NBSIR 82-1666

REVIEW OF NEEDS FOR THERMOPHYSICAL PROPERTY DATA ON SOLID FEEDSTOCKS. I. Coal

Jane E. Callanan

National Bureau of Standards
U.S. Department of Commerce
Boulder, Colorado 80303

May 1982

NBSIR 82-1666

REVIEW OF NEEDS FOR THERMOPHYSICAL PROPERTY DATA ON SOLID FEEDSTOCKS. I. Coal

Jane E. Callanan

Thermophysical Properties Division
National Engineering Laboratory
National Bureau of Standards
U.S. Department of Commerce
Boulder, Colorado 80303

May 1982

Final Report

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

CONTENTS

LIST OF TABLES

SUMMARY

In January 1981, a comprehensive survey was undertaken to determine the need for thermophysical properties of the following solid feedstocks/fuels: coal, oil shale, tar sands, gas hydrates. This report deals with that portion of the survey which concerns coal and includes the results of broad consultation with industrial, government, and academic groups as indicated in table 1.

This survey shows the need for experimental work on heat of combustion, heat capacity/enthalpy, thermal conductivity, and heat of wetting for both well-characterized premium coal samples and for samples of the type which will be used directly in conversion processes. Widely accepted, standardized measurement techniques do not exist for these properties, with the exception of heat of combustion, and must be developed; in addition, reliable data must be generated for efficient use of coal as a feedstock. Theoretical studies which will allow for modeling of properties should proceed along with the experimental investigations to allow for improvement in prediction of coal properties for process design.

The following recommendations for coal-related properties research are substantiated in this report.

1. Develop reliable measurement techniques for heat capacity, thermal conductivity, and heat of wetting. Existing measurement methods are adequate for thermal expansion and heat of combustion.

2. Evaluate the effects of coal handling on coal properties.

3. Develop a standard reference material for thermal properties of coal.

4. Conduct an interlaboratory testing program to evaluate the measurement techniques developed.

5. Deposit all data in a nationally accessible central data bank.

6. Develop theoretical models for both equilibrium and transport properties with possible extension to structural properties such as porosity.

Review of Needs for Thermophysical Property Data on Solid Feedstocks. I. Coal

Jane E. Callanan

Thermophysical Properties Division
National Bureau of Standards
Boulder, Colorado

This report, which presents the results of a comprehensive survey with respect to thermal properties of coal, is part of a broader study which also includes oil shale, tar sands, and gas hydrates. This survey shows the need for experimental work on heat of combustion, heat capacity/enthalpy, thermal conductivity, and heat of wetting for both well-characterized premium coal samples and for samples of the type which will be used directly in conversion processes. Widely accepted, standardized measurement techniques do not exist for three of these properties (heat of combustion excepted) and must be developed; in addition, reliable data must be generated for efficient use of coal as a feedstock. Theoretical studies which will allow for modeling of properties should proceed along with the experimental investigations to allow for improvement in ability to predict coal properties for process design. Recommendations for work appropriate to the National Bureau of Standards and the justification for these recommendations are included.

Key words: coal; enthalpy; heat of wetting; heat capacity; literature survey; review; solid feedstocks; thermal conductivity; thermal properties.

1. INTRODUCTION

In January 1981 a study was initiated to determine the thermophysical properties needs for solid feedstocks. The substances initially selected for study were coal, oil shale, and gas hydrates. An examination of various data bases indicated that tar sands also should be included. It was necessary first to study the nature of these solid fuels/feedstocks so that appropriate judgments could be made. For coal and oil shale, this proved a formidable task. By comparison the gas hydrates are relatively simple materials. Following an initial familiarization with coal, oil shale, and gas hydrates, a computer search of data bases, which included research-in-progress and publications, was conducted.

Perhaps the most fruitful part of the study has involved personal contacts with scientists involved in fossil-fuel research. The organizations and scientists consulted by telephone, by letter, and by personal visit are indicated in table 1; the ideas evolving from these discussions are reflected throughout this report. Additional useful discussions took place at the Coal Sample Bank Workshop sponsored by DOE/GRI (Atlanta, Georgia, March 1981), American Chemical Society meetings, and the Gordon Conference on Fuel Science, (Plymouth, New Hampshire, July 1981).

This report deals with coal. By mid-1982 a second report addressing the nature of oil shale, the status of existing thermal property data for shale, the needs of the users' community, and recommendations for experimental work on oil shale will be submitted. Another report dealing with gas hydrates is scheduled for fall, 1982. Investigations and recommendations regarding tar sands will follow in 1983.

Table 1. Summary of consultations - coal[a]

Organization	Contacts
Allied Chemical Corporation	G. Hammond, A.K.S. Murthy
Amoco Research Center	O. Mahajan
Bartlesville Energy Technology Center	B.E. Gammon, N.K. Smith
Colorado School of Mines	R. Baldwin, A. Kidnay, V. Yesavage
Exxon Research Engineering:	
Corporate Research, Linden, NJ	C.T. Ratcliffe, S.C. Mraw
Research Development, Baytown, TX	R.C. Neavel
Exxon Production Research, Houston, TX	B. Blackwell, C.H. Hewitt
Gas Research Institute	W. Staats, V. Hill
Institute of Gas Technology	K. Vorres, R. Zabransky
Kentucky Center for Energy Research	J. Elder
Massachusetts Institute of Technology	J. Boston
NASA, Huntsville	J. Austin, J. Lowery
Oak Ridge National Laboratory	L.E. McNeese, E. Fuller, E.C. Hise, B.R. Rodgers, J. de Van, J. Ficolari, B. Benjamin, M. Poutsma
Pace Engineers	P. Rolniak
Coal Research Group, Pennsylvania State University	W. Spackman, P.H. Given, P.L. Walker, Jr., P. Dolson
Pittsburgh Energy Technology Center	H. Retcofsky, E.H. Spencer
Pittsburgh Mining Technology Center	J. Murphy, R.D. Watson, C. Lazzara, J. Edwards, A. Kim
Southern Illinois University	C. Carrell
U.S. Steel	R.J. Gray, S.J. Todd, R. Schoenberger, R. Wagner, F. Huggins
University of Tennessee	J. Larsen
University of West Virginia	L. Nice

[a]This list is representative rather than comprehensive in identifying leading coal-research centers.

This report includes a discussion of the thermal properties of interest in fuel science, a short primer on coal, and an elaboration of experimental concerns. Wide-ranging experimental investigations are suggested. Finally recommendations are made that will serve as a basis for delineation of the program of thermal property measurements and studies of coal within NBS.

2. THERMAL PROPERTIES

Knowledge of thermal properties of solids, though of interest in the past, has assumed new importance today. With the emphasis on synthetic fuel development and solid fuel/feedstock conversion processes, knowledge of these properties is more widely needed than heretofore. In addition, the high cost of energy and the emphasis on environmental concerns has made the utilization of such data imperative.

Thermal properties of most interest in fuel science include heat of combustion (calorific value), heat capacity, thermal conductivity, thermal diffusivity, heat of wetting, and to a lesser extent, thermal expansion. Such data obtained for petroleum and petroleum-related materials from the 1930's through the 1960's led to knowledge which has been a great asset to chemical engineers involved in petroleum refining. It is expected that corresponding information for coal and coal-related materials will be similarly useful. A discussion of the individual thermal properties follows.

2.1 Heat of Combustion

In fossil-fuel terminology, the heat of combustion is referred to as the calorific value. For many years, for those using coal as a fuel, it was the property of greatest interest. The calorific value of coals is determined by standard ASTM procedures in a bomb calorimeter, either isothermally or adiabatically. Such calorimeters are commercially available and require no extraordinary skill for their operation.

However, more accurate calorimeters and calorimetric techniques do exist at NBS-Gaithersburg, Argonne National Laboratories, and Bartlesville Energy Technology Center. Their use might allow correlation of loss of calorific value with degree of oxidation; also, greater accuracy in the determination of the heat of combustion would allow better estimates for the heat of formation[1] of coal since the heat of formation is calculated from measured heats of combustion. This better estimate for the heat of formation would improve existing modeling capabilities for coal processing. In addition, a study of heats of combustion of coal fragments in order to find additive or predictive relationships may prove useful in improving coal charges. For this purpose or for the correlation of loss of calorific value with degree of oxidation, more accurate techniques, such as those mentioned above, might need to be utilized.

As calorific value is the most important thermal characterization parameter for fuels, measurements of this parameter do exist for a very wide spectrum of well-characterized substances. However, unlike the heat of combustion, measurements of other thermal properties of coal have been made only on isolated or poorly-characterized specimens. Thus little effort has been made to correlate thermal properties with other characteristics.

2.2 Heat Capacity

Knowledge of the heat capacity of solid fuels/feedstocks is needed for efficient design of conversion and carbonization processes and for the modeling of these processes and of properties. Because of the scarcity of reliable measurements and the demands the present-day economy makes with respect to energy efficiency, there is a new impetus for a better and systematic program of experimental measurements.

---

[1]The heat of formation of coal is a concept that generates some controversy. Strictly speaking it can be calculated, but the complexity of coal has tremendous implications for the actual measurements of the heat of combustion and for the corrections which must be applied. For this reason a physical chemist may be skeptical about the numbers assigned to heats of formation of coal; from an engineering standpoint, however, even order of magnitude information is useful and the subtleties of definitions are irrelevant.

Heat-capacity and enthalpy measurements of coals have been reported by several investigators [1-14]. The techniques used are based on the method of mixtures (e.g., ASTM C351) [5], the Bunsen ice calorimeter [7,8], a variety of adiabatic calorimeters [10,11], and drop calorimetry [11]. The best of these measurements are accurate to about 2%. Most are either mean heat capacities (i.e., measurements over wide temperature intervals), practical heat capacities (include some heat of reaction) [13], or were made at isolated temperatures and do not give reliable information about the temperature dependence of the heat capacity. Some of the investigators measured the heat capacity, at room temperature, of coals which had been heated to elevated temperatures and report these as high-temperature data [14]. Most of the investigations report increasing heat capacity with increasing temperature until decomposition begins within the plastic region. Clendenin [6] reports continuously increasing heat capacities, but his measurements were made to about 120°C and then extrapolated to higher temperatures. In general heat capacities increase with increasing temperature, increasing volatile matter content, and increasing moisture content; they decrease with increasing carbonization. However, the scatter in the data due to variations in factors such as cell design, heating rate, and pretreatment of the specimens make it almost impossible to draw any unified conclusions. Badzioch [4] and Kirov [9] thoroughly review the status of these measurements up to 1965. Table 2 presents the results obtained by Singer and Tye [11] on a Pittsburgh seam coal; these data illustrate some of the difficulties mentioned above.

In all of the above studies, very little characterization information other than elemental composition is included; it is hoped that some further information may be available upon inquiry. Though any attempt to sort out existing heat-capacity measurements seems counterproductive at this time, attempts to correlate the isolated data presently available with the newly-generated data will be made as the program develops.

The differential scanning calorimeter (DSC) is capable of accuracies of 1% and allows rapid determination of heat capacities over a wide temperature range [15]. Because the DSC requires small specimen sizes, careful attention must be given to the homogeneity of the solid fuels and replicate results. This drawback is to be balanced against the recognized lack of specimen temperature uniformity that results from the use of larger specimen sizes. Several recent experimental studies based on the DSC verify its utility for such studies [15-20]. We have decided to use a commercial DSC in preliminary NBS experiments.

Differential thermal analysis (DTA) and, more recently, DSC studies have used thermograms to evaluate general endothermic and exothermic tendencies of coals in various temperature regions [21-25]. Despite some controversy, evidence does suggest the existence of an exotherm, associated with repolymerization, in plastic or coking coals. Slow heating through the plastic region is known to reduce the degree of swelling significantly; therefore use of low heating rates may extend the range of useful thermal measurements, though the interpretation of results in the plastic region will remain difficult.

Agroskin [1] has published correlations of heat capacity with rank and with characteristics of the aromatic portions of coals. A recent paper by Benson and Schobert [18] has used high-pressure DSC thermograms to obtain some tentative correlations with several coal characteristics.

Table 2. Specific heat (C_p) of Pittsburgh seam coal and cokes[a], J kg^{-1} K^{-1}

Temperature of measurement, °C	Virgin[b]		HT 350°C[c]		HT 475°C	HT 625°C	HT 650°C	HT 850°C
	Test 1	Test 2	Test 1	Test 2				
30	860	850	1,050	1,090	1,060	1,050	1,010	870
65	920	920	NA	NA	NA	NA	NA	NA
100	1,220	990	1,300	1,340	1,190	1,150	NA	NA
125	1,660	NA	NA	NA	NA	NA	NA	NA
150	1,580	1,060	NA	1,520	1,280	NA	NA	NA
180	1,440	NA	NA	NA	NA	NA	NA	NA
200	1,360	1,130	1,600	1,710	1,380	1,250	1,200	1,120
240	1,180	NA	NA	NA	NA	NA	NA	NA
250	1,190	1,210	NA	1,910	1,480	NA	NA	NA
300	NA	NA	2,100	2,120	1,590	1,370	1,330	1,270
350	NA	NA	NA	NA	1,700	NA	NA	NA
400	NA	NA	NA	NA	1,830	1,500	1,460	1,430
450	NA	NA	NA	NA	1,920	NA	NA	NA
500	NA	NA	NA	NA	NA	1,660	NA	NA
600	NA	NA	NA	NA	NA	1,860	1,830	1,750
800	NA	NA	NA	NA	NA	NA	NA	2,220

NA Not available.
[a]After Singer and Tye [11]
[b]Virgin coal sample in test 1 was undried; sample 2 for test was predried at 110°C to constant weight to remove water.
[c]HT = temperature of carbonization.

2.3 Thermal Conductivity

Information on thermal conductivities is needed for both solid and powdered fuel specimens. For processes which utilize monoliths, thermal conductivity data are required for heat flow both parallel and perpendicular to the bedding plane. Obvious difficulties are presented in preparing solid specimens by the need for exactly planar surfaces and for specimens with no defects or cracks. Information obtained on powdered specimens is in many ways more practical. Here, however, the great difference in the thermal conductivity of the gaseous and solid phases makes the measurements very sensitive to the packing procedures used and the gases produced.

Recommended procedures for thermal conductivity include the guarded-hot-plate method (ASTM C177) and the heat flow meter (ASTM C518). Two other methods developed for heterogeneous and/or refractory developed for heterogeneous and/or refractory materials are promising. The method used by Wagner [26] on insulation materials is a variant of a hot-wire method in which resistances are measured at widely-spaced points in the specimen; such a technique seems to take microscopic heterogeneity into account more than measurements made at a single point do. Dils [27] used a modified hot-wire method with refractory materials; with auxiliary spectroscopic measurements, values for thermal conductivity that are consistent with those measured by the guarded-hot-plate method are obtained.

Badzioch [4,28] summarizes and critically evaluates the results of thermal conductivity measurements up to 1964. His discussion includes coal and coke monoliths and powdered specimens. One of the principal criticisms cited in his summary is that most of the measurements were made at room temperature on coals that had been heat-treated at elevated temperatures rather than made at the elevated temperatures themselves. The general criticism of older experimental work, that it was done with

Table 3. Thermal conductivity (λ) of Pittsburgh seam coal and cokes[a], W m^{-1} K^{-1}

Temperature of measurement, °C	Virgin		HT 350°C Test 1		HT 350°C Test 2		HT 475°C	HT 500°C	HT 625°C	HT 650°C		HT 850°C	
	⊥	||	⊥	||	⊥	||	||	⊥	||	⊥	||	⊥	||
50	0.196	0.214	0.14	0.20	0.16	0.185	0.125	0.137	0.21	0.29	0.31	0.74	0.76
150	.192	.213	.17	.22	.17	.195	NA	.154	NA	.35	.36	NA	NA
200	NA	NA	NA	NA	NA	NA	.18	NA	.30	NA	NA	NA	NA
250	.190	.212	.19	.24	NA	NA	NA	.172	NA	.40	.41	.92	.95
300	NA	NA	NA	NA	.185	.21	NA	NA	NA	NA	NA	NA	NA
350	NA	NA	.21	.25	.185	.215	NA	.186	NA	.45	.46	1.05	1.09
400	NA	NA	NA	NA	.14	.16	.26	NA	.42	NA	NA	NA	NA
475	NA	NA	NA	NA	NA	NA	.28	NA	NA	NA	NA	NA	NA
50 (cooling)	NA	NA	NA	NA	NA	NA	.12	NA	NA	NA	NA	NA	NA
500	NA	NA	NA	NA	NA	NA	.29	NA	NA	NA	NA	NA	NA
520	NA	NA	NA	NA	NA	NA	NA	.215	NA	.52	.52	1.19	1.24
50 (cooling)	NA	NA	NA	NA	NA	NA	.11	NA	NA	NA	NA	NA	NA
600	NA	NA	NA	NA	NA	NA	.45	NA	.54	NA	NA	NA	NA
500	NA	NA	NA	NA	NA	NA	.38	NA	NA	NA	NA	NA	NA
50 (cooling)	NA	NA	NA	NA	NA	NA	.17	NA	NA	NA	NA	NA	NA
650	NA	NA	NA	NA	NA	NA	.54	NA	NA	NA	NA	1.38	1.45
775	NA	NA	NA	NA	NA	NA	1.10	NA	NA	NA	NA	NA	NA
800	NA	NA	NA	NA	NA	NA	NA	NA	1.25	NA	NA	1.60	1.74
50 (final cooling)	.176	.195	.14	.19	.10	.11	.28	.14	.37	.29	.305	.75	.76

[a] Singer and Tye [11].
NA Not available.
NOTE.--HT = temperature of carbonization. ⊥ = measured perpendicular to the coal bedding plane.
|| = measured parallel to the coal bedding plane.

poorly-characterized coals, holds for the work discussed in his summary. Additional published data on the thermal conductivity of American coals include those of Clendenin [6] and Singer and Tye [11]. The recently obtained data of Singer and Tye show similar trends to those cited in Badzioch's summary for heat-treated coals, but decreasing conductivity with increasing temperature for virgin coal. Table 3 indicates the temperatures and temperature ranges of heat-treatment and measurements as well as the results.

In general, thermal conductivities of powdered coal specimens are lower than those for monoliths though some disagreement exists as to what would be expected given the nature of the devolatilized powder. The effect on thermal conductivity of factors such as moisture content, pore shape and orientation, direction of heat flow, volatile matter and mineral content, and petrographic composition also need evaluation. The reliability of thermal conductivity measurements of coals must be established and such measurements applied to different coals.

2.4 Heat of Wetting

The heat of wetting of a solid is the heat generated as the dry solid is immersed in a liquid. It is determined from the temperature rise accompanying immersion of a thoroughly evacuated, weighed, test specimen in a known volume of a suitable liquid. If there is no chemical interaction, the effect is one of physical adsorption and is proportional to the surface area wetted. A suitable wetting liquid has small molecules with good wetting properties and minimum volatility at room temperature.

Apparatus for measuring heats of wetting vary from simply constructed systems, such as described by Fuller [29], to sophisticated commercially available calorimeters.

In the past, heat of wetting measurements, particularly those using methanol, have been used to evaluate the open porosity and surface areas of coal. Because of interactions between the OH groups in methanol and the oxygen functional group on coal surfaces, such measurements have often been seriously in error. As a result of the development of other techniques for surface area measurements, heats of wetting are used less often for such determinations. A recent study [30] of an alumina and a silica-alumina used thermometric titration procedures to determine surface area and heats of adsorption with considerable success.

Liquefaction processes and the proposed use of slurries have generated a pressing need for reliable information on heats of wetting, in water, in hydrocarbon liquids, and in mixtures of hydrocarbon liquids. For conversion processes, heats of interaction with liquids are needed both upstream and downstream, i.e., for solid feedstocks going into the process and for the separation of the solids at the conclusion of the process. To say that the development of suitable measurement techniques is a challenge is perhaps an understatement; nevertheless the problems of sample homogeneity, moisture content, surface area, and evaluation of interactions must be addressed in an attempt to reduce the experimental error of these measurements from an extreme of a 50% level to one that will allow for reasonable use of the data.

2.5 Thermal Expansion

There is no strong expressed need for thermal expansion data other than that available through free swelling index (ASTM D720), the Gray-King assay, or dilatometric measurements. There is some interest in the possible contribution of the micropore system to anisotropy in thermal expansion.

2.6 Thermal Diffusivity

The heat transport property of most interest for solid fuels is the thermal diffusivity (α). Though methods are available for direct measurement, this quantity is often calculated by means of the relationship

$$\alpha = \frac{\lambda}{C_p \rho},$$

where λ is the thermal conductivity, C_p, the heat capacity, and ρ, the bulk density. For a solid sample, thermal diffusivity is measured directly by imposing a heat pulse on the front side of a disk through the relationship

$$\alpha = 0.139\ L^2/t_{0.5},$$

where L is the thickness of a disk and $t_{0.5}$ is the time required for the rear surface temperature to rise to half its maximum value.

3. COAL

Some readers of this report will be familiar with the nature of coal and its complexities and how they bear on the problems and challenges confronting the experimentalist; others will not. Section 3.1, dealing with the nature of coal, is included for the latter group of readers. Sections 3.2-3.4 deal with experimental difficulties, research opportunities, and recommendations for work by the NBS.

3.1 Nature of Coal

Coal is essentially a sedimentary rock which accumulates as peat. It is composed of macerals and minerals and contains water and gases in submicroscopic pores.

3.1.1 Formation

Macerals are the organic components of coal and arise from the partial decay of plant material in the swamp or forest which generated the coal deposit. Decaying vegetation is covered by mineral matter brought in and deposited by wind and/or water. These strata alternate in an irregular fashion to build up the coal seam. The sedimentary strata are subjected to natural geologic processes which alter them physically and chemically.

The product of these processes has been defined by Neavel [31] as a heterogeneous aggregate of microscopically distinguishable, physically distinctive, and chemically different macerals and minerals. He has compared coal to a fruitcake formed initially of a mixture of diverse ingredients and baked to a usable consistency.

3.1.2 Macerals

The macerals in coal can be traced to the specific plant tissues from which they arose and are characterized by their appearance, chemical composition, and optical properties. As the macerals develop from varied tissues such as wood, spores, cuticle, and resins, they manifest the heterogeneity of plant tissue. Thus, portions of a coal seam separated by microns will have vastly different compositions and characteristics. This heterogeneity presents tremendous challenges to the experimentalist in obtaining representative samples and repeatable measurements and data.

3.1.3 Types

The terminology for the classification of macerals is not uniform. In general, lithotypes refer to macroscopic classification and petrographic groupings to microscopic classification. The scheme suggested by Stopes, as outlined in Mackowsky [32], for lithotypes is shown in table 4.

The microscopic examination of coal, either in thin section by transmitted light or of polished faces by reflected light, allows for the petrographic classification of coal. Table 5 lists coal macerals and groups as recognized by the International Committee for Coal Petrography. The suitability of coals for various processes is related to their maceral composition. For example, vitrinite- and exinite-rich coals are useful for processes such as liquefaction or coking; an inertinite-rich coal, which is largely carbon, has no utility for such processes.

Table 4. Coal lithotypes and descriptions[a]

Lithotype	Description	
Vitrain	brilliant; glossy; uniform whole.	Bright Coals
Clarain	smooth surface if broken at angles to bedding plane; banded surface luster.	Bright Coals
Durain	close firm texture; granular; broken face has fine lumps or a mat surface rather than a smooth one.	Dull Coals
Fusain	powdery patches; detachable fibrous strands.	Dull Coals
Cannel Coal	dull black; preponderance of fungal spores and pollen.	Dull Coals
Boghead Coal	dull brown; large concentrations of algal and plankton exinite.	Dull Coals

[a]After Mackowsky [32].

Table 5. Coal macerals and maceral groups recognized by the International Committee for Coal Petrography[a]

Maceral Group	Maceral	Composed of or derived from
Vitrinite	Collinite	Humic gels; colloidal matter
	Telinite	Wood, bark, cortical tissue
	Vitrodetrinite[b]	
Exinite	Sporinite	Fungal and other spores
	Cutinite	Leaf cuticles
	Resinite	Resins and waxes
	Alginite	Algal remains
	Liptodetrinite[b]	
Inertinite	Micrinite < 10 μm	Unspecified detritus
	Macrinite 10 - 100 μm	Unspecified detritus
	Semifusinite	Carbonized woody tissues
	Fusinite	Carbonized woody tissues
	Sclerotenite	
	Inertodetrinite[b]	

[a]After Berkowitz [33].
[b]These terms refer to small entities assigned to the maceral groups on the basis of reflectivity, but not able to be unequivocally identified with any particular maceral within the group.

3.1.4 Rank

The rank of coal is related to the extent of coalification or carbonization which has taken place as a result of the geologic processes it has undergone. The classification is made first on carbon content; within some ranges of carbon content, a further classification is made on the amount of volatile matter present. For coals with a carbon content less than 69%, a further division is made on the basis of the heat of combustion, or calorific value, of the coal. Table 6 illustrates the classification of coals according to rank. The classical H/C versus O/C diagram used by van Krevelen [35] is a representation of the classification of coals according to rank.

3.1.5 Minerals

The mineral content of coals, considered to be the sum of all elements that are not part of the organic coal substance, varies from less than 5% to 35%, though it is generally less than 20% for American coals. This is true whether one considers a narrow definition of a mineral as given here, the broader concept of non-coal inorganic material [36], or all inorganic constituents [37]. The importance of mineral content to coal science and technology comes from the ability of some mineral components to affect processing to a remarkable degree. The conversion or pyrolysis reactions may be catalyzed, thus allowing for treatment and conversion under less rigorous conditions; alternatively, the mineral component may poison an added catalyst or adversely affect materials used in the processing equipment. In addition, mineral residues present potential waste disposal problems and environmental hazards.

Table 6. Classification of coals by rank[a]

Class / Group	Fixed carbon limits (%) (dry, mineral-matter-free basis)		Volatile matter limits (%) (dry, mineral-matter-free basis)		Calorific value limits, (Btu/lb) (moist mineral-matter-free basis)		agglomerating character
	>	<	>	<	>	<	
I. Anthracitic							
1. Meta-anthracite	98	--	--	2	--	--	non-agglomerating
2. Anthracite	92	98	2	8	--	--	
3. Semianthracite	86	92	8	14	--	--	
II. Bituminous							
1. Low volatile bituminous	78	86	14	22	--	--	commonly agglomerating
2. Medium volatile bituminous	69	78	22	31	--	--	
3. High volatile A bituminous	--	69	31	--	14,000	--	
4. High volatile B bituminous	--	--	--	--	13,000	14,000	
5. High volatile C bituminous	--	--	--	--	11,500	13,000	
					10,500	11,500	agglomerating
III. Subbituminous							
1. Subbituminous A	--	--	--	--	10,500	11,500	non-agglomerating
2. Subbituminous B	--	--	--	--	9,500	10,500	
3. Subbituminous C	--	--	--	--	8,300	9.500	
IV. Lignitic							
1. Lignite A	--	--	--	--	6,300	8,300	
2. Lignite B	--	--	--	--	--	6,300	

[a]Table adapted from Montgomery [34].

The spectrum of minerals present in coals varies with the geologic history of the seam and exhibits the same heterogeneity as do the macerals. The principal minerals found in United States coals are listed in table 7. One of the sources of confusion in interpreting and comparing literature data on coals is the manner in which mineral matter is, or is not, accounted for. The effect of the presence of the minerals on the measurements themselves must also be considered.

3.2 Experimental Concerns

3.2.1 Samples

A major barrier in a coal research plan is the identification, selection, and availability of well-characterized coal samples. The most extensive coal sample bank in existence is that at Pennsylvania State University. However, its coals were not mined or processed under conditions that would prevent oxidation or deterioration of the coals. Only the more recently obtained samples have been stored in an inert atmosphere. Given the potentially serious but relatively unquantified effects of oxidation on properties and the uncertain degree of oxidation of these coals, their use is less than desirable for our purpose.

Samples from the bank[2] containing vitrinite-rich coal described by Neavel et al. [38] are closer to premium, undegraded, samples than any others available in the U.S. today. Though no program of monitoring sample quality presently exists for this bank, such a program is under consideration and should be initiated in the near future. Three principal drawbacks exist, however, with the use of these samples. The first is that the bank contains only vitrinite-rich samples, which are those most useful for synthetic fuel development. A complete study should include a wider spectrum of coals, some of which are of great importance to other industrial users. Secondly, a minimum of twenty specimens must be run; this is beyond the number necessary for the development of measurement methods. Most important, however, is the question of how much information about the samples, other than the usual characterization information, will be in the public domain.

The proposed GRI/DOE Coal Sample Bank will contain a wide spectrum of coals considered to be premium samples and the information obtained will be available to all. However, the existence of the Bank is still under study; even if approved, the characterized samples will not be available for, at best, close to two years.

Another alternative would be to obtain samples through the cooperation of USGS or the Pittsburgh Technology Center. Desirable sampling techniques would have to be assured and proper preparation and characterizations obtained. While this procedure might be feasible for one or two coals, any broader use of it would mean effectively establishing and maintaining ones own Coal Sample Bank. This is an unacceptable solution because of the tremendous financial outlay that would be required for equipment and qualified personnel; also, it would represent an attempt to duplicate, unnecessarily, existing excellent characterization facilities.

---

[2]Coal Library, Baytown Research and Development Division, Exxon Research and Engineering Company, Baytown, Texas.

Table 7. Minerals frequently associated with U.S. coals[a]

Silica Minerals:	Quartz[b] (trigonal), SiO_2
Chlorite:	$(Mg, Al, Fe)_{12}[(Si, Al)_8O_{20}](OH)_{16}$
Clay minerals:	Kaolinite[b] group, $Al_4[Si_4O_{10}](OH)_8$ Illite,[b] $K_{1-1.5}Al_4[Si_{7-6.5}Al_{1-1.5}O_{20}](OH)_4$ Montmorillonite[b] group, $(1/2Ca, Na)_{0.7}(Al, Mg, Fe)_4[(Si, Al)_8O_{20}](OH)_4 \cdot nH_2O$
Feldspar group:	Alkali feldspars, $(K, Na)[AlSi_3O_8]$ Plagioclase, $Na[AlSi_3O_8]$-$Ca[Al_2Si_2O_8]$
Sulfates:	Gypsum, $CaSO_4 \cdot 2H_2O$ Anhydrite, $CaSO_4$ Hemihydrate, $CaSO_4 \cdot 1/2H_2O$ (bassanite) Barytes, $BaSO_4$ Hydrated Iron sulfate, $FeSO_4 \cdot nH_2O$ Jarosite (Na, K, Fe) sulfates
Sulfides:	Pyrite[b] (cubic), FeS_2 Marcasite (orthorhombic), FeS_2
Carbonates:	Ankerite, $Ca(Mg, Fe^{2+}, Mn)(CO_3)_2$ Calcite (trigonal), $CaCO_3$ Magnesite, $MgCO_3$ Rhodochrosite, $MnCO_3$ Siderite, $FeCO_3$ Dolomite, $CaMg(CO_3)_2$ Mixed carbonates of Ca, Mg, Mn and Fe

[a]Jenkins and Walker [36].
[b]Most commonly occurring species.

Currently the best approach seems to be to obtain well-preserved samples of well-characterized coals which come from industrially important seams and are in sufficient supply to be commercially useful for many years. The selection of coals suitable for various processes for the experimental program will help to ensure the general applicability of the methods developed.

3.2.2 Sample Characterizations

Much of the difficulty in utilizing existing data on coals stems from the fact that measurements have been made on poorly-characterized specimens. While each coal scientist may wish for knowledge of very specific properties, it has been generally agreed that the properties listed in table 8 should be supplied with samples used in coal research. The accepted procedures for determining many of these properties are those specific by ASTM. However, more modern instrumental methods give equivalent or

improved results for some of these properties though their use is not yet standardized. Slow but perceptible progress is being made with respect to the substitution of new methods.

Of the properties listed in table 8, the calorific value of coal, or more precisely, the heat of combustion, is the only thermal property included. As indicated earlier the heat of combustion is measured in standardized commercial equipment based on ASTM test methods.

3.2.3 Reference Materials

Another problem which must be addressed is that of a standard reference material suitable for use in calibrating apparatus used to make thermal property measurements on coals and related materials. Either graphites or chars are most often used; both are carbonaceous materials. Graphite has a distinctive structure and as such may not be as closely related to the carbon structure of coal as is char. Also graphites of different origin have different heat capacities. While coal does show a lamellar arrangement of aromatic moieties and the connecting aliphatic elements are the first to be expelled, the carbon backbone of the char should be more similar in structure to that of coal than is graphite, and thus be more suitable for comparison.

3.2.4 Sample Cells and Related Problems

The choice of sample cells and sample cell materials for use with the DSC presents many problems. The aluminum cells commercially available will not remain sealed at the pressures that we anticipate may develop at elevated temperatures. The reusable stainless steel cells modeled after those used at Bartlesville Energy Technology Center and those presently available commercially have the advantage of being able to withstand relatively high pressures and are machined in such a way as to make good thermal contact with the sample cavity in the instrument. However, they also suffer from several disadvantages. Their weight is large compared to the weight of the specimen; stainless steel has low thermal diffusivity; and the sulfur in coals reacts with the steel and leads to subsequent generation of hydrogen sulfide even in empty cells [40]. The last of these difficulties can be overcome by gold-plating the cells. The significance of the other disadvantages is being evaluated.

A third cell design has been considered, but cells have not been fabricated as yet. These would be disposable aluminum cells made of sufficient thickness to withstand the anticipated higher pressures and would be sealed by cold welding. Preliminary calculations have been done on the thickness of aluminum which would be needed to prevent distortion of the shape due to the build-up of pressure; the integrity of the seal must be evaluated experimentally.

Rowlinson [41] discusses measurement of heat capacity when a liquid is in equilibrium with its vapor and differentiates between C_p, C_v, and C_σ (C_{sat} or the heat capacity of a liquid maintained at all temperatures in equilibrium with its vapor). Similar considerations should be applied for solids if the solid being studied has a vapor pressure[3] in the range of those of organic liquids, which is

[3]Reference to a vapor pressure for coal does not imply the existence of an equilibrium vapor pressure from which precise thermodynamic quantities can be obtained. However, the non-negligible vapor pressure, equilibrium or not, in the sample container does require the evaluation of vaporization effects.

Table 8. Recommended characterizations for coal samples[a]

Proximate analysis
Ultimate analysis
Calorific value
Equilibrium moisture
Sulfur forms analysis
Maceral analysis
Vitrinite reflectance analysis
Mineralogical analysis
Direct determination of mineral content
Analysis of major elements in ash
Trace element analysis
Surface area
Density (helium and mercury)
Free swelling index
Carbon dioxide content
Soluble alkali and calcium (lower rank coals)
Calcium/barium exchange
Total oxygen (neutron activation)
Gieseler fluidity
Geologic and geographic information on sampling site
Full history of sample handling since collection

[a]Proceedings of Coal Sample Bank Workshop [39].

presumed to be true for coal in certain temperature regions. For this reason, the effects of specimen volume to cell volume on the measured heat capacities must be evaluated.

Mahajan and coworkers found no significant temperature gradients within their DSC specimens [20]. A similar evaluation should be made for the stainless steel cells because of the relatively large volumes (45 microliters) and the poor thermal diffusivity of the cell materials and of the samples.

3.2.5 Sample Handling

The handling of the coal samples should be carried out as far as is possible in an inert atmosphere to prevent weathering. Through the use of a controlled-atmosphere glove box, sample preparation can be done under nitrogen. With some samples, though, the weathering process will have started because of mining and transportation procedures.

The drying of the coals is another experimental procedure that presents problems which may vary to some extent with the coal and its degree of subdivision. The as-received coal is pulverized under water to prevent local heat effects from altering its properties. Water will be removed by prolonged evacuation at room temperature; if this is not sufficient, as preliminary work seems to indicate, the coal will have to be heated during evacuation until it attains a constant weight. Several

investigators follow such procedures and feel that they do not alter the coal structure significantly by this treatment [42,43]. Others maintain that both the grinding and drying processes alter the pore structure to a significant extent [44]. As indicated in sections 2.4 and 3.2.7, more experimental confirmation is needed.

3.2.6 Heterogeneity

The heterogeneity of coals presents an experimental problem which is considered by some to be insurmountable. Experienced experimentalists have estimated the degree of subdivision required, given certain total sample size and individual specimen-size limits, to assure that a sample is representative. As the DSC and TGA require very small specimens, it is necessary to evaluate the reproducibility of the measurements and determine the number of replicates needed to establish a reliable average value rather than to estimate the accuracy of individual measurements. The existence of this extreme heterogeneity in coals supports the selection of the DSC for heat capacity measurements and will be an important consideration in the development of other measuring techniques. It would seem more appropriate to have a simple, fairly rapid, technique that will allow for many replicate measurements so that an average may be obtained rather than an inherently more accurate technique that is so time-consuming that replicate measurements are not feasible.

It should be noted that many of the newer methods used in coal characterization, particularly those applied in minerological analysis, require specimen sizes as small or smaller than those used by the DSC. Thus the general use of specimens of small size and fine subdivision is becoming more common.

3.2.7 Porosity

The porosity of coal has widespread consequences with respect to properties, coal preparation and storage, and processing. The pore structure of coals contains both micropores (<2 nm) and macropores (>30 nm) in addition to pores of intermediate size [42]. The total pore volume can be determined readily from moisture content or helium and mercury densities and porosimetry. Surface areas have been determined historically from heat of wetting and gas adsorption measurements. More important than the pore volume and pore surface area, however, is the size distribution of the pores; these are determined most frequently through mercury porosimetry and nitrogen adsorption isotherms [43]. A recent study by Mraw and Naas-O'Rourke has used heat-capacity measurements at subambient temperatures to evaluate pore size and pore-size distribution [45,46]. The whole spectrum of questions concerning the surface properties and porosity of coals and chars is an active field of research today. Further study is needed in this area, particularly with reference to the applicability of thermal methods to the solution of these problems [43,47,48,49].

3.2.8 Weathering

The term weathering can be used to describe the many changes, physical and chemical, which occur in coals as a result of exposure to natural elements such as air, wind, rain, snow, and freezing. However, it is used here to refer to the oxidation of coal by natural processes. As weathering causes rapid deterioration of the heating value and suitability for processing, it has serious industrial consequences. The chemical species generated in the oxidation of coals, as a result of exposure to

air, may differ from those generated by deliberate addition of specific chemical agents. In both instances, oxidation proceeds from the surface, with surface being understood to include microfissures and accessible pores. As reactivity increases with decreasing rank, the problems associated with weathering are more severe for lower-rank coals. Indeed the combined effects of heat of wetting and weathering can readily induce spontaneous combustion, as manifested by the occurrence of mine fires.

3.2.9 Plasticity

Plasticity refers to the tendency of some coals, usually bituminous coals with moderate amounts of volatile material, to go through a softening process, become fluid, and, after expulsion of some volatile material, to resolidify. This phenomenon is essential to coke manufacture and and is beneficial also in some conversion processes; in others it is detrimental. Swelling, which may be measured with a dilatometer, and fluidity, measured most frequently with a Gieseler plastometer, are the pertinent properties most readily measured. Rank, degree of subdivision, thermal treatment, degree of oxidation, maceral content, and porosity all affect the range of the plastic region and the degree of plasticity. Thus by blending and by varied treatments, one can do much to obtain a coal with the desired plastic properties.

Many mechanisms have been proposed to explain plasticity; a critical consideration of them is not relevant to this report. A sufficient and acceptable explanation is that physical softening or melting occurs shortly before the plastic region is reached. Within the plastic region, an initial depolymerization results in smaller, more readily mobile, molecular fragments; these leave the main structure of the coal and, in most instances, eventually volatilize. Following the removal of these fragments, repolymerization and resolidification occur.

3.2.10 Mineral Content

As the specific mineral matter present in coal has such a dramatic effect on its behavior, careful attention must be given to its nature and presence. While an evaluation of the effects of mineral content in any experimental study of coal is worthwhile, it may be particularly important in the study of thermophysical properties because of its recognized effects (e.g., the presence of a small amount of pyrite greatly increases the heat capacity). Careful attention must be given to the possible effects of mineral composition on the thermophysical property measurements. It would be useful to evaluate its effect by complete removal of mineral matter and the subsequent addition of known species and amounts.

3.2.11 Subdivision

While finely-divided specimens may be suitable for research use, they are not always realistic for application to industrial processes. At some point in the development of an adequate measuring program attention should be given to comparisons between results on specimens of different degrees of subdivision. While it is true that some equilibrium thermal properties, e.g., heat capacity, should not be size-dependent, it is possible that the actual numerical results obtained will show size-dependence, as an artifact of the measuring technique. If this is so, measurements on various-sized specimens will be required in order to make adequate allowance for the phenomenon. Other properties, e.g.,

thermal conductivity, are expected to be affected by specimen size and subdivision. Equipment that will allow for measurements on appropriate specimens may need to be developed.

3.3 Possible Experimental Investigations

Acceptable measurement techniques for coals to determine thermal conductivity, heat capacity and heat of wetting must be selected.

In the course of this investigation several possible studies that would be of interest have presented themselves. The carrying out of even a portion of these would require many investigators, a long period of time, and experimental facilities that are not available presently at NBS. These studies indicate the variety of unanswered questions relating to the thermophysical properties of coal.

Heat capacity relationships of interest:

Heat capacity as a function of temperature for a diverse group of coals, to as high a temperature for each coal as is practical given variations in plastic properties.

Heat capacity as a function of rank.

Heat capacity as a function of type or maceral composition. In particular, look for additive or predictive relationships that can be used to obtain properties of blends.

Heat capacity as a function of subdivision. This investigation would require some use of an adiabatic calorimeter since the size of the sample cells in the DSC limits the size of particle that can be used. Also, the poor thermal conductivity of larger particles requires long equilibrium times; the scanning mode would not be suitable for such particles.

Heat capacity as a function of the ratio of organic to mineral matter.

Heat capacity in the presence or absence of specific minerals. For such a study, minerals could be added to demineralized coals.

Heat capacity as a function of the atmosphere surrounding the specimen. Atmospheres of interest include nitrogen, oxygen, air, pyrolysis and combustion products, and air and nitrogen with varying degrees of moisture.

Heat capacity as a function of degree of weathering. Such information is needed for combustion models and for industrial users who must work with weathered coals.

Heat capacity as a function of oxygen content and/or functionality.

Heat capacity of coal fragments formed by solvent swelling and emerging fractionation techniques.

Heat capacity of representative model compounds to provide the basis for modeling of thermal behavior.

Heat capacity of chars; of ash.

Variations of heat capacity relationships mentioned as a function of thermal history.

Thermal conductivity studies of interest:

Thermal conductivity as a function of temperature for virgin coals; for heat-treated coals, for chars, and ash.

Thermal conductivity as a function of pressure, particularly realistic mine and processing pressures.

Thermal conductivity as a function of direction of heat flow with respect to the bedding plane.

Thermal conductivity as a function of degree of subdivision.

Thermal conductivity of powdered, packed samples.

Techniques for high-temperature studies (to 1200°C) for poorly conducting materials; apply such techniques to carbonaceous materials; to insulating materials.

The variation of thermal conductivity as a function of many of the variables listed in the section on heat capacity such as weathering, maceral and mineral content, and atmosphere. The modeling of thermal conductivity is as necessary and desirable as is the modeling of heat capacity.

Heat of wetting studies:

Heat of wetting of coal as a function of subdivision.

Heat of wetting as a function of solvent (water, hydrocarbon liquids, mixtures of such liquids, typical coal processing fluids).

The variation of thermal properties with the variables mentioned has not been measured for the most part; thus no judgment can be made as to significant differences in such properties, e.g., macerals are all organic materials, though the mode of incorporation of mineral matter often differs. Measurement may show that the differences in thermal properties of the macerals are not significant or do not vary in a regular way. However, such evidence must be obtained, not guessed at.

As noted previously, the studies indicated here would require many staff-years of work. In the formulation of the recommendations which follow, the charter of the Bureau of Standards to provide

support in satisfying the most pressing needs of industry, external consultations, and NBS staff expertise were considered.

3.4 Recommendations

3.4.1 General

Indications of research needs in thermophysical properties of solid feedstocks and the implied generic rationale for their performance by the Thermophysical Properties Division are interspersed throughout this report. However, the recommendations are summarized here and the rationale restated for the convenience of the reader and for emphasis.

There was a consensus among those consulted that a strong need exists for thermophysical property data for coal. The needs identified in this report were considered urgent by some, but are only now being recognized by others.

Knowledge of these properties is needed to reduce energy consumption and its associated expense; to minimize capital expenditure for processing and transport equipment; to tailor coal feedstocks for various processes; to minimize safety and environmental hazards; and most importantly, to permit intelligent and operative design of synthetic fuel processes and to facilitate use of solid feedstocks for direct synthesis of industrially important chemicals. For the determination of the heat balance in conversion processes, these properties must be known for the substances going into the process as well as for those in the product stream.

An in-depth knowledge of the thermophysical properties of coals is important to the detailed understanding of normal combustion processes as well as solid-liquid conversion and gasification processes. Knowledge of these properties will aid in formulating acceptable correlations between process factors and properties and characteristics of coals. Measurements are needed for heat capacities, thermal conductivities, and enthalpies for raw coals, chars, and ash in various temperature regions for above-ground and in situ processes. There is also a need to know these same properties as a function of a) realistic mine pressures and b) the higher pressures encountered in processing (up to 20 MPa (3000 psi)). In addition, heats of interactions with various liquids are needed.

It is recommended that satisfactory procedures be developed for the measurement of the heat capacity of coals throughout as much of the temperature range, 0 to 700°C, as is possible. Methods for chars and mineral matter in this temperature range should be standardized. As the temperature range for useful measurements on coals may be extended significantly by slow heating, an attempt should be made to evaluate thermophysical properties as far as possible into the plastic region.

It is desirable to make thermophysical property measurements on coals in which weathering has been curtailed as far as possible. At first glance, this may seem impractical from the standpoint of industrial users. However, it is important for such users, who work with coals in various stages of weathering, to be able to relate the properties measured to the degree of weathering and thus account, and compensate, for changes in properties due to weathering as processing occurs. For this reason, it is recommended that the first study undertaken, subsequent to the development of measurement techniques, be the variation of thermophysical properties as a function of degree of weathering.

It is desirable to be able to predict the thermophysical properties of blends of coals from the properties of the individual components. Because of the importance of maceral content to suitability for processing, it would be useful to be able to predict the thermophysical properties of blends from the thermophysical properties of the component macerals. As maceral enrichment and separation techniques are presently available [50,51], a second recommended study is that of the variation of the thermophysical properties mentioned above as a function of maceral type and composition.

Given the strongly expressed consensus that heat of wetting measurements are urgently needed for coal slurries, for liquefaction processes, and for the control of spontaneous combustion, and in light of the existing uncertainties regarding methods for such measurements, it seems advisable to undertake methods research on heats of wetting. Such measurements are within the domain of the Thermophysical Properties Division.

A strong case can be made for wide-ranging investigations of a reasonable number of commercially important coals rather than a more academic study of great numbers and varieties of coals, though the latter could lead to some interesting and worthwhile correlations. From the standpoint of the industrial user the selection of coals for study should be practical, i.e., the coals studied must be those which are suitable for processing, either alone or as a component of blends, and should exist in sufficient quantity to be commercially useful for many years. Consequently it is recommended that a few coals important to coking, combustion, liquefaction, and gasification processes be sought.

That the development of satisfactory procedures for sampling and sample handling for solid fuels is integral to the development of satisfactory measurement procedures is a truism. Many years of coal research have generated recommended procedures; as the experimental program defining measurement procedures progresses, the necessity and/or effects of coal sample handling procedures should be evaluated systematically so that the final methods adopted will be sufficient for their purpose, but not precise beyond reason. More directly, sampling and sample handling techniques must be a component of our experimental program. It is recommended that such research be undertaken in cooperation with a) groups from NBS having appropriate expertise, and b) research programs recently instituted by groups such as the Gas Research Institute.

When measurement procedures are satisfactory, the development of standard reference materials for thermophysical properties will be feasible and should be undertaken. Following this, an interlaboratory testing program should be set up and, from the results, necessary refinements of measurement techniques made.

Banks of data coming into existence on well-characterized coals contain few thermophysical property data. The attempts to correlate coal properties with suitability for industrial processing have not led to generally satisfactory results. Since many of these processes depend on heat transfer, the addition of heat capacity, thermal conductivity, and heat of wetting data to these banks will enhance the possibility of improving such correlations. As the experimental work progresses, efforts should be made to develop correlations among properties and general (non-proprietary) process requirements. The probability of success in deriving correlations increases as the available data increase. It is advisable to strengthen consultation and cooperation with as broad a group of coal scientists as possible and to establish a reputation for sound experimental work in solid feedstocks/fuels with a view to encouraging the release of as much non-proprietary data as possible. The general charter and

reputation of the National Bureau of Standards should be used to facilitate, direct, and perhaps to carry out, the compilation of these data.

As the compilation of characterization and physical data proceeds, attempts should be made to develop models or predictive relationships. Such relationships do exist for heats of combustion; Kirov [9] and Gomez [8] have developed predictive relationships for specific heat and/or enthalpy based on proximate analysis and temperature, respectively. Of these Kirov's is more generally applicable, but admittedly is used in lieu of reliable data or a better model (Aspen program). Continued attempts to derive predictive relationships should be made as the matrix of reliable characterization and physical property data expands. The possibility of relating thermal properties to the structure of coals and to structural changes is intriguing and should be pursued.

Thermophysical properties of fuels may also be modeled from similar properties of selected compounds. A recent attempt by Benson and Schobert [18] to reproduce thermograms of coal with one or two compounds shows remarkable promise. Research of this sort, which represents an alternative attempt at modeling, should be conducted in conjunction with the measurement of the properties of the coals as soon as the measurement techniques are determined to be reliable.

3.4.2 Equipment

Instrumental choices for the initiation of the experimental program have been made with consideration of the nature of the materials to be tested, available instrumentation, and the needs of potential users in mind.

For heat capacity, the differential scanning calorimeter (DSC) has been selected because of its speed and simplicity of operation along with an adequate accuracy (better than 2% with pure materials over wide temperature ranges). The rapidity with which scans can be made will allow for several replicate measurements in the course of a determination; this is desirable given the variety of coals and their inhomogeneity. The need is for a simple, rapid, readily-automated method in contrast to methods inherently more accurate, but difficult, time-consuming, and expensive to carry out.

Numerous thermal conductivity techniques are described in the literature. The most suitable ones are those that involve specimens with a small thickness to cross-sectional area ratio due to the relatively low conductivity of coal specimens. The hot-wire technique and the guarded-hot-plate technique appear to be most suitable, but other longitudinal or radial heat-flow methods can be applied with success. The hot-wire technique is tentatively selected for initial investigations. Measurement uncertainties of 10% are probably acceptable for general characterization; for the establishment of standards related to solid feedstocks an uncertainty of no more than 2% is recommended.

4. REFERENCES

[1] Agroskin, A. A. and Gleibman, V. B., "Heat Capacity and Characteristics of the Molecular Structure of Coal Materials," Khim. Tverd. Topliva No. 3, 61-67, 1975.

[2] Agroskin, A. A. and Goncharov, E. I., "Determination of the Specific Heats of Coals During Carbonization," Coke and Chem. USSR pt. 11, 16-20, 1965.

[3] Agroskin, A. A., Goncharov, E. I., Makeev, L. A., and Yakumin, V. P., "Specific Heat and Heat of Pyrolysis Reaction for Some Donbas Coals," Coke and Chem. USSR, Pt. 5, 7-11, 1970.

[4] Badzioch, S., "Thermo-Physical Properties of Coals and Cokes," BCURA Rev. 200, 24(11,2), 485-520, 1960.

[5] Batchelor, J. D., Yavorsky, P. M., and Gorin, E., "Measurement of the Thermal Properties of Carbonaceous Material," J. Chem. Eng. Data 4(3), 241-6, 1959.

[6] Clendenin, J. D., Barclay, K. M., Donald, H. J., Gillmore, D. W., and Wright, C. C., "Thermal and Electrical Properties of Anthracite and Bituminous Coals," Penn. State Coll. Miner. Ind. Exp. Sta. Tech. Paper 160, 11-67, 1949.

[7] Coles, G., "The Specific Heat of Coal and Its Relation to Composition," J. Soc. Chem. Ind. 42, 435T-439T, 1923.

[8] Gomez, M., Gayle, J. B., and Taylor, A. R., Jr., "Heat Content and Specific Heat of Coals and Related Products", Bur. Mines RI 6607, 45pp., 1965.

[9] Kirov, N. Y., "Specific Heats and Total Heat Contents of Coals and Related Materials at Elevated Temperatures," BCURA Monthly Bull., Rev. 241, 29(2,1), 33-59, 1965.

[10] Melchior, E. and Luther, H., "True Specific Heats of Cokes and Coals: Measurements from 30 to 350 C," Erdoel und Kohle, Erdgas, Petrochemie, 28(8), 379-385, 1975.

[11] Singer, J. M. and Tye, R. P., "Thermal, Mechanical, and Physical Properties of Selected Bituminous Coals and Cokes," Bur. Mines RI 8364, 37pp., 1979.

[12] Terres, E., Dahne, H., Nandi, B., Scheidel, C., and Trappe, K., "Determination of the Genesis of Fusains from Their Specific Heat," Brennstoff-Chem. 37, 269, 342, 366, 1956.

[13] Voloshin, A. I., "Thermal Constants of Coal, Semicoke and Coke and the Heat of Carbonization," Koks i Khim. No. 10, 20-24, 1958.

[14] Zamuluev, V. K., "Thermal Properties of Coals Undergoing Pyrolysis," Khim. i Tekhnol, Topliva i Masel, 20-23, July 1959.

[15] Mraw, S. C. and Naas, D. F., "The Measurement of Accurate Heat Capacities by Differential Scanning Calorimetry. Comparison of d.s.c. Results on Pyrite (100 to 800 K) with Literature Values from Precision Adiabatic Calorimetry," J. Chem. Thermodynamics 11, 567-584, 1979.

[16] Mraw, S. C. and Naas-O'Rourke, D. F., "Thermodynamic Properties of Cyclohexane-d_{12}: Low-Temperature Heat Capacity and Enthalpies of Transition and Fusion From Accurate Differential Scanning Calorimetry, and the Entropy from Spectroscopic Results," J. Chem. Thermodynamics 12, 691-704, 1980.

[17] Mraw, S. C. and O'Rourke, D. F., "Accuracy of Differential Scanning Calorimetry for Heat Capacities of Organic Compounds at High Temperatures. New Method for Enthalpy of Fusion by d.s.c.," J. Chem. Thermodynamics 13, 199-200, 1981.

[18] Benson, S. A. and Schobert, H. H., "Structural Characteristics and Relationships in Low-Rank Coals", paper presented at Lignite Conference, San Antonio, Texas, June 1981.

[19] Mahajan, O. P., Tomita, A., and Walker, P. L., Jr., "Differential Scanning Calorimetry Studies on Coal. 1. Pyrolysis in an Inert Atmosphere," Fuel 55, 63-69, 1976.

[20] Mahajan, O. P., Tomita, A., Nelson, J. R., and Walker, P. L., Jr., "Differential Scanning Calorimetry Studies on Coal. 2. Hydrogenation of Coals," Fuel 56, 33-39, 1977.

[21] Berkowitz, N., "On the Differential Thermal Analysis of Coal," Fuel 36, 355-373, 1957.

[22] Glass, H. D., "Investigations of Rank in Coal By Differential Thermal Analysis," Econ. Geol. 49, 294-309, 1954.

[23] Glass, H. D., "Differential Thermal Analysis of Coking Coals," Fuel 34, 253-268, 1955.

[24] Gold, P. I., "Thermal Analysis of Exothermic Processes in Coal Pyrolysis," Thermochimica Acta. 42, 135-152, 1980.

[25] Mitra, P. K., Tarafdar, T. C., Raja, K., and Banerjee, N. G., "Devolatilization Characteristics of Carbonaceous Solid Fuels with Special Reference to Coal," Ind. J. of Tech. 15(9), 375-380, 1977.

[26] Wagner, R. A., private communication (1981).

[27] Dils, R. R., Rorrer, D. E., Allen, J. D., Francis, J. E., and McNeil, M. B., "Radiative Heat Transfer in High Temperature Hot Wire Thermal Conductivity Measurements," Seventh European Thermophysical Properties Conference, Antwerp, Belgium, June 1980.

[28] Badzioch, S., Gregory, D. R., and Field, M. A., "Investigation of the Thermal Conductivity and Thermal Diffusivity of Coal," Fuel 43, 267-280, 1964.

[29] Fuller, E. L., Jr., "Structure and Chemistry of Coals: Calorimetric Analysis," J. Coll. Interface Sci. 75(2), 577-583, 1980.

[30] Neill, P. H., "Thermometric Titrations for the Determination of Surface Areas and Acidities of Aluminas and Silica Aluminas," M.S. Thesis, University of Tennessee, Knoxville, TN, 1981.

[31] Neavel, R. C., "Coal Structure and Coal Science: Overview and Recommendations," ACS/CSJ Chemical Congress, Honolulu, Hawaii, Fuel Div. Preprints, 24, 73, 1979.

[32] Mackowsky, M.-Th., Micros. Acta 77(2), 114, 1975.

[33] Berkowitz, N., "An Introduction to Coal Technology," New York, Academic Press, 1979.

[34] Montgomery, W. J., "Standard Laboratory Test Methods for Coal," Analytical Methods for Coal and Coal Products, Vol. I, C. A. Karr, Jr., ed., New York, Academic Press, 1978.

[35] Van Krevelen, D. W., "Coal," New York, Elsevier Publishing Co., 1961.

[36] Jenkins, R. G. and Walker, P. L., Jr., "Analysis of Mineral Matter in Coal," Analytical Methods for Coal and Coal Products, Vol. II, C. A. Karr, Jr., ed., New York, Academic Press, 1978.

[37] Finkelman, R. B., "Modes of Occurrence of Trace Elements in Coal," U.S. Geological Survey, Open File Report OF 81-99, 322 pp., 1981.

[38] Neavel, R. C., Hippo, E. J., Smith, S. E., and Miller, R. N., "Coal Characterization Research: Sample Selection, Preparation, and Analyses," 180th National Meeting of the ACS, San Francisco, California, Fuel Div. Preprints, 25, 246 (1980).

[39] Proceedings of DOE/GRI Coal Sample Bank Workshop, March 1981, Atlanta, Georgia (to be published).

[40] Spackman, W., private communication (1981).

[41] Rowlinson, J. S., "Liquids and Liquid Mixtures," London, Butterworth, 1969.

[42] Gan, H., Nandi, S. P., and Walker, P. L., Jr., "Nature of the Porosity in American Coals," Fuel 51, 272, 1972.

[43] Walker, P. L., Jr., "Microporosity in Coal - Its Characterization and Its Implications for Coal Utilization," paper presented at the Royal Society meeting on "New Coal Chemistry," May 1980.

[44] Wightman, J. P. and Widany, E., "Thermodynamics and Kinetics of Immersion of Coals by n-Alcohols," Colloids and Surfaces, (in press).

[45] Mraw, S. C. and Naas-O'Rourke, D. F., "Water in Coal Pores: Low-Temperature Heat Capacity Behavior of the Moisture in Wyodak Coal," Science 205, 901-2, 1979.

[46] Mraw, S. C. and O'Rourke, D. F., "Water in Coal Pores: Part II. The Enthalpy of Fusion Reflects Pore Size Distribution," J. Coll. Interface Sci., (in press).

[47] Ismail, I. M. K. and Walker, P. L., Jr., "Rates and Heats of Oxygen Chemisorption on Saran Chars at 100 C," J. Coll. Interface Sci. 75(2), 299-312, June 1980.

[48] Mahajan, O. M. and Walker, P. L., Jr., "Porosity of Coals and Coal Products," Analytical Methods for Coal and Coal Products, Vol. I, C. A. Karr, Jr., ed., New York, Academic Press, 1978.

[49] Nelson, J. R., Mahajan, O. P., and Walker, P. L., Jr., "Measurement of Swelling of Coals in Organic Liquids: A New Approach," Fuel 59, 831, 1980.

[50] Dyrkacz, G. R., Bloomquist, C. A. A., and Horowitz, E. P., "Laboratory Scale Separation of Coal Macerals," Separation Science and Technology (in press).

[51] Harris, L. A. and Hise, E. C., "The Application of Coal Petrography to the Evaluation of Magnetically Separated Dry Crushed Coals," Process Minerology, Extractive Metallurgy, Mineral Exploration, Energy Resources, D. M. Hausen and W. C. Park, eds., Proceedings Annual Meeting, AIME, Feb. 22-26, 1981, Chicago, IL.

NBS-114A (REV. 2-8C)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET (See instructions)	1. PUBLICATION OR REPORT NO. NBSIR 82-1666	2. Performing Organ. Report No.	3. Publication Date May 1982

4. TITLE AND SUBTITLE

Review of Needs for Thermophysical Property Data on Solid Feedstocks. I. Coal

5. AUTHOR(S)

Jane E. Callanan

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

Final

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

This report, which presents the results of a comprehensive survey with respect to thermal properties of coal, is part of a broader study which also includes oil shale, tar sands, and gas hydrates. This survey shows the need for experimental work on heat of combustion, heat capacity/enthalpy, thermal conductivity, and heat of wetting for both well-characterized premium coal samples and for samples of the type which will be used directly in conversion processes. Widely accepted, standardized measurement techniques do not exist for three of these properties (heat of combustion excepted) and must be developed; in addition, reliable data must be generated for efficient use of coal as a feedstock. Theoretical studies which will allow for modeling of properties should proceed along with the experimental investigations to allow for improvement in ability to predict coal properties for process design. Recommendations for work appropriate to the National Bureau of Standards and the justification for the recommendations are included.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

Coal; enthalpy; heat of wetting; heat capacity; literature survey; review; solid feedstocks; thermal conductivity; thermal properties.

13. AVAILABILITY

☒ Unlimited

☐ For Official Distribution. Do Not Release to NTIS

☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES 32

15. Price $7.50

USCOMM-DC 6043-P80

☆ U.S. GOVERNMENT PRINTING OFFICE: 1982—578-782/242 REGION No. 8