasification reactions. About 4 mg of char contained in a platinum bucket were used for reactivity measurement. The TGA system was flushed with N_2 (100°cc/min) for 20 min to replace air. The sample was then heated up to 800°C at a rate of 20°C/min . The sample was held at 800°C until it attained a constant weight. Following this, the sample was cooled in N_2 down to reaction temperature. The temperature was kept constant for 30 min after which N_2 was replaced by CO_2 or H_2 . Decrease in sample weight due to gasification was then continuously recorded. The cation-exchanged chars used in these studies are the same as those used in the previous study.

Reactivity in Carbon Dioxide

Burn-off versus time plots for chars produced from raw, demineralized and cation-exchanged samples are shown in Figure 15.

The demineralized char is significantly less reactive than the raw char. This is presumably due to the loss of catalytic inorganic matter upon acid treatment. The following order of reactivities is observed for chars produced from raw, demineralized and cation-exchanged samples:

The higher reactivity of the raw char compared to the iron and magnesium containing chars is probably due to the presence of exchangeable calcium ion in the raw lignite. Although there was a large difference between K and Ca catalytic activity for reaction in air, no appreciable difference between those two samples is found for reactivity in CO_2 .

It is also of interest that the Mg-exchanged char has a lower reactivity than the demineralized sample. The difference in reactivity between those two samples was even more marked at 780°C .

Even though the char- O_2 and char- CO_2 reactions both involve an intermediate oxygen transfer step followed by a gasification step, the order of reactivities of chars produced from different cation-exchanged samples is not the same in the two oxidizing atmospheres. This shows the high specificity of different catalytic species. It is known that iron is a good oxidation catalyst but is soon deactivated upon the formation of its oxide.

Reactivity in Hydrogen

Burn-off plots for various char samples in H_2 are shown in Figure 16. The order of reactivities of various samples in H_2 is markedly different from that observed in the two oxidizing (air and CO_2) atmospheres. Below 45% burn-off, sodium is the most effective hydrogasification

Figure 15. BURN-OFF VERSUS TIME PLOTS IN CO_2 AT 760°C OF CHARS PRODUCED FROM RAW, DEMINERALIZED AND CATION-EXCHANGED LIGNITE

Figure 16. BURN-OFF VERSUS TIME PLOTS IN H_2 AT $790^\circ C$ OF CHARs PRODUCED FROM RAW, DEMINERALIZED AND CATION-EXCHANGED LIGNITE

catalyst; whereas at higher burn-offs iron is a better catalyst. The raw char has much more reactivity in H_2 than the potassium and calcium-exchanged chars. This is presumably due to iron in the raw lignite⁹. Although potassium and calcium are good catalysts in oxidizing atmosphere, they are poor catalysts for hydrogasification.

It is also of interest that the demineralized sample has a higher reactivity than potassium and magnesium-exchanged samples. Results of the present studies indicate the high specificity to different cations in catalyzing the char- CO_2 and char- H_2 gasification reactions. However, as pointed out in Quarterly Technical Progress Report FE-2030-15, it cannot be completely ruled out that the observed changes in reactivities in CO_2 and H_2 brought about by the exchangeable cation may be due to differences in the surface area, porosity and pore size distribution of different char samples.

CONCLUSIONS

FACET I-B: COAL CHARACTERIZATION

Task 5: Coal Characterization

In a comparison of properties of whole coals and vitrinite concentrates derived from them, the vitrinites display higher reflectance values and greater fluidities than the whole coals.

Task 7: Automation of Microscope Analytical Methods

The particle size and relative reflectance of coal components can introduce unexpected variations in automated microscope reflectograms that must be taken into account in quantitative interpretations.

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

Task 23: Operation of Isothermal Furnace

The maximum potential weight loss in the isothermal furnace is not directly measurable by a practicable number of recycles of the char.

Empirically correlating weight loss in the isothermal furnace with change in proximate volatile matter between the original coal and char provides a technique for calculating the maximum potential weight loss.

For Texas lignite, PSOC-412 the maximum potential weight loss is 66% of the daf coal and is relatively independent of particle size and temperature over the range of operating conditions.

The maximum potential weight loss exceeds the proximate volatile matter of the lignite by a factor of 1.3.

TASK IV-B: COKES AND CHARs

Task 27: Effects of Variables on Char Structure

Combined TGA, TMA studies provide a good quantitative picture of the effects of preoxidation on the caking properties of coals. Through this technique it is shown that, for a given level of oxygen uptake, the temperature of preoxidation has a marked influence on the effectiveness of oxidation in destroying plastic properties. Controlled oxidation studies indicate that addition of small amounts of oxygen (1-2% by wt) bring about drastic reduction in swelling and a steady increase in dilation temperatures. Particle size studies show that agglomeration and swelling properties are partially restored upon grinding of an oxidized coal. Finally, water vapor is shown to have an accelerating effect in reducing the plastic properties of a high swelling coal.

The tests of the applicability of small angle x-ray scattering procedures are completed. Results obtained for glassy carbon, Saran chars and coal chars have demonstrated that these techniques give much promise for the characterization of the porous nature of microporous carbonaceous solids.

Task 28: Effect of Char Structure on Reactivities

Burn-off plots for Saran char using the gas chromatograph-tube furnace system have been constructed, proving the applicability of the system. Mass spectrometer data have shown active surface area of Saran char to be some function of the conditions under which oxygen adsorption is occurring.

Task 30: Effect of Catalytic Cations on Reactivity

Ion exchange with barium acetate, as described in this and earlier reports, is an accurate and precise method for carboxyl group determination. Also, the results from the back-exchange of the barium substantiates the idea that two carboxyl groups are associated with divalent ions.

Studies of the carboxylic salts of PSOC-833 reveal that approximately 60% of the carboxyl groups are associated with cations. This suggests a pH of about 5 for the water associated with the coal. The major cations for this Montana lignite are magnesium and calcium.

Reactivities of chars produced at 800°C from a Texas lignite containing equivalent amounts of exchangeable sodium, calcium, magnesium and iron have been measured in 1 atm of CO₂ and H₂. The presence of cations in the coal precursor generally increases the reactivity of the char produced, but the extent of the increase is markedly dependent upon the nature of the cation.

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