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

Quarterly Technical Progress Report for July—September 1978

By
W. Spackman

May 1979
Date Published

Work Performed Under Contract No. EX-76-C-01-2030

The Pennsylvania State University
Coal Research Section
University Park, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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

Quarterly Technical Progress Report
July - September 1978

by
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UNITED STATES DEPARTMENT OF ENERGY

COAL RESEARCH SECTION
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA 16802

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ABSTRACT

The Penn State Sample Bank has been expanded to include an additional 13 samples from Utah, 4 samples from Pennsylvania, 6 samples from Maryland and 7 samples from West Virginia (Facet I-A). A total of 34 coal samples and 131 selected printouts of coal data were provided on request to the coal research community (Facet I-C). The Gieseler plastometer has been used to detect rapid decrease in plasticity of fine coal particles, stored in air at room temperature. Both the maximum fluidity value and the temperature range of plasticity were shown to be sensitive indices. (Facet I-B).

A flow sheet had to be designed to attempt to prepare certain maceral associations (or lithotypes) from the laboratory processing of 800 lb of hvAb coal, based on our experience in the detailed fractionation of the same coal (Facet II).

Under Task 23, experiments performed in the Hoskins furnaces produced data consistent with the hypothesis that a reduction of char forming, secondary reactions during pyrolysis will significantly enhance the yield of volatile matter. Within the scope of these experiments, the heating rate *per se* was not a controlling factor in the yield of volatile matter. Generation of weight loss versus temperature and residence time curves using the isothermal furnace continued during this quarter. For the 70 x 100 mesh portion of Darco Texas lignite, PSOC-412, the enhancement of volatile matter yield increased with residence time in the isothermal furnace (Facet IV-A).

The effects of low temperature oxidation on reducing the agglomerating properties of caking coals are being studied. A DuPont 942 TMA has been shown to be a valuable tool for quantifying swelling and softening parameters. These caking parameters show a marked dependence on heating rate, load pressing on the sample, and particle size. A standard TMA operating procedure has been established for the analysis of plasticity. From combined TMA and thermogravimetric (TGA) studies we hope to be able to quantify the effects of preoxidation on caking coals. In the same task attempts are being made to characterize the porous nature of heat-treated coals by small angle x-ray scattering (SAXS). This technique is being evaluated as a method for determining size distributions of heterogeneities in cokes and chars. A computer program is being evaluated which calculates characteristic average size parameters and size distributions from raw SAXS data. To test the applicability of the program, SAXS data generated from a well characterized glassy carbon are being examined. Preliminary results show much promise for the technique (Task 27, Facet IV-B).

Under Task 28 the effect of particle size on preoxidation in air of two highly caking coals in the temperature range 135-250°C on weight loss during pyrolysis up to 1000°C and reactivity of resultant char to air has been studied. Increase in particle size adversely affects the rate of preoxidation as well as the subsequent increase in char reactivity (Facet IV-B).

Certain important aspects of the chemical and physical composition of American lignite coals are being characterized. Firstly, an analysis of the major minerals in lignites will be performed. The second stage involves defining the total amount of carboxyl groups present, and their associated cations. The purpose of this study is to define a standard, repeatable method by which one can successfully analyze American lignite coals. This information can then be ultimately used to obtain correlations between inorganic matter in lignites and the reactivity of chars produced from them. Qualitative analysis of the major minerals in PSOC-623, a Darco Texas lignite, has been completed. The major minerals are calcite, pyrite, quartz, kaolinite and illite. Quantitative analysis of these minerals has been started, and calibration curves for infrared, x-rayed and atomic absorption analyses have been completed. In the same task reactivities of char samples produced at 800°C from a lignite coal containing different amounts of exchangeable calcium ions have been measured in 1 atm hydrogen at 790°C. The presence of calcium in the char inhibits the hydrogasification reaction (Task 30).

Differential scanning calorimetry and thermogravimetric analysis were used to study the interaction between oxygen and seventeen coal chars (40 x 100 mesh) at 100°C. At 15 min reaction time, the cumulative amount of heat liberated Q_{15} (cal/g char) was used for the purpose of characterization and comparison. As the carbon content of parent coals, from which the chars were prepared, increases, Q_{15} (as well as values of ΔH, kcal/mole) decreases. Increase in nitrogen surface areas from anthracites to lignites is associated with an increase in Q_{15} up to 62 m^2/g, whereafter Q_{15} decreases with increasing nitrogen surface area. Relations between Q_{15} (where $\tau_{0.5}$ is the time required to gasify 50% of the char), have been confirmed. When the chars are gasified in air at 405°C, Q_{15} is linearly related to $\tau_{0.5}$, thus $Q_{15} = 6.75 - 0.048\ \tau_{0.5}$. For gasification in steam at 910°C or in CO_2 at 900°C, as $\tau_{0.5}$ increases (from lignite to anthracite chars), Q_{15} drops abruptly and finally levels off. Removal of mineral matter from the coal, prior to preparing the chars, has little effect towards lowering Q_{15} compared to that obtained with the raw char.

The same techniques were used to investigate briefly the interaction between air and a highly caking coal (PSOC-337, 200 x 250 mesh size fraction) at selected isothermal temperatures in the range 100-275°C. At 15 min reaction time, the amounts of heat liberated at 100, 125, 150, 175, 200, 225, 250, and 275°C are 1.15, 3.0, 6.4, 21.5, 72.0, 175, 385 and 550 cal/g coal, respectively. At 125 and 175°C, values of ΔH, being independent of reaction time, were about 176 and 220 kcal/mole oxygen added to the coal. The significant increase in Q(cal/g coal) or ΔH (kcal/mole oxygen) with reaction temperature is attributed to (i) the possible interaction between oxygen (in the oxidant gas) and some functional groups including hydrogen, (ii) the process of cross linking occurring in the coal during oxidation, and (iii) desorption of CO complex and gasification of the coal to yield CO_2 (Task IV-F).

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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

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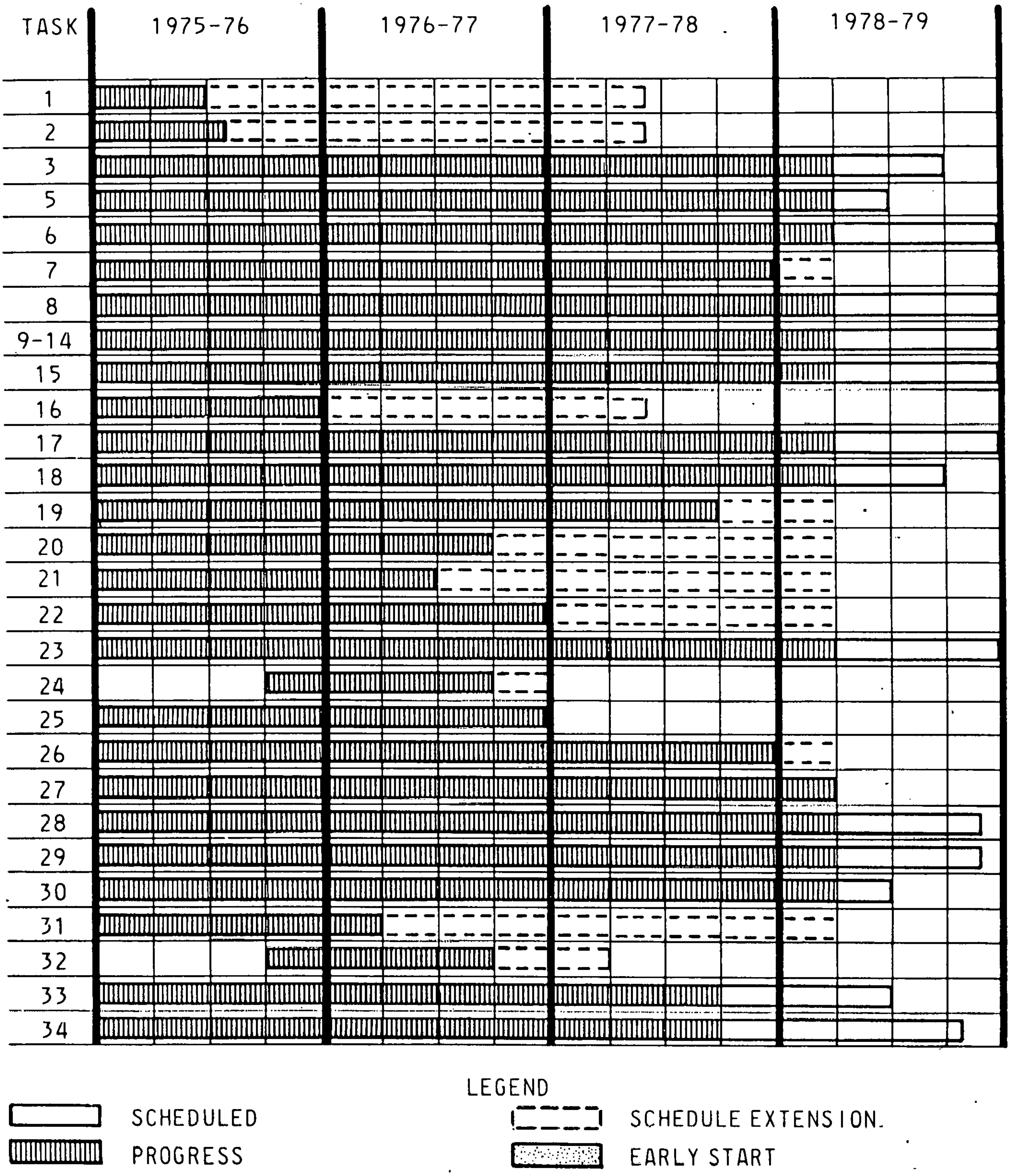
FACET VI	Project Planning, Management and Administration
Task 35	Administrative Plan and Program
Task 36	Cooperation and Collaboration with Other Agencies
Task 37	Communication of Research Results



PROJECT PLAN AND PROGRESS REPORT

Quarter Ending September 30, 1978

SUMMARY OF PROGRESS TO DATE

Thirty new coal samples from Utah, Pennsylvania, Maryland and West Virginia were collected during this quarter (Task 3). Table 1 summarizes the status of coal characterization and the Penn State/DOE Coal Data Bank. The deterioration of plastic properties, as measured by the Gieseler plastometer was determined in a set of 10 runs made during the course of 86 days (Task 5).

A total of 34 characterized coal samples and 131 printouts of selected coal data were supplied during the report period at the request of agencies engaged in coal research (Tasks 9-14).

In Task 20 of Facet II, a flow-sheet has been designed to concentrate four maceral associations (lithotypes) in the bath processing by unit operation of 800 lb of a hvAB coal.

In Facet IV-2 a new isothermal furnace with a temperature capacity of 1000°C and a residence time of 600 millisecs has been constructed and is being used to generate pyrolysis data. Darco Texas lignite, PSOC-412, has been partially characterized with respect to the kinetics of pyrolysis. Subsidiary experiments have been performed to permit more accurate interpretation of the isothermal furnace data (Task 23).

Under Task 25 a pressurized laminar-flow isothermal reactor has been designed and constructed. This unit will enable us to study reactions of coals in various atmospheres (H_2, O_2 and CO_2) at elevated temperatures ($\leq$ 1200°C) and pressures (100 atmospheres, maximum).

Task 27 of Facet IV-B involves an attempt to quantify the effects of preoxidation on the caking properties of certain coals. Several caking parameters [initial contraction, dilation, onset of softening temperature (T_s), dilation temperature (T_d), and resolidification temperature (T_r)] have been selected for this work. A DuPont 942 TMA dilatometer system has been shown to be a valuable quantitative tool for the characterization of these swelling and softening parameters. The transition temperatures and dilation values obtained with this instrument are well defined and reproducible. Studies were conducted to evaluate the effect of TMA operating conditions on the selected caking parameters. Swelling and softening data show a strong dependence on heating rate, load on the sample, and particle size of the starting coal. Over 260 TMA experiments have been carried out in an effort to establish the optimum conditions for studying plasticity. This facet of the study has been completed and a standard TMA operating procedure has been established. It has also been proved that oxygen uptake can be followed both quantitatively and reproducibly with a Fisher Thermogravimetric Analyzer (TGA) unit. Kinetic studies of oxygen sorption indicate that oxygen chemisorption is affected by intraparticle diffusion, that is, chemisorption rate increases with decrease in particle size. From combined TGA, TMA studies we hope to quantify the effects of preoxidation on the caking properties of some coals. In the same task a sophisticated computer program has been made operational which calculates characteristic average pore size parameters and pore size distributions from raw SAXS data.

Table 1. Penn State/DOE Coal Data Bank Status

Data Category	Data Elements Per Data Category	Previous OCR/ERDA Contract (OCR 14-01-001-390; ERDA E(49-18)-390)	Current ERDA/DOE Contract (DOE EX-76-C-01-2030)	Total	Current Contract Goal
Seam & Mine Information	66	300	836	1136	1300
Proximate	6	291	562	853	1300
Ultimate	7	284	557	841	1300
Equilibrium Moisture	1	18	416	434	1300
Sulfur Forms	4	288	536	824	1300
Maceral Analyses	43	300	572	1072	1300
Reflectance Analyses	67	284	545	829	1300
Free Swelling Indices	1	161	497	658	1300
Gray-King Coke Types	1	88	466	554	1300
Plastometer	6	25	7	32	150
Hardgrove Grindability	1	238	495	733	1300
Vickers Hardness	1	196	175	371	1300
Ash Fusion	8	0	495	495	1300
Low Temperature Ash	3	57			1300
Ash Analysis Related Data	1	57			1300
Major and Minor Elements	10	57	374	431	1300
Trace Elements	34	57	836	893	1300
Mercury	1	0	191	191	1300
Uranium	1	0	526	526	1300
Mineralogical	35	57	75	132	1300
Calculated Compositional Values	225	300	562	862	1300
Analysis Log	18	300	836	1136	1300
Other Categories	52	269	40	309	630

Total: 33 Data Categories 592 Data Elements

The program is being tested on data obtained for a well characterized glassy carbon (Tokai GC-30). Samples of heat-treated demineralized coals are being prepared and will be subjected to analysis by SAXS in the next quarter.

The results for the effect of preoxidation in air of two highly caking coals (PSOC-337 and 127) on weight loss during pyrolysis up to 1000°C and reactivity of resultant char to air at 470°C were presented in the last two DOE progress reports. Preoxidation was found to markedly enhance char reactivity. For a given level of preoxidation, the oxidation temperature as well as the presence of water vapor in the air had essentially no noticeable effect on char reactivity. In this report we are presenting the results of the effect of coal particle size on weight loss during pyrolysis and reactivity of resultant char to air (Task 28).

A qualitative analysis of PSOC 623, a Darco Texas lignite, has been completed. The major minerals are calcite, pyrite, quartz, kaolinite and illite. Also, significant progress has been made on the quantitative analytical technique. All calibration curves for three techniques (x-ray, infrared and atomic absorption) have been completed (Task 29).

The effect of cation exchange on the subsequent reactivity of a lignite char during gasification in 1 atm H_2 at 790°C has been studied. The presence of calcium in chars inhibits the hydrogasification reaction. This is in sharp contrast to the behavior in air, CO_2 and steam. In these atmospheres, char reactivity has been previously reported to increase linearly with increase in the calcium content of the char. With the submission of this report, about 80% of the proposed work on the effect of exchangeable cations on subsequent char reactivity has been completed (Task 30).

In Task 31, similar coal chars were used to investigate chemisorption of oxygen in a thermoparameter analyser and differential scanning calimeter.

The following Technical Report was published during the report period:

FE-2030-TR10 -- The Measurement of Reflectance of Coal Macerals -- Its Automation and Significance, A. Davis.

A list of Technical Reports produced as a result of this contract, and available from TIC, Oak Ridge, is given in Table 2.

Table 2. Technical Reports Prepared for
the Department of Energy
Contract No. EX-76-C-01-2030

FE-0390-1	Problems and Solutions in the Use of Coal Analyses--P.H. Given and R.F. Yarzab	November, 1975
FE-2030-TR2	The Characteristics of Chars Produced by Pyrolysis Following Rapid Heating of Pulverized Coal--N. ya Nsakala, P.L. Walker, Jr., and R.H. Essenhigh	February, 1977
FE-2030-TR3	Effects of Heat Treatment Conditions on Reactivity of Chars in Air--J.T. Ashu and P.L. Walker, Jr.	March, 1977
FE-2030-TR4	The Effect of Cation Exchange on the Subsequent Reactivity of Lignite Chars to Steam--E.J. Hippo and P.L. Walker, Jr.	March, 1977
FE-2030-TR5	Survey of Selected Agencies Conducted to Determine the Extent to Which the Nation's Coals are Adequately Characterized--J.M. Hower, A. Davis, C.P. Dolsen, and W. Spackman	October, 1977
FE-2030-TR6	The Effects of Impregnation of Coal with Potassium and Sodium Salts--H. Marsh and P.L. Walker	January, 1978
FE-2030-TR7	Porosity of Coals and Coal Products--O.P. Mahajan and P.L. Walker	March, 1978
FE-2030-TR8	Reactivity of Heat Treated Chars--O.P. Mahajan and P.L. Walker	March, 1978
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	March, 1978

FACET I-A: SAMPLE COLLECTION AND SEAM CHARACTERIZATION

COAL SAMPLING (TASK 3)

A coal sampling trip to Utah was made in August where thirteen samples were collected. A large channel sample (PSOC-1107) and four lithotype samples (PSOC-1108 - PSOC-1111) of coal from the old Kannel King Mine in Kane County was collected, a channel sample (PSOC-1112) and three lithotypes (PSOC-1113 - PSOC-1115) of the Blind Canyon seam in Emery County, and a channel sample (PSOC-1116) with three lithotypes (PSOC-1117 - PSOC-1119) of the Upper Sunnyside seam in Carbon County were obtained. In September we collected a channel sample (PSOC-1133), a lithotype (PSOC-1134) and two bench samples (PSOC-1135 and PSOC-1136) from the Lower Kittanning seam in Cambria County, Pennsylvania.

During this quarter we also received through our subcontract with West Virginia thirteen samples of coal from Maryland and West Virginia (PSOC-1120 through PSOC-1132).

FACET I-B: COAL CHARACTERIZATION

COAL CHARACTERIZATION (TASK 5)

Maceral analyses were completed on 28 PSOC samples during this period, along with 61 reflectance analyses and 8 fluorescence analyses. In addition the free swelling index and Gray-King Coke types were determined for 17 coals, and Hardgrove grindability for 17 coals.

The Plastic Properties of Coals and Their Influence in Conversion Processes

As a part of Task 5, we are studying the effects of progressive oxidation on the plastic properties of coals using a Gieseler Plastometer. An understanding of oxidation rates and the resultant changes in plasticity are important factors of determining the suitability of coals for conversion processes.

The coal selected for the initial study was PSOC-1099, a sample of the hvAb Pittsburgh Seam, Pennsylvania. A sample of 500 g, minus 425 μm in size, was stored at room temperature in an air atmosphere. At different time intervals, 15 g portions of the sample were removed and tested for plastic properties using the Gieseler plastometer (Table 3).

The coal showed that the maximum Gieseler plasticity number (dial divisions per minute, ddpm) decreases rapidly at first and then more slowly with increased time of aging (Figure 1). Corresponding temperatures of maximum fluidity appear to increase slightly. These results, in part, contrast with work by Jung[1]. He found temperatures of maximum fluidity to fall slightly with increased oxidation.

The coal showed an increase in softening temperature with increased time of aging. The solidification temperature, however, showed no distinct variation. Finally, the width of the softening zone remained constant at first and then decreased rapidly with increased time of aging (Figure 2).

Both maximum plasticity and softening range appear to be related to time of aging. The maximum Gieseler fluidity value was the most sensitive index of oxidation in the first three weeks of the experiment. After this time, the plastic range appeared to be the best index of oxidation.

Additional coals currently are being tested. Promising experiments are in progress with another hvAb. This coal, PSOC-1116, exhibits the same relation between the change in maximum plasticity and softening range with progressive oxidation.

Table 3

Measured Plastic Properties of PSOC-1099 with Increase In Time of Aging

Aging Time (days)	Maximum Plasticity Number (ddpm)	Maximum Plasticity Temp. (°C)	Softening Temp. (°C)	Solidification Temp. (°C)	Softening Range (°C)
0	14,681	437.5	389.3	477.8	88.5
4	10,031	437.5	386.5	475.0	88.5
10	6,008	441.0	389.8	477.3	87.5
21	5,601	439.5	387.5	477.0	89.5
34	5,655	441.5	391.0	474.5	83.5
42	4,211	441.0	394.3	476.3	82.0
57	4,090	441.0	394.5	478.0	83.0
69	2,746	442.0	395.0	475.5	80.5
78	2,637	444.0	396.3	478.5	82.0
86	2,621	443.0	400.0	478.0	78.0

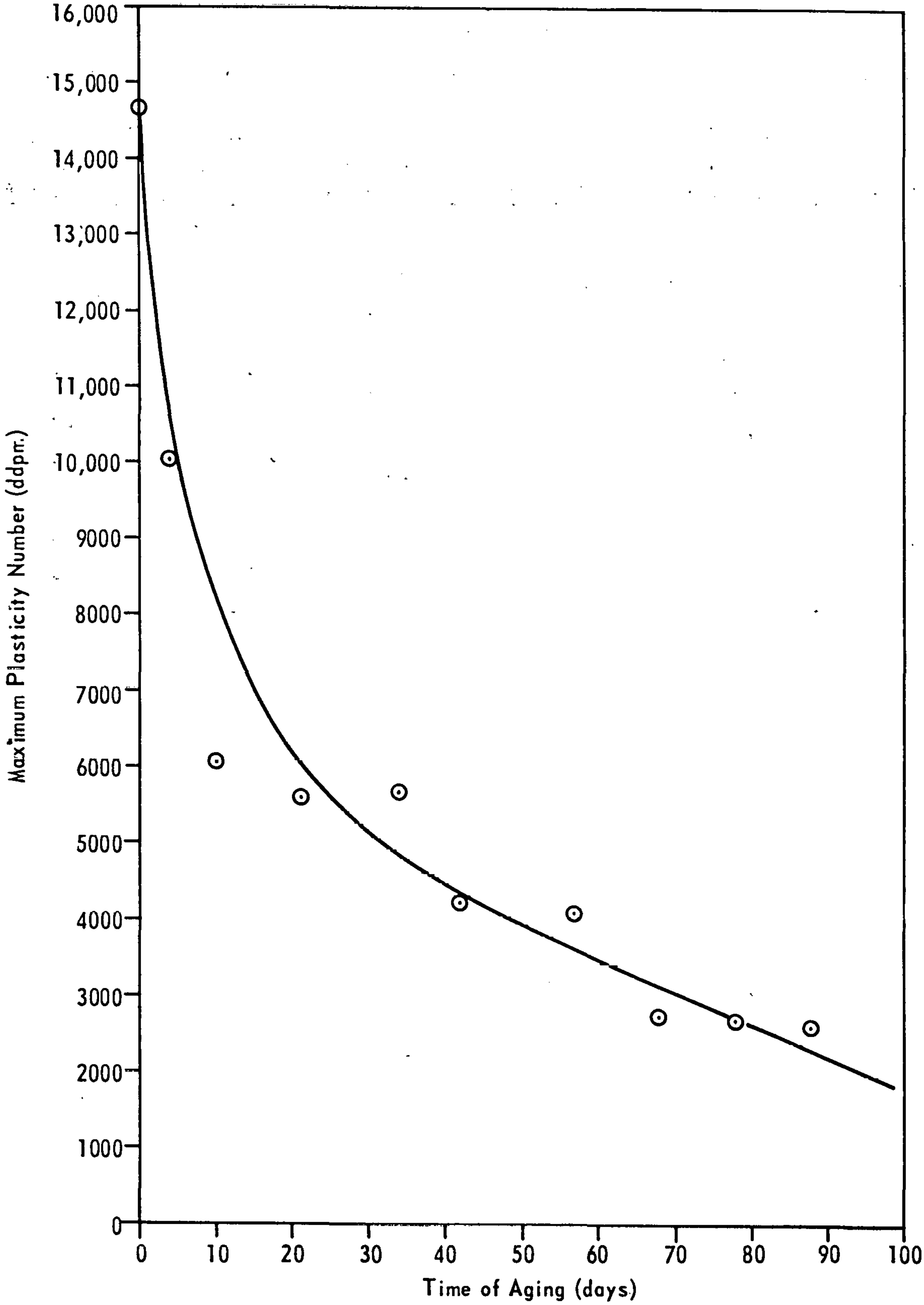


Figure 1. VARIATION IN MAXIMUM PLASTICITY WITH TIME OF AGING

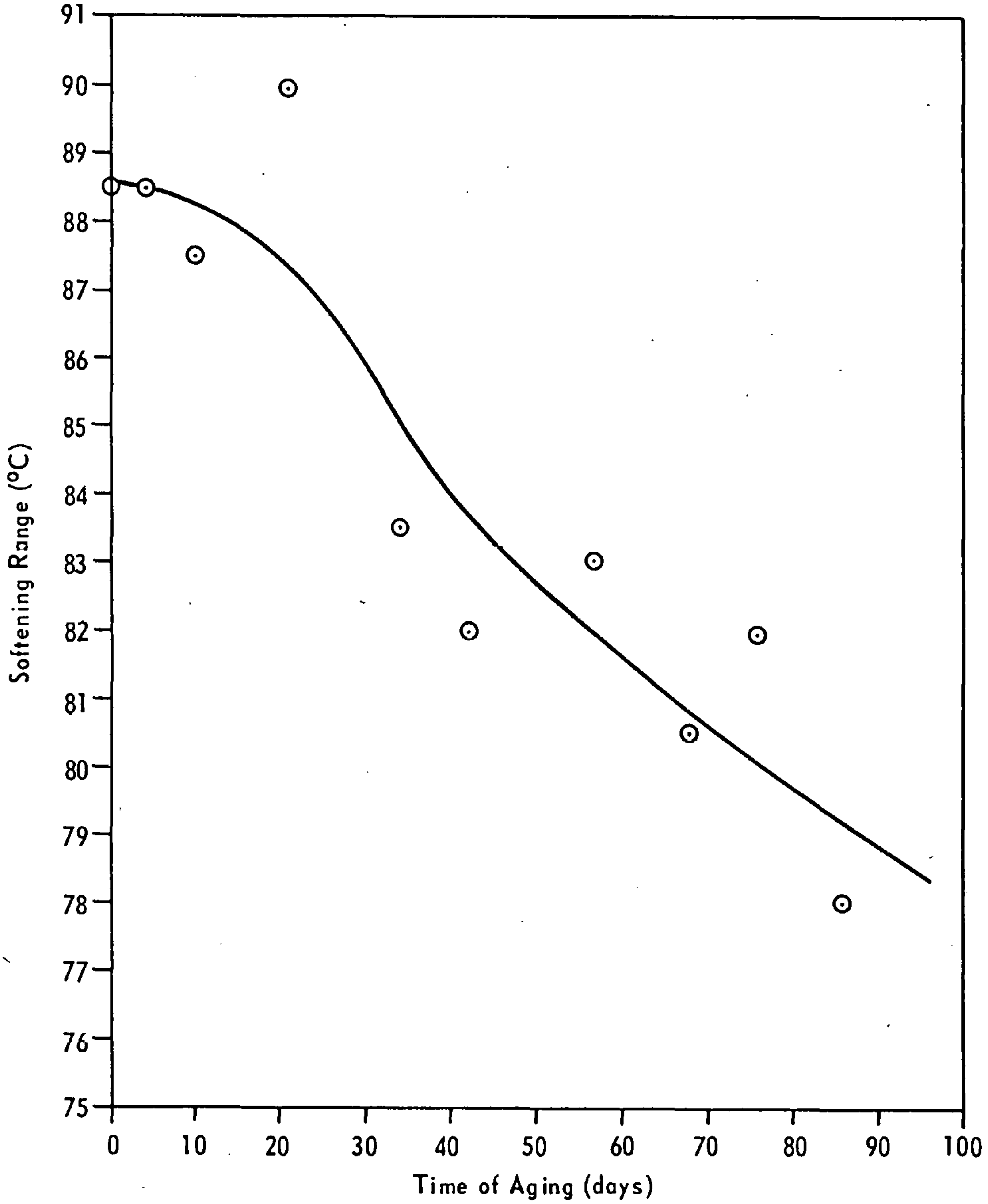


Figure 2. VARIATION IN SOFTENING RANGE WITH TIME OF AGING

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

SERVICE TO OTHER AGENCIES (TASKS 8-14)

A total of 34 characterized coal samples were supplied to other agencies who are engaged in coal research throughout the country, as well as printouts of analytical data for 128 coals. In addition, printouts of selected data for 523 coals were supplied to the Inland Steel Company, and similar data for all the coals in the Data Base were supplied to Cities Service Research Laboratories and to Applied Research Laboratories.

Other agencies requesting these materials included: The University of Southern Florida, Azcon Corporation, West Virginia University, Pittsburgh Energy Technology Center and Tufts University.

FACET II: COAL BENEFICIATION AND PRE-USE PROCESSING

TECHNIQUES FOR FRACTIONATION (TASK 20)

Introduction

The detailed fractionation of many coal seam samples has demonstrated the variations and heterogeneity of the organic and mineral components of U.S. coal seams. The studies have also demonstrated the potential capability of utilizing physical coal beneficiation to develop optimized coal conversion feed stocks for specific conversion processes (Task 18). The sampling of preparation plant products and characterization of these samples has demonstrated that existing commercial preparation plants do change the organic composition of run-of-mine coals despite the fact that existing plant design criteria are not dedicated to these objectives. It obviously follows that substantially greater coal compositional management is technically feasible should coal beneficiation facilities be designed with this objective. The potential significance of managing coal conversion feedstocks has been referred to in scattered reports; however, the subject has not been explored sufficiently in either laboratory, pilot or commercial demonstration. The potential economic, technological, and environmental implications of such applications are most impressive.

As partial fulfillment of Task 20, a 800 lb sample of No. 3 Elkhorn seam from Dean, Kentucky (PSOC-1103) has been acquired. The main effort this quarter has been the design of a laboratory flowsheet to process this coal to develop four major products: 1.) A vitrinite-micrinite concentrate; 2.) An exinite-fusinite concentrate; 3.) A middling - for calorific recovery; and 4.) A refuse product(s). The flow sheet design is based upon the characteristics of this coal as set forth by our previous studies of the same seam - PSOC 1, 2, 3, 4, and 6.

Experimental

This hvAb coal is unique in several ways - especially in hardness (HGI - 65.7. Individual fractions range from 38.6 to 57.4). The seam shows major lithotypes which are described as clarainic and durainic. It is the separation and concentration of these lithotypes which is being attempted.

Previous studies indicate a vitrinite-micrinite association of densities < 1.28 in the larger particle sizes - but softer particles. Vitrinite has the greatest tendency to concentrate. In contrast, an exinite-fusinite association tends to concentrate in the more dense fractions, in liberateable particles which are smaller and harder. The separation of the liberateable mineral matter results in fractions which separate at relatively low densities (about 1.3).

This coal will be very difficult to process owing to the extremely high levels of near-gravity material - the task is much beyond the capability of existing commercial facilities - as regards organic component concentration. It is, however, a relatively easy coal to process in terms of existing preparation goals for mineral matter and sulfur rejection.

The designed flow sheet, which will be utilized in these studies is based upon the above principles and in a mode as realistic to present commercial practice as feasible. It is noted that some processes exceed procedure not utilized but that are deemed feasible. The flow sheet is presented in Figure 3. The feed size analysis is presented in Table 4. The processing will be made batch-wise by unit operation, with appropriate sampling and analysis to detail each operation. The data will be accumulated as rapidly as the limited, available manpower permits.

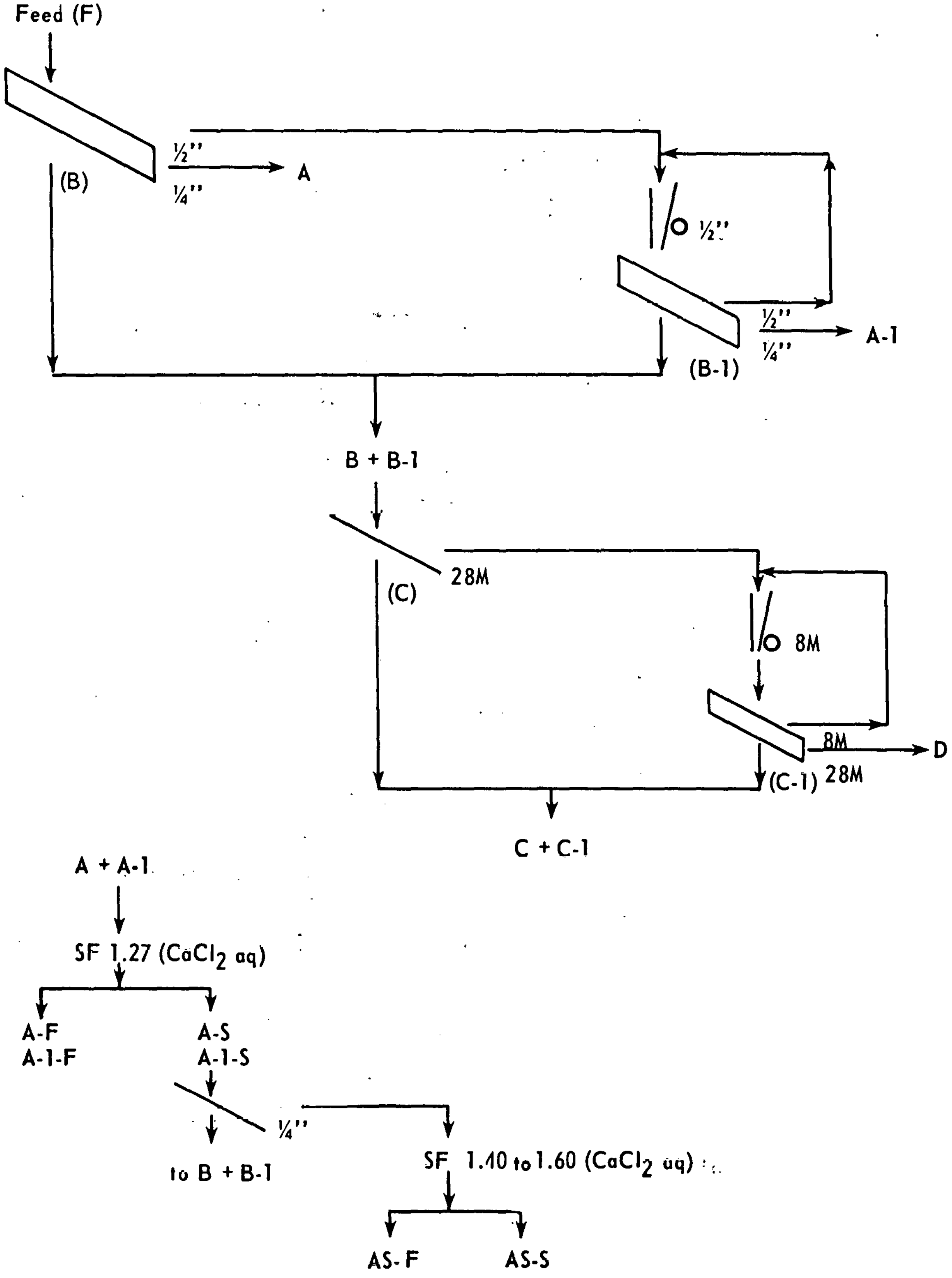


Figure 3. PROPOSED LABORATORY FLOWSHEET FOR LITHOTYPE BENEFICIATION PSOC-1103 - No. 3 Elkhorn Seam

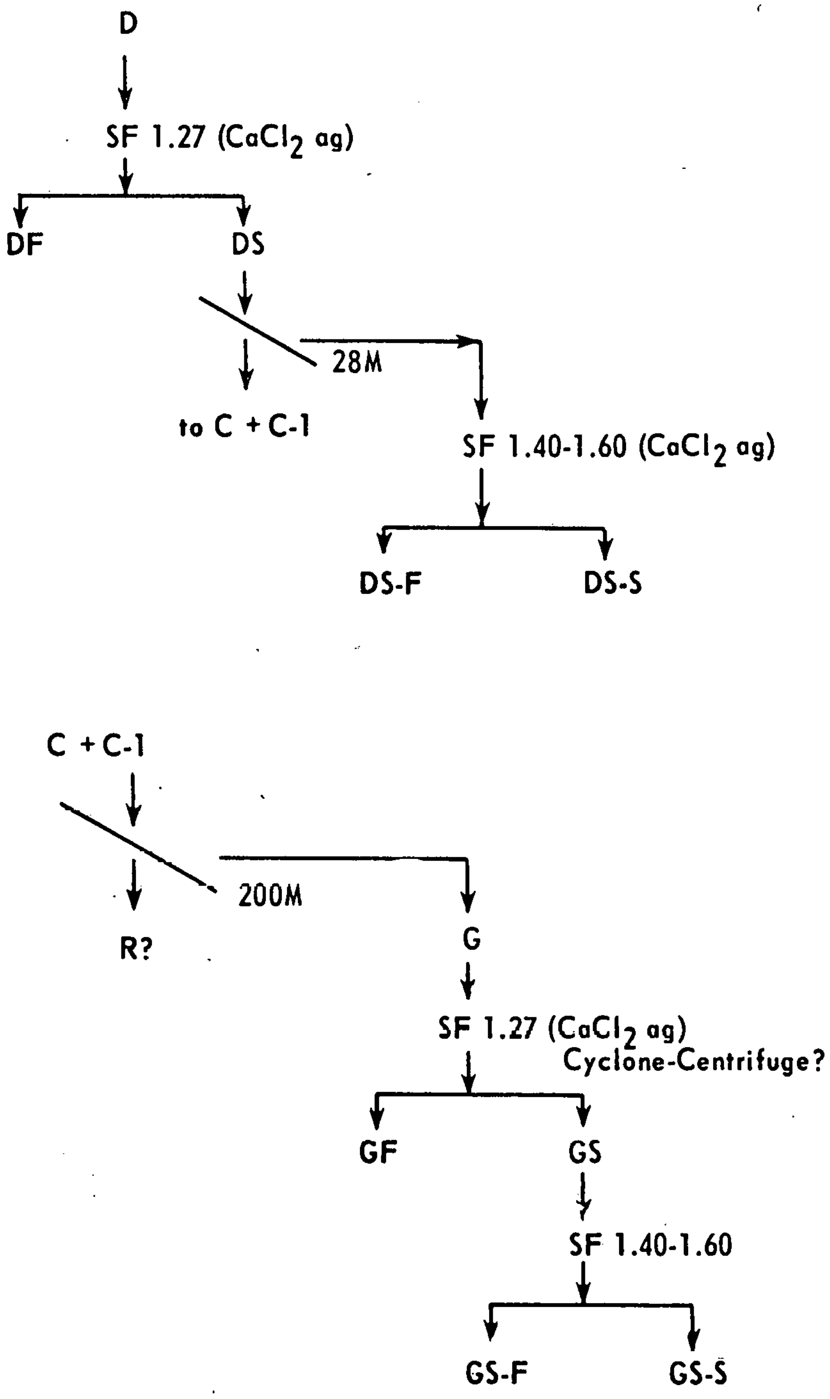


Figure 3. Continued

Table 4

Size Analysis of Head Samples
PSOC-1103 - No. 3 Elkhorn Seam
Air-Dried Basis

Passed	Retained	Wt., %	Cumulative Wt., %	
			Retained	Passed
	2-inch	15.2	15.2	100.0
2-inch	1-inch	20.8	36.0	84.8
1-inch	0.5 inch	24.9	60.9	64.0
0.5 inch	0.25 inch	14.5	75.4	39.1
0.25 mesh	16 mesh	16.3	91.7	24.6
16 mesh	30 mesh	3.2	94.0	8.3
30 mesh	100 mesh	3.1	98.0	5.1
100 mesh		2.0	100.0	2.0

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

Volatile Matter Experiments

Purpose

Performing A.S.T.M. volatile matter tests is a necessary step in the analysis of chars produced in the isothermal furnace. As reported in the January - March report the phenomenon of sparking during these tests can be eliminated by reducing the size of the test sample, but the consequence is to overestimate the A.S.T.M. yield of volatile matter in the isothermal furnance, where the sample size is effectively a single particle, is due totally or partially to this sample size phenomenon, or if there exist other factors such as a heating rate effect.

Method

The method, as outlined in the January - March, 1978 report, was again used. To modify the heating rate, however, alumina chips (99.8% Al_2O_3) were placed in the volatile matter crucible and the coal sample dispersed evenly around them. This also had the effect of reducing the porous bed for a given sample size.

Results

Figure 4 was constructed using the data of Table 5 for Darco Texas lignite, PSOC-412, sieve cut 70 x 100 mesh, with mean weight particle, $\bar{x}$, of 178 μm. The effect of adding the alumina chips is to slightly increase the volatile matter yield for a given sample size. This is consistent with the hypothesis that reduction in char forming secondary reactions due to the elimination of the porous bed causes an increase in volatile matter yield. It should be noted that the surface area of the alumina chips is an order of magnitude less than the external surface area of the coal particles in the porous bed. The data are not supportive of the hypothesis that an increase in volatile matter yield accompanies an increase in the heating rate. Since the change in heating rate is difficult to estimate accurately, it is not certain whether its change is significant. The data, therefore, should not be construed as conclusive evidence that the heating rate is not a controlling factor in a system such as the isothermal furnace.

Weight Loss Following Rapid Heating

Weight Loss Curves

Weight loss in the isothermal furnace as a function of temperature and residence time are shown in Figure 5, constructed using the data in Table 6, for the 70 x 100 mesh sieve ($\bar{x}$ = 178 μm) cut and in Figure 6 for the 270 x 400 mesh sieve cut ($\bar{x}$ = 41 μm), using the data in Table 7. These curves have not

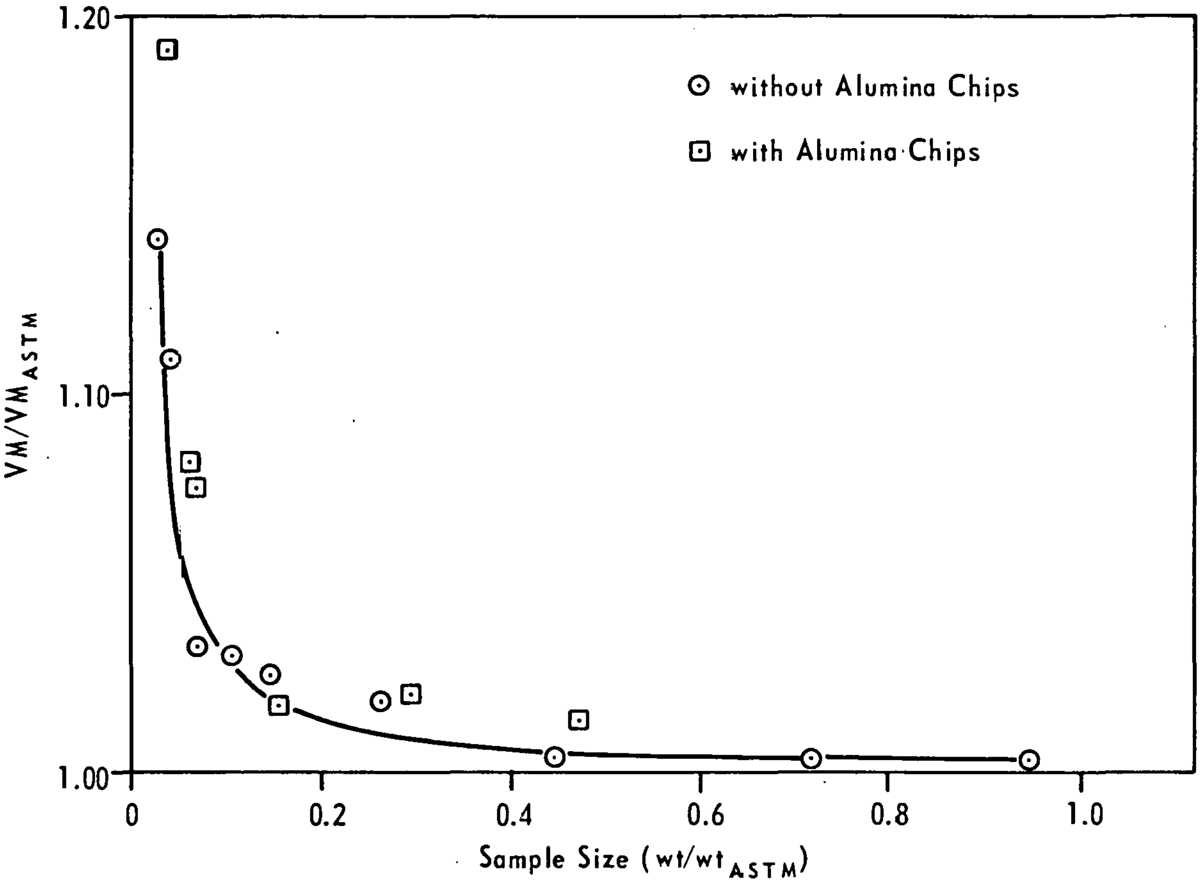


Figure 4. EFFECT OF SAMPLE SIZE ON VOLATILE MATTER YIELD FOR PSOC-412 COAL, 70 x 100 MESH

Table 5

Effect of Sample Size on Volatile Matter Test for

PSOC-412, 70 x 100 Mesh

	Wt. Sample (g)	V.M.,% daf Coal	V.M./V.M. ASTM
Without Alumina Chips			
	0.95	51.9	1.000
	0.73	52.3	1.007
	0.45	52.0	1.001
	0.26	52.7	1.016
	0.14	53.5	1.031
	0.10	53.9	1.039
	0.05	54.1	1.043
	0.04	57.6	1.111
	0.03	59.0	1.136
With Alumina Chips			
	0.47	52.8	1.016
	0.29	53.1	1.024
	0.17	52.9	1.018
	0.09	55.8	1.075
	0.06	56.2	1.083
	0.04	61.9	1.192

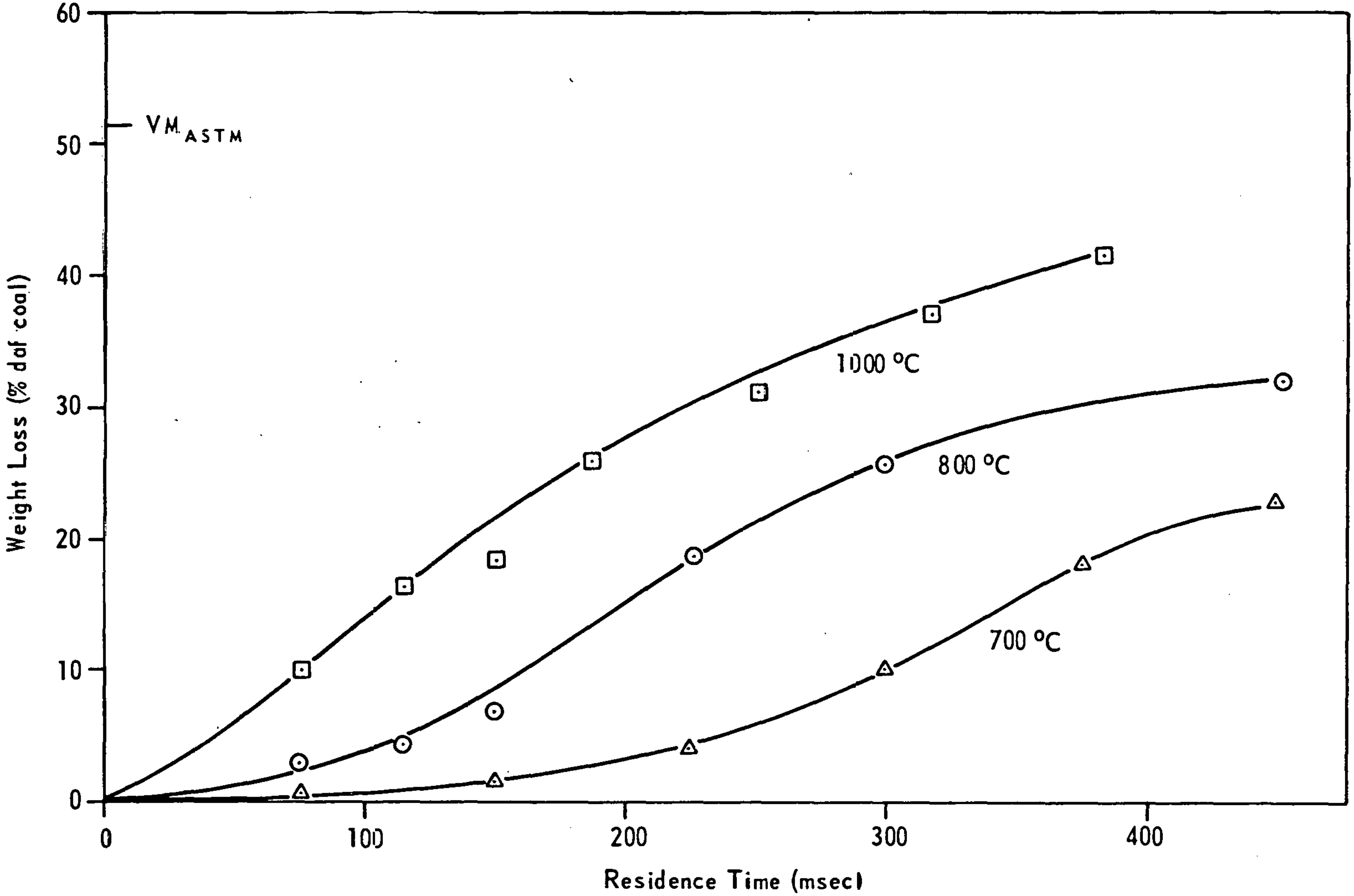


Figure 5. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME FOR PSOC-412 COAL, 70 x 100 MESH

Table 6

Weight Loss as a Function of Residence Time

for PSOC-412, 70 x 100 Mesh

Total Residence Time (secs)	Weight Loss, ΔW % daf Coal		
	700°C	800°C	1000°C
0.075	-	3.4	10.1
0.113	-	4.6	16.2
0.150	1.8	7.1	18.6
0.189	-	-	26.1
0.225	3.8	19.0	-
0.252	-	-	31.8
0.300	10.6	25.0	-
0.315	-	-	37.6
0.375	17.5	-	41.1
0.450	22.5	32.5	-

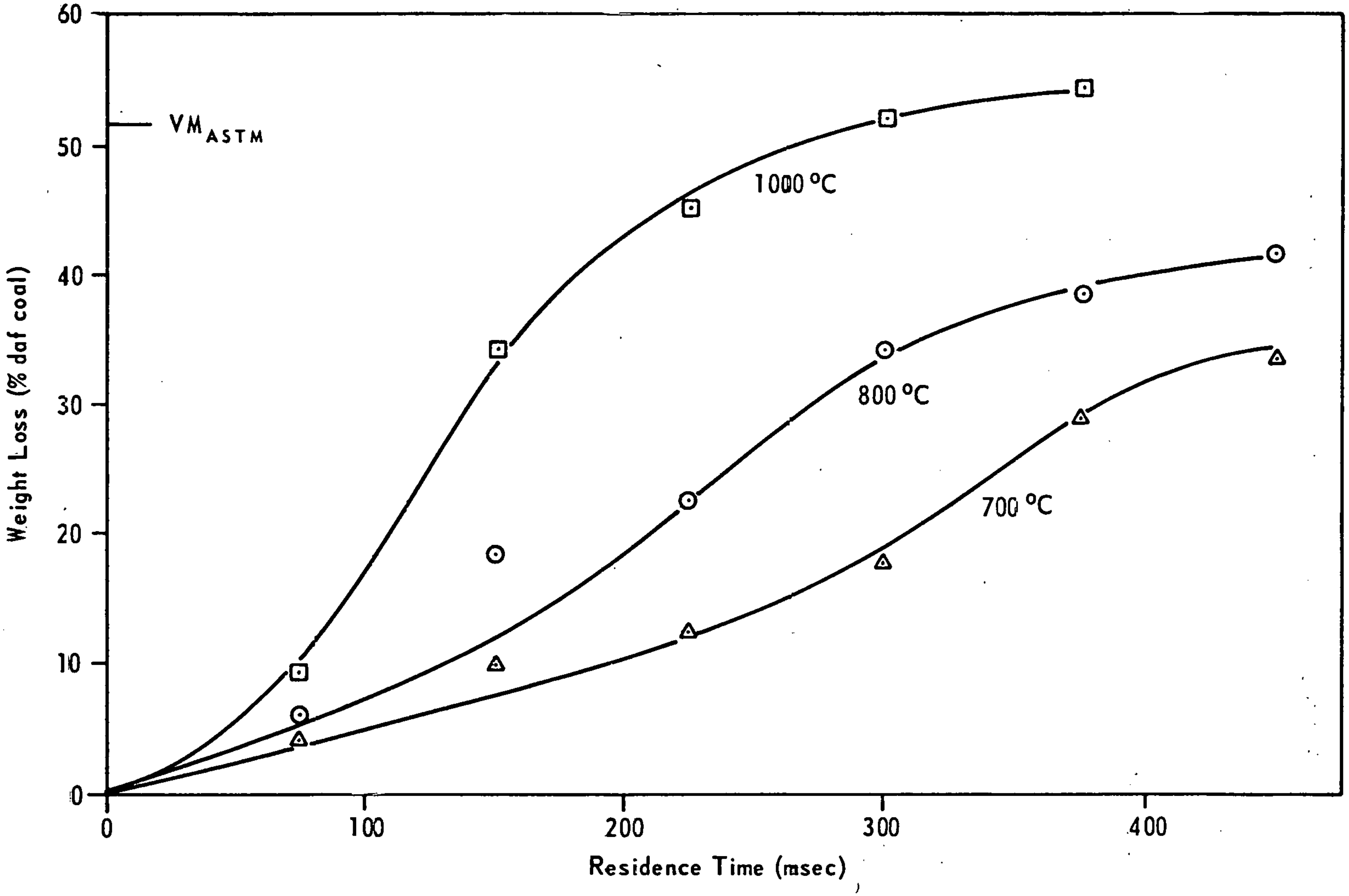


Figure 6. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME FOR PSOC-412, 270 x 400 MESH

Table 7

Weight Loss as a Function of Residence Time for PSOC-412, 270 x 400 Mesh

Total Residence Time (secs)	Weight Loss, ΔW % daf Coal 700°C	800°C	1000°C
0.075	4.9	6.1	9.9
0.150	9.9	18.5	34.6
0.225	12.7	22.7	45.3
0.300	18.4	34.3	52.3
0.375	29.8	38.1	54.5
0.450	33.6	41.8	-

been corrected for the error involved in using ash as a tracer, hence there is a constant underestimation of the weight loss as outlined in the April - June, 1978 report. These graphs are two in a series that are currently being generated over a wide range of particle size and which will be discussed in a subsequent report.

Error Involved with Ash Tracer Technique

Using ash as a tracer incorporates errors due to loss of weight by the mineral matter upon heating. The technique for determining this error was outlined in the April - June, 1978 report. Data for the 70 x 100 mesh sieve cut are given in Table 8 and plotted in Figure 7. The average error is an underestimation of the weight loss by 8.9%, representing 4.5% of the original A.S.T.M. volatile matter of the dry-ash-free coal.

Enhancement of Volatile Matter Yield

The weight loss data of Table 6 for the 1000°C pyrolysis temperature case has been corrected for the error involved in using ash as a tracer and is presented in Table 9, together with the residual volatile matter in the char, R as a % original dry-ash-free coal, also corrected for such an error. The total release of volatiles, $\Delta W + R$, shows a steady increase from the A.S.T.M. volatile matter content with increasing residence time in the isothermal furnace, as seen in Figure 8. The ΔW and $\Delta W + R$ lines will meet when $\Delta W = \Delta W_\infty$ (the maximum potential weight loss). This should become more apparent when data are collected for longer residence times and small sieve cuts.

Table 8

Error Involved in Using Ash as a Tracer for PSOC-412, 70 x 100 Mesh

Pretreatment Temperature, °C	250	350	450	550	650	750
VM_I, % daf coal	5.0	20.1	37.5	43.4	48.0	52.1
VM_{II}, % daf coal	49.8	33.0	14.3	8.6	4.6	1.5
VM_{TOTAL} ($=VM_I + VM_{II}$)	54.8	53.1	51.8	52.0	52.6	53.6
ΔW % daf coal (using ash tracer)	50.4	47.3	45.5	48.1	46.9	48.3
Error, %	8.0	10.9	12.1	7.5	10.8	9.9

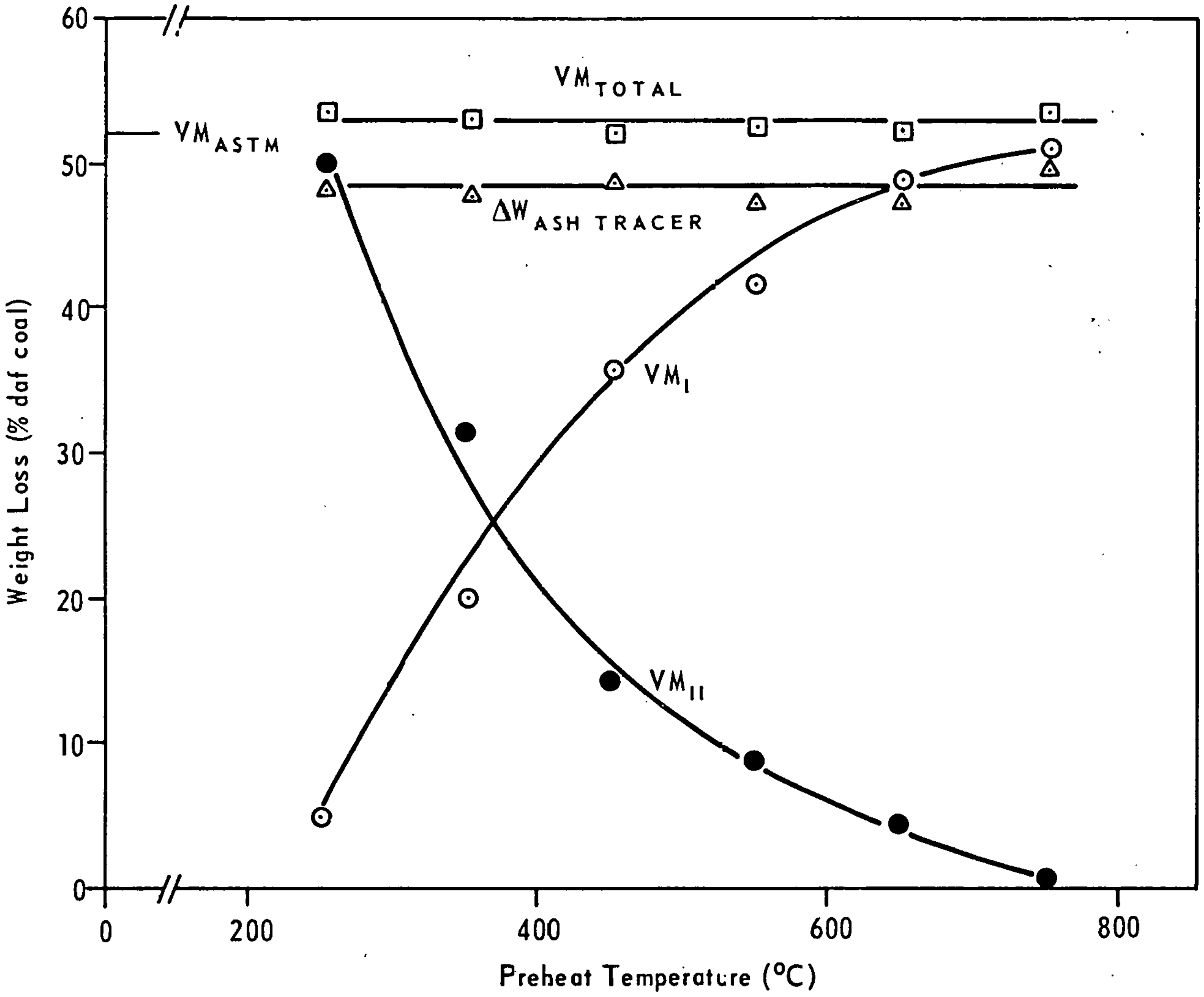


Figure 7. COMPARISON BETWEEN DIRECT MEASUREMENT AND ASH TRACER TECHNIQUE FOR PSOC-412 COAL, 70 x 100 MESH

Table 9

Relationship Between Weight Loss in Isothermal Reactor at 1000°C and Residual Volatile Matter of the Char for PSOC-412, 70 x 100 Mesh

Total Residence Time (secs)	ΔW (corrected) % daf coal	R (corrected) % daf coal	ΔW + R % daf Coal
0.075	14.6	38.2	52.8
0.113	20.7	36.0	56.7
0.150	23.1	33.5	56.6
0.189	30.6	25.3	55.9
0.252	36.3	21.7	58.0
0.315	42.1	17.4	59.5
0.378	45.6	14.3	59.9

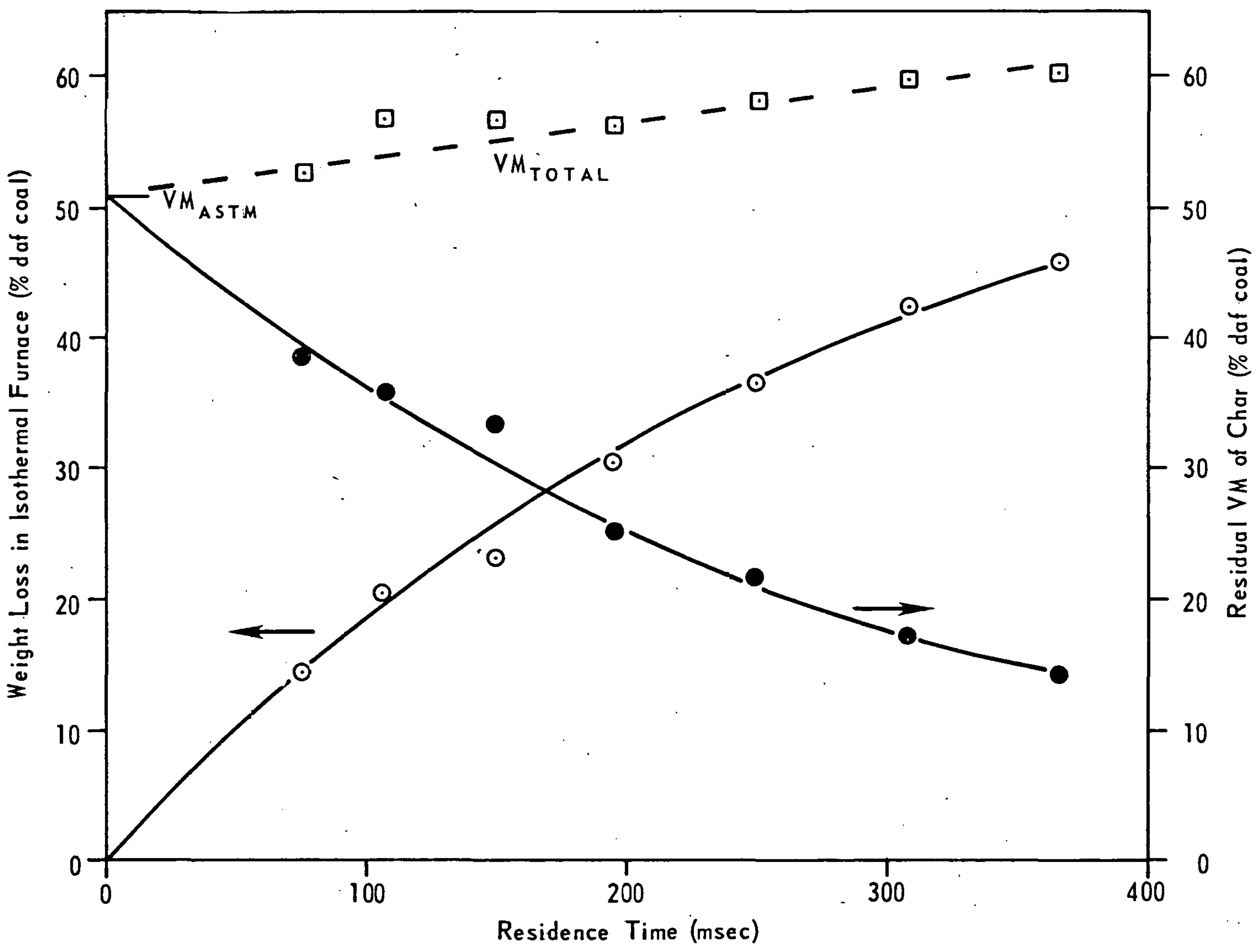


Figure 8. TOTAL RELEASE OF VOLATILE MATTER AS A FUNCTION OF RESIDENCE TIME AT 1000°C FOR PSOC-412 COAL, 70 x 100 MESH

A Computational Examination of the Effect of Coupled Heat Transport and Chemical Kinetics Upon Single Particle Coal Pyrolysis

Introduction

Published studies of the thermal decomposition of coal particles within rapid heating conditions reveal wide variation in kinetic schemes and the magnitude of kinetic parameters used to correlate weight loss data.[2,3,4] An immediate tendency is to attribute the orders of magnitude variation in rate constants to the inherent nature of coal. Even apart from the diversity of coal types used in the various studies, and as noted by Anthony and Howard,[2] other important parameters such as particle size, experimental configuration and final particle temperatures achieved, vary considerably from one study to another.

Considering the differences in experimental designs and subsequent differences in derived kinetic parameters, the question naturally arises as to the degree thermal transport pheonomen could be influencing observed results. In addition, it is of interest to ascertain if the pyrolysis process, coupled to the thermal transport phenomena, is capable of significantly influencing the temperature history of the reacting particle, and, consequently, observed thermal decay.

Physical Model and Mathematical Formulation

For the sake of computational examination, a simple physical model of coal is proposed. The solid coal material is said to consist of a thermally responsive element, the pyrolytic material, and an inert part. The global thermal response is assumed to take the form of a simple Arrhenius expression. Depending upon the particular thermal environment envisaged as well as the operating parameters chosen, the thermal response of a coal particle during rapid pyrolysis might be imagined to occur in one of three manners as illustrated in Figure 9, or as some intermediate case of these.

A simple energy balance taken on the particle as a whole leads to the following ordinary differential equation for cases 9a and 9c:

$$\rho C_p V_p (dT/dt) = hA_p(T_e - T) + \Delta H(dP/dt)V_p \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In case 8b the energy balance is performed over a volume element of the particle and leads to the following partial differential equation:

$$C_p(\partial T/\partial t) = k_e((2/r)(\partial T/\partial r) + \partial^2 T/\partial r^2) + \Delta H(\partial P/\partial t) \; . \; . \; . \quad (2)$$

In both expressions the rate of pyrolytic material decay is first order with respect to remaining material and with the rate constant expressed as:

$$k(T) = Ae^{(-E/RT)} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Discussion

The above differential equations, with appropriate initial and boundary conditions, are integrated numerically to ascertain the temperature history of the coal particle during the rapid pyrolysis process. Parameter variations, such as in particle size and driving temperature, are made systematically to determine the relative influence of each on the particle heating rate and pyrolytic decay. Some results are displayed in Figures 11-17 below. Figures 11 and 12 refer to the cases illustrated in 17a and 17c. Such a situation might well occur, for example, when coal particles entrained in a cold flow are injected co-currently into a preheated flow within a reactor whose walls are in thermal equilibrium with the preheated stream. Figures 13-17 illustrate a thermal response such as depicted in 17b. Such a situation could be envisaged upon injection of coal particles into a preheated fluidized bed.

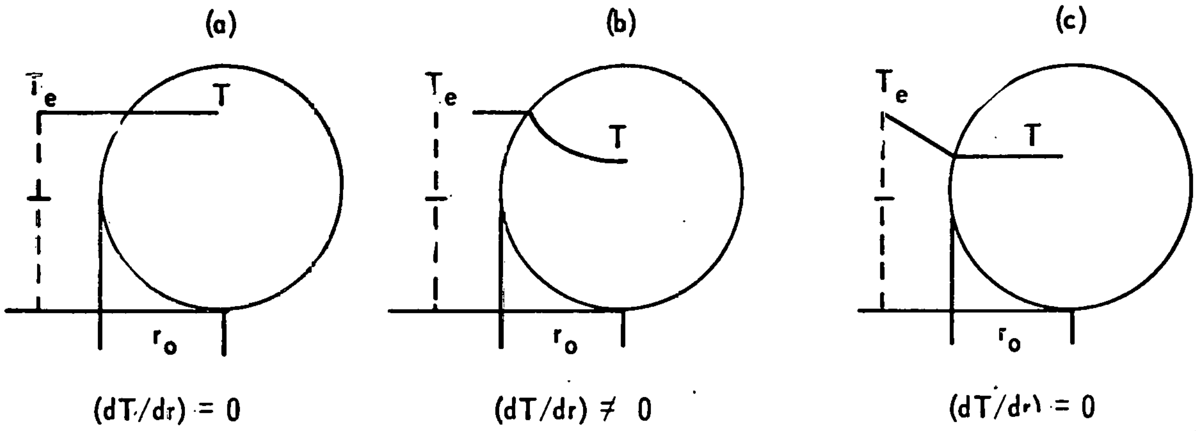
From a microscopic point of view the element of interest is the variation in the temperature response when a parameter such as particle size is changed within the same mode of thermal stimulation (Figures 11 and 13). Also from a microscopic point of view, and again depending of the parameter combination in consideration, the mode of pyrolysis can change from an essentially isothermal, volumetric process to one of a shrinking-core, non-isothermal process (Figures 14,15,16). From a macroscopic point of view, the element of interest is the resulting modification of the charter of the weight loss curves (Figures 12 and 17).

When the mode of thermal response is that depicted in Figure 10b, the apparent activation energy calculated from the weight loss curves at 50% reaction completion tends to one-half the supposed true activation energy as particle size is increased. When the mode of thermal response is that of 10c the apparent activation energy can be considerably less than E/2 as particle sized is increased. The analogy to zone theories of carbon-oxygen reactions is apparent. These results suggest that wide variation in kinetic parameters for rapid coal pyrolysis can indeed be in part due to coupled thermal transport-chemical kinetic phenomena. The mode of coupling and its magnitude depend to a large extent on the particular experimental design employed as well as the operating parameters chosen within the particular experimental design.

SYMBOLS

A = Arrhenius pre-exponential, sec^{-1}
A_p = particle geometric surface, cm^2
d_o = particle diameter, μm
C_p = particle specific heat, cal/gm-°K
E = chemical activation energy
h = heat transfer coefficient, cal/cm^2-°K-sec
k_e = particle conductivity, cal/cm-°K-sec
$k(T)$ = Arrhenius rate constat, sec^{-1}
P = pyrolytic material concentration, gm/cm^3
r = radial position within particle, cm

r_o = particle radius, μm
R = gas constant, kcal/mole-°K
T = particle temperature,°K
T_e = ambient, driving temperature,°K
V_p = particle volume, cm^3
ρ = particle density, gm/cm^3
H = heat of reaction, cal/gm



(a) $(dT/dr) = 0$ (b) $(dT/dr) \neq 0$ (c) $(dT/dr) = 0$

Figure 9. POSSIBLE DRIVING TEMPERATURE – PARTICLE TEMPERATURE RELATIONSHIPS DURING RAPID PYROLYSIS

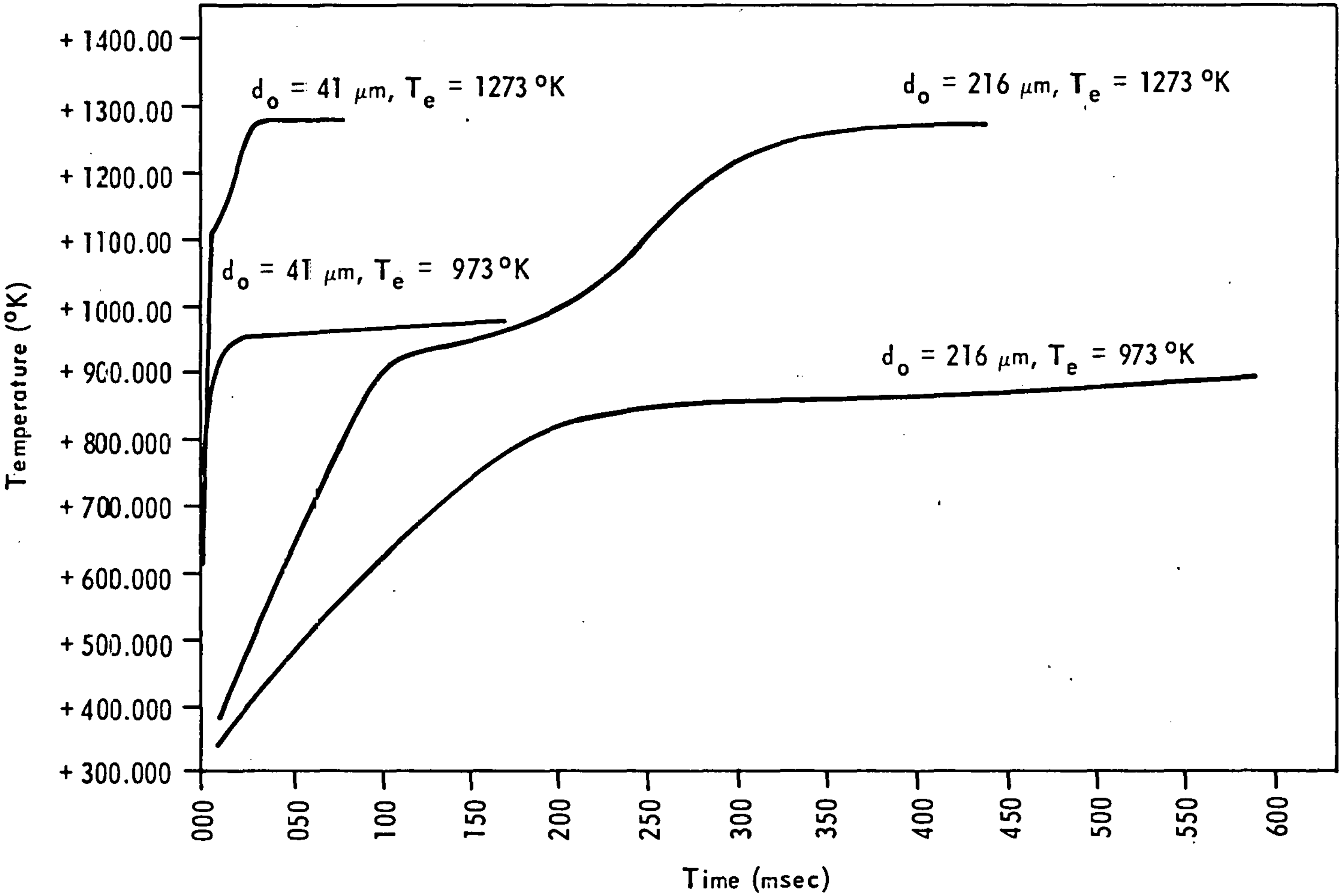


Figure 10. PARTICLE TEMPERATURE HISTORIES ILLUSTRATING CASE 9a AND CASE 9c

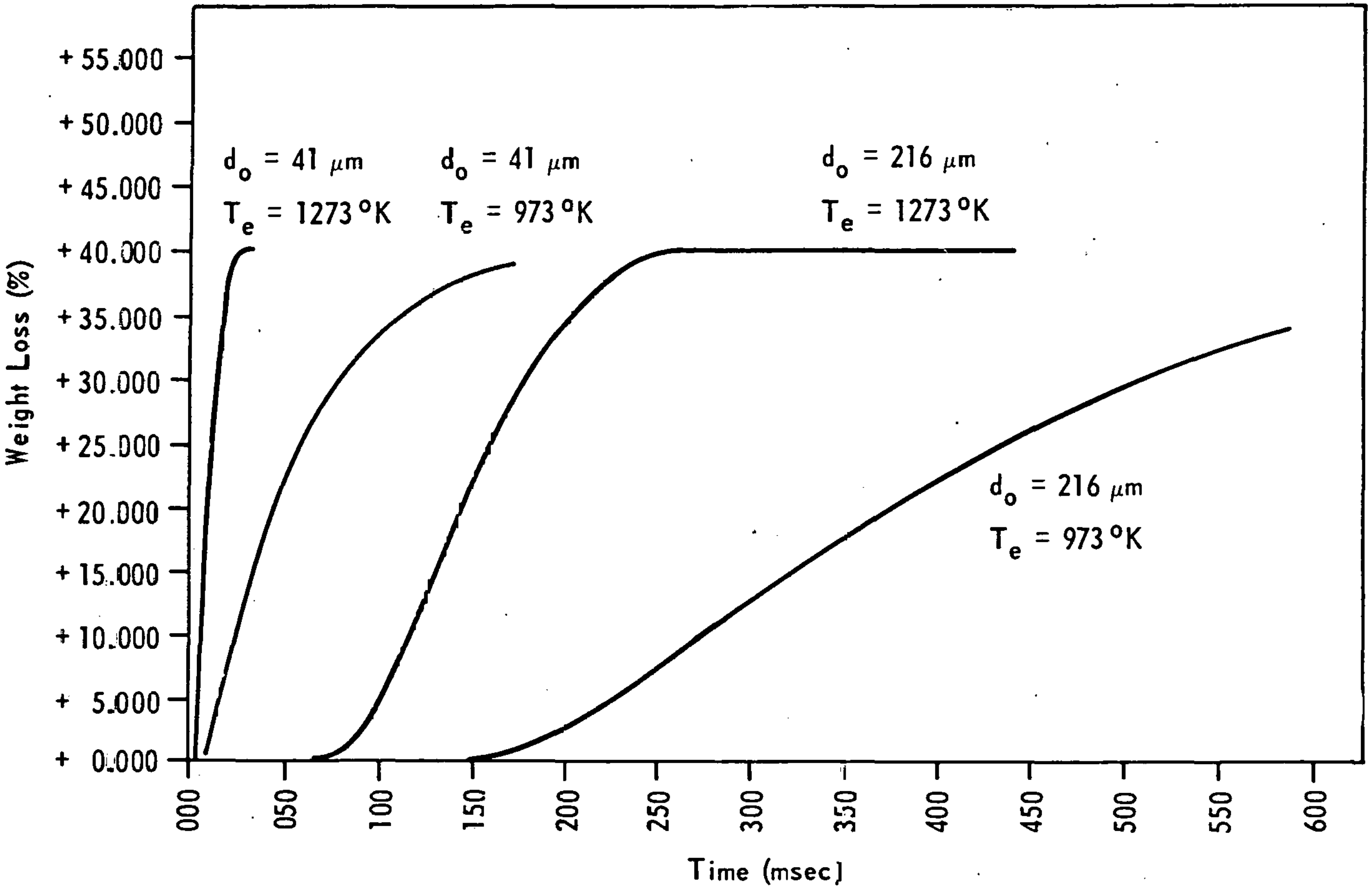


Figure 11. PERCENT WEIGHT LOSS ACCOMPANYING TEMPERATURE HISTORIES OF FIGURE 10

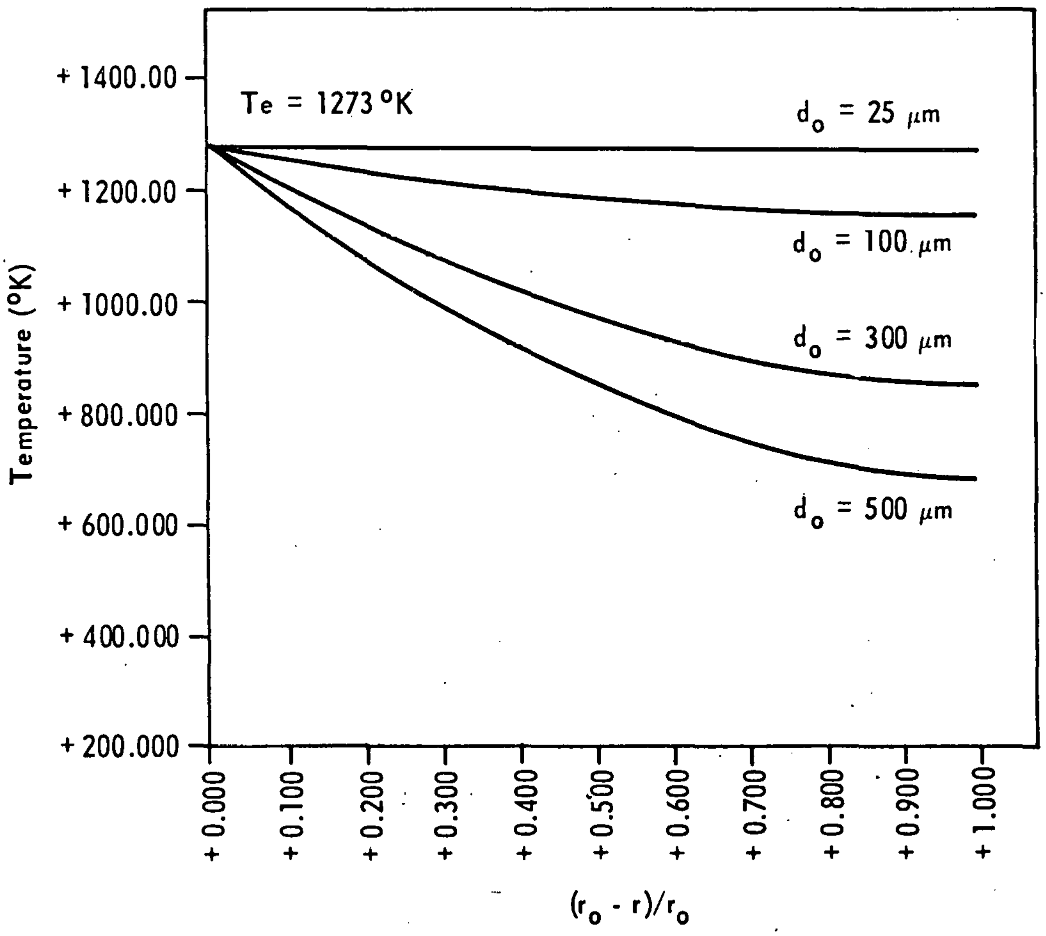


Figure 12. TEMPERATURE PROFILES AND PARTICLE SIZE ILLUSTRATING CASE 9b

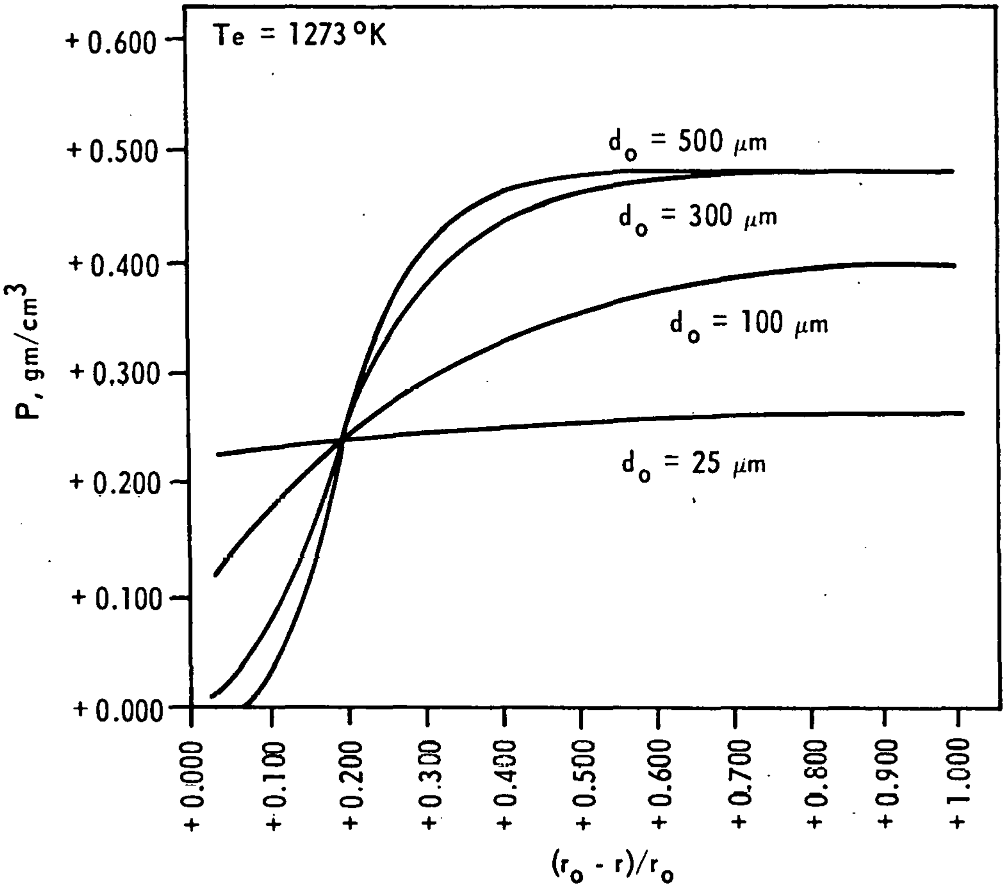


Figure 13. P-PROFILES AND PARTICLE SIZE ILLUSTRATING CASE 9b

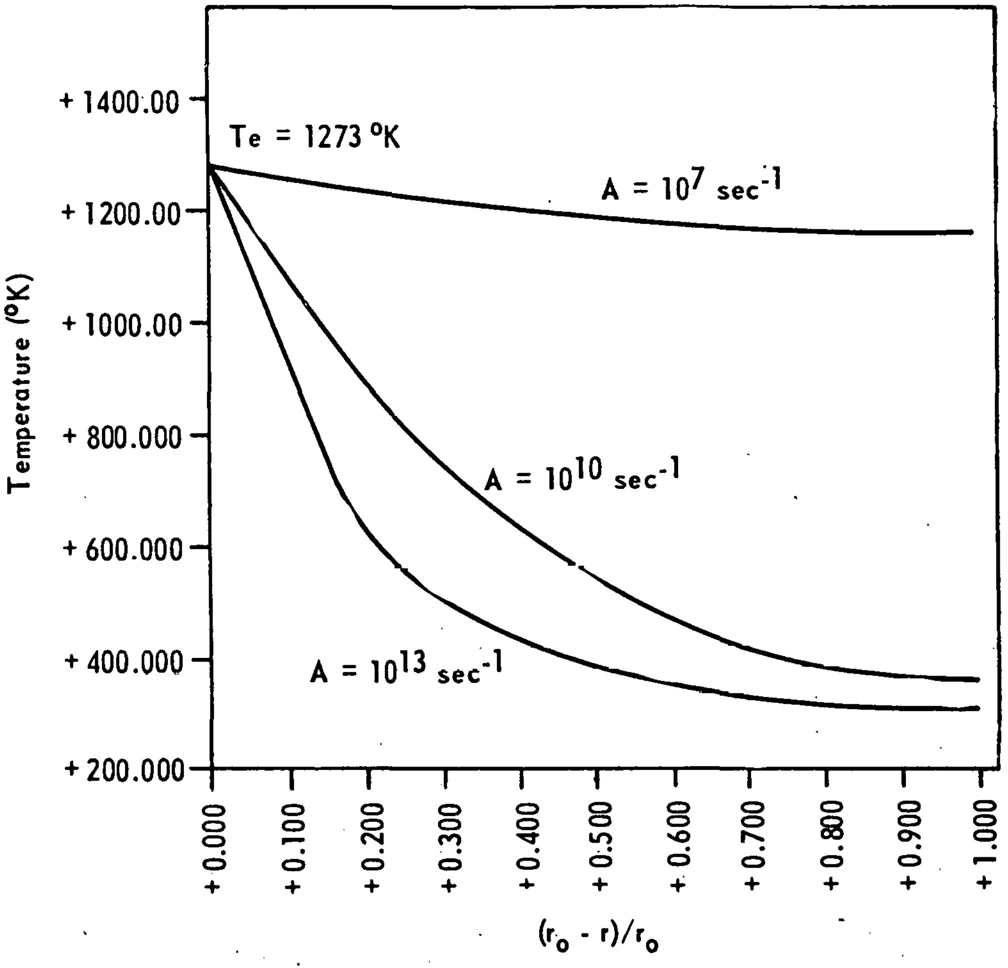


Figure 14. TEMPERATURE PROFILES AND PRE-EXPONENTIALS ILLUSTRATING CASE 9b

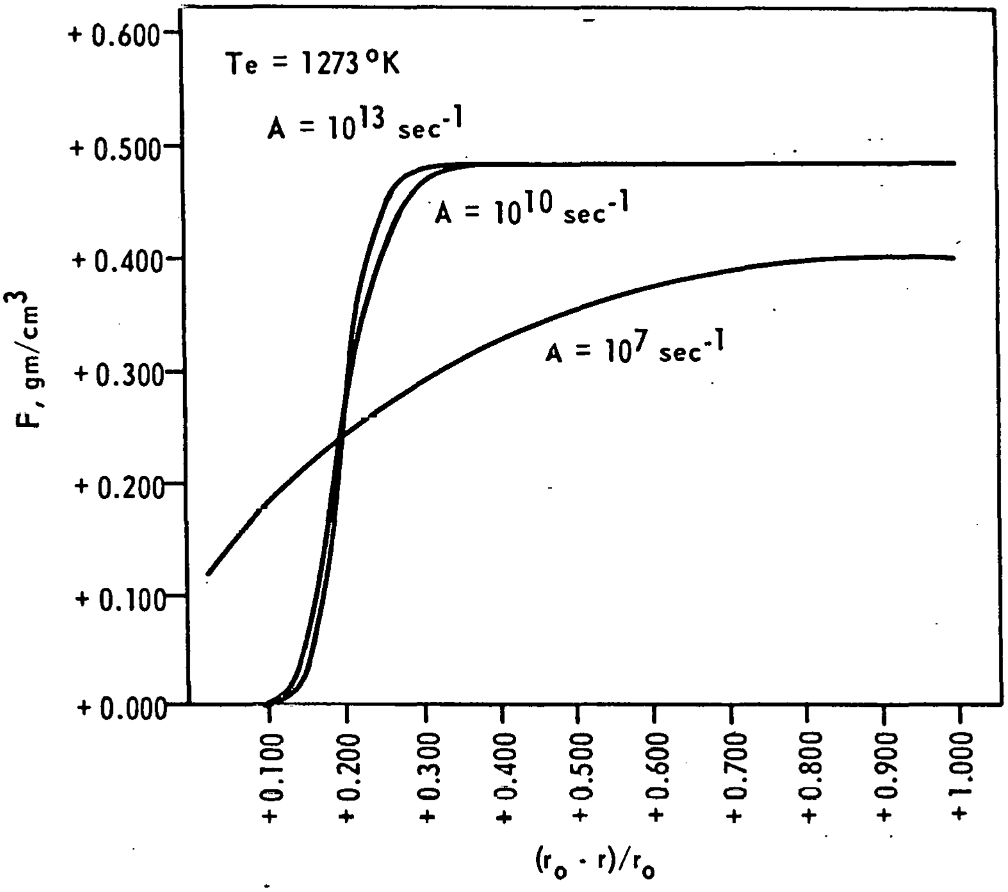


Figure 15. P-PROFILES AND PRE-EXPONENTIALS ILLUSTRATING CASE 9b

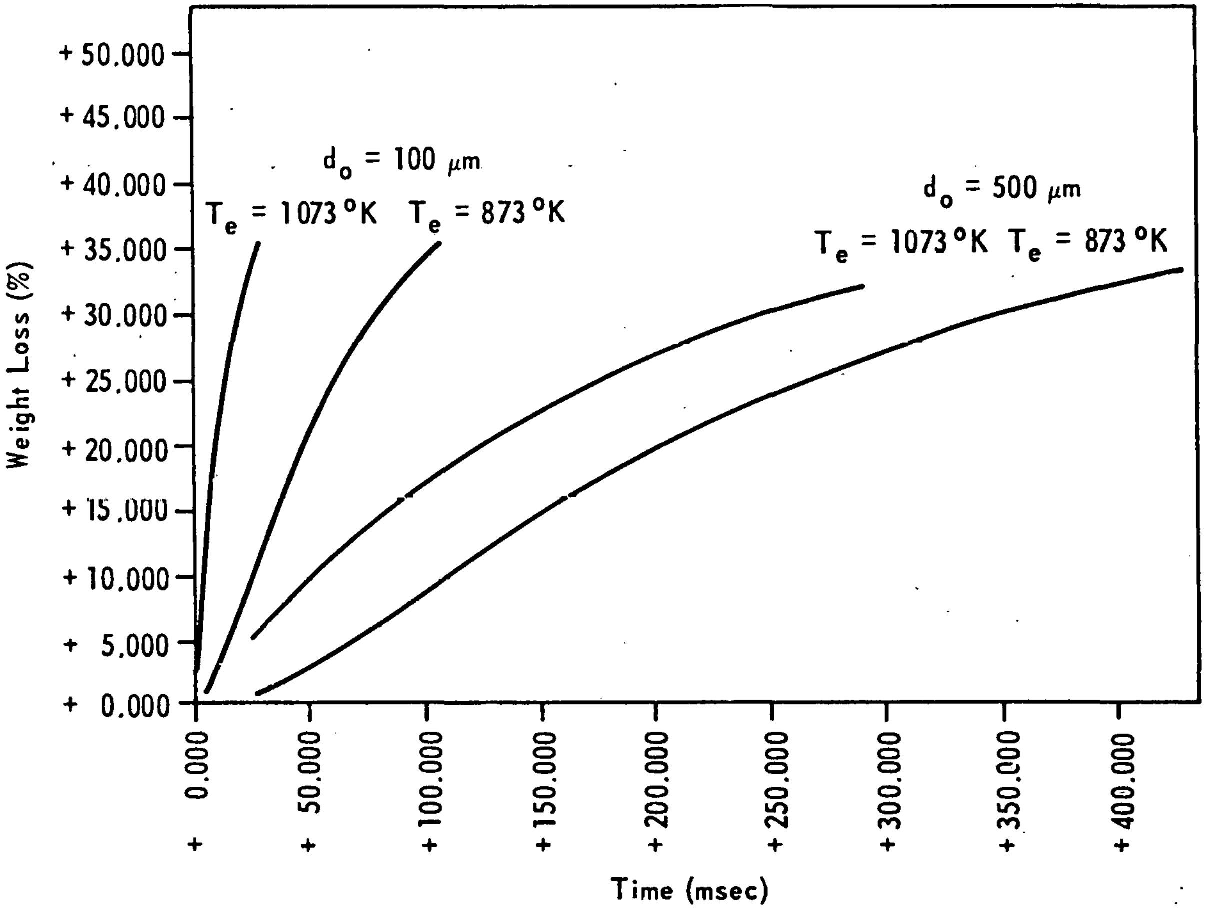


Figure 16. PERCENT WEIGHT LOSS CURVES ILLUSTRATING CASE 9b FOR PARAMETERS GIVEN

EVALUATION OF THE GASIFICATION POTENTIAL OF COALS (TASK 25)

Studies with a Pressurized Laminar-Flow Isothermal Reactor

Since delivery of the pressurized isothermal reactor from Autoclave Engineers, Inc., assembly at the Fuels and Combustion Laboratory has continued. Presently, installation of the unit is near completion; major connections involving both electrical and pressure systems have been made. Autoclave Engineers, Inc., after tests with the coal-feeder system, have suggested that modification be made to ensure efficient operations with the smallest particle size range.

Construction of the High Pressure Gas Facility has been started and has progressed well. The pressurized isothermal reactor will be housed in this facility to ensure safe operations with hydrogen. When the isothermal reactor has been completely assembled tests will be made to check its operational characteristics.

FACET IV-B: COKES AND CHARS

EFFECT OF VARIABLES ON CHAR STRUCTURE (TASK 27)

Preoxidation of Caking Coals to Deminish Their Softening and Swelling

A standard TMA operating procedure has been adopted. Over 260 TMA experiments have been conducted in an effort to optimize TMA conditions for the study of plastic properties of coals. Heating rate, load, and particle size studies have been completed for 35 x 60 mesh, 100 x 150 mesh, 200 x 250 mesh and -200 mesh coal samples (PSOC-337 hvAb coal). These data are compiled in Table 10. All data reported in this table are expressed as 95% confidence values obtained from 5 or 6 runs at each set of conditions. The 100 x 150 mesh and -200 mesh studies are the completion of work reported last quarter. The conclusions drawn here are much the same as those presented in the last report (DOE Progress Report, FE-2030-12). Plastic parameters are highly dependent on TMA variables. Contraction and dilation values show a strong dependence on heating rate, load and particle size. All transition temperatures investigated exhibit a strong heating rate dependence. The initial softening temperature (T_s) was also found to vary with particle size and load on the sample. Dilation temperatures and resolidification temperatures exhibit a slight particle size dependence but little or no relation to sample load.

From these results standard TMA operating conditions have been chosen. Plastic parameters will be studied at rapid heating conditions (50°C/min) under a 1 g sample load. To eliminate the possibility of maceral segregation the twenty unoxidized coals to be investigated will be ground to -200 mesh and analyzed under the above conditions. Eight of the twenty coals have been selected. The remaining twelve coals will be selected shortly. It is estimated that 120 TMA runs will be needed to complete this study. All of these samples should be run by the end of the next quarter.

Oxidation studies will require a different procedure. Kinetic studies of oxygen sorption show that oxygen chemisorption is affected by intraparticle diffusion (ERDA Progress Report FE-2030- 9). This eliminates the possibility of using a minus sieve fraction. For example, in a minus 200 mesh sample, the minus 325 mesh fraction will oxidize more rapidly than the plus 325 mesh fraction. For this reason, oxidation studies will be conducted on a narrow size range. The procedure for preoxidized coals will be rapid heating (50°C/min) of 200 x 250 mesh coal under a slight load (1 g). This procedure may lead to maceral segregation; therefore, a separate maceral analysis will be conducted on each of the raw sieve fractions.

The TMA unit will be used to examine the effect of O_2 sorption on three caking coals of varying vitrinite reflectance. These coals were selected on the basis of high swelling and high vitrinite content. During the next quarter these coals will be quantitatively oxidized to several different levels; and then their swelling, upon heating, will be measured with the TMA unit. It is estimated that a total of 200 runs will be required to complete this portion of the study.

Table 10

TMA Softening and Swelling Data for PSOC-337 (hvAb) Coal

size raction	Heating Rate °C/min	% Volume Expansion Under Load			Transition Temperatures Under 5 g Load			Transition Temperatures Under 1 g Load			Transition Temperatures Under No Load		
		5 g	1 g	None	T_s	T_d	T_r	T_s	T_d	T_r	T_s	T_d	T_r
200 x 250 Mesh	50	690±40	710±20	700±20	354±10	462±6	555±9	364±4	468±3	560±4	376±6	467±10	558±5
	20	280±20	380±50	420±70	337±6	453±3	551±1	346±5	454±1	551±5	368±3	457±1	548±3
	3	73±3	110±10	128±14	301±11	435±1	No Resolidification observed	320±7	435±1	No Resolidification observed	340±30	437±1	No Resoli dificatio observed
35 x 60 Mesh 40	50	105±16	396±32	382±52	339±6	433±3	556±7	346±7	432±6	557±3	349±10	425±4	555±4
	20	79±15	130±22	160±17	323±6	451±4	521±8	325±8	453±6	524±5	341±8	467±4	527±6
	3	32±4	72±8	62±9	312±6	434±3	No Resolidification observed	307±4	428±2	475±2	320±13	432±3	478±4
100 x 150 Mesh	50	335±50	504±27	500±40	356±5	468±1	554±4	357±3	471±1	555±4	362±6	477±8	561±3
	20	152±12	221±13	276±16	325±6	454±2	524±3	318±18	456±1	525±5	338±8	459±2	526±3
	3	57±9	99±5	91±9	310±4	437±5	479±6	301±13	434±1	478±5	300±6	436±2	--
-200 Mesh	50	335±77	412±70	420±33	371±7	476±1	556 4	382 4	478±3	559±2	--	479±3	560±2
	20	144±12	205±10	226±28	361±7	460±1	527 3	362 6	461±2	526±4	388±5	465±1	524±5
	3	66±7	88±11	86±13	321±8	438±2	435 8	348 13	438±1	--	378±9	441±2	--

Chacterization of Heat Treated Coals by Small Angle X-ray Scattering (SAXS)

The major objective of this study is to characterize the pore structures of cokes and chars by use of SAXS. In previous reports we have detailed the advantages of SAXS over methods which involve fluid penetration for these materials. It will be recalled that SAXS is not limited by access to the pore structure because x-ray scattering at small angles arises from the presence of heterogeneities (i.e. pores) in solid matrices. Thus, SAXS profiles are characteristic of the entire pore structure.

We have shown previously that this technique can be used to characterize the pore structures of cokes and chars in terms of characteristic average size parameters. Currently we are developing the method to describe pore structure of these materials in terms of size distribution. It is suggested that the determination of pore size distributions will lead to significant advances in char characterization.

The determination of size distributions from SAXS data requires the use of rather sophisticated computational techniques. The basis for our present work is a computer program obtained from Vonk.[5,6] This program has been adapted to determine structural parameters, size distribution functions, the correlation function and chord-size distribution functions for porous materials. Developments are being incorporated to account for fluctuations in electron density in the carbonaceous matrix.

To test the applicability of this program, SAXS data generated from a well characterized glassy carbon (Tokai GC-30) have been examined. Initial data have shown much promise. Fresh samples of heat-treated demineralized coals are being prepared and it is anticipated that they will be subjected to SAXS analysis during the next quarter. Applicability of the Vonk SAXS program will be completed during the next quarter.

RELATION OF CHAR STRUCTURE TO CHAR REACTIVITIES (TASK 28)

Effect of Preoxidation of Caking Coals on Coal and Char Properties

In the preoxidation studies carried out so far under this task, we have used 200 x 250 mesh fraction of PSOC-337 and 127 coals. In the present study we have used 40 x 70 mesh fraction of the two coals. Experimental procedures followed for measuring weight change during preoxidation, pyrolysis and reactivity runs were the same as those reported in the previous progress reports.

Results given in Table 11 show that for both the coal studied, the time required for attaining the same level of oxidation, that is weight increase, during the preoxidation treatment at a given temperature increases significantly with increase in the particle size. It is noteworthy that in the case of PSOC-337 coal it was possible to attain a 7 wt percent increase during the preoxidation of the 200 x 250 mesh fraction at 220°C. However, it was not possible to exceed 3.5 wt percent increase for the 40 x 70 mesh fraction for oxidation temperatures up to 250°C; at higher temperatures the sample started losing weight due to gasification.

Devolatilization curves for PSOC-337 and 127 coals following various oxidative treatments are plotted in Figures 17 and 18, respectively. Considering the results for PSOC-337 coal samples, it is seen that above 450°C weight loss during pyrolysis decreases with increase in the level of preoxidation of the sample. This behavior is not observed with PSOC-127 coal. In this case for samples oxidized up to 2 wt percent increase, weight loss during pyrolysis is less than that for the raw coal. However, further increase in the level of preoxidation results in an increase in weight loss during pyrolysis. For instance, a weight increase of 4.6 percent during preoxidation increases the cumulative weight loss at 1000°C from 15 to 22 percent. These results thus suggest that the preoxidation brings about significant changes in the coal structure. It was also found that at a given temperature an increase in particle size of both the raw coals from 200 x 250 to 40 x 70 mesh resulted in a decrease in weight loss during pyrolysis. The extent of the decrease in each case was found to increase with increase in the pyrolysis temperature.

Burn-off versus time plots for various chars reacted in 1 atm air at 470°C were obtained in the manner described in the earlier DOE reports. As in the previous reports, we have used $\tau_{0.5}$ (the time corresponding to a fractional burn-off of 0.5) as the reactivity parameter during char gasification. $\tau_{0.5}$ values for various char samples produced from PSOC-337 and 127 coals are given in Table 12. For the sake of comparison, results for the 200 x 250 mesh fraction are also included in Table 12. Results for the chars produced from the unoxidized coals show that an increase in particle size from 200 x 250 mesh to 40 x 70 mesh decreases the reactivity of PSOC-337 and 127 chars by factors of about 8 and 2, respectively. These results thus suggest that the gasification rates of less reactive char can be significantly enhanced by using smaller particle size in the reactor. For both the particle size fractions studied, an increase in the extent of preoxidation increases the subsequent char reactivity, that is $\tau_{0.5}$ decreases. However, for the same level of preoxidation, the char produced from the larger size fraction is less reactive

Table 11

Effect of Particle Size on Rate of Preoxidation of Caking Coals

Preoxidation Temp, °C	Wt. Increase During Preoxidation, %		Oxidation Time, min	
	200 x 250 mesh	40 x 70 mesh	200 x 250 mesh	40 x 70 mesh
PSOC - 337				
135	0.75	0.81	47	745
180	1.4	1.4	43	232
PSOC - 127				
180	0.66	0.66	120	202
220	1.9	2.0	90	384
250	3.0	3.0	37	394
250	4.5	4.6	65	945

Table 12

Effect of Preoxidation on Subsequent Char Reactivity

PSOC-337				PSOC-127			
Wt. increase during Preoxidation, %		Reactivity, $\tau_{0.5}$ min		Wt. increase during Preoxidation %		Reactivity, $\tau_{0.5}$ min	
200 x 250 mesh	40 x 70 mesh	200 x 250 mesh	40 x 70 mesh	200 x 250 mesh	40 x 70 mesh	200 x 250 mesh	40 x 70 mesh
0	0	95	610	0	0	2040	3720
0.75	0.31	47	250	0.66	0.66	129	2100
1.4	1.4	40	232	1.4	1.4	65	366
2.4	2.2	35.5	195	1.9	2.0	57	306
-	3.0	-	150	3.0	3.0	53	246
3.8	3.5	32	140	4.5	4.6	52	156

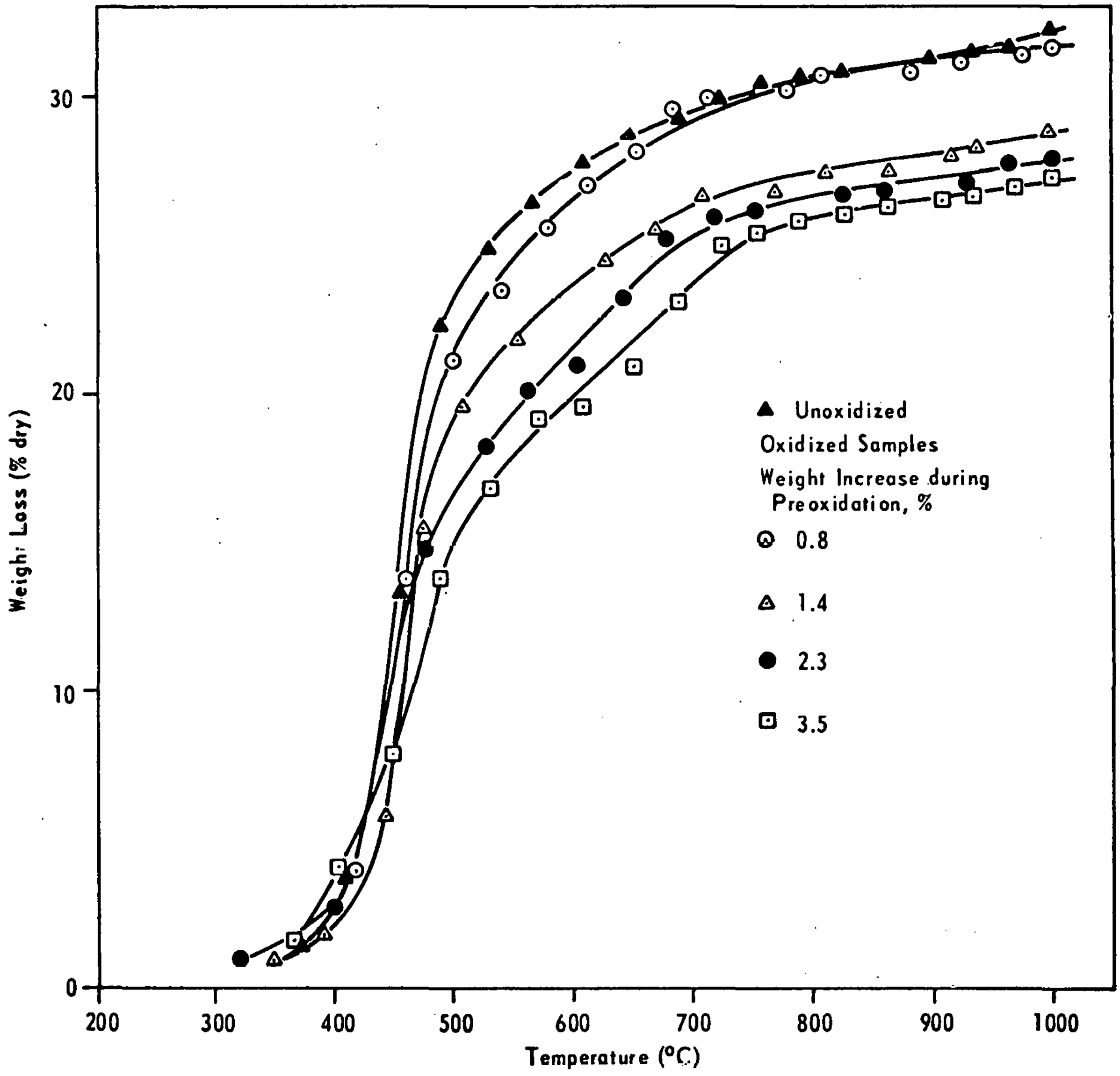


Figure 17. TGA PYROLYSIS CURVES FOR PSOC-337 COAL SAMPLES

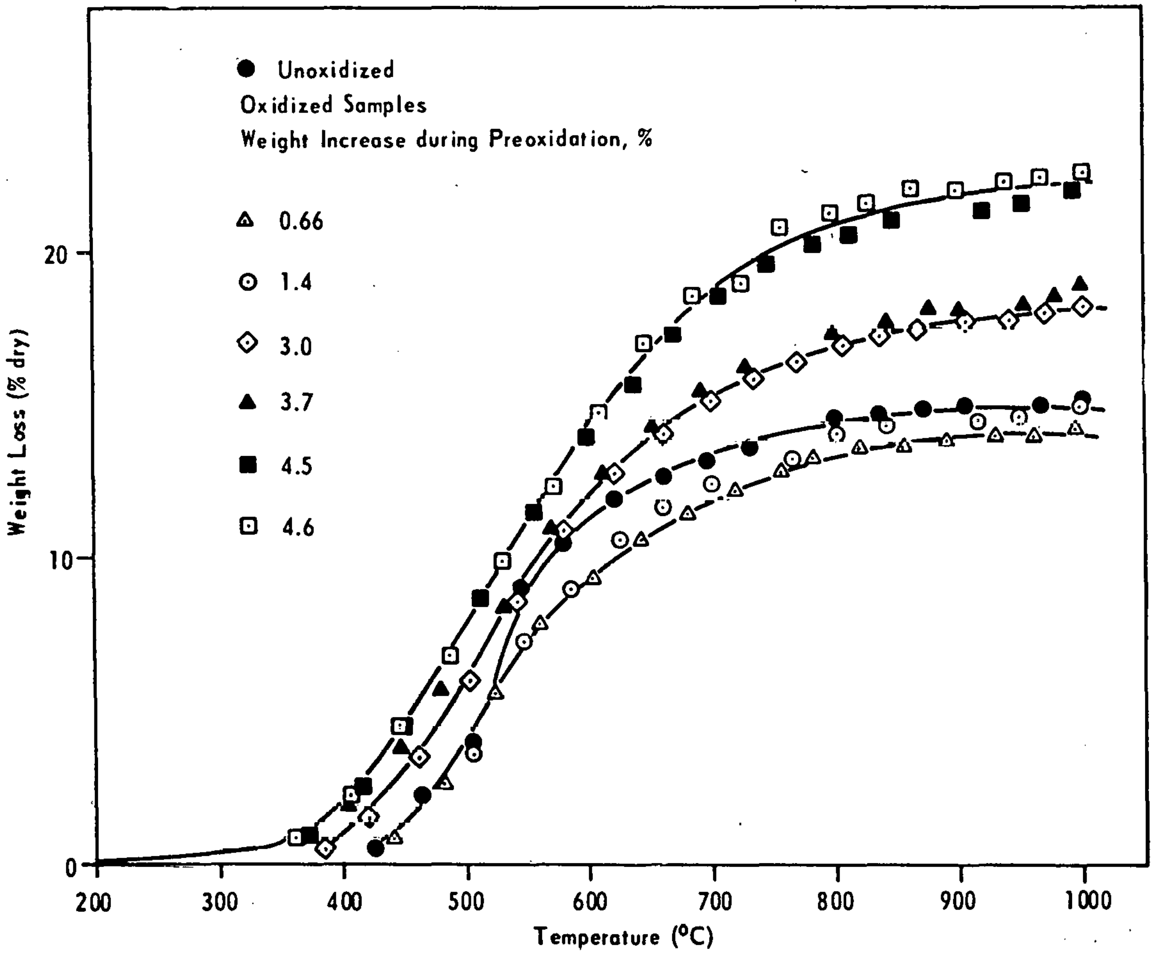


Figure 18. TGA PYROLYSIS CURVES FOR PSOC-127 COAL SAMPLES

during gasification. It is noteworthy that while for the chars produced from the 200 x 250 mesh fractions of the two coals studied $\tau_{0.5}$ values attain more or less constant values after 1.5-2.0 wt percent increase during preoxidation, $\tau_{0.5}$ values for chars produced 40 x 70 mesh coals decrease monotonically with further increase in the extent of preoxidation. The marked effect of particle size on reactivity is also shown by the fact that for the char produced from 40 x 70 mesh fractions of PSOC-337 coal oxidized to 3.5 wt percent increase $\tau_{0.5}$ is still higher than that of the char produced from the 200 x 250 mesh fraction of the unoxidized coal.

In the next quarter, effect of preoxidation of caking coals on physical properties of chars produced will be studied. These properties will be: surface area, true and apparent densities (as measured by helium and mercury displacement, respectively), total open pore volume and pore size distribution.

CATALYTIC EFFECT OF MINERALS IN GASIFICATION (TASK 29)

The inorganic constituents of lignites can be divided into 2 fractions; discrete mineral phases and inorganic species associated with the organic phase. Analysis of major discrete mineral phases is the main topic of this report. This analysis employs three techniques; infrared spectroscopy (I-R), x-ray diffraction, and atomic absorption (AA).

The first step of the major mineral analysis is their separation from the carbonaceous material of the coals. This is accomplished by use of a low temperature asher (LTA), which oxidizes the coal at a relatively low temperature ($\sim$ 170°C). Under suitable conditions very little changes occur to the discrete mineral phase. However, ashing of low rank coals can present unique problems. The carboxylic acid structures, which are only found in low rank coals, are associated with cations. During ashing the cations can form sulfates and carbonates. Hence, it can be difficult to distinguish between minerals formed during ashing and those present in the coal. This can be avoided, to some extent, by exchanging the cations prior to ashing by acid washing the coal. However, this treatment does remove acid soluble minerals.

X-ray analysis is used as both a qualitative and a quantitative tool. Qualitative analysis on PSOC-623 (Darco, Texas Lignite) revealed the presence of calcite, pyrite, quartz, kaolinite, and illite.

Quantitative analysis of an LTA residue is more difficult because of orientation effects and overlapping peaks; poorly crystaline minerals also add complexity. But, quantitative analysis of calcite, pyrite, and quartz can be determined with acceptable accuracy. The internal standard method is used which entails adding an internal standard, (CaF_2) to the sample, and comparing the peak areas of minerals to that of the standard. Calibration curves are obtained by using mixtures of known proportions. Analysis is carried out by comparing calibration data to the unknown. Calibration data has been collected for the following minerals; quartz, calcite, pyrite, and CaF_2.

Infrared spectroscopy has been used for the analysis of kaolinite and anhydrite. Quantitative analysis is carried out by the baseline method. The 910^{3}cm^{-1} and 3645 cm^{-1} bands are used for kaolinite, while the 670 cm^{-1} band is used for anhydrite. Calibration curves for these minerals have been completed. Calcium sulfate can occur either as gypsum ($CaSO_4.2H_2O$), hemihydrite ($CaSO_4.H_2O$) or anhydrite ($CaSO_4$). All forms are analyzed as anhydrite which is accomplished by heating the LTA sample to 400°C in flowing nitrogen.

The quantitative analysis of clays other than kaolinite by the previous methods is severely limited. To estimate these, a normative or rational method is employed. This entails the use of atomic absorption to analyze for silicon and aluminum. The silicon and aluminum in kaolinite and quartz are subtracted from the total, and the remainder is assigned to "other clays". Atomic absorption calibration curves are created by using series of standards of known silicon and aluminum compositions.

Quantitative mineralogical analysis of PSOC-623 should be completed during this quarter. Work will then focus on ion-exchange studies to determine the total amount of carboxylic acid groups in the selected lignites and the cations which are associated with them (Task 30).

EFFECT OF CATION EXCHANGE AND METAL ADDITION (TASK 30)

Effect of Cation Addition on Char Gasification

It was discussed in previous DOE reports that chars produced from lignites are appreciably more reactive during gasification in air, CO_2 and steam than those produced from higher rank coals. We reported that in these three oxidizing atmospheres, reactivity of a Texas lignite char increased as a linear function of the amount of calcium contained in the char. Normalized reactivities of various calcium containing chars in air, CO_2 and steam were found to be essentially the same. Since the submission of the last progress report, we have measured the reactivities in H_2 of the calcium containing chars which were previously used in the air, CO_2 and steam reactivity work. These char samples were produced at 800°C from a Texas lignite to which different amounts of exchangeable calcium ions were introduced in the manner described previously.[7]

A DuPont 951 TGA balance in conjunction with a 990 Thermal Analyzer were used to monitor weight changes during reaction. About 3 mg char contained in a paltinum bucket were used for reactivity measurements. The TGA system was flushed with N_2 (100 cc/min) for 20 min to displace air. The sample was then heated to 800°C until the sample weight became essentially constant. Following this, the sample was cooled in N_2 down to 790°C. This temperature was kept constant for 30 min after which N_2 was replaced by H_2 at the same flow rate. Decrease in sample weight due to gasification was then continuously recorded. The reactivity parameter, R, was calculated from the following equation:

$$R = \frac{1}{W_0} \cdot \frac{dw}{dt}$$

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

Burn-off versus time plots for chars produced from raw, demineralized and calcium exchanged samples are shown in Figure 19. The demineralized char is significantly less reactive than the raw char. This is presumably due to the loss of catalytic inorganic matter upon acid treatment. We have previously reported in the DOE reports that in oxidizing atmospheres reactivity of chars produced from calcium exchanged samples increased linearly with increase in the calcium content of the char. This is in sharp contrast to the behavior observed in H_2. In H_2, char reactivity decreases continuously with increase in the calcium content of the char.

Gasification rates of pure carbons are dependent upon active surface area (ASA), that is, the concentration of carbon atoms located at the edges of layer planes. It is expected that in microcrystalline carbons such as chars, the greater is the total surface area, the greater will be the ASA. In the present study, increasing calcium exchange on the lignite from 0.10 to 2.14 m mole/g resulted in a monotonic increase in total surface area (as measured by CO_2 adsorption at 25°C) of the 800°C char produced from 720 to 850 m^2/g. Ion exchange had little or no effect on char pore volume. Therefore, it may be concluded that the presence of exchangeable

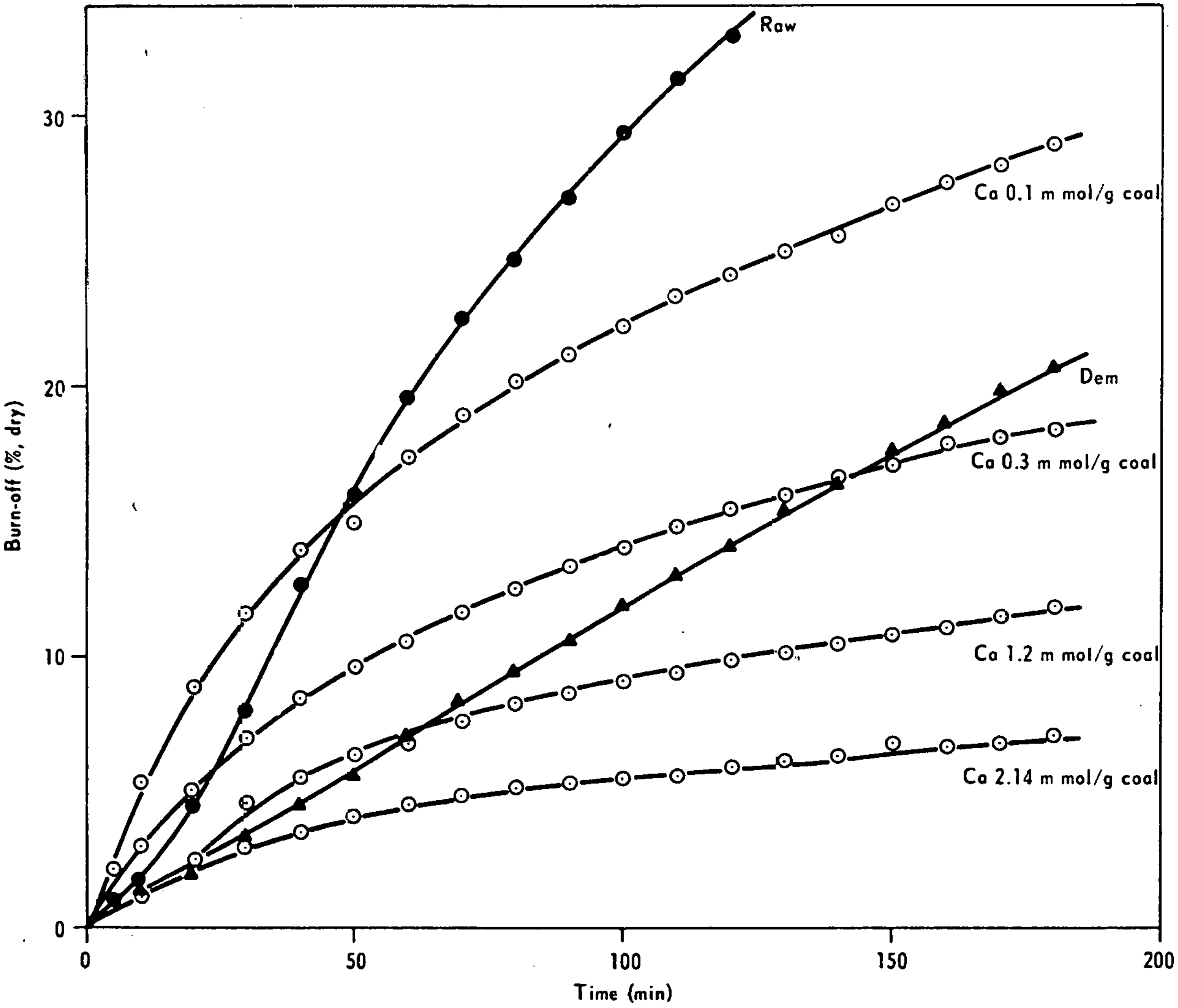


Figure 19. REACTIVITY OF RAW, DEMINERALIZED AND CALCIUM EXCHANGED CHARS IN 1 ATM H_2 AT 790°C

calcium in the lignite coal has an inhibiting effect on the subsequent reactivity of the char in H_2.

We have previously studied the possible catalytic effect of major minerals found in coals on the reactivity of a relatively pure char in H_2.[8] It was found that the presence of 5 wt percent calcite in the char-calcite mixture decreased the gasification rate in H_2 (300 psi) at 940°C by a factor of four. The results of the present study support the conclusion that calcium is an inhibitor for the char hydrogasification reaction.

In the next quarter, reactivities of chars produced from the Texas lignite (PSOC-140) containing the same amount of different exchangeable cations (Na, K, Ca, Mg and Fe) will be studied in air. Reactivities of these chars in steam have been reported previously.

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

Chemisorption of Oxygen and Gasification of Carbonaceous Solids

Seventeen coal chars (particle size 40 x 100) were used in the present study. These chars had been prepared by carbonizing the parent coals in N_2 at 10°C/min up to 1000°C and then holding at this temperature for 2 hr. The chars prepared from strongly caking coals (PSOC-171, 4, and 137) were reground to a 40 x 100 mesh fraction. Table 13 presents analysis of the coals and their chars.

For some selected coals (PSOC-91, 87, 138, 101, and 81), mineral matter was also removed prior to the carbonization process. Removal was achieved either by acid washing (10 volume percent HCl) or by demineralization (1:1 HCl-HF mixture). Chars prepared using these approaches are referred to as acid washed (AW) or demineralized (DEM) chars.

A known weight of the char under consideration was charged inside the DSC cell or the TGA reactor. The sample was outgassed, flushed with UHP-N_2 at 45CC/min, heated at 20°C/min up to 600°C, held at this temperature for 30 min, and finally cooled to room temperature. Following this pretreatment, the char was held isothermally (in N_2) at 100°C for 45-90 min to permit the attainment of thermal stability of the instruments (invariably smooth horizontal output line). Oxygen was then introduced to replace N_2 at the same flow rate. The thermograms were then started. Values of Q (cal/g char), measured by the DSC technique, or W (mg/g char) measured by the TGA unit, were computed by a 30 min reaction time. At a 15 min time interval, the cumulative amount of heat released, Q_{15} (cal/g char), was used for the sake of comparison.

Variation of Q_{15} with the carbon content of the parent coals is shown in Figure 20. As the carbon content increases from lignites to anthracites, Q_{15} tends generally to decrease. However, for the chars carbonized from high volatile bituminous coals (PSOC-26, 22, 24, 67, and 171), some deviations are seen. It is also remembered, as Table 13 indicates, that most of these five coals have significant sulphur contents. The role of the sulphur on the nature of carbonization or towards affecting the values of Q_{15} is not yet understood.

Further consideration was given to the variation of ΔH with the carbon content of parent coals. TGA runs were made to determine the weight increase due to oxygen uptake. As described elsewhere,[9] values of ΔH (kcal/mole) were calculated by

$$\Delta H = 32\ Q/W \qquad (1)$$

For a few char samples, the TGA apparatus was not sufficiently sensitive to measure accurately oxygen chemisorption. Accordingly, such data, being small in magnitude, were omitted. However, with other chars, values of W (mg/g char) were used to calculate ΔH. These are listed in Table 14. For each char studied, ΔH was independent of reaction time, thus indicating that neither physical adsorption nor gasification was taking place[9]. As seen in Table 14, as the carbon content of the parent

Table 13

Analysis of Coals and Chars

	COALS								Chars
				Ultimate Analysis (wt %, daf)					
PSOC Sample No.	ASTM Rank	State	Ash, % (dry)	C	H	N	S*	O (By Difference)	Ash, %
89	Lignite	N.D.	11.6	63.3	4.7	0.48	0.98	18.9	
91	Lignite	Mon.	7.7	70.7	4.9	0.80	0.30	22.3	11
87	Lignite	N.D.	8.2	71.2	5.3	0.56	0.46	22.5	13
140	Lignite	Tex.	9.4	71.7	5.2	1.30	0.72	21.1	12
138	Lignite	Tex.	10.3	74.3	5.0	0.37	0.51	19.8	16
98	Sbb. A.	Wyo.	8.4	74.3	5.8	1.20	1.1	17.7	12
101	Sbb. C	Wyo.	6.1	74.8	5.1	0.89	0.30	18.9	8
26	HVB	Ill.	10.8	77.3	5.6	1.10	2.3	13.6	20
22	HVC	Ill.	10.1	78.8	5.8	1.60	1.8	12.1	23
24	HVB	Ill.	11.8	80.1	5.5	1.10	2.3	11.1	14
67	HVB	Ut.	4.8	80.4	6.1	1.30	0.38	11.9	5
171	HVA	W. Va.	7.6	82.3	5.7	1.40	1.8	8.9	11
4	HVA	Ky.	2.1	83.8	5.8	1.60	0.66	8.2	2
137	MV	Ala.	7.1	87.0	4.8	1.50	0.81	5.9	19
114	LV	Pa.	9.8	88.2	4.8	1.20	0.62	5.2	12
81	Anthracite	Pa.	7.8	91.9	2.6	0.78	0.54	4.2	6
177	Anthracite	Pa.	4.3	93.5	2.7	0.24	0.64	2.9	5

*Organic Sulfur.

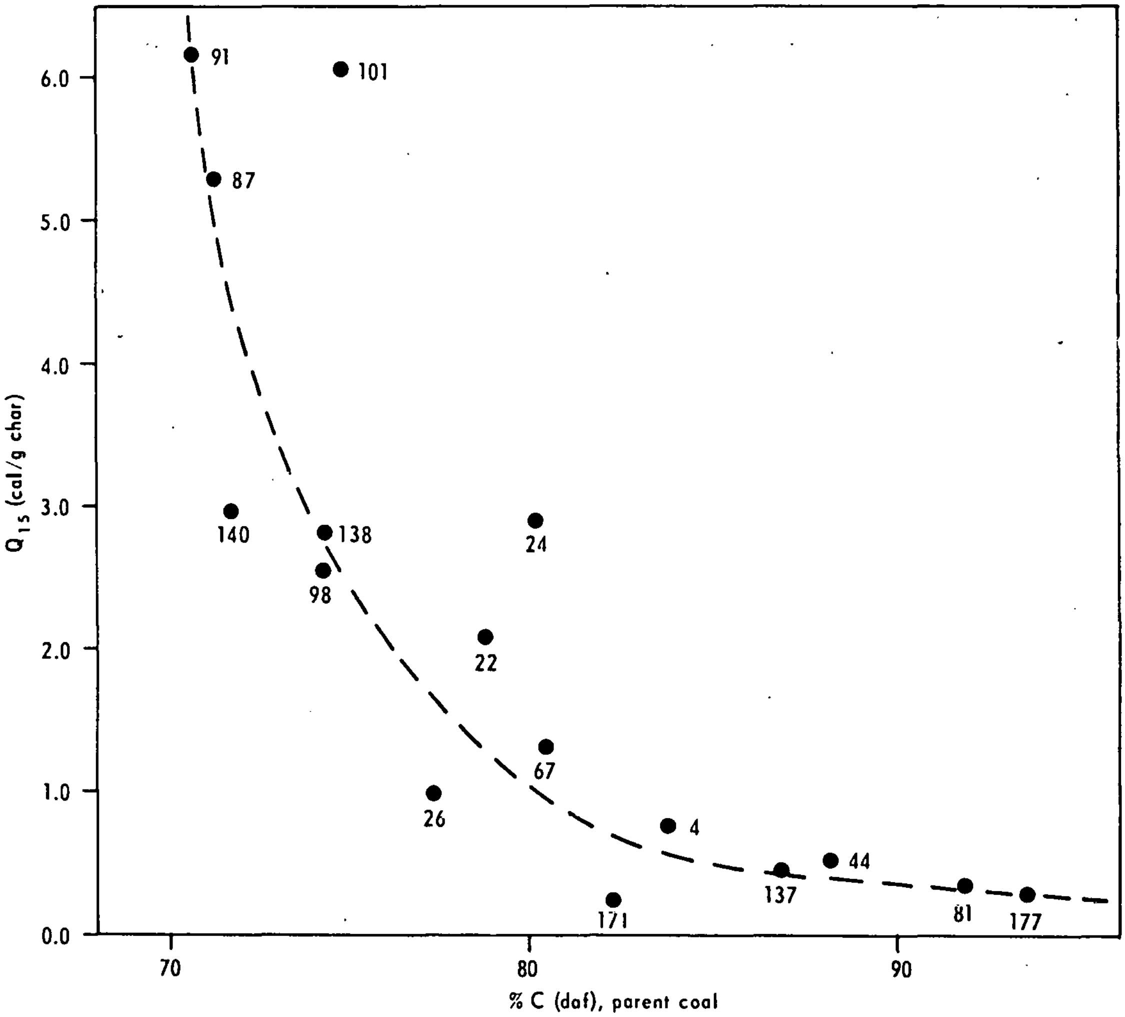


Figure 20. VARIATION OF HEAT RELEASED WITH CARBON CONTENT OF THE PARENT COAL

TABLE 14

Values of ΔH (kcal/mole) for Different Coal Chars

PSOC Sample Number	Carbon Content (%, daf)	ΔH (kcal/mole)
89	63.3	82.4
91	70.7	78-79
87	71.2	78
140	71.7	72.8
98	74.3	69-70
101	74.8	69.4
24	80.1	54.5
67	80.4	56.1

increases, ΔH decreases. This relation seems to be linear. Furthermore, values of ΔH are very much comparable to those computed for three Saran chars, 42-75 kcal/mole.

The dependence of Q_{15} on nitrogen surface areas is shown in Figure 21. As surface area increases, Q_{15} increases, passes through a maximum corresponding to a subbituminous-C char (PSOC 101), and finally decreases for lignite chars. Thus, chars having N_2 surface areas less than 25 m^2/g or greater than 125 m^2/g are shown to release comparable values of Q_{15} $\leq$ 3.0 cal/g char. This is interesting compared to Saran chars subjected to O_2 under the same experimental conditions. Although values of Q_{15} ranged between 1.7-2.9 cal/g char, nitrogen surface areas varied between 800-1200 m^2/g.[9] It is worthy to note that Saran chars were first prepared by carbonizing the parent precursor at 900°C for 4 hr. Thus, the nature of as well as the type of pores in the carbon matrix are partially affecting the amount of heat released during oxygen interaction with all these chars.

Now we further correlate Q_{15} to some reactivity data. This is illustrated in Figures 22 and 23 for reactivities in air at 405°C, in Figure 25 for reactivities in steam at 910°C, and in Figure 25 for reactivities in CO_2 at 900°C. Two reactivity parameters were used[10], R_T (for example R_{405}) and $\tau_{0.5}$. While the former is defined as the maximum rate of gasification (g/hr/g char) at temperature T (say at 405°C), $\tau_{0.5}$ is the time (in minutes) required to gasify 50 percent of the starting weight of the char. In Figure 22, it is clear that the chars showing an increase in R_{405} for gasification in air are seen to liberate more heat during oxygen chemisorption at 100°C. The relation is linear up to Q_{15} = 4.0 cal/g char. However, for very reactive chars (PSOC-87, 101, and 91), Q_{15} seems to level off at a value of 6.15 ± 0.1 cal/g char. For PSOC-140, a duplicate DSC run was made. Marked deviation of behavior of this sample cannot be explained at present.

Variation of Q_{15} with $\tau_{0.5}$ for reactivities in air (of Figure 23) is linear, thus satisfying the equation

$$Q_{15} = 6.75 - 0.048\ \tau_{0.5} \qquad (2)$$

Such a linearity would suggest that, apart from the rank of coal used to prepare the char, oxygen chemisorption is the rate determining step in the overall gasification reaction in air. However, for gasification in CO_2 or steam, as shown in Figures 24 and 25, respectively, Q_{15} decreases asymptotically with increasing $\tau_{0.5}$. Thus, for lignites, when Q_{15} is almost halved, $\tau_{0.5}$ is essentially doubled. However, for other chars of higher rank, a slight decrease in Q_{15} is associated with a large change in $\tau_{0.5}$.

The effect of mineral matter removal is illustrated by the data in Table 15. Before further considering these data, we may emphasize that more samples ought to be studied so that a better understanding could be reached. In spite of this remark, three general trends are observed. These are: (i) for the AW lignite chars (PSOC-91, 87, and 138), values of Q_{15} are essentially the same, (ii) for an anthracite char (PSOC-81),

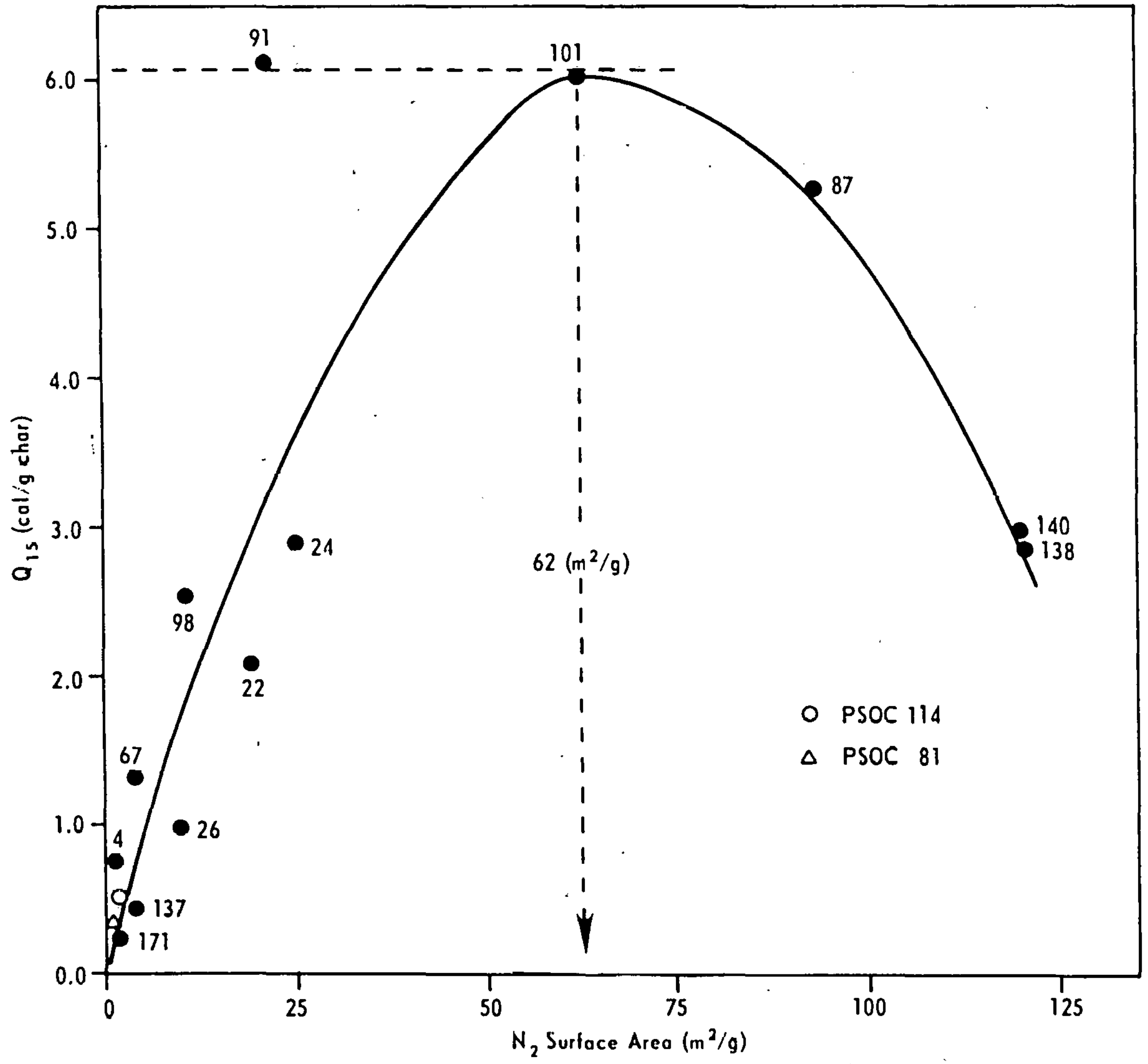


Figure 21. DEPENDENCE OF Q_{15} (CAL/G CHAR) ON NITROGEN SURFACE AREA OF CHARS

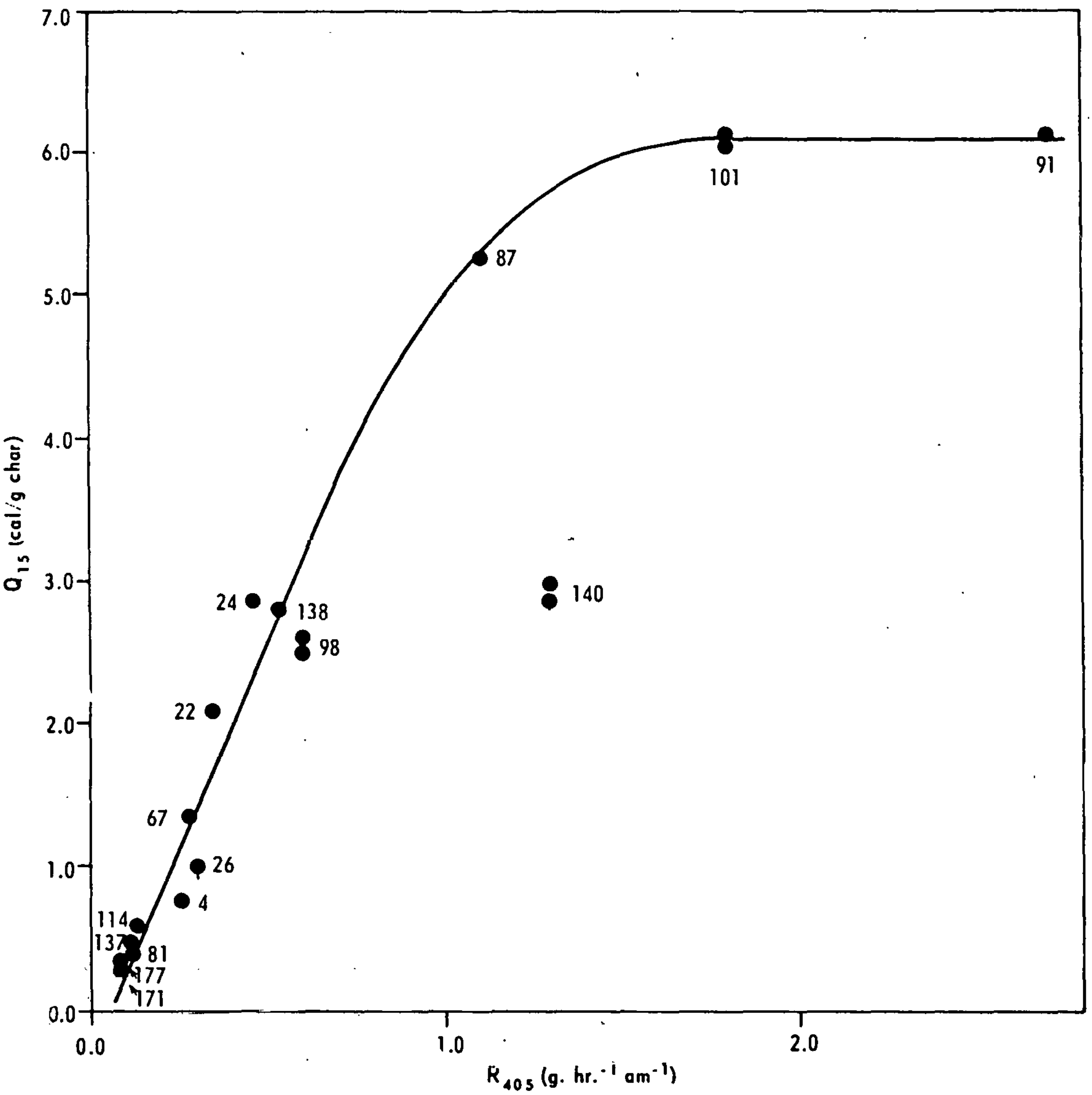


Figure 22. RELATION BETWEEN REACTIVITIES OF CHARS IN AIR AT 405 °C AND THE HEATS RELEASED IN OXYGEN AT 100 °C

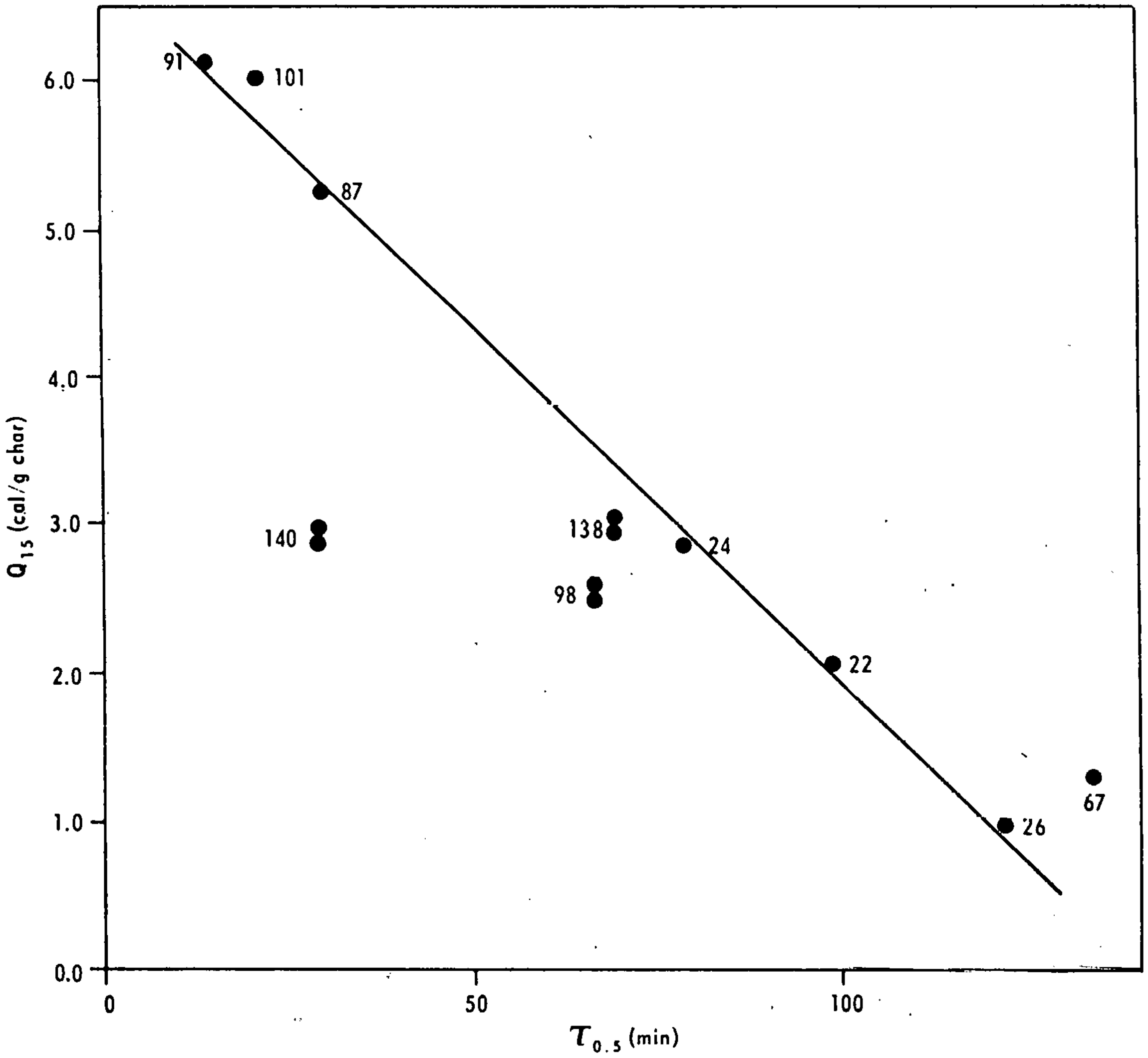


Figure 23. VARIATION OF Q_{15} WITH TIME REQUIRED TO GASIFY 50% OF CHARS IN AIR

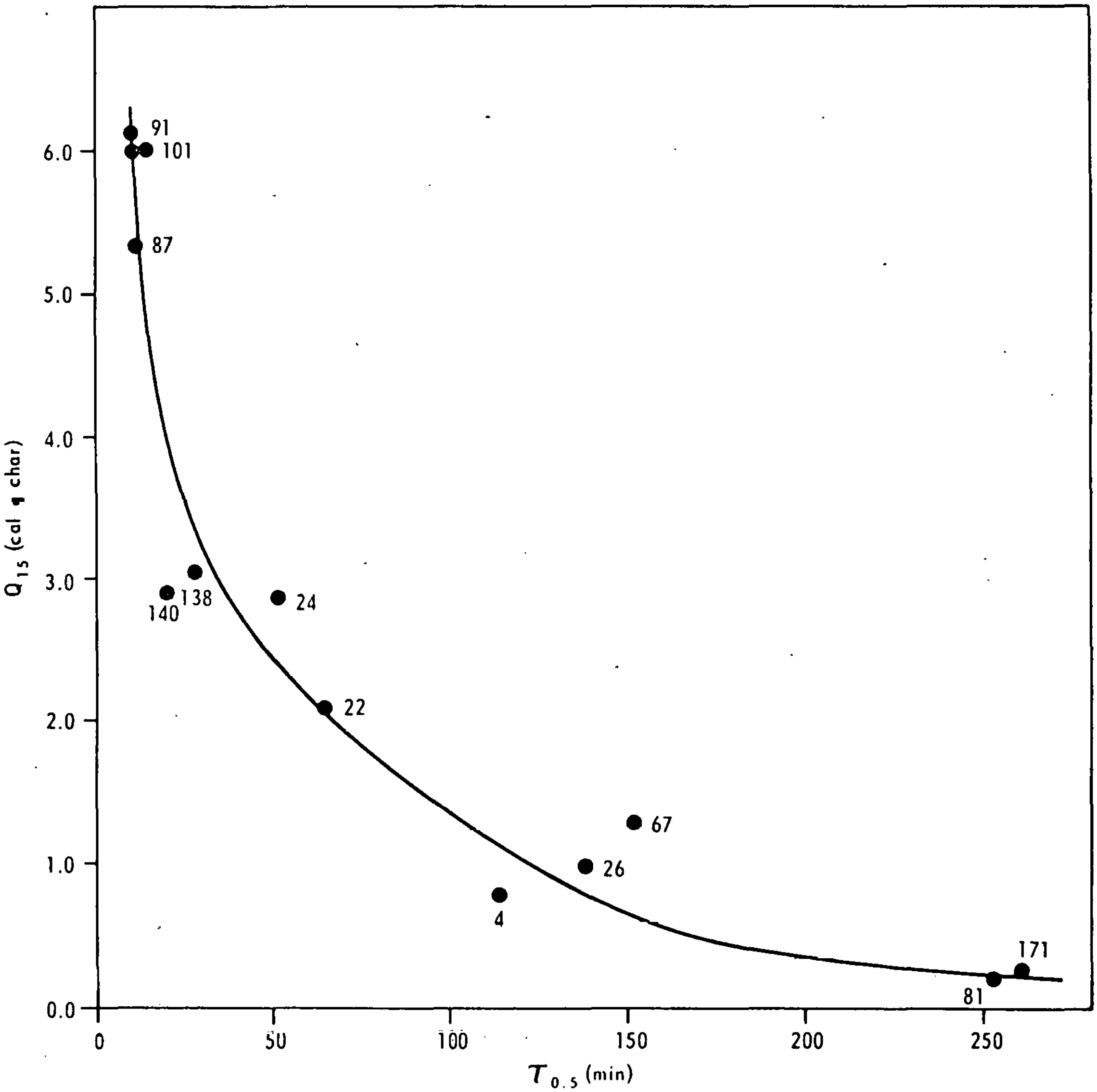


Figure 24. VARIATION OF Q_{15} IN OXYGEN AT 100°C WITH $\tau_{0.5}$ IN STEAM AT 910°C

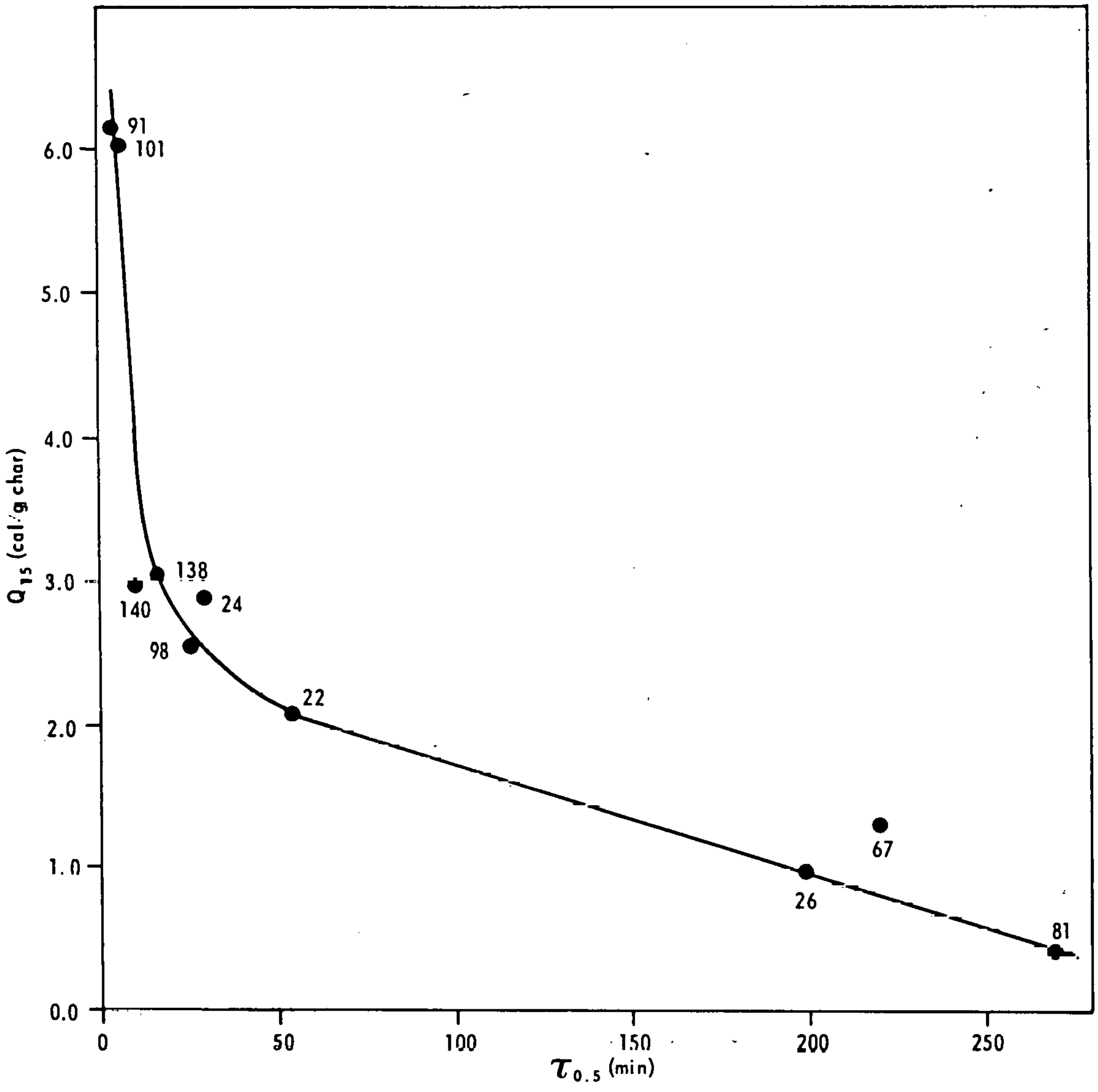


Figure 25. VARIATION OF Q_{15} IN OXYGEN AT 100°C WITH $\tau_{0.5}$ IN CO_2 AT 900°C

Table 15

Surface Areas and Reactivity Parameters for Acid Washed and Demineralized Coal Chars

PSOC Sample Number	Ash, %	Surface Areas (m^2/g) N_2	CO_2	R_{405}^* ($g.hr^{-1}.g^{-1}$)	$Q_{15}^{\#}$ (cal/g)
91	10.9	35	471	2.70	6.13
91 AW	1.3	89	924	0.12	3.07
87	13.1	107	299	1.10	5.28
87 AW	2.6	11	626	0.31	3.17
87 DEM	0.0	1	600	0.23	4.08
138	16.0	143	667	0.53	3.04
138 AW	9.6	4	752	0.31	3.27
138 DEM	0.9	47	116	0.17	0.64
101	8.2	68	501	1.04	6.04
101 AW	1.1	3	667	0.20	2.14
81	6.4	1	42	0.11	0.38
81 AW	5.8	<1	42	0.16	0.38

* in air

\# in oxygen

the Q-t plot is almost the same for the raw or AW char, and (iii) for DEM chars, Q_{15} is lower than that obtained for the raw char. It is interesting to note that (i) although inorganic removal drastically decreases gasification rate (for example values of R_{405}), it only decreases Q_{15} by a factor of 0.2 to 1.0, and (ii) the essentially complete removal of mineral matter from PSOC-87 char does not have a significant effect on the value of Q_{15}.

Application of the Differential Scanning Calorimetry Technique to the Study of Oxidation of Caking Coals

A highly caking coal (PSOC-337), particle size 200 x 250 mesh, was used in the present study. A known weight of the sample, about 15-18 mg, was charged in a DSC cell, flushed with UHP-N_2 (45 cc/min) for 15 min, held isothermally at 200°C for 15 min, and finally brought to the desired reaction temperature. When the thermal stability of the cell was reached (generally achieved when an invariably smooth output horizontal line is detected), air was introduced to replace N_2 at the same flow rate. The amount of heat liberated, Q(cal/g coal), was cumulatively computed as a function of reaction time, t (min). Values of Q were recorded for 30 min. It was noted at temperatures above 125°C that the runs could have been extended for longer periods. Figure 6 illustrates the dependence of Q (on a logarithmic scale) on reaction time and temperature. The effect of temperature on an aribtrary value of Q (say Q_{15}, that is the total heat liberated at 15 min reaction time) is more pronounced in the case of PSOC-337 coal than in the case of Saran chars.[9] Here, at 100 and 200°C, Q_{15} amounts to 1.15 and 72.0 cal/g coal, respectively (compared to 1.4 and 8.5 cal/g char in the case of an unactivated Saran char, particle size 150 x 250). It is important to add that the Saran char had been subjected to a better cleaning pretreatment condition (600°C in N_2 for 30 min) than the PSOC-337 coal. It can be speculated, therefore, that such an increase in Q with reaction temperature may be attributed to (i) an additional gasification reaction that takes place simultaneously with oxygen chemisorption at the coal surface, and/or (ii) the interaction of oxygen with some functional groups located at the coal surface. This will be considered shortly.

Under the same experimental conditions mentioned above, a home-made TGA unit was used to monitor changes in weight occurring when the coal was subjected to oxygen at different isothermal temperatures. At 100°C, the weight increase was slow, ranging between 0.3 and 0.5 mg/g coal for a 30 min exposure time. At 125, 150, and 175°C, the increase in weight was recorded up to 5 hr reaction time (cf. Figure 27). These data are in excellent agreement with those previously reported,[11] where a 951 DuPont Thermogravimetric Analyzer had been used.

Values of ΔH can be calculated. If W(mg oxygen/g coal) is the weight increase due to the amount of oxygen uptake, and Q(cal/g coal) is the heat liberated under the same experimental conditions, then

$$\Delta H = 32Q/W \qquad \text{kcal/mole oxygen}$$

Values of ΔH at three selected temperatures are listed in Table 16. It is generally observed that these values are significantly higher than those found in the case of chars. For example, when three different Saran chars were considered, ΔH for oxygen chemisorption ranged between 42-75 kcal/mole.[9] Besides, when gasification was taking place concurrently with oxygen chemisorption, ΔH was seen to increase with either reaction time or temperature. Further, for oxygen chemisorption on eight different coal chars,

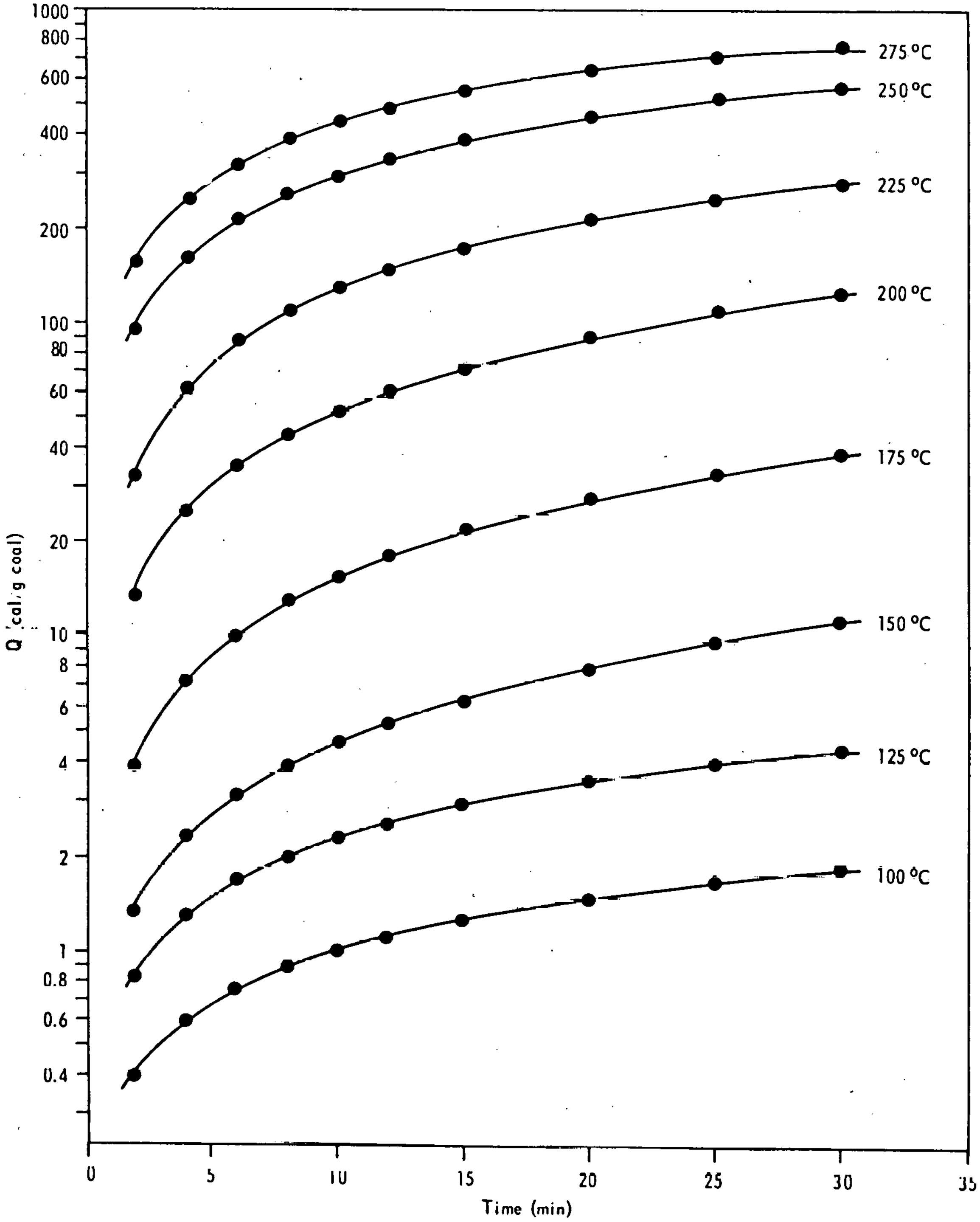


Figure 26. LOG Q - t RELATIONS FOR PSOC-337 COAL (200 x 250) SUBJECTED TO AIR AT DIFFERENT TEMPERATURES

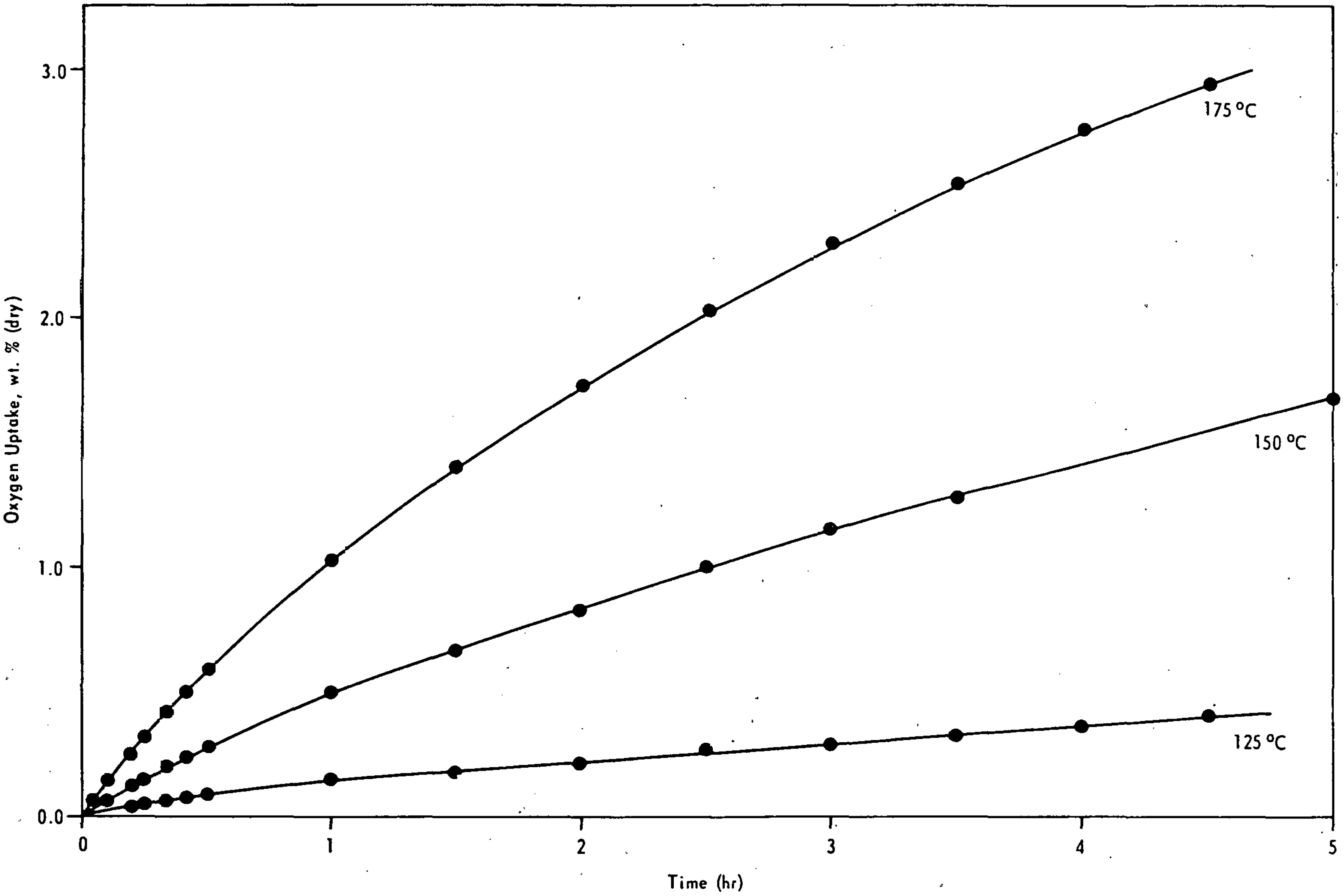


Figure 27. VARIATION OF WEIGHT INCREASE WITH REACTION TIME AND TEMPERATURE - PSOC-337 COAL (200 x 250 MESH)

Table 16

Variation of ΔH (kcal/mole) with Reaction Time and Temperature [PSOC-337 Coal (200 x 250 Mesh)]

Reaction Time (min)	ΔH (kcal/mole) Reaction Temperature (°C)		
	125	150	175
2	187	189	229
4	168	183	220
6	165	161	213
8	171	153	213
10	173	146	222
12	174	141	222
15	181	140	226
20	190	135	219
25	182	133	215
30	165	131	216

ΔH varied between 54 and 82 kcal/mole.[9] Thus, for all chars exposed to O_2 at 100°C, and in absence of gasification, ΔH never exceeds 85 kcal/mole.

With PSOC-337 coal, however, oxygen-interaction appears to be more complex. Accordingly, three major reactions (if not more) are proposed. Firstly, is the interaction between oxygen molecules and "hydrogen" (protruding from the coal surface) to form gaseous water molecules that leave the surface. As a result, nascent sites are left behind and are capable of adsorbing oxygen resulting in higher ΔH values. Further due to the weight loss of hydrogen, the total increase in sample weight is lowered and hence ΔH is elevated. Secondly, is the interaction between oxygen and the carbon matrix in the coal, with a ΔH value in the vicinity of 40-85 kcal/mole. Thirdly, is the desorption of "peroxygen" content to CO (as suggested by Van Krevelen), and/or gasification of the carbon with oxygen to form CO_2. Once more, these reactions are known to lower the total increase in sample weight and, hence, to increase the value of ΔH.

An alternative to these three reactions is the nature of exothermicity when cross linking is considered. Caking coals are converted to thermosetting precursors via the introduction of cross links between coal crystallites. This is accomplished by oxidation of the coal at selected temperatures (100-350°C). Crosslinking is known to decrease the entropy of the system. When an equilibrium stage is reached, the enthalpy of the system is also lowered; and, therefore, the reaction is seen to be exothermic. Consequently, a given value of ΔH, being proportional to the number of cross links formed, would increase with increasing oxidation temperature. The data shown in Figure 26 and Table 16 may support this argument. However, more experimental data are needed.

CONCLUSIONS

FACET I-B: COAL CHARACTERIZATION

Task 5: Coal Characterization

Maximum Gieseler fluidity was the most sensitive indiceof oxidation in the first three weeks of oxidation of a minus 452 um sample of lvAb coal. After this time, the plastic range appeared to be the best indice of oxidation.

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

Task 23: Operation of Isothermal Furnace

Hoskins furnace experiments showed no reduction in volatile matter yield with reduced heating rate. The slight enhancement of the yield is consistent with the hypothesis of reduced secondary char forming reactions.

The enhancement of volatile matter yield in the isothermal furnace for the 70 x 100 mesh, 1000°C case increases with increasing residence time.

FACET IV-B: COKES AND CHARS

Task 27: Effects of Variables on Char Structure

Combined TGA, TMA studies should enable us to quantify the effects of preoxidation on the caking properties of certain coals. Thermochemical studies have shown the DuPont 942 TMA unit to be a valuable quantitative tool for measuring swelling and plastic properties of these coals. Swelling and softening parameters are highly dependent on TMA variables (heating rate, load on sample and particle size). Optimization studies have led to the establishment of a standard TMA operating procedure which will be followed for the remainder of this study.

Initial data from the examination of the porous nature of a glassy carbon have revealed that small angle X-ray scattering can be successfully applied to the characterization of carbonaceous solids.

Task 28: Effect of Char Structure on Reactivities

Effect of particle size on preoxidation in air of two highly caking coals in the temperature range 135-250°C on weight loss during pyrolysis up to 1000°C and reactivity of resultant char to air at 470°C has been studied. An increase in particle size from 200 x 250 to 40 x 70 mesh adversely affects: i) the rate of weight gain during preoxidation, and (ii) weight loss during pyrolysis. Preoxidation increases subsequent char reactivity but for the same level of preoxidation the larger size fraction is less reactive during gasification.

Task 29: Catalytic Effect of Minerals in Gasification

Qualitative mineralogical analysis for PSOC-623, a Darco Texas lignite, has been completed. The major minerals are calcite, pyrite, quartz, kaolinite, and illite.

Task 30: Effect of Catalytic Cations on Gasification

The presence of exchangeable calcium ions in a lignite coal inhibits the subsequent reactivity of the char in H_2. This is in sharp contrast to the behavior in air, CO_2 and steam; in these atmospheres reactivity increases linearly with increase in the calcium content of the char.

FACET IV-F: DIFFERENTIAL SCANNING CALORIMETRY

Task 31: Differential Scanning Calorimetry

For oxygen chemisorption on coal chars at 100°C, the heat released at 15 min reaction, Q_{15}, can be used for the purpose of characterization.

As the carbon content of the parent coal from which the chars were prepared increases, Q_{15} decreases and finally levels off for anthracite chars. A similar general behavior is also true for values of ΔH (kcal/mole), that is ΔH decreases with increasing rank of precursor coal.

As nitrogen surface area of the chars increases, Q_{15} increases, passes through a maximum (at 62 m^2/g), and finally decreases.

Values of Q_{15} are linearly related to $\tau_{0.5}$ in air, that is time required to gasify 50 percent of the char in air at 405°C, thus $Q_{15} = 6.75 - 0.048\ \tau_{0.5}$.

For gasification in steam at 910°C or in CO_2 at 900°C, as $\tau_{0.5}$ increases, Q_{15} decreases and then levels off for anthracites.

When a caking coal (PSOC-337) is exposed to air at an isothermal temperature (in the range 100 to 275°C), the increase in Q(cal/g coal) is highly sensitive to reaction temperature. This is also true for the calculated values of ΔH (kcal/mole oxygen added to the coal). These observations are attributed: (i) the possible interaction between oxygen (in the oxidant) and hydrogen in the coal, (ii) the process of cross linking occurring during oxidation of the coal, and (iii) desorption of CO complex or gasification of the coal to yield CO_2.

REFERENCES

1. Jung, G. Glückauf, v. 71, p. 1141, 1935.

2. Anthony, D.B. and Howard, J.B. Coal Devolatilization and Hydrogasification. AIChE. Journal, v. 22, No. 4, p. 625. 1976.

3. Yellow, P.C. Kinetics of the Thermal Decomposition of Coal. BCURA Monthly Bulletin, v. 29, No. 9, p. 285, 1965.

4. Ubhayakar, S.H. Pyrolysis of Coal. AMP-538, AVCO-Everett Research Lab., Inc. July, 1977.

5. Vonk, C.G. A General Computer Program for the Processing of Small-angle X-ray Scattering Data. J. Appl. Cryst., v. 8, p. 433, 1976.

6. Vonk, C.G. On Two-methods for Determination of Particle Size Distribution Functions by Means of Small-angle X-ray Scattering. J. Appl. Cryst., v. 9, p. 433- 1976.

7. Hippo, E.J., and Walker, P.L., Jr. Effect of Cation Exchange on the Subsequent Reactivity of Lignite Chars to Steam. Technical Report 4 of The Pennsylvania State University to DOE, 137 pp. March 1977.

8. Tomita, A., Mahajan, O.P., and Walker, P.L., Jr. Catalysis of Char Gasification by Minerals. Preprints, Division of Fuel Chemistry, 173rd National Meeting, Amer. Chem. Soc., New Orleans, v. 22, pp. 1-6, 1977.

9. Ismail, I.K. and Walker, P.L., Jr. Thermochemistry and Kinetics of Oxygen Interaction with Microporous Chars. Technical Report FE-2030-TR12 to DOE.

10. Soledade, L.E.B. and Walker, P.L., Jr. Reactivity of Coal Chars in Air, (in press).

11. Spackman, W. The Characteristics of American Coals in Reaction to their Conversion into the Clean Energy Fuels. Technical Report FE-2030-10, October-December, p. 77, 1977.

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