565

5/29/80 r. s.

Sh. 1336

FE-2030-12

MASTER

FOSSIL ENERGY

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

Quarterly Technical Progress Report, April—June 1978

By
W. Spackman
A. Davis
P. L. Walker
H. L. Lovell
R. H. Essenhigh
F. J. Vastola
P. H. Given
N. H. Suhr

January 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

DISCLAIMER

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy $7.00
Microfiche $3.50

FE-2030-12
Distribution Categories UC-90a, UC-90b, UC-90c, UC-90d, and UC-90e

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

Quarterly Technical Progress Report
for the Period
April - June 1978

W. Spackman, Principal Investigator

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

1855

Date Published - January 1979

PREPARED FOR
UNITED STATES DEPARTMENT OF ENERGY

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

ABSTRACT

The Penn State Coal Sample Bank was expanded to include four new samples from southwestern Pennsylvania and four from eastern Kentucky (Facet I-A). A total of 69 coal samples and 487 selected printouts of coal data were provided to the coal research community (Facet I-C). Forty-four pyrite chord size distributions have been determined by automated reflectance microscopy; the information generated is being used to determine the number of data points necessary to obtain good replication of results.

Fractionation of the Hiawatha seam, Utah, has been completed; results indicate that a high yield of a superior coal product could be obtained. Hardgrove indices have been determined on 96 coal seam and lithotype samples (Facet II).

Under Task 23, experiments were performed in Hoskins furnaces to determine the accuracy of the ash-tracer technique as a method for calculating weight loss in the isothermal furnace. This technique was found to consistently underestimate the weight loss by about 5%. The experiments also showed that two-stage evolution of the volatile matter did not alter significantly the yield as compared with the proximate (ASTM) yield. This was true for stage 1 evolution over a temperature range of 250-800°C, and stage 2 evolution at 950°C. Experiments on the isothermal furnace showed that no significant weight loss occurred during the heating-up time, irrespective of the number of recycles (Facet IV-A).

The effects of low temperature oxidation on reducing the agglomerating properties of caking coals are being studied. A DuPont 942 Thermomechanical Analyzer (TMA) has been shown to be a valuable tool for quantifying swelling and softening parameters. In addition, Thermogravimetric studies (TGA) have shown that oxygen uptake can be followed both quantitatively and reproducibly. From combined TGA,-TMA studies we hope to be able to quantify the effects of preoxidation on the caking properties of coals. Experimental techniques are being developed to study the effect of active surface area of a char on its reactivity during gasification. Preliminary mass spectrometric data collection has begun. The effect of preoxidation in air of a highly caking coal in the temperature range 180-250°C on weight loss during pryolysis up to 1000°C and reactivity of resultant chars to air have been investigated. Preoxidation has little or no effect on weight loss during pyrolysis. However, preoxidation markedly enhances char reactivity. Important aspects of the chemical and physical makeup of lignite coals are being characterized by x-ray diffraction of low-temperature ashes to determine the mineral content and composition of the coal. Reactivities of a series of chars produced at 800°C from a lignitic coal containing different amounts of exchangeable calcium ions have been measured in 1 atm CO_2 at 760°C. Char reactivity increases linearly with increase in the calcium content of the char (Facet IV-B).

Differential scanning calorimetry has been used to measure the heat of oxygen chemisorption, Q (cal/g char), at 100°C on few selected coal chars. Reactivity data for these chars in air at 405°C, for example R_{405}, had been available from previous studies, where R_{405} is an arbitrary conventional rate of gasification. Values of Q_{15}, that is the heat liberated at 15 min chemisorption time, were plotted versus the corresponding values of R_{405}.

A possible relation between both parameters is indicated. As R_{405} increases, Q_{15} increases and finally levels off at a constant value of 6.1 cal/g char. This value holds when R_{405} exceeds 1.80 g/hr/g. Removal of mineral matter by acid-washing a parent coal (PSOC-91) prior to charring produced a less reactive char towards either gasification or oxygen chemisorption (Facet IV-F).

TABLE OF CONTENTS

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

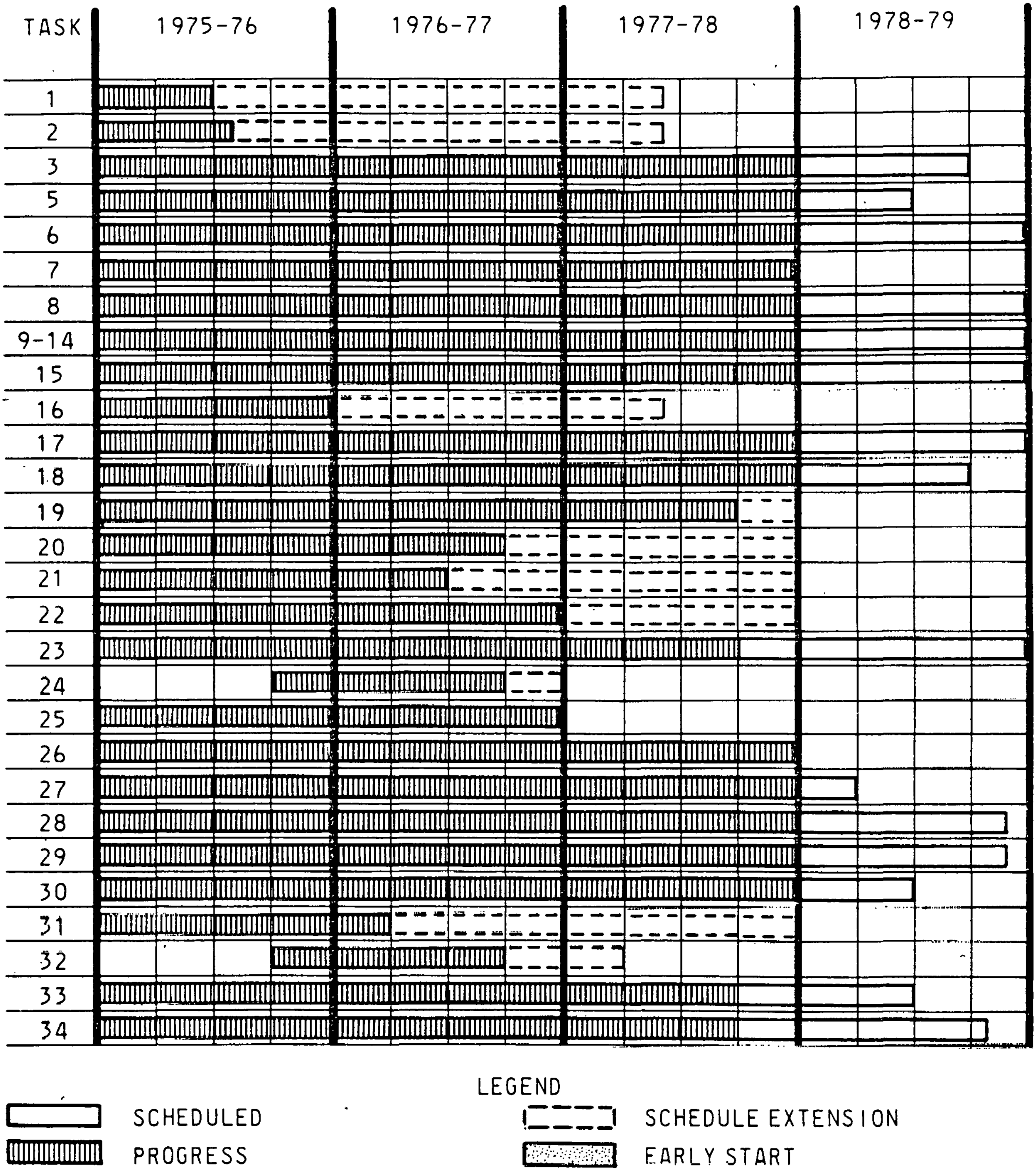
Facet IV: Significance of Coal Characteristics in Gasification Processes
    IV-A: Reactor Development and Operation
    IV-B: Cokes and Chars
    IV-D: Reactivity of Coal Chars
    IV-E: Catalysis Research
    IV-F: Differential Scanning Calorimetry

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

FACET I-A	Sample Collection and Seam Characterization
Task 1	Sampling Survey
Task 2	Sampling Plan
Task 3	Sampling
FACET I-B	Coal Characterization
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
FACET I-C	Sample Bank Operation, Maintenance and Development
Task 8	Maintenance of Coal Sample Bank
Tasks 9-14	Provision of Samples and Data to Penn State and Other Investigators
FACET I-D	Penn State/DOE Coal Data Base
Task 15	Computerization of Data
Task 16	Evaluation of the Data Base
Task 17	Structuring and Utilization of the Data Base
FACET II	Coal Beneficiation and Pre-Use Processing
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
FACET IV-A	Reactor Development and Operation
Task 23	Operation of Isothermal Furnace
Task 24	Pyrolysis of Coal Lithotypes
Task 25	Operation of Pressurized Isothermal Reactor
Task 26	Coal Reactivity
FACET IV-B	Cokes and Chars
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
FACET IV-F	Differential Scanning Calorimetry
Task 31	DSC in Evaluating Coals for Conversion
FACET V-A	Combustion of Chars and Low Volatile Fuels
Task 32	Flame Ball Combustion Model
Task 33	Plane Flame Furnace
FACET V-B	Combustion of Coal - Oil Emulsions
Task 34	Combustion of Coal - Oil Emulsions
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 June 30, 1978

SUMMARY OF PROGRESS TO DATE

Eight new coal samples from southwestern Pennsylvania and eastern Kentucky were collected during this quarter. Table 1 summarizes the status of coal characterization and the Penn State/DOE Coal Data Bank. An automated Gieseler plastometer has been installed, and is operating. Parameters of fluidity are being compared against the liquefaction behavior of coals (Task 5). Petrographic characterization of eight coals has been performed on samples submitted by other DOE contractors.

The Rapid Scan system of automated reflectance microscopy measures the size distribution of pyrite (chord sizes in linear traverses). A suite of 92 sized samples is being examined to determine the effectiveness of this technique. A new stepping stage is being interfaced with the system to obtain more resolution in characterizing the organic constituents (Task 7).

A total of 69 characterized coal samples and 487 selected printouts of coal data were supplied during the report period at the request of agencies engaged in coal research (Tasks 9-14).

In Task 18 of Facet II, a total of 25 different coals have been fractionated in the series of washability studies. Hardgrove grindabilities were determined for 96 samples (Task 20). Samples were obtained from four commercial preparation plants in order to evaluate their beneficiation operations (Task 21). Field tests of the DryFlo separator have been delayed owing to unavailability of a suitable feed location and feed properties (especially moisture content (Task 22)).

In Facet IV-A, Task 23, Darco Texas lignite, PSOC-412, has been studied extensively at an isothermal pyrolysis temperature of 800°C for residence times up to 0.3 sec. The behavior in the laminar flow, isothermal furnace has been compared with behavior during the proximate analysis. A new isothermal furnace with greater temperature and residence time capacity has been constructed and heating-up trials are in progress. The lignite then will be characterized in this furnace.

Task 27 of Facet IV-B involves an attempt to quantify the effects of preoxidation on caking properties of certain coals and to determine the effect of this pretreatment on the subsequent reactivity of chars derived from these coals. A Fisher Thermogravimetric Analyzer (TGA) unit has been shown to be an effective, quantitative technique for the measurement of low temperature oxygen sorption. Kinetic studies (using TGA) of oxygen uptake indicate that oxygen chemisorption is controlled by diffusion through the individual coal particles. These studies also show concurrent gasification and chemisorption for an hvAb coal (PSOC-337) at temperatures as low as 200°C.

A fluid bed reactor, which is to be used for preoxidation of coal samples has been designed and built. Fluidization studies of PSOC-337 have shown that all particle sizes to be investigated (35 x 60 mesh, 100 x 150 mesh and 200 x 250 mesh) can be easily fluidized. Samples of 200 x 250 mesh coal have been fluidized for periods in excess of 4 hr with minimal

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	789	1089	1300
Proximate	6	291	562	853	1300
Ultimate	7	284	557	841	1300
Equilibrium Moisture	1	18	416	434	1300
Sulfur Forms	4	288	502	790	1300
Maceral Analyses	43	300	544	844	1300
Reflectance Analyses	67	284	484	768	1300
Free Swelling Indices	1	161	480	641	1300
Gray-King Coke Types	1	88	449	537	1300
Plastometer	6	25	6	31	150
Hardgrove Grindability	1	238	478	716	1300
Vickers Hardness	1	196	175	371	1300
Ash Fusion	8	0	491	491	1300
Low Temperature Ash	3	57	75	132	1300
Ash Analysis Related Data	1	57	334	391	1300
Major and Minor Elements	10	57	334	391	1300
Trace Elements	34	57	762	819	1300
Mercury	1	0	191	191	1300
Uranium	1	0	293	293	1300
Mineralogical	35	57	75	132	1300
Calculated Compositional Values	225	300	562	862	1300
Analysis Log	18	300	789	1089	1300
Other Categories	52	269	40	309	630

Total: 33 Data Categories 592 Data Elements weight loss (4-5%) due to carryover of fines in the gas stream. In addition, temperature studies indicate that preoxidation temperatures can be maintained (±2°C) throughout the entire preoxidation period. From combined TGA and fluidization results it is believed we can quantitatively add oxygen to coal samples in the fluid bed reactor.

A DuPont 942 TMA system has been shown to be a valuable quantitative tool for the characterization of swelling and softening parameters of caking coals. Softening temperatures and dilation values obtained with the instrument are well defined and reproducible. These transition parameters are dependent on TMA variables (heating rate, load on sample, particle size). The optimum TMA conditions for studying plasticity have been determined to be rapid heating (50°C/min) of finely ground coal under a small load. Over 150 TMA experiments have been conducted to date. It is estimated that 100 more TMA trials will be needed before a standard TMA operating procedure is adopted. After a standard TMA procedure has been established, it will be used to examine the effect of oxygen sorption on three highly caking coals. In addition, the swelling and softening parameters of 20 caking coals of varying rank will be investigated.

Under Task 28, work was initiated to explore a possible correlation between the active surface area (ASA) of a char and its reactivity during gasification. The effect of bed height and particle size on reactivity of a Saran char was reported in earlier reports. In this report preliminary results of the desorption of oxygen complexes from Saran char are reported.

The results of the effect of preoxidation in air of a highly caking hvAb coal (PSOC-337) on weight loss during pyrolysis up to 1800°C and reactivity of resultant char to air at 470°C were presented in Qtr. Tech. Prog. Report FE-2030-11. It was found that weight loss during pyrolysis above 400°C decreased with increase in the extent of preoxidation. 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 limited preoxidative treatment on the reactivity of a lv bituminous coal. Preoxidation has little or no effect on weight loss during pyrolysis above 500°C. Preoxidation to the extent of 3 weight percent increases char reactivity by a factor of 40 (Task 28).

Under Task 29, qualitative x-ray analysis of three American lignites is near completion. The lignites are PSOC-90, 246, 623, from Montana, North Dakota and Texas, respectively. In Task 30, the effect of cation exchange on the subsequent reactivity of a lignite char during gasification in carbon dioxide (1 atm) at 760°C has been studied. The presence of calcium in chars has a marked accelerating effect on char reactivity. With the submission of this report, about 70 percent of the proposed work on the effect of exchangeable cations on subsequent char reactivity has been completed.

In Facet IV-F, Task 31, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study the thermal and chemical effects involved during oxidation of Saran chars at selected isothermal temperatures in the range 75-950°C. These studies have been described in DOE TR reports over the past two years. At this stage, we believe that our understanding about several experimental uncertainties associated with both techniques has been enhanced sufficiently to extend the study to coal char and/or coals.

The TGA technique was used to study reactivities of coal chars in air at 405°C and 500°C, in carbon dioxide at 900°C, and in hydrogen at 980°C. Most of these chars are still available for further investigations. Therefore, our attempts are briefly, hereafter, oriented to explore the possibility of utilizing the DSC and TGA techniques to (i) characterize these chars, and (ii) shed more light on the kinetics and mechanisms of char gasification. For example, in the case of some commerical carbons and Saran chars, the DSC technique, showing a better resolution than the TGA technique, was used to characterize the samples in terms of their reactivities towards oxygen chemisorption. Further, the combined data obtained with both techniques indicated the existence of an early gasification reaction which started at temperatures above 100°C when Saran chars were exposed to oxygen. For a particular char, it was concluded that half of the oxygen interacting with the char was chemisorbed, while the other half was involved in gasification to yield carbon dioxide. Further observations and conclusions are then predicted when the interaction between oxygen and coal char is considered.

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

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

FE-2030-TR11 -- A Review of Some Physical Methods of Coal Characterization, Their Application in Constitution Analysis and Relevance to Industrial Utilization, 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)

During June of this quarter, a sampling trip was made to southwestern Pennsylvania to collect a channel sample and three lithotypes (PSOC-1099 through PSOC-1102) of the Pittsburgh seam and to eastern Kentucky where a large channel sample and three lithotypes of the Elkhorn #3 seam were taken (PSOC-1103 through PSOC-1106).

FACET I-B: COAL CHARACTERIZATION

COAL CHARACTERIZATION (TASK 5)

Maceral analyses were completed on 108 PSOC coals with additional fluorescence analyses on 14 of these coals. Also completed were maceral analyses of the washability fractions from PSOC-313 and PSOC-326, with thirty-three fractions each. Reflectance analyses were completed on 53 PSOC samples during this period. Free swelling indices and Gray-King coke types were run on 69 coals.

The Plastic Properties of Coals and Their Influence in Conversion Processes

An automated Gieseler plastometer recently was installed and is in operation. Preliminary test runs using a series of coals of different fluidity have been conducted. The test runs indicate the equipment is performing to specifications.

The parameters of fluidity as measured by the Gieseler plastometer are presently being collected on a series of coals with known liquefaction behavior. Conversion data were obtained from work done at The Pennsylvania State University under DOE Contract EX-76-C-01-2494. Correlation between the parameters of fluidity and the liquefaction behavior of the coals is being sought. Early and very provisional results obtained on only eight coals suggests that, as the fluid range decreases, so the liquefaction conversion[1] increases (Figure 1). Additional work is needed to check this unexpected finding. The effect of oxidation on fluidity and liquefaction also will be sought.

CHARACTERIZATION OF OTHER DOE CONTRACTORS' SAMPLES (TASK 6)

Samples of eight coals from other DOE contractors were prepared and maceral and reflectance analyses performed.

RAPID SCAN AUTOMATED REFLECTANCE MICROSCOPE SYSTEM (TASK 7)

Work under Task 7 has been directed toward further utilization of the new PDP-8-based system. Forty-four analyses were run for pyrite characterization in order to determine the optimum number of data points necessary for replication. Current work includes the analysis of a suite of sized samples, involving 92 analyses. A complete report on these efforts is being prepared.

The new digital scanning stage has been partially delivered and work has begun on interfacing it with the PDP-8 computer. The completion of this work should enable precise reflectance measurements yielding a more refined reflectogram. This will enhance the ability to interpret the reflectogram for vitrinite reflectance as well as for petrographic composition. A project has also been undertaken to relate conventional reflectance data histograms to data taken by the Rapid Scan system. The information generated by this project will also improve the interpretation of automated reflectance profiles. Future work will involve interfacing the new scanning stage and developing the necessary software to provide raster scanning.

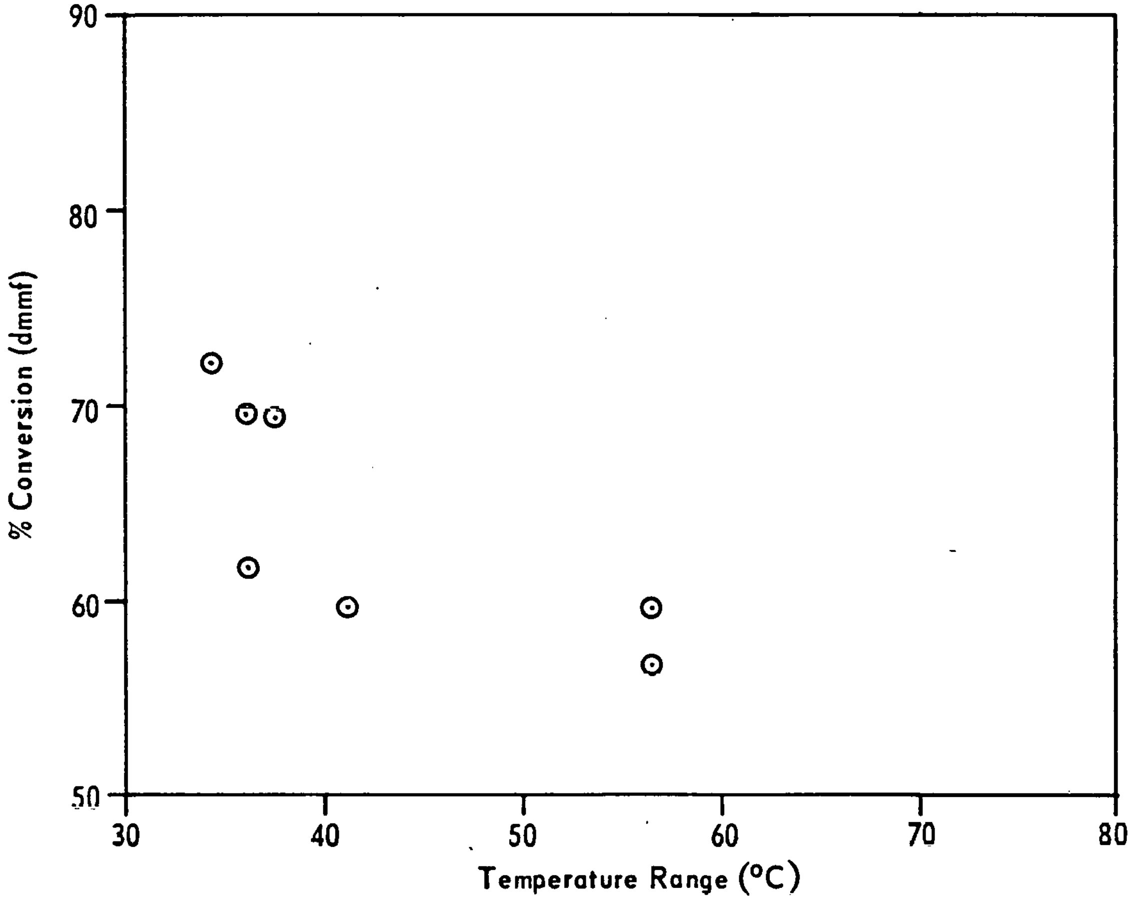


Figure 1. GIESELER FLUIDITY VS LIQUEFACTION CONVERSION[1]

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

SERVICE TO OTHER AGENCIES (TASKS 8-14)

During this second quarter of 1978, a total of 69 characterized coal samples and 487 selected printouts of coal data were supplied on request to other agencies engaged in coal research.

The requesting agencies include: TRW in California (gasifying study), Versor, Ind., Bethlehem Steel Corporation (coking), Alky Bend Mining, Inc., Colorado Geologic Survey (general), Aerospace Corporation (desulfurization), Oak Ridge National Laboratory (mineralogy), Atlantic Research Corporation (storage study), California Institute of Technology (desulfurization), University of Wyoming (general), Wyoming Geological Survey (reserves), Atlantic Richfield Corporation (sulfur study), Colorado School of Mines (mineralogy), University of Tennessee (desulfurization), Citgo Research and Development Company (liquefaction), Mobil Research and Development (exploration), Case Western Reserve University (maceral characterization), University of Southern California (electron spin resonance).

FACET II: COAL BENEFICIATION AND PRE-USE PROCESSING

WASHABILITY CHARACTERIZATION (TASK 18)

To date 25 different coals have been fractionated including PSOC-313 and those listed in Table 2 of the quarterly technical progress report for the period January-March 1978 (FE-2030-11). The fractionation of the seam sample PSOC-495 was completed during this quarter. This coal from the Hiawatha seam, Orangeville, Utah has been fractionated, the chemical analysis completed, and the fractions submitted for petrographic analysis. This coal is high volatile bituminous C in rank.

The Hiawatha seam coal (PSOC-495) is a low ash (8.12%) and sulfur (0.77%) coal. The particle densities also are low (72.2% floating at 1.35 g/cc). Based on an estimation from the dry, ash-free basis of the head sample (14,457 Btu/lb), the heat content of such a prepared product would be 13,645 Btu/lb, a high value for a coal of this rank. Individual fractions had ash values as low as 1.90 percent and sulfur as low as 0.60 percent. The reduction in sulfur was not as significant due to the organic sulfur levels. The 1.35 sink fractions (+16 M) had ash contents between 20.16 and 23.92 percent ash with sulfur in the range 0.71 and 0.78 percent. The 1.40 sink fractions (+16 M - 83.9% yield) contained between 28.95 and 37.42 percent ash and 2.33 to 3.85 percent sulfur. Accordingly, with more liberation, additional usable coal could be recovered at 1.40 g/cc or lower. Obviously a superior coal product in high yield could be obtained. The hardness variation of the particles in this coal was not great, ranging from a Hardgrove Grindability Index of 65.0 in Fraction A to 59.0 in Fraction C.

TECHNIQUES FOR FRACTIONATION (TASK 20)

Much of the activity concerned the development of grindability data for the coal data bank on recently received head samples. Hardgrove grindability was determined for 96 different samples.

The beneficiation of large samples of coals to represent lithotype concentrations are being planned with the acquisition of fresh samples. A sample of the Elkhorn No. 3 seam from Kentucky will be available in early July, with samples from the Pittsburgh seam, the Kittanning seam, and a western coal to arrive within a few weeks.

BENEFICIATION OF CONVERSION FEEDSTOCKS (TASK 21)

The pyrite liberation studies continued with pyrite fraction isolation completed through the minus 400 mesh fraction, including particle description. The size analyses and pyrite concentration analysis were completed. With the availability of these samples, trace element analyses, x-ray studies and reactivity studies can proceed.

Samples continue to be collected for various unit operations in commercial preparation plants. Additional samples were acquired from four additional plants. Evaluation of these samples, including maceral analyses and establishing unit operation performance are being made.

EVALUATION OF DRYFLO SEPARATOR (TASK 22)

Field tests of the Model DryFlo separator have been delayed by unavailability of a suitable feed location and feed properties (especially moisture content). A preparation facility has been located in western Pennsylvania which utilizes a new type of thermal dryer. Investigations are being made to establish if this location and available feed are appropriate for the DryFlo studies.

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

New Isothermal Furnace

Construction of the new isothermal furnace alluded to in previous reports was completed during this quarter. The furnace and preheater were mounted on a supporting structure, ancillary equipment (vacuum pump, flow meters, etc.) was installed and an electrical supply circuit connected. The water cooled injector and collector probes have been constructed together with the suction pryometer for gas temperature measurements. The new system is essentially a scale-up of a previous model described in detail in technical report FE-2030-TR2 and is intended to supersede that system.

Initial attempts to reach the design gas temperature of 1000°C were unsuccessful. The maximum temperature was restricted to 600°C by the capacity of the existing circuitry. New circuits have been installed to overcome this problem and heating-up trials are now in progress.

Volatile Matter Experiments

Purpose

As outlined in previous quarterly technical reports, for example FE-2030-9, weight loss in the isothermal furnace is determined using ash as a tracer. One criticism of this method is based on the probable weight loss of the mineral matter when heated. This was treated theoretically in quarterly technical progress report FE-2030-9. Further, it was shown in quarterly technical progress report FE-2030-10 that weight loss in the isothermal furnace, ΔW as % original daf coal, is greater than the change in proximate volatile matter between the original coal and char, ΔV as % original daf coal, by the so-called Q factor. Both these phenomena were investigated by experiments performed in the Hoskins furnaces used for the proximate volatile matter tests.

Method

Modified ASTM volatile matter tests were performed on Darct Texas lignite, PSOC-412, size graded to 60 x 80 mesh with a mean weight particle size, $\bar{X}$, of 216 µm. The preset furnace temperature ranged from 250-800°C for stage 1 evolution but was always 950°C for stage 2 evolution. Loss of volatile matter during stage 1, VM_I as % original daf coal, was determined by difference in weight between the coal and the resulting char, called $char_I$. During stage 2 heating, the volatile matter in $char_I$, designated VM_{II} as % original daf coal, was liberated producing $char_{II}$. The porixmate ash content of $char_{II}$ was determined by the standard method.

Results

The results are shown in Table 3, together with the standard ASTM volatile matter test. The total volatile matter, $VM_{TOTAL} = VM_{I} + VM_{II}$, is not significantly different from VM_{ASTM} for any of the pretreatment temperatures. This is clearly illustrated in Figure 2. The 800°C, stage 1 temperature case is particularly significant. Pretreatment in the 800°C isothermal reactor for this size grade of PSOC-412 resulted in a Q-factor of 1.9 (see quarterly technical progress FE-2030-11), in comparison with no enhancement of the volatile matter yield in the Hoskins furnace.

It must be remembered that other factors besides the rate of heating are different between the two furnace methods, for example, the pyrolysis medium and the existence of a porous bed of coal. It is important therefore not to construe the above as proof that the heating rate, per se is responsible for the enhancement of the volatile matter yield in the isothermal furnace. It does indicate, however, that the data are consistent with such a hypothesis.

The weight loss, ΔW, in producing $char_{II}$ from the original coal was computed using ash as a tracer and the results are included in Figure 2. The data indicate that this technique consistently understimates the directly measured weight loss. Percentage errors are given in Table 3, with the maximum error at 6.2 percent.

Unless the mineral matter undergoes drastically different changes in the isothermal furnace compared with the Hoskins furnace, the results indicate that the weight loss, ΔW, is not overestimated by using the ash tracer method (it is, in fact, underestimated) so the Q-factor cannot be explained in terms of the method of determination. The present experiments do not indicate the effect of using ash as a tracer on the estimation of ΔV, but in theory, this will change in the same direction as ΔW. Separate experiments are needed to confirm this.

Weight Loss During Heating Up

Purpose

In the quarterly technical progress report FE-2030-10, it was inferred from the data that no weight loss occurred during the 0.095 sec heating-up time for, among others, the 70 x 100 mesh size grade ($\bar{X} = 178\ \mu m$). It was reported in the quarterly technical progress report FE-2030-11 that weight loss apparently increased with recycling for a given isothermal time, assuming a heating-up time of 0.095 sec on each recycle. A series of experiments were conducted, therefore, to measure directly the weight loss, if any, during the initial heating-up time of 0.095 sec, and subsequent heating-up times for the recycle cases. It has been previously indicated that the purpose of recycling is merely to increase the range of total residence times in the furnace.

Table 3. Effect of Two-Stage Evolution of Volatile Matter on the Total Yield

Pretreatment Temperature, °C	ASTM	250	350	450	550	560	750	800
VM_I, % daf coal	0	9.5	22.3	37.4	42.5	47.2	52.1	52.2
VM_{II}, % daf coal	51.4	43.2	29.4	13.8	9.1	4.9	0.8	1.5
VM_{TOTAL} (= VM_I + VM_{II})	51.4	52.7	51.7	51.3	51.6	52.1	52.8	53.7
% ash in $char_{II}$	18.4	18.8	18.9	18.5	18.8	--	--	--
ΔW, % daf char using ash tracer	48.2	49.6	49.9	48.7	49.6	--	--	--
Error using ash tracer, %	6.2	5.8	3.4	5.3	3.9	--	--	--

Method

A sample of Darco Texas lignite, PSOC-412, size graded to 70 x 100 mesh ($\bar{X}$ = 178 μm) was injected into the isothermal furnace operating at the standard conditions (see quarterly technical progress report FE-2030-8) for a total residence time equal to the heating-up time of 0.095 sec. The sample was recycled once and twice under the same conditions.

Results

The results, given in Table 4, indicate that, within the experimental accuracy, no significant weight loss occurred during either the initial heating-up time or subsequent heating-up times. Any enhancement of the volatile matter yield on recycling for a given isothermal residence time, therefore, cannot be attributed to weight loss during the recycle heating-up time.

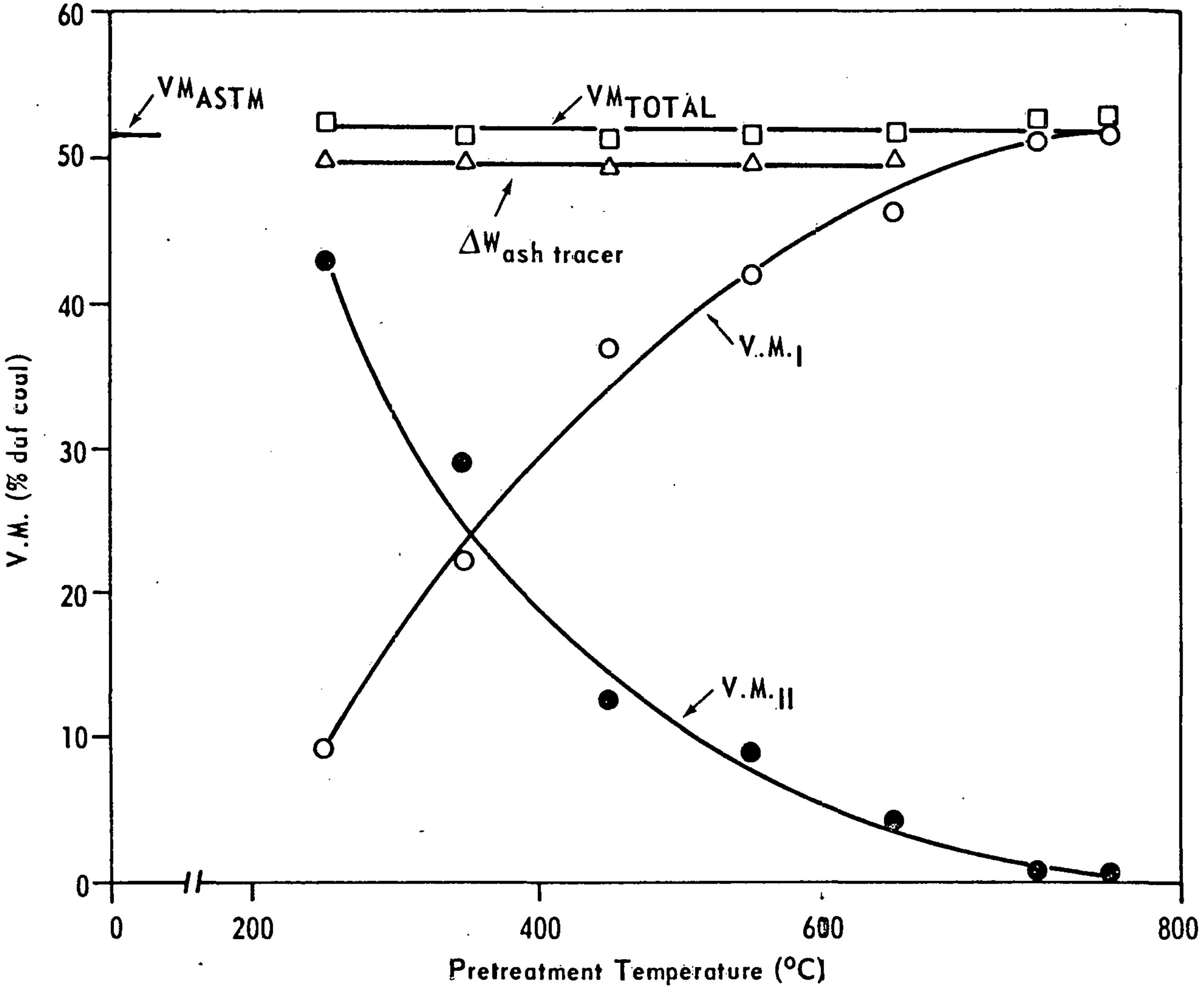


Figure 2. COMPARISON OF VOLATILE MATTER YIELD DETERMINED BY DIFFERENT TECHNIQUES

Table 4. Weight Loss During Heating-up in the Isothermal Furnace

Recycle Condition	Total Residence Time (sec)	Isothermal Residence Time (sec)	Heating-up Time (sec)	ΔW, % daf coal
None	0.095	0	0.095	-1.0
One	0.190	0	0.190	2.0
Two	0.285	0	0.285	1.0

FACET IV-B: COKES AND CHARS

EFFECT OF VARIABLES ON CHAR STRUCTURE (TASK 27)

Preoxidation of Caking Coals to Deminish Their Softening and Swelling

During this quarter, efforts were directed at establishing a standard TMA procedure for the analysis of agglomerating properties of caking coals. The DuPont 942-TMA system is a highly sensitive dilatometer equipped with a time derivatime computer. A typical TMA run yields much quantitative information about softening and swelling of coal samples. The plastic temperature region (300-600°C) observed in caking coals may be split into two zones. Zone one is the initial softening stage. In this region (300-450°C) coal samples become plastic and are easily compressed under a load. Zone two is the region in which rapid expansion occurs. This rapid expansion is followed by a significant contraction of the sample and a subseqeunt loss of plasticity. The derivative computer is invaluable for determining transition temperatures such as onset of softening (T_s), the temperature at which dilation begins (T_d) and resolidification temperature (T_r) of the coal.

Over 150 TMA experiments have been conducted in order to evaluate the effect of TMA variables:

a) heating rate (3°C/min, 20°C/min and 50°C/min)
b) load on sample (no apparent load, 1 g, 5 g)
c) particle size (35 x 60 mesh, 100 x 150 mesh and 200 x 250 mesh)

on characteristic softening and swelling parameters:

i) T_s - onset of softening temperature
ii) T_d - initial dilation temperature
iii) T_r - resolidification temperature
iv) initial contraction, expansion and final contraction

Heating rate and load studies have been completed for 35 x 60 mesh and 200 x 250 mesh coal samples (PSOC-337 hvAb coal). These data can be found in Table 5. All data reported in this table are expressed as 95 percent confidence values obtained from 5 or 6 runs at each set of conditions.

Results indicate that the initial softening temperature, T_s, increases markedly with increasing heat rate (Table 5, Figure 3). T_s also shows a strong inverse dependence on added load (Figure 4).*

---

*Note: T_s value determined at 3°C/min under no load has a high degree of uncertainty (±30°C). This is due in part to higher derivative sensitivity required at low heating rates and to a loss of some stability of the dilatometer probe in the no load mode.

Table 5. TMA Softening and Swelling Data for PSOC-337 (hvAb) Coal

Size Fraction	Heating Rate °C/min	% Volume Expansion Under Load			Transition Temperatures Under 5g Load			Transition Temperatures Under 1g Load			Transition Temperatures Under No Load		
		5g	1g	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	250±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 Resolidification observed
35 x 60 mesh	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	-	-	312±6	434±3	No Resolidification observed	-	-	-	-	-	-

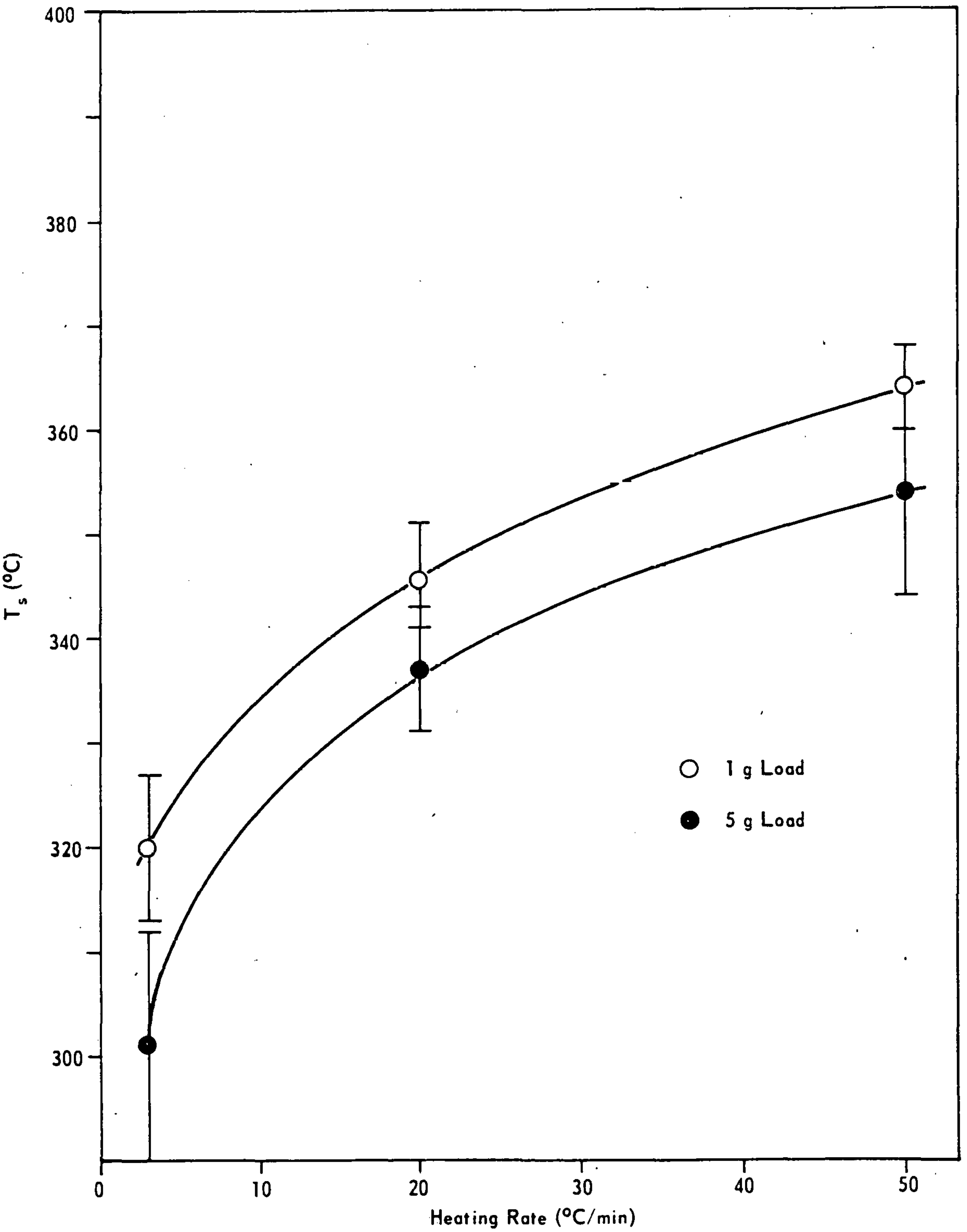


Figure 3. EFFECT OF HEATING RATE ON T_s (ONSET OF SOFTENING TEMPERATURE)

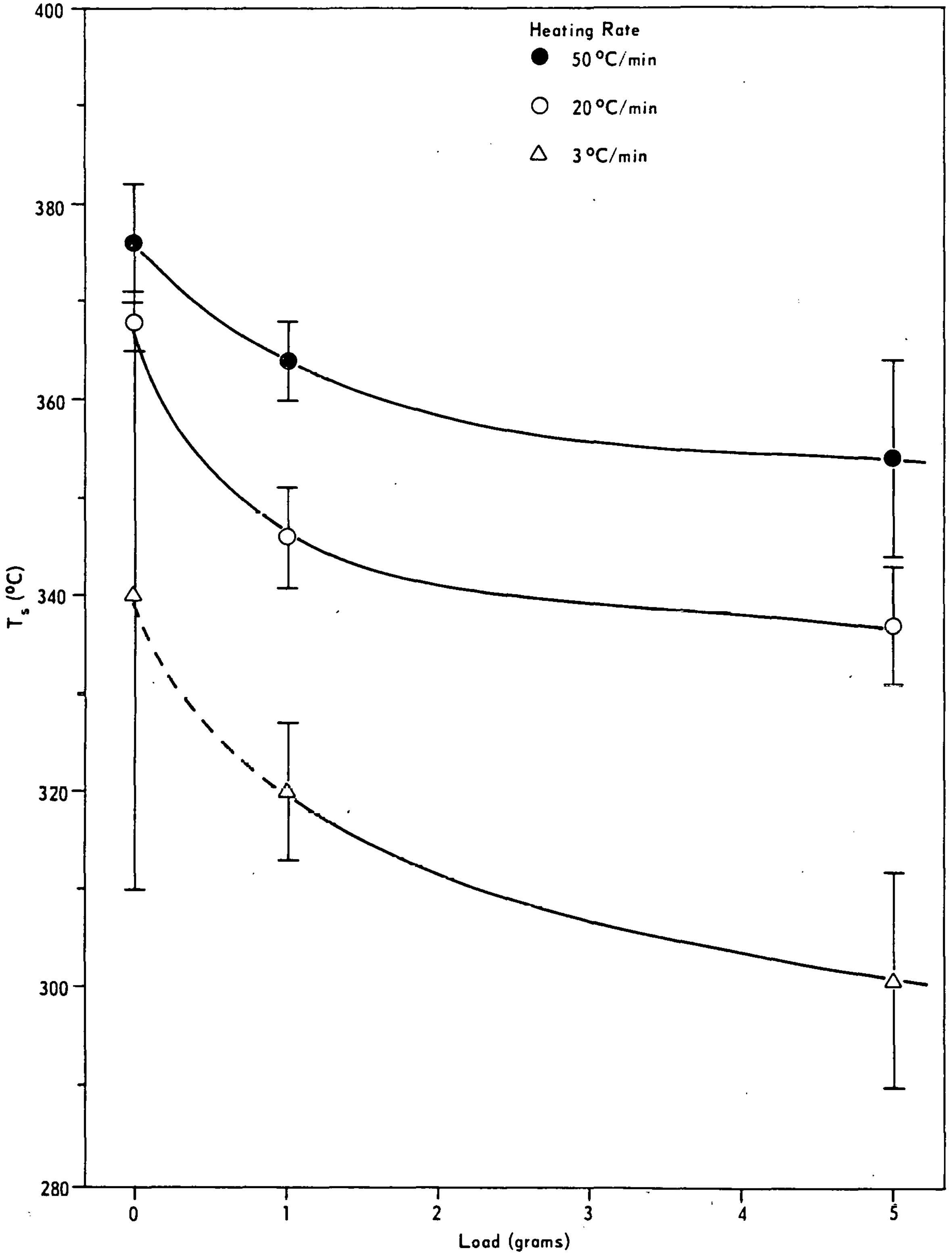


Figure 4. EFFECT OF LOAD ON ONSET OF SOFTENING TEMPERATURE (T_s)

The initial dilation temperature, T_d, is not load dependent for 200 x 250 mesh coal particles but appears to have a slight dependence for 35 x 60 mesh coal. As was the case for T_s, T_d is very sensitive to the heating rate at which it is determined. T_d values for 35 x 60 mesh fractions at 50°C/min heating rate are rather low. This is due to the shape of the dilatometric trace and as a result these temperatures should not be compared directly for the 200 x 250 mesh values.

The resolidification temperature, T_r, also shows a heating rate dependence. T_r decreases with decreasing heating rate from 50°C/min to 20°C/min. However, no resolidification temperature was observed for the 3°C/min trials. Samples heated at 3°C/min followed the usual contraction, expansion, contraction profile with an additional expansion above 600°C. T_r values are not dependent on applied load.

Attempts were made to characterize the swelling properties by correlating the contraction and expansion parameters. No meaningful correlations could be obtained. The most consistent results were obtained by defining a total dilation (D_t) parameter as:

$$D_t = \text{initial contraction} + \text{maximum expansion} \qquad (1)$$

This parameter is used to calculate the percent volume expansion ($\%V_{ex}$) of the coal sample upon heating:

$$\%V_{ex} = \frac{(D_t)(\pi r^2)}{(1/\rho_p)(W)} \cdot 100 \qquad (2)$$

D_t - is in inches

r - radius of the sample container (in.)

ρ_p - packing density of the coal in the sample vial at start of experiment (g/ in.^{2})

W - starting wt of coal in g.

Volume expansion data are summarized in Table 5 and Figures 5 and 6. Results indicate that the percent volume expansion is extremely sensitive to heating rate (Figure 5). Volume expansion is also affected by the load on the sample in some cases (Figure 6).

From these results optimum TMA operating conditions appear to be rapid heating of finely ground coal under a small applied load. Transition temperatures (T_s and T_o) are better defined under a slight load. This is due to stabilization of the dilatometer probe on the sample surface. Small loads (1g) do not present any restrictions since at rapid heating of the small particle size, a load dependence is not noticeable (Figure 6). These conditions lead to optimum dilation values (D_t) and well defined transition temperatures.

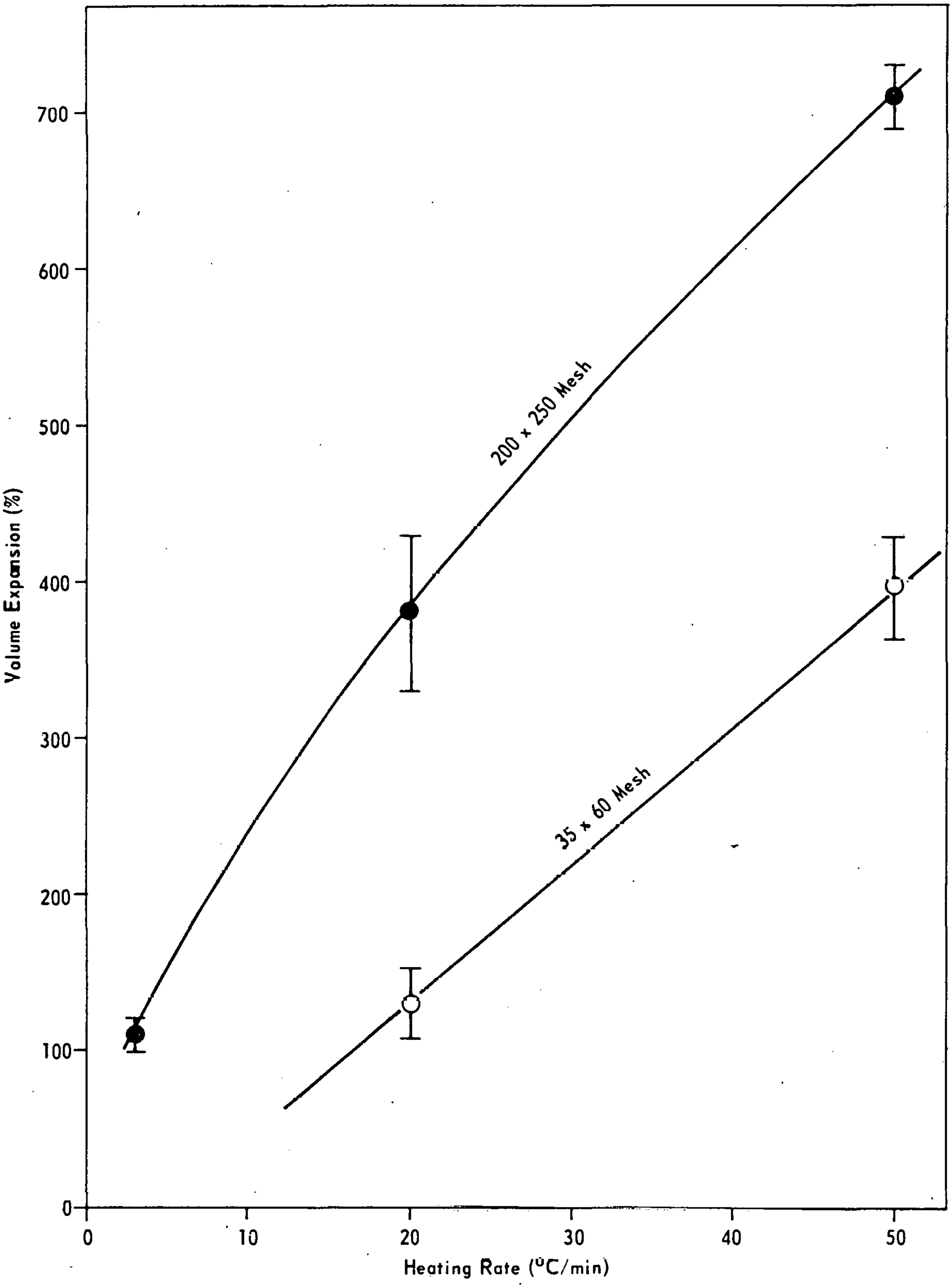


Figure 5. EFFECT OF HEATING RATE ON VOLUME EXPANSION UNDER 1 G LOAD

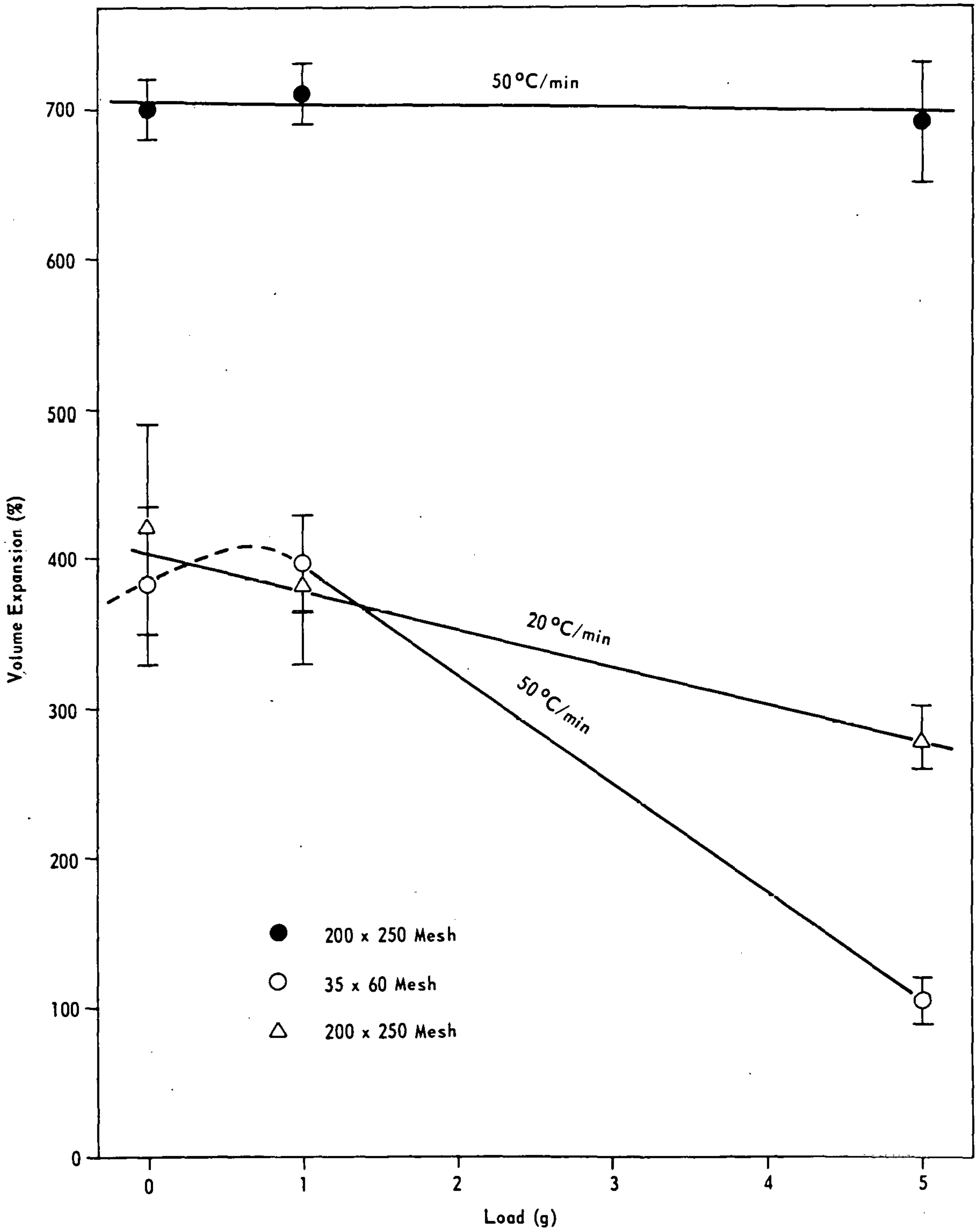


Figure 6. EFFECT OF LOAD ON % VOLUME EXPANSION

Some concern has been expressed over the possibility of maceral segregation upon grinding and separation of coal into sieve fractions. Swelling and softening are functions of component macerals. Therefore, segregation of macerals could lead to apparent particle size effects. To examine this point, -200 mesh samples of the whole coal will be prepared and run in the TMA. This procedure will remove the possibility of maceral segregation.

As noted in the previous report, investigation of heating rates during TMA runs indicates that there is a noticeable increase in heating rate corresponding to the temperature region at which maximum decomposition of the coal occurs. This behavior is a result of coal pyrolysis reactions and cannot be removed. These variations in heating rate are not precisely reproducible from run to run and are most likely responsible for experimental uncertainty in the determination of swelling and softening parameters.

Work for the next quarter will involve a continuation of TMA studies. Heating rate and load studies will be completed for 100 x 150 mesh and -200 mesh coal samples. Upon completion of this work (approximately 100 TMA runs), a standard TMA procedure will be adopted. This procedure will be used to examine the effect of oxygen sorption on three caking coals. The coals will be selected on the basis of high swelling and high vitrinite content. The three coals will have varying vitrinite reflectance. These coals will be quantitatively oxidized to several different levels (0-3% by wt, dry basis) and then their swelling upon heating measured with the TMA unit. It is estimated that a total of 150 TMA runs will be required to finish this facet of the study. Half of these runs should be completed by the end of next quarter.

Finally, the TMA technique will be applied in an effort to characterize the softening and swelling parameters of 20 coals of varying rank (all in the caking range). It is estimated that 120 TMA runs will be needed to complete this study. Ten of these samples (approximately 60 TMA runs) should be completed by the end of the quarter.

RELATION OF CHAR STRUCTURE TO CHAR REACTIVITIES (TASK 28)

Relation of Active Surface Area of Chars to Their Reactivity

During this quarter, considerable progress has been made in learning the different experimental techniques to be used in the proposed research work. These techniques include gas chromatography (GC), gas adsorption and mass spectrometry (MS).

As stated in previous technical progress reports, the GC technique will be used to monitor the concentration of carbon dioxide and carbon monoxide produced during gasification of Saran char in air. From a material balance, it will be possible to calculate the level of carbon burn-off at any stage during the gasification process, as well as char reactivity. Unfortunately, the proposed work concerning the effect of particle size and bed height on reactivity in a tube furnace has been delayed by problems concerning an unsteady baseline during temperature programming of the GC. The GC manufacturer and other experts in this area have been consulted and it is hoped that these experimental problems can be overcome in the next few days. Following this, concerted efforts will be made to expedite the research work.

The conventional volumetric adsoprtion technique will be used to determine the total surface area (TSA) of various char samples activated to different levels of burn-off.

The use of a mass spectrometer for measurement of ASA was outlined in the previous reports. Work was initiated to learn this technique using a Saran char sample (Saran char is highly microporous having a structure similar to coal derived chars). The determination of ASA requires a priori, a "clean" carbon surface. In this laboratory, ASA of non-porous carbons has been determined in the past. These carbon surfaces could be cleaned in a reasonably short period of time by outgassing at 950°C down to $<10^{-8}$ torr. However, this is not the case with the highly microporous Saran char. It takes inordinately long periods of time to thoroughly degas Saran char at 950°C.

About 20 mg of Saran char were taken for the MS study. After three days of degassing at 950°C, the char sample was thought to be clean enough for ASA measurements. Five hundred milli torr of research grade oxygen was admitted and allowed to contact the Saran char for 24 hr at 100°C. The gases in the system were then analyzed using MS. No products of combustion, that is carbon monoxide and carbon dioxide, were detected. After this the sample was outgassed at 100°C down to $<10^{-7}$ torr.

The sample was then slowly heated to 750°C. A liquid nitrogen trap was used to freeze out carbon dioxide. The temperature was then raised slowly to 950°C. Thereafter the temperature was kept constant and the pressure of the product gas monitored (Figure 7).

The plot was expected to asymptotically approach some constant value, representing the total amount of gaseous products evolved from the decomposition of surface oxygen complexes. However, the steadily increasing pressure seen in Figure 7 was thought to be due to a possible back reaction of carbon dioxide (diffusing out of the liquid nitrogen trap) with carbon. In order to examine this possibility, after about 120 hr reaction time, the reactor was isolated and the amount of carbon monoxide in the remainder of the system was measured. Following this, the liquid nitrogen trap was removed, carbon dioxide was expanded in the system and its amount determined by MS. The gases (carbon monoxide and carbon dioxide) were then pumped out of the system.

The reactor was again put in line and heating continued. It was found that the pressure still continued to rise indicating that back reaction of carbon dioxide with carbon could not account for the increasing pressure. An understanding of this phenomena is presently being sought.

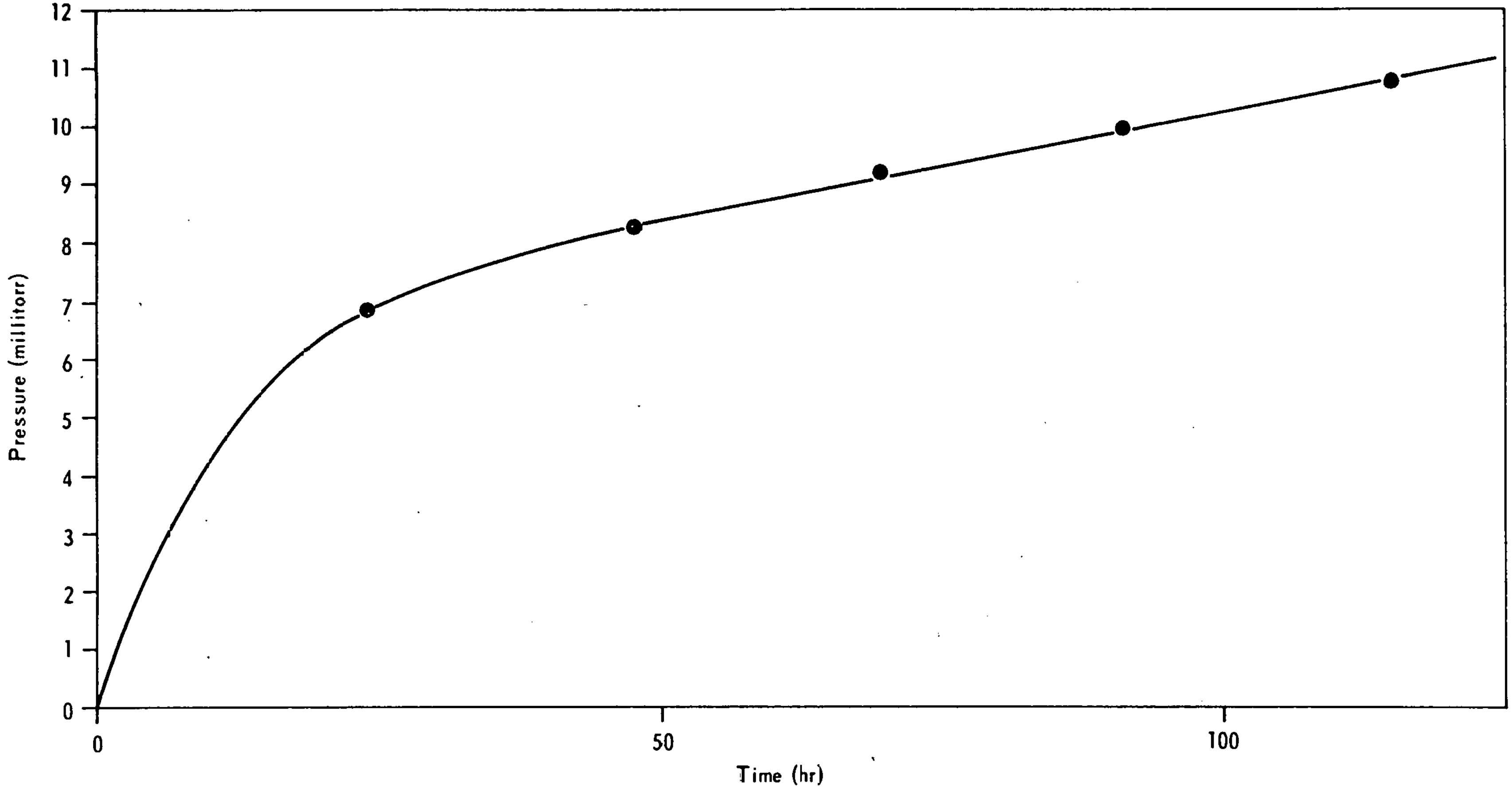


Figure 7. INCREASE IN PRESSURE OF PRODUCT GASES IN RELATION TO THE REACTION TIME UPON HEATING SARAN CARBON AT 950°C

Effect of Preoxidation of Caking Coals on Coal and Char Properties

In the previous DOE 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. We found that in air, carbon dioxide and steam the reactivity of the char produced from a lvb coal (PSOC-127) was about 150-fold less than the reactivity of the most reactive lignite char. PSOC-127 coal is a highly caking coal with a free swelling indes 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 preoxidizing the coal. During this quarter we have considered this feasibility.

Experimental procedures followed for measuring weight changes during preoxidation, pyrolysis and reactivity runs were the same as those reported in the last report (FE-2030-11).

Weight gains during preoxidation of PSOC-127 coal at different reaction temperatures when oxidation is carried out for different periods of time are given in Table 6. Effect of preoxidation on weight loss during pyrolysis is illustrated by the data given in Table 7. It is seen that oxidation increases the weight loss udring pyrolysis up to 500°C, although the increase is not related to the extent of preoxidation. At pyrolysis temperatures above 500°C, preoxidation has little or no effect on weight loss.

Burn-off versus time plots for various chars (produced from different preoxidized coals) 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) as the reactivity parameter during char gasification. $\tau_{0.5}$ values for various char samples are given in Table 6. The char produced from the unoxidized coal has a very low reactivity in air ($\tau_{0.5}$ = 2040 min). It is seen that a weight increase of only 0.45 wt percent during preoxidation of the coal leads to a dramatic increase in $\tau_{0.5}$ from 2040 min to 690 min. $\tau_{0.5}$ further decreases by a factor of over five upon increase in the extent of preoxidation from 0.45 to 0.66 percent. Thereafter, further decrease in $\tau_{0.5}$ with additional weight increase (during preoxidation) is less pronounced and when weight increase exceeds about 2 percent, $\tau_{0.5}$ attains more or less a constant limiting value. Of note is the fact that preoxidation to the extent of only 3 wt percent increases char reactivity by a factor of about 40. The results of the present study bring about clearly, perhaps for the first time, the marked effect of preoxidation of highly caking coals on subsequent char reactivity.

It was thought of interest to investigate whether for a given weight increase during preoxidation, the oxidation temperature had any effect on subsequent char reactivity. In order to study this aspect, the coal was preoxidized to a weight gain of 1.4 percent at 200, 220 and 250°C. For attaining this level of oxidation, preoxidation treatment had to be carried out for 116, 57 and 14 min, respectively. The devolatilization curves for the various samples are given in Figure 8. The reactivity plots are given in Figure 9. It is seen that for the same level of preoxidation, the oxidation temperature has essentially no effect on the devolatilization curves (Figure 8) and $\tau_{0.5}$ values (Figure 9).

Table 6. Effect of Preoxidation on Subsequent Char Reactivity

Preoxidation Temp., °C	Preoxidation Time, min	Weight Increase During Preoxidation wt % (dry)	Reactivity $\tau_{0.5}$, min
None	0	0	2040
180	62	0.45	690
180	120	0.66	129
200	118	1.4	65
220	90	1.9	57
250	37	3.0	53
250	65	4.5	52

Table 7. Effect of Preoxidation on Weight Loss During Pyrolysis

Weight Increase During Preoxidation wt % (dry)	Cumulative Weight Loss Selected Temperatures % (dry basis)							
	350°C	400	500	600	700	800	900	1000
0	0	0.2	4.3	12.1	15.2	16.7	17.2	17.5
0.45	0.7	2.6	7.6	12.6	15.3	16.9	17.4	17.7
0.67	0.8	2.7	6.4	13.0	16.0	17.4	18.4	19.0
1.4	0.9	2.0	6.0	12.0	15.0	16.5	17.2	17.5
1.9	0.0	1.9	5.9	11.8	14.9	16.7	16.4	16.8
3.0	0.8	2.3	6.0	11.3	14.7	16.6	17.2	17.7
4.5	1.2	2.8	6.5	11.5	15.0	17.4	18.5	18.8

In our preoxidation studies so far we have used a 200 x 250 mesh fraction of coal. We would like to know what effect, if any, the coal particle size has on the extent of preoxidation, and whether for the same level of preoxidation different size fractions of a coal yield chars having the same or different reactivities. The results of such a study will be reported in the next quarter. The effect of preoxidation on surface area, true and apparent densities (as measured by helium and mercury displacement, respectively), total open pore volumes and pore size distribution also will be studied.

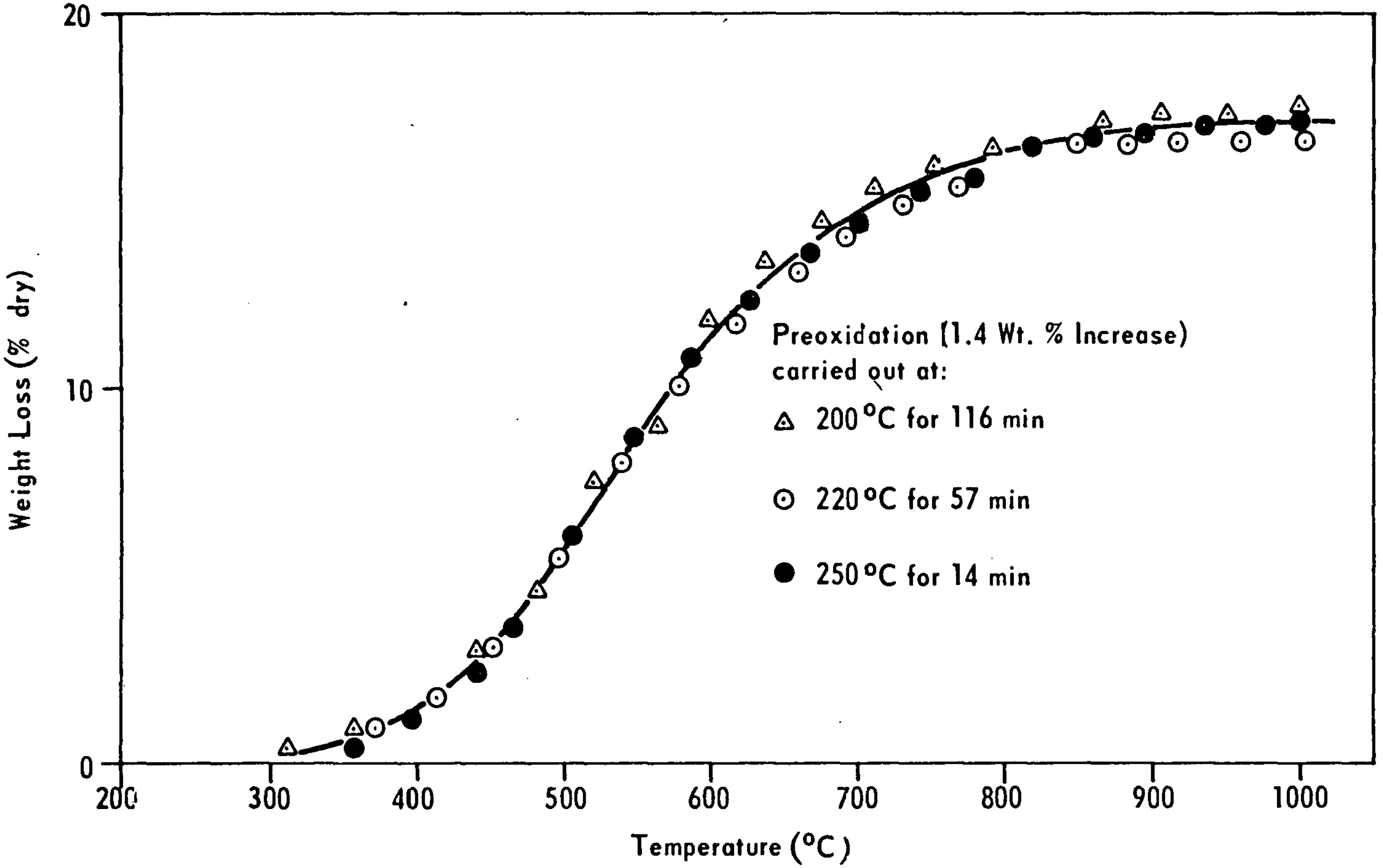


Figure 8. EFFECT OF SAME LEVEL OF OXIDATION AT DIFFERENT OXIDATION TEMPERATURES ON WEIGHT LOSS DURING PYROLYSIS

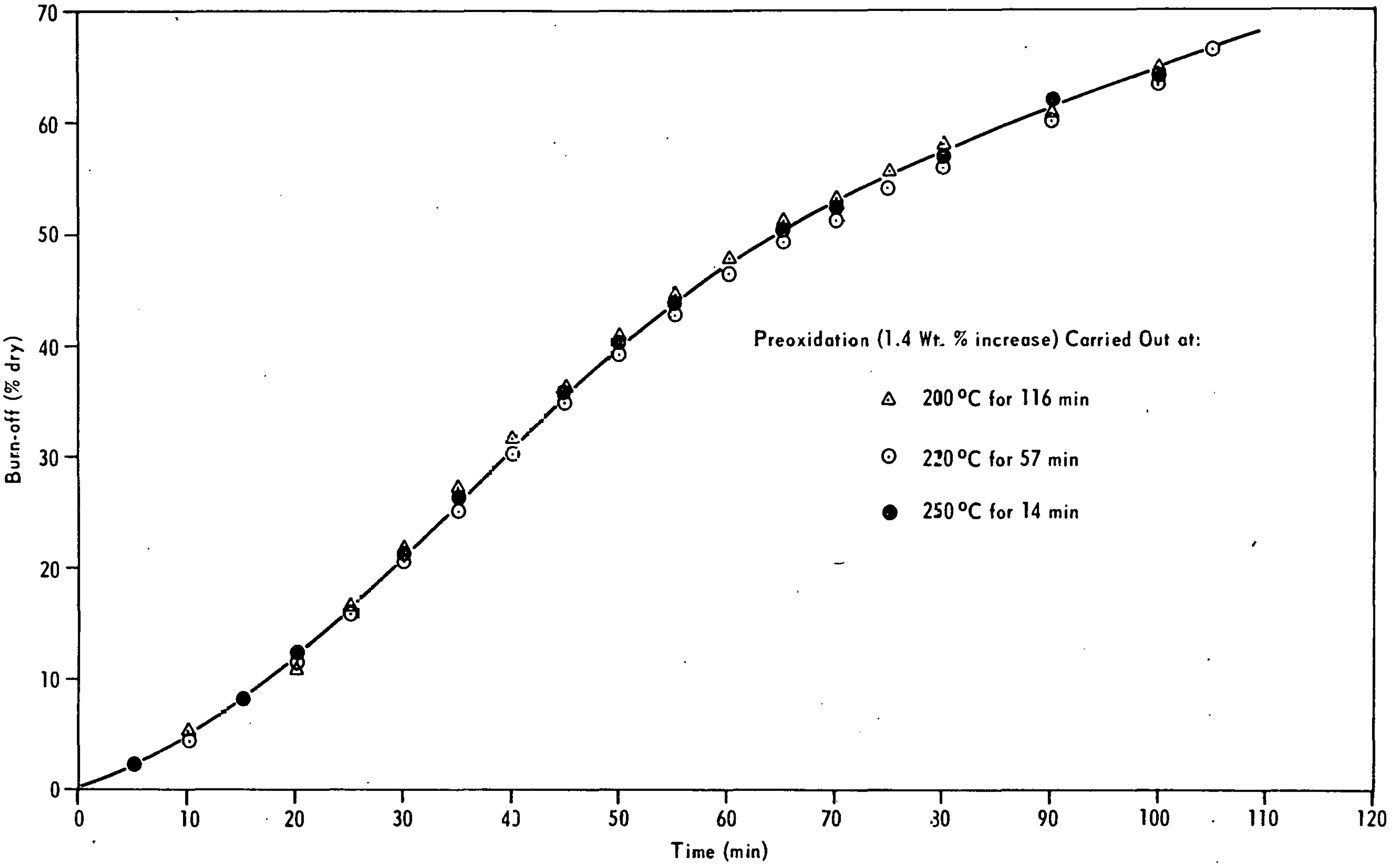


Figure 9. EFFECT OF SAME LEVEL OF PREOXIDATION OF COAL AT DIFFERENT OXIDATION TEMPERATURES ON SUBSEQUENT REACTIVITY OF CHAR TO AIR AT 470°C

EFFECT OF CATION EXCHANGE AND METAL ADDITION (TASK 30)

Carboxyl Groups and Exchangeable Cations in Lignite Coals

The analysis of the discrete mineral phases (clays, carbonates, silicates, etc.) is an important part of this study. First, it aids in a thorough understanding of the composition of the coals. Second, it may prove important in understanding the behavior of the carboxyl system under varying conditions.

This analysis is carried out with x-ray analysis of the low temperature ash (LTA) samples. LTA is a technique in which the coal sample is subjected to an oxygen plasma. Under these conditions the organic matter is oxidized quickly at low temperatures (about 48 hr at 125°C). The advantages of this technique are well known, and mainly include the oxidation of the organic matter with little disturbance of the mineral matter.

X-ray diffraction can be applied in two ways; qualitative and semi-quantitative. Qualitative analysis entails the identification of crystalline materials by their characteristic atomic spacings. Semi-quantitative analysis relates the intensity of the diffracted beams to the composition of the mixture. This is done by creating a number of calibration mixtures with known composition. An internal standard of calcium fluoride is added. The relative intensity of the mineral matter peak to calcium fluoride peak is then recorded as a function of composition. Calcium fluoride is then added to the unknown sample. By comparison of the relative intensities in this sample to the known samples, an approximate composition can be gained.

This method can only be taken as approximate for a few reasons. First, obtaining an intimate mixture of solid powders has proved to be difficult. Second, the intensity for a given mineral is dependent on the other minerals present. That is, composition is not proportional to intensity, so the calibration samples must be very close to the composition of the unknowns. Also many minerals, especially clays, have a variety of responses to diffraction. Relative intensities are highly dependent on the origin of the sample. This is due to isomorphous substitution, crystallite size, and crystal defects.

During this quarter, qualitative x-ray work on an LTA sample was conducted for three coals. The main components are similar being quartz, pyrite, kaolinite, and illite-montmorillonite. Bassanite and anhydrite (both forms of calcium sulfate) were also observed. It is believed that these were formed in the LTA as a result of the interaction of organically bound calcium with pyrite. Apparently ion-exchanged Ca-carboxylate groups can decompose under the conditions of LTA.

To study this further, the raw coal was acid treated before LTA and x-ray analysis. Treatment in 1N hydrochloric acid removes all ion exchanged minerals. After treatment no bassanite was observed. In one case pyrite was not observed in the normal LTA but was later observed in the acid-washed sample. 1N hydrochloric acid should not remove pyrite but it does remove calcium which apparently can attack pyrite. These facts display the interaction of ion exchanged inorganic with discrete mineral phases, and the importance of this section of the work.

Effect of Cation Addition on Char Gasification

In the last quarterly technical progress report (FE-2030-11) we observed that chars produced from lignites are appreciably more reactive during gasification than those produced from higher rank coals. We reported that the reactivity of a Texas lignite char in 1 atm air at 390°C varied as a linear function of the amount of exchangeable calcium ions contained in the precursor lignite. Normalized reactivities of the various calcium containing chars in air were found to be essentially the same as those found previously in 1 atm steam at 650°C.[2] Since the submission of the last progress report, we have measured the reactivities in carbon dixoide of the same set of calcium containing chars as those used in air 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.[2]

Char reactivity was measured in a DuPont TGA unit in 1 atm of carbon dioxide at 760°C. This temperature was chosen for the following reason. At this temperature the most reactive char sample, that is, the char associated with the maximum amount of calcium, had the same reactivity in carbon dioxide as in 1 atm air at 390°C. About 3 mg char were 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 until the sample weight became essentially constant. Following this, the sample was cooled in nitrogen down to 760°C. This temperature was kept constant for 30 min after which nitrogen was replaced by carbon dioxide 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:

$$R = \frac{1}{W_0} \cdot \frac{dw}{dt} \qquad (3)$$

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}).

Reactivity parameters for various char samples in carbon dioxide, air and steam are given in Table 8. As in air and steam, the reactivity parameter in carbon dioxide also increases linearly with increase in the calcium content of the char (Figure 10). The fact that the catalytic activity per unit weight of calcium is constant over such a wide range of loading (1.1 to12.9% calcium) suggests that the catalyst is highly dispersed and that the catalytic species is not sintered to any noticeable extent during heat treatment.

It was shown in the last progress report that for various char samples normalized reactivities in air and carbon dioxide were essentially the same. Whereas the reactivity versus calcium content plots for reaction in air and steam passed through the origin, the corresponding plot in carbon dioxide gives a positive intercept. This is because the demineralized char is far more reactive in carbon dioxide than in air and steam (Table 8). Therefore, in order to be consistent with the normalization procedure in all gasification atmospheres, the reactivity parameter in carbon dioxide for the

Table 8. Reactivities in Carbon Dioxide, Air and Steam of Chars Produced from Raw, Demineralized and Calcium-Exchanged Coals

Source of Char	% Ca in Char	Reactivity ($mg\ hr^{-1}mg^{-1}$) in Air	Steam	CO_2
Raw Coal	2.0	0.24	0.05	0.37
Demineralized Coal	0.2	0.02	0.005	0.25
Ca Exchanged Coals Containing mmoles Ca/g coal (daf)				
0.1	1.1	0.21	0.11	0.47
0.25	1.9	0.22	0.13	0.51
0.37	2.6	0.45	0.17	0.60
0.56	4.5	0.65	0.23	0.86
0.66	5.3	0.53	0.30	--
1.20	8.5	0.98	0.43	0.97
1.29	9.1	1.00	0.45	1.15
2.14	12.9	1.40	0.63	1.55

demineralized sample was subtracted from the reactivities of the remainder of the char samples. The 'corrected' normalized reactivities in carbon dioxide are seen to be essentially the same as those in air (Figure 11). These results thus suggest that gasification in air, steam and carbon dioxide 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 hydrogen of the same set of chars as those used in the present study will be investigated.

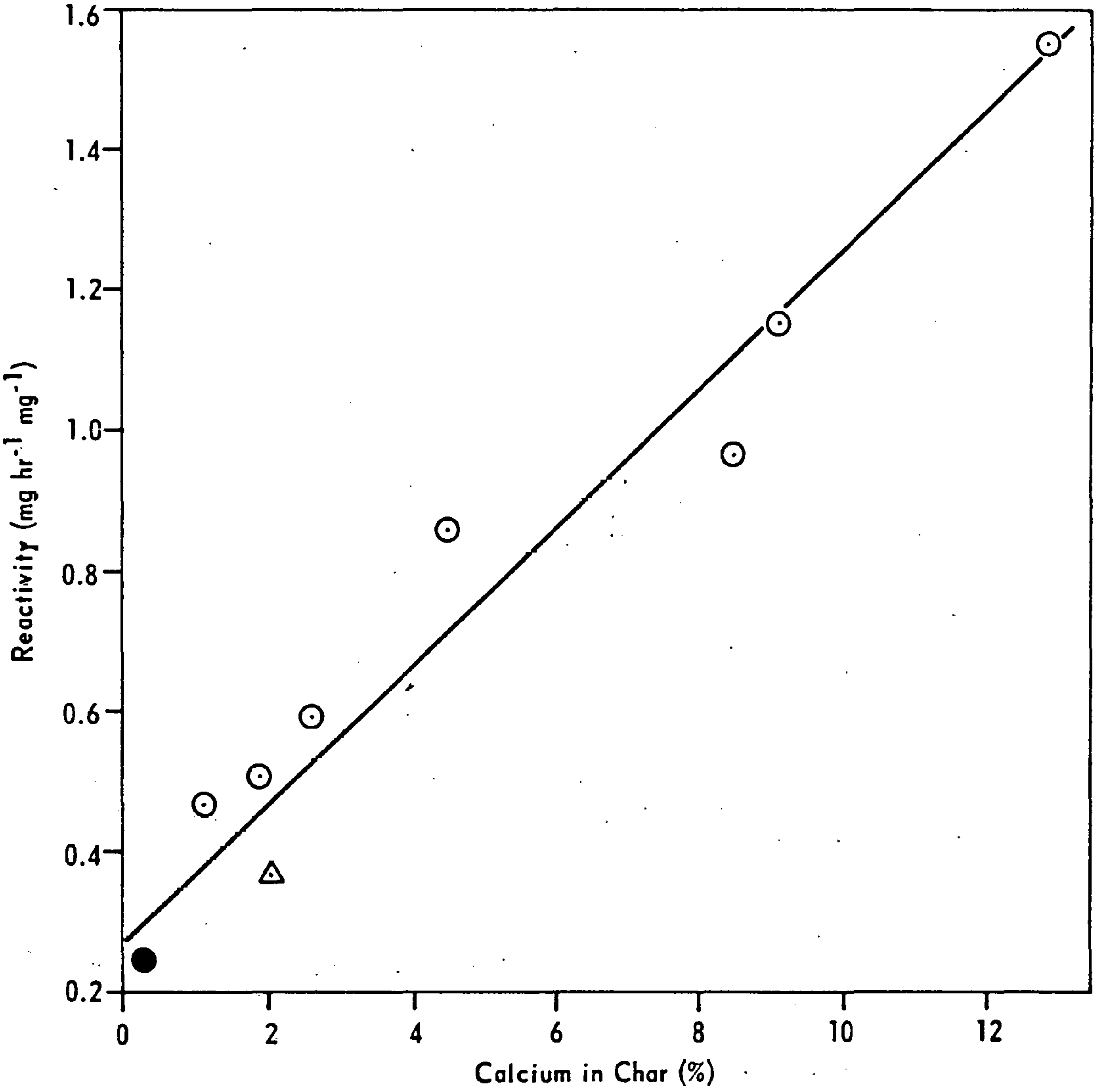


Figure 10. REACTIVITIES IN CO_2 AT 760°C OF 800°C CHARS PRODUCED FROM Ca^{++} EXCHANGED (⊙), RAW (△) AND DEMINERALIZED (●) COALS

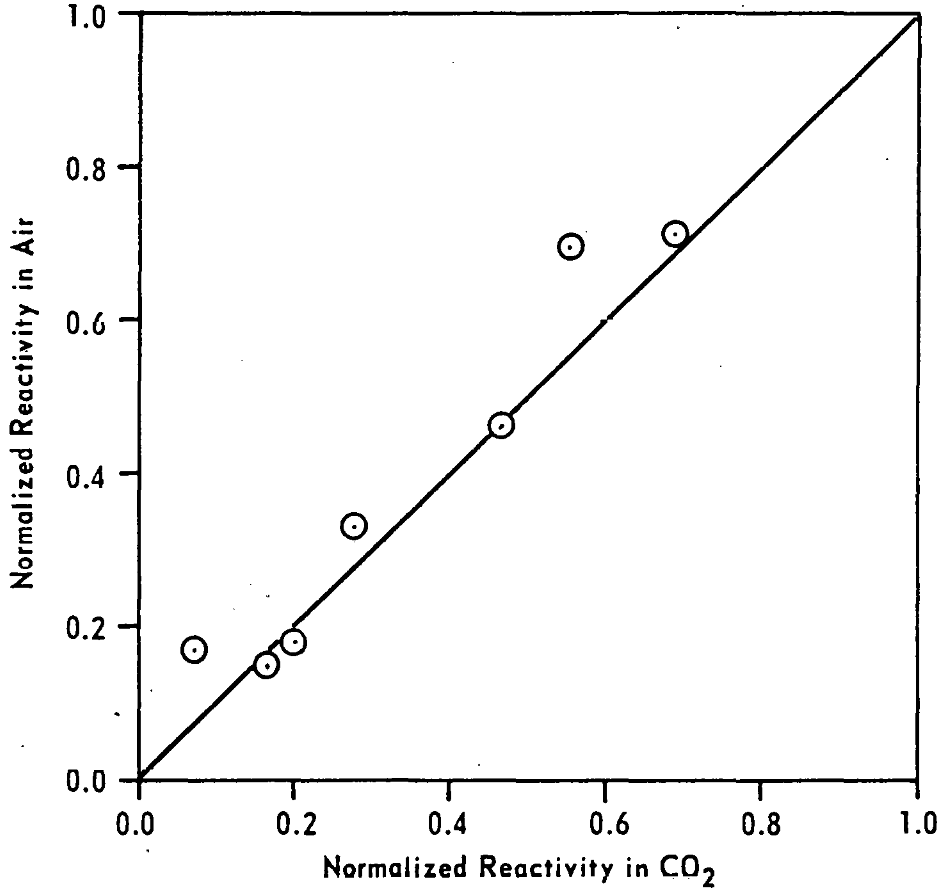


Figure 11. CORRELATION BETWEEN NORMALIZED REACTIVITIES OF VARIOUS CHARS IN CO_2 AND AIR

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

Chemisorption of Oxygen and Gasification of Carbonaceous Solids

The coal chars used in this study were prepared by carbonizing the parent coal in nitrogen at 1000°C for 2 hr. In one case, PSOC-91, the char was prepared (i) as mentioned above or (ii) by acid-washing (AW) the parent coal with hydrochloric (to partially eliminate the mineral matter associated with it) prior to the same carbonization step. The latter char is referred to as PSOC-91AW. For all chars, nitrogen-surface areas were determined. These are listed in Table 9, together with the corresponding carbon contents (%, daf) of the parent coals as well as some other parameters which will be explained shortly. Also included for comparison are some data that were previously obtained on the unactivated Saran char (150 x 250 mesh).

For each char, particle size 40 x 100 mesh, the DSC technique was used as described below. A constant known weight of the char (about 18 mg) was charged inside the cell, and then flushed with nitrogen for 5 min. The sample was outgassed, flushed with nitrogen at 45 cc/min, heated at 20°C/min up to 600°C, kept at this temperature for 30 min, and finally cooled to room temperature. Following this pretreatment, the char was held isothermally (in nitrogen) at 100°C for 45-90 min, to permit the attainment of thermal stability of the instrument (invariably smooth horizontal output base line). At this stage, oxygen was introduced to replace nitrogen at the same flow rate, and the thermogram was started. Values of Q(cal/g char) were computed for 30 min chemisorption time as described earlier.[3]

The dependence of Q at 100°C on reaction time is shown in Figure 12 for different coal chars and Saran char. Duplicate runs were made for PSOC-91 (raw), 89, and 98, thus confirming the excellent reproducibility of the DSC data points. It is worthy to note that: (i) lignite chars as well as subbituminous C char released the highest amount of heat upon oxygen chemisorption, (ii) the PSOC-91-AW sample released less heat than the original PSOC-91 char (containing all the mineral matter), and (iii) the Q-t plot for Saran char is located midway between chars produced from coals having carbon contents in the range of 63.3-93.3 percent. At 15 min reaction time, the amount of heat released, Q_{15} (cal/g char), was arbitrarily chosen for sake of comparison. Values of Q_{15} are listed in Table 9.

Let us consider the case of PSOC-91 and PSOC-91-AW. The original char has 10.9 percent (by weight) ash, while the AW-char has only 1.3 percent. These figures were directly determined by the TGA technique[4] during gasification runs. Values of R_{405} for the original and the AW-chars are 2.70 and 0.12, respectively. Thus the ratio of reactivities was 22.5. On the other hand, for oxygen chemisorption at 100°C, Q_{15} was only reduced from 6.13 to 3.06 cal/g char. That is, the ratio of reactivities was 2.0.

The latter observation was further supported by performing two identical TGA runs on the original and on the AW-91 chars. In brief, for each char, the weight of oxygen uptake, W, at 100°C was determined under conditions simulating those with the DSC runs. At 15 min reaction time, values of W for the original and AW-chars were 2.516 and 1.518 mg/g char, respectively (thus the weight of oxygen chemisorbed is reduced by a factor of 1.7).

Table 9. Characterization of Coal Chars,
Particle Size 40 x 100

PSOC Char #	Carbon Content of Parent Coal % (daf)	Nitrogen Surface Area (m^2/g)	R^*_{405}	Q_{15} (cal/g char)
89 (lig)	63.3	290	00	3.34-3.44
91 (lig)	70.7	31	2.70	6.13
87 (lig)	71.2	93	1.07	5.28
98 (Sub A)	74.3	11	0.60	2.50-2.58
101 (Sub C)	74.8	62	1.84	6.04
24 (hvBb)	80.1	25	0.46	2.88
81 (an)	91.9	1	0.11	0.38
91 (AW)	70.7	88	0.12	3.06
Saran (150 x 250)	24.7**	810-840	--	1.60

There are two possible explanations for this observed phenomenon. Probably the partial removal of mineral matter significantly eliminated those constituents which mostly catalyze gasification. Yet, the char surface was left with smaller concentrations of minerals (in the 1.3% ash content) which still were catalyzing the oxygen chemisorption reaction. It is known that for Saran chars, the addition of 80 ppm iron to the original char was associated with about a 25 percent increase in values of Q_{15} and W_{15}.[3] Thus trace amounts of iron have a significant catalytic effect on the oxygen chemisorption reaction. The other possible explanation may be directly related to the process of acid washing. It is reasonable to assume that part of the hydrochloric acid is adsorbed at the char surface, trapped inside the micropores, or is involved in forming a bond with functional groups protruding from the surface. When the char is held at 100°C, there is little chance for a chemical or a structural transformation to occur. However, at 405°C, the HCl or Cl^- ions may (i) poison the catalyst, (ii) spill over the surface and hence deactivate the sites, or (iii) change the structure of the catalyst in such a manner that it is no longer capable of dissociating oxygen. In all cases, this subject manner needs further experimental support.

In order to explore a possible correlation between Q_{15} and R_{405}, Figure 13 was constructed. For the limited number of chars studied so far, as R_{405} increases (from anthracite to lignite chars), Q_{15} increases and finally levels off at a constant value of about 6.1 cal/g char. This upper limit is found for chars having R_{405} greater than 1.8 g/hr/g. For the time being, little can be said about this relation before investigating a greater number of chars.

It is suggested that the DSC technique will be further used to scan more chars in the manner described. Chars produced from new acid treated coals will be considered. Comparative TGA runs will be made whenever needed.

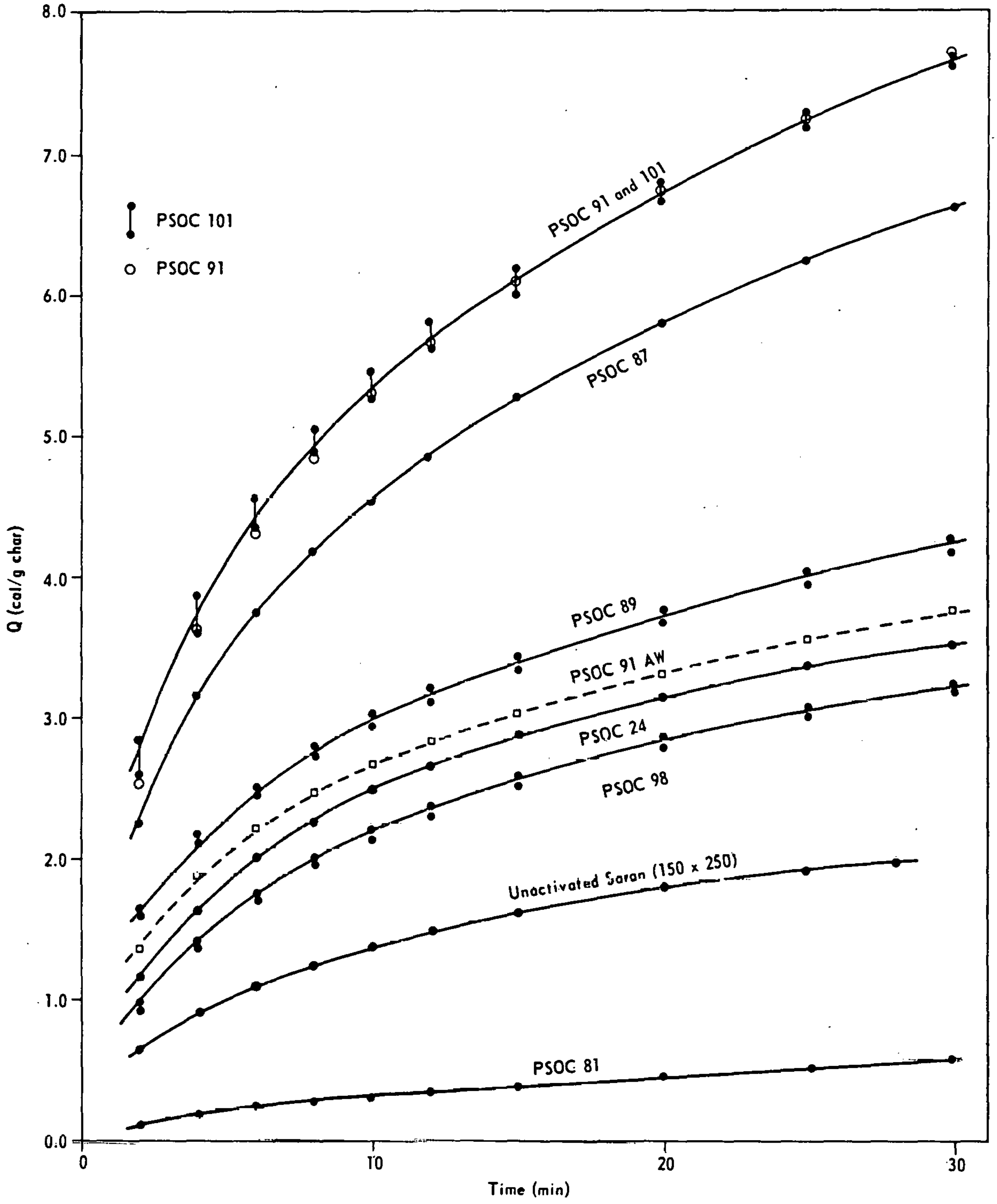


Figure 12. HEAT RELEASED FOR VARIOUS PSOC CHARS (40 X 100 MESH) WHEN EXPOSED TO OXYGEN AT 100°C

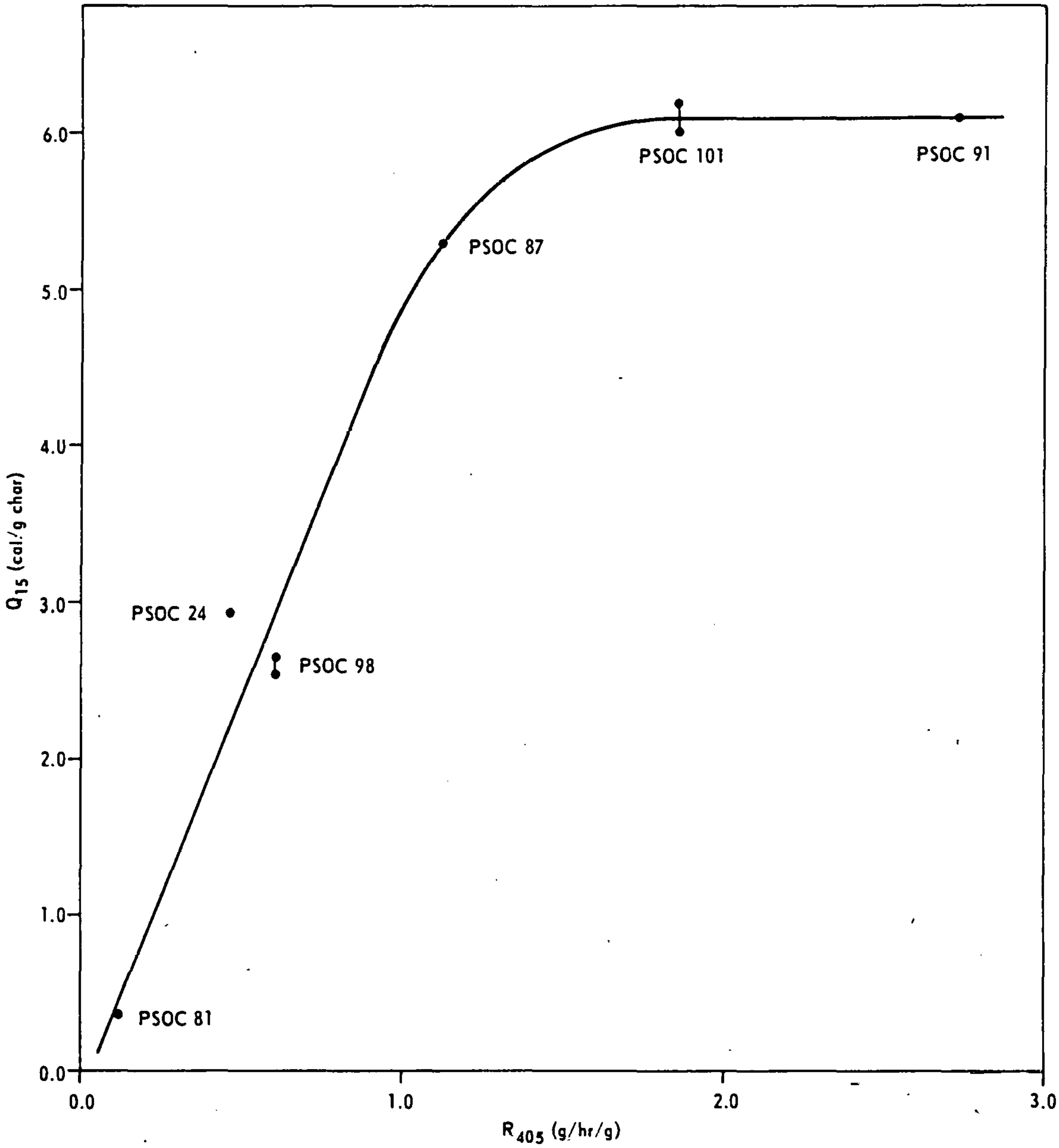


Figure 13. DEPENDENCE OF Q_{15} (CAL/G CHAR) FOR OXYGEN CHEMISORPTION AT 100 °C ON RATE OF GASIFICATION IN AIR AT 405 °C, R_{405}

CONCLUSIONS

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

Task 23: Operation of Isothermal Furnace

The volatile matter, VM_{TOTAL} liberated during a two-stage heating process in Hoskins furnaced did not differ significantly from the proximate volatile matter, VM_{ASTM}. The Q factor, or enhancement of volatile matter yield in the isothermal furnace cannot be attributed, therefore, to the two-stage heating process.

Weight loss, ΔW, determined using ash as a tracer consistently underestimated the yield of volatile matter, VM_{TOTAL} measured directly. Errors were approximately 5 percent. The Q factor is not a consequence, therefore, of using ash as a tracer to determine ΔW.

No significant weight loss occurred during the heating up time in the isothermal furnace, either initially or during subsequent recycles.

FACET IV-B: COKES AND CHARS

Task 27: Effects of Variables on Char Structure

The weight changes associated with low temperature preoxidation of coals can be followed reproducibly by use of a TGA apparatus. Thermomechanical studies have shown that a DuPont 942 TMA unit is a valuable quantitative tool for measuring swelling and plastic properties of coals. Swelling and softening parameters show a strong dependence on heating rate, load, and particle size. From these studies we conclude that the optimum TMA operating conditions to be rapid heating (50°C/min) of finely ground coal under a small load.

Task 28: Effect of Char Structure on Reactivities

The effect of preoxidation of a highly caking lvb coal on weight loss during pyrolysis up to 1000°C and reactivity of resultant char to air at 470°C have been investigated. Preoxidation markedly enhances the char reactivity; preoxidation to the extent of 3 wt percent increases char reactivity by a factor of 40. Results show that it is the extent of oxygen uptake rather than the preoxidation temperature which determines the reactivity of char produced.

Task 30: Effect of Catalytic Cations on Gasification

The reactivity of lignite char with carbon dioxide can be enhanced by the addition of calcium to the char. This is accomplished by prior addition of calcium to the precursor coal using cation exchange. Reactivity of a lignite char increases linearly with amount of calcium present up to at least 12.9 percent. Enhancement of reactivity in carbon dioxide is similar to that found previously in air and steam.

FACET IV-F: DIFFERENTIAL SCANNING CALORIMETRY

Task 31: Differential Scanning Calorimetry

For oxygen chemisorption on some coal chars at 100°C, the heat released at 15 min reaction time (for example, Q_{15}, is correlated to the corresponding reactivity in air at 405°C, R_{405}. As R_{405} increases, Q_{15} increases and finally becomes constant at 6.1 cal/g char.

Partial removal of mineral matter (PSOC-91) drastically suppresses the rate of gasification to a negligible value, but only reduces the rate of oxygen chemisorption by 50 percent.

REFERENCES

1. Abdel-Baset, M., Yarzab, R.F., and Given, P.H. Fuel, v 57, p. 89, 1978.

2. Hippo, E.J., and Walker, P.L., Jr. Effect of Cation Exchange on the Subsequent Reactivity of Lignite Chars to Stean. Tech. Rept. 4 of The Pennsylvania State University to DOE, 137 pp., March, 1977.

3. Ismail, I.K., and Walker, P.L. Thermochemistry and Kinetics of Oxygen Interaction with Microporous Chars. Tech. Rept. 12 of The Pennsylvania State University to DOE, 220 pp.,(January, 1979).

4. Soledade, L.E.B. Reactivity of Coal Chars in Air. M.Sc. Thesis, The Pennsylvania State University, May, 1976 (in press).

The following people have made contributions to this report: C.P. Dolsen, D.S. Hoover, I.K. Ismail, R. Jenkins, M. Komatsu, K. Kuehn, A. Linares, O.P. Mahajan, D. Maloney, M. Morgan, A. Scaroni, and R.L. Taylor.

☆U.S. GOVERNMENT PRINTING OFFICE: 1980-640-258/2326