DOE/PC/94063--T3

QUARTERLY TECHNICAL PROGRESS REPORT

AND KEY PERSONNEL STAFFING REPORT

NUMBER 3

PRODUCTION AND SCREENING OF CARBON PRODUCTS PRECURSORS FROM COAL

CARBON PRODUCTS CONSORTIUM

CONTRACT NO. DE-AC22-95PC94063

REPORTING PERIOD:

July 1, 1995 to September 30, 1995

Submitted to:

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Submitted by:

West Virginia University Research Corporation
on behalf of West Virginia University
617 N. Spruce Street
Morgantown, WV 26506

October, 1995

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Executive Summary

Tasks 1 and 2 involve preparation of a Project Management Plan and establishment of a Participants Agreement/Proprietary Information Agreement for members of the Carbon Products Consortium (CPC). These tasks are now complete. Task 3 is to provide a series of samples of solvent extracted coal to the CPC participants and to incorporate their feedback and suggestions into subsequent samples. As of September 30, 1995, UCAR has received two rounds of samples; Koppers has received one round of samples; ALCOA and AMOCO have not yet specified the types of samples they wish to receive; FMI has received one round of samples and has requested a rather large, five kilogram, sample of coal extracts to do multiple impregnation on a large carbon fiber preform. There are extensive communications between the WVU research team and the five industrial partners. Task 4, cooperation with MITRE on their preparation of an economic analysis of the solvent extraction, is complete. Task 5, Technology Transfer, is an on going endeavor with research team meetings, general CPC meetings, presentations of conference papers, and submission of required reports. The CPC is finally functioning as it has been envisioned, i.e., with the WVU solvent extracted coal materials being evaluated by several companies as precursor for their individual product lines. The companies are comparing the WVU materials with commercially available pitches and cokes.

1.0 Project Planning and Administration

The purpose of Task 1.0 is to prepare and submit to the DOE, a Project Management plan for the WVU portion of the Carbon Products Consortium (CPC) workplan. This Management Plan was submitted to PETC on July 2, 1995. It has been accepted by the COTR and by the contracts management staff. Task 1.0 is complete.

2.0 Consortium Administration and Reporting

The purpose of Task 2.0 is to establish a Participants Agreement (PA) and a Proprietary Information Agreement (PIA) for members of the CPC, to facilitate communications between CPC participants and the COTR, and to help secure, maintain and manage CPC funds obtained under this contract.

The PA and the PIA were finalized on September 1, 1995. It was necessary to revise the PA to define the category of Affiliated Participant for an organization which does not sign the PA or the PIA, but is involved with the work of the CPC. A copy of the revised PA was included with Monthly Status Report No. 8, September 1, 1995 - September 30, 1995.

All monthly status and quarterly technical reports have been submitted as required by the contract. In addition to the required reports, regular communications with the COTR have been maintained.

Extensive discussions and efforts are ongoing to try to maintain funding for the CPC program. The university and industrial contracts have been established as three year programs;

however, only one year of funding has been made available.

3.0 Coal Extraction

Under Task 3.0 and subtasks, WVU will provide a variety of types and sizes of samples of coal extracts to the industrial and national laboratory participants. Details of the coal extractions follow.

Equipment. During the reporting period the research team has obtained a new high temperature furnace for use in coking and calcining coal extracts. Furthermore, the WVU research team has built and is now testing a five to ten gallon capacity reactor for producing larger size batches of coal extracts.

3.1 Supplying Coal Extracts for Testing

3.1.1 Preparation of Screening Samples

Screening experiments were conducted with WVGS 13421 coal in tubing bomb reactors (nominal volume 50 mL) constructed out of stainless steel. A smaller diameter stainless steel tube was welded to the body of the reactor for purging and pressurizing with hydrogen gas.

Typically, 9 g of dried coal and 27 mL of tetralin were charged to the reactor and the system pressurized with 400 psig initial, cold hydrogen pressure. Catalytic additives were also examined to determine their effectiveness in altering pitch properties. The reactor was mounted on a shaker mechanism and agitated vertically at about 800 cycles per minute. The reactors were immersed in a fluidized sand bath heater and brought from ambient to reaction temperature. The reactors were held at the desired temperature for 1 hour after which the sand bath heater was removed and the reactors allowed to cool to room temperature slowly.

Following hydrogenation of the coal, the non-condensable gases were determined using a combined volumetric and gas chromatographic technique. N-methyl pyrrolidone (NMP) was used to wash out the reactor contents into a 250 mL flask. A condenser was attached to the flask and the mixture refluxed for 1 hour. The NMP-soluble product was separated from unconverted coal and mineral matter by vacuum filtration through a medium porosity, glass fitted filter. The filtrate was rotary evaporated to remove NMP and finally dried in a vacuum oven at 150 °C for about 1 day. The insoluble material was dried under similar conditions. Figure 1 outlines the steps used to produce the coal-derived pitches for the screening experiments.

The coal-derived pitches were sent to UCAR Carbon Company for evaluation. Their results were presented in the last quarterly report. The Department of Chemical Engineering at WVU also characterized the pitches and products, the results are presented in the following tables.

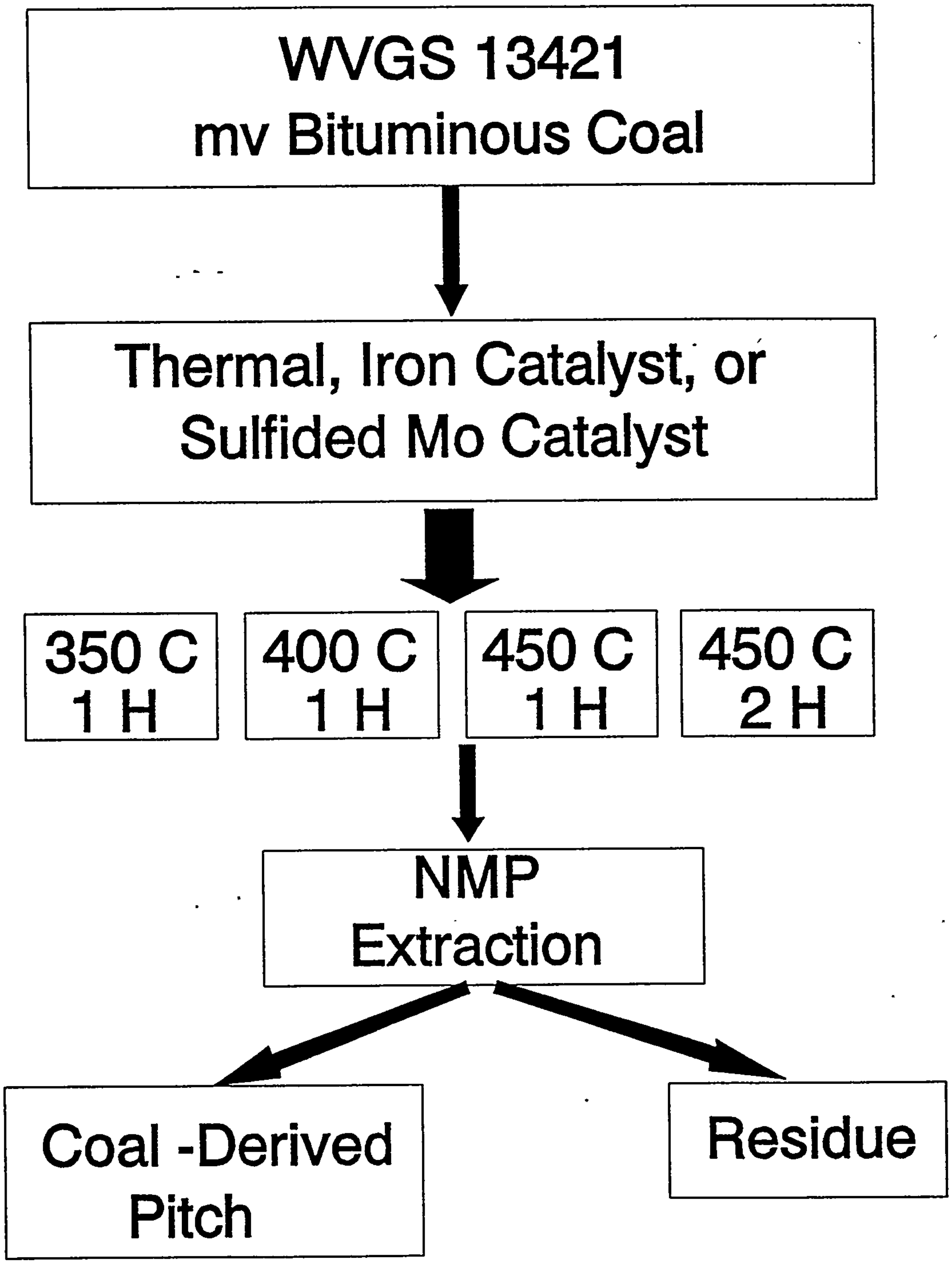

Figure 1. Process Steps for Screening Experiments.

TABLE 1

NMP-Soluble Product Yields from Hydrogenation of WVGS 13421
(3:1 tetralin:coal, 400 psig H_2 initial cold, duplicate runs)

Conditions	350°C,1H	400°C,1H	450°C,1H	450°C,2H
Thermal	74.5	89.5	88.2	87.7
Fe_2S_3	78.0	91.3	89.4	89.3
Sul'd Mo	ND	90.3	89.2	88.2

$$\text{Yield} = \frac{(\text{wt dry coal - wt dry residue})}{(\text{wt daf coal})} \times 100$$

TABLE 2

Total Gas Yield from Hydrogenation of WVGS 13421

Conditions	350°C,1H	400°C,1H	450°C,1H	450°C,2H
Thermal	0.0	0.6	4.1	6.8
Fe_2S_3	0.0	0.6	4.9	6.7
Sul'd Mo	0.0	0.6	4.8	10.0

$$\text{Gas Yield} = \frac{(\text{wt total gas})}{(\text{daf coal})} \times 100$$

TABLE 3

Gas Composition from Hydrogenation of WVGS 13421

Conditions	Gas Make	350°C,1H	400°C,1H	450°C,1H	450°C,2H
Thermal	CO_x	0.0	0.1	0.3	0.2
	CH_4	0.0	0.4	2.9	5.3
	C_2H_6	0.0	0.1	0.9	1.3
Fe_2S_3	CO_x	0.0	0.1	0.3	0.2
	CH_4	0.0	0.4	3.8	5.5
	C_2H_6	0.0	0.1	0.8	1.0
Sul'd Mo	CO_x	0.0	0.1	0.2	0.2
	CH_4	0.0	0.4	3.9	7.0
	C_2H_6	0.0	0.1	0.7	2.8

$$\text{Gas Make} = \frac{(\text{wt gas})}{(\text{wt daf coal})} \times 100$$

TABLE 4

Helium Density of NMP-Soluble Pitches (g/cc)

Conditions	350°C,1H	400°C,1H	450°C,1H	450°C,2H
Thermal	1.279	1.277	1.259	1.255
Fe_2S_3	1.274	1.253	1.261	1.256
Sul'd Mo	1.281	1.273	1.257	1.255

ASTM Method D4892-89

TABLE 5

Mettler Softening Point of NMP-Soluble Pitches (°C)

Conditions	350°C,1H	400°C,1H	450°C,1H	450°C,2H
Thermal	>350	>350	190.0	126.0
Fe_2S_3	>350	>350	155.6	123.3
Sul'd Mo	>350	>350	158.1	130.9

ASTM Method D3104-87

TABLE 6

Green Coke Yields from NMP-Soluble Products

Conditions	.350°C,1H	400°C,1H	450°C,1H	450°C,2H
Thermal	75.4	74.8	60.7	55.5
Fe_2S_3	74.0	74.7	58.7	51.4
Sul'd Mo	72.5	73.3	57.9	54.0

$$\text{Green Coke Yield} = \frac{\text{(wt green coke)}}{\text{(wt pitch)}} \times 100$$

Conditions: One-forth gram pitch in crucible packed in coke breeze. Five °C/min to 600°C and hold two hours and then cool to room temperature.

Based on the recommendations of UCAR Carbon Company, the conditions that appeared the most favorable for the production of coal-derived pitches should occur at 450 °C.

3.1.2 Bench-Scale Samples

After the small-scale screening experiments were completed, larger size materials were produced in 1-gallon autoclaves. These new products should be more typical of the kind of pitches that WVU will produce for the CPC members. Two coals were selected and the hydrogenation conditions used were 450 °C for either 1 or 2 hours. The table below identifies the pitches.

TABLE 7

Identification of Source Coal and Resultant Pitch

Coal	.... Hydrogenation Condition	Pitch ID
WVGS 13421	450°C, 1 Hour	A066
WVGS 13421	450°C, 2 Hours	A076
WVGS 13423	450°C, 1 Hour	A075
WVGS 13423	450°C, 2 Hours	A073

Typically, 600g of powdered coal and 1.8L tetralin were placed into the stirred reactor and pressurized to 200 psig, initial cold hydrogen pressure. Between 3 and 4 hours were required to reach final temperature after which several more hours were needed to reach ambient temperature.

The hydrogenated coal was transferred to a 10L rotary evaporator to remove unreacted tetralin. After tetralin removal, N-methyl pyrrolidone was added to the mixture and agitated at 140°C for 1 hour. The NMP-hydrogenated-coal slurry was transferred to a centrifuge to separate the solids from the pitch. Finally, the clean pitch was isolated from the NMP by rotary evaporation and then vacuum dried. Figure 2 outlines the steps involved in the production of the pitches. Some preliminary characterization data are also presented in the following tables.

TABLE 8

Characterization of Bench-Scale Coal-Derived Pitches

Pitch ID	[1]Mettler SP,°C	[2]Density,g/cc	[3]TI,wt%	Coke Yield,wt%
A066	155.8	1.264	22.3	62.4
A076	101.7	1.227	12.1	54.0
A075	129.3	1.220	19.8	54.7
A073	112.5	1.223	20.9	52.6

1) ASTM D3104-87, 2) ASTM D4892-89, 3) ASTM 4072-81, modified

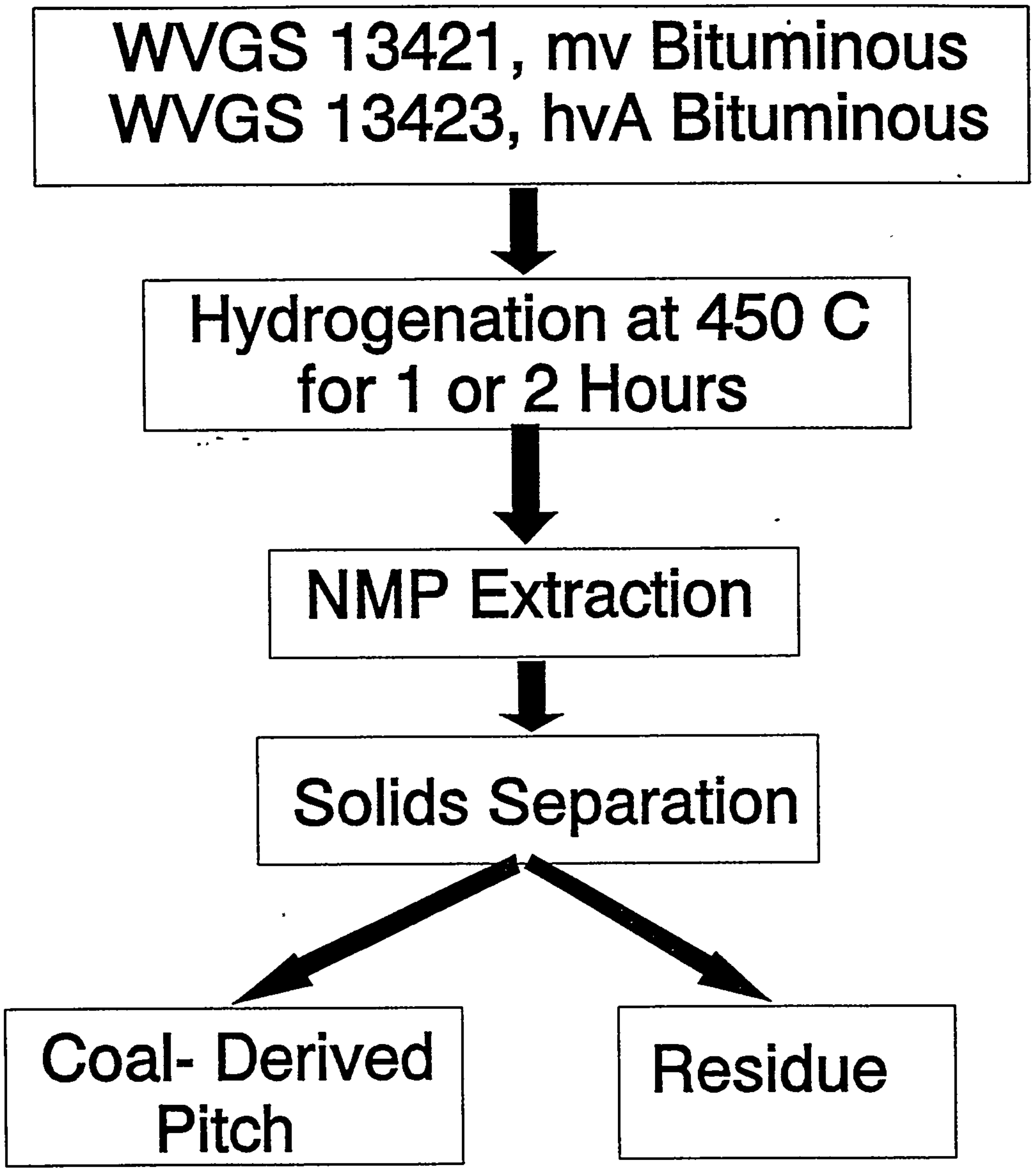

Figure 2. Process scheme for bench-scale experiments.

In order to eliminate as much NMP as possible from the coal pitch, the vacuum drying temperature and time were increased from 150 to 170°C for 48 instead of 24 hours, respectively. In some cases, the softening point values are not much different than the earlier values reported for the small-scaled experiment. These pitches were sent to UCAR Carbon Company for evaluation and testing.

3.1.3 Other Bench-Scale Pitches

About 1.5 kg of a coal-derived pitch was sent to FMI, Inc. for testing as an impregnation pitch. This material was produced by hydrogenation of WVGS 13421 at 450 °C for two hours. After the isolation of the NMP-soluble material as described above, the pitch was ground to pass a 8 mesh Tyler sieve and mixed at about 110 °C with toluene (6:1 toluene:pitch, vol:wt) for about an hour. The toluene-insoluble fraction was removed from the toluene-soluble (TS) fraction by centrifugation. After which the TS was dried in a vacuum oven overnight at about 170 °C.

Several pitches were also sent to Koppers for testing. Approximately 900 g each of three different coal-derived materials were produced. The table below identifies what the pitches are.

TABLE 9

Samples sent to Koppers for testing.

Pitch Identification	Pitch Description
D057-1	NMP-soluble extract from unhydrogenated WVGS 13423 coal.
D057-2	NMP-soluble extract from WVGS 13423 coal after hydrogenation at 450°C, 1 hour.
D057-3	NMP-soluble extract from WVGS 13423 coal after hydrogenation at 450°C, 1 hour, toluene-soluble fraction.

No characterization data are yet available, but will be reported as soon as they become available.

3.2 Production of Larger Quantities of Extracts

Work on this task is scheduled for year two of the project.

3.3 Pilot Plant Support

The WVU Chemical Engineering Department is negotiating an agreement with a large chemical company which would provide pilot plant size quantities of coal extracts.

4.0 Technical/Economic Evaluation of WVU Extraction Process

WVU provided all requested information to the MITRE Corporation for their economic analysis of the coal extraction process. A draft of the MITRE report was received in mid July, 1995 and a revised version was received in September, 1995.

The MITRE report suggests several process changes whose implementation on a larger scale could substantially reduce the cost of the coal extraction process. MITRE finds that coal extract based calcined coke for anodes could be produced for approximately $177 per ton. This is very promising since petroleum based calcined coke is already over $200 per ton in Europe and will soon exceed that amount in the United States. MITRE also recommends research on the production of isotropic carbon fibers from coal extracts of unhydrogenated coal. Such fibers are in the $8 to $10 range and the market is expected to double in the near future.

5.0 Technology Transfer

During the reporting period there have been several technology transfer sessions. Some of are listed below:

The WVU research team discussed the CPC program and market assessments of carbon products with the Dean of the College of Business and Economics at WVU.

Several members of the CPC presented papers at the International Carbon Conference in San Diego. Furthermore the CPC participants who were attending the conference had a dinner meeting to discuss UCAR results and the MITRE report. Mike Nowak of PETC attended this meeting.

UCAR, ORNL and WVU met in Pittsburgh to discuss UCAR and ORNL analysis of coal derived pitches and activated extraction residues.

The WVU research team met with NASA Langley engineers to discuss crash energy absorbing properties of carbon foams.

WVU and ORNL presented papers on CPC related work at the Pittsburgh Coal Conference. See Attachments 1 and 2.

An ORNL representative presented a paper on analysis of solvent refined coal at the International Coal Science Meeting in Spain. See Attachment 3.

WVU, Koppers, and UCAR were represented at the Great Lakes Carbon Coke Quality Conference in Houston.

ATTACHMENT 1

PRODUCTION AND STRUCTURE OF COKES DERIVED FROM COAL LIQUIDS

PETER G. STANSBERRY

JOHN W. ZONDLO AND ALFRED H. STILLER
Department of Chemical Engineering
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Morgantown,WV 26506-6102

Copy of Transparencies of Talk
Given at 1995 Pittsburgh Coal Conference
September 13, 1995

TOPIC AREAS

- Preparation of coal "pitches"
- Conversion to coke and graphite
- Characterization of carbonization process

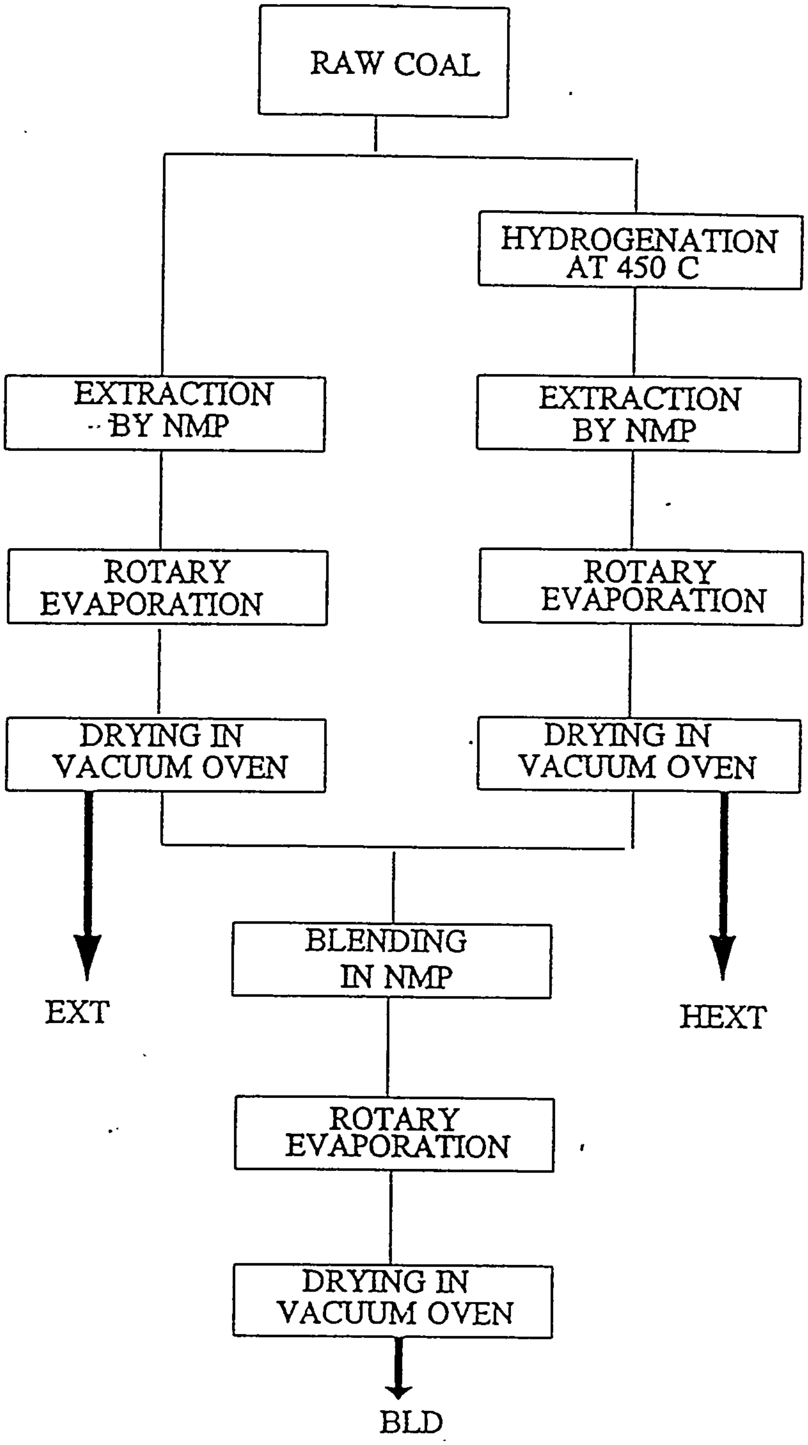
WVGS Designation	WVGS 13421	WVGS 13423
WV Geological Designated Coal Bed	Powellton	Lower Powellton
County	Raleigh	Mingo
State	West Virginia	West Virginia
ASTM Rank	mvb	hvAb
Mean-Maximum Reflectance of Vitrinite	1.111	1.002

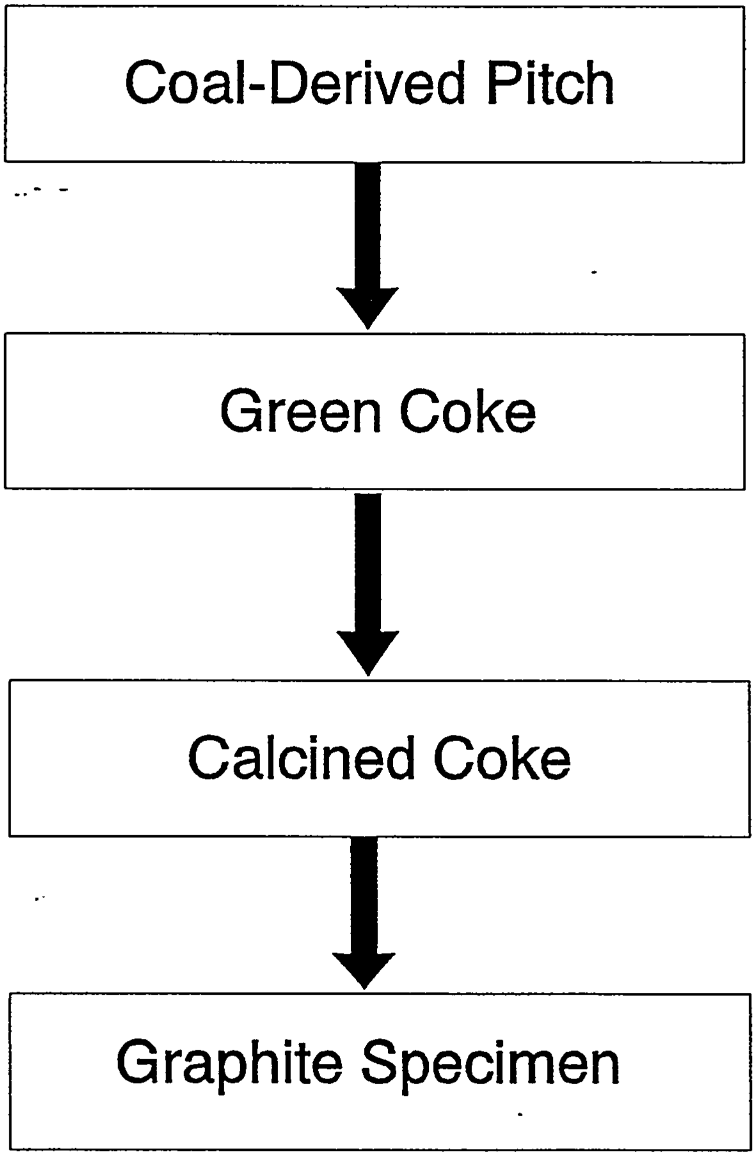
Proximation Analysis (as received)

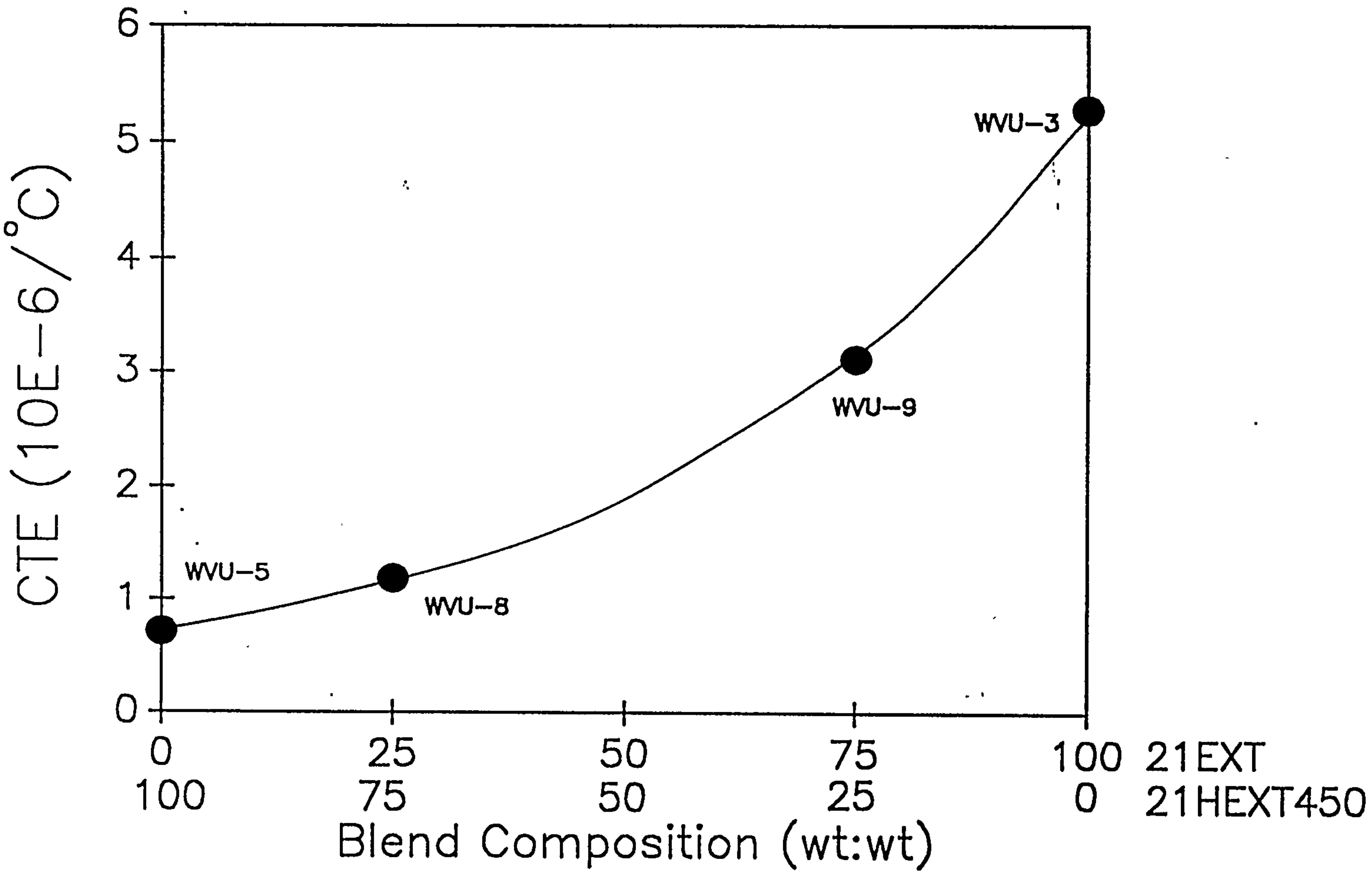
Moisture	0.98	0.82
Fixed Carbon	67.87	60.49
Volatile Matter	27.96	34.41
Ash	3.19	4.27

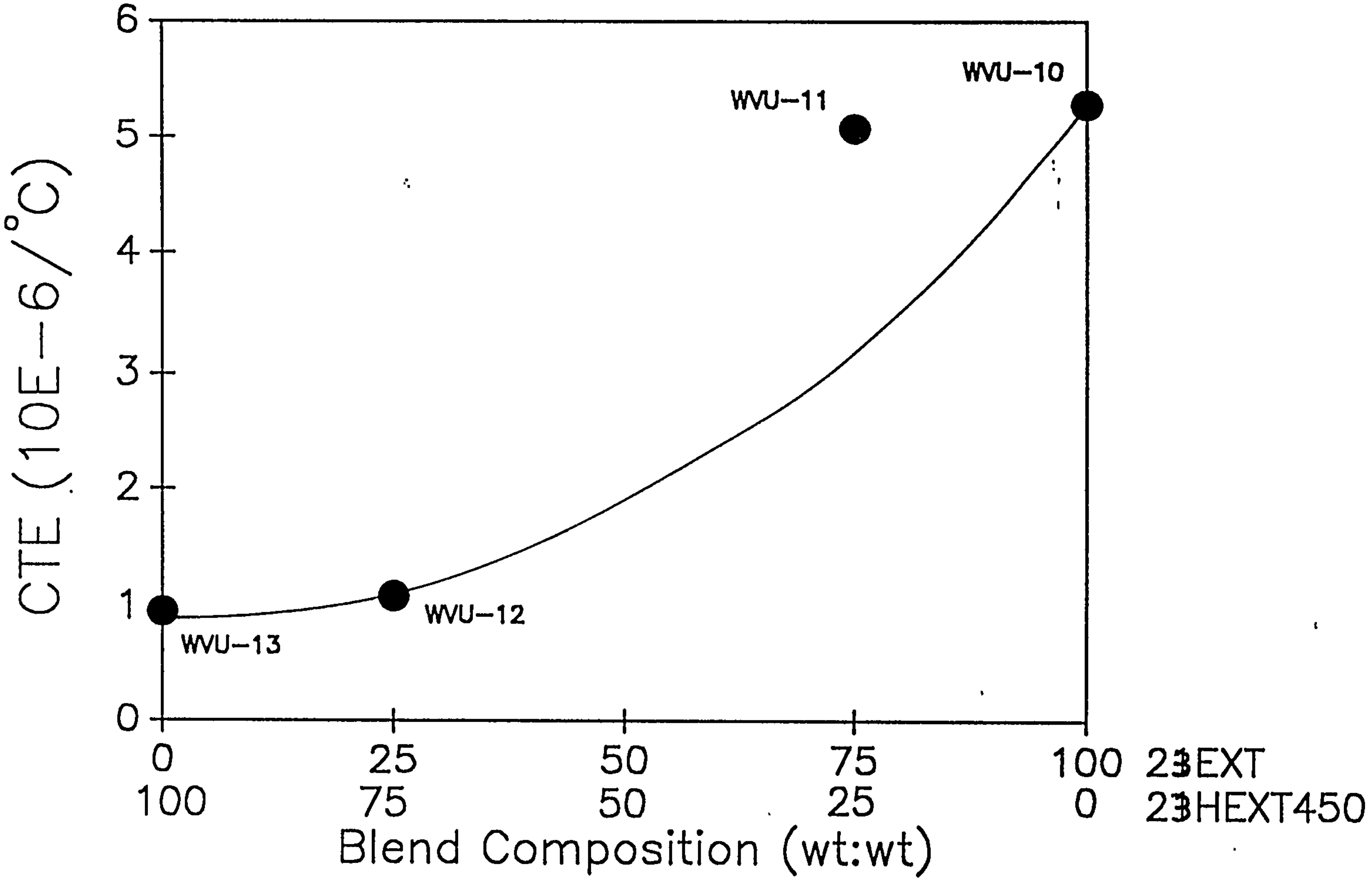
Petrographic Composition

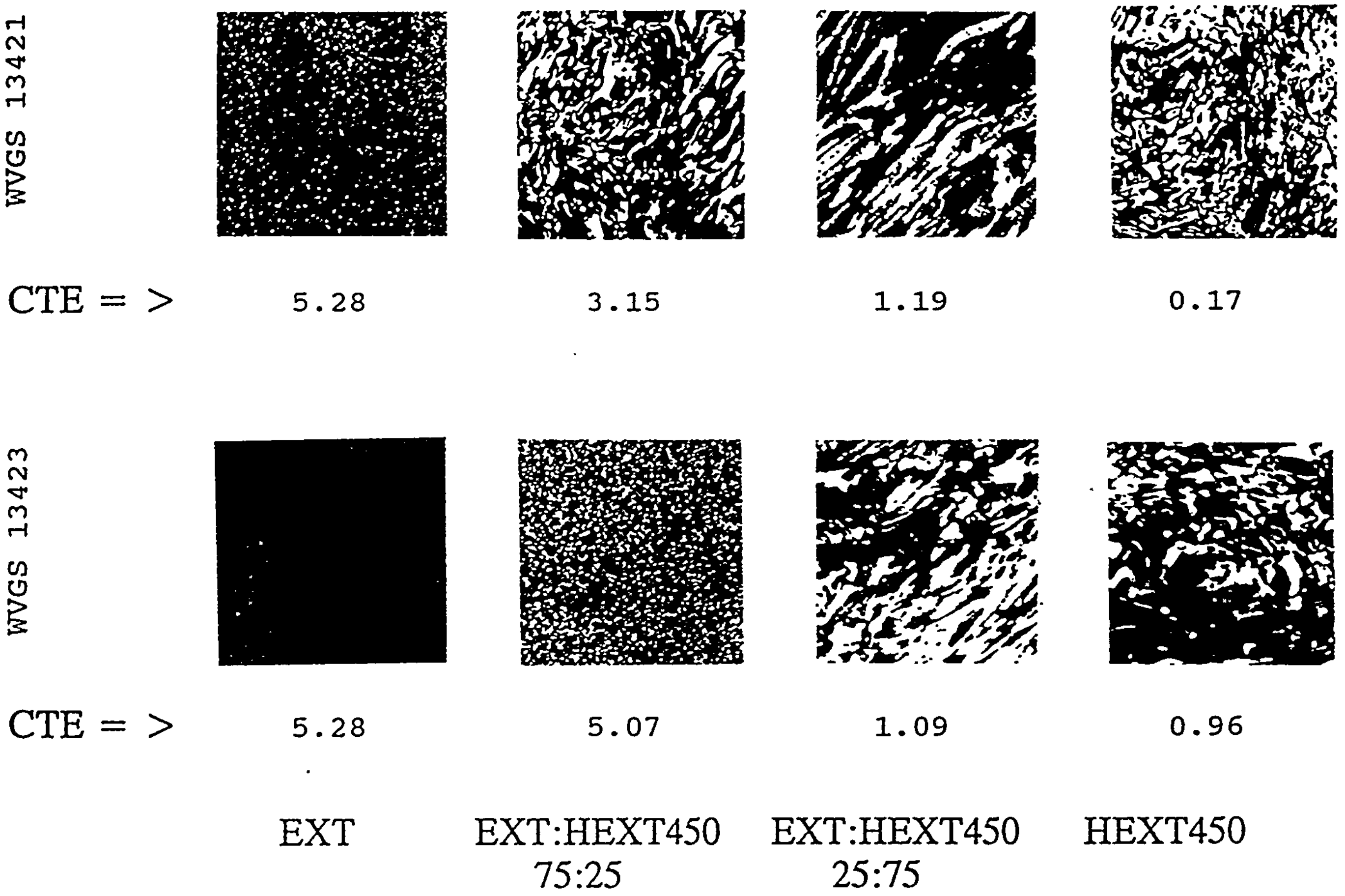
Vitrinite	63.3	71.4
Exinite	5.7	5.5
Inertinite	30.0	21.7

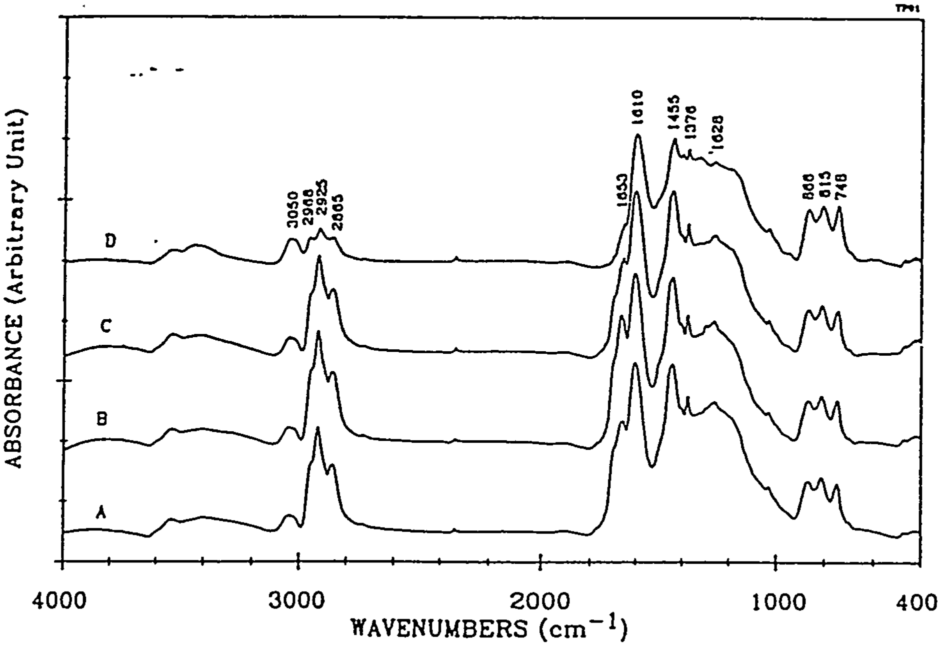

RAW COAL
HYDROGENATION AT 450 C
EXTRACTION BY NMP
EXTRACTION BY NMP
ROTARY EVAPORATION
ROTARY EVAPORATION
DRYING IN VACUUM OVEN
DRYING IN VACUUM OVEN
EXT
HEXT
BLENDING IN NMP
ROTARY EVAPORATION
DRYING IN VACUUM OVEN
BLD


Coal-Derived Pitch
Green Coke
Calcined Coke
Graphite Specimen


CTE (10E−6/°C)
6
5
4
3
2
1
0
WVU−3
WVU−9
WVU−8
WVU−5
0
100
25
75
50
50
75
25
100
0
21EXT
21HEXT450
Blend Composition (wt:wt)


CTE (10E−6/°C)
6
5
4
3
2
1
0
WVU-10
WVU-11
WVU-12
WVU-13
0 25 50 75 100 23EXT
100 75 50 25 0 23HEXT450
Blend Composition (wt:wt)


WVGS 13421
CTE = >
5.28
3.15
1.19
0.17
WVGS 13423
CTE = >
5.28
5.07
1.09
0.96
EXT
EXT:HEXT450
75:25
EXT:HEXT450
25:75
HEXT450



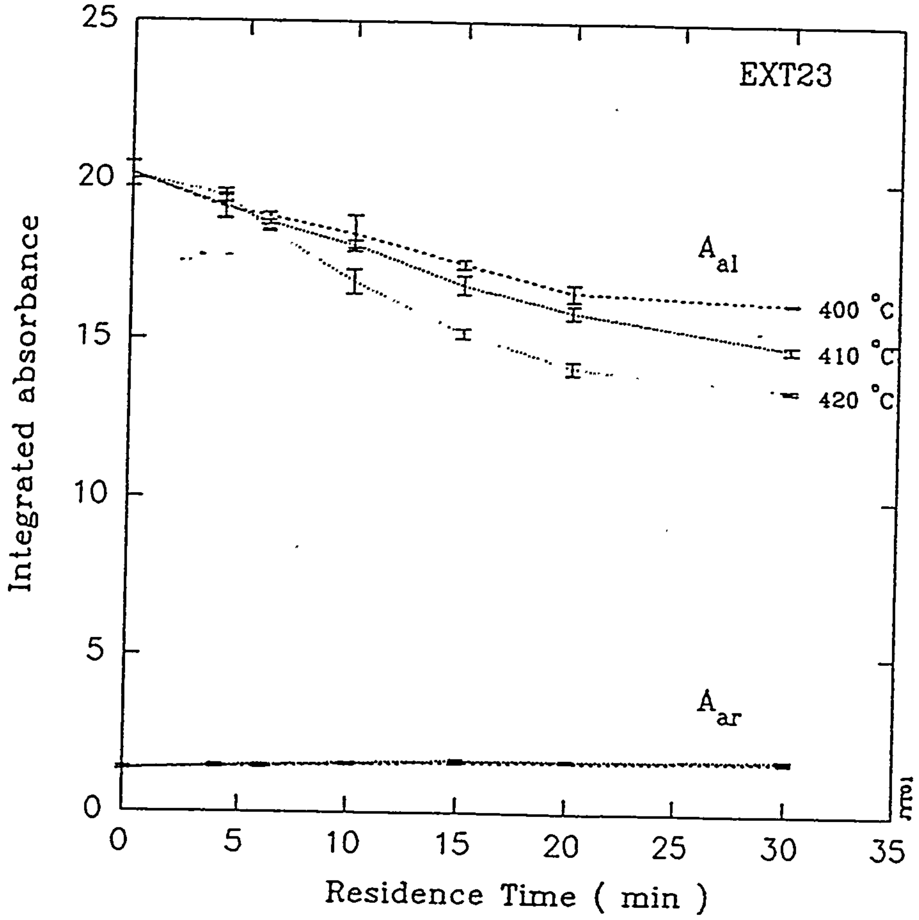
FTIR Spectra of Precursor EXT21 (A); and its Semicokes Made at 300 °C (B), 375 °C (C), and 420 °C (D) for 60 min Soak Time

QUESTION

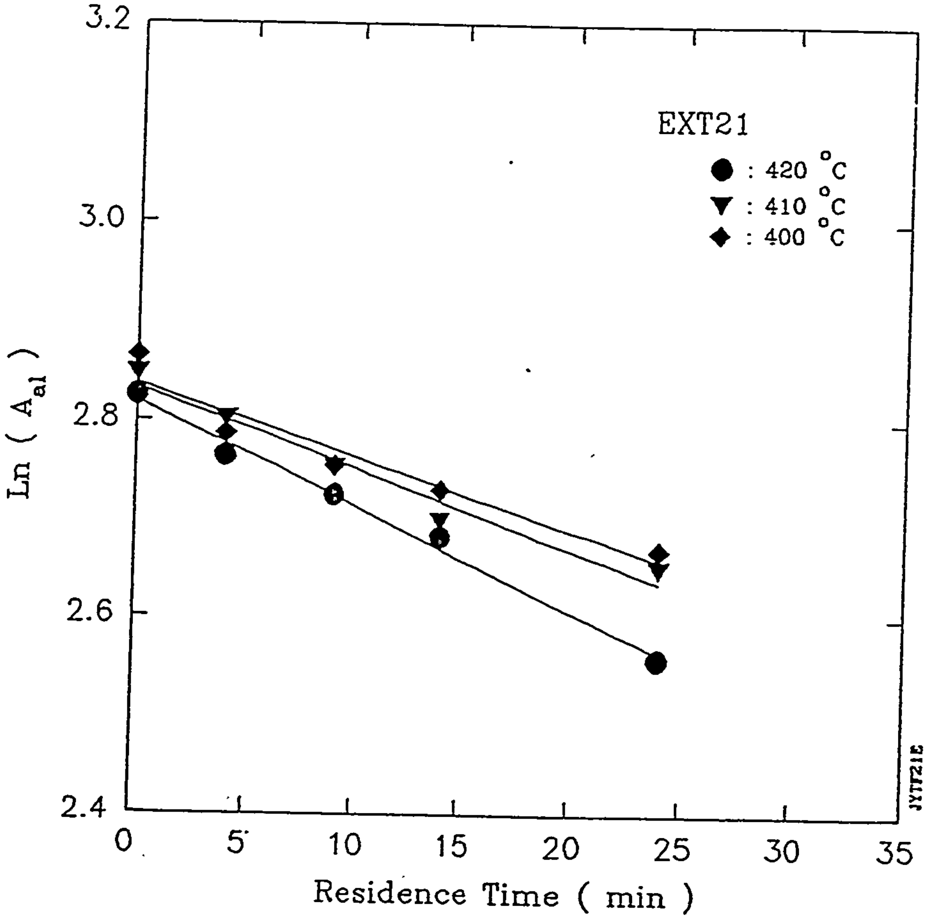
- Is the ability of HEXT to modify the carbonization of EXT-related to hydrogen utilization?

APPROACH TO PROBLEM

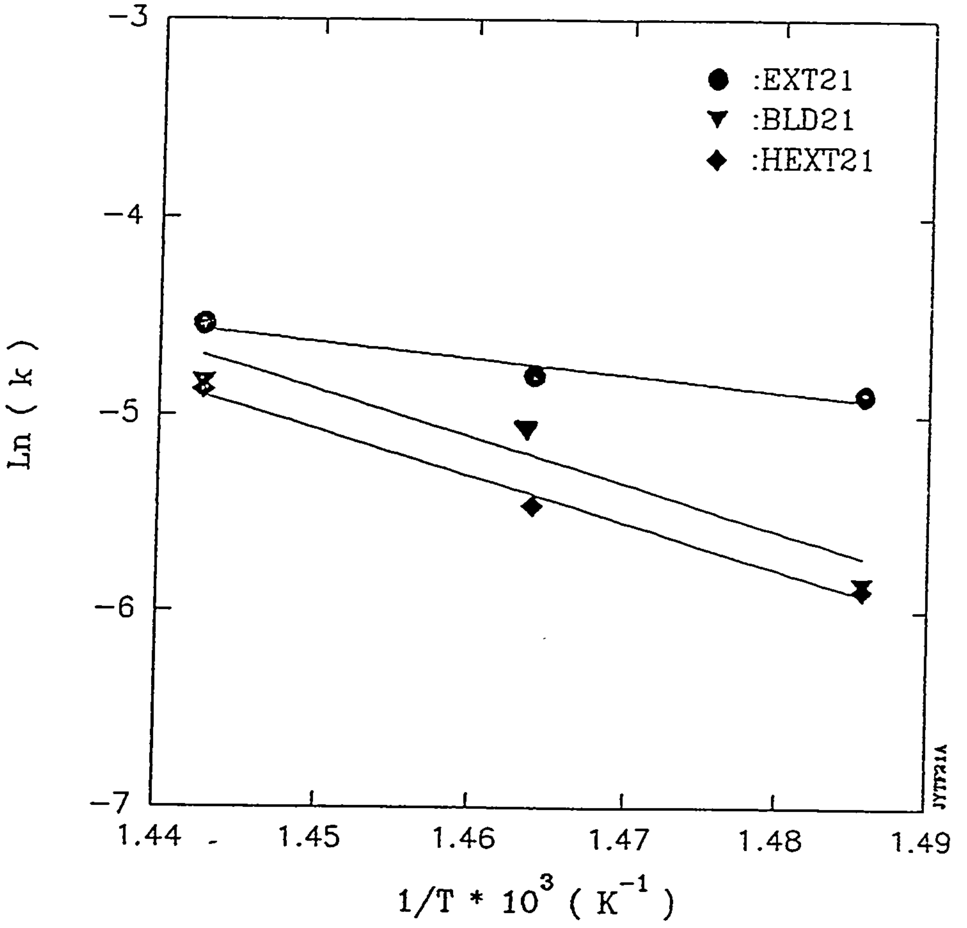
- * Prepared carbonized samples in tube reactors
- * Kept reaction times to less than 1/2 hour--view that initial events determine coke structure and properties
- * Applied quantitative FTIR to follow aliphatic (A_{al}) and aromatic (A_{ar}) hydrogen distribution
- * Modeled changes in A_{al} using first order kinetics



Effects of Temperature and Residence Time on Changes of A_{al} and A_{ar} for Precursor EXT23



Relationships between Ln (A_{al}) and Residence Time for Precursor EXT21



Arrhenius Plots for Precursors EXT21, BLD21, and HEXT21

APPARENT ACTIVATION ENERGIES

Sample	E_a(Kcal/mole)	R
EXT21	17	0.96
BLD21	48	0.90
HEXT21	47	0.99

Sample	E_a(Kcal/mole)	R
EXT23	34	0.99
BLD23	41	0.99
HEXT23	71	0.89

SUMMARY

* Coals can be converted into cokes and graphites with controlled properties

* Structure of cokes appear to be related to the fate of aliphatic hydrogen

ATTACHMENT 2

A STUDY OF SOLVENT-REFINED COAL USING THERMOGRAVIMETRY AND MASS SPECTROSCOPY

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A STUDY OF SOLVENT-REFINED COAL USING THERMOGRAVIMETRY AND MASS SPECTROSCOPY

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The authors wish to express their appreciation to Peter G. Stansberry and John W. Zondlo (Department of Chemical Engineering) and Caulton L. Irwin (National Research Center for Energy and the Environment), West Virginia University, Morgantown, WV, for making these samples and information concerning the NMP extraction process available to us for study.

Research sponsored by the U. S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program [DOE/FE AA 15 10 10 0, Work Breakdown Structure Element ORNL-3(F)] under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

INTRODUCTION

Coal is an abundant raw material for a wide variety of carbon-based products. Many applications require that the raw coal be purified to remove undesirable components (such as sulfur and mineral matter) prior to use. A coal-sourcing model was developed by the West Virginia Geological and Economic Survey (WVGES) to specify, locate, and evaluate coal resources for these purposes. As a part of the WVGES study, fifteen coals (mostly from West Virginia) were extracted using NMP (n-methyl-pyrolidone). The solvent extraction yields that were determined are strongly dependent on coal rank, and ranged from 0.0 to 66.3% by weight.

METHODS

Samples of raw coal, soluble extract, and insoluble residue were gently crushed to a coarse powder and sieved to obtain the 35-60 mesh (0.25 to 0.5 mm) fraction.

A combined thermogravimetry-mass spectrometry (TG-MS) method was used to analyze the samples. The apparatus comprises a computer-automated Mettler Thermoanalyzer (model TA-1) combined with a UTI (model 100C) quadrapole mass spectrometer for analyzing the composition of the outlet gases. Each sample was analyzed three times: 1) in pure helium (to evaluate the volatile components); 2) the residue of the previous helium pyrolysis was then oxidized in an artificial air mixture comprising 80% helium and 20% oxygen (to evaluate the oxidation of the pyrolysis residue); and 3) a new sample was subjected to oxidative pyrolysis using the same artificial air mixture as in (2) above (to evaluate the effects of oxidation during pyrolysis).

RESULTS AND DISCUSSION

The magnitude and rate of mass loss from each sample are dependent upon several factors, including the initial composition of the sample, previous treatment of the material, and the composition of the gas phase present in the chamber of the thermoanalyzer. Details of the mass losses are more readily observed on the rate (time-derivative, dm/dt) data. The mass spectroscopic data reveal the specific volatile components released and the sequence in which they are released.

Mass losses may occur for several reasons:

1. H_20, CO_2, etc., may be released from clay minerals, carbonates, and other mineral matter present in the original coal. H_20 may be released from clay minerals at temperatures below 200°C.

2. A number of volatiles are produced as degradation products when inherent functional groups in the sample combine. For example, an "XX-OH" component may combine with a "YY-OH" component to produce "XX-O-YY" plus H_20 (gas). Other reactions may produce H_2O, CO_2, N_2, etc. Methane, ethane, and more complex C-H phases (or fragments derived from them) may also be released during heating of the sample.

3. During oxidative pyrolysis, the coal ("CxHyOz") may react with O_2 (gas) to produce CO_2 (gas), CO (gas), H_2O (gas), etc.

The TG data for samples pyrolyzed in helium reveal that the percentage of sample remaining increased about 7% (insoluble residue compared with the raw coal) and decreased about 4% (soluble extract compared with the raw coal). When fresh samples are subjected to oxidative pyrolysis, oxidation begins at temperatures in the vicinity of 400°C and the reactions cease by the time 600°C is reached; however, when the residues of helium pyrolysis are subject to oxidation, temperatures in excess of 500°C are required before oxidation is renewed and the second period of oxidation does not cease until a temperature of in the vicinity of 800°C is reached.

The insoluble residue appears to contain virtually all of the mineral matter present in the raw coal with 38 wt. % of the original sample mass remaining after oxidation. On the other hand, the soluble extract appears to be nearly free from mineral matter with <1 wt. % of the original sample mass remaining after oxidation.

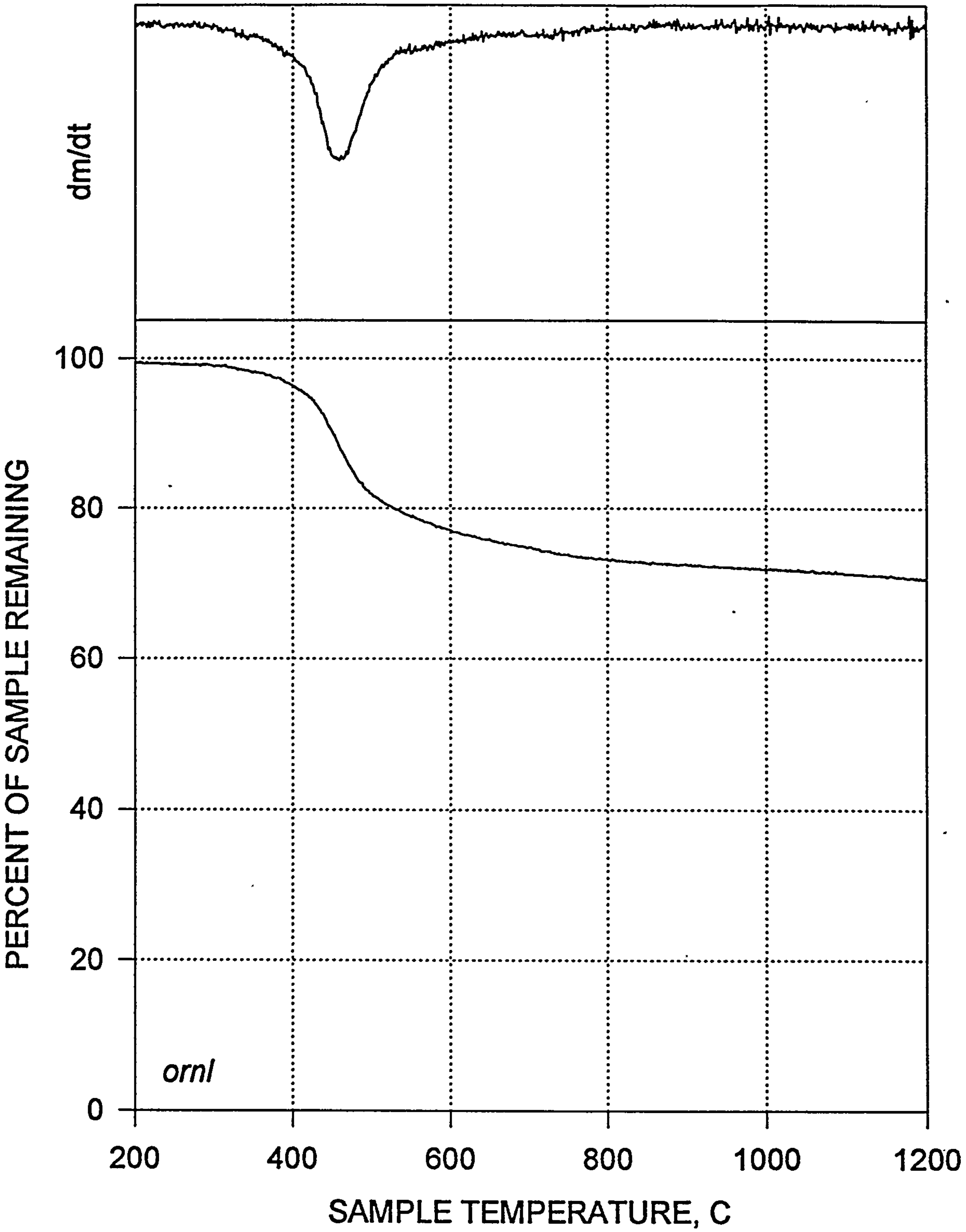
TABLE 1. Mass losses for samples pyrolyzed under different conditions.

Sample[a]	Mass remaining (wt. %)
Raw Bakerstown Coal (helium pyrolysis)	71
Raw Bakerstown Coal (oxidation after helium pyrolysis)	15
Raw Bakerstown Coal (oxidative pyrolysis)	15
Insoluble Residue (helium pyrolysis)	78
Insoluble Residue (oxidation after helium pyrolysis)	38 (see note b)
Insoluble Residue (oxidative pyrolysis)	38
Soluble Extract (helium pyrolysis)	67
Soluble Extract (oxidation after helium pyrolysis)	<1
Soluble Extract (oxidative pyrolysis)	<1

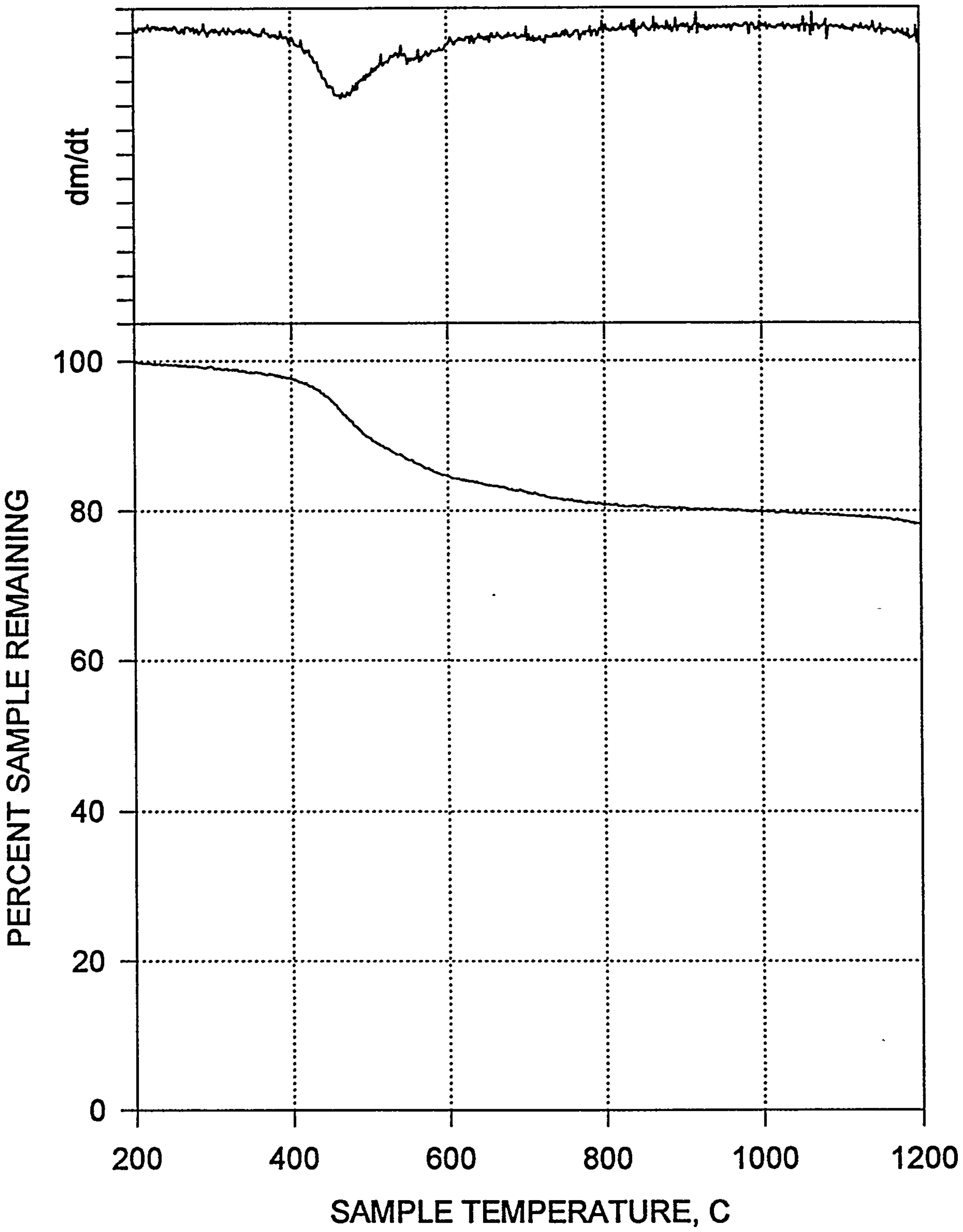
[a] The Bakerstown Coal contains 28% volatile matter on a moisture-free basis and 16% ash on a moisture-free basis.

[b] Corrected for mass change after cooling of residue of helium pyrolysis and oxidation of the residue.

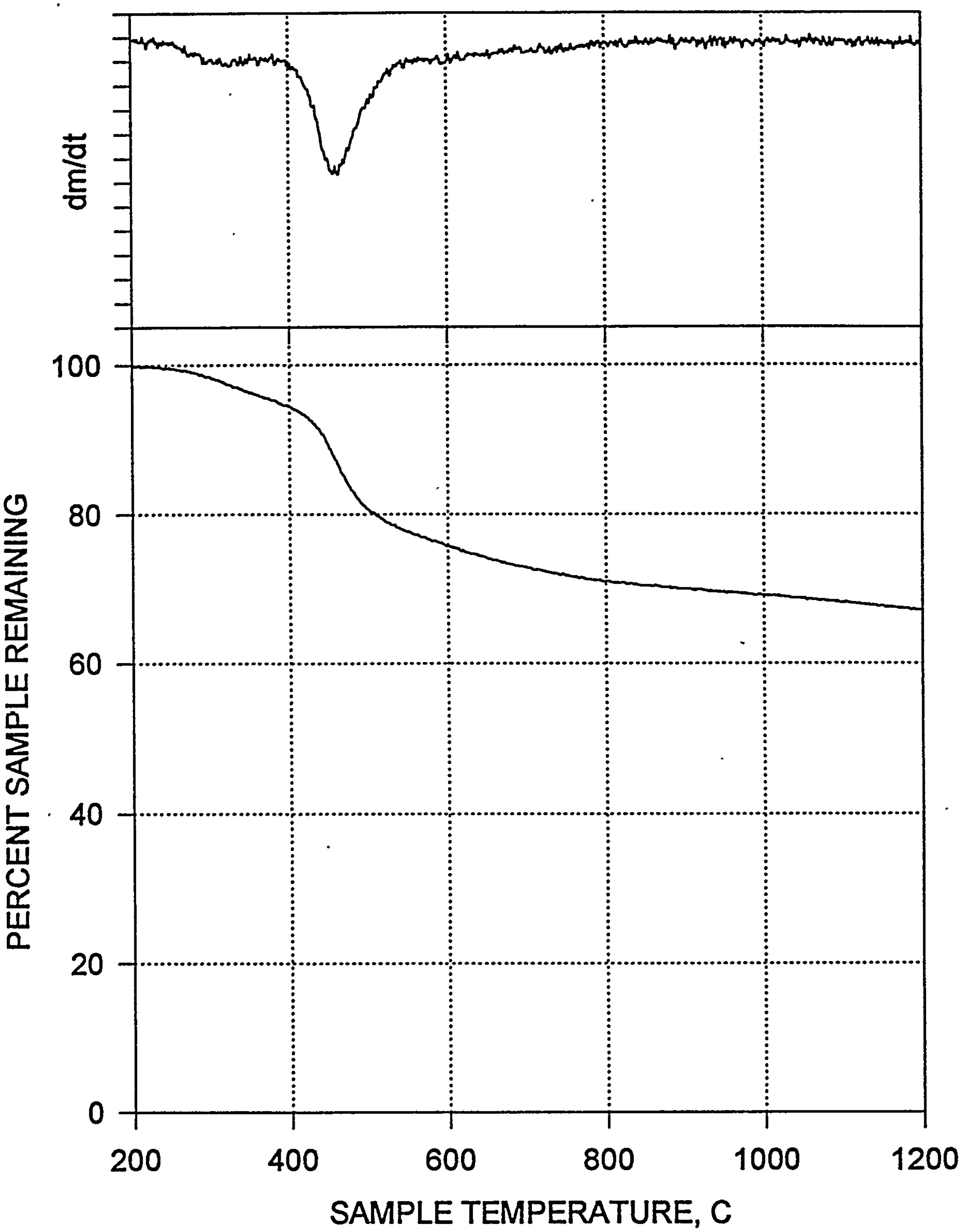
BAKERSTOWN IN HELIUM



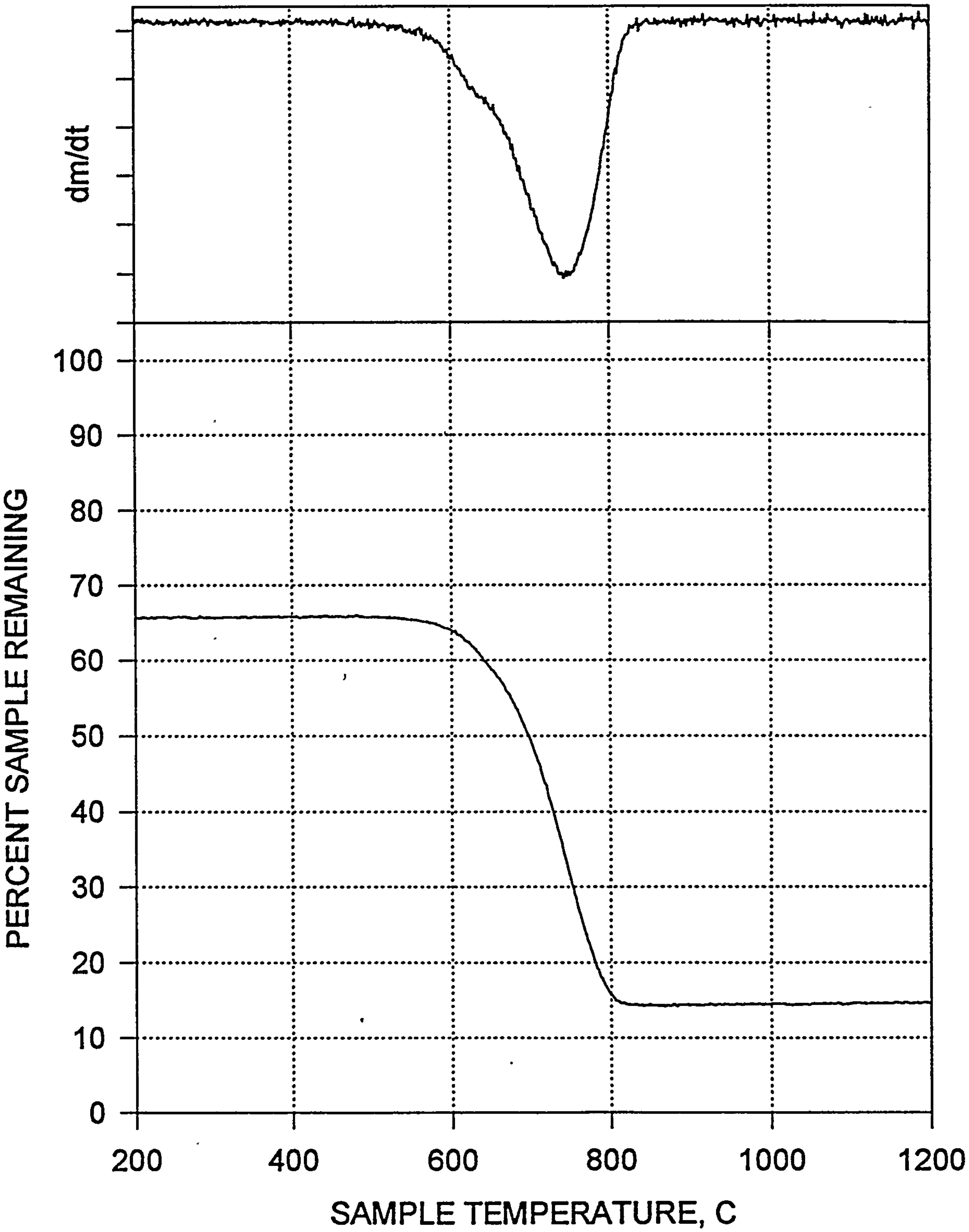
BAKERSTOWN INS0LUBLE RESIDUE IN HELIUM



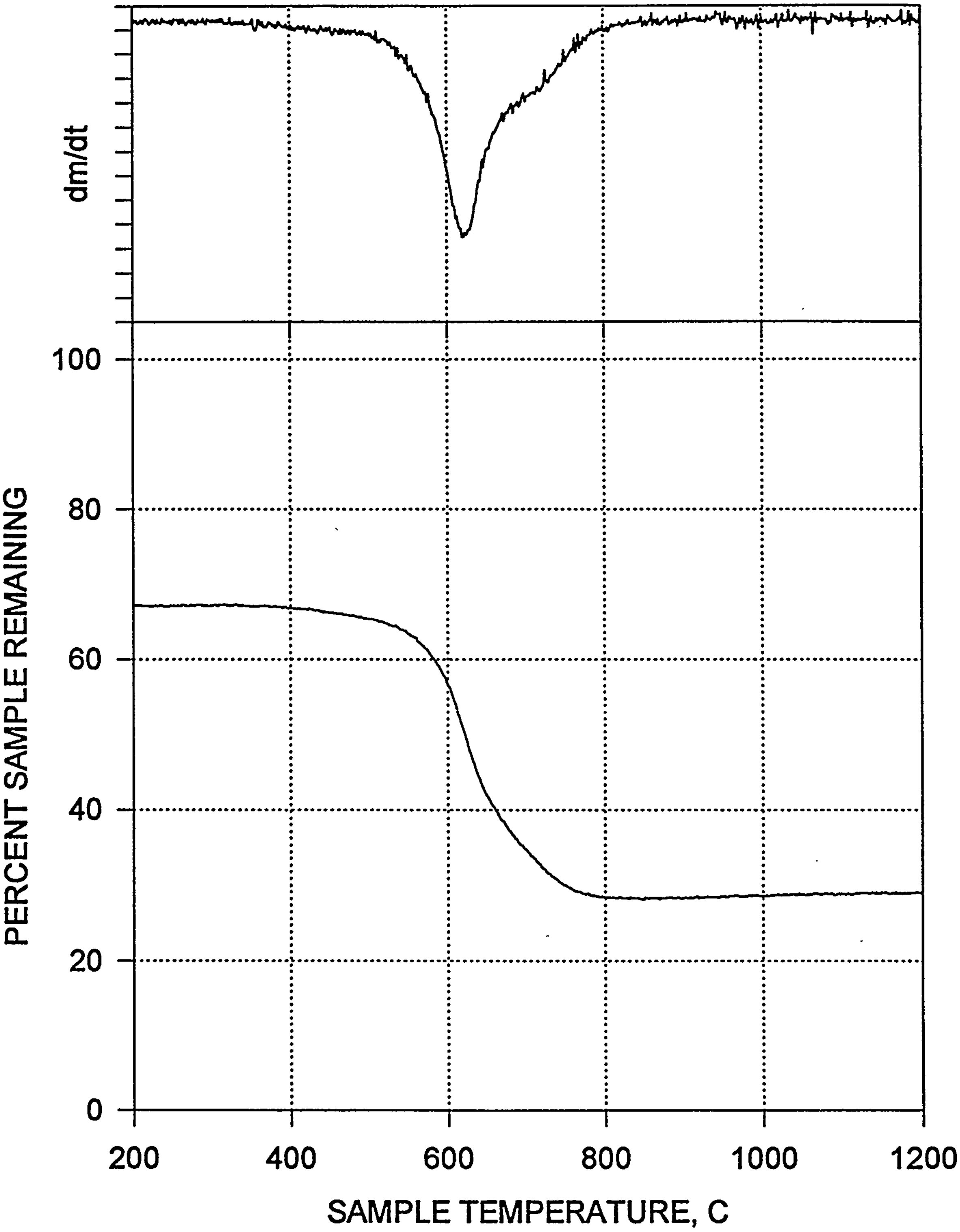
BAKERSTOWN SOLUBLE EXTRACT IN HELIUM



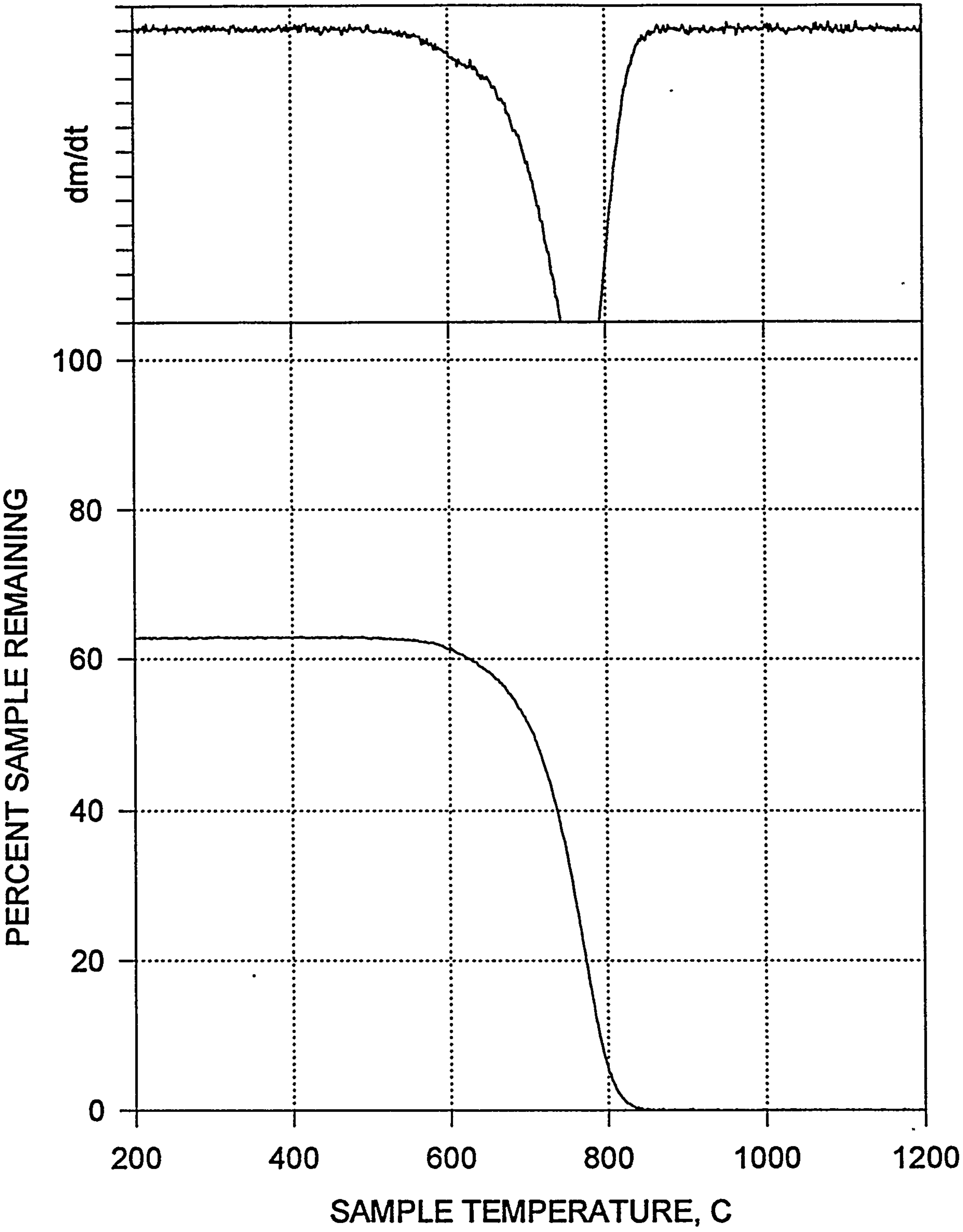
BAKERSTOWN IN 20 % OXYGEN AFTER HELIUM PYROLYSIS



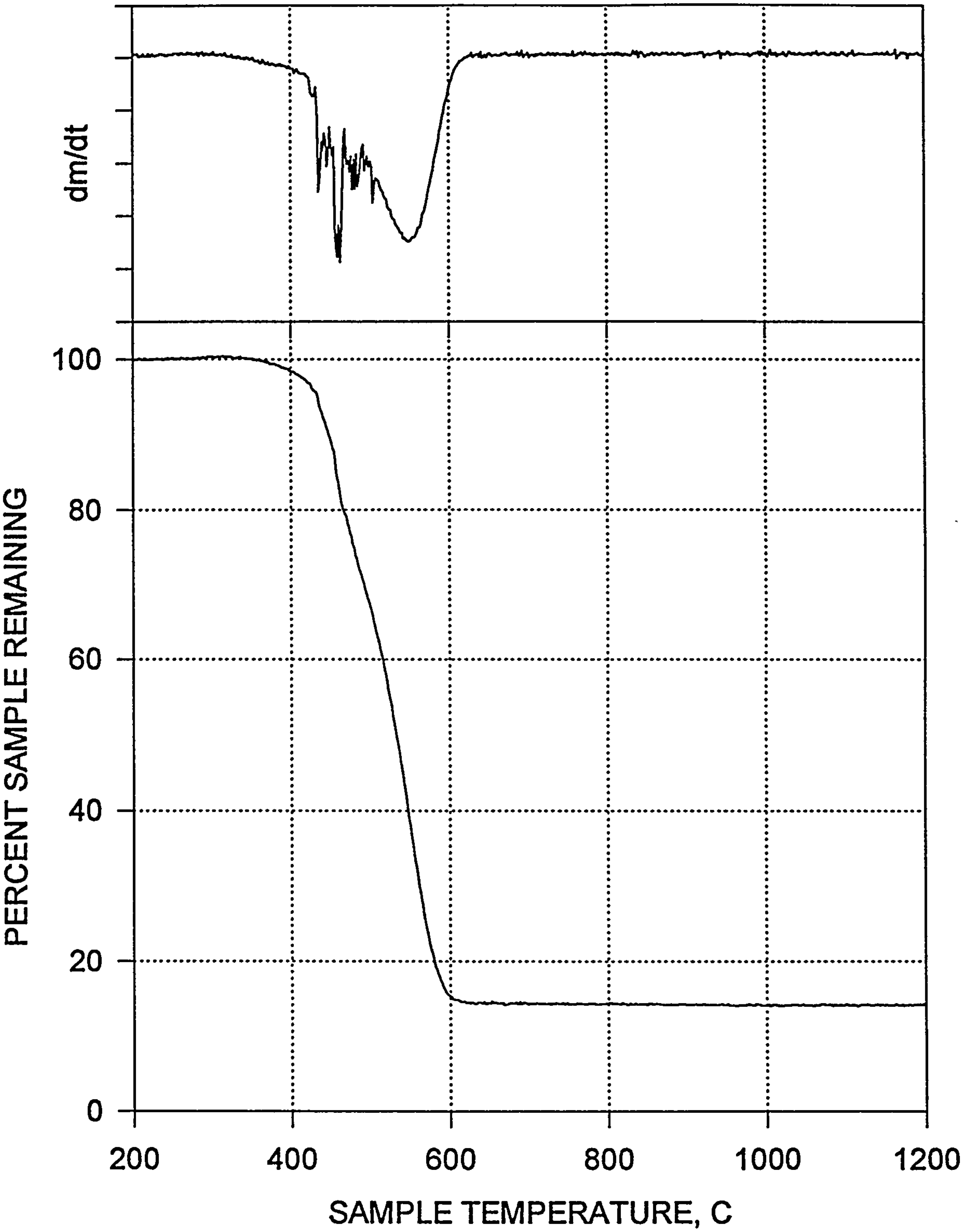
BAKERSTOWN INS0LUBLE RESIDUE IN 20 % OXYGEN AFTER HELIUM PYROLYSIS



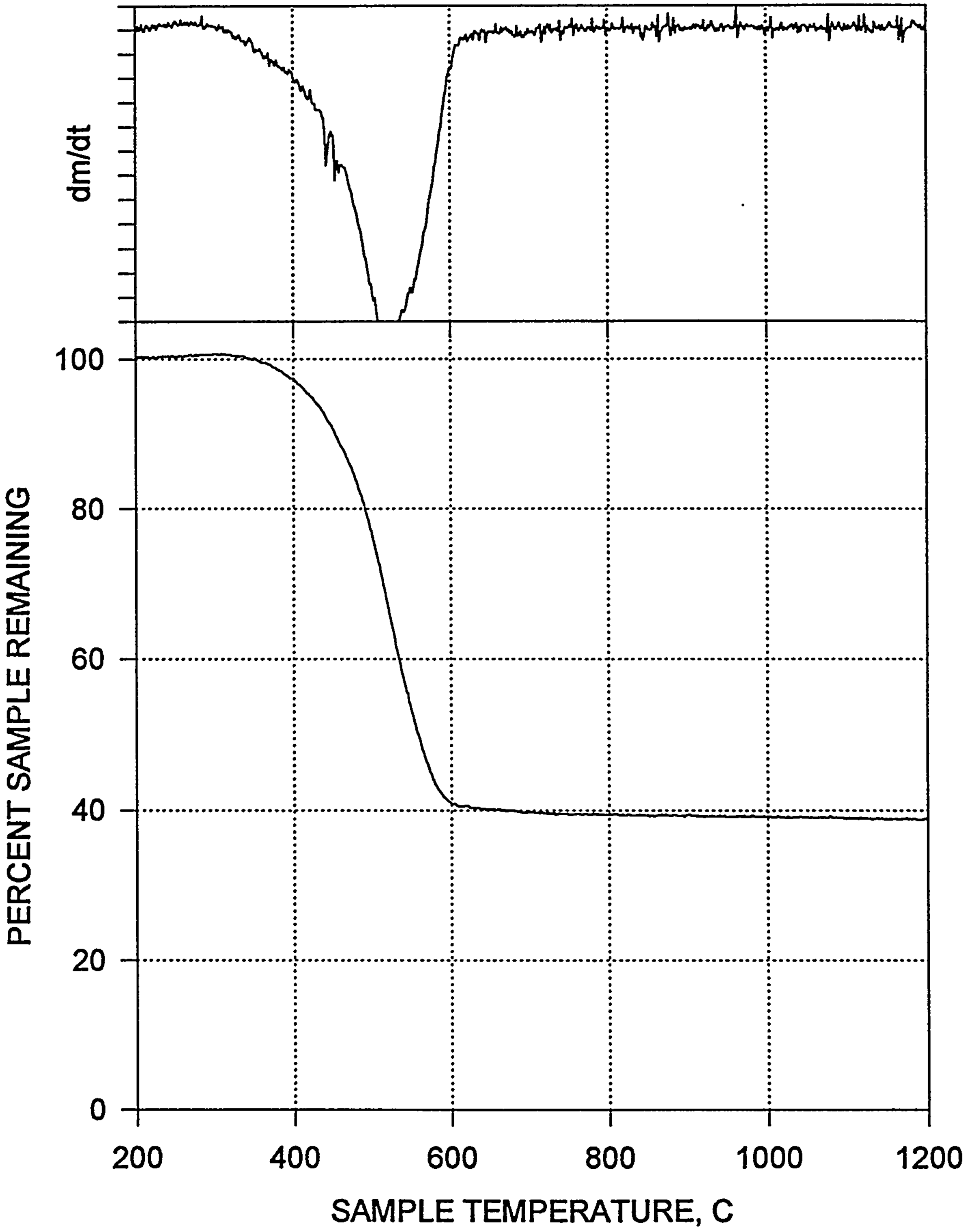
BAKERSTOWN SOLUBLE EXTRACT IN 20 % OXYGEN AFTER HELIUM PYROLYSIS



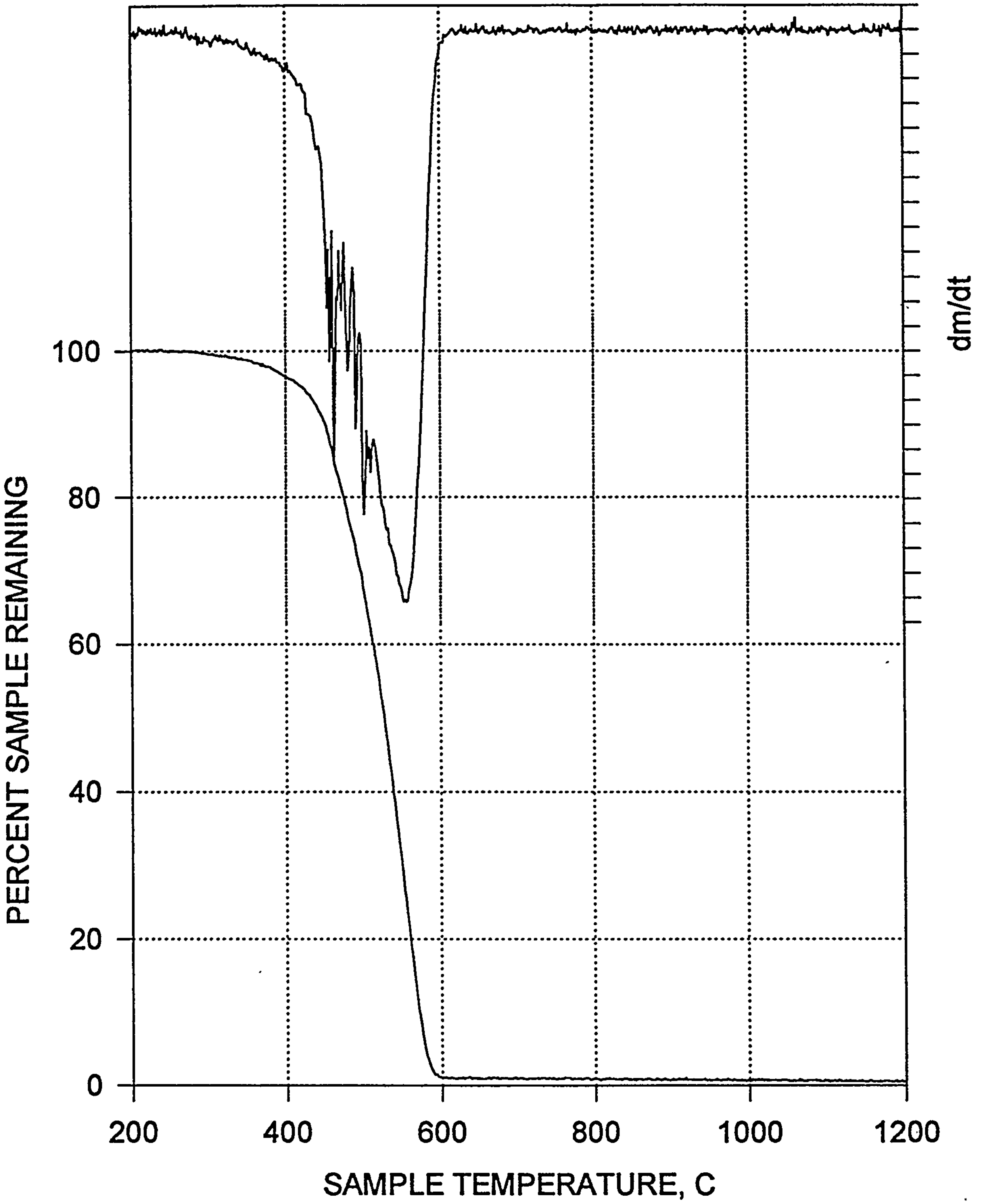
BAKERSTOWN RAW COAL
IN 20 % OXYGEN



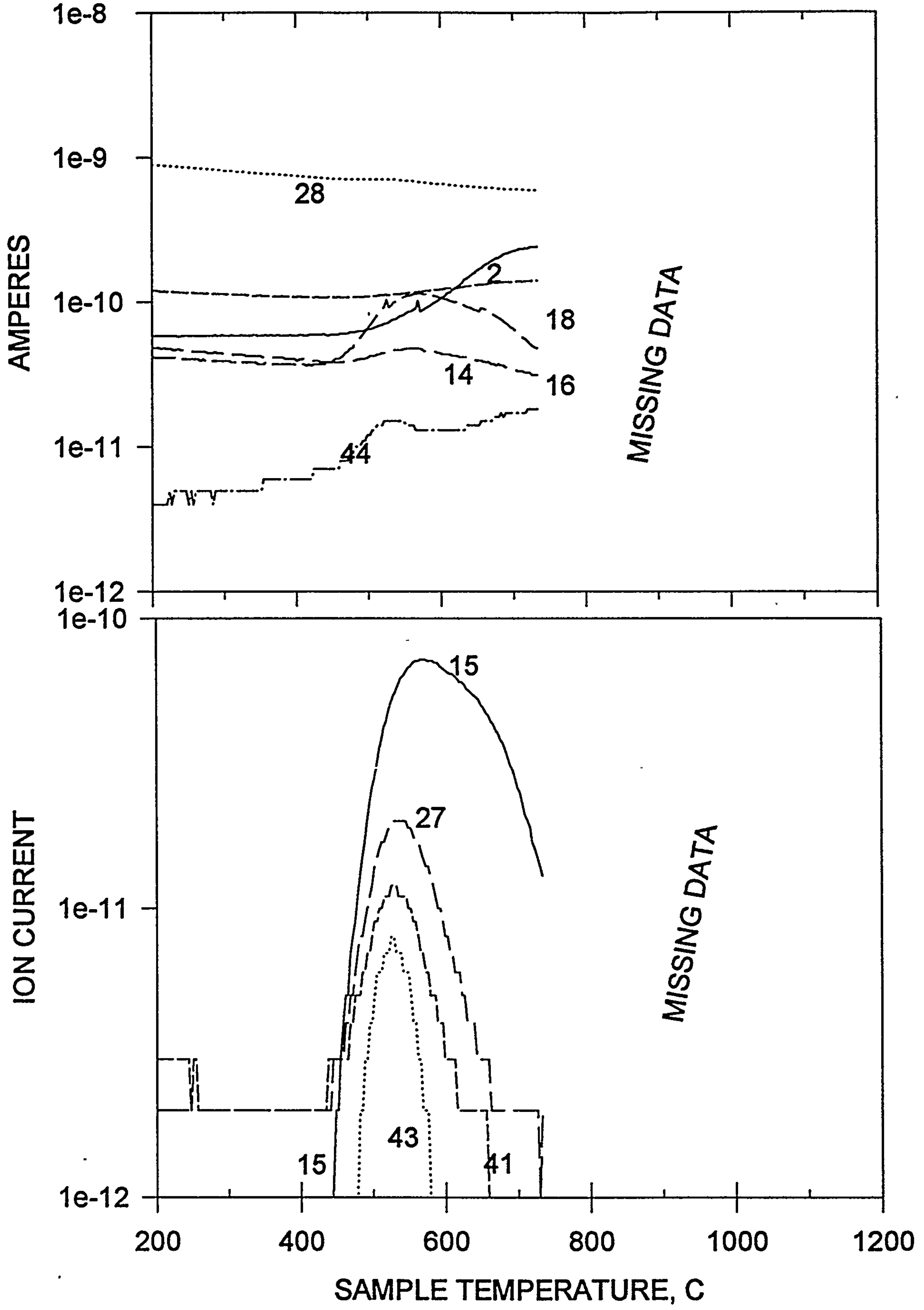
BAKERSTOWN INS0LUBLE RESIDUE IN 20 % OXYGEN



BAKERSTOWN SOLUBLE EXTRACT IN 20 % OXYGEN

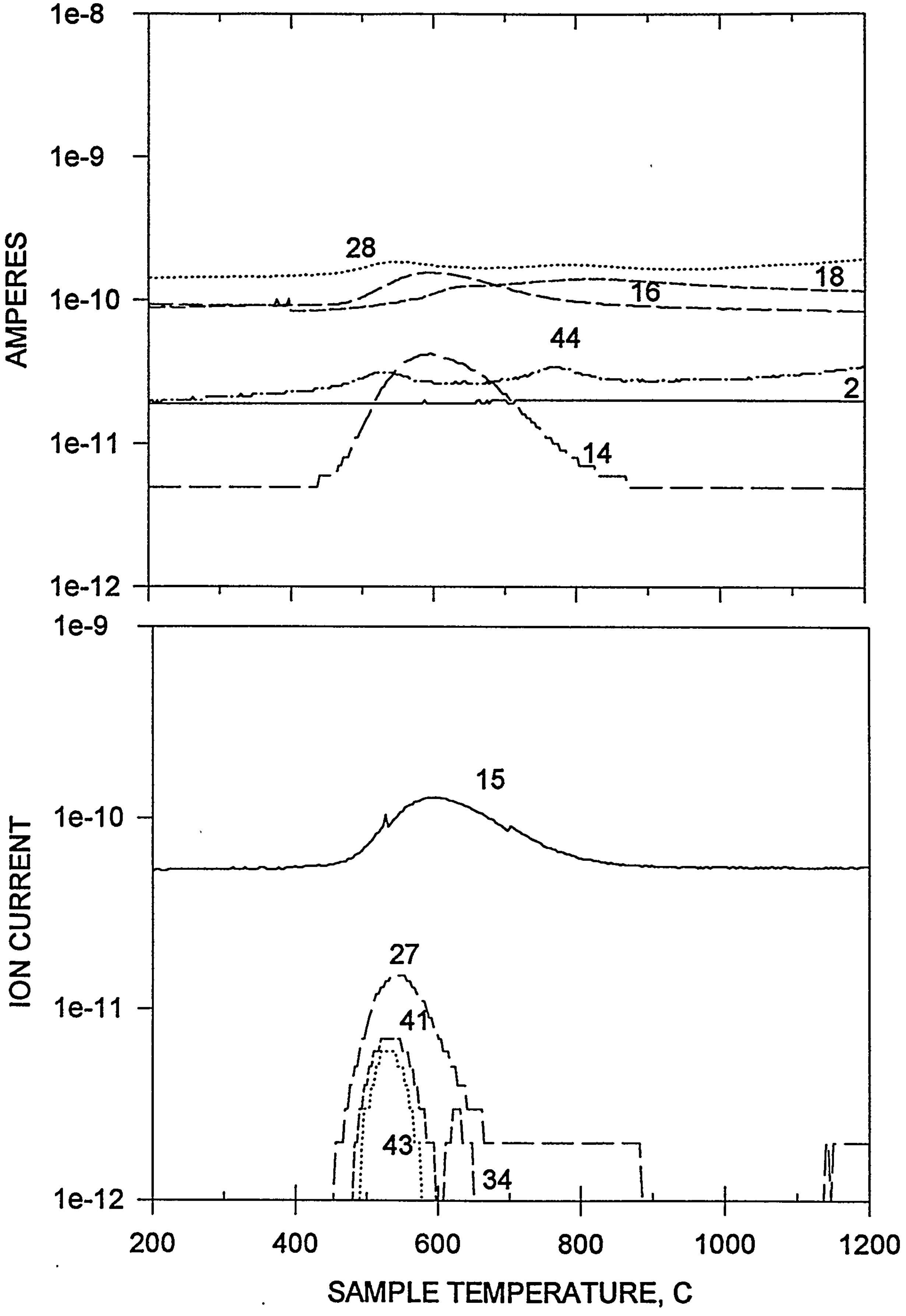


The mass spectrometry data reveal that the raw coal, the insoluble residue, and the soluble extract are similar in their volatile components and the temperatures at which they are released during heating. Peaks for several hydrocarbon species (and their molecular fragments), H_20, CO_2, CO, etc., are present in the mass spectroscopy traces, depending on the gas composition used. Two of the most noticeable differences are the diminished peak at amu = 15 (CH_3, a methane fragment) and the appearance of a very small peak at amu = 34 (H_2S) in the insoluble residue. Both of these features are consistent with a sample that represents the residue of an extraction process, i.e., the insoluble residue might be expected to be depleted in volatile phases and enriched in inorganic sulfur-bearing phases.



BAKERSTOWN IN HELIUM

BAKERSTOWN INSOLUBLE RESIDUE IN HELIUM



BAKERSTOWN SOLUBLE EXTRACT IN HELIUM

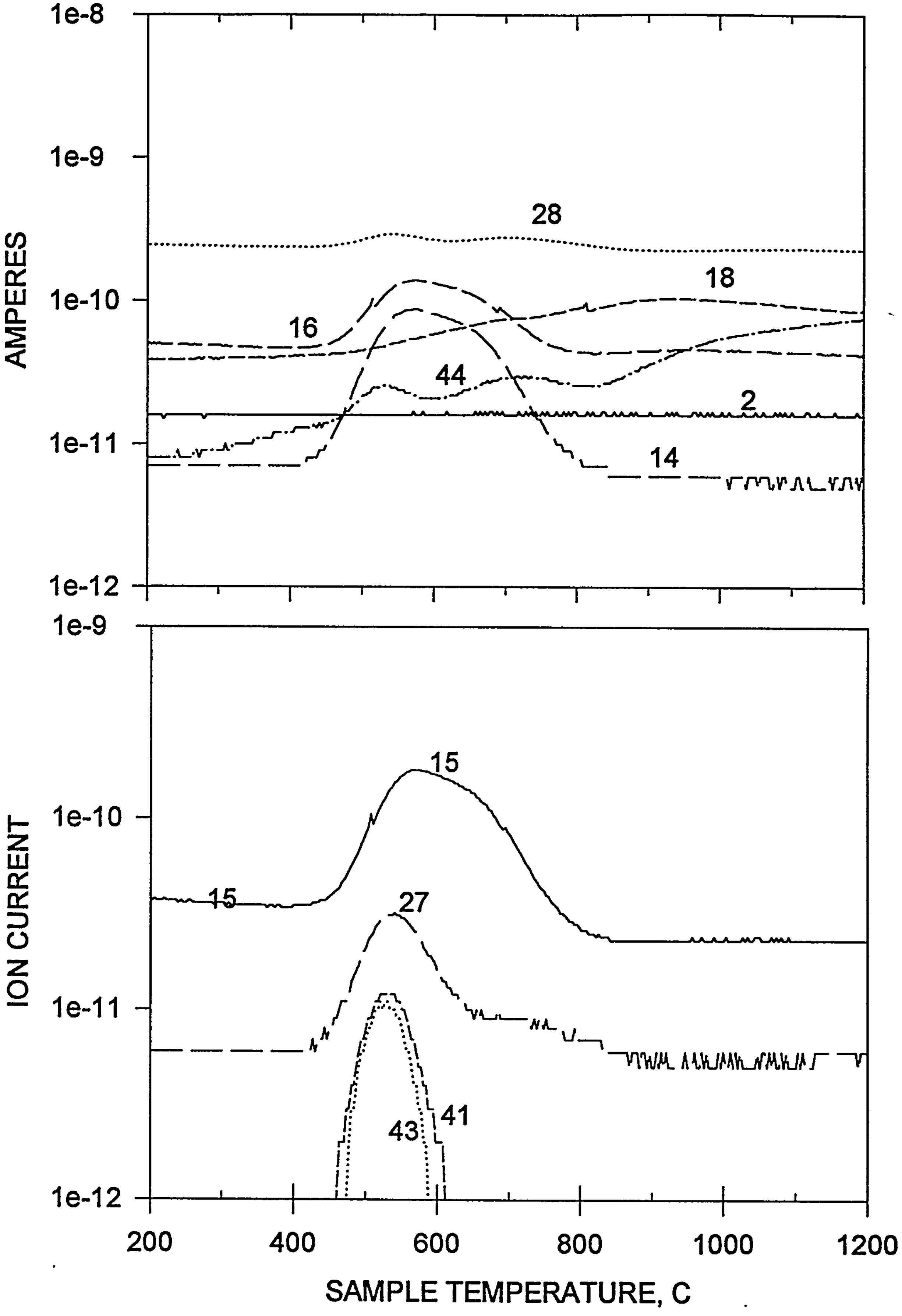


TABLE 1. Mass losses for samples pyrolyzed under different conditions.

Sample(a)	Mass remaining (wt. %)
Raw Bakerstown Coal (helium pyrolysis)	71
Raw Bakerstown Coal (oxidation after helium pyrolysis)	15
Raw Bakerstown Coal (oxidative pyrolysis)	15
Insoluble Residue (helium pyrolysis)	78
Insoluble Residue (oxidation after helium pyrolysis)	38 (see note b)
Insoluble Residue (oxidative pyrolysis)	38
Soluble Extract (helium pyrolysis)	67
Soluble Extract (oxidation after helium pyrolysis)	<1
Soluble Extract (oxidative pyrolysis)	<1

[a] The Bakerstown Coal contains 28% volatile matter on a moisture-free basis and 16% ash on a moisture-free basis.

[b] Corrected for mass change after cooling of residue of helium pyrolysis and oxidation of the residue.

CONCLUSIONS

1. The NMP extraction process appears to be remarkably efficient in decreasing the amount of mineral matter present in raw Bakerstown coal. The mass remaining after oxidation (ash content) decreased from 15% (in agreement with 16% ash reported for Bakerstown coal) to <1% ash in the soluble extract.

2. The NMP extraction process appears to be primarily physical in nature based on the observation that the volatile species released during heating do not appear to change significantly from raw coal to soluble extract. The volatile content increased from 29% (in agreement with the 28% volatile matter reported for the Bakerstown Coal) to 33% for the soluble extract using helium pyrolysis.

3. Volatilization takes place over a temperature range >300°C (and for some samples, in more than one step based on the dm/dt curves).

4. Oxidation of the residues of samples previously pyrolyzed in helium begins at higher temperatures (approximately 200°C higher) than for the oxidation of fresh samples.

ATTACHMENT 3

THERMOGRAVIMETRIC AND MASS SPECTROSCOPIC ANALYSES OF SOLVENT-REFINED POWELLTON COAL, WEST VIRGINIA (U.S.A.)

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Coal Science
J.A. Pajares and J.M.D. Tascón (Editors)

THERMOGRAVIMETRIC AND MASS SPECTROSCOPIC ANALYSES OF SOLVENT-REFINED POWELLTON COAL, WEST VIRGINIA (U. S. A.).

Fuller, E.L.[a,b], Kopp, O.C.[a,b], and Rogers, M.R.[b]

1. INTRODUCTION

Coal is an abundant source for raw materials for a number of valuable carbonaceous products. Most applications require purification of the raw coal to remove undesirable components (mineral matter, sulfur, specific macerals, etc.). The West Virginia Geological and Economic Survey (WVGES) has developed a coal-sourcing model that can specify, locate, and evaluate coal resources that can be used to produce carbon-based products. As part of the WVGES study, fifteen coals (mostly from West Virginia) were subjected to solvent extraction using N-methyl-2-pyrrolidone (NMP). The NMP solvent extraction yields are strongly dependent on coal rank, ranging from 0.0 to 66.3 percent by weight.

This study determines the nature and extent of changes wrought in the NMP solvent extraction process. How do the final products, ie., the soluble extract and the insoluble residue, differ from the starting material (raw coal) and how do they differ from each other? Measurement of the thermal and chemical properties of each allow evaluation of the pertinent parameters. Optimum use of coal resources will involve the generation of feedstocks from the hydrogen-rich components of coal and production of carbon based-products from the residual chars. Such a program requires an extensive database for coals of various ranks. Each specific coal type will require tailored processing.

2. EXPERIMENTAL

Samples of raw coal, soluble extract, and insoluble residue were provided by Dr. Peter G. Stansbury (Department of Engineering, West Virginia University, Morgantown, WV, USA). These materials were gently crushed to a coarse powder and sieved to separate the 35-60 mesh (0.25 to 0.50 mm) size fraction used in these studies.

Thermogravimetric analyses[1] supported by mass spectrometric analyses (TGA-MS) were carried out with utilizing a computer automated Mettler Thermoanalyzer (model TA-1) in combination with a UTI model 100C^{tm} quadruple mass spectrometer for analyses of outlet gas composition. Thermal treatment in air causes loss of inherently volatile material and reactive components that are oxidized (primarily by oxygen, carbon dioxide, and/or water vapor). Each material was analyzed three times as sample temperatures were increased (10 °C per minute) to 1000 °C: (1) in pure helium (for evaluation of volatile components); (2) oxidation of the residue of (1) in 20% oxygen in helium (for evaluation of oxidation processes); and (3) oxdative pyrolysis of a fresh aliquot in 20% oxygen in helium (evaluation of both volatiles and oxidation, and any synergetic effects).

3. RESULTS AND DISCUSSION

Typical thermogravimetric results are presented in Figure 1. The amount and rate of mass loss is dependent upon coal composition, gas phase composition, and previous treatment. Data below 200 °C are omitted where water loss predominates for the more hydrous coals. Three regions are noted: 450-460 °C which is generally associated with devolatization and oxidation of labile components; 600-620 °C due to oxidation of hydrocarbon materials; and >750 °C for the oxidation of carbonaceous residues. The residual material, after 1000 °C oxidation, is the ash (mineral matter) determined by classical analyses for the specific coal or modified material. Details of the process are more readily discernible in the more sensitive rate (time derivative, dm/dt) data superimposed in Figure 1.

Details of the processes are obtained from the mass spectrometric data for the effluent gases from the TGA as presented in Figure 2. The ion currents are proportional to the specific concentrations, which are proportional the rate of evolution at the noted temperatures. Three classes of effluents are generated:

1. Volatile components (water vapor, hydrogen, methane, ethane, etc.), that are expelled from the coal matrix by thermal treatment.

2. Oxidation products (carbon monoxide, carbon dioxide, water, etc.) produced by combustion:

$$\text{YY-}C_XH_YO_Z + O_2(\text{gas}) \text{ -----> } CO_2(\text{gas}) + CO(\text{gas}) + H_2O(\text{gas}). \qquad (1)$$

3. Degradation products formed from inherent functional components in the coal

$$\text{XX-COOH + YY-COOH + HEAT -----> XX-CO-O-CO-YY} + H_2O(\text{gas}) \qquad (2)$$

$$\text{XX-OH + YY-OH + HEAT -----> XX-O-YY} + H_2O(\text{gas}) \qquad (3)$$

$$\text{XX-COOH + YY-OH + HEAT -----> XX-CO-O-YY} + H_2O(\text{gas}) \qquad (4)$$

leaving anhydride, ether, and ester units in the substrate (where **XX-** and **YY-** denote different or identical, binding sites in the coal macerals).

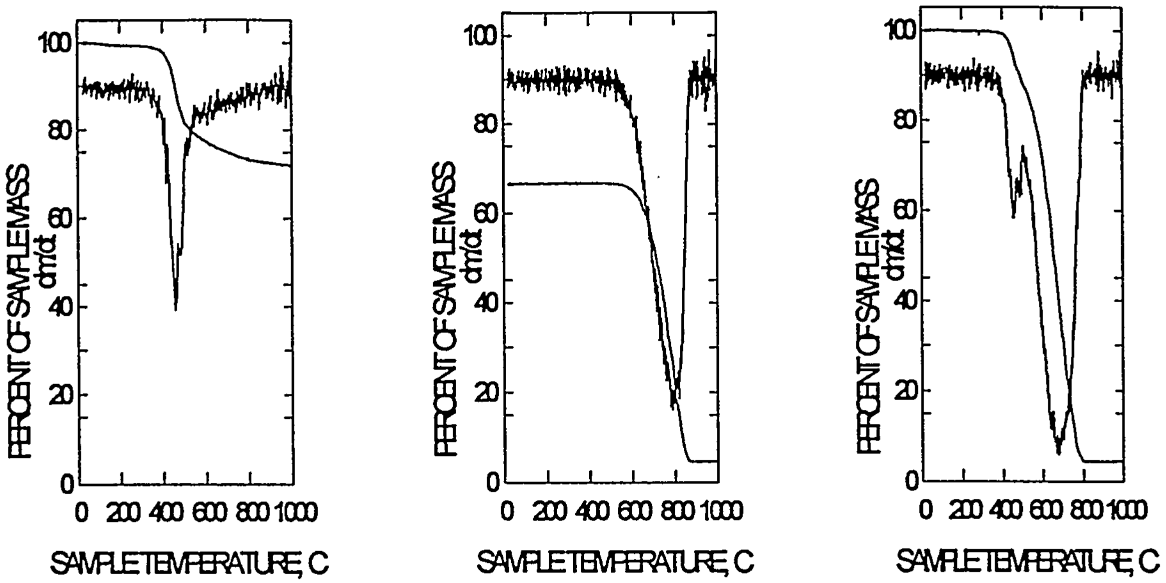

Figure 1. Thermogravimetric analyses of raw coal samples. Left: Pyrolysis in helium gas. Center: Oxidation of resdue from helium pyrolysis. Right: Simultaneous oxidation and pyrolysis of fresh sample.

Combined oxidation and pyrolysis qualitatively approximates the results of the step sequence, although there are distinct quantitative differences. The combined TGA-MS provides the data required to evaluate the detailed kinetics and mechanism to verify the thermal degradation processes occurring in the helium pyrolysis. Most of the sites for this processes are labile for oxidation and do not persist into the higher temperature regime (500 - 1000 °C).

A database has been established for each of three samples to aid in the evaluation of the chemical and physical changes wrought in the NMP extraction processes. The detailed analyses allow several conclusions:

1. The NMP extraction process of WVGES Powellton Coal is primarily physical in nature, increasing the content of volatile material from 27.9 to 32.7 percent.

2. The extraction process is quite efficient in decreasing the amount of mineral matter. The ash content was decreased from four percent to less than one percent.

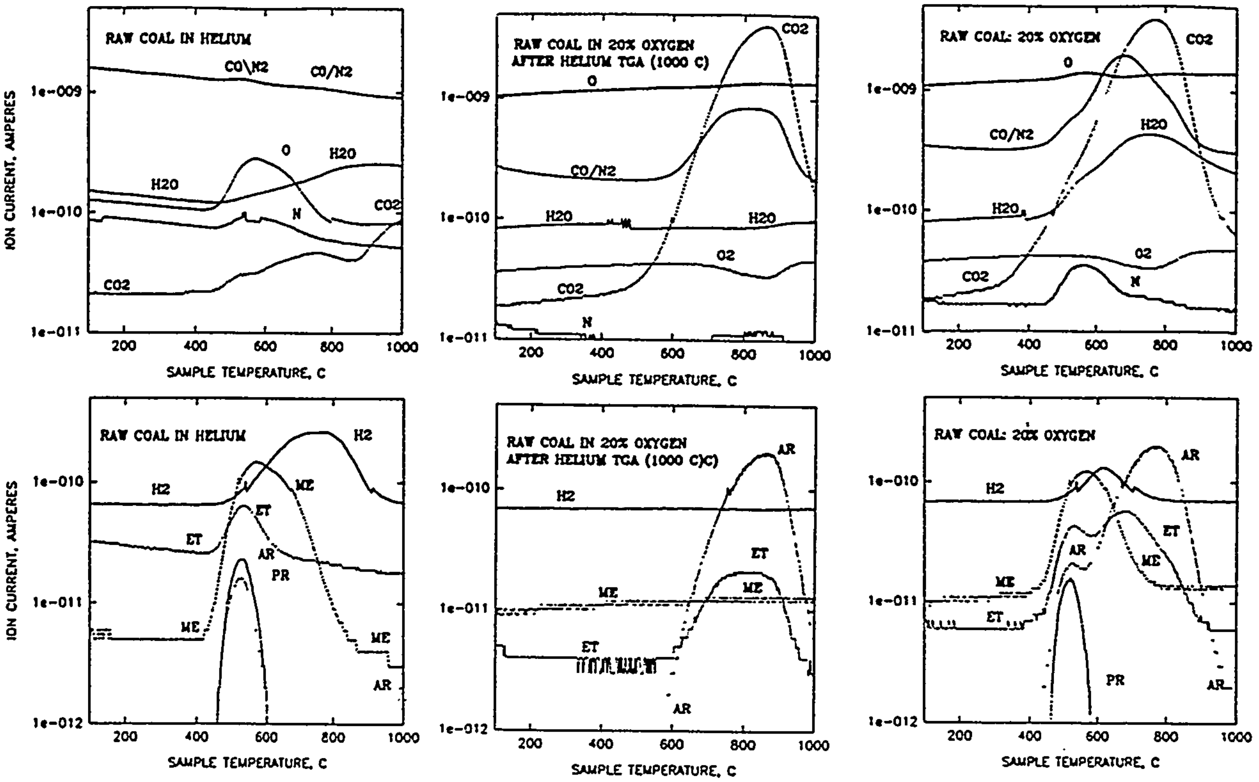

Figure 2. Mass spectrometric analyses of effluent gases from the thermogravimetric analyzer. Thermogravimetric analyses of raw coal samples. Left: Pyrolysis in helium gas. Center: Oxidation of residue from helium pyrolysis. Right: Simultaneous oxidation and pyrolysis of fresh sample.

3. Devolatization occurs in two or three distinct temperature regions.

4. Oxidation of residual carbonaceous material after pyrolysis occurs at ca. 100 °C higher temperatures than noted for fresh materials.

5. Initial rates of mass loss on oxidative pyrolysis are lower than rates of pyrolysis in an inert atmosphere.

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[1] O.C. Kopp and E.L. Fuller, Jr., "Thermogravimetric and Mass Spectrographic Study of Coal Pyrolysis and Combustion," Conference Proceedings, International Conference on Coal Science, Vol I, p. 69-72. K. H. Michaelian, ed. (Banff, Canada, September 12-17, 1993).

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THE PRODUCTION & SCREENING OF CARBON PRODUCTS PRECURSORS FROM COAL

Contract No. DE-AC22-95PC94063

KEY STAFFING REPORTS

for the period covering

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July - September, 1995

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