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

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by

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ABSTRACT

The Penn State/DOE Coal Sample Bank was expanded to include seventeen lignite seams from Texas and two samples of a western Kentucky coal (Facet I-A). A total of 253 characterized coal samples and 539 selected printouts of coal data were provided to the coal research community (Facet I-C).

Results of further coal fractionation studies confirm previous conclusions that fractions of widely differing characteristics can be developed in the laboratory, and indicate that with appropriate process development they could be produced commercially. Knowledge of the detailed occurrence, associations, and format provides the basis for pyrite rejection during coal beneficiation. A sample of Clarion seam coal is being studied seeking to isolate pyrite using procedures which will minimize the physical change of the pyrite occurrence. The morphology, distribution, and chemical nature of the pyrite forms isolated are being evaluated (Facet II).

In Facet IV-A, operation of the isothermal furnace has continued during this quarter using nitrogen as a pyrolysis medium at a temperature of 800°C. A Texas Darco lignite, PSOC-412, has been characterized extensively with respect to the effect of particle size on weight loss for times up to 300 msec. Weight loss increases as the particle size decreases, for a given residence time, down to a limiting particle size below which weight loss is independent of particle size. For 300 msec residence time the limiting particle size is about 100 μm . Combustion pot experiments to study the variation of the bed density show that the particle density remains nearly constant during gasification.

Under Facet IV-B, a study is being made into the effects of low temperature oxidation on reducing the agglomerating properties of caking coals. The ultimate aim is to thereby increase the reactivity of the chars produced. Thermogravimetric studies have shown that oxygen uptake can be followed both quantitatively and reproducibly. A DuPont 942 Thermomechanical Analyzer (TMA) is being used to study agglomerating properties. This system shows much promise in defining softening points and in supplying quantitative swelling data.

Removal of inorganic matter by acid treatment significantly changes the nitrogen and carbon dioxide areas of coals and chars. The effect is more pronounced in the case of chars.

The effect of preoxidation in air of a highly caking coal in the temperature range 120-250°C on weight loss during pyrolysis up to 1000°C and reactivity of resultant chars to air at 470°C has been investigated. Preoxidation markedly enhances subsequent char reactivity. For a given level of oxidation, the preoxidation temperature as well as the presence of water vapor in air has essentially no effect on char reactivity.

The characterization of certain, important aspects of the chemical and physical makeup of lignite coals is being undertaken. The first analysis will involve use of a LTA with x-ray diffraction to determine the mineral content and composition of the coals. The second stage involves defining the total amount of carboxyl groups present and the extent to which they have been substituted by cations. The purpose of this study is to define a standard, repeatable laboratory technique to measure these fundamental properties.

Reactivities of a series of char samples produced at 800°C from a lignitic coal containing different amounts of exchangeable calcium ions have been measured in 1 atm air at 390°C. Char reactivity increases linearly with increase in the calcium content of the char.

In research conducted under Facet IV-F, when an unactivated Saran char is subjected to oxygen at 125-227°C, chemisorption of the gas occurs simultaneously with an early gasification reaction. The former process has a constant value of activation energy which is independent of fractional surface coverage θ , where $0.92 > \theta > 0.79$. For gasification reaction, E_a is about 14.3-16.7 kcal/mole. A theoretical study on some experimental data^a obtained from both DSC and TGA techniques indicates that "such" gasification reactions yield carbon dioxide rather than carbon monoxide. A new parameter, (oxygen/carbon), is introduced. This gives the ratio between the differential counts of oxygen atoms chemisorbed and those of carbon atoms gasified. Apart from reaction temperature, the parameter decreases with increasing coverage ($\theta = 0.76-0.98$) and finally levels off at (oxygen/carbon) = 2.0.

The mathematical model of a plane flame furnace (Facet V-A) firing char and low volatile fuel is being improved with the inclusion of radiative heat transfer from the flame to the walls, and of a conduction heat loss through the walls to the ambient. The heat generation term is modified by consideration of the attackable surface area of the fuel particles. The predicted gas temperatures and flame front positions vary with fuel properties (reactivity, particle size, fuel density) and operating conditions (excess air, air preheat, etc.). The predicted peak gas temperature of about $1550 \pm 20^\circ\text{C}$ and the flame front location are in basic agreement with experimental data. Improved agreement between the model and the experimental results continues to be sought with the measurement of gas temperature profiles, gas concentrations and burn-off of solid particles.

Experiments on the combustion characteristics of coal-oil mixtures (Facet V-B) have led to minor furnace and control modifications, improvements in operating procedures, and an improved basis for evaluating experimental data. A sequence of experiments indicates that the thermal efficiency increases with amounts of coal addition through a peak of about 10 weight-percent coal, and decreases again. On the other hand NO emissions increase through the range of coal addition (16%), apparently due to increasing fuel nitrogen. The trend is similar to that observed in the previous work on coal/oil/water/air emulsions. In both cases the behavior can be explained by a balance between the flame and wall radiations.

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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

LEGEND

SCHEDULED		SCHEDULE EXTENSION
PROGRESS		EARLY START

PROJECT PLAN AND PROGRESS REPORT
Quarter Ending March 31, 1978

SUMMARY OF PROGRESS TO DATE

In Facet I, seventeen Texas lignites and two samples of western Kentucky coal were collected during the quarter (Task 3). Table 1 summarizes the status of coal characterization and the Penn State/DOE Coal Data Bank (Task 5). Rapid Scan (automated reflectance microscopy) reflectograms and pyrite chord-size analyses obtained from a newly assembled system show less variability than older data; systemic artifacts inherent in the older system are now avoided. Future work will provide suitable statistical programs to handle the pyrite and petrographic data; the pyrite study should be concluded during the next quarter (Task 7). A total of 253 characterized coal samples and 539 selected printouts of coal data were provided to the coal research community during the research period (Tasks 9-14).

In Task 18 of Facet II, 23 coals have been fractionated and chemically analyzed in the planned series of washability studies. In Task 19, two samples have been specially tested for another DOE contractor. The relationship of pyrite separation in beneficiation to its occurrence, form, and association is now being undertaken as a part of Task 21.

In Task 23 of Facet IV-A, a Texas lignite, PSOC-412, has been studied extensively at one isothermal pyrolysis temperature, 800°C, for times up to 300 msec. About twenty runs were performed to obtain the data. Construction of a 1000°C furnace is near completion which will allow the evaluation of temperature as a parameter. The new furnace offers an increased residence time of 600 msec. A similar number of runs like those already made will be performed at a minimum of two higher temperatures.

The combustion pot study of the reactivity of coal and coke has been completed (Task 26). During the course of the program a total of 61 experiments and several additional supporting experiments have been carried out to study the mechanism of reaction in a solid fuel bed. During this period experiments using coals designated PSOC-322 and PSOC-80 led to results which agree with those presented in previous quarterly reports. The activation energy obtained for coal has been found to be about 30 kcal for the carbon/carbon dioxide reaction. Several supporting experiments showed that the apparent density and bed porosity do not change appreciably during the gasification runs, indicating that internal reaction is not significant in the combustion zone. This supports the previously adopted assumption of diffusion dominant reaction in the combustion zone of the solid fuel bed reactor.

In Task 27 of Facet IV-B, the use of a Fisher Thermogravimetric Analyzer (TGA) has been shown to be an effective, quantitative technique for the measurement of oxygen sorption. As reported previously, oxygen uptake at a given temperature and particle size can be followed accurately and reproducibly (within $\pm 2\%$). Particle size studies have shown that oxygen chemisorption is controlled by diffusion through the individual particles. Finally, we have shown that even at temperatures as low as 200°C, there is concurrent gasification and chemisorption. At temperatures below 150°C no significant gasification is observed. The fluid-bed reactor, which is to be used for preoxidation of coal samples has been designed and built. Preliminary tests have shown that all particle sizes to be studied in this investigation (35 x 60 mesh, 100 x 150 mesh, and 200 x 250 mesh) can be easily fluidized. From combined TGA and

fluidization results we believe we can quantitatively add oxygen to coal samples in the fluid bed reactor. The DuPont 942 TMA system is being investigated as a method of characterizing the swelling and softening behavior of coals upon carbonization. This system shows much promise in defining softening points and in supplying quantitative swelling data. Over 40 TMA experiments have been conducted to date in an attempt to determine optimum operating conditions. It is estimated that approximately 100 more experiments will be required before a standard TMA technique can be adopted. The coal selected for use in the early stages of this study is the high volatile bituminous PSOC-337. The selection criteria were that the coal have a high FSI, low ash yield, and a high vitrinite concentration. In order to remove the possibility of preoxidation of samples during preparation and storage, all grinding, sieving and storage has been done under a nitrogen atmosphere.

With the submission of this report, the work on the effect of inorganic matter removal on surface areas of coals and chars will be discontinued. The results obtained will be reported in the form of a publication.

The effect of preoxidation in air of a highly caking coal on weight loss during pyrolysis up to 1000°C and reactivity of resultant char to air at 470°C has been studied in Task 28. Weight loss during pyrolysis above 400°C decreases with increase in weight gain during preoxidation. Preoxidation markedly enhances subsequent char reactivity; the effect is more pronounced at lower levels of preoxidation. It is only the extent of preoxidation (that is the weight gain during preoxidation) which determines the reactivity of the char produced from a caking coal. The presence of water vapor in air during preoxidation has no noticeable effect on weight loss during pyrolysis as well as on subsequent reactivity. It is planned to study one more caking coal in this program.

A literature survey was conducted and initial tests have been made on a LTA and a x-ray diffractometer as part of Task 30. Also, the effect of cation exchange on the subsequent reactivity of a lignite char during gasification in air at 390°C has been studied. The presence of calcium in the chars has a marked accelerating effect on char reactivity. Normalized reactivities of the various calcium containing chars are essentially the same in air and steam. With the submission of this report, about one-half of the proposed work on the effect of exchangeable cations on subsequent char reactivity has been completed.

Differential scanning calorimetry (DSC) and thermogravimetry (TGA) techniques have been used to study the thermal and chemical effects involved during oxidation of Saran chars in the temperature range 75-950°C (Facet IV-F, Task 31). Three samples, particle size 150 x 250 mesh, have been considered: (i) the unactivated Saran, (ii) the same sample but associated with iron (101 ppm) as a contaminated impurity during grinding via stainless steel gears, and (iii) an air-activated Saran which had been burned to a 63.8 percent level of burn-off. In spite of some major differences between the three carbons, they all have shown the same general trend (sequence of reactions) when exposed to oxygen. For example, below 100°C, physical adsorption and chemisorption of oxygen are occurring simultaneously. At 100°C, chemisorption of oxygen is the predominant process. In the temperature range 125-250°C, two processes are taking place; chemisorption of oxygen and gasification of the complex formed. The latter reaction, being observed at such low temperatures, is named hereafter as early-gasification. The combination of DSC and TGA techniques has led to the observation

of such early-gasification. As one might expect, in the temperature range 450-950°C gasification leading to a complete burn-off is certainly taking place. The kinetics of this reaction has also been studied by the thermogravimetric technique. Detailed kinetic studies on the early gasification process have been made. It has now been confirmed that the rates of early-gasification (at 125-250°C) are many orders of magnitude higher than those obtained by extrapolation of higher temperature (450-550°C) gasification data obtained to this temperature range.

In Facet V-B, Task 34, coal, oil, water and air have been mixed in a number of ratios to establish the general behavior of the mixtures, and their physical-chemical properties. Characterization of the furnace and its dynamic responses has laid the foundations for a more complete and systematic evaluation.

The combustion characteristics of coal-oil and coal-oil-water-air mixtures, and the effect of the water and coal additions on the heat transfer and NO_x production from No. 2 fuel oil have been studied. Water additions have reduced the amount of excess air at various smoke levels, although the reduction of excess air at smoke point is not significant. As coal has been added to oil-water-air emulsions, and to No. 2 fuel oil a rise in furnace efficiency has been attributed to increasing flame emissivity without significant changes in excess air requirements for complete combustion. Beyond a level of coal additions of from 5 to 10 percent, declines in furnace efficiency are attributable to the attenuation of the radiation from the walls in transmission through the flame. Trends in exhaust gas temperatures substantiate this argument.

Improvement of the mathematical model of a plane flame furnace (Facet V-A, Task 33) has continued. Assuming an infinite parallel plane geometry (properties vary only along the direction of flow) as a starting point toward further three-dimensional modelling, results have been compared with those obtained experimentally with four chars which have been burned in a plane flame furnace at common air flow rates. Modifications to the model such as uneven nodal spacing, variable radiation absorption coefficients and diffusional limitations on combustion rates have brought the model results closer to reality. The study of the infinite parallel plane model has provided insight on the effects of major variables such as combustor length and fuel reactivity.

Experimental work has been resumed with the measurement of gas temperatures and the collection and analyses of gas and solid samples.

The following Technical Reports have been submitted to DOE during the report period:

- FE-2030-TR6 - The Effects of Impregnation of Coal with Potassium and Sodium Salts, H. Marsh and P.L. Walker;
- FE-2030-TR7 - Porosity of Coals and Coal Products, O.P. Mahajan and P.L. Walker;
- FE-2030-TR8 - Reactivity of Heat Treated Chars, O.P. Mahajan and P.L. Walker;

FE-2030-TR9 - Study of the Interrelationships Among Chemical and
Petrographic Variables of United States Coals, C. Waddell,
A. Davis, W. Spackman and J.C. Griffiths

FACET I-A: SAMPLE COLLECTION

COAL SAMPLING (TASK 3)

During this period, no sampling trips were made by Penn State personnel. Our subcontract with Texas A & M University, however, resulted in the receipt of nine cores containing seventeen lignite seams from Texas. We also received two samples from PERC of a western Kentucky coal, one a raw coal sample and the other a cleaned product of the same coal.

FACET I-B: COAL CHARACTERIZATION

COAL CHARACTERIZATION (TASK 5)

Maceral analyses were completed on 79 PSOC samples, reflectance analyses on 76 samples, and fluorescence analyses on 48 samples during this quarter. In addition, maceral analyses were completed on the washability fractions of six coals, with the total number of fractions equaling 170. The free swelling index was determined for 75 coals, Gray-king coke types analyses were run on 100 coals, and Hardgrove grindability determined for 67 coals.

The current status of the coal characterization program and the Penn State/DOE Coal Data Base is summarized in Table 1.

The Plastic Properties of Coals and Their Influence in Conversion Processes

A brief description of the work relating coal fluidity to both liquefaction behavior and the degree of oxidation of coals was given in FE-2030-10. An order had been placed for a fully automated Gieseler plastometer, especially modified to provide a range of heating rates from about 1 to 12°C/min (the standard rate is 3°/min). Delivery of the instrument is expected in May.

RAPID SCAN AUTOMATED REFLECTANCE MICROSCOPE SYSTEM (TASK 7)

Work under Task 7 has been directed toward bringing the new PDP-8 computer system on line for pyrite and maceral analysis. System hardware has been tested and debugged and the necessary software modifications have been effected. All data acquisition programs have been updated and are now operable on the new facility. Refinements are still needed on the plotting software, but summary data can be made available on the line printer or terminal.

New programs are being developed to improve Rapid Scan data acquisition by taking advantage of the larger memory capacity (32K) and greater overall flexibility of the PDP-8 computer over an older model, the PDP-9. Reflectograms and pyrite chord-size analyses completed on the new system show less variability than older data. This is due primarily to the improved optics and photomultiplier stability of the Leitz MPV-2 microscope and also to a more accurate digitizing of the analog output provided by the PDP-8's analog to digital converter. Thus, the hardware improvements have made the data more reliable and provided a basis for a reasonable comparison between samples.

Prior to this time, it was difficult to tell whether the observed similarities and differences among samples were real or simply systemic artifacts. Comparisons could be made in only a general, qualitative manner.

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

SERVICE TO OTHER AGENCIES (TASKS 8-14)

At the request of other agencies engaged in coal research, we have supplied 253 characterized coal samples, ranging in quantity from 10 g to 150 lbs, and 539 selected printouts of coal data from the Penn State/DOE Coal Data Bank.

The agencies requesting these materials and their research interest include: Adelphia Center for Energy research (coal-oil water blends); General Electric Corporation (sulfur studies); Kansas State University (liquefaction studied); West Virginia Geologic and Economic Survey (x-ray scatter study); Ohio University (infra-red diffuse spectrum); PERC (coal combustion); U.S. Bureau of Mines (demethanization); California State University (thermal studies); Iowa State University (sulfur in coal); Sandia Laboratories (combustion); and Mobil Field Research Laboratory (thermal degradation).

FACET II: COAL BENEFICIATION AND PRE-USE PROCESSING

WASHABILITY CHARACTERIZATION (TASK 18)

To date 23 different coals have been fractionated and the chemical analysis completed. These are listed in Table 2. One of these, PSOC-453, was completed during this quarter. Another coal, PSOC-495 (Hiawatha Seam, Orangeville, Utah) is now in the fractionation process. These coals represent eight different ranks of widespread geographic origin. The fractions show great variation in ash, sulfur, and maceral content. The data confirm previous reported conclusions that coal fractions of widely differing characteristics can be developed in the laboratory and indicate that with appropriate process development could be produced commercially.

The Blind Canyon seam sample (PSOC-453, High Volatile A) was unusual in its low ash and sulfur content and particle density. Seventy-five percent of the sample (all plus 16M) had densities less than 1.3, an ash content of 4.21 percent, and a sulfur content of 0.43 percent. Based on an estimation on a dry, ash-free basis, the heat content of such a prepared product would be 14,055 Btu/lb, an unusually high value for this coal rank. Individual fractions had ash values as low as 3.01 percent and sulfur as low as 0.34 percent. The 1.30 sink fraction (+16M) had ash contents between 17.73 percent and 28.91 percent with a somewhat higher sulfur content. The sulfur content was decidedly higher (0.43-0.91%) which amounted to 17 percent of the coal. Undoubtedly, a low density separation of these fines would increase the yield of a superior clean coal product to over 85 percent. The hardness fractions also showed wide variation (74.7-61.5 HGI) suggesting major differences in maceral composition.

The pellets for petrographic analysis of PSOC-453 have been prepared. During the past quarter, maceral data were completed for several samples whose fractionation was previously reported. These were PSOC-183, 184, 241, 242, 383, and 609.

PSOC-183 (High Volatile B, Upper Block, Brazil, Ind.) is unusual in its low vitrinite (49.3%), high sporinite content (21.3%), and high fusinite content (11.3%). The size-density fractions confirm these characteristics, although the sporinite content tends to be lower and the fusinite content higher than found in the head sample. The vitrinite decreases with increasing particle density (66.70 to 19.10%). It also tends to increase with decreasing particle size and decrease with particle hardness. The exinite shows a reverse trend to the vitrinite and increases with particle density (8.20 to 20.8%). The exinite tends to remain with the larger sizes, but there is little distinct trend with hardness. Peculiarly, the 1/4" x 16M fraction of B hardness counters these general trends. The fusinite concentrations parallel those of the exinite, but with greater variation and concentration with particle density (13.4 to 55.2%). It contrasts with exinite in transferring to the smaller sizes which is consistent with fusinite brittleness. There is no trend with hardness. This trend of fusinite and exinite association has been observed and reported previously in these studies. This form of occurrence is not conducive to concentration of

Table 2. Listing of Coal Samples Fractionated

PSOC No.	Seam	Sample Location	Rank	Fractions Developed		
				Hardness	Size	Density
183	Upper Block	Brazil, Ind.	High Volatile B	3	5	5
184	Upper-Lower Block	Carbon, Ind.	High Volatile C	3	5	4
241	Monarch	Sheridan, Wy.	Subbituminous B	3	5	4
242	Deitz	Sheridan, Wy.	Subbituminous B	3	5	3
317	Lower Freeport	Stoystown, Pa.	Low Volatile	1*	5	6
326	Upper Kittanning	Kittanning, Pa.	High Volatile A	3	5	4
329	Brookville	Edinburg, Pa.	High Volatile A	3	5	5
337	Lower Kittanning	Brookville, Pa.	High Volatile A	3	5	4
349	Lower Clarion	Bruin, Pa.	High Volatile A	3	5	5
357	Lower Elkhorn	Mouthcard, Ky.	High Volatile A	3	5	5
367	Hazard No. 7	Hazard, Ky.	High Volatile A	3	5	4
379	B	Mildred, Pa.	Semianthracite	3	5	3
383	A	Mildred, Pa.	Semianthracite	3	5	7
399	Fort Scott	Venita, Okla.	High Volatile A	3	5	5
401	Mineral	Welch, Okla.	High Volatile A	3	5	4
416	No Name	Titus County, Tex.	Lignite	3	5	4
425	Lignite	Fairfield, Tex.	Subbituminous C	3	5	3
453	Blind Canyon	Orangeville, Ut.	High Volatile A	3	5	3
459	Lower Sunnyside	Horse Canyon, Ut.	High Volatile B	3	5	4
507	#24	Hanna, Wy.	High Volatile C	3	5	3
574	Whole	Texas	High Volatile C	1*	4	10
609	Unknown	Maverick, Tex.	High Volatile B	1*	4	10
614	Lower Clarion	Clarion, Pa.	High Volatile A	3	5	6
495	Hiawatha	Orangeville, Ut.	High Volatile B	Process in Progress		

*Inadequate sample for further hardness fractions

reactive macerals. In overall contrast, the micrinite behavior is erratic. The softer A hardness fraction shows a micrinite concentration in the 1.22 float fractions (11.6-13.9%), but is nearly constant in the 1.22 sink fractions (7.80-9.80%). The two harder fractions show an increased level of micrinite which tends to parallel the vitrinite (19.70-4.50%). This coal shows substantial hardness variation (69.1 to 60.1 HGI). As a low-ash coal, its quality could be enhanced by separation at 1.40 in a yield approaching 90 percent (6.08 to 4.64%) and the sulfur reduced from 1.27 to less than 1.00 percent.

PSOC-184 (High Volatile C, Upper and Lower Block, Carbon, Ind.) is quite different from PSOC-183, being higher in vitrinite content, similar in fusinite content, but much lower in exinite. This observation from the fractionation is not consistent with the head sample analyses. The vitrinite-fusinite dissociation of PSOC-183 is maintained, but at different levels (vitrinite 85.80-50.30%; fusinite 6.20-30.60%). An anomaly is observed in the 1.24 x 1.30 density fraction where the vitrinite is lower and the fusinite higher than in fractions on either side. The variation with particle size and hardness is less distinct than for PSOC-183. The concentrations of exinite and micrinite are more constant than in PSOC-183 (exinite 9.0-2.5%; micrinite 13.5-2.00%) being lowest in the 1.40 sink fractions. This sample showed an unusually wide spread in hardness (119.7-60.7 HGI). The coal could be prepared in good yield (> 70%) with a low ash content (6.2%) at a density of 1.40, but the sulfur reduction would be limited (from 2.60 to 2.00%).

PSOC-241 (subbituminous B, Monarch seam) is a high vitrinite coal (85.7%). The fractionation at densities less than 1.35 further concentrated this maceral by rejecting the micrinite and fusinite (85.9-92.0%). The 1.40 sink fractions were consistently low in vitrinite (55.6-70.8%). The smaller sizes showed higher levels of concentration suggesting some degree of liberation. The highest fraction showed lower levels of concentration. This is quite a hard coal showing an HGI range from 56.7 to 44.9. The other reactive maceral, exinite, was evenly distributed in all fractions ranging from 0.50 to 2.5%. Both the micrinite and fusinite increased in concentration with particle density ranging from 0.60 to 4.30 percent and 4.30 to 40.2 percent, respectively. There was no consistent trend with particle size or hardness. As a low ash and sulfur coal (4.70 and 0.50%, respectively), the improvement by cleaning at 1.40 was not great (80% yield of a 3.73% ash and 0.39% sulfur product).

PSOC-242, another subbituminous B coal (Deitz seam), differed primarily from PSOC-241 with about 5 percent greater vitrinite (90.6%) and less fusinite. There was a further concentration of vitrinite attained in the C hardness fraction (94.2-96.4%), although there appears to be little variation with particle density of particle size. The hardness range was 50.4-45.4 HGI. The exinite showed little variation between fractions (0.90-2.40%). There was a trend toward both micrinite and fusinite being concentrated in the more dense fractions (0.60-2.20% and 0.70 and 5.0%, respectively), however, the change was not great in this high vitrinite coal. Obviously, the coal is unusual in its very high vitrinite content--which may be enhanced by beneficiation. Beneficiation would accomplish little ash or sulfur reduction (head sample 4.82 and 0.50%, respectively).

PSOC-393 (semianthracite, A seam, Sullivan County, Pa.) has been considered by some as more related to the low volatile seams of Central Pennsylvania than the anthracite seams of Northeast Pennsylvania. It has 10.55% volatile matter on a Parr dmmf which is less than the low volatile grouping. Its maceral composition naturally reports no exinite, but some micrinite. It has higher fusinite content and less vitrinite than many anthracites. Thus, its fractionation is basically a two-phase separation: vitrinite and fusinite. The density distribution of these components occurs over a wide range--from less than 1.40 to greater than 1.80. Vitrinite concentrates in the lower density fractions while fusinite reports to the higher density groups showing the typical association between fusinite and mineral matter. The feed vitrinite content of 82.8 percent was concentrated to 89.4-91.6 percent in the 1.45 float, A hardness fractions and was reduced to 50.8 percent in the 1.80 sink fraction. The vitrinite concentration decreased with increasing density and hardness and decreasing particle size. The fusinite was reduced from 13.8 percent to 6.1 percent in the 1.40 float, A hardness and increased to 43.7 percent with increasing density and hardness and decreasing particle size. The distribution of the 3.4 percent micrinite was more uniform, although was reduced to less than 2.0 percent in the high vitrinite fractions and concentrated with the fusinite to a maximum of 9.4 percent. The ash content was reduced substantially from the 21.7 percent feed to a low of 6.5 percent (1.40) and to 13.7 percent with a yield of 75 percent at a density of 1.80. With further liberation of the highly disseminated mineral matter further improvement would be possible. There is some sulfur reduction from the 0.94 percent feed level to about 0.75-0.80 percent with the rejected sulfur reporting to the 1.80 sink fraction. The residual pyrite is obviously finely divided and disseminated among all the 1.80 float fractions.

PSOC-609 is a core composite of an unnamed seam of high volatile B coal found at Maverick, Texas. The limited quantity of sample did not permit development of the hardness fractions. The gravity fractionation was carried out on the +16 mesh material representing 86.3 percent of the sample. The maceral distribution was surprisingly similar to PSOC-383 containing primarily vitrinite and fusinite, although low levels of micrinite and exinite were observed. These latter minor components (0.5-3.0% and 0.4-2.6%, respectively) were uniformly distributed throughout the several densities. The density range was even greater than PSOC-383 with 24.4 percent floating at 1.3. Vitrinite decreased from a high of 94.6 percent in the 1.3 float fraction to 72.6 percent in the 2.0 sink fraction with fusinite showing the opposite trend from 3.8 percent to 26.0 percent. Again the fusinite-mineral matter association is obvious with the ash increasing from 7.7 percent to 75.2 percent over the same density range. The sulfur distribution was uniform and somewhat random with respect to density ranging between 0.28 and 1.08 percent. Apparently relatively low levels of pyritic sulfur either are liberated or associated with the mineral matter in this coal.

PHYSICAL PROPERTIES OF COAL LITHOTYPES (TASK 19)

Special tests performed for other DOE contractors were friability tests (ASTM 441-45--Tumbler Test) on POC-334 and 335. These were special coal products prepared by Ingersoll-Rand in the form of extruded briquettes.

BENEFICIATION OF CONVERSION FEEDSTOCKS (TASK 21)

The search for new approaches to innovative preparation concepts has continued with detailed pyrite form-distribution studies. Although these studies utilize pyrite reduction as a format, the approach and procedures being developed are applicable to other mineral and/or maceral components as a means to produce specialized coal composition products that would have special significance in coal conversion to liquid and gaseous fuels.

Knowledge of the detailed occurrence, associations, and form provides the basis for pyrite rejection during coal beneficiation. A sample of Clarion seam coal is being studied seeking to isolate pyrite using procedures which will minimize the physical change of the pyrite occurrence. The morphology, distribution, and chemical nature of the pyrite form isolated are being evaluated.

The pyrite is being liberated by a series of stage crushing steps (the top size of the feed was about 3 in.) with small reduction ratios followed by density separations at 2.85 as illustrated in Figure 1. The pyrite fractions isolated are sized at 11 intervals between 1-1/2 in. and 37 μm . A total of 75 pyrite fractions have been developed and are now being subject to analysis. The weight distribution of the pyrite is cited in Table 3. Until the pyrite analyses are completed it has been assumed the fractions assay 85 percent iron sulfide. The data suggest the mining process liberated about 25 percent of the pyrite with another 25 percent freed by comminution to 16M. By reduction of particle size to less than 35 μm , it appears that about 95 percent of the pyrite has been liberated. A plot of the cumulative pyrite-particle size (Figure 2) shows the absolute particle-size constant (Rosin-Rammler $\bar{x}$) to be 380 μm . About 35 percent of the pyrite occurs in particles less than 35 μm and 10 percent greater than one in. This procedure is believed to present a more accurate evaluation of the pyrite particle size distribution.

The pyrite particle morphology is being evaluated utilizing hand separation and point counting techniques. The pyrite groups being defined are:

1. Massive fine-grained crystalline masses. The forms are of irregular shape and composed of many small sized crystals.
2. Massive amorphous to fine-grained masses. The forms are of irregular shape and include, at least in part, smooth, glossy surfaces with no distinguishable crystal faces.
3. Plant structures. Generally elongate particles with remnant plant-cell structures.
4. Framboids. Spherical particles composed of many individual, highly crystalline particles, apparently grown together.
5. Single crystals.

This classification process is still in progress. It appears that the massive amorphous form predominates in particle sizes greater than 3/8 in.

Figure 1. PYRITE LIBERATION FLOW SHEET

Figure 1. PYRITE LIBERATION FLOW SHEET (Continued)

Table 3. Pyrite Particle Liberation by
Comminution Size in Clarion Seam Coal

Sample	% of Total Pyrite	Cumulative % of Total Pyrite
1	4.6	4.6
2	11.0	15.6
3	8.5	24.1
4	1.2	25.3
5	4.0	29.3
6	6.1	35.4
7	7.6	43.0
8	5.6	48.6
9	16.8	65.4
10	16.3	81.7
11	14.4	96.1

Those particles appear to be more readily liberated than the fine-grained particles. Thus it appears that the pyrite occurrence forma may be re-latable to the ease of liberation.

Preliminary analytical efforts for pyrite suggests it may be necessary to modify ASTM D-2492 procedures for forms of sulfur. Among the potential changes would be: increased nitric acid concentration and increased reaction time. The analyses completed have an average of 85 percent pyrite. Trace metal content will be evaluated including nickel, cobalt, arsenic, and manganese. Studies to evaluate the crystalline nature and reactivity of these pyrite forms is planned.

[illegible]

Point	Percentage	X, inches	Y, inches
A			
B			
Difference			

Distribution coefficient, n _____
Absolute size constant α _____

Figure 2. GRAPHICAL FORM FOR REPRESENTING DISTRIBUTION OF SIZE OF BROKEN COAL

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

OPERATION OF ISOTHERMAL FURNACE (TASK 23)

Characteristics of Chars Produced by Pyrolysis and Combustion Following Rapid Heating of Pulverized Coal

Pyrolysis of the Texas Darco lignite (PSOC-412) under the same experimental conditions (Qtr. Tech. Prog. Rept. FE-2030-8 to DOE) has been completed for the seven size grades as reported in the Qtr. Tech. Prog. Rept. FE-2030-10 to DOE (Table 6) with one exception. The 230 x 400 mesh fraction with a mean weight particle size of 50 μm has been replaced by a 270 x 400 mesh fraction with a mean weight particle size of 41 μm . This widens the overall size range (216 - 41 μm) and creates a significant size increment between the two smallest fractions, 51 and 41 μm compared with 51 and 50 μm previously. The complete size range and the proximate analysis of each size grade is reproduced in Table 4, a modification of Table 6 of the Qtr. Tech. Prog. Rept. FE-2030-10 to DOE incorporating the above mentioned change.

Limited work has been conducted on the effect of heat-up and recycling on weight loss for three size fractions with mean weight particle sizes of 178, 125, and 85 μm , respectively.

Theory--Weight Loss

The theory is presented in detail in the Qtr. Tech. Prog. Rept. FE-2030-10 to DOE. The weight loss results are again analyzed in terms of the two component hypothesis,¹ assuming that liberation of Component I is dominant within the residence time of the furnace (300 msec). This has been shown to be the case previously.² The model allows for independent, first order decomposition of Component I according to the following equation:

$$\ln (1 - \Delta W / \Delta W_{\infty}) = \ln (C_1^{\circ} / \Delta W_{\infty}) - k_1 t \quad (1)$$

where C_1° is the initial concentration (in weight %) of Component I

ΔW is the weight loss

and ΔW_{∞} is the maximum potential weight loss.

A plot of $\ln (1 - \Delta W / \Delta W_{\infty})$ vs time, therefore, yields the value of the kinetic rate constant, k .

Results--Effect of Sample Size on ASTM Volatile Matter

The ASTM volatile matter test calls for rapid heating of 1 g of sample contained in a covered nickel crucible to 960°C by plunging the crucible into a preheated Hoskins furnace. For highly volatile coals prone to sparking, a two step temperature rise is recommended; initial rapid heating to 550°C with subsequent rapid heating to 950°C. Even when the latter technique is employed, size grades of PSOC-412 coal and char below about 60 μm spark significantly making it difficult to obtain ASTM volatile matter data.

Table 4. Proximate Analysis of Different Size Grades
of Texas Darco Lignite (PSOC-412)

Original Size Grade (U.S. Mesh) [$\bar{X}$, μm]*	% Moisture	% Ash (dry)	% VM		% FC	
			(dry)	(daf)**	(dry)	(daf)
(60 x 80) [216]	14.1	10.1	45.6	50.7	44.3	49.3
(70 x 100) [178]	15.3	10.9	44.7	50.2	44.4	49.8
(100 x 140) [125]	15.2	11.0	44.5	50.0	44.5	50.0
(140 x 200) [85]	12.4	11.1	44.4	50.0	44.5	50.0
(200 x 270) [62]	12.8	12.9	43.6	50.9	43.5	49.1
(230 x 325) [51]	14.8	14.6	42.9	50.2	42.5	49.8
(270 x 400) [41]	13.8	14.5	43.2	50.5	42.3	49.5

* $\bar{X}$ = mean weight particle size

** = mean value is 50.7

Sparking can be prevented by reducing the sample size below the ASTM requirement of 1 g. The effect of the size reduction, however, is to overestimate the ASTM volatile matter as shown in Figure 3. The data, presented in Table 5, are for a representative sample of PSOC-412 coal spanning the complete size range (216 - 41 μm). It is apparent from Table 4 that the ASTM volatile matter for PSOC-412 (on a dry, ash-free basis) shows no dependence on particle size. Hence, Figure 3 can be used to correct VM data obtained using less than the required 1 g to give the equivalent ASTM volatile matter content.

The consequences are that VM data are now obtainable for the smaller size fractions and that less sample needs to be collected to perform the same number of analyses. The result is an increase in operating efficiency.

Possible reasons for this phenomenon are given elsewhere.³ The argument is basically that reducing the sample size has the effect of reducing the porous packing that can trap pyrolysis products and/or provide a surface on which they can react. This leads to a reduction in secondary cracking reactions, hence increasing the VM yield.

Figure 3. EFFECT OF SAMPLE SIZE ON ASTM VOLATILE MATTER FOR PSOC-412 COAL

Table 5. Effect of Sample Size on ASTM
Volatile Matter Test for PSOC-412 Coal

Wt. Sample (g)	Volatile Matter (% daf coal)	VM/VM ASTM
0.99	51.8	1.0
0.61	52.1	1.01
0.56	52.1	1.01
0.23	52.7	1.02
0.14	54.1	1.04
0.08	54.3	1.05

Weight Loss and Change in Proximate Volatile Matter

As indicated in the Qtr. Tech. Prog. Rept. FE-2030-10 to DOE, the data given for the smaller size fractions needed to be duplicated to increase the degree of reliability. All the weight loss (ΔW) and change in proximate volatile matter (ΔV) data given in Table 6 have high reliability at the 95 percent confidence level. Table 6 is a modification of Table 7 in the Qtr. Tech. Prog. Rept. FE-2030-10 to DOE incorporating the additional data for and reflecting the change in the smaller size fractions.

Kinetic Constants

Using the method outlined previously, values of the Q-factor, maximum potential weight loss, ΔW_{∞} , and reaction rate constant, k , are calculated for each size grade of PSOC-412 and are shown in Table 7, a modification of Table 8 in the above mentioned report to DOE. The Q-factor decreases from 19 for the 216 μm size grade to approximately 1.0 for sizes below about 50 μm . This is consistent with the concept of particle size as a controlling factor in the rate of escape of volatiles.³ As the particle diameter is reduced, the diffusional delay of escape of the volatiles is reduced, hence reducing secondary cracking reactions. It has been suggested that this effect is not significant for particles less than 50 μm in diameter.⁴ Figure 4 is a plot of $\ln(1 - \Delta W/\Delta W_{\infty})$ versus time and shows a series of straight lines of slope k . The k values are given in Table 7, and show particle size dependency down to about 50 μm . The heat up time is about 0.095 sec for particle sizes in the range 60-80 μm but is longer for larger particles and less for smaller particles.

Effect of Particle Size on Weight Loss

Figure 5 shows that weight loss for a given set of experimental conditions is a strong function of particle size in the early stages of pyrolysis over the whole range of sizes (216-41 μm). After about 300 msec, however, the weight loss loses dependency on particle size below about 100 μm .

Table 6. Extent of Pyrolysis for Different Size Grades of PSOC-412 Coal

Total Residence Time, sec	60 x 80 mesh, $\bar{X} = 216 \mu\text{m}$				70 x 100 mesh, $\bar{X} = 178 \mu\text{m}$			
	A'	VM'	ΔV	ΔW	A'	VM'	ΔV	ΔW
0.075	9.9	46.1	-1.9	-3.0	10.8	45.2	-0.7	1.4
0.113	10.0	46.2	-1.3	-1.2	11.1	45.2	0.7	1.5
0.150	10.1	46.1	-0.5	0.1	11.2	45.2	1.3	2.8
0.188	10.2	45.9	0.2	1.3	11.5	44.7	3.2	6.0
0.225	10.3	46.0	0.5	2.1	11.7	44.3	4.1	7.1
0.262	10.4	45.5	1.6	3.4	11.8	43.7	5.3	8.5
0.300	10.7	45.6	2.9	6.5	12.0	42.7	7.2	10.4
	100 x 140 mesh, $\bar{X} = 125 \mu\text{m}$				140 x 200 mesh, $\bar{X} = 85 \mu\text{m}$			
	A'	VM'	ΔV	ΔW	A'	VM'	ΔV	ΔW
0.075	11.0	45.2	0.1	0.3	11.3	43.1	2.9	1.6
0.113	11.4	44.4	2.9	4.6	11.6	42.8	4.8	5.1
0.150	11.4	--	--	4.5	11.8	42.2	5.9	6.4
0.188	11.6	44.1	4.0	6.3	12.1	40.5	8.9	9.4
0.225	12.0	41.7	8.1	10.1	13.1	38.7	13.6	16.7
0.262	13.0	40.6	12.2	17.4	13.5	36.1	17.2	19.6
0.300	14.0	37.8	17.4	24.2	14.6	34.1	21.5	27.0
	200 x 270 mesh, $\bar{X} = 62 \mu\text{m}$				230 x 325 mesh, $\bar{X} = 51 \mu\text{m}$			
	A'	VM'	ΔV	ΔW	A'	VM'	ΔV	ΔW
0.075	--	--	--	--	14.9	41.8	2.9	2.7
0.113	--	--	--	--	15.2	41.5	5.1	7.2
0.150	13.9	42.7	4.9	7.6	16.1	40.1	8.0	10.7
0.188	14.4	41.2	8.0	11.2	16.7	38.4	11.4	14.7
0.225	15.4	39.0	13.2	18.5	16.8	36.2	13.8	15.2
0.262	15.1	38.0	18.2	16.2	17.0	35.1	15.3	16.2
0.300	16.4	34.2	19.7	24.2	17.6	32.2	19.5	19.9
	270 x 400 mesh, $\bar{X} = 41 \mu\text{m}$							
	A'	VM'	ΔV	ΔW				
0.075	15.1	39.0	7.4	5.5				
0.113	15.3	41.3	4.9	6.2				
0.150	16.4	40.8	8.8	14.1				
0.188	17.2	39.2	12.1	18.4				
0.225	17.4	37.0	14.7	19.6				
0.262	18.2	31.9	21.1	24.2				
0.300	18.8	32.0	22.0	27.1				

* Symbols defined in the text.

Table 7. Kinetic Constants for Pyrolysis of PSOC-412 Coal

Original Size Grade U.S. Mesh ($\bar{X}$ μm)	Q	ΔW_{∞} , %	k (sec^{-1})
60 x 80 (216)	1.9	95.0	0.4
70 x 100 (178)	1.5	74.8	0.7
100 x 140 (125)	1.4	68.9	1.7
140 x 200 (85)	1.3	66.3	2.1
200 x 270 (62)	1.1	59.6	2.3
230 x 325 (51)	1.0	53.1	1.7
270 x 400 (41)	1.1	57.7	2.6

Effect of Pyrolysis on Particle Size

Table 9 of the Qtr. Tech. Prog. Rept. FE-2030-10 to DOE is repeated here as Table 8, incorporating the change in mean weight particle size of the smallest size grade. As previously indicated the reduction in particle size during pyrolysis is attributed to shrinkage rather than decrepitation.

Effect of Recycling on Weight Loss

Table 9 shows initial data for the effect of recycle on weight loss for three size grades of PSOC-412. For recycling, or interruption of the pyrolysis reactions, to have no effect on weight loss lines 1, 3 and 6 of Table 9 should be equal for each size grade. These lines represent the same isothermal pyrolysis time (205 msec) with either zero, one or two recycles. More data is necessary before firm conclusions can be drawn but the initial indication is that at the two recycle level significant enhancement of weight loss occurs.

Figure 4. PLOTS OF $\ln(1 - \Delta W / \Delta W_\infty)$ VS TOTAL PARTICLE RESIDENCE TIME FOR DIFFERENT SIZE GRADES OF PSOC-412 COAL

Figure 5. VARIATION OF WEIGHT LOSS WITH MEAN WEIGHT PARTICLE SIZE AT VARIOUS TOTAL RESIDENCE TIMES FOR PSOC-412 COAL

Table 8. Mean Weight Particle Sizes for PSOC-412 Coal and Chars

Original Size Grade (U.S. Mesh)	Mean Weight Particle Size of Coal $\bar{X}$ (μm)	Mean Weight Particle Size of Chars after 0.3 sec Residence Time $\bar{X}$ (μm)
60 x 80	216	201
70 x 100	178	155
100 x 140	125	111
140 x 200	85	79
200 x 270	62	52
230 x 325	51	44
270 x 400	41	30

Table 9. Effect of Recycling on Weight Loss for PSOC-412 Coal

Recycle Condition	Total Time (msec)	Isothermal Time (msec)	Heating Time (msec)	Weight Loss, % daf coal		
				178	$\bar{X}$ μm 125	85
None	300	205	95	10.4	24.1	26.2
None	197	102	95	6.5	15.0	--
One	395	205	190	12.8	21.7	28.9
None	163	68	95	3.4	10.7	--
One	326	136	190	8.1	21.1	--
Two	490	205	285	19.6	30.9	--

Future Work--Effect of Temperature on Pyrolysis

Construction of 2-in. high temperature furnace is almost complete. A supporting structure still has to be built and the ancilliary equipment installed. Including temperature as one of the variables will allow measurement of further kinetic constants (activation energy, frequency factor, velocity constant) as well as indicate the effect of temperature on weight loss. The new furnace has a larger isothermal zone (twice the existing) which will aid in determining the maximum weight loss. Installation and start up of this furnace will be given top priority in the next quarter.

COAL REACTIVITY (TASK 26)

During this quarter the study of the reactivity of coal was completed with experiments using bituminous coal PSOC-322 and anthracite PSOC-80. The size of the particles used in these experiments was 0.625 in. (± 0.125). The data were analyzed and the results compared with previous results (PSU coke, Koppers coke, and other sizes of PSOC-322 and PSOC-80 coals). These data will be presented in a subsequent technical report.

Supporting experiments were carried out to study the variation of apparent density and bed porosity through the bed as evidence of the extent of internal reaction. Reaction in the combustion pot was stopped part way through a run by removing the pot from under the exhaust hood and covering it with a steel plate until cold. After the bed was removed in horizontal layers, the apparent and bulk densities were measured for each layer.

The apparent (particle) density was determined by the water displacement method, using the relation

$$\rho = \frac{A}{B + (C - A)} \quad (2)$$

where A is the weight of the dry sample, B is the weight of the water displaced by the sample and (C - A) is the correction term for the porosity of the sample particles.⁵

The bulk density (σ) was calculated from the weight and volume of each 6 to 7.5 cm thick horizontal layer. The bed density was then calculated from

$$\epsilon = (1 - \frac{\sigma}{\rho}) \quad (3)$$

where ϵ is the bed porosity.

Figure 6 is a plot of bulk and apparent densities and the porosity against mean particle diameter in each section. From the figure it is clear that the bulk and particle densities decrease towards the bottom of the bed (smaller particle diameter in Figure 6). The change in particle density through the bed is not appreciable. The porosity tends to increase toward the bottom of the bed, evidence that the bed does not collapse significantly as the particle burns out in the lower part of the bed.

The relatively small change in apparent density is in clear support of the earlier view that the combustion reaction is mainly external to the particles and the reaction is controlled by film diffusion.

Figure 6. APPARENT DENSITY, BULK DENSITY AND POROSITY OF EACH SECTION VS AVERAGE PARTICLE DIAMETER IN EACH SECTION

FACET IV-B: COKES AND CHARs

EFFECTS OF VARIABLES ON CHAR STRUCTURE (TASK 27)

Preoxidation of Coking Coals to Retard Their Softening and Swelling

Fluidization studies of PSOC-337 (a hvAb coal) were continued this quarter. Samples of 200 x 250 mesh coal (10-15 mg) were fluidized for periods in excess of 4 hr. Weight losses, due to carry-over of fines in the gas stream, were shown to be minimal (4-5%). In addition, temperature studies indicate that preoxidation temperatures can be well maintained throughout the entire experimental period. These results indicate that the fluid bed is suitable for use in the latter stages of this investigation.

Extensive work was done this quarter directed at developing the TMA technique as a method for characterizing the fluid and swelling properties of coals. The DuPont 942 TMA is a highly sensitive dilatometric system equipped with a derivative computer. Vertical displacement of the dilatometer probe (which rests on the top of the sample) is recorded as a D.C. voltage. This voltage is linearly proportional to the vertical displacement and can be recorded. Thus the instrument records, simultaneously, displacement and its first derivative with respect to time as a function of temperature. This system affords the advantages of small sample size, which limits thermal gradient effects, and rapid turn around time (~ 90 min). A typical TMA run will yield much quantitative information about the softening and swelling of coal samples (Figure 7). The derivative trace shown is invaluable for determining transition temperatures such as the onset of softening (A), the initial dilation temperature (B), and the resolidification temperature (C) of the coal. The plastic temperature region (A-C) is split into two zones. Zone one (A-B) is the initial softening stage of the coal. In this region the coal sample is easily compressed (D') under a load. Zone two (B-C) is the region in which rapid expansion (E') occurs. This rapid expansion is followed by a significant contraction of the sample and a subsequent loss of plasticity.

Early TMA work is aimed at optimization of the TMA technique. The effect of TMA variables 1) heating rate (3°C/min, 20°C/min, and 50°C/min), 2) load on sample (no load, 1 g, 5 g), and 3) particle size (35 x 60 mesh, 100 x 150 mesh, and 200 x 250 mesh) on softening temperatures (A, B, and C) and dilation values (D' and E') is being investigated. In addition to obtaining softening information, we are looking for correlations between the initial contraction, expansion and final contraction parameters. This type of information should prove invaluable when evaluating the effects of preoxidation on coal behavior.

Reproducibility studies have been conducted to determine the useful limits of the TMA. Transition temperatures from 16 identical trials (50°C/min, 1 g load) show excellent reproducibility:

A - onset of softening	364 ± 2°C	95% confidence
B - initial dilation	469 ± 1°C	95% confidence
C - resolidification	575 ± 2°C	95% confidence

Figure 7. TYPICAL TMA OUTPUT FOR PSOC-337 (HVA COAL) 50°C/MIN HEATING RATE 20mg Sample, 1gm Load

Reproducibility for dilation values is also acceptable (Standard Deviation 2.5%).

Investigation of heating rates during TMA runs indicate that there is a marked increase in heating rate (~ 10-15%) corresponding to the temperature region in which maximum decomposition of the coal occurs. These variations in heating rate occur in every case studied, however, variations are not exactly reproducible from run to run. Since swelling is highly dependent on the rate of heating, these fluctuations in heating rate lead to a wider spread in experimental data. Efforts are now being made to reduce these fluctuations in heating rate so as to improve reproducibility.

Work for the next quarter will involve continued use of the TGA unit. Projected experiments will examine 1) the effect of grinding in air on oxygen uptake and 2) the behavior of the 35 x 60 mesh and 100 x 150 mesh size fractions at different temperatures (100, 125, 150, and 200°C).

TMA studies will also be continued. Efforts will be made to minimize variations in the heating rate. TMA variables will be studied in an attempt to optimize the system. Upon standardization of a TMA procedure, samples of PSOC-337 will be preoxidized to different levels (0-7%) and analyzed by TMA. Finally 20 to 30 coals, in the range high volatile B to low volatile bituminous, will be selected for characterization in the TMA unit.

Effect of Inorganic Matter Removal on Surface Areas of Coals and Chars

In the earlier DOE progress reports, we have reported the reactivities of a wide spectrum of chars in air, carbon dioxide, steam, and hydrogen. It was found that in each gasification atmosphere, partial or complete removal of inorganic matter from raw coals prior to charring or from chars produced (by acid washing with hydrochloric or demineralizing with a hydrochloric-hydrofluoric mixture) decreased the reactivities of lower rank chars whereas reactivities of higher rank chars increased. These changes could not be attributed solely to the removal of catalytic inorganic impurities by acid treatment because it was found that concomitant with the changes in reactivities chars produced from acid-washed coals or raw chars had surface areas which were markedly different from those of the chars produced from the process which involved no acid treatment. In the present study we have investigated systematically the effect of mineral matter removal on surface areas of coals and chars.

Coals (40 x 100 mesh) varying in rank from anthracite to lignite were used in the present study. Partial removal of inorganic matter from the coals was affected by acid-washing with 10 volume percent hydrochloric acid at 60°C. The inorganic matter content of some of the acid-washed coals was further reduced by treatment with a 1:1 hydrochloric-hydrofluoric mixture; these coals are referred to as demineralized (Dem) samples in the text.

Selected raw, acid-washed and demineralized coals were carbonized at 1000°C in a nitrogen atmosphere in the manner described in the earlier DOE progress reports. In a few cases, chars produced from raw coals were acid washed with hydrochloric acid. Chars produced from acid-washed coals are referred to as AW in the text, the acid-washed chars are referred to as AW* and chars produced from demineralized coals are referred to as Dem chars.

Surface areas of coals and chars were determined from nitrogen adsorption at 77°K using the BET equation and from carbon dioxide adsorption of 298°K using the Polanyi-Dubinin equation. Prior to making an adsorption run, coals were outgassed at 110°C and chars at 500°C for 16 hr at a pressure of 10^{-6} torr. For each point on the nitrogen and carbon dioxide isotherms, an arbitrary adsorption time of 30 min was allowed.

The effect of inorganic matter removal on surface areas of coals is illustrated by the data given in Table 10. It is seen that in some cases acid treatment brings about significant changes in surface areas. In general, the relative change in nitrogen surface area of a given coal upon inorganic matter removal is more pronounced than the change in carbon dioxide area. It is also seen that in some cases acid treatment increases the nitrogen area but decreases the carbon dioxide area and vice versa.

The effect of removal of inorganic matter on surface areas of chars is brought out clearly in Table 11. On a relative basis, the changes in surface areas brought about by acid treatment are more pronounced for chars than coals. The effect of inorganic matter removal on surface areas of chars is markedly dependent upon the manner in which inorganic matter is removed, that is, whether the acid treatment is given to the coal precursor prior to charring or to the chars produced from the raw coals. With the exception of PSOC-91 char, the nitrogen areas of the lignite and subbituminous AW samples are lower and the carbon dioxide areas are higher than the corresponding areas of the AW* samples.

RELATION OF CHAR STRUCTURE TO CHAR REACTIVITIES (TASK 28)

Effect of Preoxidation of Caking Coals on Coal and Char Properties

In the last progress report (Qtr. Tech. Prog. Rept. FE-2030-10 to DOE) we reported the effect of preoxidation (in air) of a highly caking coal at different temperatures on weight loss during pyrolysis up to 1000°C and reactivity of resultant chars to air at 470°C. Preoxidation had essentially no effect on weight loss during pyrolysis below 450°C; at higher temperatures preoxidation resulted in a decrease in weight loss. It was found that preoxidation markedly enhanced the subsequent char reactivity. In order to understand better the effect of preoxidation on subsequent char reactivity, we have carried out additional work on the effect of preoxidation temperature and time on char reactivity. We have also investigated the effect of the presence of water vapor contained in air on preoxidation of coal and subsequent char reactivity. Whether for a given level of preoxidation, the oxidation temperature has any effect on char reactivity has also been studied.

The experimental procedures followed for studying weight loss during coal pyrolysis and subsequent char reactivity were the same as those reported in the last progress report.

The work described in the present report is a continuation of that presented in the last progress report. Therefore, in order to unify the results and thus to have a meaningful understanding of the overall results obtained so far, we have included in the present report some of the results included in the last report.

Table 10. Effect of Inorganic Matter Removal on Surface Areas of Coals

PSOC Coal No.	ASTM Rank	State	C,%(daf)	Ash,%(dry)	N ₂ Surface Area, m ² /g			CO ₂ Surface Area, m ² /g		
					Raw	Acid- Washed	Dem	Raw	Acid- Washed	Dem
91	Lignite	Montana	70.7	7.7	21	-	7	287	236	273
87	Lignite	North Dakota	71.2	8.2	7	20	26	191	218	184
245	Lignite	North Dakota	72.0	13.5	15	-	14	143	-	239
100	Sbb-D	Wyoming	72.1	5.0	14	-	17	246	-	184
138	Lignite	Texas	74.3	10.3	9	10	16	191	178	184
230	Sbb-B	Montana	75.3	9.2	33	-	14	266	-	256
232	HVC	Kentucky	78.0	10.2	12	-	17	198	-	239
127	LV	Pennsylvania	89.6	5.7	<1	-	10	232	242	239

Table 11. Effect of Inorganic Matter on Surface Areas of Chars

PSOC Sample No.	ASTM Rank	C(daf), %	Char Ash, %	Surface Area, m ² /g	
				N ₂	CO ₂
91	Lignite	70.7	10.9	31	420
91AW*			7.2	17	470
91AW			1.3	88	912
87			13.1	93	260
87AW*	Lignite	71.2	6.0	106	500
87AW			2.6	11	610
87DEM			0.0	1	600
138			16.0	120	560
138AW*	Lignite	74.3	11.6	11	497
138AW			9.6	4	680
138DEM			0.9	47	115
101			8.2	62	460
101AW*	Sub-C	74.8	5.4	17	359
101AW			1.1	3	670
127			6.7	2	12
127DEM			0.0	4	37
81	Anthracite	91.9	6.4	1	39
81AW*			6.1	<1	47
81AW			5.8	<1	40
81DEM			0.9	<1	56

The extent of weight gain during preoxidation of the 200 x 250 mesh fraction of the coal (PSOC-337) when oxidation is carried out for a maximum of 4 hr (except at 250°C) is shown graphically in Figure 8. At 250°C, oxygen uptake attained a maximum value after about 2 hr, thereafter the sample weight started to decrease. Probably preoxidation of coal at each oxidation temperature studied involves both chemisorption of oxygen as well as gasification of carbon. The results in Figure 8 suggest that except at 250°C, weight increase due to chemisorption offsets any weight decrease due to gasification.

Devolatilization curves obtained following the various oxidative treatments are plotted in Figure 9. The results for raw coal are also included in Figure 9 for the sake of comparison. The results show that oxidative treatment at different temperatures (up to a maximum of 220°C) has essentially no effect on weight loss during pyrolysis up to 450°C. Preoxidation at 120°C has no noticeable effect on weight loss during pyrolysis over the entire temperature range studied. However, for preoxidation treatment above 120°C, weight loss at a given temperature during pyrolysis decreases more or less regularly with increase in the oxidation temperature.

Burn-off versus time plots for various chars (produced from different preoxidized samples) reacted in 1 atm air at 470°C were obtained in the manner described in the last report. As in the last report, we have used in the present study $\tau_{0.5}$ (the time corresponding to a fractional burn-off of 0.5)

Figure 8. WEIGHT GAIN OF COAL AT DIFFERENT TEMPERATURES AS A FUNCTION OF TIME IN AIR

Figure 9. TGA PYROLYSIS CURVES FOR VARIOUS OXIDIZED SAMPLES

as the reactivity parameter during char gasification. $\tau_{0.5}$ values for various chars are given in Table 12. It is seen that a weight increase of only 0.45 wt percent during oxidation of the caking coal at 120°C leads to a dramatic decrease in $\tau_{0.5}$ from 95 min to 54 min. Further decrease in $\tau_{0.5}$ with additional weight increase is less pronounced and when weight increase exceeds 3.8 percent, $\tau_{0.5}$ attains more or less a limiting value.

So far we have preoxidized the coal at different temperatures and following maximum uptake of oxygen at each temperature after 4 hr we have studied the effect of preoxidation on devolatilization behavior of the coal and subsequent reactivity of the char produced. It was thought of interest to investigate whether for a given uptake of oxygen the preoxidation temperature has any effect on subsequent char reactivity. This study was carried out in the following manner. The coal was preoxidized to a weight increase of 1.4 percent at each of the following temperatures: 120, 150, 180, 220, and 250°C. For attaining this level of oxidation, oxidation had to be carried out for 22 hr, 4 hr, 43 min, 11 min, and 3 min at 120, 150, 180, 220, and 250°C, respectively (see Figure 8). The devolatilization curves for the various preoxidized samples are given in Figure 10. The reactivity plots, that is burn-off versus time plots for chars produced from the preoxidized coal samples, are given in Figure 11. It is noteworthy that the preoxidation temperature has essentially no effect on the devolatilization curves (Figure 10) and $\tau_{0.5}$ values (Figure 11). Similar results were also obtained when the coal was preoxidized at 180, 220, and 250°C to a weight gain of 3.75 percent. These results thus show that it is only the extent of weight increase during preoxidation and not the temperature of preoxidation which determines the reactivity of the char produced from a caking coal.

Since the preoxidation of a caking coal increases the subsequent reactivity of the char, it is reasonable to assume that the treatment of the preoxidized coal with hydrogen should result in a decrease in the char reactivity. In order to see if such was the case, the coal preoxidized with air at 220°C for 4 hr was subsequently treated with hydrogen (1 atm) at 220°C. It was found that under these conditions hydrogen did not react with the oxidized coal, that is the oxidized coal did not undergo any weight loss upon treatment with hydrogen. This is perhaps not surprising because it is known that in the case of the higher rank coal, exothermic reaction with hydrogen at 800 psi occurs at temperatures far in excess of 220°C.⁶

So far preoxidation of the coal was carried out with dry air. However, in commercial gasification and combustion units preoxidation of caking coals is carried out with air which is invariably associated with some amounts of water vapor; the amount of water vapor present is dependent upon the relative humidity. We have investigated the role which water vapor contained in air during preoxidation has on subsequent char reactivity. Air used for preoxidation was bubbled through distilled water maintained at 15°C, the partial pressure of water vapor in the mixture was 12.8 torr. The coal was oxidized to the same level of weight gain (1.4%) in dry and wet air at 180°C. To achieve the same level of oxidation (weight increase) it takes significantly more time in wet air than in dry air (Figure 12). The presence of moisture has no noticeable effect on weight loss during pyrolysis (Figure 13) as well as on subsequent reactivity (Figure 14).

Table 12. Effect of Preoxidation on Subsequent Char Reactivity

Preoxidation Temp., °C	Weight Increase During Preoxidation, Wt% (dry)	Reactivity, $\tau_{0.5}$, min
None	0	95
120	0.45	54
135	0.75	47
150	1.4	40
160	1.8	37.5
170	2.4	35.5
180	3.8	32
220	7.0	30
250	6.0	30

So far we have carried out the preoxidation of the caking coal at relatively low temperatures for extended periods of time. In industry, preoxidation is carried out at higher temperatures (~ 400°C) using much shorter residence times. In the next quarter we will preoxidize the coal in air in an isothermal reactor at 400°C using residence times up to a maximum 300 msec. The effect of preoxidation on devolatilization behavior and subsequent char reactivity will be studied.

In the previous DOE technical progress reports we have reported the reactivities of chars in air, carbon dioxide, steam, and hydrogen. The chars were produced from a wide spectrum of coals varying in rank from anthracite to lignite. It was found that in oxidizing atmospheres the reactivity of the char produced from a lvb coal (PSOC-127) was about 150-fold less than the reactivity of the most reactive char. PSOC-127 is a highly caking coal with a free swelling index of 9. The low reactivity of the char produced from this coal may be due to the caking character of the precursor coal. If so, the char reactivity can possibly be enhanced by preoxidation of the coal. In the next quarter, this feasibility will be explored in length.

EFFECT OF CATION EXCHANGE AND METAL ADDITION (TASK 30)

Carboxyl Groups and Exchangeable Cations in Lignite Coals

Lignite coals loom as the largest untapped energy reserve this country has. Thus, current projections for coal production include lignite as the most significant fraction of coal mined by 1985.

One property that is almost exclusive to lignite coals is the occurrence of carboxyl groups. In the raw coal, these groups are often substituted with cations such as calcium, sodium, potassium, and magnesium. The reactivity of the char in the carbon-steam reaction is significantly enhanced by the addition of such cations and, therefore, affected by the naturally occurring ones. There has been, however, a lack of understanding of the fundamental physical makeup of this carboxyl system.

Figure 10. EFFECT OF SAME LEVEL OF OXIDATION AT DIFFERENT OXIDATION TEMPERATURES ON WEIGHT LOSS DURING PYROLYSIS

Figure 11. EFFECT OF THE SAME LEVEL OF PREOXIDATION OF COAL AT DIFFERENT OXIDATION TEMPERATURES ON SUBSEQUENT REACTIVITY OF CHAR TO AIR AT 470°C

Figure 12. OXYGEN UPTAKE ON COAL IN DRY AND WET AIR AT 180°C

Figure 13. EFFECT OF SAME LEVEL OF PREOXIDATION IN DRY AND WET AIR ON WEIGHT LOSS DURING PYROLYSIS

Figure 14. EFFECT OF THE SAME LEVEL OF PREOXIDATION OF COAL IN DRY AND WET AIR ON SUBSEQUENT REACTIVITY OF CHAR TO AIR AT 470°C

Lignite coals from the four major lignite areas will be studied: Texas, Wyoming, Montana, and North Dakota. The first stage of the research involves use of a Low Temperature Asher (LTA) which allows reaction of the carbon in the coal with minimal destruction of the mineral matter present. This technique will be followed by x-ray diffraction, which can identify and, to some extent, quantify the mineral constituents.

The amount of major exchangeable cations on each coal will be determined using ion exchange with barium or ammonium salt solutions at constant pH. The resultant solution will be analyzed by atomic absorption to find the concentration of cations in the original coal. The total acidity of each coal also will be defined. To do this, two methods are being considered. They are ion-exchange and non-aqueous titration. This data will then be analyzed to determine the amount of sites that are available for cation exchange. The main part of the next quarter will be spent using LTA and x-ray diffraction to get a basic understanding of the lignite constituents.

Effect of Cation Addition on Char Gasification

We have reported in previous technical progress reports that chars produced from lignites are more reactive during gasification than those prepared from higher rank coals. The presence of exchangeable cations, which are associated with carboxyl acid groups found most abundantly in lignites, are believed to be responsible for the enhanced reactivity of chars produced from lignites. Hippo and Walker⁷ have studied systematically the role which cations in lignites play in the subsequent reactivity of chars to steam. They found that the reactivity of a lignite char in 1 atm of steam at 650°C was a linear function of the amount of exchangeable calcium ions contained in the precursor lignite. In order to see if the presence of exchangeable calcium ions also enhances the gasification rates in other atmospheres of interest (air, carbon dioxide, and hydrogen), we have measured the reactivities in air of the same set of calcium-containing chars and those used by Hippo and Walker in their steam reactivity work. These char samples were prepared at 800°C from a Texas lignite to which different amounts of exchangeable ions were introduced. The experimental details for preparing the calcium exchanged lignite samples and subsequently chars therefrom are described elsewhere.⁷

In the present study, char reactivity was measured in a DuPont TGA unit in 1 atm of air at 390°C. About 3 mg char was taken in a platinum pan. The TGA system was flushed with nitrogen (100 cc/min) for 20 min to displace air. The sample was then heated to 800°C at a heating rate of 10°C/min. Heating was continued at 800°C until the sample weight became essentially constant. Following this, the sample was cooled in nitrogen down to 390°C. This temperature was kept constant for 30 min after which nitrogen was replaced by air at the same flow rate. The extent of gasification (weight loss) was followed as a function of time. The reactivity parameter, R, was calculated from the following equation:

$$R = \frac{1}{W_0} \cdot \frac{dW}{dt} \quad (4)$$

where W_0 is the starting weight of the char on a daf basis and dW/dt is the maximum rectilinear weight loss rate (mg hr^{-1}).

Burn-off versus time plots for selected char samples given in Figure 15 bring out clearly the effect of exchangeable calcium ions present in the coal precursor on subsequent char reactivity in air. The gasification rate of the char containing no calcium, that is the char produced from the demineralized coal, is very low. For instance, it takes about 200 min to gasify 10 percent of the char. In contrast, this time is reduced to only 40 min when the char contains only 1.1 wt percent calcium.

The reactivity parameter increases linearly with increase in the calcium content of the char (Figure 16). The fact that catalytic activity per unit weight of calcium is constant over such a wide range of loading (1.1 to 12.9% calcium) suggests that the catalyst is highly dispersed and that the catalytic species is not sintered to any noticeable extent during heat treatment.

Reactivity parameters for the various char samples in air and steam are given in Table 13. Although absolute reactivity parameters for various char samples in air are higher than those in steam, normalized reactivities are essentially the same in the two atmospheres (Figure 17). These results thus suggest that gasification on air and steam of chars produced from calcium exchanged coal samples involves essentially the same mechanism, that is, an oxygen transfer step followed by a gasification step.

In the next quarter, reactivities in carbon dioxide of the same set of chars as those used in the present study will be investigated.

Table 13. Reactivities in Air and Steam of
Chars Produced from Raw, Demineralized and Calcium Exchanged Coals

Source of Char	% Ca in Char	Reactivity ($\text{mg hr}^{-1}\text{mg}^{-1}$) in	
		Air	Steam
Raw Coal	2.0	0.24	0.05
Dem. Coal	0.2	0.02	0.005
Ca Exchanged Coals			
Containing			
<u>mmoles Ca/g coal (daf)</u>			
0.1	1.1	0.21	0.11
0.25	1.9	0.22	0.13
0.37	2.6	0.45	0.17
0.56	4.5	0.65	0.23
0.66	5.3	0.53	0.30
1.20	8.5	0.98	0.43
1.29	9.1	1.00	0.45
2.14	12.9	1.40	0.63

Figure 15. BURN-OFF CURVES IN AIR AT 390°C OF CHARS PRODUCED FROM DEMINERALIZED AND Ca^{++} EXCHANGED SAMPLES

Table 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	772	1072	1300
Proximate	6	291	461	752	1300
Ultimate	7	284	455	739	1300
Equilibrium Moisture	1	19	400	418	1300
Sulfur Forms	4	288	458	746	1300
Maceral Analyses	43	300	436	736	1300
Reflectance Analyses	67	284	431	715	1300
Free Swelling Indices	1	161	411	572	1300
Gray-King Coke Types	1	88	380	468	1300
Plastometer	6	25	0	25	150
Hardgrove Grindability	1	238	383	621	1300
Vickers Hardness	1	196	175	371	1300
Ash Fusion	8	0	424	424	1300
Low Temperature Ash	3	57	75	132	1300
Ash Analysis Related Data	1	57	290	347	1300
Major and Minor Elements	10	57	290	347	1300
Trace Elements	34	57	584	641	1300
Mercury	1	0	166	166	1300
Uranium	1	0	293	293	1300
Mineralogical	35	57	75	132	1300
Calculated Compositional Values	225	300	461	761	1300
Analysis Log	18	300	772	1072	1300
Other Categories	52	269	36	305	630

Total: 33 Data Categories

592 Data Elements

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FACET IV-F: DIFFERENTIAL SCANNING CALORIMETRY (TASK 31)

Chemisorption of Oxygen and Gasification of Carbonaceous Solids

The kinetics of early-gasification observed with the unactivated Saran carbon have been studied theoretically. In order to achieve a reasonable understanding on this subject matter, it was clearly important to first obtain a complete picture for the oxygen chemisorption reaction occurring simultaneously with gasification. A literature survey on oxygen interaction with carbons has been reviewed elsewhere.⁸ Most of the articles cited concerned either oxygen-chemisorption on carbon or gasification of a char or coal above 400°C. Few articles have emphasized the simultaneous occurrence of chemisorption and gasification.^{9,10,11}

As indicated earlier (Qtr. Tech. Prog. Rept. FE-2030-10 to DOE), the terms W_{exp} , W , and W_g have been introduced. $W(\text{mgO}_2/\text{gC})$ is the calculated weight of total oxygen uptake if the early-gasification reaction were not taking place. W_g (mg gasified/gC) was calculated by assuming that carbon dioxide was the only evolved gas. The actual weight of oxygen uptake measured experimentally, W_{exp} , is in fact the difference between W and W_g .

Dependence of W on reaction temperature was studied in the following manner. For each reaction temperature, where W - t plots were constructed, the rate of oxygen uptake was calculated at a given value of fractional surface coverage θ . The procedure used to calculate θ is standard. In brief, if W_t is the total weight of oxygen chemisorbed (mg/gC) on the ultra-clean surface of the carbon under consideration (generally determined by a mass spectrometer), then

$$\theta = (W + W_{\text{pre}})/W_t \quad (5)$$

where W_{pre} is the weight of pre-existing oxygen attached to the surface, thus being not-desorbable under the conventional pretreatment procedure used for this work. Values of θ varied between 0.72 and 0.95 for reactions occurring at 125-227°C.

Aarhenius plots, illustrated in Figure 18, were then made at three selected constant values of θ : 0.79, 0.84, and 0.92. The straight lines obtained are parallel, and, therefore, give rise to a constant value of activation energy, E_a , amounting to 11.5 ± 0.3 kcal/mole. Contrary to the general findings in the literature (where, in most cases E_a increases with θ) one may reach the following conclusion: Since this chemisorption process is practically associated with the early-gasification reaction, free nascent sites are created on the carbon surface. These sites are known to have lower values of E_a than the originally existing ones. The chemisorption reaction continues on the nascent as well as on the "old" sites. Values of E_a should be lower for the former but higher for the latter. The net value of E_a would then remain constant.

Figure 18. ARRHENIUS PLOTS FOR TYPICAL OXYGEN CHEMISORPTION ON THE UNACTIVATED SARAN CARBON (150 x 250 MESH)

The same plots were also constructed to investigate the dependence of (dW_{exp}/dt) or (dW_g/dt) at constant coverages on the reciprocal of absolute temperature. These are shown in Figure 19. Due to the short-term runs (28 min), it was only possible to construct one line in the former case and two lines for the latter. For the early-gasification reaction, the activation energy lies within the range 14-16 kcal/mole. In this regard, a value of $E_a = 42$ kcal/mole has been reported for the same sample at 450-550°C (see Qtr. Tech. Prog. Rept. FE-2030-10 to DOE). Therefore, for the early gasification reaction, E_a is about one-third of that obtained at higher temperatures.

Attempts were then directed to explore any possible dependence of W_g on W or W_{exp} . Three major regularities, in general, were found:

1. The cumulative values of W_g , W_{exp} , or W increase with reaction time or temperature.
2. The rate of any of these parameters decreases with reaction time but increases with temperature.
3. The ratio between W (weight of oxygen chemisorbed) and W_g (corresponding weight of carbon gasified) is always greater than unity. This ratio decreases with increasing reaction time or temperature.

The later observation was further examined in the following manner. For each reaction time, the increment in the values of ΔW and ΔW_g was calculated. The value of θ was also determined. This procedure was repeated for all other reaction times and temperatures. Taking into consideration the atomic weights of carbon and oxygen being 12 and 16 respectively, the term $(O/C)_{t,T}$ was computer, where

$$(O/C)_{t,T} = 0.75 (\Delta W / \Delta W_g)_{t,T} \quad (6)$$

Thus, this term determines the ratio between the incremental number of oxygen atoms chemisorbed and that of carbon atoms gasified. The plot of (O/C) versus the corresponding values of θ is shown in Figure 20 for all reaction temperature. As the value of θ increases (either by raising the temperature or via longer exposure to oxygen), the ratio (O/C) decreases and finally levels off at 2.0 for $\theta = 0.92-0.99$.

At this stage, it is believed that the combination of the DSC and TGA techniques has increased our understanding towards chemisorption and gasification of a typical clean carbon which is not associated with mineral matter or other foreign materials as in the case of coals and chars. In the near future, we are planning to consider some of the thermal and kinetic effects involved during the oxidation of some selected coal chars. Uptake of oxygen in the chars will be compared with previous results on gasification measured at higher temperatures.

Figure 19. ARRHENIUS PLOTS FOR EARLY GASIFICATION AND SIMULTANEOUS CHEMISORPTION/GASIFICATION REACTIONS – UNACTIVATED SARAN (150 x 250 MESH)

Figure 20. DEPENDENCE OF (O/C) ON θ – UNACTIVATED SARAN 150 x 250 MESH

FACET V-A: COMBUSTION OF CHARS AND LOW VOLATILE FUELS

PLANE FLAME FURNACE (TASK 33)

A one-dimensional model of a plane flame furnace firing char and low volatile fuels has been described in previous reports. In partial agreement with measured data, it has predicted gas temperature profiles sharply increasing after ignition, and the very fast burn-off of char particles. The other major predicted variables are oxygen concentration and fixed carbon content, verification of which require more experimental data.

The basic energy balance equation for steady state conditions was presented in a previous quarterly report:

$$\dot{Q}_{\text{conv}} = \dot{Q}_{\text{rel}} + \dot{Q}_{\text{rad}} - \dot{Q}_{\text{loss}} \quad (7)$$

where the rates of heat transfer are due to convective flow, generation by combustion, radiation absorbed by the combustion medium, and losses by radiation to the sidewalls. Two important changes in the balance equation have corrected a bookkeeping error, and generalized the heat release term in order to more suitably model the experimental flame system.

In particular, the radiation to the side walls, $\dot{Q}_{\text{loss}}$, has been absorbed into the term for the radiation contribution:

$$\begin{aligned} \dot{Q}_{\text{rad}} = & -4\sigma k (T^4 - T_w^4) + 2\sigma k T_{w1}^4 E_2(\tau) + \\ & 2\sigma k T_{w2}^4 E_2(\tau_L - \tau) + 2\sigma k \int_0^{\tau_L} T^4(t) E_1(|\tau - t|) dt \end{aligned} \quad (8)$$

where each of the parameters was defined in the previous report. Previously, the entire loss term represented radiation loss to the ambient without inclusion of a conductive wall loss (as though the flame were not separated from the ambient by a wall). The balance equation now includes the transfer rate through the furnace walls:

$$\dot{Q}_{\text{cond}} = U (T - T_{\text{amb}}) \quad (9)$$

where U is a heat transfer coefficient, so that

$$\dot{Q}_{\text{conv}} = \dot{Q}_{\text{rel}} + \dot{Q}_{\text{rad}} + \dot{Q}_{\text{cond}} \quad (10)$$

The heat release term has been generalized by including a coefficient γ in consideration of the attachable surface area of fuel particles:

$$\dot{Q}_{\text{rel}} = -\gamma \dot{M}_q T_0 / T \quad (11)$$

where the rate of mass consumption $\dot{M}$ can be expressed in terms of R_s , the

rate of carbon burned per unit surface area of fuel particles, and $S_t = 4\pi r^2 N_{r,0}$, the total surface area of $N_{r,0}$ particles per unit volume:

$$\dot{M} = - S_t R_s \quad (12)$$

For an assumed shrinking sphere model, reaction taking place on the particle surface is first order with respect to the oxygen partial pressure at the surface:

$$R_s = k_c P_s = k_d (P_g - P_s) \quad (13)$$

where k_c and k_d are the chemical and diffusional reaction rate coefficients, respectively, and P_g and P_s are the oxygen partial pressures at ambient and at the particle surface.

In previous calculations of the heat release rate ($\gamma = 1$), for 25 μm particles at 1500°C, the calculated $Q_{rel} = 2.5 \times 10^6 \text{ Btu/h ft}^3$ exceeded the maximum yield in the combustion of pulverized coal. Two factors contributed to the high value: too high values of specific surface reaction rate R_s , and too high values of attackable surface area in the shrinking sphere. Just as the first factor was previously accommodated by the inclusion of a multiplicative factor β for the chemical reaction rate, the second factor is accommodated by a similar factor α dependent on the ash content of the char particles, so that $\gamma = \alpha\beta$ in application to equations in which both surface area and reaction rate appear.

The ash (noncombustible material) comprises about 28 percent by weight of the Exxon and FMC chars. Assuming that for a shrinking sphere model the reactive area can be approximated by that of a sphere with 72 percent of the char volume:

$$m' = (1 - A\%) m_0 = .72 m_0, (r')^3 = .72 (r_0)^3 \quad (14)$$

Therefore, the sphere has a radius .9 times that of the nominal particle size. Hence, the correction coefficient for the reacting surface area is $\alpha = (.9)^2 = 0.8$.

Results of Modelling Calculations

Temperature profiles for several values of β are presented in Figure 21. These differ from those previously obtained because of the correction in the heat rate balance equation. All subsequent results were generated and are presented for $\beta = 0.75$. Figure 22 illustrates the percent burn-off versus residence time, comparing a previously reported result with that obtained from the modified equations.

Temperature profiles for three fuel feed rates equivalent to combustion intensities of 75,000, 100,000, and 150,000 Btu/hr are presented in Figure 23,

Figure 21. GAS TEMPERATURE VS DISTANCE FROM THE TUBE BANK WITH β VARYING

Figure 22. BURN-OFF PERCENT OF FUEL VS RESIDENCE TIME

Figure 23. FUEL FEED RATE VARIATION

for constant excess air. One percent burn-off has been taken as an index of flame front position, and occurs at (ignition) temperatures of about 950°C. As combustion intensity increases, the model predicts that the flame front moves from the head of the furnace and that the mean gas temperature increases.

As illustrated in Figure 24, increased excess air also causes the flame front to move further from the burner due to higher input velocities. The peak gas temperature also decreases as excess air increases.

With other factors such as excess air and fuel feed rate kept constant, heat generation by chemical reaction in the combustion chamber varies with particle size. The maximum rate of heat generation per unit volume doubled with the halving of particle diameter. However, the temperatures increase more sharply, then decrease more rapidly with the smaller particle sizes (Figure 25).

Figure 26 shows that the temperature profiles for two fuel densities such as found in Exxon char and anthracite are similar. Gas temperature profiles are also quite insensitive to air preheat, as indicated by Figure 27.

Experimental Study

Experimental work has continued with testing the performance of solid and gas sampling probes described in a previous report.

For sea coal and Exxon Wyodak char, the measuring of gas temperature has not been without problems. For temperatures above 1400°C the molten particles become sticky and have clogged the suction line, necessitating the redesign of the suction pyrometer. The radiation shield for the suction pyrometer has been redesigned and constructed as illustrated in Figure 28.

Measured temperature profiles are presented in Figures 29 and 30. The average difference between the measured gas and wall temperatures is about 220°C for the char and about 180°C for the coal. The true gas temperature is possibly closer to 250°C and 200°C above the wall temperature for these fuels.

Figure 24. EXCESS AIR VARIATION

Figure 25. PARTICLE SIZE VARIATION

Figure 26. FUEL DENSITY VARIATION

Figure 27. TEMPERATURE PROFILE WITH PREHEAT AIR

Figure 28. WATERCOOLED SUCTION PYROMETER

Figure 29. TEMPERATURE PROFILE (BITUMINOUS COAL)

Figure 30. TEMPERATURE PROFILE (WYODAK CHAR)

FACET V-B: COMBUSTION OF COAL-OIL EMULSIONS (TASK 34)

Previous quarterly reports have described results obtained from studies on the combustion of oil-water-air (MGD) emulsions, with and without coal additions. However, as pointed out in recent reports, a significant amount of additional work has since been applied to characterizing the behavior of the hot wall furnace, and assessing the effects of using different burners. During this quarter a series of experiments using coal-oil mixtures has been run with improved control techniques and understanding of the system and its responses derived from the recent furnace characterization work.

Using the coal-oil feeding system described in the previous quarterly report, a mixture of 50 percent coal and 50 percent No. 6 oil (by weight) has been fed with No. 2 oil to the burner. By recycling the dense mixture by a gear pump, sedimentation is prevented. The flow rate of the mixture is controlled by monitoring the rate of drop of its level in the storage tank. Other flow rates (No. 2 oil, atomizing and secondary air) were controlled manually while monitoring rotameters and exhaust gas composition (carbon dioxide, oxygen).

Maintaining a firing rate of 25.6×10^4 kcal/hr (1.016×10^6 Btu/hr) on the basis of net calorific values, a typical firing history consists of burning No. 2 oil until equilibrium conditions are approached, combustion of the experimental coal-oil mixture, and occasionally a return to No. 2 oil at the end of a run. This procedure is evident in the histories of the exhaust gas temperature and thermal efficiency illustrated in Figure 31. The efficiency, defined as the percentage of heat extracted by the water tubes from the total thermal input, varies with amounts of coal addition.

The measurement of the furnace characteristic time has been repeated with each run. In contrast to the value $\tau = 8.1$ hr reported in a previous technical progress report, the characteristic time has since been evaluated at $\tau = 2.8 - 0.7$ hr independent of firing rate (Figure 32). A comparable value ($\tau = 2.9$ hr) has been obtained by calculation from a simple mathematical model of the furnace wall.

The increase of water-tube thermal efficiencies with amounts of coal addition peaks with additions of about 10 percent as revealed in Figure 33 for the entire furnace length, and for integrations over the first third and first two-thirds of the length. The exhaust gas temperatures (Figure 34), measured by suction pyrometer, mirror this trend. On the other hand, no production (from fuel nitrogen) increased monotonically with the addition of coal in greater amounts (Figure 35).

Figure 36 illustrates the spread of roof temperature and heat flux data and Figure 37 shows these profiles for various coal additions. In addition to the peaking of thermal efficiency and exhaust gas temperatures with amounts of coal addition at 10 percent, it is evident that the profiles are shifted toward the burner. A qualitative explanation is that the addition of coal increases the flame emissivity and the volume of significantly radiating gases.

Figure 31. TYPICAL HISTORY OF THERMAL EFFICIENCY AND EXHAUST GAS TEMPERATURE

Figure 32. FURNACE RESPONSE CHARACTERISTIC TIME

Figure 33. THERMAL EFFICIENCY AGAINST COAL ADDITION

Figure 34. EXHAUST GAS TEMPERATURE AGAINST COAL ADDITION

Figure 35. NO EMISSION AGAINST COAL ADDITION

Figure 36. TYPICAL SCATTER PLOT OF THE ROOF TEMPERATURE AND HEAT FLUX PROFILE

Figure 37. ROOF TEMPERATURE AND HEAT FLUX PROFILE OF VARIOUS COAL ADDITION

This increases the flame contribution to the radiative heat transfer. However, radiative heat transfer from the roof and walls to the water tubes is reduced by interception by the particulate cloud. Although the net transfer initially increases, the balance between the increase from the flame and the decrease in the radiation from the roof and wall surfaces peaks at about 10 percent coal addition.

Similar trends were observed previously in the studies on coal-oil-water-air mixtures.

CONCLUSIONS

FACET II: COAL BENEFICIATION AND PRE-USE PROCESSING

Task 18: Washability Characterization

Washability fractions of 23 different coals show great variation in ash yield, and sulfur and maceral contents. Fractions of widely differing characteristics can therefore be developed in the laboratory, and the results indicate that with appropriate process developments, the same could be achieved on a commercial scale.

Task 21: Beneficiation of Conversion Feedstocks

It appears that the mode of pyrite occurrence in coals may be relatable to the ease of liberation in preparation plants.

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

Task 23: Operation of Isothermal Furnace

For a given pyrolysis time, weight loss increases with decrease in particle size down to a limiting particle size after which the weight loss is independent of particle size. For 300 msec pyrolysis time at 800°C in a nitrogen atmosphere, the limiting particle size is about 100 μm .

Reducing the sample size in the ASTM volatile matter test results in the overestimation of volatile matter by as much as 5 percent. This can be explained in terms of reduced volatile matter cracking and capture within the porous bed.

The Q factor decreases with decrease in particle size (from 1.9 at 216 μm to 1.0 at 50 μm). This also may be the result of reduced volatile matter cracking and capture within the particle itself.

The reaction rate constant (k) is particle size dependent down to about 50 μm .

Task 26: Coal Reactivity

The reactivity study of coal provides agreement with the previous findings regarding both combustion and gasification reaction mechanisms. Additional supporting experiments showed that the particle density and bed porosity variations through the bed are not appreciable, supporting the diffusion dominance mechanism for the combustion zone.

FACET IV-B: COKES AND CHARs

Task 27: Effects of Variables on Char Structure

It has been shown that by use of the TGA apparatus the weight changes associated with preoxidation can be followed reproducibly. Combined TGA and fluidization results indicate that we can quantitatively add oxygen to coal samples in the fluid bed reactor. Thermomechanical studies have shown the DuPont TMA unit to be a valuable quantitative tool for measuring swelling and plastic properties of coals.

Removal of mineral matter by acid treatment brings about significant changes in surface areas of coals. Generally, the relative change in nitrogen surface area of a given coal is more pronounced than the corresponding change in its carbon dioxide area. Relative to the coals, the effect of inorganic matter removal on changes in surface area is more pronounced in the case of chars, the extent of the change depending upon the manner in which the inorganic matter is removed.

Task 28: Relation of Char Structure to Char Reactivities

Preoxidation in air at 120-250°C markedly enhances the char reactivity; the effect is more pronounced with smaller uptakes of oxygen. The results show that it is the extent of oxygen uptake rather than the preoxidation temperature which determines the reactivity of the char produced from a caking coal. The presence of moisture in air has no noticeable effect on weight loss during pyrolysis as well as on subsequent char reactivity.

FACET IV-F: DIFFERENTIAL SCANNING CALORIMETRY

Task 31: Differential Scanning Calorimetry

For the oxygen chemisorption reaction on the unactivated Saran carbon (150 x 250 mesh) at 100-227°C, the activation energy, E_a , is independent of fractional surface coverage θ , provided that $0.92 > \theta > 0.79$.

The value of E_a amounts to $11.5 \pm .3$ kcal/mole.

For the early-gasification reaction, occurring simultaneously with chemisorption at 127-227°C, E_a is 14-16 kcal/mole.

FACET V-A: COMBUSTION OF CHARs AND LOW VOLATILE FUELS

Task 33: Plane Flame Furnace

In order to provide better agreement between the results of the computer model of a plane flame furnace burning chars and low volatile fuels, and experimental data, the energy balance equation was corrected and modified. The good agreement between the flame temperature profile prediction and experimental data has been illustrated and indicates the successful completion of

this aspect of the plane flame modelling. These conclusions are still subject to further verification, especially with respect to solids and gas samples analyses.

FACET V-B: COMBUSTION OF COAL-OIL EMULSIONS

Task 34: Combustion of Coal-Oil Emulsions

As coal amounts added to No. 2 fuel oil are increased, the efficiency with which heat is transferred to water tubes in the experimental hot-wall furnace initially rises. However, as the net balance between radiative heat transfer from the flame and from the roof and walls changes with the coal loading, the efficiency peaks at 10 percent coal addition and falls.

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