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DMF Extractability as a Predictor of Plasticity in Bituminous Coals

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Whitt,

Jana Mefford

1983

DMF EXTRACTABILITY AS A PREDICTOR OF PLASTICITY IN BITUMINOUS COALS

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Jana Mefford Whitt
June 1983

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DMF EXTRACTABILITY AS A PREDICTOR OF PLASTICITY IN BITUMINOUS COALS

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DMF EXTRACTABILITY AS A PREDICTOR OF PLASTICITY IN BITUMINOUS COALS

Jana Mefford Whitt 73 pages

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Plasticity is a phenomenon of certain coals that is not completely understood. Some bituminous coals go through a softening and swelling state upon heating before they resolidify. It is this softening and swelling state that is labeled as the "plastic state" of the coal. Concurrent with the plastic state of the coal, thermal decomposition of the coal takes place. Several low molecular weight gases are also evolved. These occur at a temperature of approximately 450°C.

The plasticity of a coal is a good indication of the coking ability of a coal. Plastic coals tend to give higher yields in liquefaction reactions than do nonplastic coals, a fact very useful to the synfuel industry. Fluidized bed reactors are impaired by the use of plastic coals, as they tend to agglomerate in the bed. Currently the ASTM approved method used to determine plasticity is by using a Gieseler plastometer. Gieselers are inconsistent and an easier, more efficient method is needed.

It is currently thought that the bitumen in the coal, the extractable portion of the coal, is responsible for initiating the plasticity mechanism. It is logical, then, to assume that the amount of bitumen in the coal could be used as a predictor of the degree of plasticity.

Dimethylformamide (DMF) was used as the solvent for the Soxhlet extraction of 43 highly characterized bituminous coals. A correlation between the DMF extraction data and the coal plasticities shows that DMF extraction is a reasonable technique to use to predict plasticity.

CHAPTER 1

INTRODUCTION

The plasticity of a coal is a characteristic that is difficult to measure. Presently, the only way to obtain decent fluidity measurements is by using a Gieseler plastometer. However, Gieselers are inconsistent and good reliable data is hard to obtain. A method which is consistent, inexpensive and relatively simple is needed to measure or predict the plasticity of coals.

Plasticity results from the softening and swelling of some bituminous coals as they are heated. The plastic state of the coal is the softening and swelling state. After the coal leaves its plastic state it resolidifies into a semi-coke. The mechanism of coal plasticity is not completely understood, but it is presently thought that it is the bitumen of the coal which serves as an initiator of the process. The bitumen of the coal is that part which is extractable with organic solvents. Bitumen is rich in hydrogen and has a low melting point. It is reasonable, then, to suspect that the amount of bitumen in a coal would be related to its plasticity. Solvent extraction was done using dimethylformamide as the solvent on 43 bituminous coals. These 43 coals were highly characterized. DMF was chosen as the solvent because of its small size (making it easier to enter the pore system of the coal), its availability of electron pairs on the nitrogen and oxygen atoms, and the polarity of the molecule. These characteristics of a solvent make it especially efficient in removing the bitumen from a coal. It was the intent of this research to prove that the amount of bitumen extracted would be related to the degree of plasticity.

The plasticity of a coal is important for a number of reasons. Plastic coals are the prime coking coals. Coke manufacture is the second largest use of coal today behind the direct combustion of coal. Plastic coals also tend to give higher yields in some liquefaction reactions than nonplastic coals. A place where plastic coals are not welcome would be in fluidized bed reactors. Here plastic coals tend to agglomerate and impair the reaction process. It can be seen from these examples that the industrial world needs a simple, consistent, and inexpensive method to measure and/or predict the degree of plasticity in coals.

CHAPTER II

HISTORICAL

Certain coals, upon heating, pass through a softening and swelling state. As the temperature increases,they then resolidify into a more or less distended cellular coke mass. This softening and swelling state is called the plastic state of the coal. Coals exhibiting this behavior are called plastic coals, or sometimes coking coals. The temperature of the plastic state of the coal coincides approximately with the temperature of active decomposition of the coal. Concurrent with the plastic phenomenon then, thermal decomposition of the coal occurs. This happens at a temperature around 450°C. Several low molecular weight gases are evolved during this time.

Historically, the first evidence of plasticity in bituminous coals undoubtedly was observed directly in a coal-fire fuel bed. Proof that there is a surface flow of the heated coal during the formation of coke has been demonstrated by numerous investigations through the years.(1)

Plasticity is an important phenomenon of coal because it is a good indicator of the best coals to use in the commercial coking processes. The more plastic coals are the better coking coals. Basically, coke and its properties are the result of the coal properties and the conditions used to convert the coal into coke. Since there is no question that the plastic state and the properties of the plastic mass determine this technical process, all parameters that influence the plastic stage and the properties of the plastic mass are important.(2)

The plasticity of a coal also is an indicator of which coals are better for fluidized bed processes. In general, high fluidity of coal and a wide plastic range are unfavorable for operations in fluidized beds. Fusion of the coal needs to be avoided in a fluidized bed, and the tendency of the coal to agglomerate (form into a rounded mass) depends on the time that the softened coal requires to solidify to semi-coke under process conditions, and also depends on the fluidity and the actual stickiness of the molten coal mass.(3)

Plasticity data on coals could play an important role in the future of coal liquefaction. The most reactive high volatile bituminous coals in liquefaction processes are those that develop maximum plasticity.(4) Neavel proposes that plasticity is essentially a transient, hydrogen-donor liquefaction process and that an understanding of plastic development may lead to insights into liquefaction mechanisms.(5)

As a general rule, plastic behavior is only encountered among the high-volatile A, medium volatile and low volatile bituminous coals. The strongest appearance of plasticity is among the medium-volatile bituminous coals (with C content = 86-89%). There is no sharp dividing line between plastic and nonplastic coals, however, and plastic behavior can vary widely in this range.(6)

Coal is composed of macerals. A maceral is defined as a microscopic constituent of coal. Of the four common macerals found in coal, only vitrinite and exinite exhibit plastic behavior. Fusinite and micrinite have not been found to exhibit plasticity. Except for a very few unusual coals, only vitrinite in coals of bituminous rank has plastic capability.(5) Vitrinite and exinite seldom show plastic behavior if their carbon content is below 80.5% or above 91.0%.

In general, plastic properties become evident in coals when the content of volatile matter exceeds 12-15%, becomes more pronounced as the volatile content increases to 30-35%, becomes less pronounced and then disappears when the coal contains about 40% volatiles. In the same manner, coal plasticity is related to coal porosity. The most plastic coals are also the least porous. Exceptions are found to these generalizations, as are found in most generalizations concerning coal.(7)

Plastic properties are extraordinarily sensitive to changes in ambient conditions. Increasing the heating rate will increase the maximum fluidity and degree of swelling. It will also raise the temperature at which maximum fluidity and the onset of swelling are observed. Preheating the coal in an inert atmosphere to temperatures less than 200°C for a period of time will steadily decrease fluidity and swelling. Coals with high ash contents can have their plastic properties enhanced by reducing the mineral matter in the coal. Oxidation will narrow the plastic range and lower the maximum fluidity, and will eventually destroy plastic behavior. The coals being studied should be stored under N_2 in a freezer to help retard degradation of the coal and its plastic properties. Mild hydrogenation broadens the plastic range and increases fluidity and swelling. Manifestations of plasticity can be suppressed by pyrolyzing the coal in vacuo or enhanced by heating it under pressure.(8)

The dependence of coal plasticity on ambient conditions has made it extremely difficult to develop a comprehensive, self-consistent theory of plasticity. Various attempts have been made during the past 100 years, and two widely accepted, plausible, but insufficient mechanisms have emerged.

The earliest proposed mechanism was established by R. V. Wheeler.(9) In the years 1915-1924, Wheeler and Jones,(10,11) Fischer and Gluud,(12) Bone et al.(13,14) postulated that the coals which exhibit plastic behavior contain a fusible portion, or bitumen, which is responsible for their softening and swelling. This fraction, sometimes referred to as the "coking principle," is found in certain coal extracts.(15) The bitumen portion is defined as that portion of the coal which is extractable with organic solvents. It is characteristically low in molecular weight, rich in hydrogen and melts at temperatures less than 200°C.

Audibert(16) in 1926 suggested a homogeneous melting of all the coal within its plastic range. This supported the bitumen theory, but may be misleading, as this phenomenon might occur only in the case of high concentration of such a maceral component as pure vitrinite. In general, exinite, micrinite, fusinite and mineral matter occur to a certain degree in all coals.

The bitumen theory was also supported by the early observation that the extractable 'fusible fraction' when added to nonplastic coals confers plasticity and by evidence that initial melting is (more or less) a reversible phenomenon.(9)

An early proposal which is somewhat related to the bitumen theory was postulated by Blayden et al.(17) in 1944 and by Hirsch(18) in 1954. They suggested a turbostratic lamellar model based on x-ray studies, which assumes that coal may be represented as flat poly-condensed aromatic "lamellae" whose average dimensions and degree of ordering increase with rank. This theory explains the softening of coal by assuming that the smaller lamellae become mobile at higher temperatures and act as a lubricant for the bigger lamellae.

Bangham et al.,(19) in 1949, inferred the existence of units called "micelles" with diameters of about 200 Å. As the rank of coal increases, the micelle arrangement becomes more compact. The plasticity mechanism was explained by Bangham by assuming that these colloidal particles were covered by surface films that become fluid when heated. Such a concept may be considered as being halfway between the "bitumen" and the "lamellae" theories.

The other major theory, and the one most widely accepted in the past 30 years, is due mainly to Van Krevelen and his associates.(20,21,22) Others before Van Krevelen, however, had articulated the theory that plasticity arises from pyrolytic generation of small molecules.(23,24,25) In 1956, Fitzgerald(26) and in 1957, Chermin and Van Krevelen(27) proposed a mathematical model for the carbonization process.

An unstable intermediate product, "metaplast" is formed during the first reaction. This is a depolymerization reaction, and the metaplast formed is responsible for the plastic behavior. A cracking process follows, in which non-aromatic groups are split off. Recondensation of the metaplast units then occurs, and a semi-coke is formed. The last reaction is a secondary degasification in which the semi-coke units polymerize as methane evolves and, at higher temperatures, as coke in formed hydrogen evolves.

This theory is supported by the work of many others. Brown and Brown(28,29) have shown the substantial effects of heating rates upon plasticity, effects which are consistent with pyrolytic reactions but not with simple melting. Russell and Perch(30) and many others have shown an extremely sharp suppression of plastic behavior by very mild partial oxidation, an observation hard to reconcile with simple mass melting. Loison and his co-workers strongly support this metaplast theory in their comprehensive review of plasticity for Lowry.(31)

A more recent theory, presented by Neavel, encompasses parts of both theories, and seems to be the most plausible at this time. Neavel believes that three properties of coal appear to be necessary and sufficient for plastic behavior: (1) lamellae-bridging structures that can be thermally broken; (2) an indigenous supply of hydroaromatic hydrogen, and (3) an intrinsic capability of micelles and lamellae to become mobile independently of quantitatively significant bond rupture (to "melt").(5)

If one examines recent representations of coal, such as the Peter H. Given model given in Figure 1, one can see that coal does have all of Neavel's structural requirements. Given's model is the most generally accepted representation, although it is important to realize that vitrinite from coals of different ranks will vary somewhat. Lamellar size, heteroatom content, aromaticity, degree of condensation, and functional group characteristics all vary--even within a given vitrinite.

Vitrinite is used for this model since it is the vitrinite in bituminous coals which exhibits plastic behavior. The vitrinite is composed of packets (micelles) of more or less aligned molecular units (lamellae) of variable structures typified by condensed ring systems connected by bridging atoms. Attached to the rings are various functional groups (=O, -COOH, -OH, $-C_nH_m$). Some of the ring carbons may be saturated with hydrogen (hydroaromatic structures). As shown in part (b) of Figure 1, imperfect packing of the molecular units and the micelles leads to microporosity. Hydrogen bonds, Van der Waals forces, structural bridges such as ether linkages and methylene linkages bind the lamellae and micelles together.

About 20% or less of unbonded, relatively low molecular weight material, referred to as bitumen in earlier theories, is readily extracted through the pore system by solvents.(5)

In the ideal case, Neavel postulates that plastic development proceeds as follows:

1. General mobility of micellar units (physical melting) commences around 350-400°C as Van der Waals forces and

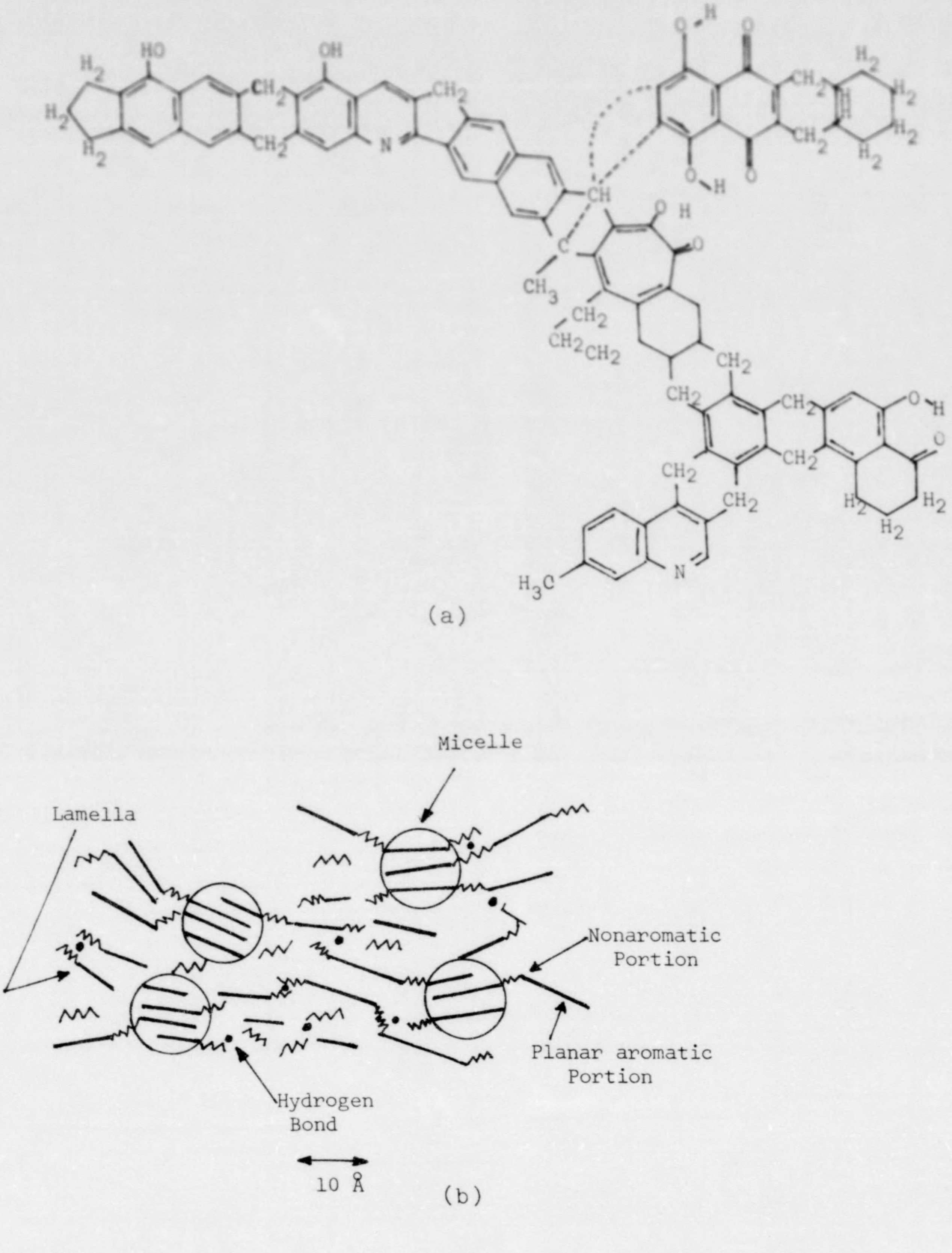


Figure 1. Representation of idealized molecular structure of vitrinite in bituminous coal: (a) molecular unit or layer; (b) composite alignment of layers(5)

hydrogen bonds become weakened, the bitumen serving as a necessary solvating vehicle and hydrogen donor early on during this phase. Some minimal cleavage of covalent bonds (especially ethers) may be involved in this phase.

2. Viscosity decreases progressively as mean molecular size is reduced at a rate reflecting the thermal rupture of covalent bonds that bridge stable molecular units, but only so long as the free radicals thereby formed are stabilized by indigenous donatable (hydroaromatic) hydrogen.

3. As the limited donor hydrogen inventory becomes consumed through the transfer of hydrogen and loss of volatile hydrogen-rich species, free radicals, which continue to be formed, increasingly "stabilize" by repolymerization. Viscosity, having reached a minimum then increases progressively as the molecular weight of the residual material increases.

4. Repolymerization then becomes the dominant fate of free radicals, and the metaplast solidifies as a semi-coke. In coals where premature cross-linking is not significant, molecular moieties align to form anisotropic mesophase structures.(5)

As suggested in early theories, bitumen removal, slow heating rates, and high concentration of relatively weak bonds would and do reduce plastic capability. These all appear to promote cross-linking before the temperature is reached at which melting can take place. Therefore, contact between indigenous donatable hydrogen and free radicals formed at high temperatures is prevented, and possibility of plastic behavior is reduced. Direct dehydrogenation, oxidation and bitumen removal all result in reduced availability of hydrogen and also reduce plastic capability. The reduction of donor hydrogen content allows premature repolymerization of thermally produced free radicals.

This theory explains other observations of coal plasticity. Also, the non-plasticity of low-rank coals can be explained by their high oxygen contents and consequent formation of strong cross-linkages from reactions at temperatures in the range below the coal softening point along with high unproductive consumption of donatable hydrogen by oxygen-associated reactions. The scarcity of bitumen and the relatively high extent of initial cross-linking explains the non-plastic behavior of anthracites and highly ranked coals.(7)

Neavel's theory seems to grasp important truths in both theories of plasticity. Often in the scientific world, the best of two schools of thought are combined to create a better theory.

The methods of measuring plastic behavior are as varied as the theories on the mechanisms of plasticity. One is not dealing with the determination of melting point, density or viscosity of a pure compound, but rather with attempts to describe and characterize in a useful manner a group of changes, both physical and chemical, that take place concurrently and sequentially, as the coal is heated.(12)

Some of these important changes include the development of a degree of fluidity; the development of a stickiness or tackiness that enables the particles to cohere or to adhere to "inert" particles, the evolution of gas that may escape readily, or may be effectively trapped in a tough, viscous mass, causing considerable swelling; and the setting to a firm solid as higher temperatures are attained. Thus, there are a large number of quantities an investigator may be interested in. He could be interested in such things as temperature at which fluidity develops and setting occurs, in the degree of fluidity attained; in the amount of swelling that occurs when no restraint is imposed, or in the pressure that develops if the mass of coal is held at essentially constant volume; in the strength of the solid residue that remains after setting has occurred, or the strength of the mass if an inert solid was admixed with the coal before heating; or in the variation of any or all of these properties with the rank of the coal, in the petrographic composition of the coal, or with changes in the test conditions, such as rate of heating.(12)

Several tests have been designed to measure swelling characteristics. The free swelling index is perhaps the most popular indicator of degree of swelling. In this test, which is an ASTM (American Society for Testing and Materials) procedure, one gram of -60 mesh coal is heated in a fused silica crucible to 820 ± 5°C in 2-1/2 minutes. The free swelling index (FSI) is determined by comparing the resultant "button" with a series of standard profiles. Coal which will not form a button is given a FSI of 0. Indices of 2 or 3 are usually taken as implying that the coal is weakly coking. (See Figure 2, next page)

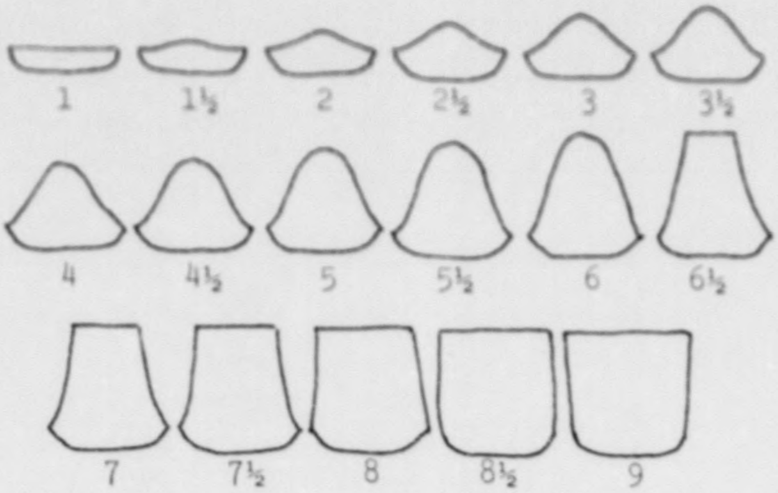


Figure 2. Standard coke button profiles and corresponding free swelling indices approximately 2/3 full scale.(33)

An alternative method used in some European countries assesses the mechanical strength rather than the distension of a coke button. In the Roga test, 1 gram of -0.2 mm coal is mixed with 5 grams of -0.4 mm anthracite compacted for 30 seconds under 6 kg and heated to 850°C in 15 minutes. The resultant button is then weighed (W), screened to remove -1 mm material, reweighed (a), and rotated in a 20 cm diameter drum for three 5-minutes periods, with -1 mm particles being removed after each. The Roga index (R) is calculated from

$$R = \frac{\frac{1}{2}(a+d)+b+c}{3} \times \frac{100}{W}$$

where b, c, and d are the weights of the residual button after the first, second and third period of rotation and can assume any value between 0 and 80.(34)

Coking properties can also be assessed by comparing the pyrolyzed residues from 600°C Gray-King assays with a series of "standard cokes" labeled as A, B,....G. Coals designated as A will not form a good coke pencil, coals designated as G yield residues that are quite distended.

The FSI, Roga index and Gray-King coke type are widely used industrially to provide practical guides to the behavior of coal. They are also used for laboratory screening of coals for particular end uses. The three tests have been shown to correlate well, although correlations of free-swelling index with the others are somewhat more complex. However, none of these offers much information about the complex rheological behavior of coal in its plastic state. Such information must be found by using suitable standardized plastometric or dilatometric methods.

Two methods of considerable interest involve plastometers. Plastometers measure resistance to shear in a heated coal mass. Both involve a cylindrical charge of coal in which is imbedded a coaxial stirrer having rabble arms. As the coal is heated, torque is applied to the coal charge or to the stirrer.

In the Davis plastometer the coal charge is rotated at a constant speed of 1.5 rpm, and the charges in torque are recorded throughout the temperature range 300-500°C. The temperature is increased at 3°C/min. In the unchanged coal charge resistance to rotation is low, but as the coal begins to soften, resistance increases rapidly. It decreases as sufficient fluidity develops, then increases during resolidification. The coke formed then breaks apart, and resistance returns to a very low value. The softening temperature, the plastic range and the solidification temperature are all obtained, as well as a measure of the fluidity and its changes as the test progresses.(35,36) The Davis plastometer, however, has been found not to give useful results with coals of low plasticity.(15)

The ASTM approved method involves using a Gieseler plastometer. The Gieseler is a modified constant torque plastometer and evaluates the apparent fluidity of plastic coal. This instrument (see Figure 3) measures the rotation

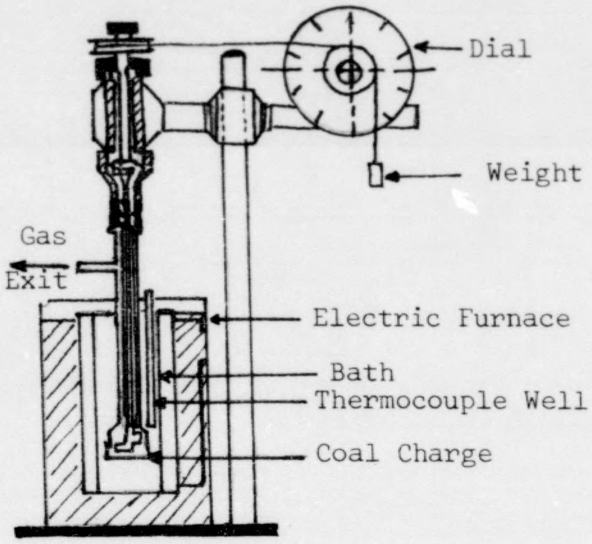


Figure 3. Simplified schematic of a Gieseler plastometer.(37)

of a specially designed rabble-armed stirrer in a compacted 5 gram coal charge. The coal is heated from a temperature of 300°C at 3 ± 0.1°C/min. The instrument records the fluidity in dial divisions per minute (ddpm).(38) The stirrer shaft is fitted with a dial which is divided into 100 dial divisions. The minimum deformation which is read is that occurring when the stirrer shaft makes one hundredth of a revolution per minute, i.e., one dial division per minute. The driving motor always operates at 300 rpm; consequently, the highest possible reading for an extremely fluid coal is 30,000 ddpm. All measurements of plastic or fluid properties obtained in Gieseler plastometers are given by numbers between 1 and 30,000 ddpm.(39)

Critical points in a Gieseler determination are the softening temperature (T_s), the temperature of maximum fluidity (T_m), and the resolidification temperature (T_r). T_s and T_r are defined in ASTM as the temperatures where the ddpm equals 1, or can be conventionally defined. The width of the plastic range is defined as T_r-T_s. A typical Gieseler curve is shown in Figure 4.(38)

Gieseler plastometers are sometimes not consistent or reliable. Rees and Pierron,(40) in 1955, evaluated the Gieseler and found it to be useful in obtaining qualitative or semiquantitative data on plastic properties, but not satisfactory for quantitative interpretation. Kirov and Stephens have criticized the Gieseler as furnishing misleading information during the early stages of coal plasticity.(7) It seems that although this method is not extraordinarily reliable, it is the best method for evaluating the fluidity at the current time.

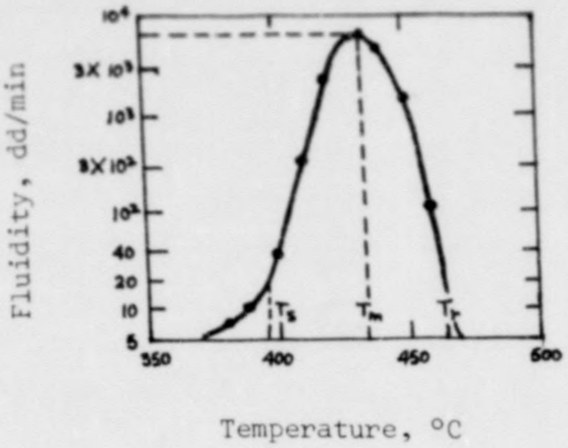


Figure 4. Typical (Gieseler) fluidity curve. T_s, T_m and T_r denote the softening, maximum fluidity, and resolidification temperatures.(34)

Isothermal plastometry has been carried out using a constant torque Gieseler plastometer, maintaining the temperature constant rather than a 3°C/min. ramp. Coal is reduced to -40 mesh, stored under inert gas at -40°C until the day of use, and is then loaded and packed into the Gieseler crucible assembly following ASTM procedures.

During the run the temperature is normally constant within approximately ± 1°C. For all isothermal runs a standard deviation of temperature is reported. Melting and coking slopes for the coal at the experimental temperature must be determined as the first step. The linearity of the coking slope under isothermal conditions, first noted by Fitzgerald,(41) is a general characteristic of plastic coals, including coal blends. The linearity of the melting slope has been shown in recent studies to be similarly well defined.(39)

Figure 5 illustrates a typical isothermal plasticity curve. The tangent slopes are calculated by a least-squares fitting routine, using all data with fluidity greater than one ddpm and less than 25% of the highest observed fluidity.

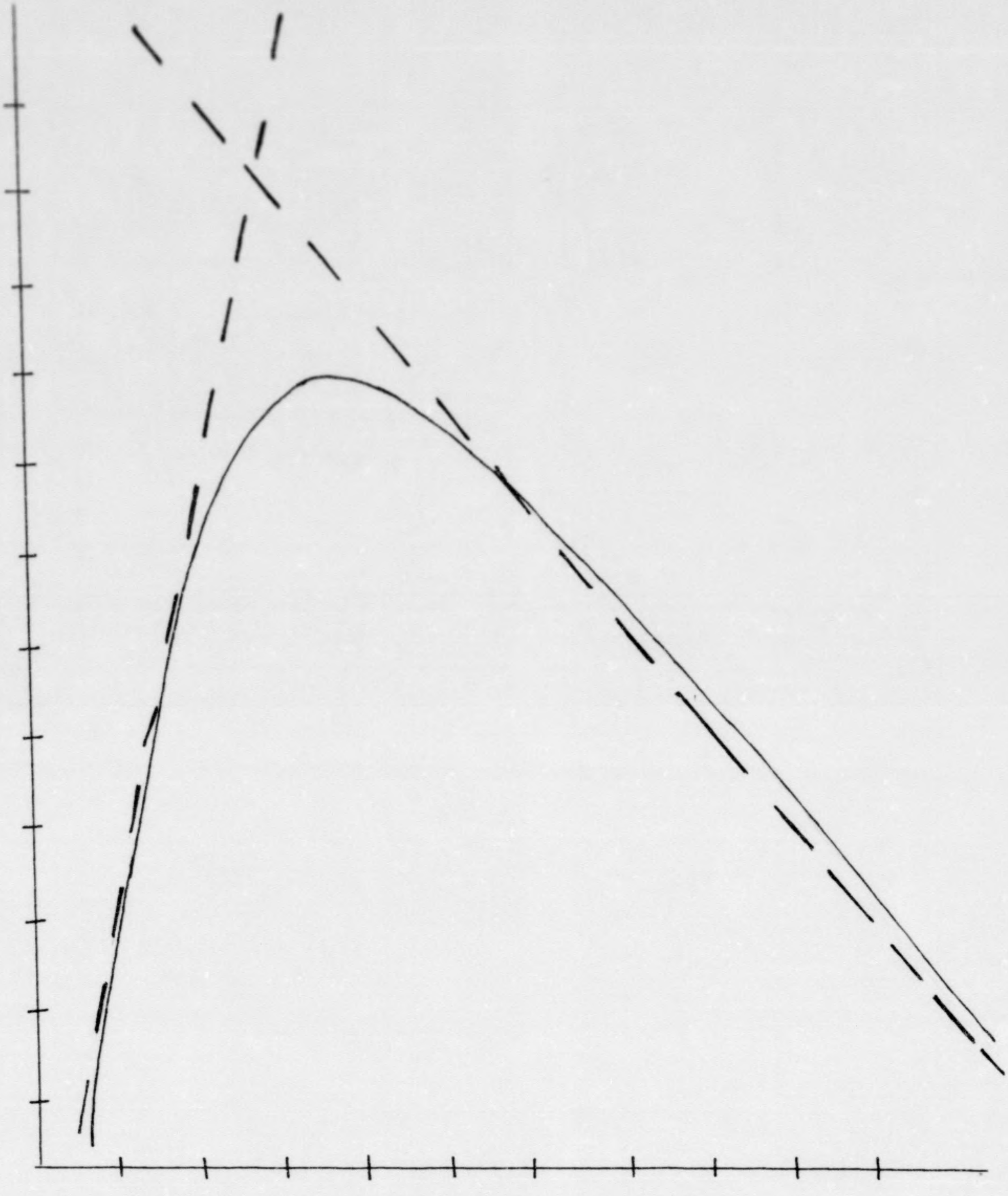
Figure 5 illustrates another aspect of analysis of the plastic curve. The maximum observed fluidity is relatively poorly defined, as real curves typically have flattened maxima. Furthermore, for highly fluid coals the sample is often outgassing in the neighborhood of maximum fluidity, affording irregular and irreproducible observed maxima. The intersection of the melting and coking slopes, however, is independent of these uncertainties and may provide a more precise and consistent measure of coal fluidity.(41)

Volume changes that accompany the heating of a coking coal through its plastic range are conveniently measured with a dilatometer, and several such instruments have been specifically developed for this purpose. The best known and most commonly used are the Audibert-Arner, Sheffield, and Ruhr dilatometers. All operate on the same basic principle. They record the vertical displacement of a piston that rests on a compacted coal charge, but differ

Figure 5. Typical Isothermal Fluidity Curve.

USDOE COAL #25

At 386.0 ± 0.2 Deg. C



HORIZONTAL AXIS: TIME IN MINUTES Maximum Value = 100
VERTICAL AXIS : LN(FLUIDITY IN GIESELER DDPM) Maximum Value = 8
Tangents are least-squares slopes.
Experimental data: ——
Calculated slopes: — —

in such details as piston weight and diameter, and the degree of compaction of the charge.(24,42,43)

Although the number of investigations and the improvement of measuring methods have led to distinct progress in the study of the plastic properties of coal, many phenomena are not completely explained. Because of the complex nature of coal, sufficient information about its plastic behavior cannot yet be obtained.

One technique used to study plasticity and many other aspects of coal is solvent extraction. Development of solvent extraction as a technique for investigating coal compositions and producing waxes, resins, or other coal derivatives of potential commercial use dates from Bedson's(44) discovery in 1902, that bituminous coals are substantially soluble in hot pyridine. Coal extractions, however, were done as early as 1860, when De Marsilly(45) extracted coals with various solvents. Much of the early work centered on efforts to isolate a presumed coking principle, i.e., substances then believed to be responsible for coking properties and is now only of interest because it demonstrated the occasional presence in coal of small amounts of loosely associated material that differed from the bulk of the coal substance.(46) Full commercial significance was not realized until the investigations of Bergius in 1913 (47) and of Pott and Broche(48) in 1933. Pott and Broche's classical work was the forerunner of the noncatalytic liquid phase dissolution process. Bergius' work with later developments helped to build the German coal hydrogenation processes during World War II.

Numerous studies on various aspects of coal extraction have been done. The precise mechanism of coal extraction is still unknown, however. An examination in considerable detail has led to the suggestion that extraction occurs by the removal of units of colloidal size directly from the coal. The effect of various changes in extraction conditions on the yield of extract and on imbibition of solvent by the residue, coupled with the further conclusion that extracts and residues are fundamentally similar in type led to this suggestion, and to the proposal of the following model. A matrix of larger and more strongly linked micelles, which can be partly and progressively dispersed in a suitable solvent by increasing the temperature, is associated with a proportion of smaller, less strongly bonded micelles. These smaller micelles are normally trapped within this matrix unless it is first swollen by solvent. The difference between these two classes of micelles was supposed to be one of degree rather than of kind. Possible they formed a continuous series, the dividing line being determined by temperature. The micelles, assumed to be rigid and relatively indestructible, would be extracted as individuals by diffusion through the swollen pores of the matrix. It has been shown, however, that the large permanent micelle in the Bangham sense does not exist in coals. It may be taken also to refer to single molecules or to aggregates with strong resistance to disintegration.(49,50)

This conception of extraction mechanism has many similarities with the models proposed by Agae and Hubertus(51) and Kreulen, but there are some differences. It is supported by the close correlation observed between yield of extract and degree of imbibition of solvent.(53) If solvent is imbibed into spaces between the large units, the sizes of the spaces between these units will increase with the degree of imbibition, and the smaller units will then more easily escape from the structure. It can be seen that if a continuous distribution of sizes of units, over a considerable range, is postulated, the observed gradual increase in degree of extraction with increase of temperature or with the use of more powerful solvents can be qualitatively explained. The extracts and residues would then be fractions in terms of size rather than of chemical type, and the observed similarity between extracts and residues would also be expected. This view may be summarized as the "micellar sieve extraction mechanism."

A more recent model of coal extraction has been worked out on the basis of experimental data, by Marzec and Sobkowiak.(54) This data included extract yields, donor and acceptor numbers of the models (numbers worked out by Gutmann), and mass spectrometric analysis of the extracts.

The presence of two types of donor-acceptor bonds binding together the extractable molecular and macromolecular network of coal is assumed in the model. Extraction will occur if a solvent molecule can substitute one or the other partner in the donor-acceptor bond (see Figure 6). A substitution reaction may occur if ΔH of the existing in coal donor-acceptor bond and is also higher than the ΔH of interaction

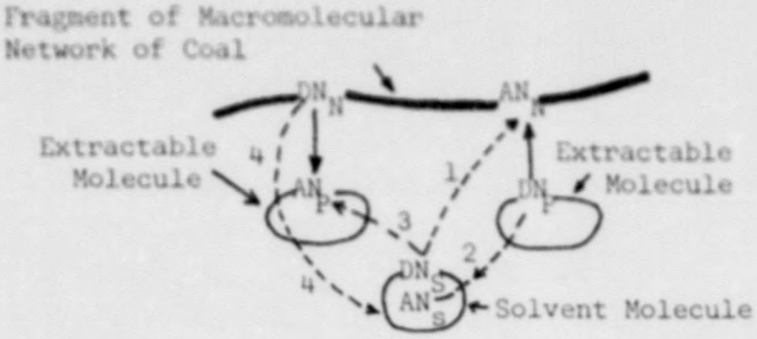


Figure 6. Coal Extraction Model

between solvent molecules themselves. Limits for elimination of donor-acceptor bonds between molecular (extractable) substances and macromolecular network in coal via substitution activity of the solvent, in terms of donor and acceptor numbers were derived. Solvents were characterized according to these limitations.(54)

The kinetics of coal extraction have not been extensively explored. Results of studies have shown that the depth of extraction is found to be primarily a function of the amount of hydrogen transferred and relatively independent of the solvent composition employed (these studies involved a hydrogen donor type solvent). The hydrogen-transfer results were interpreted in terms of a free radical mechanism wherein the rate-determining step is the rupture of covalent bonds.(55)

All but the most mature coals, upon contact with a solvent under the right conditions, will dissolve. Extract yields depend, therefore, as much on coal composition and extraction procedures as on the nature of the solvent.

The solubility of coal in a designated solvent is rank dependent. The solubility tends to decrease with increasing rank, all other matters being equal. The extract yield approaches zero at approximately 92% carbon content. Below the onset of thermal decomposition, extract yields may vary directly with the extraction temperature. Thermal decomposition occurs at approximately 450°C. Even near the boiling point of the solvent, the process of coal dissolution is protracted unless there is direct contact between coal and solvent. Essentially complete extraction also depends on using suitably fine coal.

There are three basic categories of compounds isolated in the solvent extraction of coal. These are historically classified based on the solubility behavior of the extracted products. The three categories are oils, asphaltenes, and preasphaltenes. The major relative amount of material formed in each category depends upon the nature of the coal being extracted, the solvent used, and the extraction technique employed. Oils are defined as being materials which are soluble in hexane. They generally have molecular weights of 500 or less, and consist largely of hydrocarbon materials. Oils comprise a rather wide range of aliphatic and aromatic materials. The lower rank coals tend to contain a greater percentage of aliphatic compounds than do the higher rank coals. Asphaltenes are defined as being soluble in benzene but insoluble in hexane. The asphaltenes have a relatively high oxygen content, especially in the form of phenolic hydroxyl. Heterocyclic and ether linkages are also present. The majority of the compounds in the asphaltene class are aromatic or hydroaromatic in nature. In general, these materials are more polar and less volatile than the oils. The preasphaltenes are distinguished from the oils and asphaltnees by their higher molecular weight. Molecular weights of preasphaltenes generally range above 1000. They have a high degree of functionality, there are more -OH groups per preasphaltene unit than is commonly found in oils or asphaltenes. Accordingly, the preasphaltenes have also been called "asphatols." These are believed to be the materials initially formed on the thermal decompositon of coal.(56)

There are four basic types of extraction procedure which have been applied to coal.(57) The first of these is called nonspecific extraction. Nonspecific extractions generally take place at temperatures of less than 100°C. Solvents such as benzene, toluene or chloroform are used. Extract yields run from 1-10% of the dry ash free weight of the coal being extracted. Nonspecific solvents extract coal selectively and dissolve mainly waxy and resinous substances. The waxes and resins are not integral components of the coal structure. Since the temperature at which the extraction is carried out is too low to give much, if any, decomposition of the matrix, these products are most likely those substances found within the pore structure and capillaries of the coal particle.

Normally the products obtained in the benzene extraction of a coal or maceral include alkanes, alkenes, cycloalkanes, hydroaromatics, alkylbenzenes, and alkylnapthalenes. Higher rank coals tend to have much less aliphatic material and more aromatic and hydroaromatic material. Extraction of peat and lignite with benzene-methanol mixtures and then fractionation of the crude extract yields valuable montan waxes and resins and has been commercially done this way. The waxes are mainly aliphatic long chain C_{24}-C_{32} acids and their esters, or C_{24}-C_{32} alcohols. The resins consist of derivatives of mono and dibasic C_{12}-C_{32} acids. As the rank of the extracted coal increases, the amounts of extractable waxes and resins decrease.(58) The second type of extraction procedure is called specific extraction. This procedure employs solvents such as pyridine, dimethylformamide, or dimethylsulfoxide. These solvents are nucleophiles and have electron-donor capacity. Specific extractions take place at temperatures less than 200°C, and the yield of extractable material is typically between 10 and 30% of the dry ash free weight of the coal. Specific solvents dissolve nonselectively, and the extracted material almost always resembles the insoluble residue so closely that it is virtually indistinguishable from it. It is reasonable to attribute this near-identity of extract and residue to the fact that specific solvents disperse as well as dissolve coal material. There is persuasive evidence that such extracts are colloidal suspensions. Pyridine extract solutions commonly form light precipitates within hours or days when allowed to stand under nitrogen.(59) The third type of procedure may be called extractive pyrolysis. Extractive pyrolysis is usually run at a temperature above 400°C, and a wide variety of solvents are used. This is basically a pyrolysis reaction carried out in the presence of a solvent and can lead to reasonably high yields of extraction products. The yield of extractables usually runs around 30% by any ash free weight, but the actual yield depends upon the solvent, the extraction temperature and the rank of the coal. The last type of extraction procedure is probably the most widely studied. Reductive extraction is carried out with solvents which are good hydrogen donors. It may also be carried out under a hydrogen atmosphere in the presence of a hydrogenation catalyst. Reductive extraction is the basis for some of the liquefaction schemes in the synfuel industry. It is a pyrolytic reaction with the temperature typically 400°C or above. The yield of extractables can be greater than 90% of the dry ash free weight of the coal.

One of the newest methods of extracting coal involves a supercritical gas. A supercritical gas is one which is above its critical temperature and pressure. A gas cannot be liquefied above its critical temperature regardless of how high the pressure is. This method was pioneered by the National Coal Board in Britain and is based on the fact that the vapor pressure of a solid or liquid can be greatly increased by bringing it into contact with a compressed gas. The greater the density of the gas the more pronounced the effect will be--thus gases are used at their critical temperature. Gases have their greatest density at their critical temperature. Under appropriate conditions and with a suitable gas, it is therefore possible to transfer into a vapor phase substances that are otherwise substantially nonvolatile.(60)

Supercritical gas extraction is particularly suitable for the recovery of liquids formed when coal is heated to greater than 400°C. The liquids formed at this temperature are not sufficiently volatile to distill at 400°C. If the temperature is increased, these heavy molecules polymerize to form heavier and larger molecular species and evolve as gases and liquids. Supercritical gas extraction offers a means of recovering these liquids as they are formed and thereby avoids the undesirable decomposition reactions. Since the extraction takes place at temperatures below those at which the volatile matter is evolved by destructive distillation, extensive thermal decomposition of the coal is avoided. Operating conditions demand that the critical temperature of the gaseous solvent should be close to the decomposition temperature of coal and the extraction temperature. The pressure should be above the critical pressure of the solvent. Yields vary with the volatile matter contents of the raw feed coal. The extracts prove to be virtually ash-free low-melting solids with a significantly greater hydrogen content than the feed coal.

Many investigations have been devoted to various methods of extraction and to the use of the most effective coal solvents. It has been concluded that the best solvents for coals have structures containing nitrogen or oxygen atoms possessing unshared electron pairs. It is known that the unshared electron pairs of nitrogen and oxygen can partially accept a hydrogen atom, attacking other molecules in order to form a hydrogen bond. They also can form coordination bonds with other atoms.(61)

Pyridine is one of the most extensively used solvents for the extraction of coal. Pyridine will, for example, extract approximately 20% of a low-rank bituminous coal. Lignitic coals usually give lesser amounts of pyridine extract than the higher rank coals. Pyridine extraction yields peak at around 88.5% carbon content, then decrease rapidly to virtually zero at 92% carbon. The infrared spectrum of the extract closely resembles that of the parent raw coal, suggesting that the extracted material retains the structural characteristics of the raw coal. Useful information about the structure of coal should be gained from the study of pyridine extracts.(62)

It has been proposed that the enhanced solubility of coal in pyridine is at least partially due to the swelling of the coal particles that occur on treatment with this and similar solvents. The enlarged pore structure should allow for a more efficient removal of the organic material contained within the capillary system. Pyridine does have polar and nucleophilic character which allows for more solubility of materials that would not be soluble in low polarity solvents like benzene and toluene. Pyridine extracts of bituminous coals contain oils, asphaltenes and preasphaltenes.(32)

Dipolar aprotic solvents possess a high dielectric constant and large dipole moments. Important solvents of this group are dimethylformamide, dimethylacetamide, dimethyl sulfoxide, and acetone. Dimethylformamide (DMF) is highly effective as a solvent because of its high polarity, electron donating properties of the carbonyl oxygen, and the screening of the nitrogen atom by the methyl groups. Characteristic of this solvent is the absence of hydrogen bonds between its molecules.

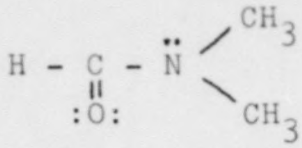


Figure 7. DMF Molecule

In a recent study by Ekoterinina,(61) et al., two conclusions about DMF extraction were drawn: (1) The yield of extracts obtained from coals with the aid of DMF depends on the content of active acid groups and changes in accordance with the stage of coalification. In the extraction of coals by DMF the selective formation of hydrogen bonds between the solvent and certain structural groupings with the coal structure is observed. (2) The coal fractions insoluble in DMF are characterized by lower contents of aliphatic and alicyclic structures, and, in the case of hard coals, also by lower contents of carbon-oxygen bonds. However, the insoluble fractions have higher contents of quinoidaromatic compounds as compared with the soluble fractions. In an earlier study by Ekaterinina,(63) the coal extracts were characterized by higher hydrogen contents and H/C atomic ratios and lower oxygen contents than the residues.

DMF has a high affinity for the coal matrix and is sometimes difficult to remove from the residue. Washing the residue with a solvent such as methanol and vacuum drying it at a high temperature (150°C) seems to remove all the DMF from the residue.

DMF was chosen as the solvent for use in this project for numerous reasons. DMF has a relatively low boiling point (153°C) and is easy to work with. As previously mentioned, DMF has excellent solvent characteristics for use with coal. It is a small molecule and enters the capillary system of the coal easily. DMF removes everything which is nonclassically bound to the coal matrix.

Tetralin is an example of a very good hydrogen donating solvent that has been widely used in the reductive extraction of coal. A subbituminous coal, for example, was converted into approximately 80% tetrahydrofuran soluble products within two hours by reaction with tetralin at 427°C.(64) Vapor pressure osmometry indicates a drop in the number average molecular weight from approximately 1200 at 10 minutes reaction time to a value of approximately 500 at 30 minutes or longer, and suggests an initial rapid cleavage of relatively few "active" bonds to form preasphaltenes. This action is followed by a slower further conversion of the preasphaltenes to the lower molecular weight asphaltenes and oils.(64)

Some work relating the plasticity of coal with solvent extraction has been done. E. D. Pierron(15,65) in the late

1950's and early 1960's studied the relationship using several types of solvents. He mainly focused his work on pyridine extractions, however. In 1959, Pierron, Rees, and Clark(15) extracted two coals of similar chemical analyses and plastic temperature characteristics but different maximum fluidities (Gieseler) with pyridine. A part of one of the coals was oxidized and then also extracted. The high volatile bituminous coals' pyridine extracts were then extracted with n-hexane. The coals and their extracts and residues were analyzed and the atomic H/C and O/C ratios were calculated. They were also investigated by x-ray scattering and infrared spectroscopy. Several conclusions were drawn from the studies of the three series of coals. The plastic behavior of a fluid coal was destroyed by pyridine extraction, and the yield of extract for each solvent appeared to be proportional to the fluidity of coal. Chemical, x-ray, and infrared data showed a relative increase in aliphaticity of each extract with each progressive extraction. In each series, as the progressive scheme of extraction is carried out, each extract possesses a lower melting point, a lower molecular weight, and a similar thermal decomposition temperature range. In each series, the pyridine, chloroform, and n-hexane extracts are similar to the corresponding extracts of the other coals studied. The oxidized coal, in spite of showing no Gieseler fluidity, still yielded 13.6% of pyridine extract. This was tentatively interpreted as the possible inability of the Gieseler plastometer to detect very low fluidity.(10)

In 1960, Pierron and Rees(65) further studied the relationship for additional coals of different ranks and levels of fluidity. Data were presented to show that, for the coals studied, yields of extracts are proportional to maximum fluidities although not necessarily directly proportional. Further data presented indicate that return of the extracts to inert residues restores fluidity beyond that of the original coal. For the eight coals studied, the pyridine, chloroform, and n-hexane extracts for each coal showed similar analyses. The data also indicated that fluidity is related to the quantity of extract obtained rather than to difference in kind of extract.

Since it has been shown that bitumen, the extractable portion of coal, is involved in the plasticity mechanism, and that removal of bitumen by pyridine does destroy plasticity, it is reasonable to predict that the plasticity of a coal is related to its extractables. It is our intent to use DMF as a solvent for extracting a series of highly characterized bituminous coals and use the data to predict the fluidity of the coals.

CHAPTER III

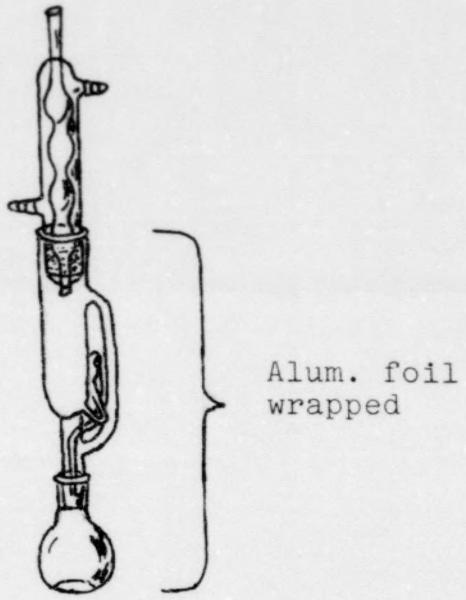
EXPERIMENTAL

A. Instrumentation and Reagents

Solvent extraction work was done using a standard Soxhlet extracter. Each Soxhlet was insulated with glass wool wrapped in aluminum foil to help prevent heat loss. It was hoped that any heat loss would be confined to the condenser.

Figure 8.

Soxhlet Extraction Apparatus



A system of six Soxhlets was set up, three in a series. The three Soxhlets on the left were used for THF extraction work. The DMF extraction work was carried out in the three Soxhlets on the right.

A Glas-Col six unit heating mantle was used for the heating of the Soxhlet system.

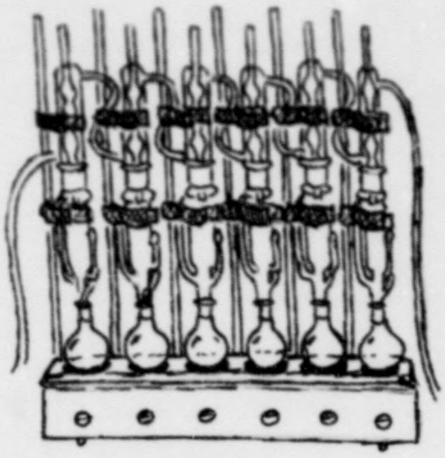


Figure 9.

Six unit heating apparatus with Soxhlet set-up.

The vacuum ovens used were from Forma Scientific, Inc. in Marietta, Ohio. They were the "Forma Vac" model, catalog number 3062. The vacuum gauge attached to the oven was used to judge the amount of vacuum being pulled. The ovens were 115 volts, 4 amps. Temperature inside the vacuum oven was measured with a standard mercury lab thermometer placed on a tray inside the oven. The vacuum was pulled with a Hyvac 7 pump, from Central Scientific Company.

Weighings were done on a Sartorius Analytical Balance, model number 2402. These weighings were done to the nearest mg. The balance was accurate to the nearest 0.1 mg.

The dimethylformamide used was from J. T. Baker Chemical Company, Phillipsburg, New Jersey, and met A.C.S. reagent grade specifications. The assay by gas chromatography was 99.9%, and it had a boiling point range of 1.3°C. No extra purification was done to the DMF before using it.

The methanol used was from Fisher Scientific Company, Fair Lawn, New Jersey. The methanol was A.C.S. certified and had a boiling point range of 0.5°C. The assay was 99.9%, and no extra purification was done.

The raw coal was received in five pound bags. It was crushed to -8 mesh coal and split, then crushed further into -60 mesh for use. The crushed coal was stored in the freezer under nitrogen until it was used.

B. Procedure

The procedure used for the solvent extraction work was developed at the Institute for Minerals and Mining Research by Art Fort.(39) All samples are run in triplicate, and the criterion for good procedure and technique is close agreement of results for members of each group.

1. Dry a beaker at 100-110°C (1 hr. or more), cool in a desiccator, and weigh to nearest mg. All subsequent weighings will be to nearest mg. Weigh in 10 g of -60 mesh raw coal.

2. Dry the samples in a vacuum oven at 60 ± 4°C for a period of six hours. Cool to room temperature in a desiccator and weigh to obtain moisture loss percent. Dry marked thimbles, cool and weigh along with the coal samples. Place the dried coal sample in its thimble and weigh again to obtain the weight of dried coal to be extracted.

3. Extract the dried coal samples for a period of 22 ± 2 hours, with 100 ml of dimethylformamide. Insulate the Soxhlet extraction assembly well to minimize heat loss (we desiremost of the heat loss to occur in the condenser). Inspect the extraction assembly from time to time to insure that DMF drips rapidly from the condenser drop tip.

4. After cooling, replace DMF with methanol and bottle the DMF extract. Extract the coal sample with methanol for a period of five to six hours.

5. Remove the thimble from the extraction assembly, allow bulk of methanol to drain and evaporate under the hood. Place the thimble in a vacuum desiccator over calcium chloride lumps (replace $CaCl_2$ lumps periodically as they show evidence of moisture). Evacuate desiccator for a period of one-half hour. Seal vacuum, and allow sample to remain over-night under vacuum.

6. Transfer sample to vacuum oven and dry at 150°C for a period of six hours (vacuum). Turn the oven off and leave the samples in the overn under vacuum until they cool to below 50°C (approximately 3 hours). Cool to room temperature (desiccator) and weigh to obtain extraction loss. Store in desiccator under vacuum.

7. Repeat 150°C dryings for 2 hours, allowing the samples to cool to below 50°C before removing them. Continue these 2 hour dryings until the extraction losses are reproducible.

8. Store extracted samples in screw-cap vials. Label each vial and place it in a freezer.

The original procedure called for drying the extracted samples at 60°C rather than 150°C. FTIR spectra showed that all the DMF was not being removed at this temperature. The drying temperature was then increased to 150°C. FTIR analysis showed that drying at the higher temperature did remove all the DMF. IMMR also determined this to be true on the basis of nitrogen analysis of extraction residues and suggested the 150°C drying temperature.(66)

The last Soxhlet condenser in each series did not exchange well in the summer months. The procedure was modified at this time to using 150 ml of solvent in the last flask, rather than the original 100 ml. This solved the problem.

CHAPTER IV

RESULTS

The bituminous coals used in this research have all been highly characterized. Classical characterization of the coals included proximate and ultimate analyses, free swelling index, heating value, forms of sulfur, sulfate in ash, maceral composition, total reactive macerals, Parr mineral matter and vitrinite maximum reflectance. The Institute for Mining and Minerals Research (IMMR) in Lexington, Kentucky, analyzed each of these coals and provided the information in Tables 1 through 7.

The coals used in this study have been freshly collected from freshly mined coal and from cleaning plants using freshly mined coal of known local origin.(67) Table 1 lists the sources of the coals used, the sample size, and the nominal rank.

Table 2 contains the proximate and ultimate analyses of the coals. All data are on a dry basis except for moisture, which is as determined.

Table 3 presents, for the same coals, the forms of sulfur, ash sulfate, heating value, free swelling index, and rank (by ASTM D388). These data are not quite complete, lacking forms of sulfur and ash sulfate for the last four coals obtained.

Table 1

Sources of Western Kentucky Coals

no.	IMMR no.	Seam	Vertical location	Source key	County	Sample size	Nominal rank
1	9021	KY #9	high	G1	Daviess	6 x 2"	hvCb/subA
2	9022	KY #9	high	G1	Daviess	2 x 1/2"	hvCb/subA
3	9029	Elm Lick	middle	S1	Ohio	CS	hvCb/hvBb
4	9036	Bancroft	high	B1	Muhlenberg	3 x 1/2"	hvBb
5	9037	Bancroft	high	B1	Muhlenberg	1/2 x 1/4"	hvBb
6	9045	Bancroft	high	O	Muhlenberg	3 x 1/2"	hvCb
7	9046	Bancroft	high	O	Muhlenberg	1/2 x 1/4"	hvCb
8	9052	KY #9	high	C1	Ohio	6 x 1-1/2"	hvCb
9	9055	KY #9	high	C1	Ohio	1-1/2 x 1/4"	hvCb
10	9064	KY #9	high	F1	Hopkins	1-1/4" x 28m	hvCb
11	9398	KY #14	middle	B1	Muhlenberg	3 x 1/2"	hvCb
12	9399	KY #14	middle	B1	Muhlenberg	1/2 x 1/4"	hvCb
13	9072	KY #9	high	H1	Union	6 x 1-1/4"	hvBb
14	9077	KY #9	high	H1	Union	1-1/4 x 28m	hvBb
15	9085	KY #9	high	H2	Union	6 x 1-1/4"	hvCb
16	9089	KY #9	high	H2	Union	1-1/4 x 28m	hvCb
17	9099	KY #9	high	G2	Muhlenberg	6 x 1-3/4"	hvCb
18	9100	KY #9	high	G2	Muhlenberg	1-3/4 x 1/4"	hvCb
19	9109	KY #11/#12	high	R1	Muhlenberg	4 x 1-1/2"	hvCb
20	9110	KY #11/#12	high	R1	Muhlenberg	1-1/2 x 1/4"	hvCb
21	9121	KY #9	high	D1	Webster	2 x 28m	hvBb/hvAb
22	9127	KY #6	middle	P1	Union	3 x 1/2"	hvAb
23	9129	KY #6	middle	P1	Union	- 1/2"	hvAb
24	9158	KY #11	high	C2	Union	5 x 1"	hvCb/subA
25	6083	Mason	---	---	Bell	run of mine	hvAb
26	7625	KY #10	---	---	Webster	run of mine	hvAb
27	7626	KY #9	---	---	Union	run of mine	hvAb
28	8055	Indiana Lower Block	---	---	Spencer (IN)	run of mine	hvCb

continued

Table 1, continued

no.	IMMR no.	Seam	Vertical location	Source key	County	Sample size	Nominal rank
29*	9145	KY #9/#11	high	K1	Ohio	1-1/2 x 3/4"	hvCb
30	9146	KY #9/#11	high	K1	Ohio	3/4 x 1/4"	hvCb
31	9159	KY #11	high	C2	Union	1 x 3/16"	hvCb/subA
32	9335	KY #9	high	P2	Hopkins	1-1/4 x 28m	hvBb
33	9342	KY #11	high	P3	Union	3 x 1/2"	hvAb
34	9344	KY #11	high	P3	Union	- 1/2	hvAb
35	9418	KY #11/#12	high	C3	Hopkins	6 x 5/8"	hvCb
36	9419	KY #11/#12	high	C3	Hopkins	+ 6	hvCb
37	9556	IL #6	----	Y	Williamson	3 x 1/2"	hvBb
38	7701	Amos	channel	----	Butler	----	hvBb
39	7704	Amos	channel	----	Butler	----	hvBb
40	7707	Amos	channel	----	Butler	----	hvBb
41	7708	Amos	channel	----	Butler	----	hvBb

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*Coal no. 29 will be dropped from the final analysis. Coal no. 30, from the same site, will be retained.

Table 2

Proximate and Ultimate Analyses*

Coal	Moisture	Ash	Volatile Matter	Fixed Carbon	%C	%H	%N	%S	%O**
01	10.03	8.69	42.9	48.4	73.86	5.41	1.73	4.10	6.19
02	7.86	10.77	42.6	46.5	71.67	5.05	1.62	3.41	7.44
03	6.75	5.40	41.6	52.9	77.60	5.38	1.60	2.02	7.96
04	5.33	6.44	46.8	46.6	76.48	5.37	1.60	3.29	6.79
05	4.08	6.50	45.0	48.4	74.55	5.33	1.40	2.79	9.40
06	5.02	7.86	44.5	47.5	72.19	5.09	1.11	3.68	10.04
07	5.21	6.48	44.8	48.6	76.46	4.78	1.04	3.20	8.00
08	7.76	8.79	41.4	49.7	73.16	5.43	1.52	3.13	7.94
09	7.08	9.05	41.5	49.4	75.00	5.58	1.54	3.37	5.43
10	6.32	8.49	41.7	49.7	75.08	4.30	1.13	3.14	7.83
11	5.94	17.71	38.4	43.8	63.32	4.61	1.25	3.40	9.69
12	4.72	17.75	38.7	43.5	66.27	4.82	1.28	3.45	6.40
13	6.92	8.44	41.8	49.6	74.15	5.24	1.23	3.21	7.71
14	6.70	7.60	41.1	51.2	74.12	5.21	1.35	2.75	8.93
15	6.31	10.38	41.3	48.3	73.18	5.47	1.54	3.77	5.62
16	6.20	8.42	41.0	50.5	75.03	5.61	1.46	3.03	6.42
17	7.97	8.42	41.2	50.2	74.94	5.04	1.39	3.60	6.59
18	7.09	8.36	40.6	50.9	74.08	5.11	1.50	3.59	7.34
19	7.55	10.16	41.2	48.6	73.28	5.20	1.31	3.18	6.84
20	7.77	9.70	43.5	46.7	74.06	5.28	1.22	2.92	6.79
21	2.57	8.68	40.3	50.9	75.41	5.27	1.07	3.35	6.18
22	2.45	9.60	39.4	50.9	75.98	5.42	1.44	2.91	4.63

continued

Table 2, continued*

Coal	Moisture	Ash	Volatile Matter	Fixed Carbon	%C	%H	%N	%S	%O**
23	2.61	8.25	40.1	51.5	77.04	5.44	1.47	2.66	5.11
24	7.87	7.15	42.8	49.9	75.68	5.55	1.51	3.56	6.52
25	1.68	6.79	40.2	52.9	77.79	5.33	2.04	1.38	6.64
26	2.12	14.20	32.2	53.5	69.87	4.43	1.50	2.76	7.22
27	2.86	8.12	40.0	51.8	76.18	5.17	1.54	3.53	5.43
28	10.96	8.26	42.2	49.5	76.65	5.78	1.58	1.42	6.28
29	6.17	6.50	43.3	50.1	74.22	5.42	1.57	3.63	8.63
30	6.44	8.95	42.3	48.7	74.67	5.41	1.54	4.01	5.37
31	7.42	7.85	43.6	48.5	75.43	5.26	1.39	3.48	6.56
32	2.94	7.23	42.8	49.9	76.05	5.37	1.65	3.00	6.66
33	2.24	10.76	40.7	48.5	72.90	5.22	1.43	3.14	6.53
34	2.28	8.03	41.0	50.9	74.36	5.25	1.45	2.77	8.11
35	6.59	10.61	39.3	49.9	73.77	5.10	1.25	4.06	5.18
36	7.00	12.58	38.2	49.1	70.38	4.91	1.29	4.06	6.76
37	3.30	12.48	37.2	50.2	72.88	4.91	1.53	2.90	5.28
38	9.89	3.41	40.5	56.0	81.75	5.64	1.65	0.83	6.69
39	7.63	13.41	38.5	48.0	70.57	5.12	1.56	1.91	7.40
40	9.29	3.75	39.6	56.5	81.33	5.68	1.73	0.80	6.68
41	7.78	2.77	42.1	55.0	80.73	5.74	1.61	1.06	8.06

*Moisture as determined, other values on a dry ash-included basis.

**By difference.

Table 3

Forms of Sulfur, Ash Sulfate, Heating Value, FSI and ASTM Rank*

Coal	Forms of Sulfur			% SO_3 in ash	Heating Value Btu/lb	F S I	ASTM Rank
	Pyritic	Sulfate	Organic				
01	2.04	0.06	1.98	5.58	12,948	2 1/2	hvCb
02	1.43	0.02	1.96	5.96	12,622	4 1/2	hvBb
03	0.98	0.01	1.02	0.42	13,715	4	hvBb
04	2.22	0.13	0.92	0.74	13,647	3 1/2	hvBb
05	1.70	0.25	0.83	0.77	13,479	3 1/2	hvBb
06	1.38	0.02	2.27	0.37	13,297	6	hvBb
07	1.08	0.03	2.08	0.72	13,587	3 1/2	hvBb
08	1.16	0.05	1.91	4.30	13,096	5	hvBb
09	1.25	0.12	1.99	2.89	13,054	4 1/2	hvBb
10	1.18	0.10	1.85	2.83	13,332	4	hvBb
11	1.61	0.14	1.63	1.14	11,769	2 1/2	hvBb
12	1.78	0.09	1.57	0.72	11,754	2 1/2	hvBb
13	1.34	0.04	1.82	3.97	13,332	4 1/2	hvBb
14	0.93	0.05	1.76	9.02	13,408	4	hvBb
15	1.62	0.05	2.10	6.63	12,850	4 1/2	hvBb
16	1.17	0.05	1.81	4.18	13,336	4 1/2	hvBb
17	1.57	0.13	1.90	0.48	13,158	5	hvBb
18	1.47	0.25	1.86	1.13	13,023	4 1/2	hvBb
19	1.43	0.15	1.59	2.88	12,882	4	hvBb
20	0.92	0.29	1.71	2.30	12,913	5	hvBb
21	1.33	0.08	1.93	2.16	13,537	8 1/2	hvAb
22	1.45	0.10	1.35	2.04	13,490	8	hvAb

continued

Table 3, continued

Coal	Forms of Sulfur			% SO_3 in ash	Heating Value Btu/lb	F S I	ASTM Rank
	Pyritic	Sulfate	Organic				
23	1.22	0.05	1.39	3.14	13,718	8 1/2	hvAb
24	1.22	0.05	2.27	1.23	13,296	4	hvBb
25	0.19	0.01	1.17	0.87	14,249	7	hvAb
26	0.48	0.08	2.20	0.70	12,607	7	hvAb
27	0.48	0.07	2.97	0.46	13,650	7	hvAb
28	0.80	0.02	0.59	6.13	13,241	2 1/2	hvCb
29	1.37	0.27	1.98	1.07	13,215	3 1/2	hvBb
30	1.46	0.32	2.23	1.44	13,007	4 1/2	hvBb
31	1.26	0.07	2.14	1.35	13,220	4	hvBb
32	0.92	0.03	2.05	1.92	13,733	5	hvAb
33	1.16	0.02	1.95	0.62	13,277	5 1/2	hvAb
34	1.08	0.01	1.67	1.92	13,671	6 1/2	hvAb
35	2.05	0.09	1.91	12.41	12,775	6	hvBb
36	2.22	0.11	1.72	10.21	12,468	4 1/2	hvBb
37	1.70	0.03	1.16	3.92	12,740	4 1/2	hvAb
38	---	---	---	---	14,171	3	hvBb
39	---	---	---	---	12,525	3	hvBb
40	---	---	---	---	14,154	2 1/2	hvBb
41	---	---	---	---	14,281	3	hvBb

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*Forms of sulfur and heating value on a dry, ash-included basis.

Tables 4 and 5 present the maceral composition, total reactive macerals, Parr mineral matter content, and maximum vitrinite reflectance, all on a dry basis.

Fluidities of each coal are determined by means of the standard ASTM constant-torque Gieseler plastometer procedure. Quadruplicate plastometer runs were made with each coal. The averages reported in Table 6 are arithmetic averages of the individual temperature determinations and are geometric averages of the maximum fluidities. When the distribution of the four replicate determinations is such that an outlier value lies more than three standard deviations from the average of the remaining three data, the outlier is rejected; otherwise all data are used.

The second group of plasticity data is that attained under isothermal conditions. This requires 20-25 determinations for each coal, and has now been completed for 28 coals. The isothermal characterization data are summarized in Table 7.

Table 8 includes the individual determinations from the three DMF extractions run on each coal. Each determination is listed in Table 8, and the numerical average of the three runs is given in most cases. In some instances, the best two of three determinations was used for the average. The six sigma test was used to determine which coals to use only two determinations for. A complete description of the procedure used in the solvent extraction work is given in the experimental section of this paper.

Tables 1 through 8 are taken from reference 67.

Table 4

Maceral Composition of Coals[1]

Coal	Vitrin[2]	PseudoV[2]	Exinite	Resin[2]	Fusin[2]	SemiF[2]	Micrin[2]	Macrin[2]
1	75.9	0.8	2.9	0.4	4.3	3.2	0.8	0.4
2	66.3	0.1	6.0	1.2	4.1	3.3	5.5	0.0
3	84.4	0.8	4.7	0.3	1.5	0.6	0.7	0.0
4	70.3	4.1	7.1	0.5	2.7	3.2	3.0	0.3
5	73.6	4.1	6.0	0.3	3.2	2.2	1.8	0.2
6	72.0	6.4	3.2	1.0	2.1	1.9	3.0	0.0
7	78.1	3.8	1.9	0.8	2.6	2.2	1.8	0.0
8	67.6	3.6	3.3	1.0	4.3	5.3	3.2	0.4
9	73.3	2.1	3.9	0.3	5.1	2.7	0.8	0.3
10	73.1	2.4	2.5	0.3	5.9	3.2	1.5	0.1
11	67.5	2.2	2.1	1.1	1.9	3.0	0.9	0.2
12	66.0	3.5	2.7	0.4	2.0	2.8	1.5	0.1
13	69.9	0.9	7.2	1.6	2.6	3.6	3.4	0.0
14	73.4	5.7	2.6	0.5	3.2	3.3	1.3	0.4
15	69.4	2.3	3.5	0.2	5.6	3.9	1.6	0.3
16	72.7	2.4	3.2	0.4	3.7	4.0	3.5	0.2
17	74.6	2.2	2.8	0.4	3.9	2.9	1.7	0.1
18	76.1	1.2	3.5	0.4	3.3	3.6	1.7	0.2
19	76.1	3.2	2.3	1.0	2.1	1.8	0.9	0.3
20	77.2	2.7	1.9	1.0	2.2	2.3	0.9	0.1
21	68.0	7.5	2.5	1.8	3.4	3.0	2.4	0.1
22	70.7	5.3	3.2	0.5	3.5	2.8	1.9	0.1

continued

Table 4, continued

Coal	Vitrin[2]	PseudoV[2]	Exinite	Resin[2]	Fusin[2]	SemiF[2]	Micrin[2]	Macrin[2]
23	73.3	3.9	3.5	0.9	5.0	1.8	1.3	0.0
24	76.8	3.4	2.5	0.7	2.3	2.5	0.9	0.1
25	69.2	6.5	4.0	1.7	2.4	5.0	2.8	0.1
26*	62.2	10.0	1.5	1.2	1.9	5.0	0.5	0.4
27	64.1	7.0	2.7	0.9	4.1	8.6	1.2	0.2
28	67.5	1.5	6.9	0.9	3.1	1.4	9.0	0.8
29	Petrographic data irreproducible; sample to be dropped from further study							
30	66.3	2.1	7.4	2.2	4.2	2.5	3.3	0.0
31	80.6	0.5	2.7	0.9	1.8	2.2	0.9	0.1
32	75.6	2.9	1.8	1.3	2.6	3.0	2.9	0.5
33	72.6	5.7	1.7	1.7	1.2	1.9	1.6	0.2
34	74.2	6.3	2.1	1.8	2.7	1.4	2.1	0.2
35	74.8	2.7	1.9	0.8	2.7	2.2	1.2	0.1
36	74.2	2.0	2.3	0.2	3.1	1.6	0.8	0.1
37	69.4	5.9	2.0	0.4	3.2	2.3	1.4	0.3
38	71.2	5.5	7.6	0.8	4.5	3.0	3.5	0.0
39	68.9	3.3	6.8	0.8	1.0	1.4	2.3	0.0
40	74.0	6.1	6.4	1.5	2.4	1.5	3.5	0.0
41	79.0	6.7	6.3	0.9	0.4	0.7	2.7	0.0

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* Sample is visibly weathered.

[1] dry basis, not corrected for mineral matter content

[2] abbreviations: Vitrin = vitrinite, PseudoV = pseudovitrinite, Resin = resinite, Fusin = fusinite, Micrin = micrinite, and Macrin = macrinite

Table 5

Maceral and Mineral Composition and Vitrinite Reflectance of Coals*

Coal	Reactive macerals	Inert macerals	Mineral matter	Vitrinite maximum reflectance	Standard devn of max reflect
1	81.7%	6.8%	11.6%	0.61	± 0.047
2	80.2	6.3	13.5	0.42	0.038
3	91.1	1.9	7.0	0.70	0.042
4	86.1	5.1	8.8	0.59	0.032
5	86.5	4.9	8.6	0.56	0.031
6	86.2	3.4	10.5	0.57	0.038
7	87.1	4.1	8.8	0.60	0.032
8	80.5	8.2	11.3	0.53	0.033
9	81.2	7.2	11.6	0.58	0.038
10	80.9	8.3	10.9	0.57	0.036
11	74.8	4.1	21.0	0.56	0.042
12	75.0	4.0	21.1	0.55	0.039
13	84.2	5.0	10.9	0.61	0.030
14	84.6	5.8	9.7	0.58	0.043
15	78.3	8.5	13.3	0.61	0.037
16	83.5	6.6	10.8	0.54	0.047
17	82.6	5.9	11.1	0.54	0.042
18	84.1	5.9	11.0	0.54	0.041
19	84.1	3.6	12.4	0.57	0.042
20	84.5	3.8	11.8	0.53	0.035
21	83.2	5.5	11.2	0.71	0.026
22	82.5	5.5	12.0	0.73	0.032
23	83.5	6.2	10.4	0.74	0.035
24	85.1	4.1	9.7	0.60	0.049
25	85.8	6.1	8.1	0.87	0.041
26	77.0	5.7	17.3	0.87	0.041
27	78.7	10.6	10.7	0.76	0.032
28	86.3	4.0	9.7	0.64	0.034
29	Petrographic data irreproducible; sample to be dropped				
30	82.1	6.0	11.9	0.58	0.037

continued

Table 5, continued

Coal	Reactive macerals	Inert macerals	Mineral matter	Vitrinite maximum reflectance	Standard devn of max reflect
31	86.3	3.3	10.4	0.59	0.041
32	85.5	5.0	9.5	0.65	0.037
33	83.8	2.9	13.3	0.72	0.030
34	87.0	2.8	10.2	0.69	0.047
35	82.1	4.2	13.7	0.58	0.030
36	80.0	4.2	15.8	0.58	0.032
37	79.9	5.0	15.1	0.66	0.042
38	89.6	6.5	3.9	0.67	0.031
39	82.5	1.9	15.6	0.65	0.026
40	92.0	3.4	4.6	0.70	0.036
41	95.8	0.9	3.3	0.67	0.031

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* Maceral compositions on dry basis, not corrected for mineral matter content; mineral matter content by Parr procedure; vitrinite reflectance in oil at 546 nm. Reactive macerals are calculated as the sum of vitrinite, pseudovitrinite, exinite, resinite, micrinite, and one third of the semifusinite; other maceral components (Table 4) are counted as inert.

Table 6

ASTM Gieseler Plasticity: Standard Data*

coal	T(softening)		T(max fluidity)		T(solidificn)		ln(max fluidity)		Max fluidity
01	386.0	± 2.6	418.3	± 2.6	437.4	± 2.1	2.565	± .454	13.0
02	384.6	0.4	422.7	0.6	437.8	0.4	2.259	.033	9.6
03	390.4	3.7	432.0	0.0	450.3	1.4	3.343	.046	28.3
04	382.8	0.6	428.3	1.0	451.5	0.5	6.300	.099	544.
05	390.9	1.8	430.8	1.5	452.8	0.6	4.456	.023	86.1
06	381.7	1.0	421.0	1.0	457.3	0.6	9.888	.254	19,690
07	383.0	0.1	425.5	2.9	453.2	0.7	6.653	.029	775.
08	387.0	4.2	427.5	4.4	448.1	1.2	3.927	.135	50.7
09	389.3	2.8	426.3	0.6	446.9	0.2	3.744	.101	42.3
10	389.8	2.2	426.3	0.6	450.0	1.2	4.502	.070	90.2
11	390.8	0.6	424.5	2.3	448.5	0.2	4.594	.044	98.9
12	387.8	0.6	423.0	0.0	450.5	0.3	5.431	.011	228.
13	376.4	0.3	422.3	0.6	451.8	0.6	6.292	.185	540.
14	385.7	3.9	425.0	4.7	452.7	3.8	5.214	.036	184.
15	378.9	0.9	424.0	0.0	449.9	1.1	5.992	.116	400.
16	384.1	4.1	423.5	1.3	445.7	1.8	4.164	.122	64.3
17	392.8	3.8	430.0	5.4	448.7	3.1	3.812	.320	45.3
18	388.3	2.5	428.0	0.8	446.5	0.4	3.287	.106	26.8
19	383.3	1.2	428.0	1.0	450.4	2.6	4.756	.046	116.
20	383.2	1.6	423.3	1.5	448.8	0.2	4.513	.117	91.2
21	374.8	0.3	(419-428°)		463.4	0.6	10.315	.019	30,000.
22	375.7	0.5	(422-435°)		467.0	0.4	10.318	.015	30,000.
23	383.5	1.5	(422-434°)		467.1	1.7	10.326	.006	30,000.
24	384.8	1.7	423.7	0.6	444.6	1.0	3.551	.056	34.9
25	391.2	0.4	428.3	2.8	471.4	1.4	10.323	.010	30,000.
26	402.1	1.5	437.7	0.6	461.4	0.6	4.768	.047	118.
27	378.8	1.5	422.6	4.2	464.1	1.2	10.113	.185	25,150.
28	396.6	0.8	437.3	1.0	451.2	1.9	2.924	.332	18.6

continued

Table 6, continued

coal	T(softening)		T(max fluidity)		T(solidifcn)		ln(max fluidity)		Max fluidity
29	393.8	± 5.7	428.0	± 4.6	448.0	± 3.0	3.678	± .296	39.6
30	389.2	2.7	426.3	1.5	442.9	1.1	2.786	.052	16.2
31	387.0	1.4	424.3	0.6	445.3	0.8	2.889	.003	18.0
32	376.7	2.7	418.0	3.4	461.3	1.4	10.298	.018	30,000.
33	377.3	2.1	(415-431°)		464.8	2.3	10.3	---	30,000.
34	380.6	1.2	419.8	3.2	465.4	0.3	10.3	---	30,000.
35	375.0	0.8	421.6	0.5	457.6	2.0	9.262	.022	10,530.
36	385.1	0.1	427.0	3.6	456.0	1.0	5.220	.174	185.
37	382.0	3.0	431.0	0.0	457.3	0.3	6.046	.089	423.
38	396.0	0.5	433.5	2.4	458.6	1.5	5.230	.064	187.
39	395.5	2.2	433.0	0.0	456.9	1.2	5.414	.052	224.
40	401.0	3.0	435.8	1.5	454.0	3.0	3.096	.517	22.1
41	397.7	0.9	436.0	1.6	459.0	1.2	5.379	.137	217.

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* Data are averages of quadruplicate runs by constant-torque Gieseler plastometer, using ASTM Standard D2639 (reference 6). T(softening) is the temperature (°C) at which the initially melting mass attains afluidity of 1 d.d.p.m. (approximately comparable to a Newtonian viscosity of 10 megapoise). T(solidifcn) is the temperature at which fluidity of the coking coal mass falls to 1 d.d.p.m. The maximum fluidity is in dial divisions per minute (d.d.p.m.) and is averaged geometrically (i.e., by averaging the logarithms of the individual maximum fluidities). When the distribution of the individual data is such that an outlier falls more than three standard deviations outside the average of the remaining three data, the reported average is that of the best three determinations.

Table 7

Maximum Isothermal Fluidities of some Bituminous Coals

coal	runs	T range	ln(maximum observed fluidity, ddpm)					ln(maximum calculated fluidity, ddpm)				
			E(a), kcal	s.d.	@ 380°	@ 400°	@ 420°	E(a), kcal	s.d.	@ 380°	@ 400°	@ 420°
02	16	406-423°	35.2	3.7	0.380	0.852	1.822	40.8	5.1	0.408	1.038	2.504
03	18	408-433°	41.3	3.4	0.273	0.704	1.715	41.0	6.7	0.445	1.138	2.758
04	16	406-431°	33.2*	1.8	1.327	2.837	5.803	25.5	1.1	2.041	3.656	6.334
06	17	393-418°	28.4	1.3	2.956	5.668	10.470	23.3	1.1	3.587	6.109	10.089
07	17	404-426°	23.6	1.3	2.581	4.428	7.363	18.6	1.5	3.361	5.147	7.692
09	20	403-427°	51.1	3.6	0.252	0.813	2.447	44.4	4.3	0.484	1.336	3.483
10	18	405-429°	38.5	2.3	0.651	1.572	3.608	30.7	3.2	1.178	2.382	4.623
11	17	412-432°	30.8	2.5	0.631	1.277	2.478	31.2	2.5	0.856	1.748	3.424
14	20	398-422°	27.5	1.3	1.613	3.027	5.478	20.5	1.1	2.424	3.877	6.035
15	18	400-427°	21.9	1.1	2.100	3.467	5.561	22.4	1.2	2.264	3.781	6.132
18	20	398-424°	47.1	2.4	0.428	1.258	3.474	35.9	2.5	0.907	2.062	4.472
20	22	401-428°	41.9	1.3	0.616	1.607	3.965	27.7	1.6	1.415	2.669	4.854
21	22	387-410°	22.6	1.4	4.836	8.107	13.191	16.8	1.7	5.912	8.679	12.462
22	20	389-413°	22.0	1.1	4.052	6.707	10.784	20.0	1.5	4.958	7.840	12.074
24	20	405-431°	36.9	2.8	0.394	0.916	2.030	23.7	3.4	1.024	1.762	2.939
25	16	404-420°	1.9	0.7	9.520	9.934	10.340	-0.2	1.3	11.096	11.040	10.988
26	17	412-436°	27.9	2.2	1.178	2.229	4.066	21.0	1.3	1.924	3.110	4.890
27	19	379-404°	28.7	1.3	4.371	8.428	15.647	19.5	1.1	5.643	8.810	13.404
28	19	413-437°	32.8	2.0	0.160	0.339	0.687	27.2	3.0	0.314	0.585	1.053
32	21	389-411°	18.0	1.1	5.564	8.403	12.394	12.6	1.2	6.918	9.230	12.111
34	20	390-409°	7.3	1.2	8.240	9.738	11.398	12.4	1.7	7.602	10.096	13.189
35	17	400-419°	20.9	1.3	3.631	5.865	9.214	17.4	1.3	4.356	6.493	9.459
36	16	404-425°	23.9	1.0	1.998	3.456	5.789	21.2	1.1	2.526	4.107	6.491
37	22	406-432°	23.8	1.4	1.975	3.404	5.615	19.3	1.1	2.717	4.229	6.415
38	16	411-436°	26.2	0.7	1.485	2.702	4.750	25.0	1.1	1.730	3.066	5.257
39	19	410-435°	24.3	1.8	1.739	3.029	5.110	22.6	1.4	2.041	3.426	5.581
40	20	417-443°	36.1	2.1	0.476	1.088	2.372	16.3	1.5	1.993	2.892	4.107
41	20	412-438°	21.6	1.0	1.952	3.199	5.096	19.7	0.8	2.347	3.681	5.625

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* Calculated by least-squares using 18 isothermal runs.

Table 8

Coal Fractions Extractable by DMR: Individual Determinations

Coal	Sample 1	Sample 2	Sample 3	Average
01	24.21%	24.16%	22.98%	24.18%*
02	22.49	24.21	20.69	22.46
03	18.71	20.18	18.96	18.84
04	20.89	24.65	22.70	22.75
05	21.13	24.53	23.10	22.92
06	22.62	23.44	23.03	23.03
07	23.91	24.53	24.17	24.20
08	22.94	24.16	21.23	22.78
09	23.75	23.79	22.37	23.77*
10	22.63	22.22	22.05	22.30
11	25.06	24.56	23.61	24.41
12	24.62	23.78	24.31	24.24
13	31.43	27.24	28.38	29.02
14	32.25	26.54	28.20	29.00
15	23.38	25.57	26.38	25.11
16	26.37	25.05	26.98	26.13
17	23.51	24.43	26.40	24.78
18	20.98	23.00	21.26	21.12*
19	20.48	23.70	26.19	23.45
20	21.39	23.13	24.84	23.12
21	31.93	34.11	32.09	32.01*
22	33.09	34.31	33.52	33.64
23	31.29	32.19	32.96	32.14
24	23.01	23.37	22.72	23.03
25	27.28	28.68	28.71	28.69*
26	21.53	22.21	22.62	22.11
27	34.17	36.05	35.15	35.12
28	18.66	17.64	18.91	18.79*
30	22.95	23.29	24.23	23.49
31	24.08	22.52	23.85	23.97*
32	26.05	26.41	30.19	26.23*

Table 8
(Continued)

Coal	Sample 1	Sample 2	Sample 3	Average
33	33.51	27.31	27.50	27.41*
34	34.59	34.34	35.67	34.47*
35	27.44	27.63	27.42	27.43
36	27.05	25.83	25.63	25.73
37	25.78	23.21	. . .	24.50*
38	22.63	22.67	21.88	22.65*
39	23.79	22.67	22.22	22.89
40	20.87	19.43	18.82	19.71
41	20.97	23.30	24.67	22.98
42	24.78	26.11	24.92	25.27
43	34.33	35.86	34.78	34.99

*average of best two of three determinations (six sigma test).

CHAPTER V

DISCUSSION

Table 9 represents the extraction data for the bituminous coals. Listed is the ASTM maximum observed fluidity, the average percent loss of dry coal with DMF, and the standard error.

The DMF extraction data shows a systematic relationship to ASTM maximum fluidity. The coals can be divided into four groups according to their ASTM maximum fluidities. Group I includes 11 coals with fluidities of less than 50 ddpm. Group II includes coals with fluidities between 51 and 100 ddpm. There are six coals in this group. In group III there are 10 coals with fluidities between 101 and 500 ddpm. Group IV includes the 13 coals with fluidities greater than 500 ddpm. The eleven Group I coals show an average DMF-extractable content of 22.06 (±2.24) percent. The six Group II coals (slightly more plastic) show an average DMF extractable content of 23.61 (±1.42) percent, marginally higher. The ten Group III coals show an average DMF-extractable content of 24.28 (±2.00) percent, and the thirteen Group IV coals show an average DMF-extractable content of 29.75 (±4.28) percent. Seven of these thirteen coals exhibit a maximum Gieseler fluidity above 30,000 ddpm; the average DMF-extractables for this most plastic subgroup is 31.21 (±2.83) percent.

Table 9

Coal Fractions Extractable: Average % Loss

Coal Number	ASTM Maximum Fluidity	Average % Loss	Standard Error
01	13.0	23.78	0.40
02	9.6	22.46	1.02
03	28.3	19.29	0.45
04	544	22.75	1.09
05	86.1	22.93	0.98
06	19,690	23.03	0.24
07	775	24.20	0.18
08	50.7	22.78	0.85
09	42.3	23.30	0.47
10	90.2	22.30	0.17
11	98.9	24.41	0.43
12	228	24.24	0.24
13	540	29.02	1.25
14	184	29.00	1.70
15	400	25.11	0.89
16	64.3	26.13	0.57
17	45.3	24.77	0.86
18	26.8	21.75	0.63
19	116	23.45	1.65
20	91.2	23.12	1.00
21	30,000	32.71	0.70
22	30,000	33.76	0.47
23	30,000	32.15	0.48
24	34.9	23.03	0.19
25	30,000	28.22	0.47
26	118	22.12	0.32
27	25,150	35.12	0.54
28	18.6	17.59	0.65
29	39.6	coal withdrawn-incomplete data	
30	16.2	23.45	0.35
31	18.0	23.48	0.48
32	30,000	27.55	1.32
33	30,000	29.43	2.03

Table 9

(Continued)

34	30,000	34.81	0.36
35	10,530	27.50	0.07
36	185	26.17	0.44
37	423	24.43	1.31
38	187	22.39	0.26
39	224	22.89	0.47
40	22.1	19.71	0.61
41	217	22.98	1.08
42		25.27	0.42

Group III can be subdivided into two groups of coals with varying sulfur contents. Seven of the 10 coals contained "normal" sulfur amounts and show an average DMF-extractable content of 24.94 (±2.19) percent. The three remaining coals contained low amounts of sulfur and showed a lower than expected DMF-extractable content. The average value is 22.75 (±0.31) percent. These three coals also showed inconsistent data in the other parts of the project, and a separate study may be done relating the sulfur content to plasticity.

The results were statistically tested to determine the existence of any significant differences in the percent DMF-extractable contents between the four groups. In all cases there did exist significant differences to at least the 95% confidence level (using the Student t test).

An SAS program (statistical analysis system) was run using the extraction data and several types of fluidity measurements. Correlation coefficients were found between the extraction data and the fluidity measurements.

A correlation coefficient of 0.764 was found when relating the Gieseler ASTM ln maximum observed fluidity and the percent DMF extractables from the coals. This is the correlation coefficient we were most interested in, since we are using the data of the standard method of measuring plasticity. We feel that 0.764 is a reasonably good correlation coefficient when you take into account the nature of coal and the somewhat unpredictable Gieseler measurements. Comparing the Gieseler ASTM ln maximum calculated fluidity with the percent extraction losses, a correlation coefficient of 0.768 is obtained. This, of course, removes some of the data inaccuracy, since the intersection of the melting and coking slopes is used as the maximum fluidity. This eliminates the problem of flattened maxima. One would expect a somewhat better correlation for this reason.

The best correlation coefficients, however, existed with the isothermal fluidity data. Only 28 coals were used in this correlation, since these were the only coals for which isothermal data was available. Using the ln maximum observed fluidity at 400°C with the percent extraction losses, one obtains an 0.823 correlation coefficient. At 420°C, this increases to 0.832. The calculated isothermal results gives good coefficients also. At 400°C a correlation coefficient of 0.813 is found. At 420°C, the correlation coefficient is the best of all the results, 0.852.

Isothermal curves are useful in obtaining both fundamental information and data of predictive value. In each run, four experimentally determined properties are examined. These include the melting slope, coking slope, maximum observed fluidity, and maximum fluidity by slope intersection. All of these properties are functions of temperature and exhibit an Arrhenius relationship. This permits the determination of empirical activation energies associated with melting, coking, and fluidity, as well as estimation of the melting and coking constants.(41)

Another use of the Arrhenius relationship is that it permits the comparison of properties of various coals at precisely the same temperature.

The possibility of increasing the correlation coefficients by using DMF extraction data with other parameters was also investigated. This data is summarized in Table 10, presenting the best combinations in each of the six types of fluidity measurements and the corresponding coefficients.(67)

It can be seen that combining DMF with other parameters does increase the correlation coefficients. Pyrolysis work shows up consistently in the combination parameters. Since most standard labs are not equipped with a pyrolysis/gas chromatograph unit, a program excluding the pyrolysis data was run. The 13 variables with the highest predictive values were used to run 36 regressions to estimate the six maximum fluidities listed in Table 10. DMF was not locked in as one of the variables this time; however, DMF was present in all 36 regressions. This information is summarized in Table 11. All the correlation coefficients are quite good, proving that DMF extraction data in combination with other easily accessible data can be used to predict plasticity.

The correlation coefficients which were based on the DMF extraction data alone can be explained by reviewing the proposed mechanisms for coal plasticity. It is the bitumen, the extractable portion of the coal, which is thought to be responsible for initiating the plasticity process. The bitumen contains mainly aliphatic materials which are rich in hydrogen, and serves as a lubricant and hydrogen donor early in the softening and swelling process. Since bitumen melts at temperatures less than 200°C, it would be available early in the process for use as a vehicle. It is reasonable,

Table 10

Correlation Coefficients Using More Than One Parameter

Fluidity Measurements (ln)	Parameters	Correlation Coefficients
Gieseler Maximum Observed Fluidity	Pyrtotal, DMF	0.857
	Pyrct4, pseudo, DMF	0.878
	Pyrct4, reflect, THF, DMF	0.901
Gieseler Maximum Calculated Fluidity	Pyrtotal, DMF	0.881
	Pyr4, Pyrtotal, DMF	0.899
	Pyrct4, reflect, THF, DMF	0.923
Maximum Observed Fluidity at 400°C	Pyrtotal, DMF	0.902
	Pseudo, Pyrtotal, DMF	0.914
	Pyr4, Pyrtotal, pyrquot,DMF	0.934
Maximum Observed Fluidity at 420°C	Pyrtotal, DMF	0.866
	Reflect, THF, DMF	0.905
	Pyr4, FSI, THF, DMF	0.882
Maximum Calculated Fluidity at 400°C	Pyrtotal, DMF	0.897
	Pseudo, pyrtotal, DMF	0.915
	Pyr4, pyrtotal, pyrquot,DMF	0.930
Maximum Calculated Fluidity at 420°C	Pyrtotal, DMF	0.891
	Reflect, THF, DMF	0.916
	Pyrtotal, reflect, THF, DMF	0.930

Pyrtotal = Pyrolysis, total counts per microgram coal

Pyrct4 = Pyrolysis, counts per microgram in 13-16 minutes

Pseudo = % Pseudovitrinite

Reflect - Maximum % vitrinite reflectance

THF = % extracted by hot THF

Pyr4 = % of total pyrolysis in 4 minute window

Pyrquot = (14-15 minute count/17-18 minute count)

FSI = Free swelling index

This data is available in reference 67.

Table 11

Correlation Coefficients Excluding Pyrolysis Data

Fluidity Measurements (ln)	Parameters	Correlation Coefficients
FOBSRAMP	PSEUDO DMF	.817
	REFLECT DMF	.805
	PSEUDO DMF THF	.848
	REFLECT DMF THF	.865
	PSEUDO REFLECT DMF THF	.872
	ORGANIC REFLECT DMF THF	.878
FCALRAMP	PSEUDO DMF	.812
	REFLECT DMF	.819
	VOLMAT REFLECT DMF	.836
	REFLECT DMF THF	.870
	SULFUR REFLECT DMF THF	.874
	ORGANIC REFLECT DMF THF	.887
FOBS400	RESINITE DMF	.867
	BTU DMF	.871
	RESINITE MACERAL1 DMF	.888
	BTU RESINITE DMF	.907
	RESINITE REFLECT DMF THF	.914
	BUT EXINITE RESINITE DMF	.915
FOBS420	DMF THF	.863
	THF ASPHALT*	.863
	BTU DMF THF	.885
	REFLECT DMF THF	.903
	BTU VITRIN DMF THF	.910
	VITRIN REFLECT DMF THF	.913
FCAL400	RESINITE DMF	.859
	BTU DMF	.872
	REFLECT DMF THF	.889
	BTU RESINITE DMF	.904
	RESINITE REFLECT DMF THF	.913
	BTU RESINITE EXINITE DMF	.917

Table 11 (Continued)

Fluidity Measurements (ln)	Parameters				Correlation Coefficients
FCAL420	DMF	THF			.879
	BTU	DMF			.882
	BTU	DMF	THF		.901
	REFLECT	DMF	THF		.916
	VOLMAT	REFLECT	DMF	THF	.920
	RESINITE	REFLECT	DMF	THF	.921

The following labels, along with those listed in Table 10, are used in Table 11:

Organic = % organic sulfur, dry basis

Volmat = % volatile matter

Sulfur = % sulfur, dry-ash included

Resinite = % resinite

BTU = Heating value

Maceral = Vitrinite, pseudovitrinite, exinite, resinite, and one-third of semifusinite

Exinite = % exinite

Asphalt = % DMF extractabel - % THF extractable

Vitrin = % vitrinite, dry-ash included

then, to expect the amount of extractables to be related to the degree of fluidity. This is shown with the high correlation coefficients which were found.

Further verification of this is found in Pierron's work in the late 1950's and early 1960's. He found that the yield of pyridine extract seemed to be proportional to the degree of fluidity, and that pyridine extraction destroyed the fluidity of the coal.(65) Re-introduction of the extract into the coal not only restored the plasticity of the coal, but actually enhanced the plasticity.(15)

CHAPTER VI

SUMMARY

In this research the goal was to study the possibility of using dimethylformamide extraction data to predict the plasticity of bituminous coals.

Plasticity is a phenomenon of coal which is not completely understood. Some bituminous coals, upon heating, go through a softening and swelling state before they resolidify. This softening and swelling state is called the plastic state of coal. The plastic state usually occurs around 450°C, and is concurrent with the thermal cecomposition of coal. Only bituminous coals exhibit this behavior. Not all bituminous coals exhibit plasticity to the same degree, however.

The current popular mechanism of plasticity is attributed to Richard Neavel.(5) He stated that it is the bitumen in the coal, the extractable portion of the coal, that is responsible for initiating the plasticity process. Dimethylformamide removes the bitumen of the coal. It is logical to assume, then, that the percent loss of extractables using DMF as a solvent would be an indicator of the degree of plasticity in a coal.

Forty-three coals were extracted in triplicate using DMF as the solvent. DMF was chosen because of its high polarity and small size. The average percent loss was calculated for each coal.

Statistical analyses show that there is indeed a good correlation between the percent DMF extractables and the degree of fluidity. The correlation coefficient for the relationship between the ASTM maximum observed fluidity and the percent DMF extractables was 0.764. This is a reasonably good correlation, taking into account the nature of coal and the inadequacy of the Gieseler plastometer. Correlation coefficients dealing with isothermal fluidities were higher, as were correlation coefficients in which DMF was used in combination with other parameters to predict the fluidity.

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