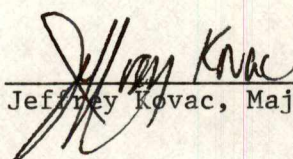
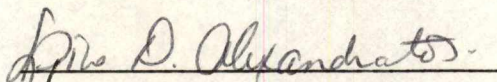
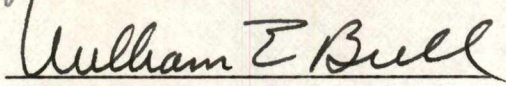
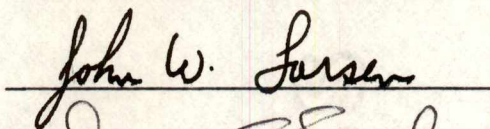
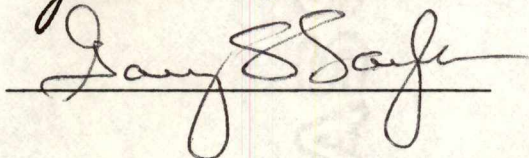


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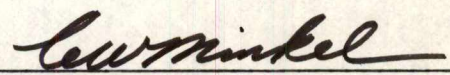
I am submitting herewith a dissertation written by Susan E. Shawver entitled "The Macromolecular Structure of Low Rank Coals and Lignites." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


Jeffrey Kovac, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:


Vice Provost
and Dean of The Graduate School

THE MACROMOLECULAR STRUCTURE OF
LOW RANK COALS AND LIGNITES

A Dissertation
Presented for the
Doctor of Philosophy
Degree

The University of Tennessee, Knoxville

Susan E. Shawver

March 1986

DEDICATION

To my family.

ACKNOWLEDGEMENT

I wish to express my appreciation to Dr. John W. Larsen whose patience, guidance, and support made the work presented here possible. In addition, the support of Dr. Jeffrey Kovac is gratefully acknowledged. Appreciation is also extended to Dr. Spiro Alexandratos whose confidence and faith was an inspiration to achieve the seemingly impossible.

Appreciation is extended to the Department of Energy, University of Tennessee, and Lehigh University for their financial support.

This work is dedicated to my family, especially my father and brother who mined the focus of this work-coal.

ABSTRACT

The low rank coals, lignites and subbituminous coals, are considered to be three dimensionally covalently crosslinked macromolecules. The solvent swelling methodology used to characterize the macromolecular structure of bituminous coals is extended to the lower rank coals. The pyridine-extracted subbituminous coal obeyed the predictions of regular solution theory, while the pyridine-extracted lignites did not. The non-polar solubility parameter of the pyridine-extracted subbituminous coal was estimated to be $9.5 (\text{cal/cm}^3)^{1/2}$. The O-acetylated and O-methylated subbituminous coals were assigned solubility parameters of $9.2 (\text{cal/cm}^3)^{1/2}$. Solubility parameters of 9.2 and $9.1 (\text{cal/cm}^3)^{1/2}$ were assigned to the two O-acetylated lignite samples. Flory Interaction Parameters were calculated for a series of non-polar solvent-coal pairs. The Flory-Rehner and Kovac Equations were applied to the solvent swelling data to estimate crosslink densities and the number average molecular weight between crosslinks of the O-acetylated lignites and pyridine-extracted subbituminous coal. The low rank coals contain hydrogen bonds which serve as crosslinks in the coal network. Solvent swelling experiments with non-polar solvents indicated the removal of ionic bonds was found to have little effect on the macromolecular structure of the lower rank coals.

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CHAPTER I

INTRODUCTION

Coalification is an extremely complex process in which peat is transformed via a wide spectrum of physical and chemical processes into coal. In the early stages of coalification, lignite and subbituminous coals are formed. The bituminous and anthracite coals are formed as the coalification process continues. The goal of numerous research projects has been to characterize the macromolecular structure of coals. Coals are now generally accepted to be three dimensionally crosslinked macromolecular networks. An impressive piece of evidence supporting the macromolecular network is the observed swelling of coals in solvents. Many of the research efforts, however, have focused solely on the bituminous coals; the lower rank coals have received much less attention. The work performed in this dissertation is an investigation of the macromolecular structure of the lignite and subbituminous coals. The experimental approach employed is solvent swelling.

Several key features distinguish the bituminous and lower rank coals. First, the lower rank coals have a much higher as-mined moisture content. The effect of the presence of water on the macromolecular structure of the lower rank coals is undetermined. The lower rank coals also have a higher percentage of organic oxygen, often as much as twenty five weight percent of the coals. As a result, the lower rank coals are more polar than the bituminous coals.

Much of the oxygen in the lower rank coals is found in carboxyl and hydroxyl groups which can participate in hydrogen bonding. One of the goals of the work performed is to begin to characterize the hydrogen bond network in the lower rank coals.

Coals are heterogeneous materials composed of both organic and mineral matter. In the bituminous coals, the mineral matter is often found in discrete phases, such as quartz and clay minerals. In the lower rank coals, a significant portion of the mineral matter consists of ion-exchangeable alkali and alkaline earth metals which are dispersed throughout the coal and are bound ionically to the organic portion of the coal. The presence of the ionic bonds may or may not have an effect on the macromolecular structure. A series of experiments designed to address this question has been performed.

The experimental approach used to gain information on the macromolecular structure of the lower rank coals is solvent swelling, a classical polymer technique. Similar to other crosslinked networks, when exposed to a solvent a coal will swell. The swelling is dependent on two factors: 1) the amount of interaction between the network and the solvent and 2) the amount of crosslinking in the network structure. By applying the theories of rubber elasticity, regular solution, and polymer solutions to the swelling data, information on the macromolecular structure can be obtained. A prime example of the information to be gained is whether the network is tightly bound forming a rigid material or loose and flexible. This approach has proved to be quite successful with bituminous coals. Thus application of the solvent swelling technique to the lower rank

coals is a natural extension. A detailed discussion of the success of the efforts to apply the solvent swelling technique to the lower rank coals will be provided later, however, the extension of the technique has proven useful but less successful than with bituminous coals.

CHAPTER II

COAL-SOLVENT INTERACTIONS

A. Coal Structural Model

Coals are now generally¹⁻⁷, but not universally,^{8,9} accepted to be macromolecular in nature. Of course, the term macromolecular suggests polymeric, but coals are not polymeric in the strictest sense. The structural units which comprise the coal molecule are not discreet monomers, but encompass a wide variety of types of molecules with a wide distribution of molecular weights. To complicate the issue further, coals are not pure materials. Coal is comprised of both inorganic and organic components.^{1,10} In turn, each of these portions of the coal do not consist of single substances. To illustrate this point, the inorganic portion of the coal consists of a variety of ion-exchangeable cations, clay minerals, quartz, and other inorganic species such as pyrite. The organic portions of the coal, the macerals, also consist of a variety of materials. The composition of a maceral is dependent on the environment and the conditions of coalification. Obviously, coals are very complex substances.

X-ray diffraction and depolymerization studies¹¹ have shown that the organic structural units in coal consist of aromatic and hydroaromatic clusters with a wide range of molecular weights. The clusters are connected via short aliphatic chains such as methylene groups and other bridging groups such as ether linkages.¹² Based on

extensive chemical and physical evidence several workers have suggested structures for coal. Although several models for coal structure exist,¹²⁻¹⁶ only two will be shown here. Wiser¹² proposed the coal structure illustrated in Figure 1. Based on the liquefaction behavior of bituminous coals Shinn¹⁶ proposed the structure in Figure 2. Neither structure is meant to specify a particular coal molecule, but rather to suggest how the various types of molecules and linkages known to be present in the coal might be arranged.

The term macromolecular does not necessarily define a structural model for coals. Certainly coals have very high molecular weights, even after degradation.¹⁷ Several macromolecular structural models have been proposed. A key distinguishing feature between the models is how the molecules in the coal are held together. Several of the various models that have been proposed are 1) the micelle model¹⁸⁻²² 2) the Sternberg model^{23,24} 3) the entanglement model²⁵⁻²⁹ and 4) the three dimensionally crosslinked macromolecular model.^{3,5,6,30-35} The work presented here is based on the three dimensionally crosslinked macromolecular structure. An illustration of the model is presented in Figure 3. The aromatic and hydroaromatic clusters are connected by covalent bonds. Some of the clusters are tri- and tetravalent leading to a network structure. Not all of the linkages are covalent, however. Hydrogen bonds and ionic bonds may also be present. Those secondary interactions are indicated by hashed lines. Other weaker forces such as van der Waals forces play roles yet undefined. The possibility of some entanglement of the network chains is not dismissed. In addition, some of the clusters are not attached to the

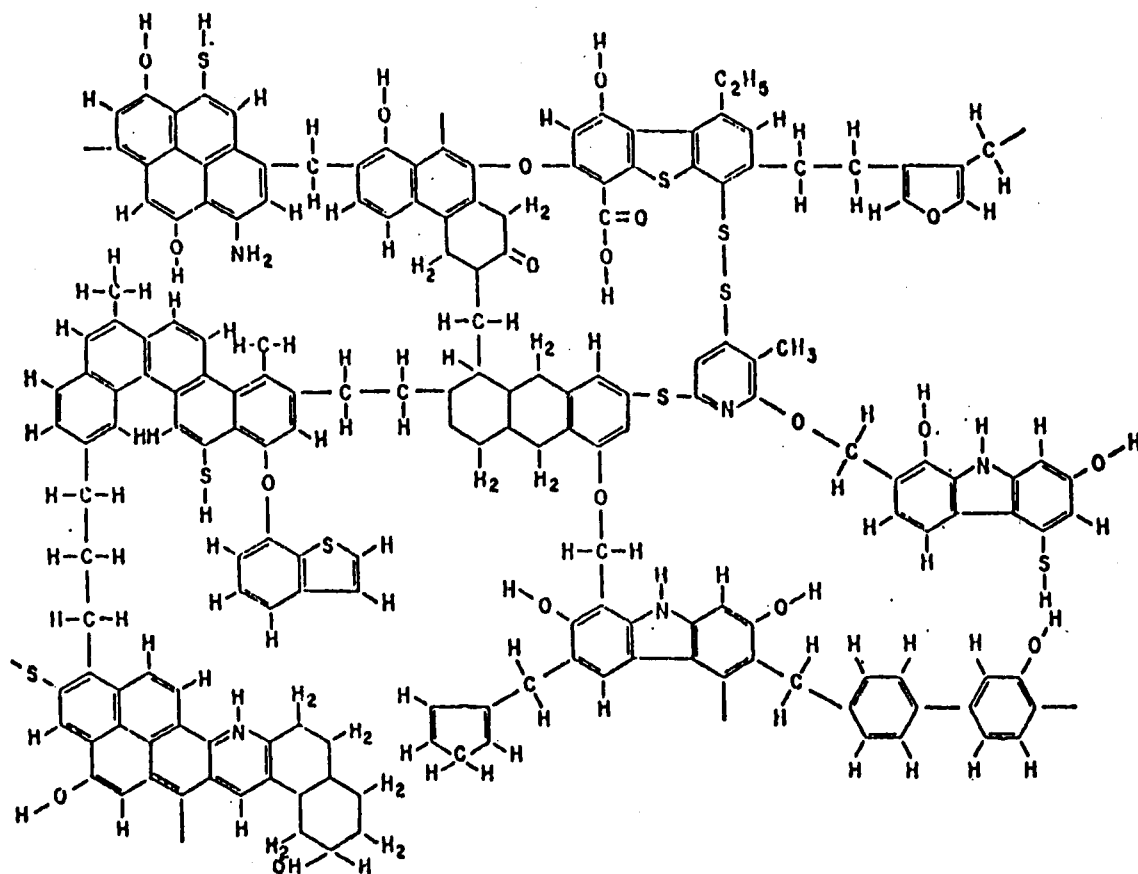


Figure 1. Wiser Model of Coal Structure.

Source: W. H. Wiser, Prepr. Pap., Am. Chem. Soc., Div. Fuel Chem., 20(2), 122 (1975).

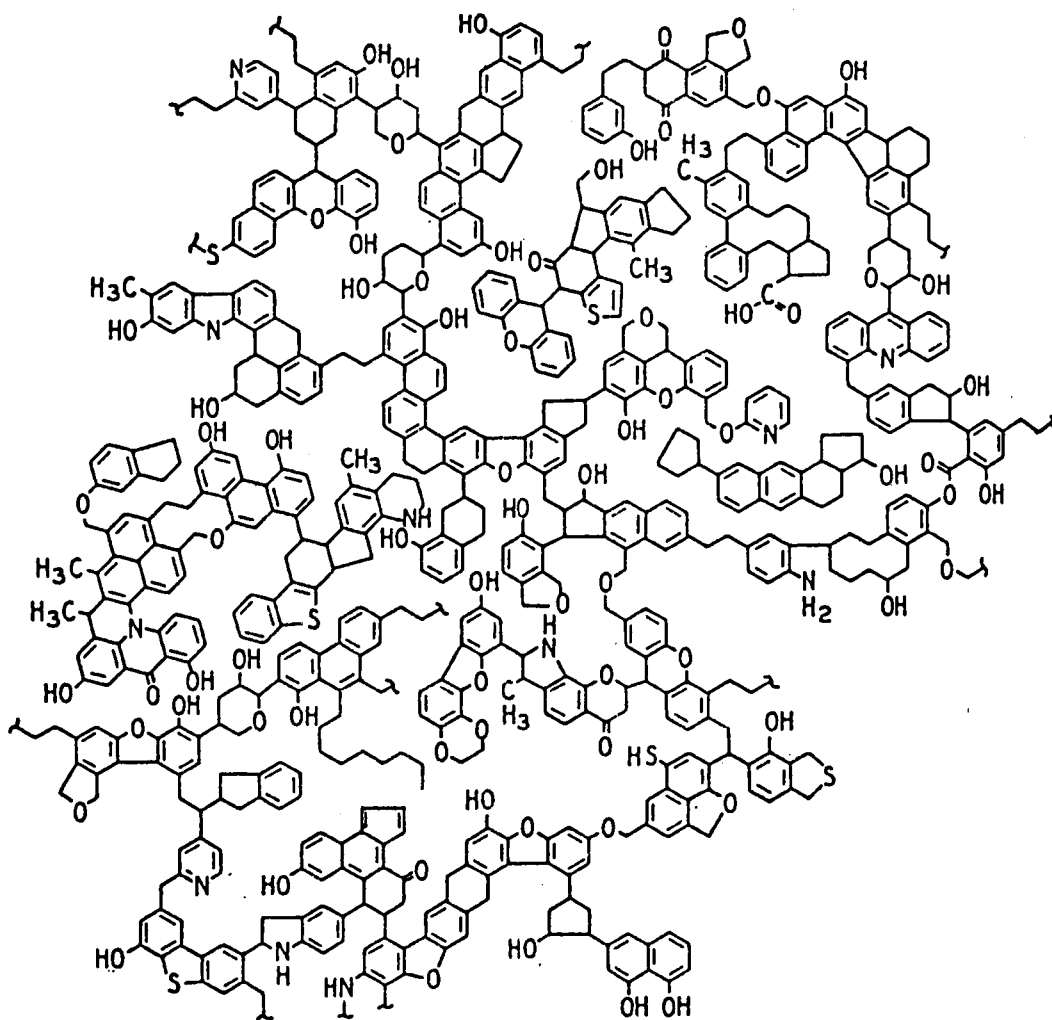


Figure 2. Shinn Model of Coal Structure.

Source: J. H. Shinn, Fuel, 63, 1187 (1984).

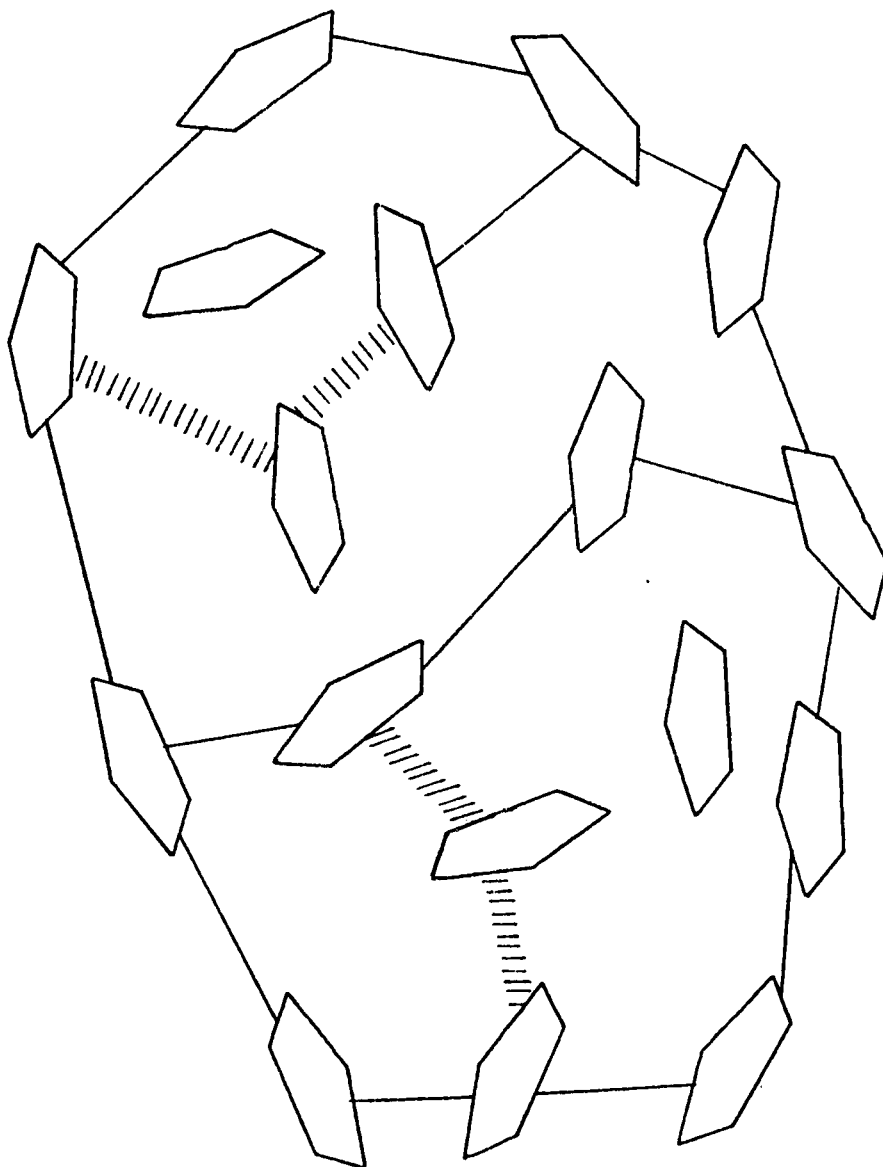


Figure 3. Coal Network Model.

coal network. Some of the unattached molecules reside in the pore structure of the coal and some are dissolved in the coal matrix. The entrapped molecules may be extracted from the coal with a suitable solvent. Each of the structural models listed has been critically reviewed.⁶ Therefore, only the evidence for the three dimensionally crosslinked macromolecular structure will be briefly reviewed.

van Krevelan³ likened the process of coalification to a three-dimensional polycondensation in which the coal "monomers", formed from decomposed plant material, combine to form a three-dimensional structure. The theoretical framework on which the polycondensation is based was developed by Flory.³⁶ At the lignite stage, a crosslinked structure is formed with soluble material dissolved in the network. As coalification continues the network continues to grow at the expense of the soluble material. Since the soluble material decreases as the process of coalification increases, the extent of coalification can be estimated from the exhaustive solvent extraction yields of the coal. Obviously, the model is oversimplified, but van Krevelan was able to model the process of coalification with reasonable success. This picture of the coalification process has been questioned, but not the ideas on which it was based.³³ In another series of experiments, van Krevelan¹ obtained additional evidence of the macromolecular structure of coal. The soluble material extracted from coals which had been subjected to hydrolysis, pyrolysis, and mild oxidation was studied. The extracts and insoluble residue were macromolecular and very similar to the untreated coal. The coal behaved as if it were a very large molecule being cleaved.

Vahrman³⁰⁻³² also described the coal molecule as an insoluble crosslinked network which contained soluble small molecular weight material. Based on solvent extraction studies, the majority of the soluble molecules were thought to reside solely in the extensive pore system of the coal. Wiser³⁷ later demonstrated that some of the soluble material was trapped in the coal matrix and could be extracted if a solvent which swells the coal matrix to allow solvent access to the soluble material was employed.

Obviously, the observation that a portion of the coal does not dissolve upon solvent exposure is not sufficient to demonstrate that the coal is a three-dimensionally crosslinked network. Hombach²⁵⁻²⁸ argues in a series of papers that the coal molecules are merely entangled and do not form a covalently crosslinked structure. If the molecules were not covalently crosslinked then the entire sample would dissolve upon continued exposure to solvent. This behavior is not observed. Consider a coal extracted with pyridine, one of the best solvents for coal. The insoluble residue exposed to pyridine for an additional one and half years does not show any signs of further dissolution.⁶ The coal molecules would have to be highly entangled to explain this behavior.

Another piece of evidence supporting a three-dimensionally crosslinked network arises from the bulk mechanical properties of coals. Larsen and Kovac³⁴ point to the study of Morgans and Terry³⁸ as an excellent example. A constant stress was placed on a bituminous coal sample and the elongation as a function of time measured. After an initial increase the elongation became constant with time. After

removal of the stress, all but 0.5% of the deformation of the sample was recoverable. This behavior is observed in crosslinked polymers. If the coal molecule were held together only by hydrogen bonds and other weaker forces the constant elongation and elastic behavior would not be observed.

The last piece of evidence supporting the three-dimensionally crosslinked structure to be discussed is the behavior of coals upon solvent exposure. Many researchers have observed that coals swell when exposed to solvents.^{6,39-42} In good solvents, a doubling in volume has been observed.⁶ In addition, the swelling is reversible. In an elegant study, Brenner⁵ exposed thin slices (approximately 15 microns thick) of vitrinite from Illinois #6 coal to n-propyl amine vapor and monitored the behavior of the coal. The coal nearly doubled in size and after removal of the solvent, the coal returned to nearly its original size and shape. The swelling procedure was repeated and the coal exhibited the same behavior, demonstrating the reversibility of the swelling process. In a later study, Brenner³⁵ provided direct evidence for a crosslinked macromolecular structure. In addition, information concerning the physical state of the coal, glassy versus rubbery, could be determined. Thin slices of an Illinois #6 vitrinite were exposed to various solvents which included pyridine, THF, and toluene. The optical anisotropy, an indication of the orientation of a material, of the coal was monitored via transmission optical microscopy. After exposure of the coal to pyridine, a good hydrogen bond accepting solvent, the optical anisotropy was completely relaxed, indicating the orientation of the coal network chains which were

maintained solely by hydrogen bonding and other weaker forces was removed. Clearly, pyridine is capable of disrupting all hydrogen bonds in the coal. The study indicated that the pyridine-immersed coal was rubbery.

In the Brenner study,³⁵ the coal was also derivatized to remove the hydrogen bond network using Liotta's⁴³ O-methylation procedure. The O-methylation procedure has been shown to remove the hydrogen network in coals. Thus, if pyridine is capable of disrupting all the hydrogen bonds present, the behavior of the untreated and O-methylated coals will be similar upon exposure to pyridine. The pyridine swelling of the untreated coal and O-methylated coals gave very similar results. This indicates that pyridine is capable of disrupting hydrogen bonds present in the coal. This observation implies the remaining bonds in the coal are primarily covalent. Thereby, direct evidence is provided for a three-dimensionally crosslinked network.

B. Theory

Many of the approaches taken to provide evidence for the macromolecular structure of coals have relied on the interaction of a solvent with the coal network,^{1-7,35} for example, solvent extraction and solvent swelling experiments. Regular solution theory is a thermodynamic model which describes the mixing of a pair of liquids or of a liquid and a polymeric system.⁴² Its principle assumptions are that mixing is random and that no specific interactions occur. The

purely statistical spatial distribution of molecules or molecule segments is not perturbed by specific interactions, the only intermolecular interactions occurring being van der Waals forces. It is an extension of the ideal solution. In both, mixing is random, but where ideal solution theory assumes that the heat of mixing is zero, regular solution theory contains a provision which allows the heat of mixing to be calculated. It has been very successful in treating non-polar systems. It is a simple theory, easily visualized and powerful, so its application to coals is reasonable and enlightening.

A brief review of regular solution theory is now provided. An ideal solution obeys Raoult's Law. In order for ideal solution behavior to be exhibited over a range of compositions and temperatures the following conditions must be met: 1) the heat of mixing, ΔH_{mix} , must be zero 2) the volume change upon mixing of the solute and solvent must be zero 3) the mixing of the solute and solvent must be random. Failure to fulfill any of these criteria results in a deviation from ideal behavior. For example, solutions in which the solute is a high molecular weight polymer are known to deviate from ideal behavior.³⁶ Flory³⁶ discussed the factors which contribute to the nonideality of polymer solutions and concluded that the observed deviation is primarily a consequence of the failure of the solution to obey the following expression for the entropy of mixing:

$$\Delta S_{\text{mix}} = -k (n_1 \ln N_1 + n_2 \ln N_2) \quad (1)$$

where n_1 and n_2 are the number of molecules of solvent and solute, respectively; N_1 and N_2 are the mole fractions of solvent and solute

respectively. Equation 1 is suitable for application to solutions in which the solute and solvent are similar in molecular size and shape and have similar attractive fields.⁴⁴ When the solute is a polymer, the huge disparity between molecular size of the solvent and solute (and consequently the mole fractions of the solute and solvent) leads to non-ideal behavior. Flory³⁶ and Hildebrand⁴⁴ independently derived a more suitable expression for the entropy of mixing incorporating volume fractions, rather than mole fractions, to replace Equation 1:

$$S_{\text{mix}} = -k(n_1 \ln v_1 + n_2 \ln v_2) \quad (2)$$

where v_1 and v_2 are the volume fractions of solvent and solute, respectively. v_1 and v_2 are given by Equations 3 and 4:⁴⁴

$$v_1 = n_1 / (n_1 + x n_2) \quad (3)$$

$$v_2 = x n_2 / (n_1 + x n_2) \quad (4)$$

where x is the ratio of the molar volumes of the solute and solvent. The approach used by Flory³⁶ to derive Equation 2 was based on liquid lattice theory. The primary assumption in this model is that the configurations of both the pure components and of the solution may be described by the same lattice.³⁶ This model also ignores contributions to the entropy from specific interactions. In addition, the model does not distinguish between varying degrees of polymer density, thus

limiting the use of the model to concentrated solutions of polymers. Briefly, the approach used by Hildebrand⁴⁴ does not employ the liquid lattice model, but assumes that the available free volume is accessible to both the solvent and polymer. The free volume is equal to the sum of the free volumes of the solvent and polymer. This approach yields the same equation as Flory's.

The enthalpy of mixing will now be discussed. In solution intermolecular interactions are large. The enthalpy of mixing is the difference between the total interaction energy of the solution and the total interaction energy of the pure components.⁴⁴ The enthalpy of mixing of two liquids is not necessarily zero. Scatchard⁴⁵ proposed the following semi-empirical relationship to define the enthalpy of mixing:

$$\Delta H_{\text{mix}} = \phi_1 \phi_2 [(E_1/V_1)^{1/2} - (E_2/V_2)^{1/2}]^2 \quad (5)$$

where V_1 and V_2 are the molar volumes of the solvent and solute, respectively; ϕ_1 and ϕ_2 are the volume fractions of the solute and solvent; E_1 and E_2 are the energies of vaporization of the solvent and solute; (E/V) is defined as the cohesive energy density (CED) of the liquid. It is the amount of energy required to break all the intermolecular interactions in a mole of liquid.⁴⁴ It is roughly a measure of the liquids interaction with itself. The square root of the CED, $(CED)^{1/2}$, is defined as the solubility parameter, δ . Equation 5 may be written as:

$$\Delta H_{\text{mix}} = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (6)$$

When $\delta_1 = \delta_2$, ΔH_{mix} has a value of zero. For all other regular solutions, ΔH_{mix} will be positive ie, endothermic. Again random mixing is assumed and specific interactions such as hydrogen bonding are not allowed. Essentially, the difference between δ_1 and δ_2 determines whether mixing will or will not occur. To illustrate this point, if the difference between δ_1 and δ_2 is large, the solute and solvent will separate since the favorable entropy change will not be sufficient to counteract the endothermic heat of mixing. If the difference between the solubility parameters is small, mixing will occur. This is a quantitative expression of the familiar chemical expression "like dissolves like".

Development of an expression for the enthalpy of mixing for a solvent and polymer has been described in detail by Flory.³⁶ The resulting expression is:

$$\Delta H_{\text{mix}} = kT \chi n_1 v_2 \quad (7)$$

n_1 is the number of solvent molecules and v_2 is the volume fraction of the soluble polymer. χ is the Flory Chi, or interaction parameter. χ is defined as the interaction energy per solvent molecule divided by kT . It is a dimensionless quantity and may be separated into entropic and enthalpic contributions:³⁶

$$\chi = \chi_H + \chi_S \quad (8)$$

χ_S is the interchange entropy, an empirical term, and its value generally varies between 0.3 and 0.4.⁴⁵⁻⁴⁷ χ_H is given by the following expression:

$$\chi_H = v_1 / RT (\delta_1 - \delta_2)^2 \quad (9)$$

The difference between δ_1 and δ_2 ultimately determines the magnitude of χ_H and consequently the magnitude of ΔH_{mix} . Thus the difference of the solubility parameter of the solvent, δ_1 , and the solubility parameter of the polymer, δ_2 , determines whether mixing will or will not occur.

Expressions for the entropy and enthalpy of mixing have been obtained. From these expressions an equation for the free energy of mixing may be derived:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (10)$$

Substituting the expression obtained for ΔH_{mix} and $T \Delta S_{\text{mix}}$ (Equations 2 and 7):

$$\Delta G_{\text{mix}} = kT \chi n_1 v_2 + kT (n_1 \ln v_1 + n_2 \ln v_2) \quad (11)$$

The solution thermodynamics discussed apply to systems in which the solute is soluble in the solvents. Not every polymer or macromolecule is soluble. For example, a rubber stopper placed in an

organic solvent such as benzene does not dissolve. What it does do is swell. This behavior is seen with macromolecular networks. Similar behavior is exhibited by coals. The amount of swelling of a coal sample, or any crosslinked material, is dominated by the degree of crosslinking in the network and the magnitude of the solvent interaction with the network. Thus, solvent swelling experiments can provide information concerning the network structure of a macromolecule. In particular, information can be gained on the number average molecular weight between branch points, $\overline{M}_c$, and the crosslink density of the macromolecule. A representation of a macromolecular coal is shown in Figure 4.⁴⁸ The branch points or crosslinks in the network are indicated by the closed circles. A brief review of the theory of swelling is now provided.

When a macromolecule is placed in contact with a solvent, the solvent begins to mix with the network chains. As more solvent is imbibed, the chains in the network are stretched and a retractive force opposing the swelling force due to solvent imbibition becomes dominant. At equilibrium, these opposing forces are balanced. Thus the free energy change (ΔG) upon mixing of the solvent and macromolecule is controlled by two factors: 1) the free energy of mixing of the solvent and network (ΔG_{mix}) and 2) the elastic free energy of the expansion of the network (ΔG_{el}). The free energy change is defined as:³⁶

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{el}} \quad (12)$$

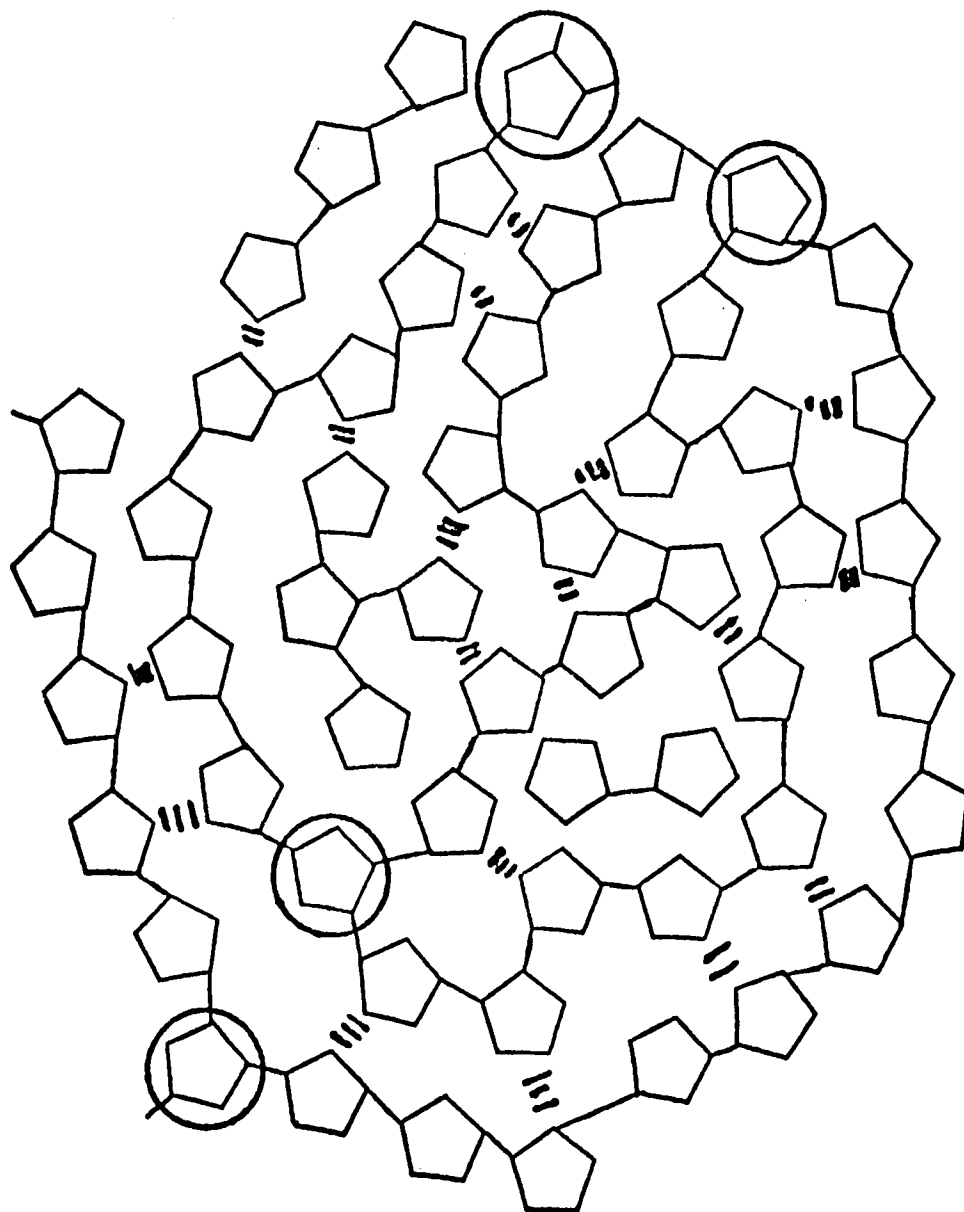


Figure 4. Macromolecular Structure for an Illinois No. 6 Coal.

Source: J. W. Larsen, D. Lee, and S. E. Shawver, Fuel Proc. Tech., in press.

ΔG_{mix} is given by:³⁶

$$\Delta G_{\text{mix}} = kT (n_1 \ln V_1 + n_1 V_2) \quad (13)$$

ΔG_{el} may be related to the term $-T\Delta S_{\text{el}}$ where ΔS_{el} is the change in entropy upon network deformation.³⁶ From a deviation not presented here,^{36,49} $\overline{M}_c$, the number average molecular weight between crosslinks, may be calculated from the following expression:³⁶

$$\overline{M}_c = v_2^{1/3} \rho V_1 / -[\ln(1-v_2) + v_2 + \chi v_2^2] \quad (14)$$

ρ is the density of the network, V_1 is the molar volume of the solvent, v_2 is the volume fraction of the swollen network at equilibrium. χ is the Flory Chi parameter. The assumptions made to derive Equation 14 include: 1) the elastic restoring force in the network is entropic in origin 2) the individual chains deform affinely (the chain deformation is of the same factor as is the macroscopic deformation) 3) the solvation process can be described by a modification of regular solution theory.⁵ Obviously, the coal network which is composed of aromatic and hydroaromatic clusters is not adequately described by the Flory-Rehner Equation. A more suitable model, which incorporates the effects of non-Gaussian chain statistics was developed by Kovac⁵⁰ and has been successfully applied to bituminous coals.⁶ The Kovac equation is given by Equation 15:⁵⁰

$$\overline{M}_c = (\rho v_2^{1/3} V_1 + V_1 \rho / N v_2^{1/3}) / -[\ln(1-v_2) + v_2 + \chi v_2^2] \quad (15)$$

The Kovac Equation is similar to the Flory-Rehner Equation, but contains an additional term which includes the parameter N which is defined by:⁵⁰

$$N = \overline{M}_c / \overline{M}_o \quad (16)$$

$\overline{M}_o$ is the number average molecular weight of the coal clusters.

Essentially, N is a measure of the deviation of the coal network from Gaussian behavior.

The determination of $\overline{M}_c$ permits the calculation of the crosslink density of the network, ρ_x , by the following expression:³⁶

$$\rho_x = 1/(\overline{M}_c v_2) \quad (17)$$

The quantities required to determine the $\overline{M}_c$ are χ and v_2 , the volume fraction of the swollen network. χ is measured independently from v_2 . χ is also temperature and concentration dependent. Orwoll⁵¹ has written an excellent review describing various techniques of determining χ . Among the techniques available are vapor sorption, osmotic pressure, and light scattering. Focusing on the work performed on coals, v_2 is obtained by exposing the coal to a solvent and measuring either the weight increase (gravimetric) or volume increase (volumetric). The volumetric method of measuring v_2 is easy⁶ but is not free of complications. If the coal is unextracted, the solvent may extract uncrosslinked material from the coal changing the

chemical potential of the solvent. In addition, the packing of the coal particles may change after swelling due to changes in their size. The gravimetric method also suffers from complications. Coals are highly porous materials. Some of the solvent imbibed by the coal will fill the pores and not contribute to swelling of the network. Therefore the observed weight gain must be corrected for the pore volume of the coal. While coals are not completely soluble, a portion of the coal (the uncrosslinked material) will dissolve upon exposure to solvent. The extraction of material from the coal into the solvent will lower the vapor pressure of the solvent causing additional solvent to condense. This will increase the time required to reach equilibrium swelling and the observed weight increase is greater than that due to swelling of the coal.

C. Literature Review

Many studies of coal have focused on the interaction of the coal network with a solvent. Often these coal-solvent interactions have been discussed within the framework of regular solution theory. The use of solubility parameters to assist in predicting maximum extraction yields or maximum swelling is common. In addition, the determination of solubility parameters to ultimately gain information on the macromolecular structure of coals is well-documented. The use of the solubility parameter concept to coals is not restricted to the examples mentioned above, however. Some research efforts which have attempted to relate solubility parameters and coal reactivity and/or

behavior have proved successful, others less so. A critical assessment of the application of solubility parameters to coals will now be presented.

M. W. Kiebler⁵² measured the amount of material extracted from bituminous coals by a variety of solvents, the extractions being performed at 150°, 200°, 250°, and 300 °C. The dependence of the extract yield on the following properties of the solvents was examined: internal pressure (equivalent to the square of the solubility parameter), surface tension, dipole moment, dielectric constant, latent heat of vaporization, refractive index, specific refraction, molar volume, parachor, and the ratio of the square of the dipole moment to the dielectric constant. In the study, Kiebler demonstrated that at temperatures from 150° to 300 °C, the effectiveness of a solvent is directly proportional to its internal pressure.

The extractions were performed in stainless steel bombs, under inert atmosphere, for a maximum of 120 hours at temperatures of 150° to 300 °C. After extraction, the bombs were washed with a 1:1 mixture of 95% ethanol and benzene. The solution was filtered and the coal residue Soxhlet extracted 120 hours with an ethanol-benzene solution under nitrogen. The ethanol-benzene solution was removed from the residue after which the residue was dried overnight at 110 °C, weighed, and an elemental analysis performed. The extracted material was isolated by removing the ethanol-benzene solution by distillation. In some cases, precipitation in either aqueous hydrochloric acid or sodium hydroxide, depending on the solvent, was necessary after

distillation. The precipitated extract was then filtered from solution and dried. The yield of extract was reported in terms of the recovery of soluble organic material:

$$\frac{\text{Wt. of extract} - \text{ash}_e \times 100}{\text{Wt. of extract} + \text{Wt. of residue} - \text{ash}_{\text{total}}} = \% \text{ Yield} \quad (18)$$

where ash_e is the weight of ash in the extract.

Table I⁵² contains the extraction yields for several solvents at various temperatures and the internal pressure of the solvents. A statistical analysis was performed on the yield of extract and the various physical properties of the solvent at 200 °C. Of the physical properties mentioned previously, only the internal pressure demonstrated a relationship with the yield of extract. The statistical analysis approach was then extended to 300 °C, utilizing the solvents which were employed at 200 °C and which were stable at 300 °C. Select solvents from 200 °C were used in the 150 °C and 250° C analysis.

Figure 5⁵² is a plot of the yield of extract versus the internal pressure at 200° and 300 °C. Figure 6⁵² is a plot of the yield of extract versus the internal pressure of the solvents at 150°, 200°, 250°, and 300 °C. The other physical properties of the solvents were shown to have no influence or were accounted for by the internal pressure. A significant correlation was observed at 200 °C for surface tension and yield only with aliphatic solvents. Since this correlation was not observed for the 300 °C extractions, it was regarded as spurious. Although Kiebler did not directly relate the

TABLE I

YIELD OF EXTRACT FROM PITTSBURGH SEAM COAL AT VARIOUS TEMPERATURES
AND INTERNAL PRESSURE, P_i , OF THE SOLVENT

Solvent	% Yield	Internal Pressure, P_i
Temperature 150 °C		
Ethylbenzene	4.5	53.5
Toluene	5.7	52.5
Phenol	21.0	120.0
Temperature 200 °C		
Heptane	4.8	21.6
Ethanol	8.3	54.4
Benzene	9.7	35.8
Biphenyl	14.0	69.8
Pyridine	20.0	56.9
Aniline	24.4	77.1
Temperature 250 °C		
Ethylbenzene	11.7	30.0
Naphthalene	17.8	49.7
o-Phenylphenol	33.2	70.4
Temperature 300 °C		
Toluene	16.0	8.5
Ethylbenzene	20.0	16.3
Bibenzyl	34.0	48.7
Aniline	48.4	47.7

Source: M. W. Kiebler, Ind. Eng. Chem., 32, 1389 (1940).

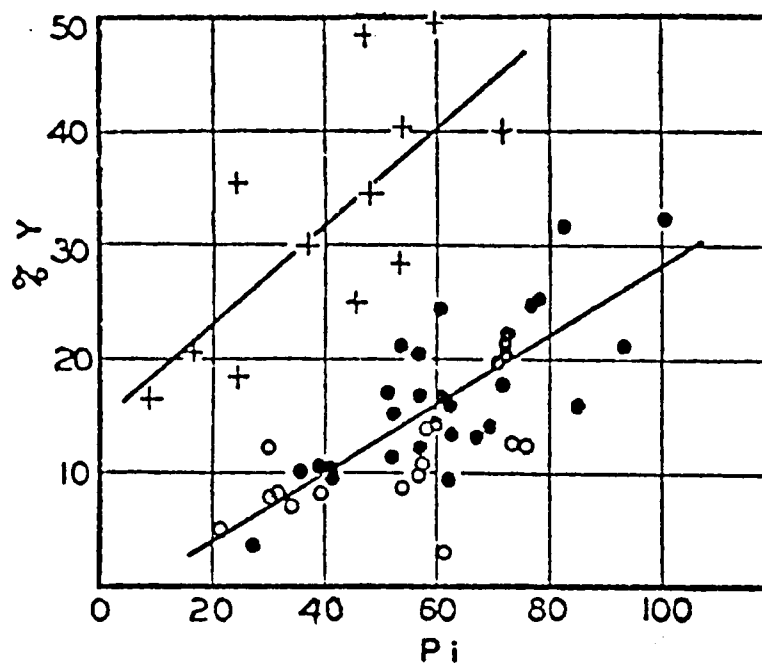


Figure 5. Plot of Yield of Extract Versus Internal Pressure (P_i) at 200° and 300°C. O, Aliphatic Solvents at 200°C; ●, Non-aliphatic Solvents at 200°C; +, Nonaliphatic Solvents at 300°C.

Source: M. W. Kiebler, Ind. Eng. Chem., 32, 1389 (1940).

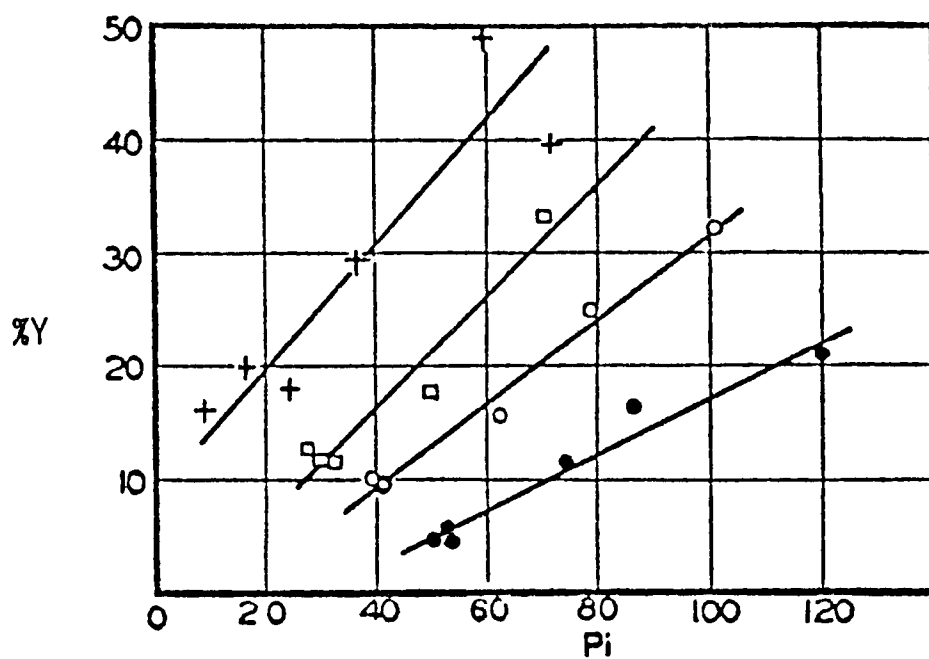


Figure 6. Plot of Yield of Extract Versus Internal Pressure (Pi) at (●) 150°, (○) 200°, (□) 250°, and (+) 300°C.

Source: M. W. Kiebler, Ind. Eng. Chem., 32, 1389 (1940).

yield of extract to the solubility parameter of the solvent, he applied the terminology of the cohesive energy density, he was among the first to relate extract yields to solvent properties.

In a series of papers, van Krevelan^{2,3} introduced the concept of coalification as a progressive polycondensation reaction. The result of the condensation reaction is the formation of a three-dimensionally crosslinked network, treatable by classical polymer techniques. The details of the approach will not be discussed here, the focus of this discussion will be on the determination of the solubility parameter of the coal.

While van Krevelan introduced the concept of coal as a macromolecule, he did not apply standard polymer techniques, such as solvent swelling, to determine the solubility parameter of coal. van Krevelan applied the method of P. A. Small.⁵³ A detailed description of Small's method is found in the literature.⁵³ Essentially, Small argued that the cohesive energy density (and therefore the solubility parameter) of a substance is the sum of the various contributions of certain atom groups to the cohesive energy density(CED):

$$(\text{CED})^{1/2} = \delta = \Sigma F_i / V_m \quad (19)$$

V_m is the molar volume and F_i is the contribution of various atom groups (the molar attraction constants) to the cohesive energy.

Values of F_i were derived by Small.⁵³ The values of F_i were derived for small molecules, and application of those values to coal may be misleading. As a result, van Krevelan derived a new set of F_i values

which would more accurately reflect the contribution of the groups of atoms in coals. Table II³ includes examples of the F_i values.

For application to coal, Equation 19 was modified:³

$$\delta = \frac{\sum_i (N_i/c) F_i}{\text{Molar Volume per Carbon Atom}} = \frac{\sum c}{W_c/d} \quad (20)$$

where N_i/c denotes the atom ratio H/C, O/C, S/C, etc. W_c is the molecular weight per carbon atom:

$$W_c = 12.00 + 1.008H/C + 16.000O/C + \dots \quad (21)$$

Originally, van Krevelan used the symbol M_c for W_c . The notation was changed to avoid confusion with $\overline{M}_c$, the number average molecular weight between crosslinks.

Substitution of values from Table II³ combined with the atom ratios gives:

$$\sum c = 68.5 H/C + 300 O/C + 115 N/C + 225 S/C + 66.5 fa \quad (22)$$

The values for the atom ratios and aromaticities are given elsewhere.¹ In Equation 22 some simplifications were used. For example, the average contribution of oxygen was chosen as 300 and the contribution of non-aromatic rings and branching in the aliphatic chain were ignored.

TABLE II

VALUES OF F_i FOR VARIOUS GROUPS AND FUNCTIONALITIES
IN COAL

Atom (or group)	$F_i ((\text{cal}/\text{cm}^3)^{1/2} \text{mole}^{-1})$
C	0
H	68.5
O	
ether	125
phenolic	250
alcoholic (1°)	360
N	
aliphatic (1° amine)	100
aromatic (1° amine)	65
non-aromatic ring	60
conjugation of double bonds	25
2 hydroxyl's on adjacent carbon atom	-190

Source: D. W. van Krevelan, Fuel, 45, 229 (1966)

The results of the calculation of the solubility parameter for a series of coals of increasing rank are contained in Table III.³ A maximum and minimum value is given for the solubility parameter because of use of two different values for the aromaticity of the coal. The results are shown graphically in Figure 7.³ From Figure 7,³ the solubility parameter of the coal decreases until a minimum is reached at a carbon content of approximately 89%, after which the solubility parameter increases. This result is consistent with the observation by van Krevelan that each solvent has a maximum extraction yield at a specific degree of coalification. The solubility parameters calculated by van Krevelan are very reasonable in magnitude. The method employed is only an approximation as specific effects such as hydrogen bonding, are ignored and it would be difficult to derive F_1 values for each of the numerous functionalities or groups of atoms in the coal structure. Aside from all the approximations made, the values of the solubility parameters determined are very similar to values obtained by other researchers as will be shown later.

Sanada and Honda^{40,54,55} studied the solvent extraction and solvent swelling of coals in order to: 1) examine the relationship between the yield of extract and the solubility parameter of the solvent; 2) determine the solubility parameter of the coal and 3) determine the number average molecular weight between crosslinks, $\overline{M}_c$, of the coal network. Determination of the relationship between the yield of extract and solubility parameter of the solvent echoes work done by Kiebler⁵² in 1940. The determination of the equilibrium swelling of a coal allows the solubility parameter of the coal to be

TABLE III
SOLUBILITY PARAMETERS CALCULATED BY VAN KREVELAN FOR A SERIES OF
COALS

% Carbon Content	$\delta(\text{cal/cm}^2)^{1/2}$	
	Maximum	Minimum
70.5	15.2	14.6
75.5	14.2	13.3
81.5	12.7	11.8
85.0	11.9	11.3
87.0	11.5	10.9
89.0	11.3	10.7
90.0	11.3	10.7
91.2	11.3	10.7
92.5	11.4	10.7
93.4	11.5	10.7
94.2	11.5	10.8
95.0	11.5	10.9
96.0	11.6	11.2
(100)	12.3	12.3

Source: D. W. van Krevelan, Fuel, 45, 229 (1966).

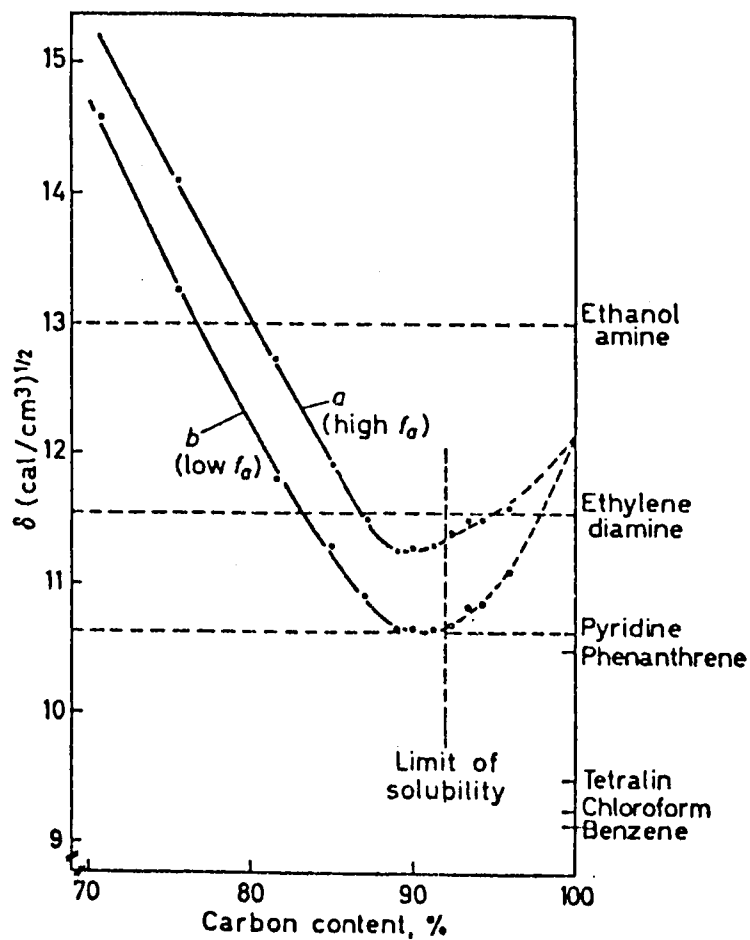


Figure 7. Plot of Calculated Solubility Parameter Versus Percent Carbon of Various Coals.

Source: D. W. van Krevelan, Fuel, 45, 229 (1966).

calculated. Essentially, the solubility parameter of the solvent which swells the coal the most is assumed to be the solubility parameter of the coal.

In the extraction studies⁵⁴ the coals were Soxhlet extracted for 48 hours. The extraction yield was determined by weighing the residue after drying for 7 hours at 110-180 °C under vacuum. In the solvent swelling studies,^{40,55} the coal was exposed to solvent vapor at 25 °C and 50 °C and allowed to swell until constant weight was attained. The swelling ratio is given by:^{40,55}

$$Q = \text{Swollen Volume/Unswollen Volume} \quad (23)$$

$$Q = 1 + (\rho_2 / \rho_1)(q_w - 1) \quad (24)$$

where ρ_2 and ρ_1 are the densities of the coal and solvent, respectively. q_w is the weight ratio calculated from the weights of the swollen and unswollen samples. No corrections were made for solvent filling the pores of the coal.

The results of the solvent extraction study are listed in Table IV.⁵⁴ δ_b is the solubility parameter of the solvent at its boiling point. Figure 8⁵⁴ is a plot of the yield of extract versus the solubility parameter of the solvent. The yield of extract increases with the increasing value of the solubility parameter of the solvent (δ_1) until δ_1 is approximately 10, then the yield of extract decreases with increasing values of δ_1 . Deviations from the curve may result from specific interactions between the solvent and coal.⁵⁴

TABLE IV

YIELD OF EXTRACT AND SOLUBILITY PARAMETERS OF SOLVENTS FOR YUBARI
AND ASHIBETSU COALS

Solvent	δ_b	Yield of extract d.a.f.,%	
		Yubari	Ashibetsu
Chloroform	8.7	2.6	2.3
Methanol	13.7	0.9	1.5
Ethanol	11.6	0.6	1.8
Ethyl methyl ketone	8.5	3.4	7.0
Benzene	8.3	1.8	1.6
Pyridine	9.6	33.2	23.8
Ethylene diamine	10.3	26.2	34.9
Butanol	9.5	0.8	5.0
Dimethyl formamide	10.3	26.2	34.9
Butanol	9.5	0.8	5.0
Dimethyl formamide	9.3	24.0	25.6
Cyclohexanone	9.4	25.0	29.1
Cyclohexanol	8.8	13.0	13.5
Phenol	9.4	32.0	21.9
Cresol	9.3	30.7	32.6
Acetophenone	8.6	35.6	29.1

Source: Y. Sanada and H. Honda, Bull. Chem. Soc. Jpn.,
35(8), 1358 (1962).

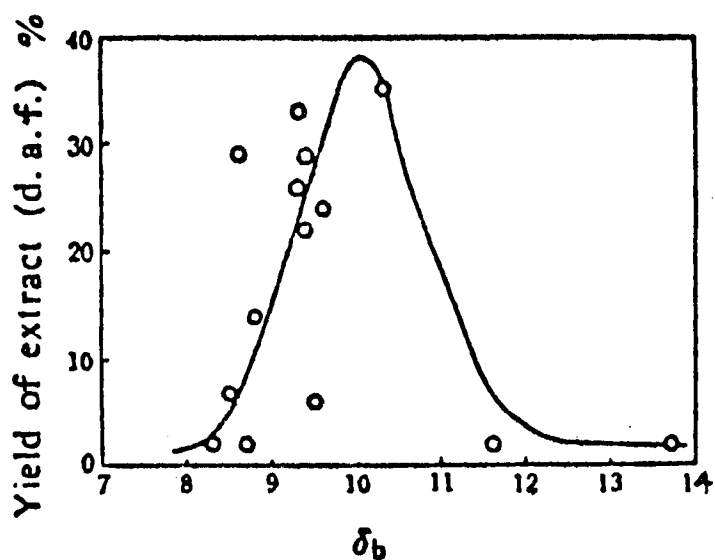


Figure 8. Plot of Yield of Extract Versus Solubility Parameter of Solvent for Ashibetsu Vitrain.

Source: Y. Sanada and H. Honda, Bull. Chem. Soc. Jpn., 35(8), 1358 (1962).

Some error may also result from the estimation of the CED at the boiling point.⁵⁴ In addition, the coals may not have been exhaustively extracted since the extractions were performed for 48 hours. Equilibrium is usually attained after four days for most coals. It is obvious, however, that a relationship between the extraction yield and δ_1 does exist.

From the solvent swelling experiments, it was found that the equilibrium swelling ratio, Q , increases with increasing δ_1 , until δ_1 is 10.8. Any further increase in δ_1 results in a decrease in Q . This result is illustrated in Figure 9.⁵⁵ When $\delta_1 = \delta_2$ the coal will achieve maximum swelling. This approach is valid only when no specific interactions between solvent and coal exist. Of the solvents used in the study, several are known to interact with the coal. Therefore the coal solubility parameter values are qualitative not quantitative.

$\overline{M}_c$ is also determined from solvent swelling experiments. The Flory-Rehner equation which allows determination of $\overline{M}_c$ is given by Equation 14. v_2 was obtained from the solvent swelling experiments. χ was determined from osmotic pressure measurements of coal extracts.⁵⁶ The determination of χ is based on the following assumptions: 1) χ is independent of the concentration of the extract in the solvent; 2) χ is the same for a given coal rank and 3) the coal extract has the same χ value as the coal network.⁵⁵ Unfortunately, the $\overline{M}_c$ values calculated by Sanada and Honda were incorrect due to a failure to include the molar volume of the solvent in the Flory-Rehner equation. Figure 10 is a plot of the results of the corrected $\overline{M}_c$ values from Equation 14

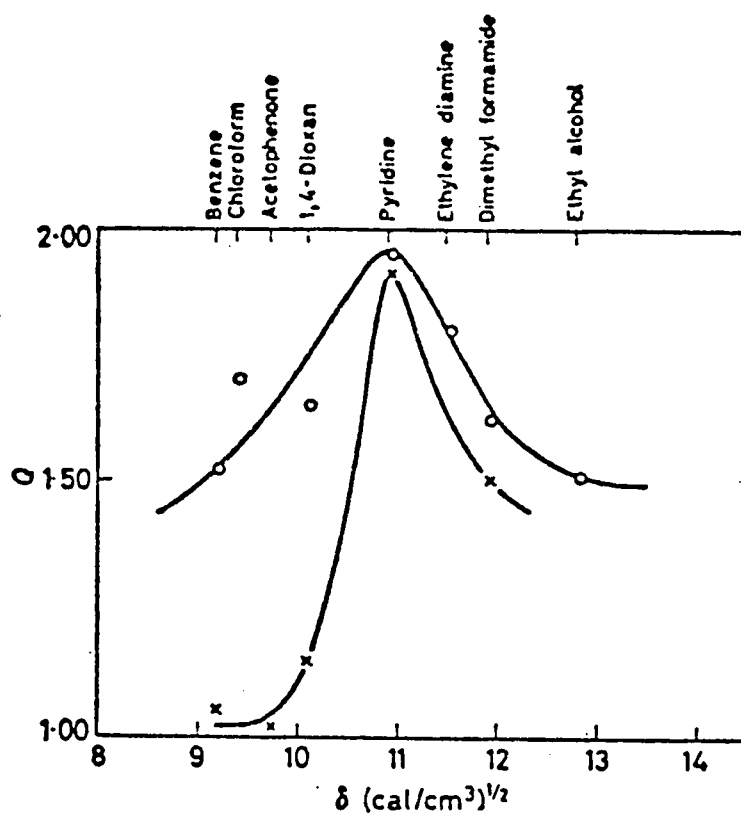


Figure 9. Plot of Swelling Ratio Versus Solubility Parameter for Ashibetsu Bituminous Coal and Odaira Lignite.
O, Ashibetsu Bituminous Coal; X, Odaira Lignite.

Source: Y. Sanada and H. Honda, Fuel, 45, 451 (1966).

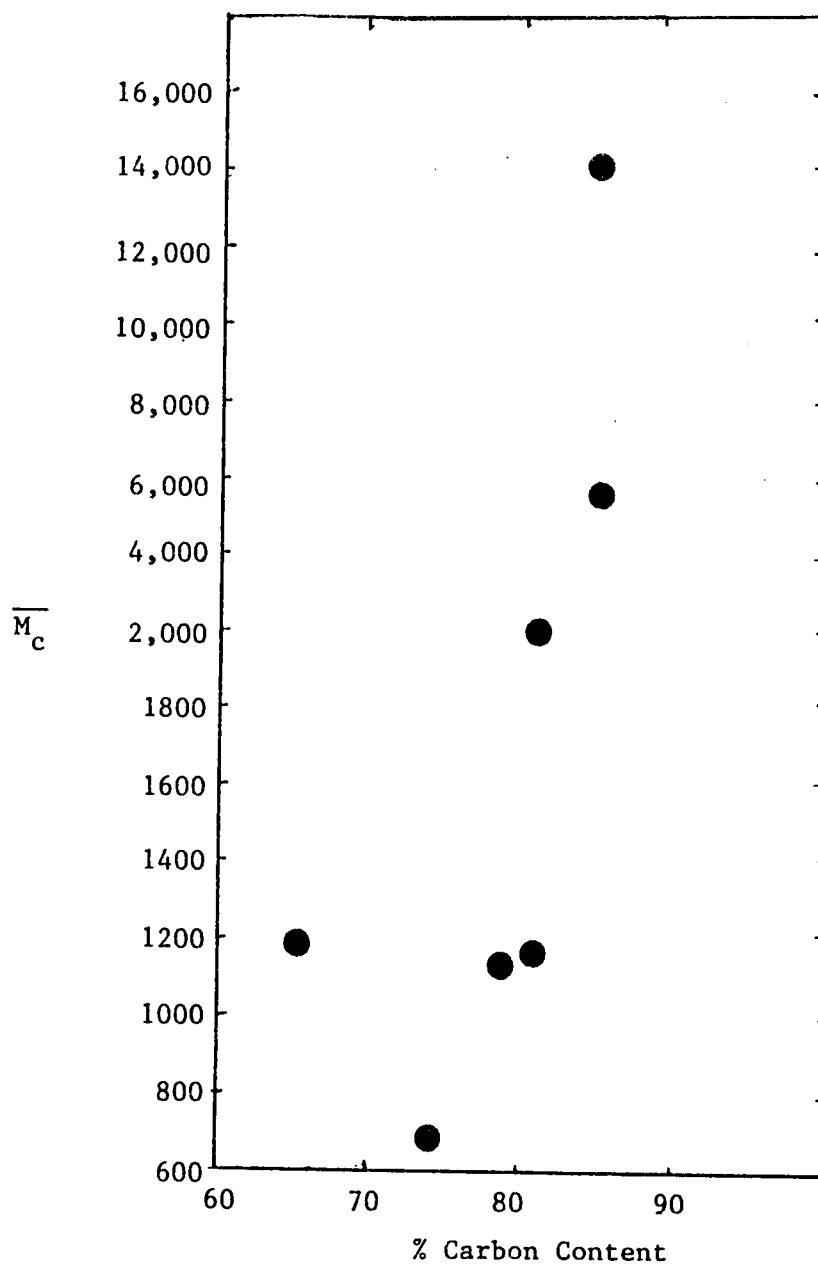


Figure 10. The Number Average Molecular Weight Between Crosslinks Versus Percent Carbon of Various Coals.

versus the percent carbon of a series of coals. The value of $\overline{M}_c$ is approximately constant from 65 to 80% carbon content. Then $\overline{M}_c$ increases sharply until approximately 85% carbon content. Since no values were estimated for coals with carbon contents greater than 85%, additional values of $\overline{M}_c$ were not reported. It would have been interesting to continue the plot, however. Even though the calculations were incorrect, Sanada and Honda were the first to attempt to measure the $\overline{M}_c$ for a coal. Their work was insightful and paved the way for further research.

Kirov, O'Shea, and Sergeant³⁹ used coal swelling measurements to determine the solubility parameters for three Australian coals. Each coal was Soxhlet extracted successively with dimethylformamide, pyridine, benzene, acetone, and methanol. The insoluble coal residues were dried under vacuum at 100 °C for 24 hours. The coal residues were then exposed to solvent for four days to ensure that equilibrium was reached. After blotting with absorbent paper until the surface was dry, the residues were weighed and v_2 obtained from the weight increase. No corrections were made for the pore volume.

Table V³⁹ lists the values of v_2 from the swelling measurements for each coal. Using the experimental data, the solubility parameter of the coal, δ_2 , was calculated by substituting v_2 and χ values into Equation 25:³⁹

$$\chi = \beta + (V_1/RT)(\delta_1 - \delta_2)^2 \quad (25)$$

V_1 is the molar volume of the solvent and a value of 0.3 was assumed for β . χ was determined using an iterative technique. In the first

SWELLING RATIOS CALCULATED FROM KIROV ET AL. AND
SOLUBILITY PARAMETERS OF SOLVENTS FOR HEBE,
GRETA, AND BULLI PYRIDINE-EXTRACTED COALS

Solvent	δ_1	Hebe Residue	Q Greta Residue	Bulli Residue
Cyclohexane	8.2	2.13	1.89	1.67
Xylene	8.8	2.33	2.33	1.72
Toluene	8.9	2.33	2.50	1.79
Benzene	9.1	2.33	2.27	1.56
Chloroform	9.3	2.33	2.13	1.82
Carbon Tetrachloride	9.5	1.49	2.22	1.64
Methyl Ethyl Ketone	9.8	2.56	2.44	1.82
Dioxan	9.9	2.86	2.27	1.85
Nitrobenzene	10.0	2.78	2.45	1.61
Acetone	10.0	2.56	2.27	2.70
Aniline	10.4	3.33	2.78	1.89
Pyridine	10.6	3.13	2.00	1.92
Quinoline	10.7	2.78	2.86	1.89
Dimethyl Formamide	11.5	3.03	2.78	1.92
n-Propanol	11.9	3.03	2.78	1.92
Ethanol	12.7	2.78	1.82	1.75
Methanol	14.5	2.70	1.61	1.72

Source: N. Y. Kirov, J. M. O'Shea, and G. D. Sergeant,
Fuel, 47, 415 (1967).

step, a series of χ values were calculated by steps of 0.1 in Equation 25. The χ values were then used in a linear regression of Equation 14 to obtain the value of δ_2 which best fit the experimental data. The calculated δ_2 value for each of the coals is listed in Table VI.³⁹ Kirov, et al. originally used the average molecular volume between crosslinks rather than $\overline{M}_c$. The $\overline{V}_c$ values were converted to $\overline{M}_c$ values assuming a density of 1.3 g/ml for each coal.

Table VII³⁹ lists δ_2 values obtained when solvents known to interact with the coal such as pyridine, acetone, methyl ethyl ether, quinoline, and dimethylformamide were excluded. Again $\overline{V}_c$ values were converted to $\overline{M}_c$ assuming a density of 1.3 g/ml for each coal.

Figure 11³⁹ is a plot of Q , the swelling ratio, versus δ_1 for the coal residues. Q is defined as $1/v_2$. From this plot, the maximum swelling occurs at solubility parameter values of 10.8, 10.8, and 11.1 for Hebe, Greta, and Bulli coal residues, respectively. The maximum swelling is observed with the lowest rank coal (Hebe). From this plot, and Tables VI and VII, it appears that as the rank of a coal increases the molecular weight between crosslinks decreases. This result contradicts the work of Sanada and Honda^{40,55} who observed $\overline{M}_c$ increases until the % carbon of the coal reaches 85%C.

The iterative technique used by Kirov et al.³⁹ to obtain solubility parameters for coals relies on the assumption that the $\overline{M}_c$ of a coal is constant. This is not likely. Coals contain hydrogen bonds, some of which serve as crosslinks. The hydrogen bonds are broken in varying amounts by solvents capable of accepting hydrogen

TABLE VI

SOLUBILITY PARAMETERS AND $\bar{M}_c$ VALUES CALCULATED BY KIROV ET AL.
OBTAINED USING ALL SOLVENTS FOR HEBE, GRETA, AND BULLI COALS

	Hebe	Greta	Bulli
δ_{coal}	9.6	10.6	10.7
V_c	1996	1612	725
$\bar{M}_c$	2595	2100	940

Source: N. Y. Kirov, J. M. O'Shea, and G. D. Sergeant,
Fuel 47, 415 (1967).

TABLE VII

SOLUBILITY PARAMETERS AND $\bar{M}_c$ VALUES CALCULATED BY KIROV, ET AL.
USING SELECTED SOLVENTS FOR HEBE, GRETA, AND BULLI COALS

	Hebe	Greta	Bulli
δ_{coal}	9.8	9.5	9.3
V_c	1530	1202	522
$\bar{M}_c$	1989	1563	679

Source: N. Y. Kirov, J. M. O'Shea, and G. D. Sergeant,
Fuel 47, 415 (1967).

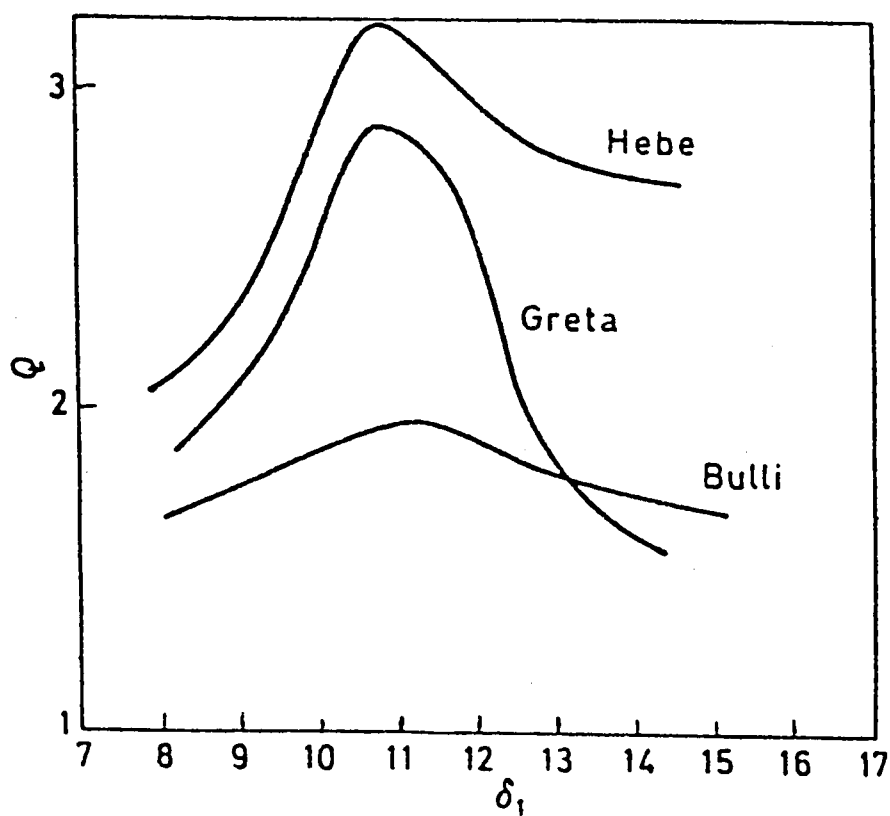


Figure 11. Swelling Ratio Versus Solubility Parameter for Hebe, Greta, and Bulli Coals.

Source: N. Y. Kirov, J. M. O'Shea, and G. D. Sergeant, Fuel, 47, 415 (1967).

bonds. Thus, depending on the solvent and its ability to interrupt the hydrogen bond network, $\overline{M}_c$ may not remain constant. In addition, regular solution theory does not allow specific interactions between solvent and solute. The use of solvents such as nitrobenzene and ethanol would not be allowed. As a result of the violation of regular solution theory and the improbability that $\overline{M}_c$ is constant, the solubility parameters obtained are unreliable.

Angelovich, Pastor, and Silver⁵⁷ studied the liquid-phase catalytic hydrogenation of a subbituminous coal to determine whether any correlation existed between the non-polar solubility parameter of the reaction solvent and the liquefaction yield. Before continuing with the discussion, a definition of the non-polar solubility parameter will be useful. For a non-polar solvent such as benzene, the non-polar solubility parameter is the same as the solubility parameter. For a polar solvent, such as pyridine, the solubility parameter and non-polar solubility parameters are not the same. Blanks and Prausnitz⁵⁸ extended the work of Burrell⁵⁹ and showed that a solubility parameter may be divided into polar and non-polar components:

$$\delta^2 = \tau^2 + \lambda^2 \quad (26)$$

where τ and λ are the polar and non-polar solubility parameters, respectively. Recall that the solubility parameter is the square of the cohesive energy density (CED). In turn, the cohesive energy density is the energy of vaporization divided by the molar volume.

The energy of vaporization of a polar solvent may be separated into polar and non-polar components,⁶⁰ thus defining the polar and non-polar solubility parameters:

$$\text{Non-polar solubility parameter} = \lambda = (\Delta E_{np}/v_i)^{1/2} \quad (27)$$

$$\text{Polar solubility parameter} = \tau = (\Delta E_p/v_i)^{1/2} \quad (28)$$

where ΔE_{np} and ΔE_p are the non-polar and polar contributions to the energy of vaporization of the solvent. This approach rests on the homomorph⁶¹ concept. A homomorph is a non-polar molecule which has nearly the same size and shape as the polar molecule of interest. The homomorph approach allows separation of the polar and non-polar contributions of the energy of vaporization. Thus, the polar energy of vaporization is the difference of the total energy of vaporization of the solvent and the energy of vaporization of the non-polar homomorph at the same reduced temperature. Once the polar energy of vaporization is determined the polar and non-polar solubility parameters may be calculated from Equations 27 and 28. The technique is quite useful, but again specific interactions such as hydrogen bonding are not allowed.

Fourteen solvents were used in the study: hexane, benzene, cyclohexane, phenol, tetralin, five coal tar fractions, two hydrogenated coal oils, road tar, and a hydrogenated road tar. The non-polar solubility parameters of the solvents are listed in Table VIII.⁵⁷ The experimental procedure was as follows. Approximately 100

NON-POLAR SOLUBILITY PARAMETERS USED IN ANGELOVICH ET AL. LIQUE-
FACTION STUDY

Solvent	Non-Polar Solubility Parameter, $(\text{cal}/\text{cm}^3)^{1/2}$
Hexane	7.3
Benzene	9.2
Cyclohexane	8.2
Phenol	9.9
Tetralin	9.4
Coal tar fraction A	9.7
Coal tar fraction B	9.8
Hydrogenated coal oil A	9.3
Coal tar fraction C	10.2
Hydrogenated coal oil B	10.4
Hydrogenated road tar	10.3
Coal tar fraction D	10.0
Coal tar fraction E	10.4
Road tar	10.5

Source: M. Angelovich, G. R. Pastor, and H. F. Silver, Ind. Eng. Chem., Process, Des. Dev., 9(1), 106 (1970).

grams of coal, impregnated with 0.5 weight percent ferrous iron catalyst, and 400 grams of solvent were charged to a rocking reactor. The purpose of the catalyst was to diminish differences in solvent effectiveness due to hydrogen donor characteristics of some of the solvents employed. The reactor was flushed three times with extra dry grade hydrogen and pressurized to 2000 psi. The rocking reactor was activated and the temperature raised to 400 °C and maintained for three hours. After cooling, the reactor contents were removed, and the liquid product distilled to 315 °C cut point. The distillation residue and any unreacted solid products were extracted with benzene at 37 °C.

The extent of coal hydrogenation was measured by the conversion α , the ash-free benzene soluble product, $I_o - I_f$, divided by the ash-free benzene insoluble reactor charge:

$$\alpha = (I_o - I_f)/I_o \quad (29)$$

Figure 12⁵⁷ is a plot of the conversion versus the non-polar solubility parameter of the solvent. The plot indicates that the solvents yielding the highest conversion have non-polar solubility parameters of approximately $9.5 \text{ (cal/cm}^3)^{1/2}$. The solvent giving the highest conversion was tetralin (greater than 90%). This is not particularly surprising. Tetralin is known to be an excellent hydrogen donor in liquefaction processes. In a subsequent study,⁶² using benzene, tetralin, and a coal tar, the presence of the catalyst had a greater effect on the conversion when tetralin was used as the

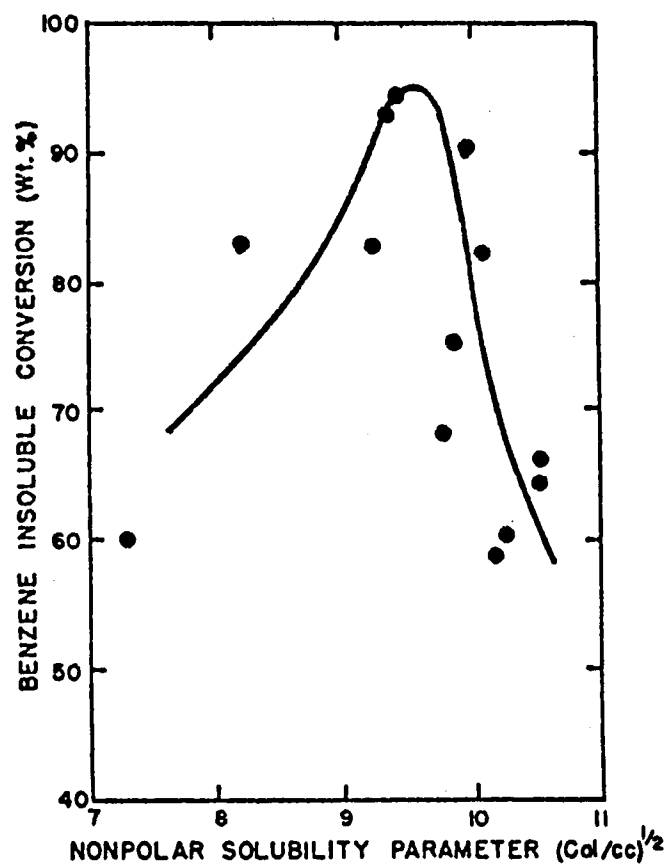


Figure 12. Plot of Benzene Insoluble Conversion Versus Non-Polar Solubility Parameter.

Source: J. M. Angelovich, G. R. Pastor, and H. F. Silver, Ind. Eng. Chem. Process, Des. Dev., 9(1), 106 (1970).

solvent. When the liquefaction process was performed without a catalyst, the highest conversion was again obtained using tetralin as the solvent. Examination of Table VIII⁵⁷ and Figure 12⁵⁷ indicates a hydrogenated coal tar also gave an excellent conversion.

The question of whether the conversion is a function of the solvent or non-polar solubility parameter remains to be answered. A recent study by Clarke et al.⁶³ showed that cycloalkanes participated in solvent extractions performed at 430 °C using solvent mixtures of cycloalkanes and aromatic compounds. The coal tars, oils, etc, used by Angelovich et al.⁵⁷ are certainly participating in the liquefaction process. From these results, it is difficult to ascertain whether the enhanced conversion in the liquefaction process is a function of the nonpolar solubility parameter of the solvent or a function of the solvents ability to participate in hydrogen donation. The best hydrogen donors have solubility parameters around $9.5 \text{ (cal/cm}^3)^{1/2}$.

The use of supercritical solvents in coal extraction processes is very promising. Yields twice that of lower temperature extractions have been reported. The increased yield is a result of the ability of supercritical gas to increase the volatility of a solute, in this case coal. The possibility of pyrolytic depolymerization occurring is not dismissed, however. Another advantage of supercritical gases in extraction processes is the ease of solvent and extract separation minimizes solvent losses. The yield of a supercritical gas extraction is dependent on solvent properties such as density and "solvent power". The extraction process is also temperature dependent. Giddings et al.⁶⁴ reported a correlation between the solvent capacity

of a supercritical gas and its solubility parameter. The solubility parameter was defined by⁶⁴

$$\delta = 1.25 P_c^{(1/2)} \rho_r / \rho_l \quad (30)$$

where P_c is the critical pressure of the medium in atmospheres, ρ_r is the reduced density and ρ_l is the reduced density of liquids, approximately 2.66.

Blessing and Ross⁶⁵ applied the correlation between solvent capacity and solubility parameter in the study of the supercritical gas extraction of an Illinois #6 coal using a variety of solvents. The solvents used were: methanol, n-heptane, 3-methylhexane, methylcyclopentane, benzene, toluene, and ethyl benzene. The supercritical extractions were performed in the batch mode in a stirring autoclave at 335 °C for 90 minutes. The reaction product was separated into a filtrate and solids fraction. The filtrates were completely pyridine soluble. The pyridine solubility of the solid fraction was determined by stirring 0.5 g of solid in 50 ml of pyridine for one hour at room temperature followed by filtration. The pyridine solubility of the entire reaction product was defined by:⁶⁵

$$PS = (\% \text{ Filtrate}) + [((100\% - \text{filtrate})/100) (\% \text{pyridine solubility of solids})] \quad (31)$$

The percent pyridine solubility of the various extractions was plotted versus the solubility parameter of the supercritical gas as defined by

the relationship of Giddings et al.⁶⁴ The plot is illustrated in Figure 13.⁶⁵ As the solubility parameter of the supercritical gas increases so does the percent pyridine solubility. Solvents with very high solubility parameters, when the extractability would be expected to decrease, were not used, however, since the pyridine extractability of the original coal is 13%, the use of some of the solvents at the lower densities is a disadvantage rather than an advantage. Since the product yields are temperature dependent as is the solubility parameter it is difficult to distinguish whether the increase in extraction yield is the result of the increase in temperature or a correlation of the solubility parameter with the coal products. In any event, supercritical gas extractions are an interesting approach to obtaining moderate extraction yields from coals and lignites.

Kershaw and Jezko⁶⁶ studied the supercritical gas extraction of South African coals using semi-continuous reactors. Their study investigated both coal properties and solvent properties. The effect of the coal properties will not be discussed here, our focus will remain on the solvent properties. Eighteen solvents were used in the study. Extractions were performed as follows. One-liter stirred autoclaves were charged with 25 g of coal and 800 ml of solvent. At 150 °C, solvent was added via a dip tube at the rate of 4 l/hr to the bottom of the autoclave and then passed through the coal bed. The temperature was raised to 450 °C and the extraction was continued until the condensate was clear. The pressure during the extraction was maintained at 20 MPa. The residue was removed from the autoclave using toluene, filtered, washed with acetone, and dried at 110 °C. The effect is seen for all temperatures employed.

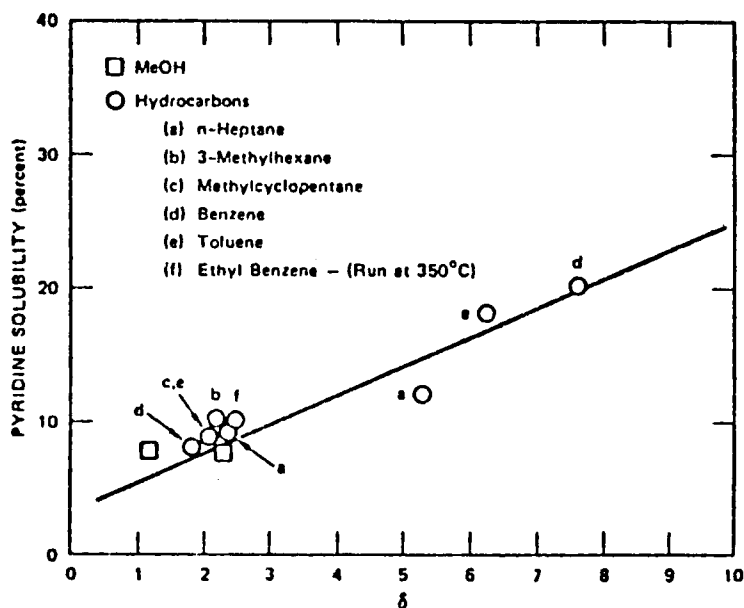


Figure 13. Plot of Percent Pyridine Solubility Versus Solubility Parameter.

Source: J. E. Blessing and D. S. Ross in "Organic Chemistry of Coal," A.C.S. Symp. Ser., No. 71, J. W. Larsen, Ed., 1978, p. 171.

The overall conversion of the coal to extract and gaseous products was defined by:⁶⁶

$$\% \text{ Conv} = 100 \times \frac{(\text{Wt. Dry Ash Free Coal} - \text{Wt. Dry Ash Free Residue})}{(\text{Wt. Dry Ash Free Coal})} \quad (32)$$

Figure 14⁶⁶ is a plot of the percent conversion versus the solubility parameter of the solvent at the reaction conditions. The solubility parameter was calculated using Equation 30.⁶⁴ From the plot, it is clear that as the solubility parameter of the solvent increases, so does the percent conversion. Again, solvents having very high solubility parameters were not used. A plot of the critical temperature of the solvent versus the percent conversion gives similar results. Since the solubility parameter is temperature and density dependent, it is difficult to distinguish which effect is dominant in the extraction process.

Kershaw, Gray, and Jezko⁶⁷ realized that by changing the pressure, the solubility parameter can be varied without changing the chemical structure of the solvent. Toluene was used as the solvent and extractions were performed at 350°, 450°, and 550 °C. The different pressures used were 10, 20, 30, and 40 MPa. A plot of the solubility parameter versus the percent conversion at the various experimental conditions is illustrated in Figure 15.⁶⁷ From the plot, the percent conversion increases with the increase in the solubility parameter until a maximum is reached, after which the percent conversion decreases with increasing solubility parameter.

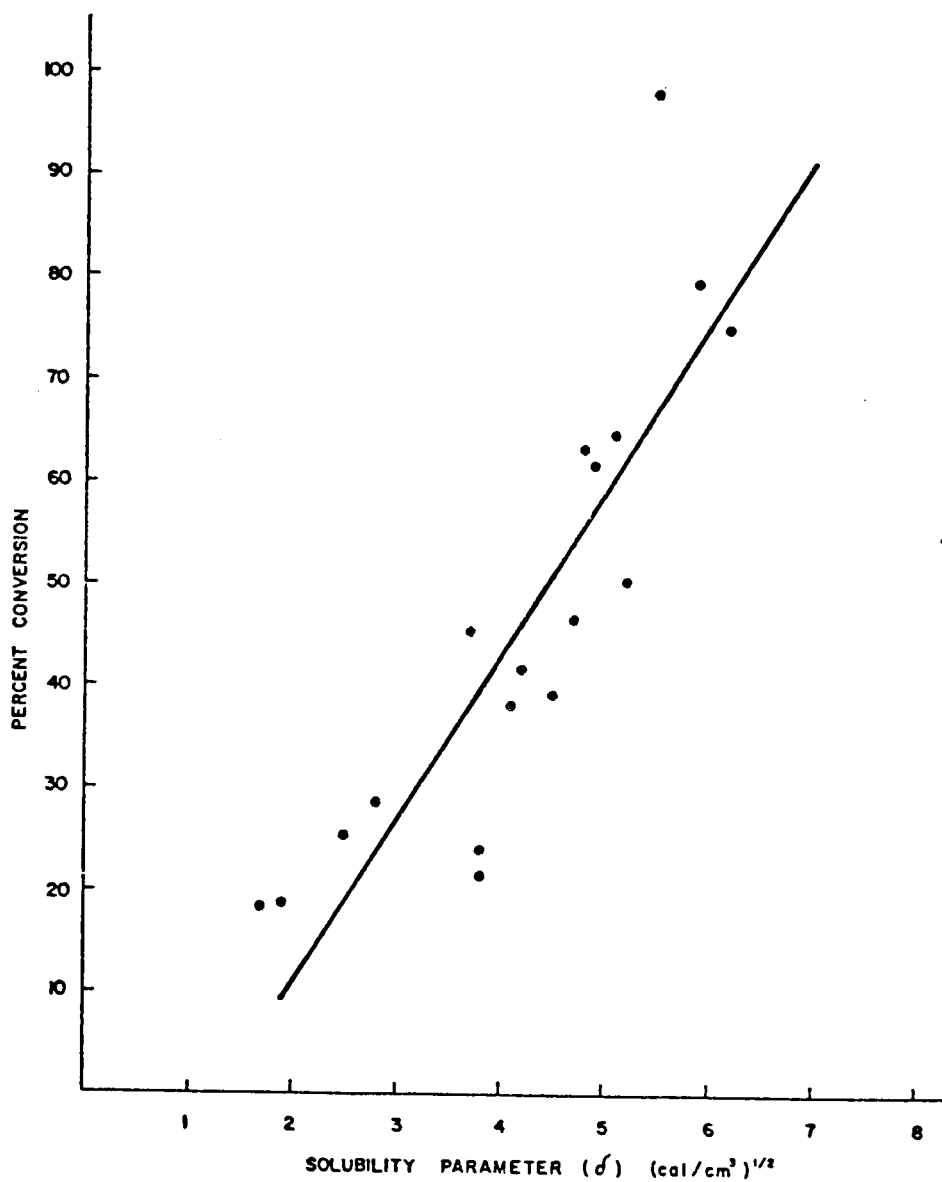


Figure 14. Plot of Percent Conversion Versus Solubility Parameter for Waterberg Coal.

Source: J. R. Kershaw and J. Jezko, Sep. Sci. and Tech., 17(1), 151 (1982).

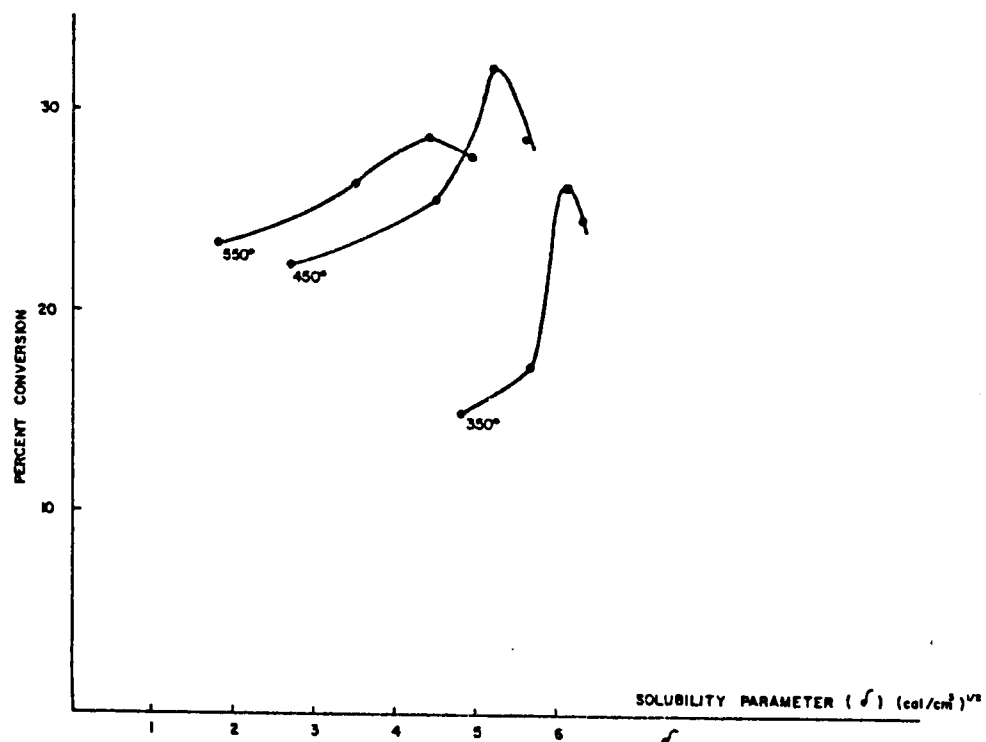


Figure 15. Plot of Percent Conversion Versus Solubility Parameter for Toluene Extraction of Waterberg Coal at Various Experimental Conditions.

Source: J. Jezko D. Gray, and J. R. Kershaw, Fuel Proc. Tech., 5, 229 (1982).

Amestica and Wolf⁶⁸ also studied the supercritical gas extraction of an Illinois #6 coal using toluene and ethanol as solvents. They attempted to correlate extraction yields with the solubility parameter using their density data but did not obtain a linear correlation.

Hombach⁶⁹ used a mixed solvent system to determine the solubility parameters of a set of coals. The approach treats the ternary system of coal/solvent 1/solvent 2 as quasi-binary. The solubility parameter of the solvent mixture, δ_{mix} , is given by:⁶⁹

$$\delta_{\text{mix}} = \phi_1 \delta_1^2 + (1 - \phi_1) \delta_2^2 \quad (33)$$

where ϕ_1 is the volume fraction of solvent 1 and δ_1 and δ_2 are the solubility parameters of the two solvents employed. The mixed solvent was composed of a tertiary amine (either N,N dimethylamine or trimethylamine) and an alcohol (methanol or ethyleneglycol-monomethylether). The coals employed in the study ranged from 84%C to 93%C (wt. %, daf).

The swelling ratios were measured by placing coal in cylindrical glass tubes and measuring the initial height of the coal bed (H_1). Approximately 1.5 ml of the solvent mixture was added and mixed thoroughly with the coal. After one week, the height of the coal bed was measured again (H_2). The swelling ratio, Q , is given by H_2/H_1 . The supernatant solvent was removed from the tube and its UV-Visible absorbance measured in a 1 mm cell.

The swelling of the coals in the mixed solvent was measured and plotted versus the solubility parameter of the mixed solvent. Figure 16⁶⁹ demonstrates the solvent swelling results. A maximum in swelling was observed and the solubility parameter of the mixture which produced the most swelling was assigned to the coal.

In some cases, the higher rank coals, the solvent swelling technique could not be used due to poor swelling of the coals. Assuming the material extracted from the coal has the same solubility parameter as the insoluble matrix, the limiting wavelength of the supernatant layer removed from the coals after swelling at 1% transmission in the UV-Visible spectrum was plotted versus the solubility parameter of the solvent mixture. Figure 17⁶⁹ indicates that a maximum occurs with δ_{mix} equal to approximately $10(\text{cal/cm}^3)^{1/2}$. This approach is contingent upon the swelling of the coal being proportional to the extractability. This is not unreasonable as demonstrated by Dryden.⁷⁰ The solubility parameters estimated by Hombach follow the same general trend with coal rank as do the solubility parameters calculated by van Krevelan.³

The mixed solvent system assumes that no specific interactions occur between the solvents and that neither solvent is preferentially absorbed by the coal. Green^{5,71} has shown that coals do act as selective sorbents. The details of that study will be presented later, but briefly, using a series of amines and alcohols, it was demonstrated that alcohols bind to specific, but unspecified, sites in the coal. Thus the solvent composition, and therefore the solubility parameter of the mixture, on the outside of the coal is not necessarily the same as in the interior of the coal. Thus the value

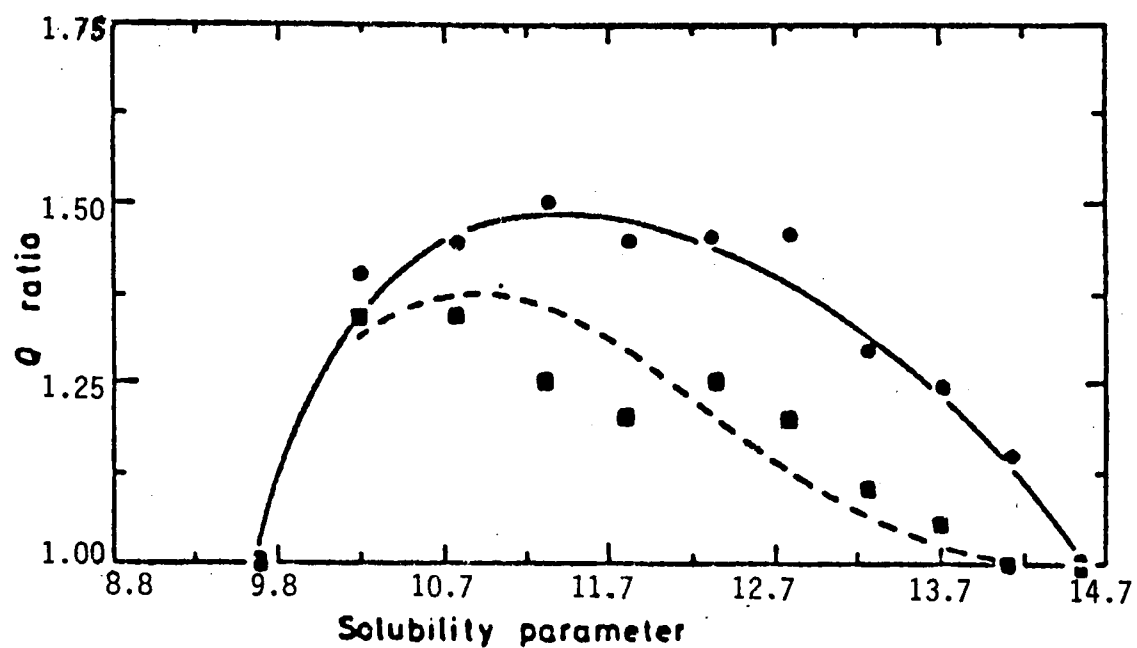


Figure 16. Plot of Swelling Ratio Versus Mixed Solubility Parameter of Two Coals.

Source: H. P. Hombach, Fuel, 59, 465 (1980).

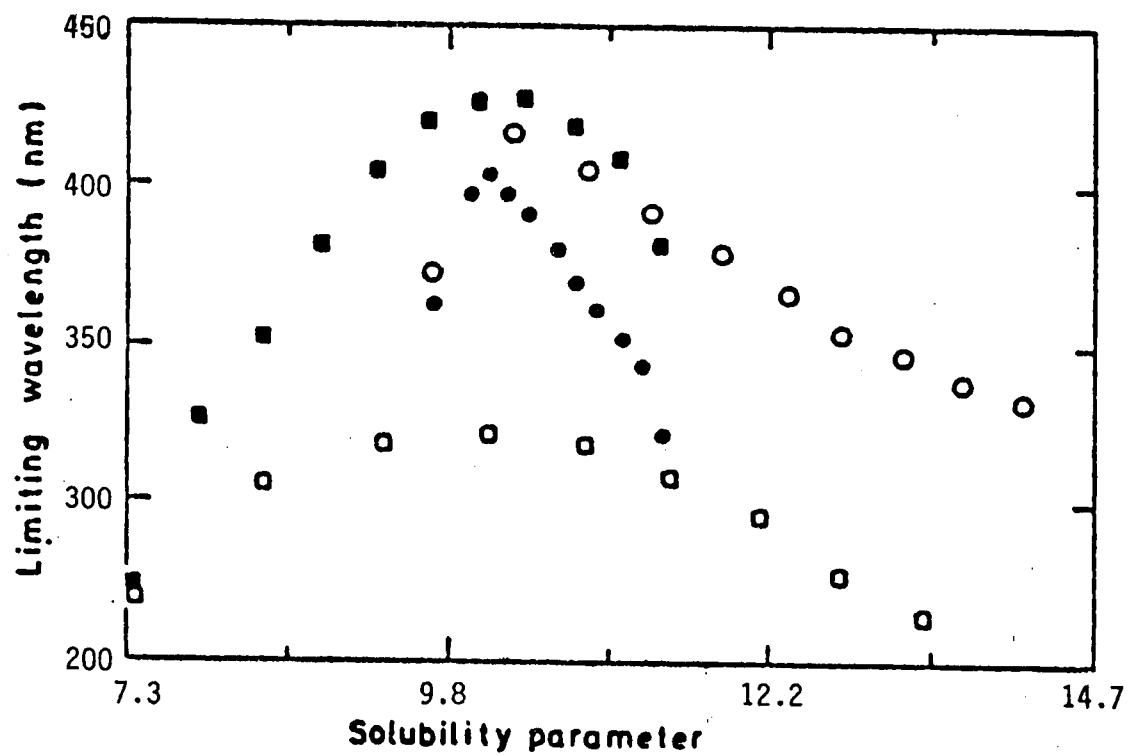


Figure 17. Plot of Limiting Wavelength Versus Mixed Solubility Parameter.

Source: H. P. Hombach, Fuel, 59, 465 (1980).

of the solubility parameter assigned to the coal using the mixed solvent system is unreliable.

Hsieh and Duda^{72,73} studied the sorption of various organic vapors on PSOC-375 (high volatile a bituminous coal, 84.5%C, dmmf) at 25 °C and a solvent activity of 1, to correlate the solubility parameter of the solvent and solvent uptake by the coal. A series of twelve solvents were employed. Pyridine extracted and untreated (native) coal was used for swelling. The procedure for measuring the solvent uptake was as follows. Approximately 0.1 g of coal is placed in a vial and weighed. The coal (covered with filter paper) and appropriate solvent were placed in a diffusion chamber and sealed. The chamber was placed in a temperature controlled box at 25 °C. The vial was removed for weighing once a week.

The measurement of solvent uptake on the untreated coals is illustrated in Figure 18.⁷² No relationship exists between the solubility parameter of the solvent and the solvent uptake. Several of the solvents employed will extract significant quantities of uncrosslinked material from the coal, resulting in long equilibrium times. Hsieh and Duda reported that equilibrium was not attained after 61 days of exposure using DMSO as the solvent. If the systems had not reached equilibrium, it would be nearly impossible to correlate the solubility parameter with solvent uptake. The use of pyridine extracted coals will alleviate the complication of extraction by solvents. The pyridine extracted coal was exposed to the same series of solvents. Figure 19⁷² is a plot of the results. The plot indicates no apparent correlation between the solubility parameter and

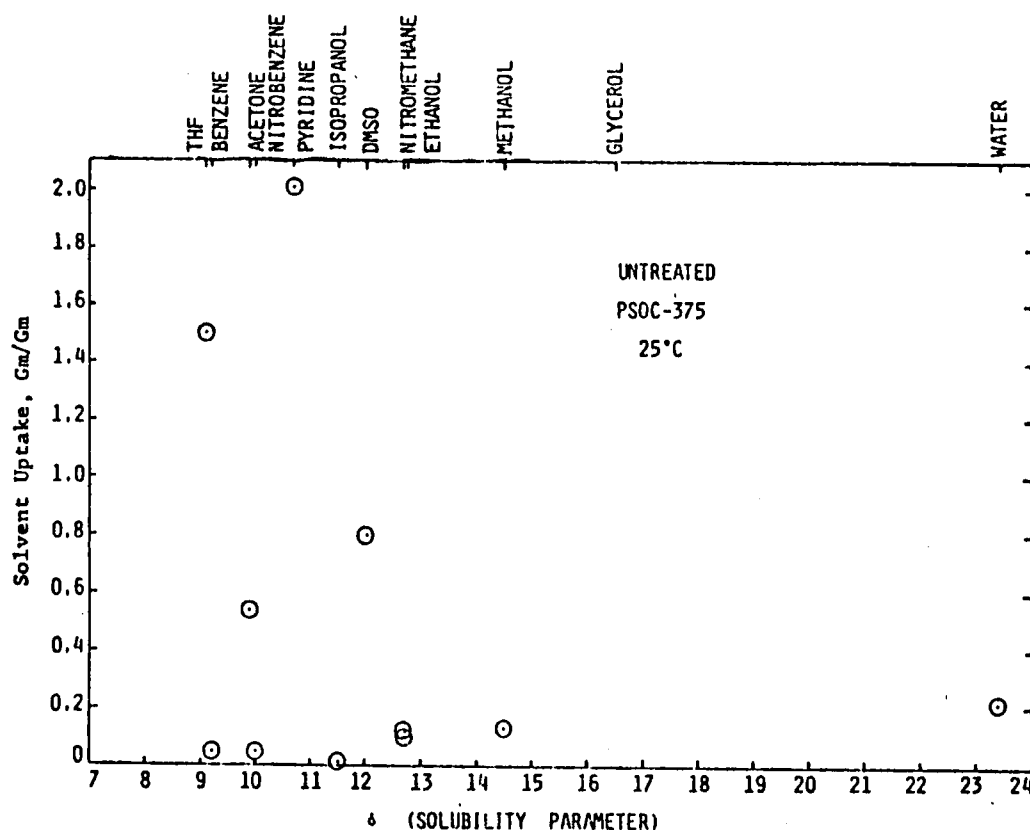


Figure 18. Plot of Solvent Uptake Versus Solubility Parameter for PSOC-375 Coal.

Source: S.-T. Hsieh and J. L. Duda, "The Dependence of Liquefaction Behavior on Coal Characteristics; Part V.: The Penetration of Solvent Vapor into Coal Particles," Final Technical Report for the Period March 1981 - February 1984, DOE Contract No. AC22-81PC40784, April, 1984, p. 52.

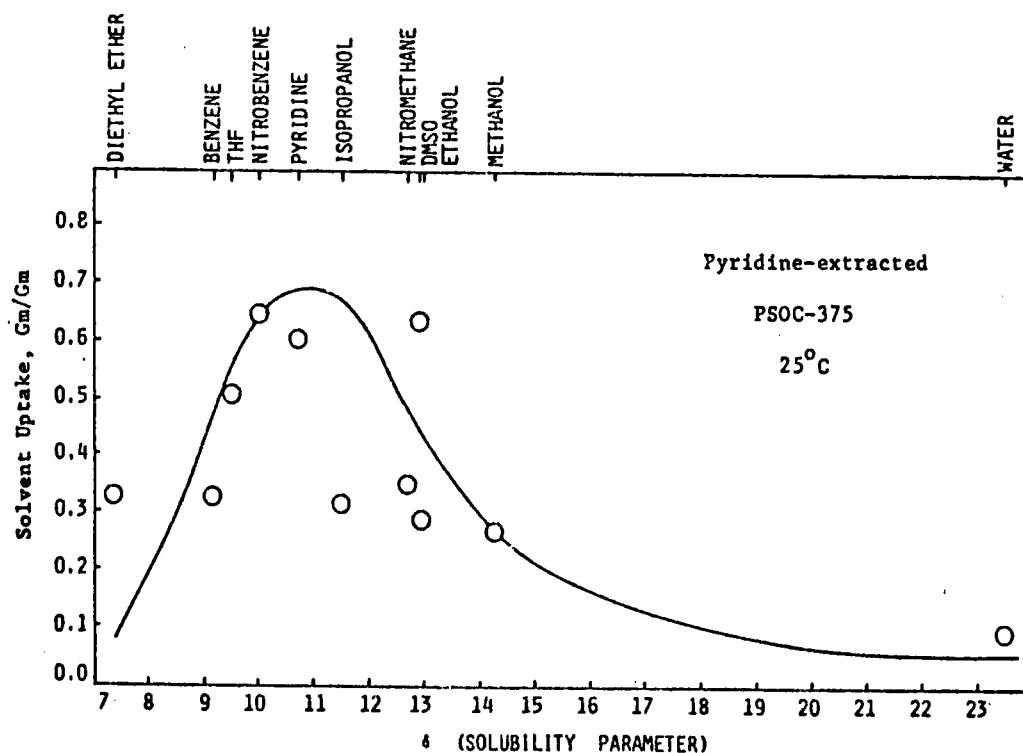


Figure 19. Plot of Solvent Uptake Versus Solubility Parameter for Pyridine-Extracted PSOC-375 Coal.

Source: S.-T. Hsieh and J. L. Duda, "The Dependence of Liquefaction Behavior on Coal Characteristics; Part V.: The Penetration of Solvent Vapor into Coal Particles," Final Technical Report for the Period March 1981 - February 1984, DOE Contract No. AC22-81PC40784, April, 1984, p. 58.

the solvent uptake. Several of the solvents used will associate strongly with the coal by hydrogen bonding, for example. Strong interactions between the solute and solvent, such as hydrogen bonding, are not treatable within the framework of regular solution theory. Thus no correlation between the solubility parameter and solvent uptake is expected.

Hsieh and Duda^{72,73} also studied the sorption of toluene at several solvent activities on pyridine extracted PSOC-375 at 110 °C to gain information on the macromolecular nature of the coal. The goal of this series of experiments was to determine the values of $\overline{M}_c$ and χ of the coal. The experiment consists of exposing the coal to toluene at various solvent activities and measuring the volume fraction of the swollen coal. Substitution of the experimental data into the Flory-Rehner equation (Equation 14) gave values for χ and $\overline{M}_c$ of -4.86 and 20.1, respectively. These values are unrealistic. Literature values indicate that χ is small in magnitude (usually less than 1) and positive.⁵¹ The value of $\overline{M}_c$ is unreasonably small. By comparison other studies have reported values of $\overline{M}_c$ greater than 400.⁵ Since the Flory model was not developed to account for the irregularities of the coal network, Hsieh and Duda employed the equations developed by Lucht and Peppas⁷ and Kovac⁵⁰ to re-analyze their experimental data. Table IX^{72,73} contains the results of the comparison of the various models.

The results from all three models indicate unrealistic values of $\overline{M}_c$ and χ . The method of Hsieh and Duda assumes that χ is constant over the range of solvent activities. As χ is both concentration and temperature dependent⁵¹ this is not likely. While the assumption of a

TABLE IX

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS AND
CHI VALUES FROM THREE DIFFERENT EQUATIONS CALCULATED BY
HSIEH AND DUDA

Equation	N	χ	$\bar{M}_c$
Flory-Rehner	-	-4.86	20.1
Lucht and Peppas	9.24	-5.15	31.2
Kovac	20.67	-7.70	31.1

Source: S-T. Hsieh and J. L. Duda, Proc. Am. Chem. Soc. Div. Polymeric Mat., Sci. and Eng., 51, 703 (1984).

concentration independent χ works well for some polymer systems,⁵¹ it⁶⁶ is much less likely to be satisfactory for the very heterogenous, internally hydrogen bonded coals. Also, with non-polar solvents at very low swelling levels, the coals may remain in a glassy state, and not be rubbery.³⁵ This vitiates the use of the Flory-Rehner equation and its extensions.

In a series of papers^{74,75} Anna Marzec has proposed a mechanism for the extraction of coals. This model is based on the assumption that electron donor-acceptor, (EDA), complexes exist in the coal structure. The EDA complexes result from electron donor and electron acceptor interactions between the extractable portion of the coal and the macromolecular network of the coal. The mechanism for extraction of a coal is merely a substitution of a solvent molecule for the extractable material. The effectiveness of a particular solvent was measured by its electron donor and electron acceptor properties as defined by Gutmann.⁷⁶ No correlation between the yield of extract and solubility parameter of the solvent was found.

Marzec et al.⁷⁷ later extended the concept of donor-acceptor complexes in coal to include the mechanism of solvent swelling. A series of 21 solvents were used to swell a high volatile bituminous coal(81%C, daf basis). The swelling ratio obtained, Q, was plotted versus the electron-donor number and the solubility parameter of the solvent. The coals were swollen as follows. Approximately 5 cm³ of coal was placed in a graduated cylindrical glass tube and approximately 5 ml of solvent was added. The coal was dried at 107 °C under vacuum before swelling. The tube was shaken, to remove air

bubbles, and the coal allowed to settle. The height of the coal bed, H_1 , was measured. The tubes were sealed with glass stoppers and maintained at 25 °C. After several days, the height of the coal bed was measured by carefully inserting a stainless steel piston into the tube until the top of the coal bed was reached. Measurements were made until no change in the height of the coal bed was detected (2-7 weeks). The final height was recorded as H_2 . The stainless steel piston was necessary for measurement of the height of the coal bed because uncrosslinked material extracted from the coal darkened the supernatant layer of solvent. The swelling ratio was calculated by H_2/H_1 .

The swelling ratios obtained and the solvents used are listed in Table X.⁷⁷ Table X⁷⁷ also includes the donor number, acceptor number, and solubility parameters of the solvents. The swelling ratio, Q , is plotted versus the donor number of the solvent in Figure 20⁷⁷ and versus the solubility parameter in Figure 21.⁷⁷

From Figures 20⁷⁷ and 21,⁷⁷ there appears to be a correlation of the donor numbers of the solvent with the swelling ratio while the swelling ratio appears to show no correlation with the solubility parameter of the solvent. These results led Marzec et al.⁷⁷ to the conclusion that coal macromolecules are bound together by EDA interactions and electron-donor sites in the coal have donor numbers of approximately 16-30. The apparent lack of correlation of Q with the solubility parameter of the solvent is not particularly surprising. Regular solution theory does not provide for specific interactions between solute and solvent. Examination of the solvents

TABLE X

SWELLING RATIOS FOR A HIGH VOLATILE BITUMINOUS COAL WITH SOLUBILITY
PARAMETERS AND DONOR-ACCEPTOR NUMBERS OF SOLVENTS

Solvent	Solvent Number	Swelling Ratio, Q	Donor Number	Acceptor Number	Solubility Parameter ($\text{cal}^{1/2}\text{cm}^{-3/2}$)
Benzene	1	1.0	0.1	8.2	9.2
Nitrobenzene	2	1.1	4.4	14.8	11.1
Isopropyl alcohol	3	1.14	20.0	33.5	11.44
Acetonitrile	4	1.15	14.1	18.9	11.8
Diethyl ether	5	1.15	19.2	3.9	7.4
Dioxane	6	1.16	14.8	10.8	9.8
Nitromethane	7	1.18	2.7	20.5	11.0
Methanol	8	1.19	19.0	41.3	12.9
Propan-1-ol	9	1.23	-	-	10.2
Ethanol	10	1.25	20.5	37.1	11.2
Ethyl acetate	11	1.26	17.1	-	8.6
Acetone	12	1.30	17.0	12.5	9.4
Methyl acetate	13	1.32	16.5	10.7	9.2
Methyl ethyl ketone	14	1.49	-	-	9.45
Tetrahydrofuran	15	1.59	20.0	8.0	9.1
1,2-Dimethoxy- ethane	16	1.60	24.0	-	-
Dimethylformamide	17	1.69	26.6	16.0	11.5
Dimethylsulphox- ide	18	2.04	29.8	19.3	12.8
Pyridine	19	2.08	33.1	14.2	10.4
Ethylenediamine	20	2.08	55.0	20.9	-
1-Methyl-2-pyr- rolidinone	21	2.38	27.3	13.3	-

Source: J. Szeliga and A. Marzec, Fuel, 62, 1229 (1983).

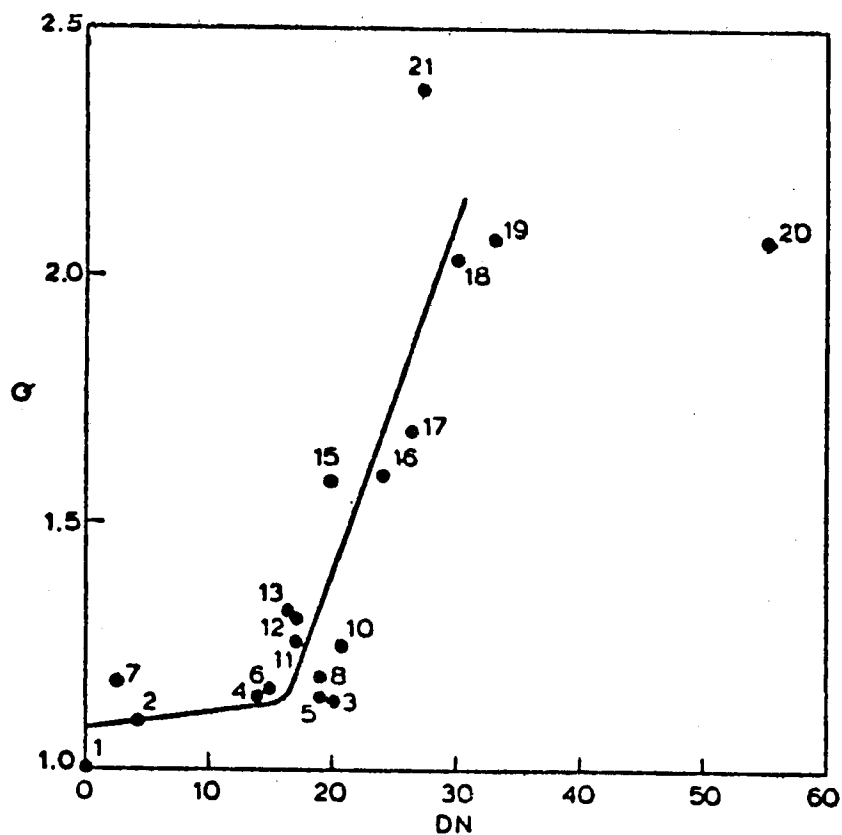


Figure 20. Plot of Swelling Ratio Versus Electron-Donor Number of Solvent. Numbers Indicate Solvents Listed in Table X.

Source: J. Szeliga and A. Marzec, *Fuel*, **62**, 1229 (1983).

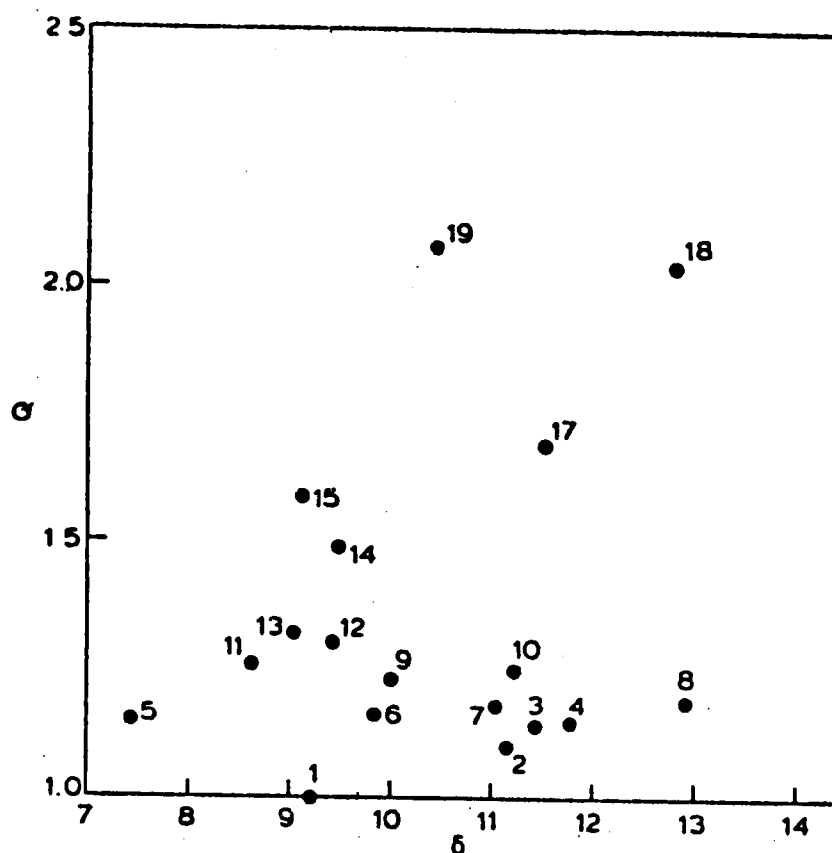


Figure 21. Plot of Swelling Ratio Versus Solubility Parameter of Solvent. Numbers Indicate Solvents Listed in Table X.

Source: J. Szeliga and A. Marzec, Fuel, 62, 1229 (1983).

contained in Table X⁷⁷ indicates that with few exceptions, the solvents used interact strongly with coal, via hydrogen bonding, for example. The approach using the electron donor-acceptor numbers of the solvents is essentially a measure of the ability of a solvent molecule to interact via electron donation or acceptance with another molecule. Thus the correlation between electron donor number and swelling is expected. One further consideration of the results. Some of the swelling ratios obtained appear to be rather low. For example, the swelling ratio obtained with nitrobenzene was 1.1. Other workers have obtained volumetric swelling ratios of 1.6 using nitrobenzene as a solvent for a bituminous coal.⁶ The low swelling may be result of the experimental procedure. The coal and solvent are mixed before the initial height is measured. It has been observed that swelling begins as soon as the coal is exposed to solvent. Thus the coal is swelling before H_1 is measured. The use of an apparent H_1 rather than a true initial value for H_1 may result in erroneous swelling ratios.

Weinberg and Yen⁷⁸ investigated coal and coal liquefaction products by employing solvent swelling. Rather than using pure solvents, mixed solvents were used. The solubility parameter of the mixed solvent is given by:⁷⁸

$$\delta_{\text{mix}} = \phi_1 \delta_1 + \phi_2 \delta_2 \quad (34)$$

where δ_1 and δ_2 are the solubility parameters of the pure solvents and ϕ_1 and ϕ_2 are the volume fractions of the solvents. The solvent mixture solubility parameters ranged from 7.0 to 23.4(cal/cm³)^{1/2}.

The solvents used included: 2-methyl pentane, cyclohexane, cyclohexanol, hydroxyethyl methacrylate, and water.

The work performed was divided into two parts. In the first part, a dried coal and pyridine-extracted coal (PSOC-102, a high volatile bituminous coal) was swollen with the mixed solvents and the swelling ratios measured. In the second part, coal liquefaction products from the PAMCO and Synthoil processes were extracted with the same series of mixed solvents and the extractability measured. Beginning with the solvent swelling experiments on dried and pyridine-extracted coals, the coals were soaked with the mixed solvent and the swelling measured volumetrically. No details were available on the actual swelling procedure or coal preparation. The swelling was plotted versus the mixed solubility parameter. Figure 22⁷⁸ illustrates the results obtained for the dried coal and Figure 23⁷⁸ is a plot of the results for the pyridine extracted coal. The pyridine extract was separated into three fractions: pentane soluble, benzene soluble, and benzene insoluble. The extractability of the benzene soluble and benzene insoluble fractions in the mixed solvent scheme was measured and the results are plotted in Figure 24.⁷⁸ 100% dissolution is observed in the range of 9 to 11 (cal/cm³)^{1/2}.

In the second part of the work, the coal liquefaction products were separated into pentane soluble, benzene soluble, and benzene insoluble fractions and extracted with the same series of mixed solvents. Complete dissolution occurred between approximately 9 and 14 (cal/cm³)^{1/2}.

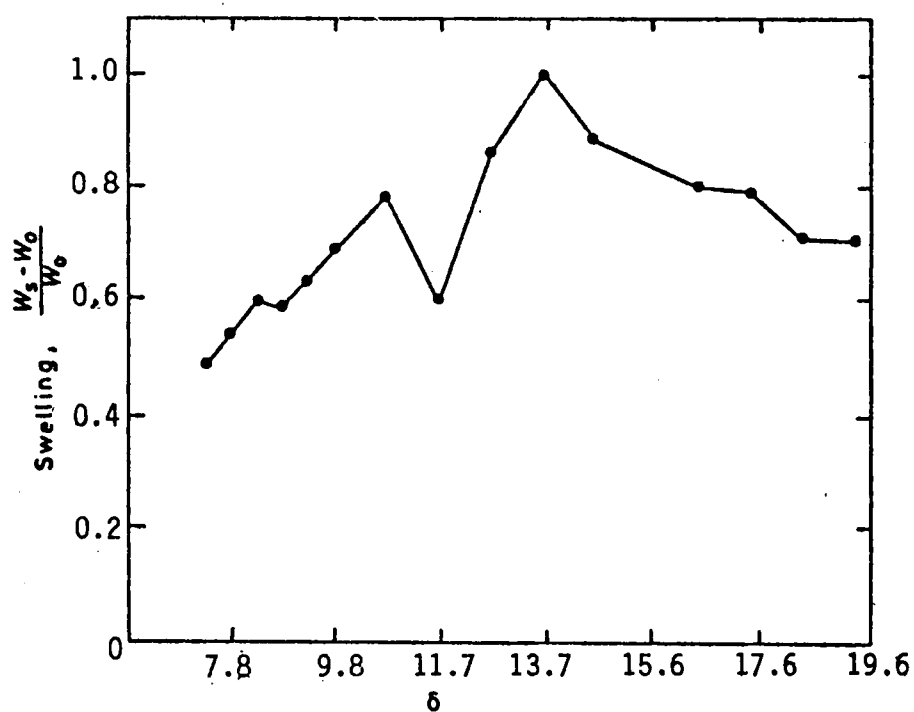


Figure 22. Plot of Swelling Versus Mixed Solubility Parameter of Solvent for PSOC-102 Coal.

Source: V. L. Weinberg and T. F. Yen, Fuel, 59, 287 (1980).

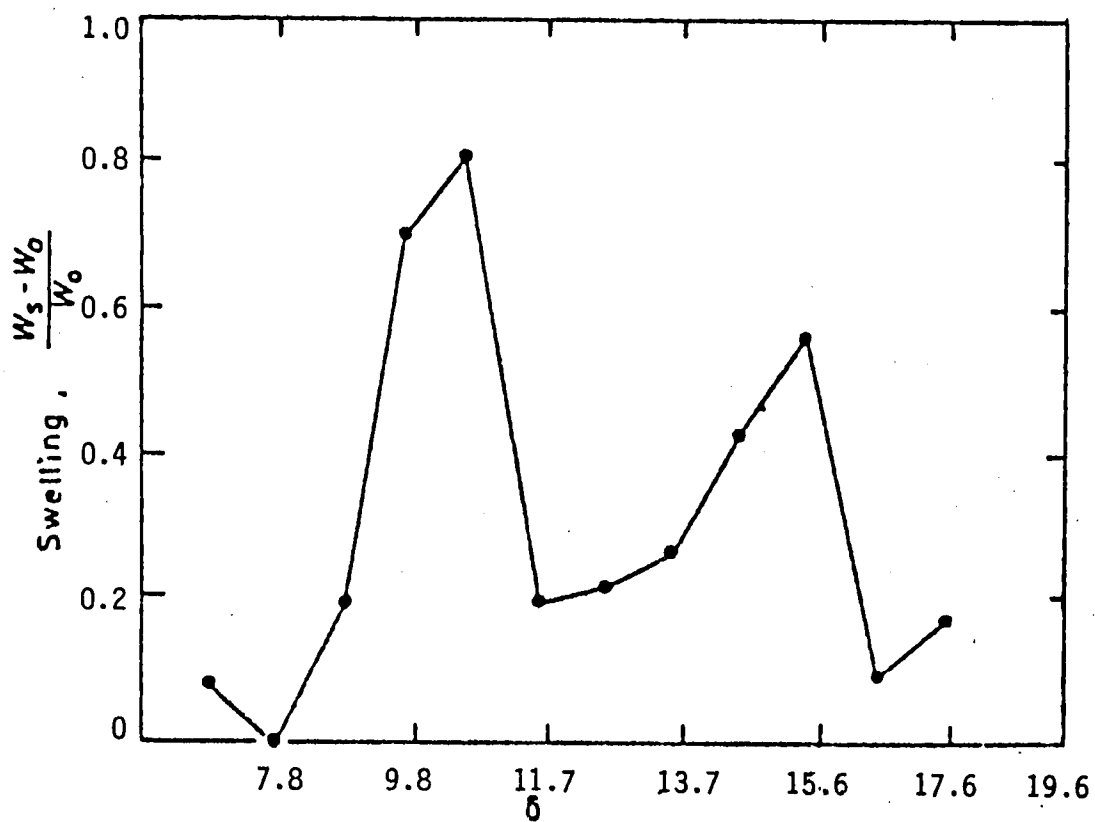


Figure 23. Plot of Swelling Versus Mixed Solubility Parameter of Solvent for Pyridine-Extracted PSOC-102 Coal.

Source: V. L. Weinberg and T. F. Yen, Fuel, 59, 287 (1980).

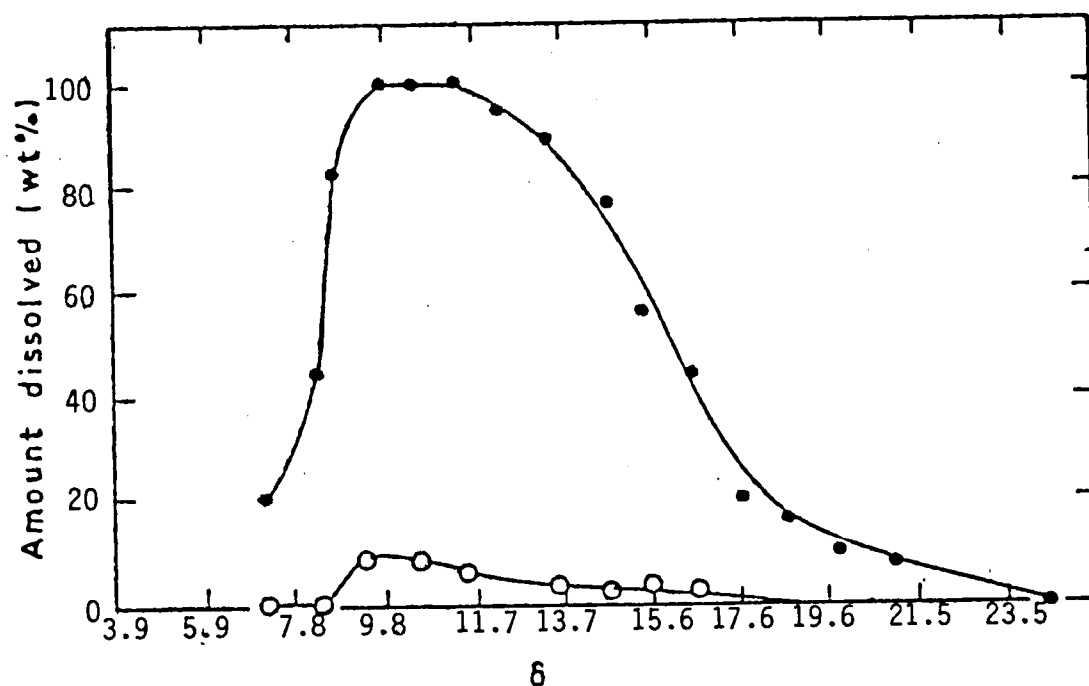


Figure 24. Plot of Percent Dissolved of Benzene Soluble and Insoluble PSOC-102 Coal Extracts Versus Mixed Solubility Parameter. ●, Benzene-Soluble Fraction; ○, Benzene-Insoluble Fraction.

Source: V. L. Weinberg and T. F. Yen, Fuel, 59, 287 (1980).

Figure 22⁷⁸ indicates a maximum in swelling at approximately $14(\text{cal/cm}^3)^{1/2}$. Generally, the maximum in swelling for coals has been observed at approximately $10.8(\text{cal/cm}^3)^{1/2}$. This may be the result of the solvent composition. The mixed solubility parameter concept is useful if one of the solvents used is not selectively absorbed. As previously discussed, swelling experiments performed by Green^{6,71} indicate that coals do act as selective sorbents. Clearly, the solubility parameter of the starting mixture will be erroneous, although it is not possible to say by how much.

In addition to studying the swelling behavior of coals, sorption studies have also been used to characterize the macromolecular nature of coal. Nelson⁷⁹ employed the solvent swelling technique to determine the number average molecular weight between crosslinks, $\overline{M}_c$, of coal. A series of coals ranging in rank from lignite to low volatile bituminous were used. The sorbates used were benzene, tetralin, and methanol. $\overline{M}_c$ values were calculated by the method of Rogers, et al.⁸⁰ This method rearranges the Flory-Rehner equation (Equation 14) into the following form:⁸⁰

$$[\ln(a_1/v_1)^{-2} - v_2]v_2^2 = \chi_o + (v_1\rho/v_2^2 \overline{M}_c)[v_2^{1/3} - v_2/2] \quad (35)$$

where a_1 is the activity of the solvent ($\sim P/P_o$), v_1 is the volume fraction of the solvent, v_2 is the volume fraction of the swollen coal. If the equilibrium swelling is known for a variety of relative vapor pressures, a graph of $[\ln(a_1/v_1)^{-2} - v_2]v_2^2$ versus $(v_1\rho/v_2^2)(v_2^{1/3} - v_2/2)$ will result in a linear plot, assuming $\overline{M}_c$ is constant, with the slope equal to $1/\overline{M}_c$ and the intercept equal to χ_o .

Realizing the limitation of the Flory-Rehner equation, Nelson also applied the method of Rogers et al.⁸⁰ to the Lucht and Peppas⁷ equation to calculate $\overline{M}_c$. The Lucht and Peppas equation similar to the Kovac equation,⁵⁰ was developed to accommodate the non-Gaussian behavior of the coal network.

In a previous study, Nelson and coworkers⁸¹ determined that in gravimetric swelling studies failure to correct for solvent which fills the pores in the coal could lead to serious errors in the determination of $\overline{M}_c$. Their results indicate that only 40-70% of the total uptake of sorbate was due to swelling. So in the present study, Nelson corrected for the pore volume in the coal in order to improve the values of $\overline{M}_c$ obtained.

The coals were swollen with solvent vapors at 25 °C using a McBain balance. Two samples of polystyrene (P816 and P818) were used for models of sorption. Polystyrene was used as a model because it is highly crosslinked. Apparent equilibrium was reached in several days for the coal samples swollen with methanol and polystyrene samples swollen with benzene. The coal samples swollen with benzene and tetralin under similar conditions reached apparent equilibrium after 4-7 weeks. The coals were dried at 110 °C under vacuum before swelling but were not pyridine extracted. The problem of possible extraction of uncrosslinked material in the coal, resulting in an excessive amount of solvent condensing on the coal, was minimized by judicious choice of solvents. Although the long equilibrium times suggest some extraction may have occurred, this is not confirmed. The porosity of a sample was measured by its density in benzene, tetralin,

and methanol and in mercury at 0.41 MPa. From a comparison of sorbate uptake values of tetralin and methanol on a lignite sample, it was assumed that above relative vapor pressure(r.v.p.) of 0.2-0.3 methanol sorption was the result of swelling. Below this range, sorbant uptake was due to physical adsorption.

Application of the method of Rogers et al.,⁸⁰ for methanol sorption was possible for only two coals, a lignite and subbituminous B coal. All other coals did not exhibit sufficient linearity to be used. Figure 25⁷⁹ shows a plot of $[\ln(a_1/v_1) - v_2]/v_2^2$ versus $(v_1\rho/v_2^{-2})/(v_2^{1/3} - v_2/2)$. $\overline{M}_c$ is obtained from the slope of the linear portion of the plot.

Figure 25⁷⁹ also includes the data for the polystyrene samples. The sorption values corrected for pore filling are also included. For the polystyrene samples, correction for pore volume improves the resulting $\overline{M}_c$ values. The calculated $\overline{M}_c$ values for the lignite and subbituminous coal were 70 for both samples. Use of the Lucht and Peppas equation increases the calculated $\overline{M}_c$ values to 117 and 128 for the lignite and subbituminous coals, respectively. Both sets of $\overline{M}_c$ values are much less than values reported in the literature.⁸¹ Correction for the pore volume does improve the value of $\overline{M}_c$, however.

The determination of the surface area of coals has received a great deal of attention. The techniques employed include the sorption of various gases and organic vapors. The use of these techniques is complicated by the highly porous nature of the coals. The measured sorption uptake will include contributions from physical adsorption and pore filling. Ideally, the molecular probe does not interact with

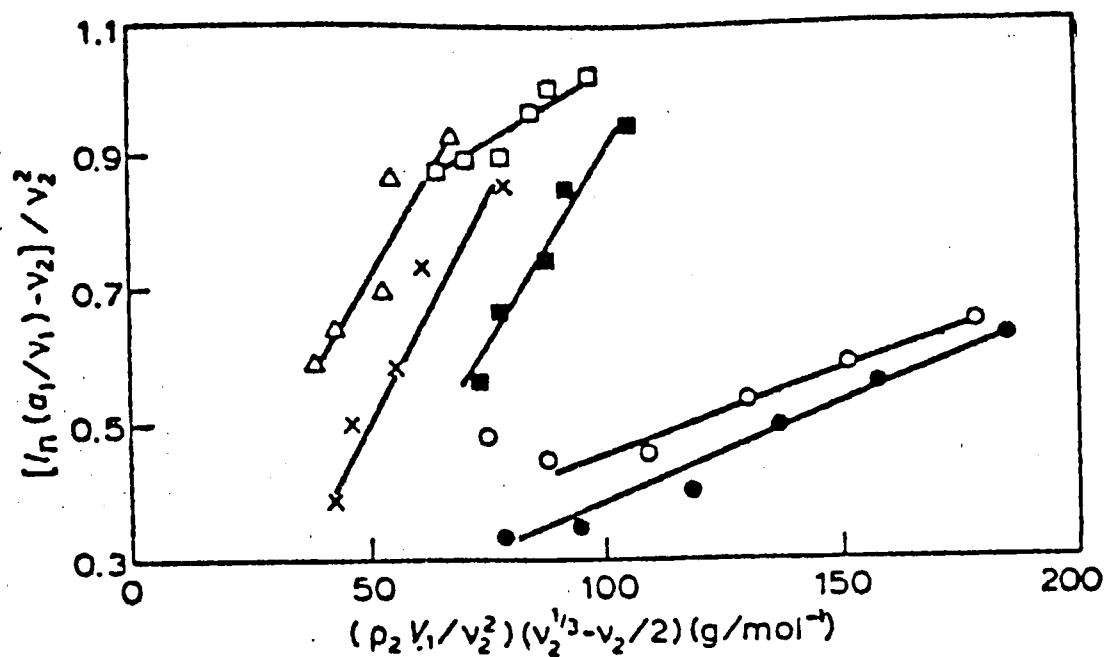


Figure 25. Plot Illustrating Use of Equation 35 to Determine the Number Average Molecular Weight Between Crosslinks for Various Coals and Polystyrene Samples. ○, ●, Polystyrene P818; □, ■, Polystyrene P816; Δ, PSOC-242 Coal; X, PSOC-246 Coal.

Source: J. R. Nelson, Fuel, 62, 112 (1983).

the coal matrix. Clearly, coals do interact with solvents. As a result, swelling of the coal matrix by a material assumed only to adsorb on the surface may lead to erroneous surface area measurements. In a study using Kentucky No. 12 coal (78%C, daf basis), Reucroft and Patel⁸² used a series of gases and organic vapors with solubility parameters in the range of $6-24(\text{cal}/\text{cm}^3)^{1/2}$ to determine if swelling effects were present at low relative vapor pressures (0.1-0.3 r.v.p.) and influencing surface area measurements. In addition, the same series of sorbates were employed at r.v.p. greater than 0.3 to obtain information on swelling of the samples.

The experimental procedure for measuring the equilibrium isotherms is described in detail elsewhere,⁸² but essentially, approximately 550 mg of coal was suspended from the balance arm of a Cahn R. G. electromicrobalance in a previously tared glass container and the weight increase due to sorption was measured as a function of the sorbate pressure. Brunauer-Emmett-Teller (BET) and Dubinin-Polanyi (DP) surface areas were determined from the equilibrium isotherm data.

At relative vapor pressures of approximately 0.9, the swelling parameter, Q , was determined:

$$Q = 1/v_2 = 1 = \rho_2/\rho_1(q_w - 1) \quad (36)$$

where ρ_1 and ρ_2 is the density of the sorbate in the liquid state and density of the coal in the liquid sorbate, respectively. v_2 is the volume fraction of coal in the swollen coal sample at equilibrium; and

q_w is the mass of coal at equilibrium/initial mass. In Equation 36, the volume of the swollen sample is assumed to be equal to the sum of the coal volume and sorbate volume. The mass of sorbate adsorbed will include a contribution from pore filling as discussed by Nelson.⁷⁹ An accurate determination of the amount of swelling must correct for sorbate that merely fills the pores. Since sorption data using n-hexane, cyclohexane, and carbon tetrachloride, solvents not expected to swell the coal, indicate that Kentucky No. 12 coal has a low sorbant uptake ($0.01 \text{ cm}^3/\text{g}$), no pore volume corrections were made. Green et al.⁸³ have demonstrated, however, that the solvent uptake using cyclohexane was approximately to the pore volume of the Illinois #6 and Bruceton coals studied. Thus the low solvent uptake by the Kentucky No. 12 coal is surprising.

The surface area of the coal was calculated from BET and DP theories using the sorption data obtained at r.v.p. ranges of 0.001-0.3 and 0.001-0.2, respectively. Figure 26⁸² is a plot of the DP and BET surface areas versus the solubility parameter of the sorbate. The surface area increases with increasing solubility parameter until a maximum is reached at approximately $10 (\text{cal}/\text{cm}^3)^{1/2}$, afterwhich the surface area decreases with increasing solubility parameter. Also, the DP surface areas are larger than the BET surface areas. This was attributed to inclusion of pore volume filling in the DP theory.⁸² Figure 26⁸² implies the surface area of the coal is influenced by the sorbate used. The sorbates with the greatest influence on the surface area are those which have solubility parameter values similar to that estimated for coals. The surface

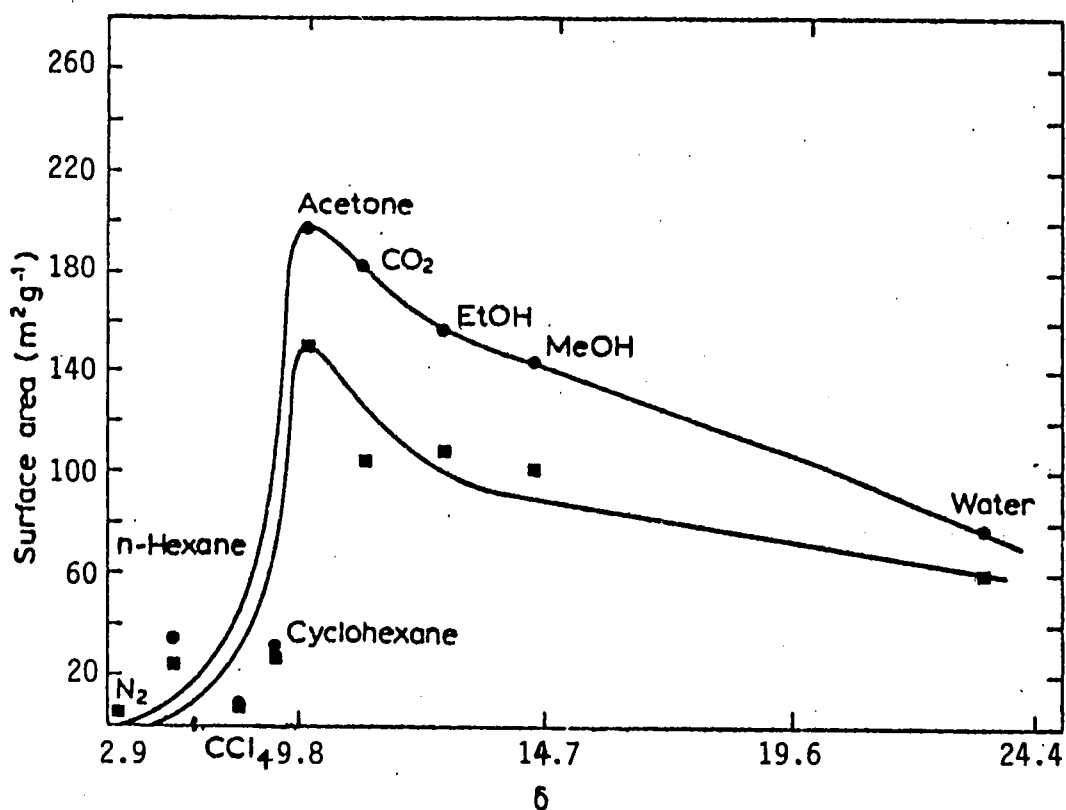


Figure 26. Plot of Surface Area Versus Solubility Parameter for Kentucky No. 12 Coal.

Source: P. J. Reucroft and K. B. Patel, *Fuel*, **62**, 279 (1983).

area calculated using pyridine was not included in the plot because the scattering in the BET and DP plots was significant.

Reucroft and Patel⁸² also note that sorption-desorption hysteresis always occurs and often the hysteresis loops do not close. The amount of hysteresis was influenced by the sorbate used. The sorbates which had solubility parameters close to the solubility parameter of the coal showed the largest amount of hysteresis. This was attributed to the inability to remove strongly sorbed sorbates from the coal sample.

The Kentucky No. 12 coal was also exposed to sorbates at a r.v.p. of approximately 0.9 to determine the swelling parameter, Q , as defined by Equation 36. Figure 27⁸² is a plot of Q versus the solubility parameter of the sorbate. Q increases with increasing solubility parameter until a maximum is reached at $10.6(\text{cal}/\text{cm}^3)^{1/2}$ thereafter Q decreases with increasing solubility parameter. This type of behavior is well documented in coals. From the plot of Q versus the solubility parameter, the solubility parameter of the coal is assigned as $10.6(\text{cal}/\text{cm}^3)^{1/2}$. The swelling parameter, Q , for pyridine appears to be unusually low. Often coal samples when exposed to pyridine more than double in volume.⁶ The low value of Q may be the result of the solvent and coal not reaching equilibrium. Also, the Kentucky No. 12 coal was not pyridine extracted prior to swelling and the uncrosslinked material would be extracted by the pyridine lowering the chemical potential of the system thereby causing an excess amount of solvent to condense. In addition, extremely low

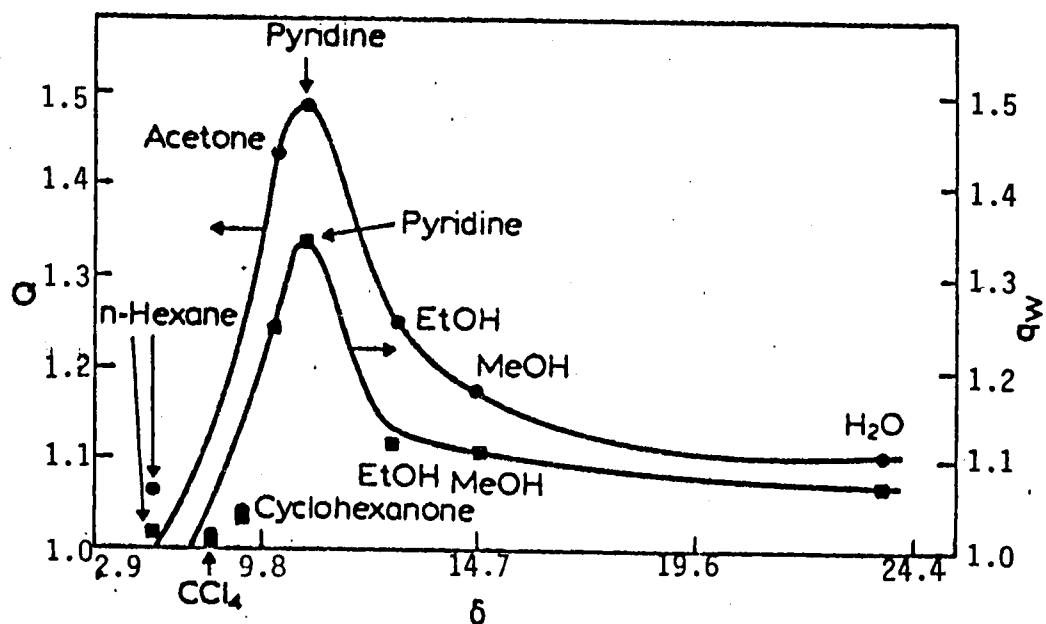


Figure 27. Plot of Swelling Ratio Versus Solubility Parameter for Kentucky No. 12 Coal.

Source: P. J. Reucroft and K. B. Patel, Fuel, 62, 279 (1983).

equilibrium times would be observed. This may occur with other solvents which associate strongly with the coal as well.

The authors conclude that since Figures 26⁸² and 27⁸² appear to be very similar, swelling of the coal is occurring even at low r.v.p. Therefore, the surface areas determined from equilibrium sorption isotherms show a dependence on the sorbate used. In particular, since the calculated solubility parameter of CO₂ is $11.3(\text{cal/cm}^3)^{1/2}$, close to the solubility parameter of the coal, the high surface areas found using CO₂ may be the result of swelling of the coal.

The imbibition of solvents by brittle, carbonaceous materials results in an expansion of the material which may exceed the critical fracture stress of the solid, resulting in spontaneous fracture of the material. The material literally breaks apart. This phenomenon has been observed with coals and is referred to as slaking. Solvents which interact strongly with coal are more likely to be imbibed by the network and lead to spontaneous fracture. A convenient indicator of the interaction of a solvent with coals is the solubility parameter. Thus Keller and Smith⁸⁴ studied the effect of ammonia ($\delta = 14.5(\text{cal/cm}^3)^{1/2}$) and several solvent mixtures containing ammonia with a range of solubility parameters in order to predict a relationship between the solubility parameter of the solvent and the size of the fractured coals. The main idea being as the solubility parameter of the solvent approaches that of the coal, swelling would be enhanced, the coal will fracture, and the size of the fractured coal may be related to the degree of swelling. Another goal of the study was to see if the slaking process improves the separation of pyrite and mineral matter from the coal.

Among the bituminous coals used in the study were: Waynesburg, Sewickley No. 9, Upper and Lower Freeports, Illinois #5 and #6, and Powelton. The details of the sample preparation and experimental apparatus are given elsewhere.⁸⁴ Both bench scale and pilot plant studies were conducted. Essentially, a coal was exposed to either pure ammonia or a mixture of ammonia and one of the following solvents: nitrobenzene, diethylamine, ethylene diamine, methylamine, ethylamine, methanol, or ethanol. The solvent mixtures were observed to swell the coal approximately 40%.⁸⁴ The size consist of the coal was measured after excess solvent removal by evaporation. Ammonia will evaporate readily, but the amine and alcohol solvents are not expected to be removed by mere evaporation. The entire sample was separated via a sink-float technique with heavy liquids whose specific gravity was either 1.4 or 1.5.

From Table XI,⁸⁴ which lists representative size consists observed with the ammonia solutions, it is clear that all of the size reductions for the mixtures are similar to those observed for pure ammonia. Keller and Smith⁸⁴ indicated the lack of variation of the size consist was consistent with a strain-energy model which predicts the change in particle size is governed by the amount of swelling to the minus two-thirds power. Thus, unless the amount of swelling changes drastically, to less than 10% for example, little variation in the size consist with the swelling is expected. In addition, no improvement in the separation of the mineral matter was observed.

Aldrich⁸⁵ suggested the strain-energy model, however, applies only to fractures which occur at the coal-mineral interface. In

TABLE XI

SIZE CONSIST OF SEWICKELY COAL AFTER TREATMENT
WITH VARIOUS AMMONIA SOLUTIONS

Solution	$+\frac{3}{8}$ in	+5 mesh	+10 mesh	+30 mesh	+60 mesh	+100 mesh
5%CH ₃ OH	1.9	8.6	24.4	69.6	92.5	97.6
20%C ₆ H ₅ NO ₂	0.5	5.1	23.3	69.0	93.7	98.9
20%NH ₂ C ₂ H ₄ - NH ₂	0	13.9	40.5	79.8	95.6	98.4
10%(C ₂ H ₅) ₂ NH	1.2	20.1	46.4	82.2	95.7	98.0
10%CH ₃ NH ₂	0.8	18.7	46.4	82.3	95.3	97.7
100%NH ₃	0.5	7.9	26.5	68.3	93.9	98.1
Run of Mine	70.5	82.5	90.4	95.3	98.1	99.1

Source: D. V. Keller, Jr. and C. D. Smith, Fuel, 55, 273 (1976).

addition, Aldrich proposes that the swelling observed is not swelling in the normal sense, but the result of bond breakage at coal-mineral interfaces and the formation of a mixture of solvent, coal, and minerals.

Asphaltenes are generally defined as the portion of a crude petroleum or bitumen that is soluble in benzene or toluene but insoluble in hexane or n-pentane. Mitchell and Speight⁸⁶ measured the solubility of asphaltenes, derived from an Athabasca bitumen, in a variety of solvents and two solvent blends and correlated the amount of asphaltene precipitated with the solubility parameter of the solvent. In the study the solubility parameter was defined as the $CED^{1/2}$ or by the following equation:⁸⁶

$$\delta = \gamma V^{-1/3} \quad (37)$$

where γ is the surface tension and V is the molar volume.

The solubility of the asphaltenes was measured two ways. The asphaltenes were mixed with the appropriate solvent and the soluble and insoluble fractions measured. In the second procedure, the Athabasca bitumen was fractionated by addition of an equal volume of benzene followed by dilution of the soluble portion with 40 volumes of the specified solvent or solvent blend. The solvent blends used in the study were benzene/n-pentane and pentane/bitumen. Each blend was prepared on a wt:wt basis.

Several of the results of the study are contained in Table XII.⁸⁶ The yield of the asphaltene precipitated is based on the weight

TABLE XII
YIELDS OF ASPHALTENE PRECIPITATION AND SOLUBILITY
PARAMETERS OF VARIOUS SOLVENTS

Solvent	δ		Precipitate (wt% bitumen, mmf)
	$\gamma V^{1/3}$	$(\Delta H_{\text{vap}} - RT/V)^{1/2}$	
Pentane	3.2	7.0	16.9
Heptane	3.8	7.5	11.4
Decane	4.1	7.7	9.0
Isopentane	3.1	6.8	17.6
Hexene	3.6	7.3	13.0
Octene	4.0	7.6	9.0
Cyclohexane	5.3	8.2	0.7
Decalin	5.5	8.6	0
Benzene	6.5	9.2	0
Tetralin	6.9	9.5	0
Cyclohexene	6.0	8.5	0
Neopentane	2.4	6.2	12.5
Pyridine	8.6	10.6	0
Chloroform	6.3	9.2	0
Blend (mol:mol)			
benzene	n-pentane		
0.14	2.09	3.4	7.2
0.78	1.58	4.3	7.7
1.12	1.32	4.7	8.0

Source: D. L. Mitchell and J. G. Speight, Fuel, 52, 273 (1976).

percent of bitumen. The solvents giving the highest yield of asphaltene(21.5-8.5%) had solubility parameters in the range of $6-8(\text{cal/cm}^3)^{1/2}$. The aromatic solvents employed dissolved all (or nearly all) of the asphaltene material. The difference in solubility was rationalized by treating the asphaltenes as micelles in which the outside of the micelle consists primarily of aliphatic and naphthenic hydrocarbons. The inner portion of the micelle was primarily composed of more polar species, for example resins. Thus a solvent capable of dissolving the asphaltenes must have sufficient ability to penetrate the micelle. The ability to dissolve the asphaltene is a characteristic of the solvent power of the solvent, which may be related to the solubility parameter of the solvent. Figure 28⁸⁶ is a plot of δ versus the amount of asphaltene precipitated. From Figure 29,⁸⁶ as the solubility parameter increases the amount precipitated decreases. Or to put it another way, as the solvent power of the solvent increases, the amount of the asphaltene dissolved also increases. This behavior was also seen in the mixed solvent studies. In addition to variation of asphaltene yield with the solubility parameter, the authors noted that the structure of the solvent employed had an effect; variations of up to fifteen percent were found.

The ability to precipitate the asphaltenes in two steps revealed some information on the mineral matter distribution of asphaltenes. The majority of the mineral matter of the bitumen is contained in the asphaltenes precipitated in the first stage. This observation implies

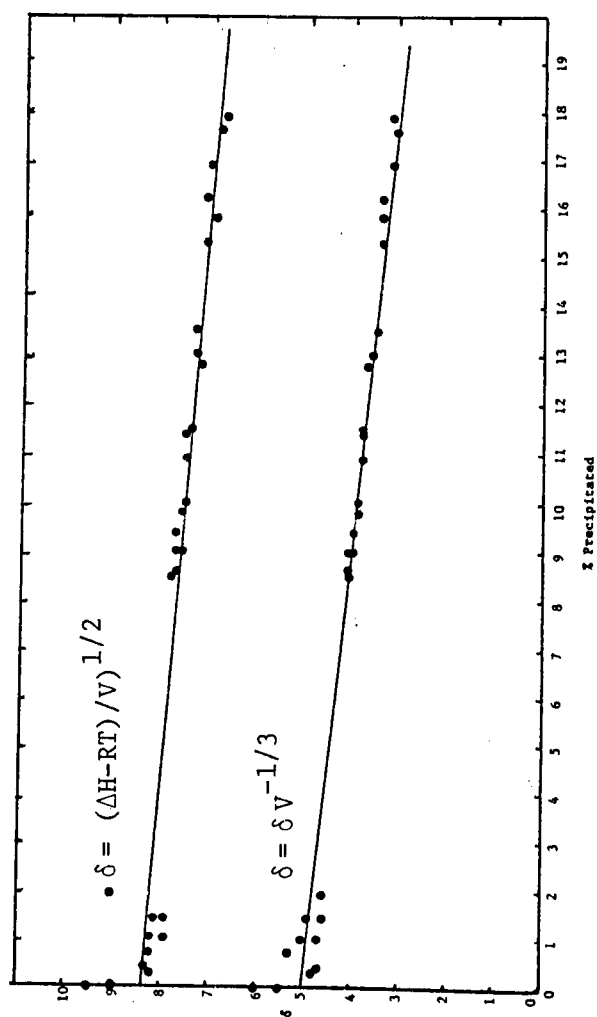


Figure 28. Plot of Solubility Parameter Versus Percent Asphaltene Precipitated.

Source: D. L. Mitchell and J. H. Speight, Fuel, 52, 149 (1973).

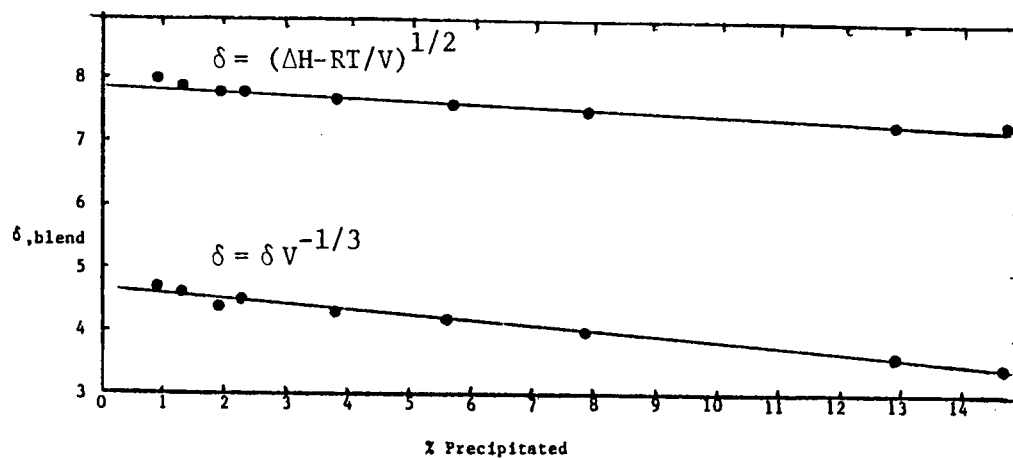


Figure 29. Plot of Solubility Parameter of Solvent Blend Versus Percent Asphaltene Precipitated.

Source: D. L. Mitchell and J. G. Speight, Fuel, 52, 149 (1973).

that the majority of the mineral matter in the bitumen can be removed by precipitation thus reducing the poisoning of cracking catalysts.

Baltisberger et al.,⁸⁷ measured the chemical composition and structural features of the asphaltene and preasphaltene fractions from a variety of lignite and bituminous coal samples to establish which of the following characteristics were dominant in determining the solubility of the asphaltenes and preasphaltenes in either pyridine or tetrahydrofuran: 1) molecular weight distribution, 2) fraction of total carbon as aromatic carbons, 3) fraction of total aromatic carbon present as edge aromatic carbons, 4) fraction of oxygen present as phenolic and etheral oxygen, and 5) relative amount of hydrogen to phenolic content based on total sample.

The coal derived liquids were obtained over a temperature range of 400° to 480 °C under various donor solvent conditions.⁸⁷ The asphaltenes and preasphaltenes were separated using tetrahydrofuran and pyridine. The asphaltenes and preasphaltenes were further fractionated using preparative gel permeation chromatography(GPC). The elemental composition, number average molecular weight from vapor pressure osmometry, hydroxyl content, and nmr spectra were determined for the GPC fractions.

Baltisberger et al.⁸⁷ realized the solubility activity coefficient could be related to the solubility parameters of the solvent and solute by the following equation:⁸⁸

$$RT \ln \gamma_1 = V_1 (\delta_1 - \delta_2)^2 \quad (38)$$

where γ_1 is the activity coefficient of the solute and V_1 is the molar volume of the solute. This equation assumes regular solution behavior.⁸⁹ From Equation 38, the solubility activity coefficient of the solute increases with an increase in the molar volume of the solute. Thus Baltisberger et al.⁸⁷ studied the relationship between molar volume and acidity of the asphaltene and preasphaltene fractions in the determination of the solubility of the asphaltenes and preasphaltenes. This approach proved to be unsuccessful; however, no correlation was found between the molecular weight (+ H/C ratio) and acidity of the GPC fractions studied. Aside from the fact that the molar volume is not the same as the molecular weight, the preasphaltenes and asphaltenes would be expected to have some overlapping molecular weights perhaps due to incomplete fractionation which would make the correlation impossible. Of the various parameters previously listed, the study revealed that the hydrogen and phenolic oxygen content was the most important in determining the solubility of the asphaltenes and preasphaltenes in pyridine and tetrahydrofuran.

The mixed solubility parameter concept has also been used in conjunction with the desulfurization of coal. Corcoran et al.⁹⁰ found the desulfurization of coal by chlorinolysis is enhanced by using a solvent mixture with a solubility parameter which also produces maximum coal swelling. This idea is to facilitate the mass transfer of chlorine into the coal using a solvent mixture which will either swell and/or solubilize the coal. The mixed solvents used consisted of either methanol, water, or carbon tetrachloride.

In order to determine which solvent mixture produced the most swelling and/or dissolution, approximately one gram of PSOC-190 coal was suspended in 10 ml of a mixed solvent and after five days, the weight increase of the coal was measured. The percent swelling was then plotted versus the solubility parameter of the mixture. The plot is shown in Figure 30.⁹⁰

Two major peaks in swelling are indicated in the plot. Nearly 300% swelling is observed when the solubility parameter of the mixture is approximately $15(\text{cal}/\text{cm}^3)^{1/2}$, and another peak is found at $\delta = 10.7(\text{cal}/\text{cm}^3)^{1/2}$. The authors suggest the two peaks are representative of two different coal-solvent interactions. The peak at $\delta = 15.2$ was attributed to a maximum in coal swelling, while the peak at $\delta = 10.7$ corresponded to a maximum in coal dissolution.⁹⁰ Using a 1:1 (by volume) mixture of methanol and carbon tetrachloride ($\delta_{\text{mix}} = 11.5$) in the chlorinolysis reaction, the percent total sulfur in the PSOC-190 coal was reduced by 55.5% and removal of 85.1% and 44% of the pyritic and organic sulfur, respectively was also observed. A similar result was obtained using PSOC-276 coal. The result supported the contention that maximum desulfurization occurs when the coal is swollen thereby reducing mass transfer limitations.

The mixed solvent procedure assumes no specific interactions between the coal and the solvents. This is not the case for methanol which is known to bind to specific sites in the coal.⁶ It is also interesting that the solvent mixture with a solubility parameter of $15.2(\text{cal}/\text{cm}^3)^{1/2}$ produced the maximum swelling. Typically, bituminous coals exhibit maximum swelling with amine solvents which have solubility parameters near $11(\text{cal}/\text{cm}^3)^{1/2}$.⁶ In addition, methanol

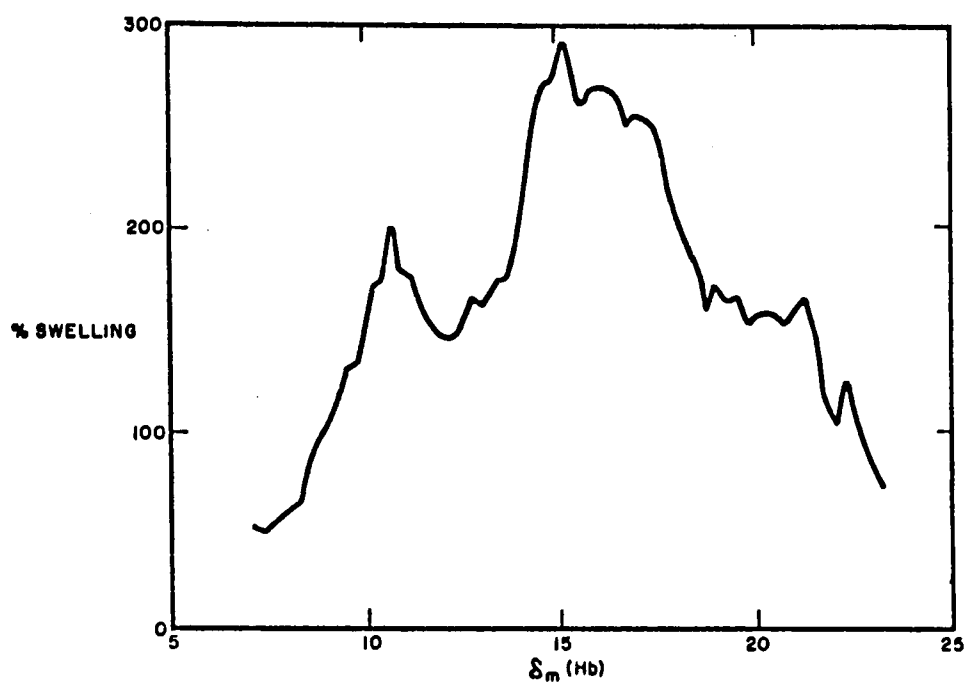


Figure 30. Plot of Percent Swelling Versus Mixed Solubility Parameter for PSOC-190 Coal.

Source: W. H. Corcoran, N. P. Vasilakos, and D. D. Lawson,
U. S. Patent No. 4,334,888.

generally produces less swelling in bituminous coals^{6,39,77} than the 260% reported by Corcoran et al.⁹⁰ It is not clear from the experimental procedure whether pore volume corrections were made. If not, the amount of swelling measured will be erroneous as discussed by Nelson.⁸¹

Lucht and Peppas^{7,91,92} support a three-dimensionally crosslinked macromolecular structure for coals, and using gravimetric swelling data have calculated the $\overline{M}_c$ values for a series of coals ranging in rank from lignite to anthracite. The $\overline{M}_c$ values were calculated from the following equation, referred to as the Lucht and Peppas equation:^{7,91,92}

$$\frac{1}{\overline{M}_c} = \frac{(\overline{v}/V_1)[\ln(1-v_2) + v_2 + \chi v_2^2][1 - 1/Nv_2^{2/3}]^3}{[\frac{1}{2}v_2 - v_2^{1/3}][1 + 1/Nv_2^{1/3}]^2} \quad (39)$$

where $\overline{v}$ is the specific volume of the coal, v_2 is the volume fraction of the swollen coal, V_1 is the molar volume of the solvent, and χ is the Flory Chi parameter. N is given by Equation 16.⁵⁰ Equation 39 attempts to correct for the non-Gaussian behavior of coals and is similar to the Kovac equation (Equation 15).

The gravimetric solvent swelling experiments were performed as follows.⁹² A pyridine extracted coal was exposed to pyridine vapor at a specified temperature (either 35°, 60°, or 80°C) for 5-12 weeks, after which the coal sample was reweighed. Corrections were made for the pore volume. The value of χ was calculated from the following equation:⁹²

$$X = 0.0116(\%C) - 0.4901$$

(40)

Equation 40 is based on the solubility parameters determined for various coals by Kirov et al.,³⁹ who used a regular solution theory approach to determine the solubility parameters. As the Lucht and Peppas swelling experiments were performed at temperatures greater than 25 °C, the appropriate corrections in the values of the solubility parameters were made.

In the determination of the $\overline{M}_c$ values, $\overline{M}_0$ was assumed to be 130 for lignites, 170 for bituminous coals with 86%C(dmmf) or less, and 370 for coals with carbon contents greater than 87%C. The values of $\overline{M}_0$ in the Lucht and Peppas work are probably too low. Various workers^{1,93-95} have argued that the average molecular weight of the coal clusters varies between approximately 300 and 700.

As shown in Figure 31,⁹² the $\overline{M}_c$ values vary with the carbon content of the coal, from approximately 750 to 1250. As shown in Figure 32,⁹² the value of N increases slightly from 7.0 to 8.5 until the carbon content of the coal reaches approximately 83%C. As the carbon content increases the value of N drops until a value of 2.2 is reached at 91.5%C. These results contradict earlier work by Lucht and Peppas^{7,91} when they observed no rank dependence on either N or $\overline{M}_c$. In the previous work, however, the amount of pyridine absorbed by the coals was unusually low and suggested the coals had not reached equilibrium.

The last series of papers to be reviewed is that of the research performed by Larsen, Green, and Kovac.^{71,83,96} Based on the model

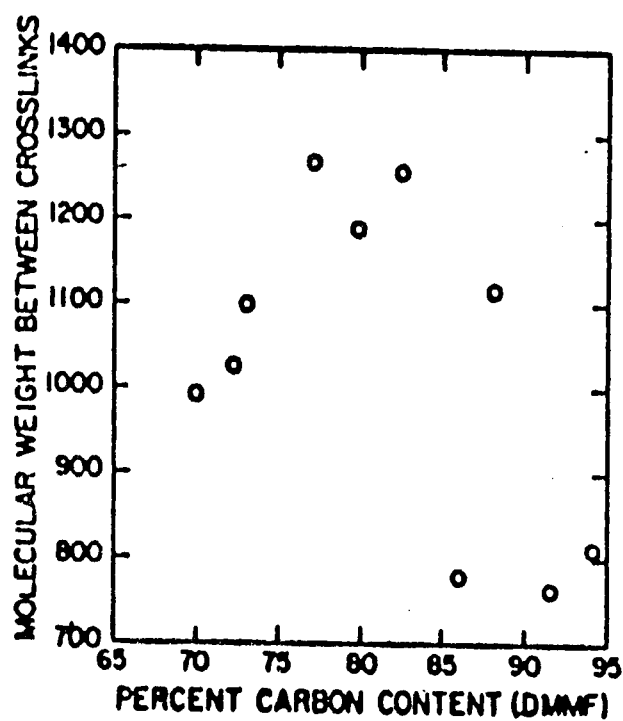


Figure 31. Plot of Number Average Molecular Weight Between Crosslinks Versus Carbon Content.

Source: L. M. Lucht and N. A. Peppas, Prepr. Pap., Am. Chem. Soc., Div. Fuel Chem., 29(1), 213 (1984).

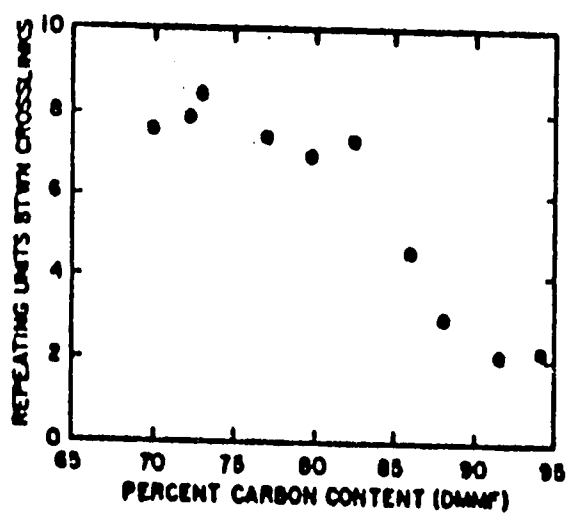


Figure 32. Plot of N Versus Carbon Content.

Source: L. M. Lucht and N. A. Peppas, Prepr. Pap., Am. Chem. Soc., Div. Fuel Chem., 29(1), 213 (1984).

that coals are three-dimensionally covalently crosslinked macromolecular networks, regular solution and physical-polymer theories were applied to determine the crosslink density and $\overline{M}_c$. The presence of hydrogen bonds in coals is accepted, but the role which the hydrogen bonds play in the macromolecular structure is ill-defined. Thus coals which were derivatized by O-acetylation to remove hydrogen bonds were also studied. The experimental technique used was solvent swelling.

Before any information on the macromolecular network could be obtained the coals must be shown to obey regular solution theory behavior and the solubility parameter of the coals must be determined. Each coal was swollen in a series of non-polar solvents and the swelling ratios measured. The solvent swelling procedure can be performed either volumetrically or gravimetrically as described in Chapter II Section B. Green^{6,83} demonstrated that the volumetric technique gives the same result as the gravimetric procedure if a correction is made for the pore volume in the later method. In the same study, it was shown that from plots of the volumetric versus gravimetric swelling the pore volume of a coal may be determined. Non-polar solvents were used to satisfy the requirements of regular solution theory. The coals demonstrated the bell-shaped curves which are expected if regular solution theory is obeyed. From the maximum in the curves, non-polar solubility parameters of $9.5(\text{cal/cm}^3)^{1/2}$ were assigned to both the Illinois #6 and Bruceton coals.

With the assignment of the solubility parameters, χ values were calculated for the coal-solvent pairs. $\overline{M}_c$ was then calculated using

the solvent swelling data and χ values, from the Flory-Rehner and Kovac equations (Equations 14 and 15, respectively). The results from the Flory-Rehner treatment on the native, pyridine extracted, and O-acetylated coals are presented in Table XIII.⁹⁶ All of the $\overline{M}_c$ values are unrealistically low. This result is attributed to the inability of the Flory-Rehner equation to adequately describe the coal network. Application of the Kovac equation produces $\overline{M}_c$ values which are more reasonable. The results using the Kovac treatment are presented in Tables XIV⁹⁶ and XV.⁹⁶ The $\overline{M}_c$ values may not be quantitatively accurate, but are indicative of general trends.

Comparison of the native, pyridine extracted, and O-acetylated coals indicates that hydrogen bonds do play an active role in the macromolecular structure of the bituminous coals. Larsen et al.⁹⁶ estimate that Bruceton coal has 4.5 times as many hydrogen bond crosslinks as covalent crosslinks. Illinois #6 showed five times as many hydrogen bond crosslinks. In addition, Green^{6,96} has shown that in native coals, the strength of the hydrogen bonds ranges from 5 to 8 kcal/mole.

The solvent swelling technique has not only provided information on the macromolecular structure of coals, but also has been used to study the interaction of solvents with specific sites in coals. Green and Larsen⁷¹ extended the mixed solvent study of Hombach⁶⁹ to determine whether one solvent of a solvent pair is selectively absorbed by coal.

The volumetric swelling procedure used in the study has been previously described.^{6,83} The swelling in the solvent mixtures was

TABLE XIII

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE BRUCETON
AND ILLINOIS NO. 6(2) COALS USING THE FLORY-REHNER EQUATION

Illinois No. 6(2)				
Solvent	χ	Unextracted	Extracted	O-acetylated
o-xylene	0.40	---	430	---
Toluene	0.36	100	410	700
Benzene	.31	110	360	630
Tetralin	0.30	---	540	990
Naphthalene	0.33	---	380	---
CS ₂	0.32	60	190	380
Average		90	390	680
Bruceton				
o-xylene		---	550	---
Toluene		190	500	1420
Benzene		150	410	1120
Tetralin		---	690	---
Naphthalene		---	520	---
CS ₂		110	210	590
Average		150	480	1040

Source: J. W. Larsen, T. K. Green, and J. Kovac, J. Org. Chem., 50, 4729 (1985).

TABLE XIV

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE
ILLINOIS NO. 6(2) COAL USING THE KOVAC EQUATION

		$\bar{M}_c$			
Unextracted	N	0.4	0.5	1.0	2.0
Toluene		430	310	200	150
Benzene		400	340	220	170
CS ₂		240	200	130	100
Average		360	280	190	140
$\bar{M}_o$		900	560	190	70
Extracted	N	1.0	1.25	2.0	3.0
o-xylene		980	870	710	620
Toluene		940	830	670	580
Tetralin		1250	1100	900	780
Naphthalene		860	760	620	540
CS ₂		430	390	310	270
Average		880	780	640	550
$\bar{M}_o$		880	620	320	180
O-acetylated	N	1.5	2.0	3.0	4.0
Toluene		1370	1200	1030	950
Benzene		1260	1110	950	870
Tetralin		1920	1680	1440	1320
CS ₂		740	650	560	510
Average		1320	1160	1000	910
$\bar{M}_o$		880	580	330	230

Source: J. W. Larsen, T. K. Green, and J. Kovac,
J. Org. Chem., 50, 4729 (1985).

TABLE XV

THE NUMBER AVERAGE MOLECULAR WEIGHT PER CROSSLINK OF THE
BRUCETON COAL USING THE KOVAC EQUATION

		$\bar{M}_c$				
		N	0.5	0.75	1.0	2.0
Unextracted						
Toluene			630	490	410	300
Benzene			440	330	270	190
CS ₂			370	280	240	180
Average			480	370	300	220
$\bar{M}_o$			960	490	300	110
Extracted						
	N	1.0	1.5	2.0	3.0	
o-xylene			1290	1080	920	800
Toluene			1180	950	840	730
Benzene			970	780	690	600
Tetralin			1650	1330	1170	1020
Naphthalene			1240	1000	880	760
CS ₂			470	380	340	300
Average			1130	920	810	700
$\bar{M}_o$			1130	610	400	230
O-acetylated						
	N	2.0	3.0	4.0	5.0	
Toluene			2630	2230	2030	1910
Benzene			2100	1780	1610	1520
CS ₂			1070	910	830	780
Average			1930	1640	1490	1400
$\bar{M}_o$			970	550	370	280

Source: J. W. Larsen, T. K. Green, and J. Kovac, J. Org. Chem., 50, 4729 (1985).

performed by adding the appropriate solvent mixture to a known amount of coal(either Illinois #6 or Bruceton) in an 8mm o.d. Pyrex tube. The solvent mixture consisting of chlorobenzene and pyridine or N,N-dimethylaniline and an alcohol(either methanol, ethanol, 2-propanol, or t-butanol). The tube was sealed, shaken periodically, and the swelling allowed to reach equilibrium. The tubes were opened and the supernatant liquids analyzed by g.c. The absolute volume of the solvent components absorbed by the coal was calculated according to the following equation:⁷¹

$$V_{i,abs} = V_{i,total} - x_i [V_{total} - (Q_{v,dry} - 1)w_{c,dry} / \rho_{c,dry}] \quad (41)$$

where $V_{i,abs}$ is the volume of component i absorbed by the coal, $V_{i,total}$ is the total volume of component i, x_i is the volume fraction of component i in the supernatant, $Q_{v,dry}$ is the swelling ratio, $w_{c,dry}$ is the weight of the dry coal, and $\rho_{c,dry}$ is the density of the dry coal in cyclohexane.

The results of the alcohol-amine mixtures indicate that approximately the same amount of alcohol is absorbed by the coal(Bruceton) regardless of the identity of the alcohol. Only with t-butanol was the amount of alcohol absorbed diminished, probably due to steric effects. This result suggests that alcohols bind to specific sites in the coal. The pyridine-chlorobenzene swelling results indicate that pyridine interrupts the hydrogen bond network permitting an increased amount of chlorobenzene into the coal. Also from the results, it appears that one pyridine molecule hydrogen bonds

to each hydroxyl group in the coal. Thus the sites which specifically interact with pyridine can be "counted" by monitoring the composition of the solvent absorbed by the coal.

CHAPTER III

EXPERIMENTAL PROCEDURES

A. Coal Preparation

1. Rawhide Coal

The Rawhide coal supplied by Dr. Ron Liotta of Exxon Research and Engineering Corp. was stored under water in approximately one inch chunks. Before grinding, the chunks of coal were reduced in size under water in a glove bag using a mortar and pestle and transferred to a round bottom flask. The water was removed from the coal using a rotary evaporator at approximately 30 °C. The coal was ground to -100 Tyler mesh under nitrogen using a ball mill. The ground coal was separated into fractions using a riffler in a dry box under nitrogen.

2. Texas Lignite

The Texas Lignite, also supplied by Dr. Liotta, was received in 1/8" chunks. The sample was fractionated using a riffler under nitrogen and the two 1/8 fractions were ground to -100 Tyler mesh using a coffee mill in a dry box.

3. Big Brown Lignite and South Beulah

The lignite samples were previously ground -70 Tyler mesh and were ground to -100 Tyler mesh using a coffee mill in a dry box.

4. Illinois #6

The Illinois #6 coal, obtained from Southern Illinois University, was previously ground to -70 Tyler mesh. The coal was ground to pass -100 Tyler mesh using a coffee mill in a dry box. The elemental analyses of the coals employed in the study are listed in Table XVI.

B. Solvent Purification

All solvents were purified by standard procedures^{97,98} except carbon disulfide, cyclohexane, and tetrahydrofuran which were purchased in high purity (Aldrich, Gold Label) and did not require further purification. The THF was inhibited with butylhydroxytoluene. The solvents employed in the study, their solubility parameters and assigned solvent numbers are listed in Table XVII.

C. Volumetric Swelling Measurements

Approximately 0.4-0.8 g of coal (-100 Tyler mesh) was placed in an 8 mm o.d. pyrex tube (sealed on one end) under nitrogen atmosphere. The tube was placed in a Fisher centrifuge (1725 or 3400 rpm) and repeatedly centrifuged and tapped by hand on a hard surface until the coal bed reached a minimum height, H_1 . The packed coal bed was broken up by tapping the tube against a hard surface. This coal was then distributed along the tube to prevent clumping due to rapid swelling when solvent was added. 2-3 ml of solvent was added to the tube and

Weight Percent Elemental Analyses^{a,b} of Dry Coals

Coal	% C	% H	% N	% S	% O ^c	% MM
Rawhide	69.27	4.42	0.96	0.56	24.30	8.36
Big Brown Lignite	69.69	5.11	1.35	1.40	24.07	11.03
Texas Lignite	70.31	5.12	1.42	1.84	23.66	16.03
Illinois #6	80.65	4.97	1.90	1.79	12.63	12.18

^aCHN analyses performed on a Perkin-Elmer 240C Elemental Analyzer by Susan E. Shawver; sulfur analyses performed by Galbraith Laboratories, Knoxville, TN.

^bDMMF basis; % MM = 1.08ASH + 0.55S.

^c% O by difference.

TABLE XVII

SOLVENTS USED IN SOLVENT SWELLING

Solvent	Solvent Number	$\delta, (\text{cal}/\text{cm}^3)^{1/2}$
n-Pentane	1	7.2
Cyclohexane	2	8.2
O-xylene	3	8.8
Toluene	4	8.9
Tetrahydrofuran	5	9.1
Benzene	6	9.2
Chlorobenzene	7	9.5
Tetralin	8	9.5
1,2-dichloroethane	9	9.8
Carbon Disulfide	10	10.0
Nitrobenzene	11	10.0
Biphenyl	12	10.6
Pyridine	13	10.7
N-methyl-2-Pyrrolidone	14	11.0
Acetonitrile	15	11.9
Ethanol	16	12.7

mixed thoroughly with the coal. The tube was allowed to stand vertically for a minimum of 24 hours. The tube was again centrifuged and tapped by hand until the measured height of the coal bed reached a minimum height, H_2 . The volumetric swelling ratio on a dry basis, $Q_{v,dry}$, is defined as:

$$Q_{v,dry} = H_2/H_1 \quad (42)$$

$$Q_{v,dry} = (v_{c,dry} + v_s)/v_{c,dry} \quad (43)$$

where v_s is the volume of solvent absorbed by a unit volume of dry coal, $v_{c,dry}$. The reproducibility of the swellings was good. For example, the average of six measurements using Illinois #6 coal and toluene gave a swelling ratio of 1.5 ± 0.04 r.s.d. This procedure is very similar to that published, and has been shown to give results identical to gravimetric swelling measurements.⁶

Normally in a solvent swelling experiment the initial height of the coal bed, H_1 , is measured visually. In the case of the O-acetylated coals, the direct observance of H_1 was difficult, if not impossible. The O-acetylated coal clings to the side of the pyrex tube obscuring the coal bed. Clearly this is undesirable. Since the height of the coal bed is related to the amount of coal in the tube, a method was sought to normalize the height of the coal bed relative to the amount of coal. An expression equivalent to the ratio H_2/H_1 was used:⁹⁹

$$H_2/H_1 = \overline{(WT/H_1)}(H_2/WT) \quad (44)$$

where $\overline{(WT/H_1)}$ is the average of the weight of an O-acetylated sample divided by the initial height. The use of the average values $\overline{(WT/H_1)}$ assumes that the apparent bulk density of the coal does not change and that any variation in $\overline{(WT/H_1)}$ is due to errors in measuring H_1 .

H_1 is measured as follows. The internal height of the tube is measured when the tube is weighed (to 0.1 cm). After addition of the coal and repeated centrifugation and tapping (assuming that when the other samples have reached the minimum H_1 the tube in question has also reached the minimum H_1), a ruler cut to fit inside the 8mm tube is gently inserted into the tube until it rests lightly on the top of the coal bed. The height from the top of the coal bed to the top of the tube is measured. The difference in the internal height of the empty tube and height measured from the top of the coal bed is taken as H_1 .

D. Removal of Inorganic Matter

1. Citric Acid Wash Procedure¹⁰⁰

Approximately 10 g of coal was weighed into a 500-ml round-bottom flask and 250 ml of 1M aqueous citric acid solution added. The solution was refluxed for approximately 20 hours under nitrogen. After cooling, the mixture was filtered through a weighed, dried Soxhlet extraction thimble. The thimble and coal were placed in a Soxhlet extractor charged with 250 ml of distilled water. After 4-5

days the extraction was stopped. Litmus paper was used to detect the presence of citric acid in the siphon liquid and the extraction was continued until the wash water was neutral. The thimble containing the coal was dried overnight in a vacuum oven at 105-110 °C.

2. Demineralization Procedure

The demineralization procedure developed by Radmacher and Mohrhaurer¹⁰¹ was used here with slight modification.¹⁰²

Approximately 6 g of coal was weighed into a Nalgene beaker.

Approximately 40 ml of 49% aqueous HF solution was added and the mixture heated to 55-60 °C for approximately one hour with stirring under nitrogen. The coal/HF solution was diluted to 600 ml, cooled, and filtered through a medium porosity sintered glass funnel and washed with an additional 150 ml of warm distilled water. The coal was transferred to a glass beaker, approximately 50 ml of 5N HCl added, and the solution heated to 55-60 °C for approximately one hour with stirring under nitrogen. The coal/HCl solution was diluted to 250 ml, filtered through a medium porosity sintered glass funnel and washed with 600 ml of warm distilled water in 25 ml portions. Litmus paper was used to check for acidity in the wash water. The coal was transferred to a tared bottle and dried in a vacuum oven at 110 °C overnight.

E. Hydroxyl Derivatization

1. O-Acetylation

Following the procedure of Blom et al.,¹⁰³ approximately 10 g of dry coal was weighed into a 250-ml round-bottom (rb) flask. 200 ml

of a mixture of acetic anhydride and pyridine (1:2 by volume) was added. The mixture was refluxed with stirring under nitrogen for 24 hours. The mixture was then cooled and transferred to a 1000 ml erlenmeyer flask containing 500 ml of distilled water. This mixture was filtered through a medium porosity Whatman filter using a Buchner funnel under nitrogen. The O-acetylated coal was washed with warm distilled water until free of acid (the wash water was tested with litmus paper) and placed in a vacuum oven at 110 °C to dry overnight. The complete derivatization of the hydroxyl groups was confirmed by diffuse reflectance FT-IR. The FT-IR spectra were obtained by Andrew J. Baskar at Lehigh University.

2. O-Methylation

The basic procedure developed by Liotta et al.¹⁰⁴ was used with a few modifications. Approximately 10 g of coal was weighed into a 500-ml round-bottom flask. 34.5 ml of 1M aqueous tetrabutylammonium hydroxide, 100 ml THF, and 17.5 ml of methyl iodide were added. The mixture was allowed to stir overnight under nitrogen. The mixture was tested with litmus paper and not found to be basic. The mixture was then filtered through a dried Soxhlet extraction thimble (under nitrogen) and washed with an additional 1.5-2.0 l of hot distilled water. The thimble was placed in a Soxhlet extractor charged with approximately 250 ml of distilled water and washed for 5-6 days, under nitrogen. The thimble containing the coal was dried in a vacuum oven

at 105° - 110 °C overnight. Complete O-methylation was confirmed by diffuse reflectance FT-IR. The FT-IR spectra were obtained by Andrew J. Baskar at Lehigh University.

F. Solvent Extraction

1. Pyridine Extraction

Approximately 10 g of dried coal was placed in a dried, tared Whatmann cellulose thimble (30mm x 70mm). The thimble was placed in a Soxhlet extractor which contained 230-250 ml of pyridine. The extraction was continued until the siphon liquid was colorless or nearly so under nitrogen. On the average, each extraction required 7 days for completion. The thimble containing the insoluble coal residue was removed from the extractor and dried under vacuum at 110°C overnight. The pyridine was removed from the siphon liquid using a rotary evaporator. The extract was dried under vacuum at 110 °C overnight.

2. N-Methyl-2-Pyrrolidone Extraction

Approximately 10 g of dried Illinois #6 coal was placed in a dried, tared Whatmann cellulose thimble. The thimble was placed in a Soxhlet extractor which contained approximately 230 ml of freshly distilled N-methyl-2-pyrrolidone (NMP). The extraction was continued until the siphon liquid was pale yellow (the color of pure N-methyl-2-pyrrolidone). All extractions were performed under nitrogen. On the average, each extraction required 12 days for

completion. The temperature of the extraction was measured by suspending a thermometer in the Soxhlet extractor such that the thermometer was in contact with the coal in the thimble. The average extraction temperature was $165^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The boiling point of NMP is 202°C at 760 mm Hg and it is difficult to remove by ordinary vacuum drying. As a result, after completion of the initial NMP extraction, a second solvent was used to wash the residual NMP from the insoluble coal. One of three solvents was used: methanol, tetrahydrofuran (THF), and water. The second extraction continued for an additional seven days. After the NMP extraction, the excess NMP was removed from the extract using a rotary evaporator and the NMP extract was dried under vacuum at approximately $140\text{--}150^{\circ}\text{C}$ overnight. After the second solvent wash, the thimble containing the insoluble coal residue was removed from the extractor and dried in a vacuum oven at 110°C overnight.

G. Repetitive Swelling Measurements

0.3 to 0.8 g of dried, pyridine-extracted Illinois #6 coal was placed in an 8 mm pyrex tube. As before, the tube was placed in a centrifuge and after centrifugation, the height of the coal bed was measured (H_1). Approximately 1-3 ml of solvent was added to the tube, mixed thoroughly with the coal and the tube allowed to stand vertically for a minimum of 24 hours. The tube was recentrifuged and the height of the coal bed measured (H_2). The volumetric swelling ratio, $Q_{v,dry}$, is given by H_2/H_1 . The supernatant solvent was removed

by evaporation with nitrogen. The tube containing the moist coal was placed in a vacuum oven overnight at 110 °C to remove residual solvent. The procedure was repeated an additonal two times using the same sample and tube. H_1 was remeasured each time.

CHAPTER IV

RESULTS AND DISCUSSION

A. Repetitive Swelling

Solvent swelling studies provide an impressive piece of evidence supporting the macromolecular nature of coals. The work presented here is based on the three dimensionally crosslinked macromolecular structural model for coals. Solvent swelling experiments are employed to characterize the network structure of the coal. In particular, the crosslink density, ρ_x , and number average molecular weight between crosslinks, $\overline{M}_c$, may be determined from the solvent swelling studies. Recently, the estimation of the crosslink density and $\overline{M}_c$ via solvent swelling studies in non-polar solvents has been criticized.⁷² In the Hsieh and Duda⁷² study, a high volatile bituminous coal was swollen gravimetrically with a series of non-polar solvents at various solvent activities. The solvent activity was varied by controlling the vapor pressure of the solvent in the system. The solvent was then desorbed and the same coal sample reswollen. Upon reswelling, the coal sample did not absorb the same amount of organic vapor. The gravimetric swellings were not reproducible. The results of the gravimetric swellings using tetralin as a solvent at 110 °C are illustrated in Figure 33.⁷² An explanation suggested⁷³ for the observed behavior is that the coal/solvent system did not reach equilibrium. If equilibrium

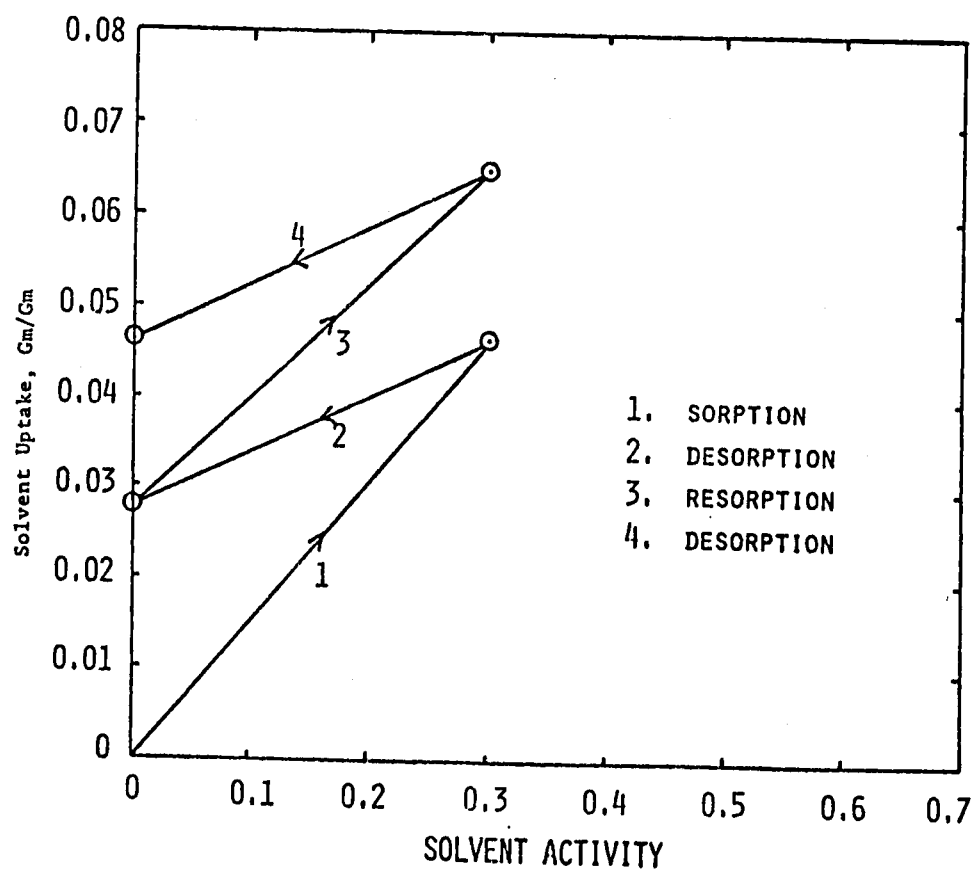


Figure 33. Plot of Solvent Uptake Versus Solvent Activity for PSOC-375 Coal at 110°C.

Source: S.-T. Hsieh and J. L. Duda, "The Dependence of Liquefaction Behavior on Coal Characteristics; Part V.: The Penetration of Solvent Vapor into Coal Particles, "Final Technical Report for the Period March 1981 - February 1984, DOE Contract No. AC22-81PC40784, April, 1984. p. 98.

is not reached, the swelling data cannot be used to determine $\overline{M}_c$ and crosslink density of the coal.

The volumetric swelling procedure has been shown to be equivalent to the gravimetric method when corrections are made for the pore volume.⁶ Repetitive volumetric swelling measurements were performed on pyridine-extracted Illinois #6 coal using three non-polar solvents to test the reproducibility of the method. If thermodynamic equilibrium is being reached, repetitive swelling of the same sample should give the same results. The results of the repetitive swellings are presented in Table XVIII. Clearly, the volumetric swellings are reproducible indicating the samples reach thermodynamic equilibrium. In addition, Brenner³⁵ has observed reversible swelling when polar organic solvents were used as the swelling solvent.

The observed discrepancy between the repetitive gravimetric and volumetric swellings is not readily explained but several factors may play a role. The swelling of coal by organic vapors may be restricted by layers of gas trapped in the coal pore system.⁶ Green⁶ observed different swelling rates, but not final swelling values, between evacuated and unevacuated samples when exposed to solvent vapors at the same solvent activity. In addition, different swelling rates have been observed between liquid and vapor at the same activity. Hsieh and Duda^{72,73} did evacuate the coal samples prior to the initial swelling so stagnant gas layers cannot account for the discrepancy in the swelling methods. Regardless, the observation of non-reversible gravimetric swelling^{72,73} in itself is not sufficient evidence to disprove the macromolecular nature of coals, but merely emphasizes the complex nature of coals.

TABLE XVIII

REPETITIVE SWELLINGS OF PYRIDINE EXTRACTED ILLINOIS #6 COAL
IN THREE NON-POLAR ORGANIC LIQUIDS

Solvent	First Measurement	$Q_{v,dry}$	
		First Repeat	Second Repeat
Chlorobenzene	1.5	1.5	1.5
	1.6	1.6	1.5
	1.5	1.5	1.5
	1.5	1.5	1.5
Toluene	1.5	1.5	1.5
	1.5	1.5	-
	1.6	1.5	1.5
	1.5	1.5	1.5
	1.5	-	-
	1.5	1.5	-
THF	2.0	1.9	1.9
	2.0	1.8	2.0
	2.1	1.9	-
	2.0	1.9	-
	2.1	1.9	1.9
	2.1	1.9	1.9

Hsieh and Duda^{72,73} simultaneously calculated the $\overline{M}_c$ and Chi parameter, χ , of a bituminous coal using swelling data obtained at four different solvent activities using the same solvent. Table XIV⁷², p. 104, contains the resulting χ and $\overline{M}_c$ values.⁷² $\overline{M}_c$ was calculated using the Flory-Rehner,³⁶ Lucht and Peppas,⁷ and Kovac Equations.⁵⁰ Obviously, the values of $\overline{M}_c$ and χ are unreasonable. The analysis of the data hinges on one key assumption: χ is concentration independent. This is generally not true.^{36,51} In some simple polymeric systems, the assumption is not unreasonable since the concentration dependence of χ was shown to be very small.¹⁰⁵ Even in some well-characterized polymeric systems, however, χ is strongly concentration dependent.^{51,80} By definition, χ is a measure of the "goodness" of a solvent^{36,51} and depends on the interactions of the solvent with the coal network. Coal is much more complex than the polymeric systems referred to previously. The presence of hydrogen bonds and the possibility of significant London forces, and other weaker interactions also complicate the overall picture. Any assumption that χ is concentration independent is not justified without experimental verification.

B. Presence of Hydrogen Bonds

Solvent swelling has been successfully applied to bituminous coals⁶ to characterize the number average molecular weight between crosslinks, $\overline{M}_c$, the crosslink density, ρ_x , and the number of hydrogen bonds.⁶ This technique has not been applied to lignites and

subbituminous coals. The purpose of the work described in this section is twofold: first, to ascertain whether the solvent swelling approach can be applied to the lower rank coals and second, to characterize the hydrogen bond network in the lower rank coals.

The role of hydrogen bonds in coals has received a great deal of attention. Several models for coal structure have included the presence of hydrogen bonds. Brown and Waters^{21,22} proposed that the micellular structure of coals was bound by hydrogen bonds and weaker van der Waals forces. The Sternberg model^{23,24} of coal structure promotes the concept that coals consist of a wide distribution of macromolecules which are held together by dispersion forces and hydrogen bonds. Hombach²⁵⁻²⁸ proposed in a series of papers that coal consists of highly entangled macromolecules. The three-dimensionally crosslinked macromolecular structure model acknowledges the presence of hydrogen bonds in addition to covalent crosslinks.^{6,7,96}

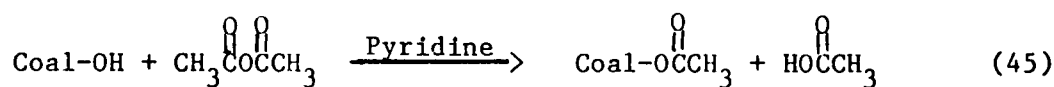
Low rank coals are rich in hydroxyl and carboxyl^{1,93,103} groups which are capable of participating in the formation of hydrogen bonds. The presence of hydrogen bonds in coals has been demonstrated by a variety of experimental approaches. Padrick and Lockwood¹⁰⁶ depolymerized a Wyodak subbituminous coal under mild conditions and proposed that the depolymerization was a result of the disruption of hydrogen bonds. The presence of hydrogen bonds in bituminous coals was demonstrated by Green,⁶ using solvent swelling techniques. The hydrogen bonds were shown to play an important role in the macromolecular structure of the coals studied. In addition, Larsen et al.⁷⁷ demonstrated using the solvent swelling technique that in native

bituminous coals, the strength of the hydrogen bonds ranges from 5 to 8 kcal/mole. Brenner³⁵ was able to obtain information on the hydrogen bonding in coals by examining the swelling of thin slices of coal upon exposure to a variety of solvents using optical transmission spectroscopy. Larsen and coworkers¹⁰⁷ argued that most hydroxyl groups in coals are hydrogen bonded. In the study, the hydroxyl groups in the coal were converted to the $-\text{OSnBu}_3$ derivatives and analyzed using Sn Mossbauer spectroscopy. The IR spectra of coals also indicate the presence of hydrogen bonds.¹⁰⁸⁻¹¹⁰ Liotta^{43,104} also demonstrated the presence of a hydrogen bond network in bituminous and lower rank coals by selectively O-methylating the hydroxyl groups. The complete derivatization of hydroxyl groups in the coal was confirmed by FT-IR and ^{13}C NMR.

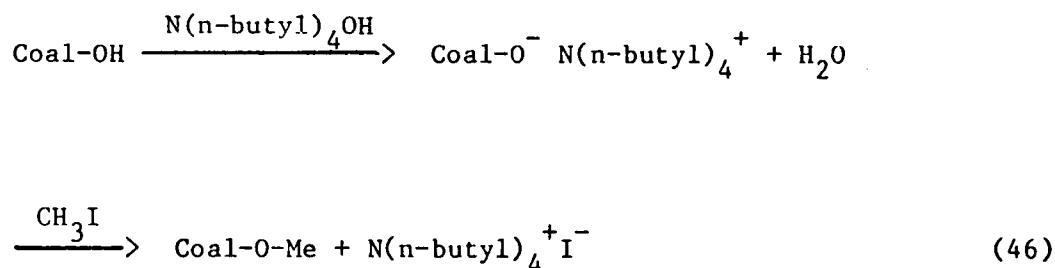
The presence of hydrogen bonds need not necessarily have an impact on the macromolecular structure of a coal. A hydrogen bond may form on a network chain without effecting the three dimensional structure. Or the hydrogen bond may form at two sites on the network chain and create a loop which will have an influence. A hydrogen bond will have an effect on the network structure of the coal if it is formed between two different network chains. The basic idea of the solvent swelling experiment is straightforward. The coal with hydrogen bonds intact is swollen with a series of solvents. The hydroxyl groups are derivatized to eliminate hydrogen bonding and the coal swollen in the same series of solvents. The swelling ratios of the coal before and after derivatization are then compared. If the

hydrogen bonds did play an active role in the macromolecular structure of the coal, the swelling will be enhanced after derivatization.

Two methods were employed for derivatization of the hydroxyl groups are 1) O-acetylation and 2) O-methylation. The O-acetylation reaction is a well-established procedure¹⁰³ and consists of refluxing the coal in a 2:1 mixture of pyridine and acetic anhydride.



Generally, the extent of reaction is confirmed by examination of the 3400 cm^{-1} region in the FT-IR spectrum. Synder et al.¹¹¹ demonstrated the O-acetylation procedure does derivatize all the hydroxyl groups present. The O-methylation procedure was developed by Liotta,^{43,104} and consists of reacting the coal in an aqueous THF solution of tetra-n-butyl ammonium hydroxide, followed by addition of methyl iodide.



Again the extent of reaction was determined spectroscopically. In order to demonstrate the effectiveness of the derivatization procedures, in the work presented here, the diffuse reflectance FT-IR

spectra of the dry, O-acetylated, and O-methylated Rawhide coals are presented in Figures 34, 35, and 36, respectively. Clearly, the complete derivatization of the hydroxyl groups is demonstrated.

While the two procedures employed produce the same net effect, the derivatization of the hydroxyl groups, there are some notable differences, particularly in the solvents employed. The O-acetylation reaction uses pyridine at reflux temperature as a solvent and, as a result, considerable material is extracted from the coal. The coal is simultaneously extracted and acetylated. The O-methylation reaction uses THF as a solvent at room temperature. Under these reaction conditions, very little material is expected to be extracted from the coal. The coal is methylated without being extensively extracted.

Non-polar solvents were used for the swelling experiments to satisfy the requirements of regular solution theory. In addition, the non-polar solvents cannot disrupt the hydrogen bond network. If hydrogen bonds do serve as crosslinks, then a given non-polar solvent should swell the coal which has been derivatized to remove hydrogen bonds more than the native coal which has its hydrogen bond network intact. Essentially, the coal derivatized to remove hydrogen bonds will have a lower crosslink density. If the hydrogen bonds that are present do not serve as network active crosslinks, there should be no difference in the swelling behavior.

The volumetric swelling ratios, $Q_{v,dry}$, were measured on the dried, pyridine extracted, O-acetylated, and O-methylated Rawhide, Big Brown Lignite, and Texas Lignite using non-polar solvents with a variety of solubility parameters. The swelling ratios obtained are

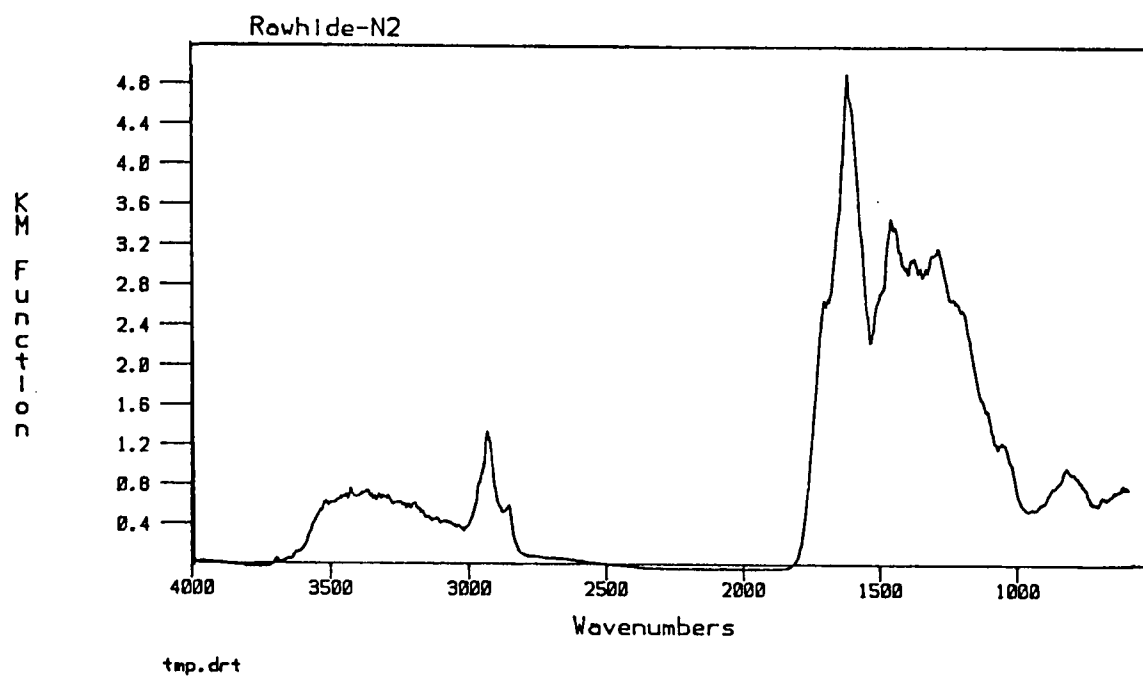


Figure 34. Diffuse Reflectance FT-IR Spectrum of Dry, Unextracted Rawhide Coal.

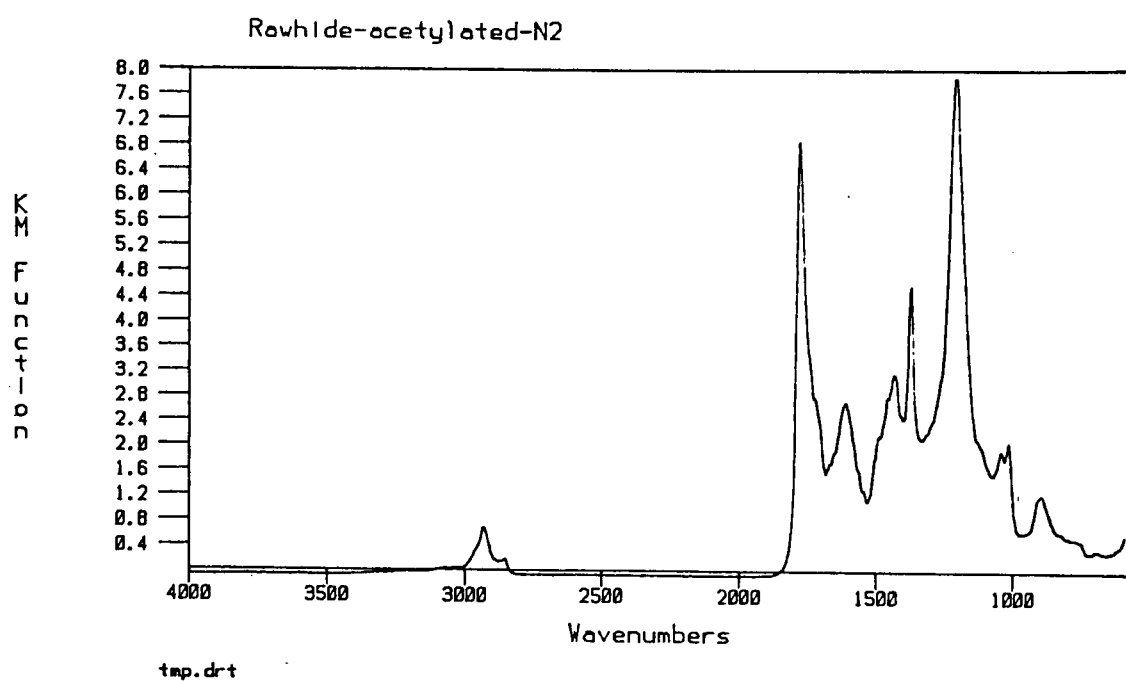


Figure 35.. Diffuse Reflectance FT-IR Spectrum of Dry, O-Acetylated Rawhide Coal.

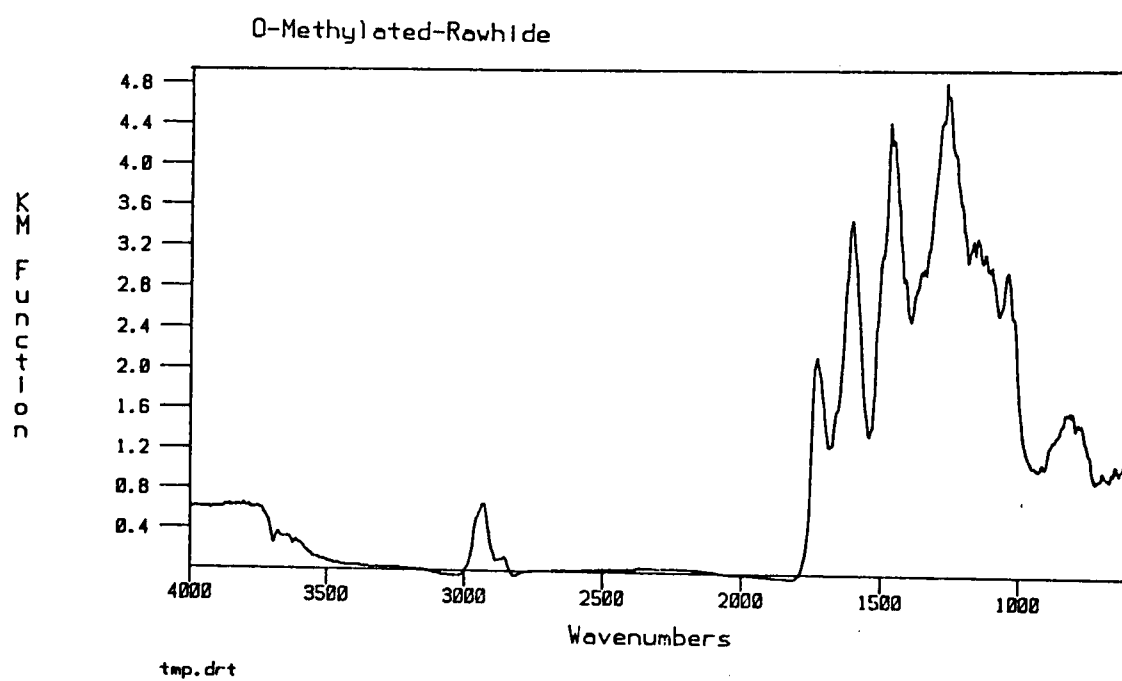


Figure 36. Diffuse Reflectance FT-IR Spectrum of Dry, O-Methylated Rawhide Coal.

listed in Tables XIX, XX, and XXI. Big Brown Lignite and Texas Lignite are coals from the same seam, but the Big Brown Lignite has been subjected to adventitious mild oxidation. The swelling ratios were also plotted versus the solubility parameters and are shown in Figures 37, 38, and 39.

Examination of the swelling ratios contained in the Tables XIX-XXI indicates that the swelling in the non-polar solvents with solubility parameters in the range of 9 to 10 (cal/cm³)^{1/2} increases after derivatization of the hydroxyl groups by O-acetylation or O-methylation. If the hydroxyl groups form hydrogen bonds which are serving as effective crosslinks in the coal network, the swelling is expected to increase after removal of the hydrogen bond network, as is observed.

From Tables XIX-XXI, the pyridine extracted coals generally do not show an enhancement in swelling compared with the native coal. The pyridine extractabilities of the Rawhide, Texas Lignite, Big Brown Lignite, and S. Beulah coals are presented in Table XXII. In the case of bituminous coals⁶, it was observed that the pyridine extraction partially disrupted the hydrogen bond network. The pyridine extracted coals were observed to swell (in non-polar solvents) to an intermediate level between the native coals and the coals derivatized to remove the hydrogen bonds. Green⁶ suggested two rationales for the observed intermediate swelling of the pyridine-extracted bituminous coals. The first rationale acknowledges the possibility that uncrosslinked material may be hydrogen bonded to two separate network chains, effectively linking the two chains together. After removal of

TABLE XIX

VOLUMETRIC SWELLING RATIOS, $Q_{v,dry}$, OF DRIED, PYRIDINE-EXTRACTED, O-ACETYLATED, AND O-METHYLATED RAWHIDE COAL USING NON-POLAR SOLVENTS

Solvent	$Q_{v,dry}$			
	Dry	PEXT ^a	ACT ^b	MET ^c
Benzene	1.1	1.2	1.4	1.5
Toluene	1.2	1.1	1.3	1.5
O-xylene	1.1	1.0	1.3	1.4
Cyclohexane	1.0	1.0	1.0	1.1
n-Pentane	1.0	1.0	1.1	1.1
Tetralin	1.2	1.2	1.6	1.5
Chlorobenzene	1.3	1.2	1.5	1.6
Carbon Disulfide	1.3	1.3	1.2	1.3
Acetonitrile	1.4	1.4	1.4	1.4

^aPEXT = Pyridine extracted.

^bACT = O-Acetylated.

^cMET = O-Methylated.

TABLE XX

VOLUMETRIC SWELLING RATIOS, $Q_{v,dry}$, OF DRIED, PYRIDINE-EXTRACTED, O-ACETYLATED, AND O-METHYLATED BIG BROWN LIGNITE USING NON-POLAR SOLVENTS

Solvent	Dry	$Q_{v,dry}$		
		PEXT ^a	ACT ^b	MET ^b
Benzene	1.2	1.3	1.6	1.5
Toluene	1.2	1.2	1.6	1.4
Carbon Disulfide	1.3	-	1.4	1.5
O-xylene	1.2	1.1	1.6	1.5
Cyclohexane	1.1	1.1	1.4	1.1
Tetralin	1.2	1.2	1.6	1.5
Acetonitrile	-	1.4	1.4	1.2

^aPEXT = Pyridine extracted.

^bACT = O-Acetylated.

^cMET = O-Methylated.

TABLE XXI

VOLUMETRIC SWELLING RATIOS, $Q_{v,dry}$, OF DRIED, PYRIDINE-EXTRACTED, AND O-ACETYLATED TEXAS LIGNITE USING NON-POLAR SOLVENTS

Solvent	Dry	$Q_{v,dry}$	
		PEXT ^a	ACT ^b
Benzene	1.2	1.2	1.5
Toluene	1.2	1.2	-
Carbon Disulfide	1.2	1.2	1.2
O-xylene	1.1	1.1	1.4
Cyclohexane	1.1	1.1	1.1
Tetralin	1.1	1.1	-
Acetonitrile	1.4	1.4	1.5

^aPEXT = Pyridine-extracted.

^bACT = O-Acetylated.

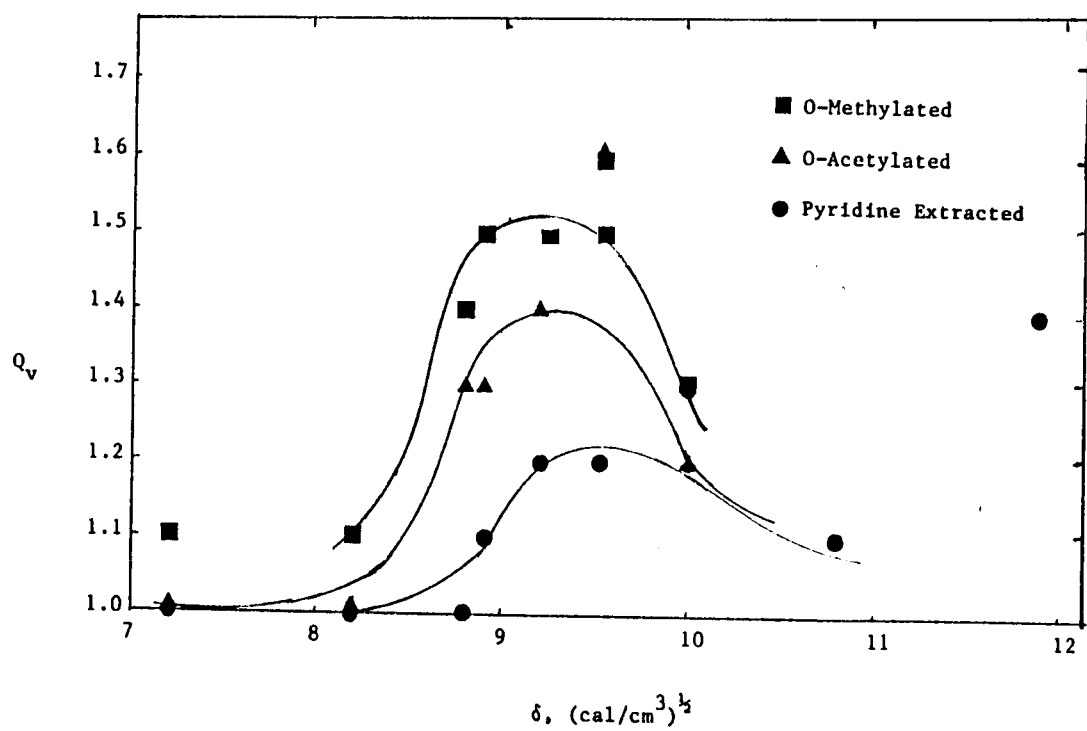


Figure 37. Plot of Swelling Ratio Versus Non-Polar Solubility Parameter of Solvent for Rawhide Coals.

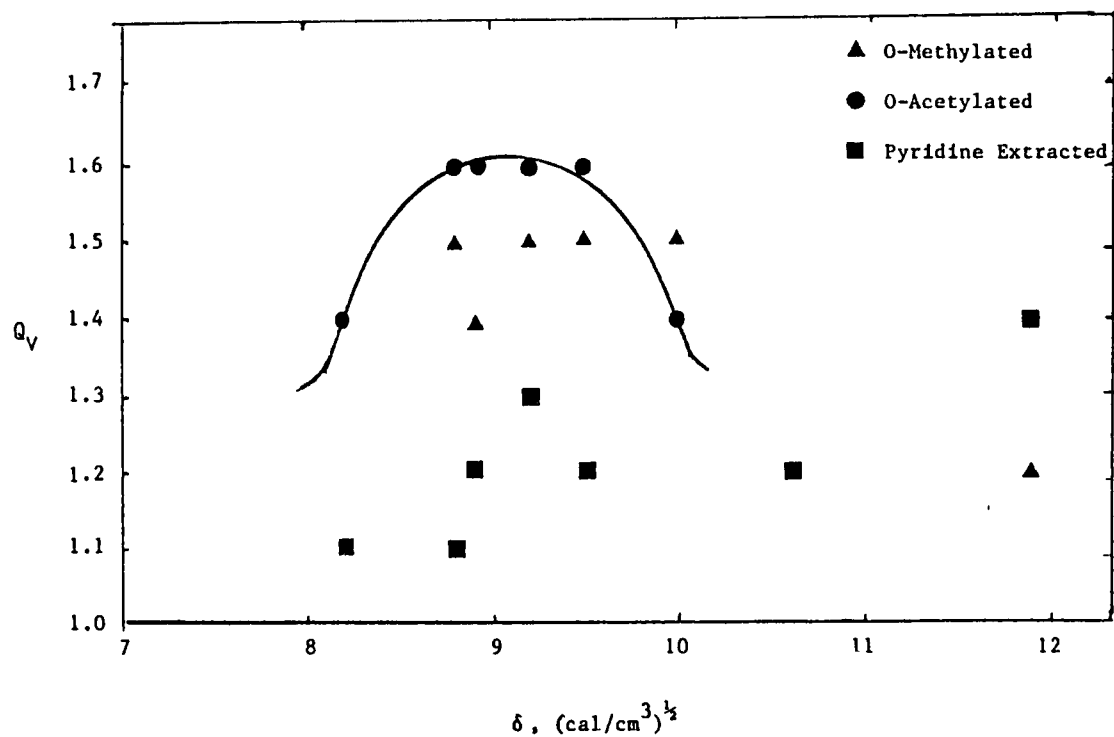


Figure 38. Plot of Swelling Ratio Versus Non-Polar Solubility Parameter of Solvent for Big Brown Lignites.

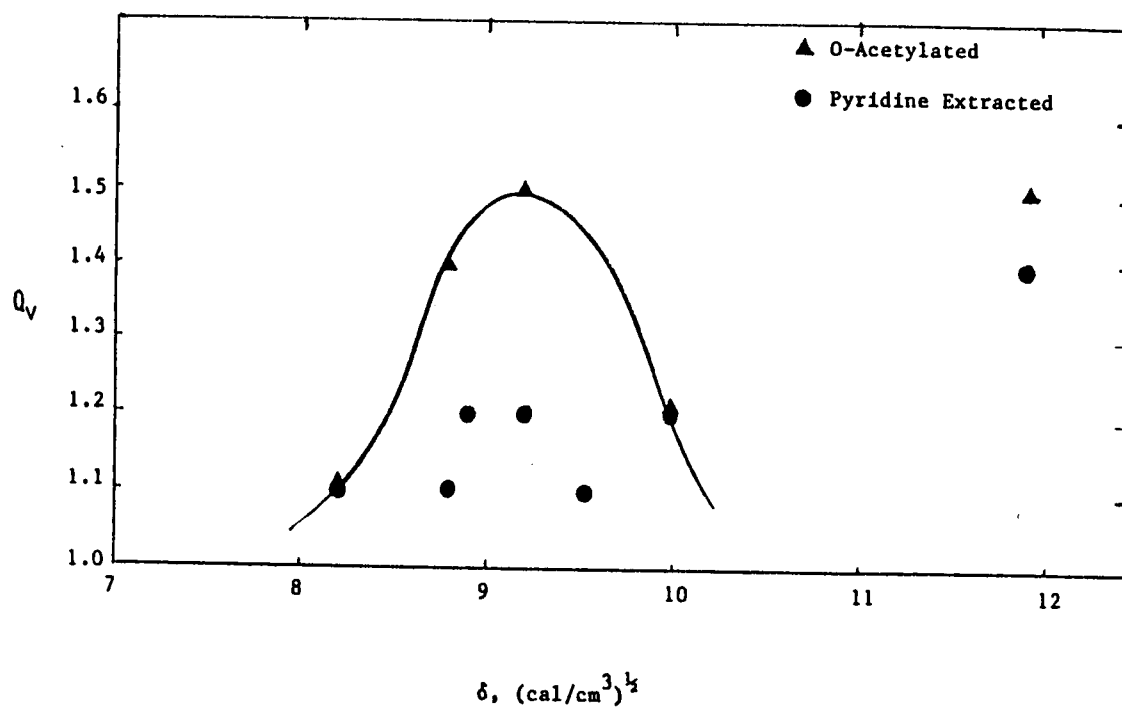


Figure 39. Plot of Swelling Ratio Versus Non-Polar Solubility Parameter of Solvent for Texas Lignites.

TABLE XXII

THE PERCENT PYRIDINE EXTRACTION OF RAWHIDE, TEXAS LIGNITE, BIG
BROWN LIGNITE, AND SOUTH BEULAH COALS

Coal	% Extraction ^a
Rawhide	5.35
Texas Lignite	5.90
Big Brown Lignite	7.47
South Beulah	6.99

^aBased on yield of extract.

the uncrosslinked material by solvent extraction, the network chains bridged by the uncrosslinked material are no longer bound to one another. Essentially the coal network is loosened. Subsequently, the two network chains may or may not participate in hydrogen-bonding, to reform the crosslink, but the possibility exists. The second rationale focuses on the formation of hydrogen bonds between different network chains. Pyridine, a good hydrogen bond acceptor, can disrupt a hydrogen bond between two functional groups. After removal of pyridine, the displaced hydrogen bond complex may or may not reform. The possibility that pyridine does not disrupt all the hydrogen bond complexes also exists. Neither rationale completely explains the observed behavior of the lower rank coals which show little difference in swelling after pyridine extraction. Brenner³⁵ has elegantly demonstrated, however, that pyridine does interrupt all the hydrogen bonds in bituminous coals and that the hydrogen bonds do reform after the pyridine has been removed from the coal.

Perhaps the key lies in the differences of the pyridine extractabilities of the bituminous and lower rank coals. In the case of the bituminous coals, the weight percent of coal extracted by exhaustive Soxhlet extraction with pyridine is approximately 20%⁶. The pyridine extractability of the lower rank coals is often 10% or less. There may be less material in the coal which is not a part of the network, a requirement for solubility. The removal of the uncrosslinked material would then have only a small effect on the network structure. Another possibility is that pyridine is not the optimum solvent for extraction of the low rank coals. It is important

to note, however, that pyridine is one of the best solvents for swelling the low rank coals. Swelling ratios of 2.4, comparable with those exhibited by higher rank coals, have been observed. If pyridine were a poor solvent for the lower rank coals, one might expect the solvent swelling results would reflect the solvent extraction results. Regardless of the explanation, the overall effect of the pyridine extraction on the swelling behavior of the low rank coals is negligible.

The solvent swelling studies are merely a general indication of the behavior of the coals before and after removal of the hydrogen bond network. The next step in the analysis is the determination of the number average molecular weight between crosslinks, $\overline{M}_c$, and the crosslink density, ρ_x , of the coal, which requires the determination of the solubility parameters for the coals and χ values for the coal-solvent pairs. The determination of the solubility parameters will now be discussed.

C. Solubility Parameters of Coals

The determination of $\overline{M}_c$ requires two experimental quantities: v_2 and χ . v_2 is easily obtained from the volumetric swelling measurements. The approach used in this work to determine χ is regular solution theory. Since the regular solution theory approach was shown to work well for bituminous coals,⁶ it was a natural extension to apply the methodology to the low-rank coals. As previously discussed, this approach requires the knowledge of the

solubility parameter of the coal. This section focuses on the determination of the solubility parameter of the coals studied.

Extensive compilations of solubility parameters are found in the literature. The solubility parameters used in this work were taken from the review articles of Hansen,¹¹² Barton,^{89,113} and Gardon.¹¹⁴ The determination of the solubility parameter of an elastomer, in this case coal, was described in Chapter II, Section B and will not be repeated here. In order to assign solubility parameters to the coals studied, the volumetric swelling ratios of the pyridine-extracted Rawhide, Texas Lignite, and Big Brown Lignite were plotted versus the solubility parameters of the solvents. The results for the above coals are shown in Figures 40, 41, and 42, respectively. Clearly, no correlation between the solubility parameter of the solvents and swelling ratio $Q_{v,dry}$, exists. The points appear to be random.

One of the primary assumptions of regular solution theory is that mixing is random. No specific interactions between the elastomer and solvent are allowed. The only interactions permitted are van der Waals interactions. Many of the solvents used are capable of either accepting or donating hydrogen bonds. These interactions are a violation of regular solution theory. As a result, it is not surprising there is no correlation between the observed swelling ratios and the solubility parameters of the solvents.

The only solvents expected to satisfy the requirement of random mixing are the non-polar solvents. Therefore, the swelling ratios of the pyridine extracted coals were plotted versus the solubility parameters of the non-polar solvents. The results are shown in

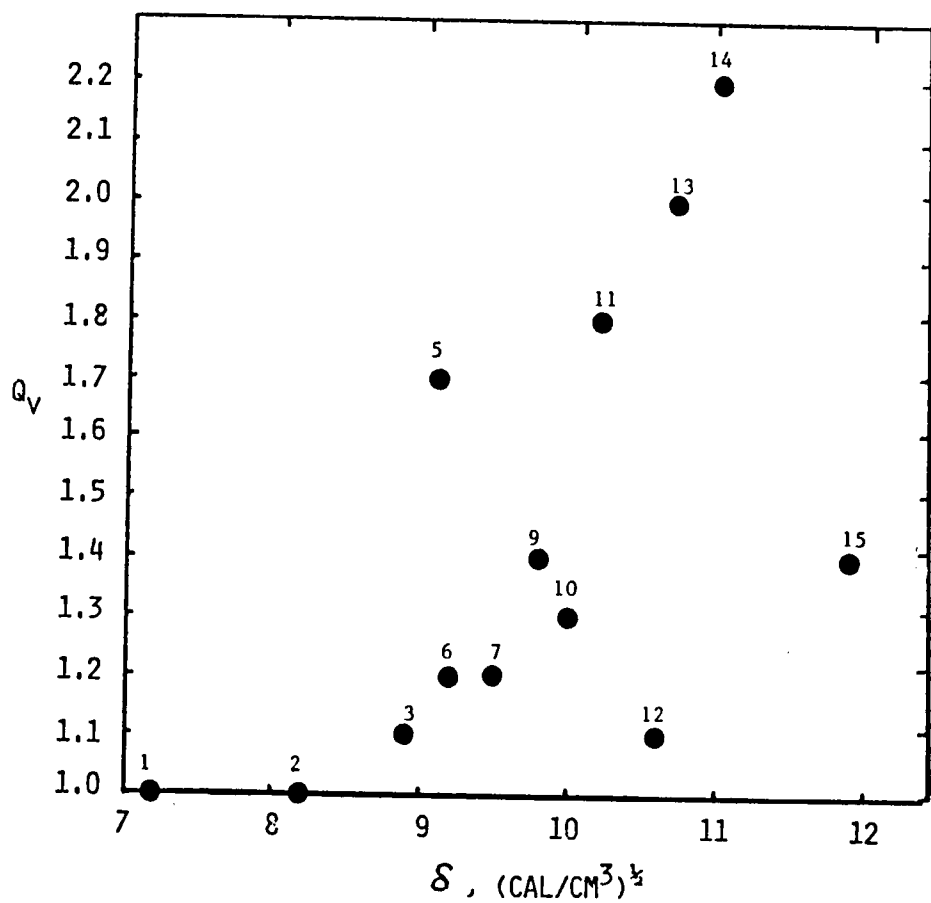


Figure 40. Plot of Swelling Ratio Versus Solubility Parameter of Solvent for Pyridine-Extracted Rawhide Coal. Numbers Indicate Solvents Listed in Table XVII.

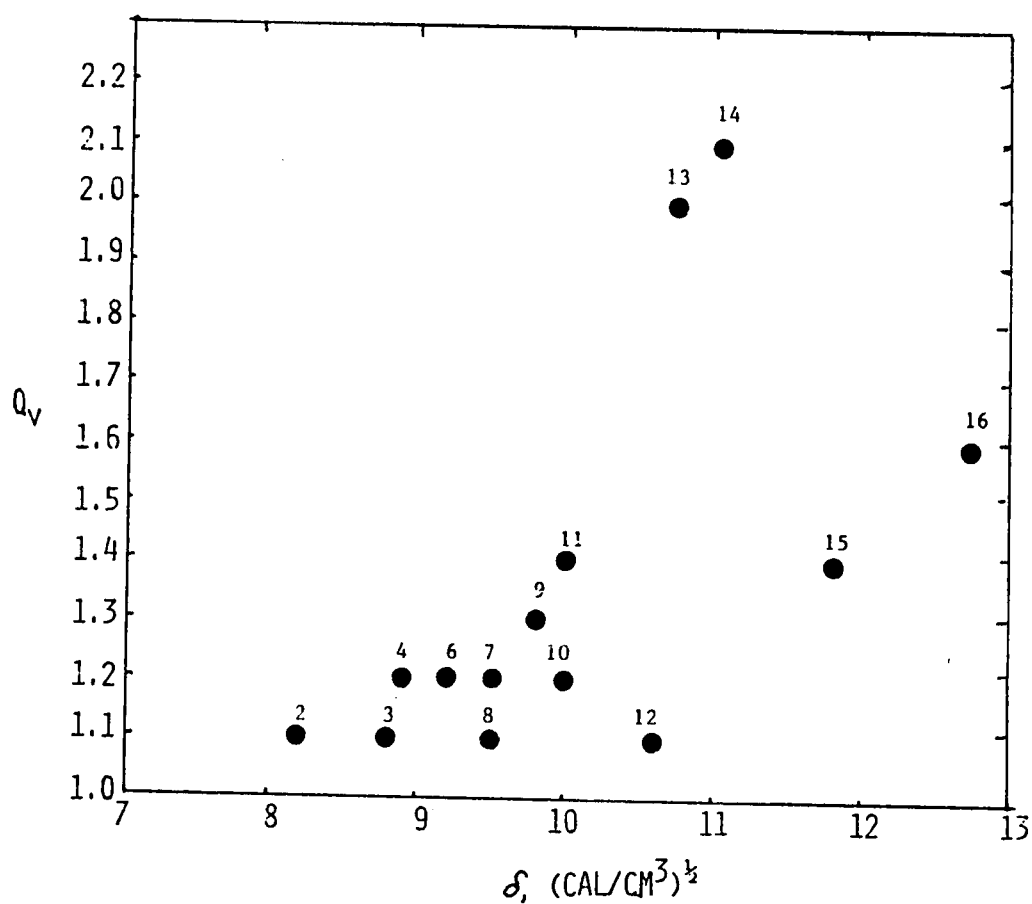


Figure 41. Plot of Swelling Ratio Versus Solubility Parameter of Solvent for Pyridine-Extracted Texas Lignite. Numbers Indicate Solvents Listed in Table XVII.

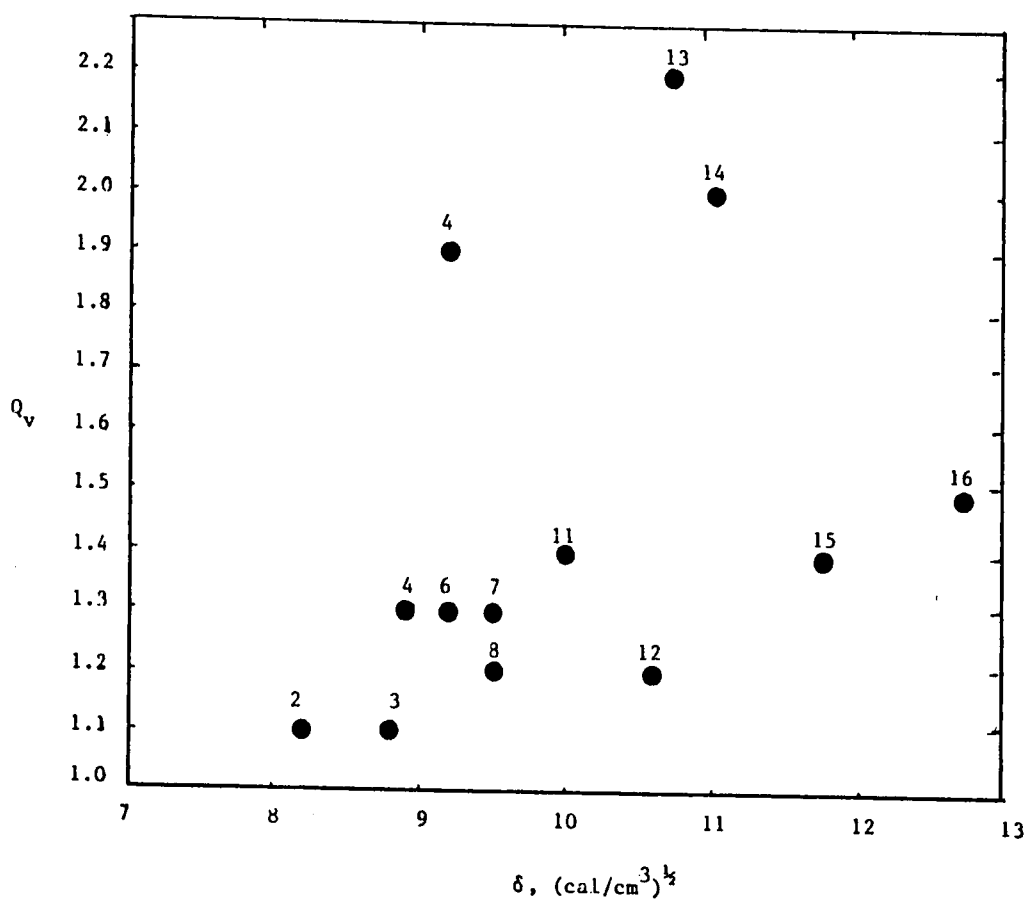


Figure 42. Plot of Swelling Ratio Versus Solubility Parameter of Solvent for Pyridine-Extracted Big Brown Lignite. Nubmers Indicate Solvents Listed in Table XVII.

Figures 43, 44, and 45. The Rawhide subbituminous coal demonstrates regular solution behavior, although not as ideally as the bituminous coals. The two lignite samples indicate a degeneration in regular solution theory behavior. From Figures 44 and 45 the assignment of a solubility parameter for the lignite samples is questionable. From Figure 43, however, the pyridine-extracted Rawhide coal is assigned a solubility parameter of $9.5 \text{ (cal/cm}^3)^{1/2}$.

Clearly, as the rank of the coal decreases, the regular solution theory behavior degenerates. The failure of the regular solution theory approach in the lignite samples is not necessarily surprising. Consider the differences between the bituminous coals and lignites. The bituminous coals have a higher carbon content but lower oxygen content than the lower rank coals. The lignites contain as much as twenty percent more oxygen than the bituminous coals.⁹³ The overall effect of the increased oxygen content in the lignites is a more polar network. Thus the non-polar solvent-coal interactions would be reduced. Essentially, the non-polar solvents are not as effective at swelling the more polar lower rank coals which are expected to be extensively hydrogen bonded.

Thus the coals were derivatized to remove hydrogen bonds by O-acetylation and O-methylation and swollen in the same series of non-polar solvents. Figures 37-39 are plots of the swelling ratios versus the solubility parameters for Rawhide, Big Brown Lignite, and Texas Lignite, respectively. From Figure 37, the O-acetylated and O-methylated Rawhide coals were assigned solubility parameters of $9.2 \text{ (cal/cm}^3)^{1/2}$. From Figures 38 and 39, the O-acetylated Big Brown

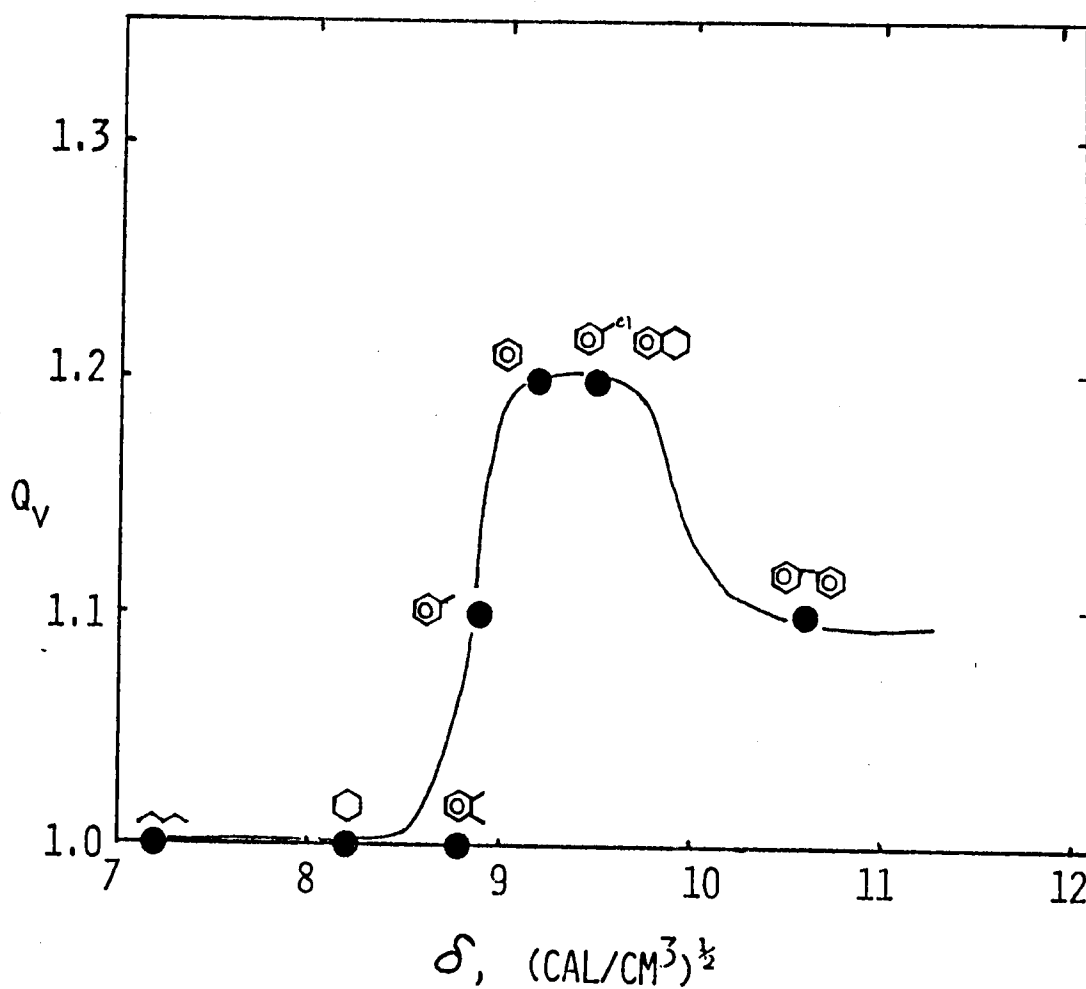


Figure 43. Plot of Swelling Ratio Versus Non-Polar Solubility Parameter of Solvent for Pyridine-Extracted Rawhide Coal.

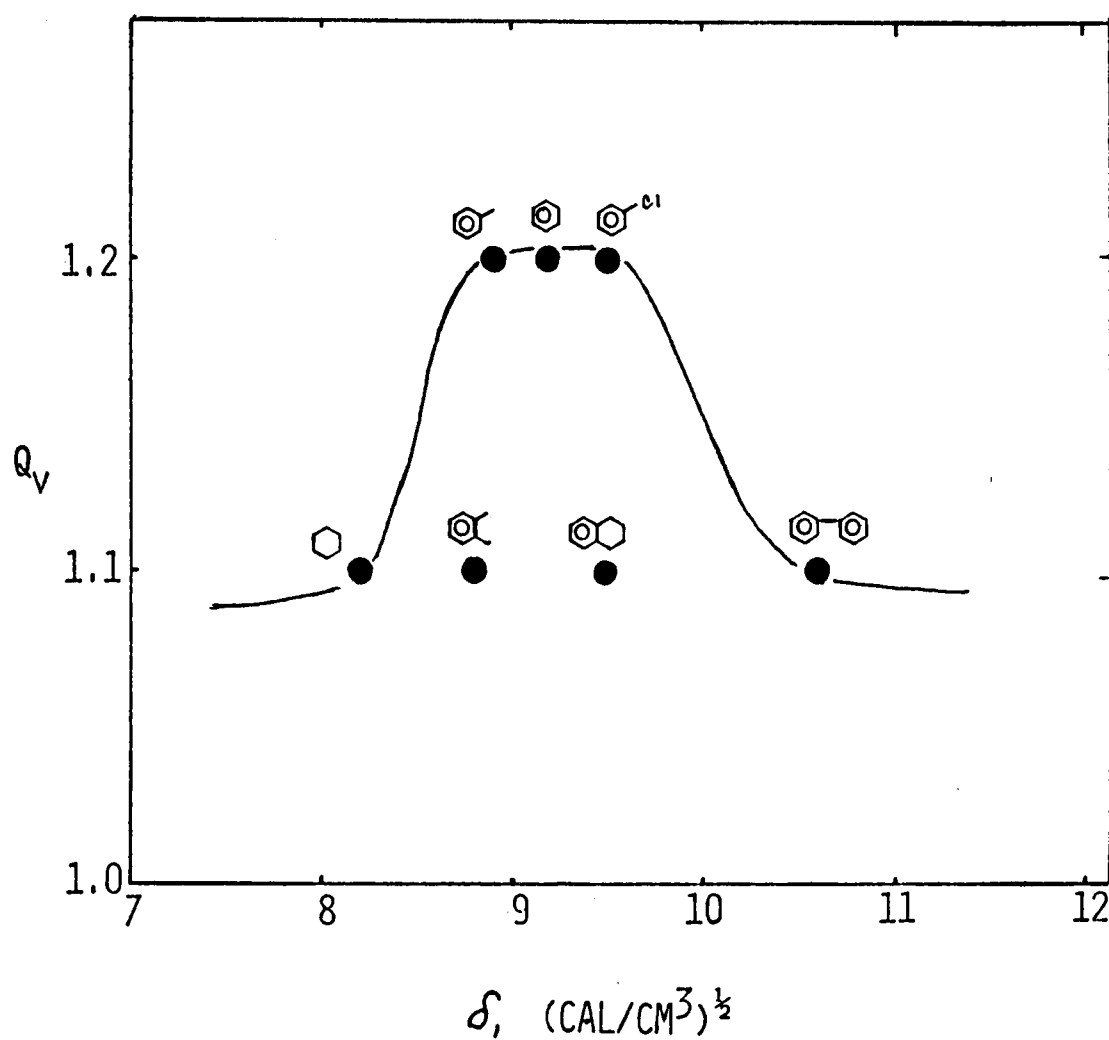


Figure 44. Plot of Swelling Ratio Versus Non-Polar Solubility Parameter of Solvent for Pyridine-Extracted Texas Lignite.

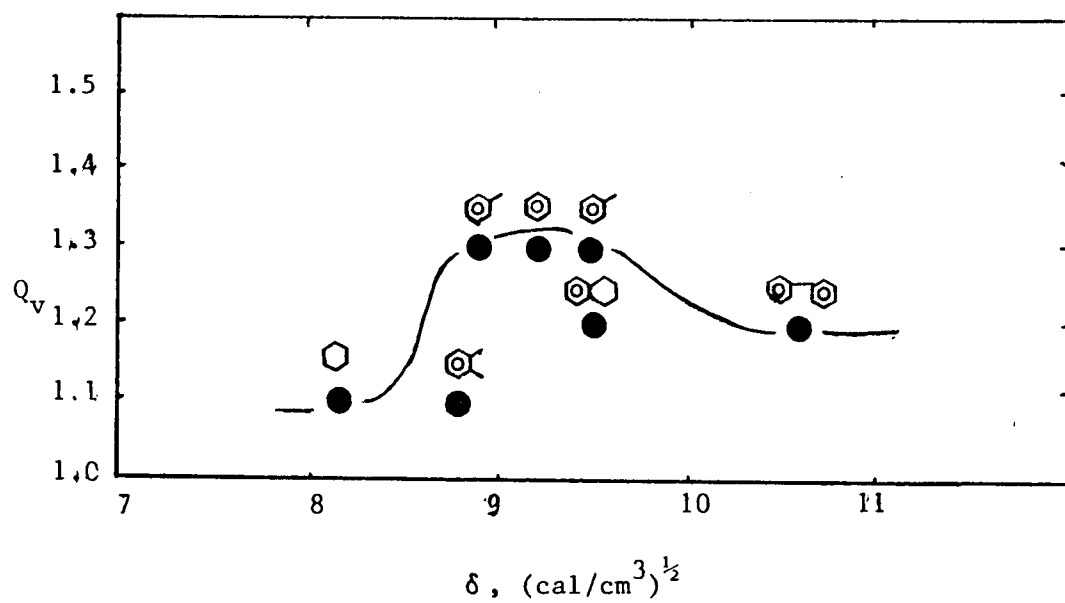


Figure 45. Plot of Swelling Ratio Versus Solubility Parameter of Non-Polar Solvent for Pyridine-Extracted Big Brown Lignite.

Lignite and Texas Lignite follow regular solution theory well enough to allow assignment of solubility parameters. The Big Brown Lignite was assigned a solubility parameter of $9.1(\text{cal}/\text{cm}^3)^{1/2}$. The Texas Lignite was assigned a solubility parameter of $9.2(\text{cal}/\text{cm}^3)^{1/2}$.

The determination of the solubility parameters for the lower rank coals allows calculation of the χ parameters for the coal-solvent pairs and in turn the number average molecular weight between crosslinks, $\overline{M}_c$. The results of those calculations will be presented in Chapter IV, Section E.

D. χ Parameters of Coals

The determination of the χ parameter for a given solvent-elastomer pair requires a knowledge of the solubility parameters of both the solvent and elastomer. The solubility parameters of the coals were determined as described in Chapter IV Section C., using non-polar solvents. The use of non-polar solvents was required to ensure random mixing, thus allowing the calculation of the χ parameters for the coal-solvent pairs using Equation 8. The results are presented in Tables XXIII-XXV. In the calculation of χ , a value of 0.3 was chosen for the entropic contribution, χ_s . This choice of the value of χ_s is arbitrary, but not unreasonable. While χ_s is not independent of the size and shape of a given polymer, other studies have shown for a variety of solvent-polymer systems, the average value of χ_s was found to be approximately 0.3.^{46,58} Green⁶ has shown that use of a constant χ_s does not significantly change the

TABLE XXIII

X PARAMETERS FOR THE NON-POLAR SOLVENTS AND PYRIDINE-EXTRACTED,
O-ACETYLATED, AND O-METHYLATED RAWHIDE COAL

Solvent	$\delta, (\text{cal/cm}^3)^{1/2}$	$V_1 (\text{cm}^3/\text{mol})$	PEXT ^d		ACT, MET ^e	
			X_H^b	X^c	X_H^e	X^c
n-Pentane	7.2	116.2	1.042	1.342	0.788	1.088
Cyclohexane	8.2	108.7	0.311	0.611	0.184	0.485
O-xylene	8.8	121.2	0.101	0.401	0.033	0.333
Toluene	8.9	106.8	0.065	0.365	0.016	0.316
Benzene	9.2	89.4	0.014	0.314	0.000	0.300
Chlorobenzene	9.5	102.1	0.000	0.300	0.016	0.316
Tetralin	9.5	136.0	0.000	0.300	0.021	0.321
Carbon Disulfide	10.0	60.0	0.025	0.325	0.065	0.365
Biphenyl	10.6	154.1	0.316	0.616	0.312	0.612

^a At 25 C.

^b Calculated from Equation 9; the solubility parameter of the pyridine-extracted Rawhide Coal estimated to be $9.5(\text{cal/cm}^3)^{1/2}$.

^c Calculated from Equation 8; X_S equal to 0.3.

^d PEXT = Pyridine-extracted.

^e ACT = O-Acetylated, MET = O-Methylated; Calculated from Equation 9, the solubility parameter of the O-Acetylated and O-Methylated Rawhide Coals estimated to be $9.2(\text{cal/cm}^3)^{1/2}$.

X PARAMETERS FOR THE NON-POLAR SOLVENTS AND O-ACETYLATED BIG BROWN LIGNITE

Solvent	$\delta_1 (\text{cal/cm}^3)^{1/2}$	χ^a	χ_H^b
Chlorobenzene	9.5	0.328	0.028
Benzene	9.2	0.302	0.002
Toluene	8.9	0.307	0.007
O-xylene	8.8	0.318	0.018
Cyclohexane	8.2	0.449	0.149
Carbon Disulfide	10.0	0.382	0.082
Acetonitrile	11.9	0.999	0.699
1,2-Dichloroethane	9.8	0.366	0.066

^aCalculated from Equation 8 ; χ_s equal to 0.3.

^bCalculated from Equation 9 ; the δ of the Big Brown Lignite estimated to be $9.1(\text{cal/cm}^3)^{1/2}$.

X PARAMETERS FOR THE NON-POLAR SOLVENTS AND O-ACETYLATED TEXAS
LIGNITE

Solvent	$\delta_1 (\text{cal/cm}^3)^{1/2}$	χ^a	χ_H^b
Chlorobenzene	9.5	0.316	0.016
Benzene	9.2	0.300	0.000
Toluene	8.9	0.316	0.016
O-xylene	8.8	0.333	0.033
Cyclohexane	8.2	0.484	0.184
Carbon Disulfide	10.0	0.365	0.065
1,2-dichloroethane	9.8	0.348	0.048
Acetonitrile	11.9	0.950	0.650
Tetralin	9.5	0.321	0.021
Biphenyl	10.6	0.812	0.512

^aCalculated from Equation 8 ; χ_s equal to 0.3.

^bCalculated from Equation 9 ; the δ of the Texas Lignite estimated to be $9.2(\text{cal/cm}^3)^{1/2}$.

average value of $\overline{M}_c$ for a coal, but does reduce the experimental scatter.

The determination of the χ parameter and volume fraction of the swollen coal for each coal-solvent pair permits the calculation of the number average molecular weight between crosslinks, $\overline{M}_c$.

E. Calculation of $\overline{M}_c$ Values

The number average molecular weight between crosslinks, $\overline{M}_c$, was calculated from the Flory-Rehner equation (Equation 14). The results of the calculations are presented in Tables XXVI-XXVIII. In all the calculations, the density of the coal was assumed to be 1.3 g/ml. v_2 , the volume fraction of the swollen coal, is defined as $1/Q_{v,dry}$.

Examination of the results in Tables XXVI-XXVIII indicates the following trend in the average $\overline{M}_c$ values: unextracted $\sim$ pyridine extracted < O-acetylated < O-methylated. The result that the O-acetylated and O-methylated samples have larger $\overline{M}_c$ values than the extracted and unextracted coal is expected. Removal of hydrogen bonds increases the chain length between crosslinks. The observation that the unextracted and extracted coals have approximately the same $\overline{M}_c$ is not entirely expected. As discussed previously, the pyridine extraction of a coal will disrupt all accessible hydrogen bonds. After removal of the pyridine some of the hydrogen bonds will reform, but the probability that all the hydrogen bonds reform would appear to be small. The results of the $\overline{M}_c$ calculations in Tables XXVI-XXVIII imply that nearly all the hydrogen bonds disrupted by the pyridine do

TABLE XXVI

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF THE
 DRY, PYRIDINE-EXTRACTED, O-ACETYLATED, AND O-METHYLATED
 RAWHIDE COAL USING THE FLORY-REHNER EQUATION

Solvent	$\overline{M}_c$			
	Dry	Pyridine Extracted	ACT ^a	MET ^b
Chlorobenzene	235	167	398	487
Benzene	92	144	270	341
Toluene	186	113	250	417
Carbon Disulfide	142	142	104	-
O-xylene	132	-	289	383
1,2-Dichloroethane	-	-	325	483
Average	138 ^c	142	273	422

^aACT = O-Acetylated; $\delta_{\text{coal}} = 9.2(\text{cal/cm}^3)^{1/2}$.

^bMET = O-Methylated; $\delta_{\text{coal}} = 9.2(\text{cal/cm}^3)^{1/2}$.

^cDoes not include chlorobenzene data.

TABLE XXVII

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF
BIG BROWN LIGNITE USING THE FLORY-REHNER EQUATION

Solvent	PEXT ^a	$\bar{M}_c$	MET ^c
		ACT ^b	
Chlorobenzene	242	706	498
Benzene	206	417	342
Toluene	176	503	325
Carbon Disulfide	-	203	235
o-Xylene	125	412	474
Cyclohexane	123	409	123
1,2-dichloroethane	263	502	-
Acetonitrile	-	-	245
Average	189	449 ^d	353 ^e

^aPEXT = pyridine-extracted.

^bACT = O-acetylated.

^cMET = O-methylated.

^dExcludes carbon disulfide and chlorobenzene data.

^eExcludes cyclohexane data.

TABLE XXVIII

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF TEXAS
LIGNITE USING THE FLORY-REHNER EQUATION

Solvent	$\bar{M}_c$	
	Pyridine Extracted	O-Acetylated
Chlorobenzene	169	589
Benzene	146	341
Toluene	177	-
Carbon Disulfide	104	104
O-xylene	126	383
Cyclohexane	126	126
1,2-dichloroethane	193	573
Tetralin	289	-
Biphenyl	238	-
Average ^a	174	239

^aExcludes chlorobenzene and 1,2-dichloroethane data.

reform. It is also possible that since pyridine is a poor extraction solvent for the lower rank coals that some hydrogen bonds are not affected by the presence of pyridine. This is not likely, however. The solvent swelling of the subbituminous coal with pyridine indicates that pyridine is one of the best swelling agents for the low rank coals (see Tables XIX-XXI, pp. 132-134). Therefore, the suggestion that pyridine does not interact strongly with the coal network is unwarranted. Examination of the solvent swelling ratios using non-polar solvents supports the similarity in $\overline{M}_c$ values for the extracted and unextracted coals. From Tables XIX-XXI, the solvent swelling ratios are nearly the same in all cases. Thus very similar $\overline{M}_c$ values are expected. One further comment concerning the results in Table XXVI. The $\overline{M}_c$ value for the O-methylated coal is greater than that of the O-acetylated coal. Since both derivatizations have been shown to remove the hydrogen bond network,^{43,103,104} the difference in the $\overline{M}_c$ values is not expected. It may be due to bond breaking during O-methylation.

Recall that the Flory-Rehner equation was derived for long flexible aliphatic chains which obey Gaussian statistics. Clearly, the coal network which consists of large, planar aromatic and hydroaromatic clusters would not be adequately described by the Flory-Rehner equation. Application of the Flory-Rehner equation yields values of $\overline{M}_c$ which are indicative of general trends but are not quantitatively realistic. Therefore the Kovac equation (Equation 15),⁵⁰ which was derived to accommodate the non-Gaussian coal network, was applied. The results are presented in Tables XXIX-XXXI.

TABLE XXIX

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF THE
 DRY, PYRIDINE-EXTRACTED, O-ACETYLATED, AND O-METHYLATED
 RAWHIDE COAL USING THE KOVAC EQUATION

		$\overline{M}_c$				
Dry	N	0.5	0.75	1.0	2.0	3.0
O-xylene		413	319	272	202	179
Toluene		605	464	395	290	256
Benzene		287	221	189	140	124
Carbon Disulfide		620	506	451	366	338
Tetralin		724	557	474	348	306
Average		530	414	356	269	241
$\overline{M}_o$		1059	552	356	135	80
Pyridine-Extracted	N	0.5	0.75	1.0	2.0	3.0
Benzene		483	371	315	232	204
Toluene		348	275	235	174	154
Tetralin		725	557	502	348	306
Average		518	401	351	251	221
$\overline{M}_o$		1037	535	351	126	74
O-Acetylated	N	0.5	0.75	1.0	2.0	3.0
Chlorobenzene		1443	1095	921	659	572
Benzene		945	720	608	439	382
Toluene		845	647	548	399	349
O-xylene		979	749	634	462	404
1,2-Dichloroethane		1179	894	752	539	468
Average ^a		1078	821	692	499	435
$\overline{M}_o$		2156	1095	692	250	145
O-Methylated	N	0.5	0.75	1.0	2.0	3.0
Chlorobenzene		1820	1375	1153	820	709
Benzene		1234	936	787	564	489
Toluene		1510	1145	963	690	599
O-xylene		1341	1021	862	622	542
1,2-Dichloroethane		1859	1401	1171	827	713
Tetralin		1936	1475	1242	891	775
Average		1616	1226	1030	736	638
$\overline{M}_o$		3233	1634	1030	368	213

^a Does not include tetralin data.

TABLE XXX

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF BIG
BROWN LIGNITE USING THE KOVAC EQUATION

		$\bar{M}_c$					
Pyridine Extracted	N	0.5	0.75	1.0	2.0	3.0	
Chlorobenzene		819	627	531	387	338	
Benzene		696	533	451	328	288	
Toluene		572	440	374	275	242	
O-xylene		390	302	257	191	169	
Cyclohexane		384	297	253	188	166	
1,2-dichloroethane		921	701	592	427	373	
Average		630	483	410	299	263	
$\bar{M}_o$		1260	644	410	150	88	
O-Acetylated	N	0.5	0.75	1.0	2.0	3.0	
Chlorobenzene		2795	2098	1785	1232	1058	
Benzene		1560	1179	989	703	608	
Toluene		1879	1420	1191	847	732	
Cyclohexane		1432	1091	920	665	579	
1,2-dichloroethane		1935	1458	1219	861	742	
Average		1921	1449	1476	862	744	
$\bar{M}_o$		3842	1932	1476	431	248	
O-Methylated	N	0.5	0.75	1.0	2.0	3.0	
Chlorobenzene		1860	1406	1179	839	725	
Benzene		1238	939	790	566	491	
Toluene		1140	868	732	529	461	
Carbon Disulfide		943	716	602	431	374	
O-xylene		1720	1305	1097	786	682	
1,2-dichloroethane		1548	1170	981	698	603	
Acetonitrile		798	614	521	383	337	
Average		1321	1003	843	605	525	
$\bar{M}_o$		2642	1337	843	303	175	

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF TEXAS
LIGNITE USING THE KOVAC EQUATION

		$\bar{M}_c$				
Pyridine Extracted, Dry	N	0.5	0.75	1.0	2.0	3.0
Chlorobenzene		552	425	361	265	233
Benzene		476	366	311	229	201
Toluene		578	444	377	277	244
Carbon Disulfide		340	262	222	163	144
O-xylene		394	305	260	333	171
Cyclohexane		394	305	260	193	171
1,2-dichloroethane		653	500	423	308	270
Tetralin		438	339	289	215	190
Biphenyl		744	575	491	364	322
Average		508	391	333	261	216
$\bar{M}_o$		1016	521	333	131	72
O-Acetylated	N	0.5	0.75	1.0	2.0	3.0
Chlorobenzene		2265	1706	361	1008	868
Benzene		1233	936	787	564	—
O-xylene		1341	1021	862	622	542
1,2-dichloroethane		2270	1705	1422	998	856
Average		1777	1342	858	798	755
$\bar{M}_o$		3554	1789	858	399	252

The Kovac equation is similar to the Flory-Rehner equation, but contains an additional term which includes the parameter N . N is the number of repeating units between crosslinks in the short chain model. N is defined as the ratio of the number average molecular weight between crosslinks, $\overline{M}_c$, and the number average molecular weight of the cluster, $\overline{M}_0$, and is given by Equation 16.⁵⁰ N essentially describes the deviation of the coal network from Gaussian behavior. When N becomes infinite, the Kovac equation reduces to the Flory-Rehner equation. The value of N was varied from 0.5 to 3.0.

From the definition of N , the estimation of an $\overline{M}_c$ requires a value of either N or $\overline{M}_0$. The various values of N were then plotted versus $\overline{M}_0$ for the coals. The results are shown in Figures 46-48. N cannot be randomly assigned, therefore a value for $\overline{M}_0$ is necessary to calculate $\overline{M}_c$. A value of 300 was assumed for $\overline{M}_0$. The assignment of a value for $\overline{M}_0$ allows determination of a value of N , and subsequently, $\overline{M}_c$, from Figures 46-48. The results are presented in Tables XXXII-XXXIV.

The results obtained by application of the Kovac equation indicate the same general trends as those found by application of the Flory-Rehner equation. The Kovac equation does yield values which are larger and perhaps more realistic than those obtained by application of the Flory-Rehner equation. The standard deviation of the data in the Texas Lignite and Big Brown Lignite samples is large and therefore there is no significant difference in the $\overline{M}_c$ values reported. As a result, the following discussion will focus on the Rawhide coal results.

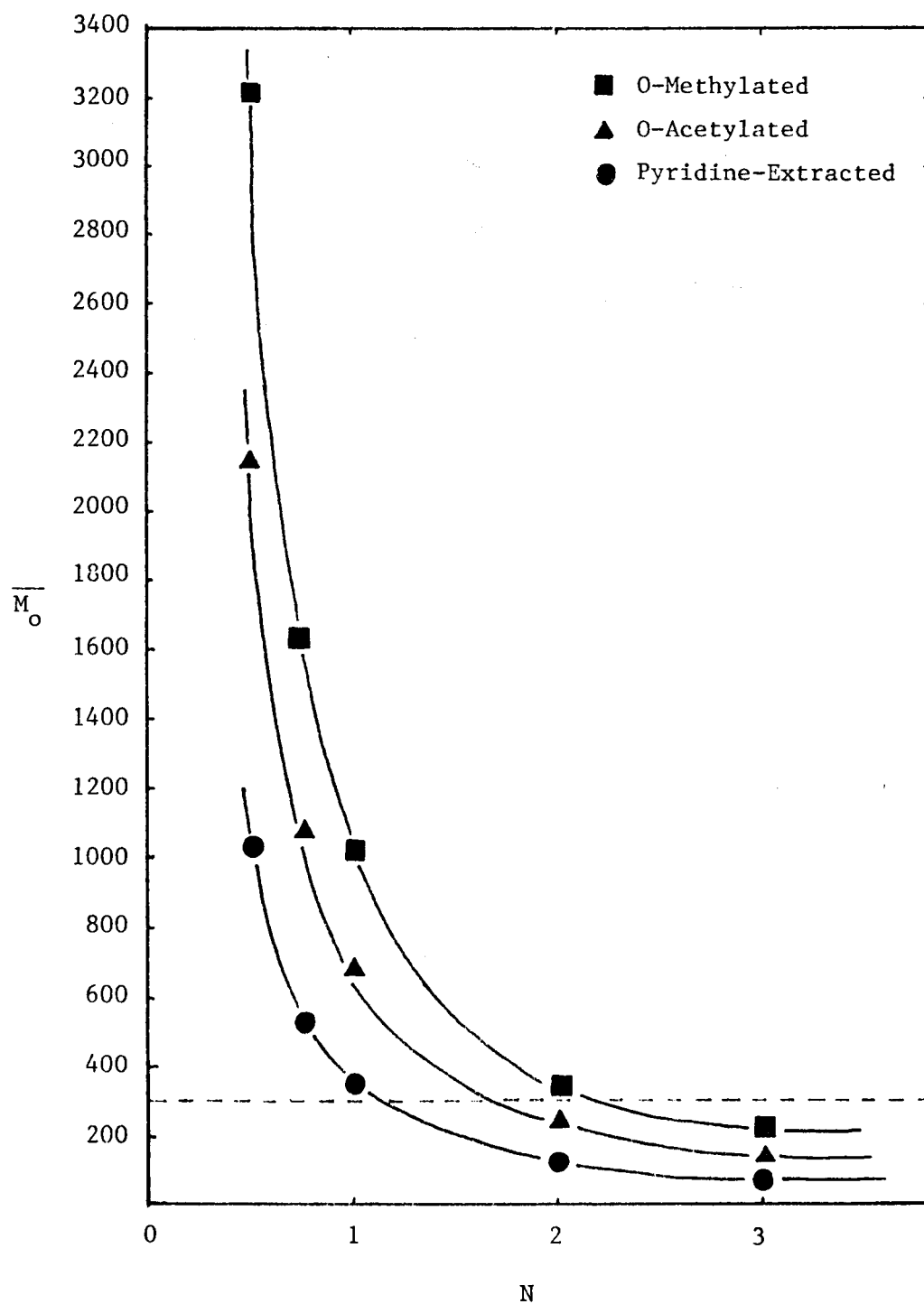


Figure 46. Plot of $\overline{M}_o$ Versus N for Rawhide Coals.

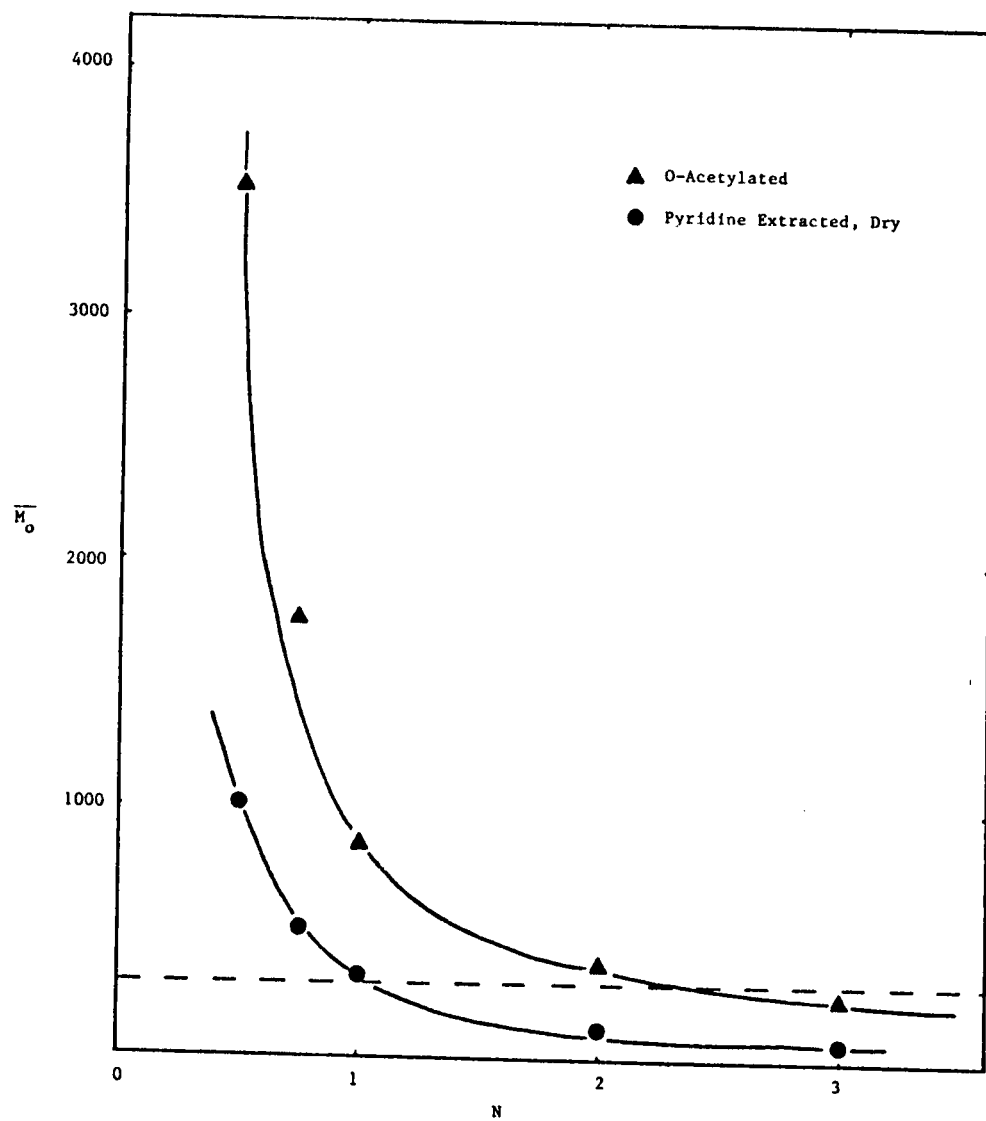


Figure 47. Plot of $\overline{M}_O$ Versus N for Texas Lignites.

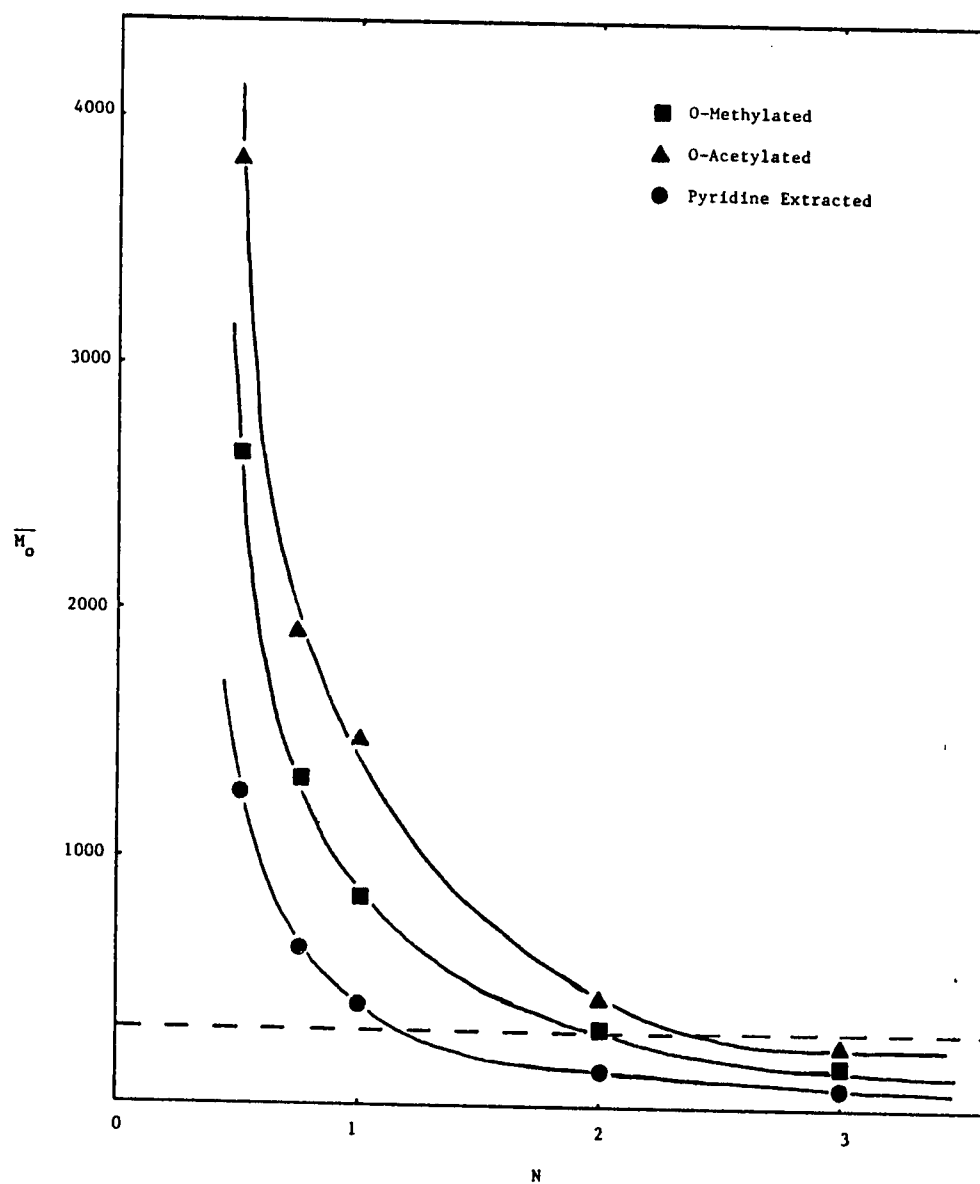


Figure 48. Plot of $\overline{M}_o$ Versus N for Big Brown Lignites.

TABLE XXXII

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS
OF RAWHIDE COAL USING THE KOVAC EQUATION
ASSUMING AN $\bar{M}_0$ OF 300

	Pyridine- Extracted	O-Acetylated	O-Methylated
N	1.2	1.8	2.3
$\bar{M}_c$	360	540	690

TABLE XXXIII

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN
CROSSLINKS OF THE BIG BROWN LIGNITE
USING THE KOVAC EQUATION ASSUMING
AN $\overline{M}_0$ OF 300

	Pyridine- Extracted	O-Acetylated	O-Methylated
N	1.2	2.4	2.0
$\overline{M}_c$	360	720	600

TABLE XXXIV

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN
CROSSLINKS OF THE TEXAS LIGNITE USING
THE KOVAC EQUATION ASSUMING
AN $\overline{M}_0$ OF 300

	Dry, Pyridine Extracted	O-Acetylated
N	1.1	2.4
$\overline{M}_c$	330	720

The determination of $\overline{M}_c$ allows the calculation of the crosslink density of the derivatized and native coal using Equation 16. Any changes in the amount of crosslinking in the coal network will be clearly reflected by the crosslink density. A density of 1.3 g/ml was assumed in all calculations. The results are presented in Table XXXV.

The results in Table XXXV indicate that unextracted and pyridine extracted coals have higher ρ_x 's than the O-acetylated and O-methylated coals. This is expected and reflects the removal of hydrogen bonds after O-acetylation and O-methylation. The unextracted coal has a ρ_x which reflects both the covalent and hydrogen bonds in the coal network. If the coal is derivatized to remove the hydrogen bonds, then the ρ_x due to the covalent bonds can be estimated simply by taking the difference of the ρ_x of the unextracted coal which has both covalent and hydrogen bonds and the ρ_x of the the O-acetylated and O-methylated coal:

$$\rho_{x,h-bond} = \rho_{x,unext} - \rho_{x,O-acet} \quad (47)$$

$$\rho_{x,h-bond} = \rho_{x,unext} - \rho_{x,O-met} \quad (48)$$

The results are listed in Table XXXVI. The number of hydroxyl groups in the coal is also listed for comparison. The number of hydroxyl groups in the Rawhide coal was not determined directly, but is reported in the literature,^{43,104} thus the literature value of 7.35 mmol/ml is presented. The $\rho_{x,h-bond}$ was calculated using Equations 47 and 48. A comparison of the results obtained from the Flory-Rehner and Kovac treatments indicates the Flory-Rehner treatment gives larger

TABLE XXXV

CROSSLINK DENSITIES OF THE DRIED, PYRIDINE-EXTRACTED,
O-ACETYLATED, AND O-METHYLATED RAWHIDE COAL

	ρ_x , mmol/ml of coal			
	DRY	PEXT ^a	ACT ^b	MET ^c
Flory-Rehner	9.4	9.2	4.8	3.1
Kovac	3.6	3.6	2.4	1.9

^aPEXT = Pyridine-extracted.

^bACT = O-Acetylated.

^cMET = O-Methylated.

TABLE XXXVI

ESTIMATION OF THE HYDROGEN BOND CROSSLINK DENSITY OF RAWHIDE COAL

	$\rho_{x,h-bond}$		No. of hydroxyl groups
Flory-Rehner	4.6 ^a	6.3 ^b	7.35 mmol/ml
Kovac	1.2 ^a	1.7 ^b	

^aCalculated from Equation 47.^bCalculated from Equation 48.

ρ_x 's than the Kovac treatment, as is expected. In addition, the ρ_x 's calculated from Equation 48 indicate that the O-methylated coal has a larger hydrogen bond crosslink density than the O-acetylated coal. This result is interesting considering neither derivatized coal has hydrogen bonds. Obviously, there should be no difference in the crosslink densities.

The difference in the calculated ρ_x 's of the O-acetylated and O-methylated coals is not expected. Both procedures are well-documented in the literature and have been shown to derivatize all available acidic sites as evidenced by FT-IR.^{104,111} Possible explanations for the discrepancy in the O-methylated and O-acetylated coals are as follows. The O-acetylation and O-methylation procedures may selectively derivatize different -OH populations in the coal. From the experimental data presented, however, no evidence exists to support this possibility. The O-methylation procedure utilizes a quaternary ammonium hydroxide which is difficult to remove from the coal. This possibility is easily explored by examination of the elemental analysis of the coal. The unextracted, dry coal has 0.96% N(dmmf basis). The O-methylated coal has 1.09% N. Obviously, an increase in the %N but not large enough within experimental error to account for the increase in the ρ_x . A third possibility is that the O-methylation procedure is breaking bonds in the coal network. The only functional group in the coal which would be labile under the conditions of the O-methylation procedure is the ester group. Low rank coals do contain ester groups,^{1,93} although in low concentration. Thus the possibility of bond breakage exists and the increased ρ_x of

the O-methylated coal, relative to the O-acetylated coal, may be the result of the bond breakage. Liotta¹⁰⁴ noted an increase in the extractability of an Illinois #6 coal and Rawhide subbituminous coal after O-methylation using three non-polar solvents. The increase in extractability was attributed to a decrease in the hydrogen bonding network of the coal, rather than the possibility of bond breakage.

Solvent swelling with pyridine may lend some insight into the situation. Pyridine is capable of completely disrupting the hydrogen bond network, so theoretically the solvent swelling ratios will be the same regardless of whether or not the coal is derivatized to remove hydrogen bonds. If significant bond breakage is occurring in the O-methylated coal, the pyridine swelling ratio of the derivatized coal will be greater than that of the unextracted coal. The volumetric swelling ratio of the dry, unextracted coal is 2.4 compared with the swelling ratios of 1.8 and 2.1 for the O-acetylated and O-methylated coals, respectively. From the solvent swelling data, no bond breakage is occurring. In fact, the solvent swelling ratios are decreased suggesting the coal is more tightly crosslinked after derivatization, or that the coal-pyridine interactions are strong enough in the coal to cause greater swelling. The latter explanation is more reasonable.

F. Comparison of $\overline{M}_c$ Values for Various Coals

The chemical processes which occur during coalification are poorly understood.¹¹⁵ Essentially two schools of thought exist on the nature of coalification. One faction views the coalification process

as a degradation of biological macromolecules followed by a condensation polymerization of the smaller molecular weight material.^{1,3,116-121} The other view treats coalification as a polyfunctional condensation of humic acids.¹²² In both models a condensation polymerization occurs so the two models are not mutually exclusive.

The coalification model supported by van Krevelan has received a large amount of attention. In the van Krevelan model,^{1,3} the coalification process is likened to a trifunctional polycondensation. The theoretical framework for the model is provided by Flory.³⁶ This model oversimplifies the coalification process in that the coal "monomers" are not all of the same species, but are actually a complex mixture of various types and sizes of molecules. From the polymer theory, if the amount of soluble material in the network is known, and the molecular weight distribution of that extracted material is known, the extent to which the network has been polymerized may be calculated. The molecular weights of the extracts should be small in the lignite stages and increase as coalification proceeds, if the coalification process is indeed a condensation polymerization. Thus van Krevelan obtained the extracts from four coals, measured the molecular weight distribution of the extracts, and was able to predict the degree of coalification with some success. The experimental technique used by van Krevelan has been criticized,³³ but it was also the best at that time.

Various workers^{33,115} have questioned the van Krevelan model, based on other experimental evidence available. Green et al.⁵ point

to the evidence that between approximately 75%C and 86%C, the crosslink density of coals decreases. In addition, Larsen et al.³³ measured the molecular weight distribution of the pyridine extracts of bituminous coals and found results which contradict those of van Krevelan^{1,3}. This observation led to the conclusion that the coalification process is not merely a condensation polymerization, but that degradation processes are also occurring. If degradation reactions are occurring, the $\overline{M}_c$ of the coal is expected to increase as coalification proceeds. The coal network is becoming less crosslinked. Extraction studies and measurement of the mechanical properties are not the only experimental techniques available for probing the macromolecular structure of coal. Green⁶ has demonstrated that solvent swelling techniques also provide information concerning the network structure of coals. The extension of the solvent swelling technique to the lower rank coals should provide additional insight to the coalification process.

The $\overline{M}_c$ values of a subbituminous coal and two lignite samples has been determined as described in Chapter IV, Section E. The results are listed in Table XXXVII. Also contained in Table XXXVII are the $\overline{M}_c$ values determined by Green⁶ for two bituminous coals. Clearly, the $\overline{M}_c$ values for the two lower rank coals are smaller than those of the bituminous coals. This result supports the conclusion of Larsen et al.³³ that coalification is not merely a condensation process, but that degradation reactions do occur during coalification. On the other hand, there is no regular increase in $\overline{M}_c$ with increasing rank as

TABLE XXXVII

COMPARISON OF NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS
USING THE KOVAC EQUATION FOR VARIOUS O-ACETYLATED COALS

Coal	Rank	$\bar{M}_c$
Illinois #6 ^b	Bituminous	1125
Bruceton ^b	Bituminous	825
Rawhide	Subbituminous	420
Texas Lignite	Lignite	720
Big Brown Lignite	Lignite	720

^a $\bar{M}_o$ assumed to be 300.

^b $\bar{M}_c$ values from Green⁶.

one might expect is the coalification process is merely a degradation process.

G. Presence of Ionic Bonds

Coals are very complex substances, composed of both inorganic and organic phases. The composition of each of these phases is dependent on the conditions of coalification and the plant material and inorganic species from which the coal was formed.^{123,124} The inorganic portion of the coal, the portion of the coal which is obviously not organic, is loosely defined as "mineral matter". The expression mineral matter does not imply a specific substance but encompasses a broad distribution of inorganic substances. The sources of the mineral matter in coals have been generalized into the following categories:¹²³⁻¹²⁵ 1) detrital minerals-minerals deposited from slowly moving water or wind currents 2) syngenetic minerals-minerals formed in the peat before it was buried by other sediments 3) epigenetic minerals-minerals found in the cracks and fractures 4) residues of the minerals present in the plant tissue from which the peat was derived and 5) decomposition products of minerals and the interaction of the minerals and the organic portion of the coal. The mineral matter present in a coal will depend on the geological age of the coal as well as its environment.

Given the wide variety of minerals known to exist, and the infinite number of combinations possible for the mineral matter composition of a particular coal seam, the attempts to ascertain the identity and impact the mineral matter has on the utilization of a

coal may seem overwhelming. Watt¹²⁴ suggests that since most of the minerals found in coals are of low concentration, realistically one only need consider six mineral species: one or two clays, a few carbonates, pyrite, and quartz. The most common clay minerals found in coals are illite, montmorillinite, and kaolinite.¹²⁴ The clays are aluminosilicates with a wide variety of ion-exchangeable cations, such as calcium, sodium, and magnesium. The most common carbonates found in coals are calcium carbonate, ankerite($\text{Ca}(\text{Mg}, \text{Fe}^{+2}, \text{Mn})(\text{CO}_3)_2$), and iron carbonate.¹²⁴

As the process of coalification proceeds, the mineral matter content in coals decreases. This is primarily due to changes in the chemical structure of the older coals. In the younger coals, the lignite and subbituminous coals, a large portion of the mineral matter is in the form of ion-exchangeable cations which are associated with the carboxyl, hydroxyl, and phenoxyl groups via ionic bonds.¹²³ As a coal increases in rank, the concentration of carboxyl and hydroxyl groups decreases thus fewer sites are available for ionic bonding. The predominant cation associated with coals is calcium.¹²³⁻¹²⁵ Other ion-exchangeable cations include sodium, barium, and magnesium. Fowkes¹²³ has demonstrated that low valency cations may be displaced by cations of higher valency, for example, calcium ions will displace sodium ions. In addition, Fowkes¹²⁶ has demonstrated that washing a coal with dilute acid (3% HCl) could displace 92-98% of the sodium ions present in a lignite sample. The focus of this section is one aspect of the interaction of the mineral matter with the organic portion of the coal; in particular the role that cations bound

ionically to carboxyl acid anions have in the macromolecular structure of the low rank coals and lignites.

As with hydrogen bonds, the presence of ionic bonds in low rank coals may or may not have an effect on the macromolecular structure. The experimental approach used to measure the effect of ionic bond formation is solvent swelling. The logic of the experiment is the same as that used to investigate the effect of hydrogen bonds.

Before discussing the solvent swelling results, the two procedures used to remove the ionic bonds will be briefly described. As previously mentioned the ion-exchangeable cations are ionically bound to the coal matrix. The removal of these cations is well-documented.^{123,126-130} Two common procedures involve treatment of the coal with dilute hydrochloric acid or ammonium acetate. The hydrochloric acid treatment suffers from the potential disadvantage of dissolving carbonates present in the coal.¹²⁷ Also Starsinic et al.¹³¹ recently demonstrated using FR-IR spectroscopy that the ion-exchange process is not 100% complete, only 90% of the cations were exchanged by Schafer's method which uses barium acetate for the ion-exchange. The procedure used in this study uses 1M aqueous citric acid. As the citric acid wash treatment (referred to as CAW in the text) is an ion-exchange process, the other inorganic components present in the coal are not affected.

The clay minerals and other inorganic species such as pyrite and quartz require more strenuous treatment for their removal. Often the mechanical processes applied to the removal of these materials, such as sink-float methods, produce less than satisfactory results.^{123,124}

Several chemical methods for the "total" demineralization of coal (removal of the cations as well as clays and other inorganic matter) exist.¹³²⁻¹³⁴ The method employed here is the HF/HCl treatment originally devised by Radmacher and Mohrhauer¹⁰¹ and later modified by Bishop and Ward.¹⁰² Throughout the rest of the text the HF/HCl treatment will be referred to simply as demineralization. The procedure is not without difficulties, as discussed by Given,¹³⁵ but within the scope of this work the complications discussed are not considered to have a major impact. A potentially serious consequence of the demineralization procedure, however, is reaction of the organic portion of the coal with the HF or HCl used in the procedure. Both are known as catalysts in Friedel-Crafts alkylation and acylation reactions.¹³⁶

Kuczynski and Andrzejak¹³⁷ observed that the amount of material extracted from a brown coal after demineralization using a 70:30 mixture of benzene and ethanol as the extraction solvent was increased. The authors suggested a "loosening" of the polymeric structure of the coal. In addition, the extracted material had a lower hydrogen content than the extract from the unextracted coal. Pyridine extractions of the Rawhide and Big Brown Lignite after demineralization indicated the same trend. The pyridine extractability (based on yield of extract) increased from 5.4% to 17.5% in the case of the Rawhide coal. The pyridine extractability of the Big Brown Lignite increased from 7.4% to 15.9%. The increase in extractability may be the result of disruption of ionic and/or hydrogen bonds present in the coal, releasing trapped, uncrosslinked

material. Covalent bond breakage is an alternative explanation. These can be distinguished by comparing the swelling of demineralized and citric acid washed coal. Brooks and Sternhell¹³⁸ have shown the content of the oxygen functionalities does not change after demineralization. The oxygen containing functionalities, are likely sites for reaction so these results do not support covalent bond breakage.

Wachowska and coworkers¹³⁹ found the dilatometric properties of coals increased significantly after demineralization. The changes in the plastic properties of the coals were attributed to adsorption of the HCl and/or HF on the basic nitrogen functionalities and physical adsorption of the acids rather than covalent bond breakage.

In order to ascertain if ionic bonds do have an effect in the structure of the low rank coals, the swelling ratios of the dried, untreated coals were compared with the swelling ratios of the CAW (citric acid washed) coals. The swelling ratios of the demineralized coals were also compared with the dried, untreated coals and the CAW coals to investigate the possibility of covalent bond breakage during demineralization. The elemental analyses of the coals are listed in Table XXXVIII. Several non-polar solvents were used to swell the coals. Recall non-polar solvents must be used to ensure random mixing and thereby satisfy the requirements of regular solution theory. The results of the solvent swelling experiments on the dry, CAW, and demineralized coals are presented in Tables XXXIX, XL, and XLI. Comparison of the swelling ratios of the dry, untreated coal and CAW coal provides information on the ionic bonding in the coal.

TABLE XXXVIII

WEIGHT PERCENT ELEMENTAL ANALYSES^a OF THE DRY, CITRIC ACID WASHED,
AND DEMINERALIZED COALS

Coal	%C	%H	%N	%O+S	%ASH	%Ca ^b
Rawhide, DRY ^c	63.48	4.42	0.96	24.91	6.24	1.2
Rawhide, CAW ^d	68.98	4.76	1.06	22.92	6.28	0.013
Rawhide, DEM ^e	69.22	4.69	1.06	24.88	0.14	0.049
BBL, DRY ^f	62.00	4.55	1.20	22.67	9.58	1.52
BBL, CAW	65.96	4.81	1.32	23.52	4.39	0.44
BBL, DEM	68.50	4.85	1.32	24.58	0.75	0.13
Texas Lignite, DRY	59.03	4.30	1.19	21.42	14.06	1.41
Texas Lignite, CAW	63.49	4.38	1.28	22.30	8.55	0.023
Texas Lignite, DEM	69.52	4.85	1.40	23.74	0.49	0.047
S. Beulah, DRY	54.85	3.40	0.83	26.54	14.38	1.51
S. Beulah, CAW	62.96	3.68	0.97	26.45	5.94	0.043
S. Beulah, DEM	66.45	3.74	0.99	27.62	1.20	0.040

^aCHN and Ash analyses performed on a Perkin-Elmer 240C elemental analyzer by Susan E. Shawver.

^bAnalyses performed by Galbraith Laboratories, Knoxville, TN.

^cDRY = Dried at approximately 110°C overnight under vacuum.

^dCAW = Citric acid washed.

^eDEM = Demineralized.

^fBBL = Big Brown Lignite.

TABLE XXXIX

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS OF DRIED, CITRIC ACID
WASHED, AND DEMINERALIZED RAWHIDE COAL

Solvent	$Q_{v,dry}$		
	Dry	CAW ^a	DEM ^b
n-Pentane	1.0	-	1.0
Cyclohexane	1.0	1.0	1.1
o-Xylene	1.1	1.2	1.2
Toluene	1.2	1.2	1.3
Benzene	1.1	1.2	1.3
Chlorobenzene	1.3	1.3	1.3
Tetralin	1.2	1.2	1.2
1,2-Dichloroethane	1.3	1.4	1.4
Carbon Disulfide	1.3	1.3	1.3
Acetonitrile	1.4	1.3	1.4

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

TABLE XL

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS OF DRIED, CITRIC ACID
WASHED, AND DEMINERALIZED BIG BROWN LIGNITE

Solvent	Dry	$Q_{v,dry}$	
		CAW ^a	DEM ^b
Cyclohexane	1.1	1.0	1.1
o-Xylene	1.2	1.2	1.2
Toluene	1.2	1.3	1.3
Benzene	1.2	1.2	1.3
Chlorobenzene	1.2	1.3	1.4
Tetralin	1.2	1.2	1.2
1,2-Dichloroethane	1.3	1.3	1.4
Carbon Disulfide	1.3	1.2	1.3

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

TABLE XLI

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS OF DRIED, CITRIC ACID
WASHED, AND DEMINERALIZED TEXAS LIGNITE

Solvent	Dry	$Q_{v,dry}$	
		CAW ^a	DEM ^b
Cyclohexane	1.1	1.0	1.1
o-Xylene	1.1	1.1	1.3
Toluene	1.2	1.2	1.3
Benzene	1.2	1.2	1.2
Chlorobenzene	1.2	1.3	1.5
Tetralin	1.1	1.0	1.2
1,2-Dichloroethane	1.3	1.3	1.5
Carbon Disulfide	1.2	1.2	1.4
Acetonitrile	1.4	1.3	1.4

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

Information on changes in the coal structure after demineralization may be obtained by comparing the dry and demineralized results. Again, the Texas Lignite and Big Brown Lignite samples are from the same coal seam, however, the Big Brown Lignite has been subjected to mild oxidation, the extent of which is unknown.

The results indicate that after removal of the ion-exchangeable cations by citric acid wash treatment little change occurs in the solvent swelling behavior. No enhancement in the swelling ratios is observed. Examination of the results for the demineralized samples shows that the HF/HCl treatment also has little effect on the solvent swelling results. Some enhancement in the swelling ratios of the demineralized Texas Lignite is observed, however. Thus the demineralization procedure seems to have little effect on the macromolecular structure of the coal. The non-polar solvent swelling experiments on the CAW coals suggest that few, if any, ionic crosslinks are present in the coal. But this observation ignores the fact that the functional groups present are capable of forming hydrogen bonds. Removal of the cations and hence ionic bonds returns the carboxylate and hydroxyl groups, which participate in ionic bonding, to the protonated form. If these hydroxyl groups form hydrogen bonds in place of the lost ionic bonds, no change in swelling is expected. Since the predominate cation is divalent calcium, presumably associated with two carboxylate anions which must be close to each other, this is not unreasonable behavior.

The non-polar solvents used for the swelling measurements cannot disrupt hydrogen bonds. If any information is to be gained concerning

the ionic bonds, then solvents such as pyridine which can interrupt the hydrogen bond network must be used in the swelling experiments. The methodology is the same as before. The swelling ratios of the dried, native coals will be compared with the swelling ratios of the CAW and demineralized coals. An enhancement in the solvent swelling ratios is expected if ionic bonds are acting as crosslinks. The results of the swelling experiments using hydrogen bond accepting solvents are listed in Tables XLII, XLIII, and XLIV. Clearly, the swelling ratios are enhanced after the coals are citric acid washed or demineralized.

The obvious conclusion is that ionic bonds do serve as crosslinks in the coals. Disruption of the hydrogen bond network by the polar solvents allows the effect of the ionic crosslinks to be seen. The polar solvents would not disrupt any ionic bonds present in the native coals. Another observation concerning the results using polar solvents is that the CAW and demineralized samples generally show similar swelling ratios. This observation implies that the demineralization procedure does not have a significant effect on the macromolecular structure of the coal. If the demineralization process was breaking or making bonds swelling ratios different than those found for the citric acid washed coals would be expected, since the CAW treatment is merely an ion-exchange process and reaction of the coal network is not expected.

Another rationalization of the enhanced swelling, using polar solvents, after CAW treatment and demineralization is as follows. In the ionic form, the carboxylate and hydroxyl functionalities would not

TABLE XLII

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS OF DRIED, CITRIC ACID WASHED, AND DEMINERALIZED RAWHIDE COAL USING POLAR SOLVENTS

Solvent	$Q_{v,dry}$		
	Dry	CAW ^a	DEM ^b
Pyridine	2.4	2.7	2.5
N-methyl-2-pyrrolidone	2.3	2.6	3.1
Tetrahydrofuran	1.7	2.1	2.3
Nitrobenzene	1.2	1.6	1.7
Ethanol	1.6	1.6	1.7

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

TABLE XLIII

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS OF DRIED, CITRIC ACID
WASHED, AND DEMINERALIZED BIG BROWN LIGNITE USING
POLAR SOLVENTS

Solvent	Dry	$Q_{v,dry}$ CAW ^a	DEM ^b
Pyridine	2.0	2.8	2.9
N-methyl-2-pyrrolidone	1.8	3.0	2.9
Tetrahydrofuran	1.7	2.3	2.3
Nitrobenzene	1.2	1.5	1.6
Ethanol	1.6	1.6	1.7

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

TABLE XLIV

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS OF DRIED, CITRIC ACID WASHED, AND DEMINERALIZED TEXAS LIGNITE USING POLAR SOLVENTS

Solvent	Dry	$Q_{v,dry}$	DEM^b
		CAW ^a	
Pyridine	2.2	2.8	3.1
N-methyl-2-pyrrolidone	2.1	2.9	3.3
Tetrahydrofuran	1.6	2.1	2.2
Nitrobenzene	1.2	1.5	1.5
Ethanol	1.6	1.5	1.7

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

be effected by the presence of polar solvents. Removal of the ion-exchangeable cations, followed by reprotonation and subsequent hydrogen bond formation increases the number of sites available for solvent complexation. It is important to realize that not all the cations participating in ionic bonds are divalent. The sites occupied by monovalent cations are now available for solvent complexation. Thus the enhanced swelling may be the result of the coal network expanding to accomodate the increased amount of solvent capable of complexing with the coal matrix, and not necessarily the result of the presence of ionic crosslinks. In thermodynamic terms, the solvent-coal interactions are increased leading to enhanced swelling. Comparison of the swelling data for the O-acetylated and O-methylated coals with the CAW and demineralized coals should allow a distinction to be made between the two possibilities, the presence of ionic crosslinks or increased coal-solvent interactions, discussed for the enhanced swelling observed after CAW treatment and demineralization.

Before discussing the solvent swelling data, it will be useful to review the types of bonding interactions in each derivatized coal. In the native coal, both hydrogen and ionic bonds are present. In the CAW and demineralized coals the ionic bonds are replaced by hydrogen bonds. In the O-acetylated and O-methylated coals, the hydrogen bond network has been removed and the ionic bonds are assumed to be removed. Now consider the swelling of the native and derivatized coals in the polar solvents which can disrupt the hydrogen bond network. The swelling ratios obtained for the Rawhide, Texas Lignite, and Big Brown Lignite samples are listed in Tables XLV-XLVII.

TABLE XLV

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS FOR VARIOUS RAWHIDE COAL
DERIVATIVES USING POLAR SOLVENTS

Solvent	Dry	$Q_{v,dry}$			
		CAW ^a	DEM ^b	ACT ^c	MET ^d
Pyridine	2.4	2.7	2.5	1.8	2.1
NMP ^e	2.3	2.6	3.1	1.8	2.3
Tetrahydrofuran	1.7	2.1	2.3	1.8	1.8
Nitrobenzene	1.2	1.6	1.7	1.3	1.9
Ethanol	1.6	1.6	1.7	1.3	1.1

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

^cACT = O-Acetylated.

^dMET = O-Methylated.

^eNMP = N-Methyl-2-pyrrolidone.

TABLE XLVI

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS FOR VARIOUS BIG BROWN
LIGNITE DERIVATIVES USING POLAR SOLVENTS

Solvent	Dry	CAW ^a	Q _{v,dry}		
			DEM ^b	ACT ^c	MET ^d
Pyridine	2.0	2.8	2.9	1.7	2.0
NMP ^e	1.8	3.0	2.9	2.1	2.2
Tetrahydrofuran	1.7	2.3	2.3	1.9	1.9
Nitrobenzene	1.2	1.5	1.6	2.3	2.0
Ethanol	1.6	1.6	1.7	1.5	-

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

^cACT = O-Acetylated.

^dMET = O-Methylated.

^eNMP = N-methyl-2-pyrrolidone.

EQUILIBRIUM VOLUMETRIC SWELLING RATIOS FOR VARIOUS
TEXAS LIGNITE DERIVATIVES USING
POLAR SOLVENTS

Solvent	$Q_{v,dry}$		DEM ^b	O-Acetylated
	Dry	CAW ^a		
Pyridine	2.2	2.8	3.1	2.0
N-Methyl-2-Pyrrolidone	2.1	2.9	3.3	3.2
Tetrahydrofuran	1.6	2.1	2.2	-
Nitrobenzene	1.2	1.5	1.5	1.7
Ethanol	1.6	1.5	1.7	1.4

^aCAW = Citric Acid Wash.

^bDEM = Demineralized.

The native coal should exhibit the least amount of swelling due to the presence of ionic bonds, some of which may serve as ionic crosslinks. The CAW (or demineralized coal) and O-acetylated (or O-methylated) coals should exhibit greater swelling than the native coal since in both cases ionic bonds are not present and the polar solvents can disrupt any hydrogen bonds in the CAW coal. The only difference between the two treated coals is that the hydroxyl groups are derivatized in the O-acetylated coal. In addition, the CAW and O-acetylated coals should exhibit the same swelling ratios if no additional driving forces such as increased coal-solvent interactions are present. Another approach to illustrate the point is to examine the ratio of the swelling ratios of the derivatized coals. The ratio of the $Q_{v,dry}$ values of the CAW and O-acetylated coals, Q_{rel} , will be equal to one if the enhanced swelling after CAW treatment is the result of the removal of ionic crosslinks. If the observed enhanced swelling is due to increased coal-solvent interactions resulting from additional complexation sites for the solvent, Q_{rel} will be greater than one. Table XLVIII lists the Q_{rel} values obtained for the CAW and O-acetylated Rawhide, Texas Lignite, and Big Brown Lignite samples using a variety of polar solvents. The same treatment holds for the demineralized and O-methylated coals but for clarity only the $Q_{v,dry}$ values of the CAW and O-acetylated coals are listed.

In almost all cases, Q_{rel} is greater than one. This result indicates that when the polar solvents are employed the enhanced swelling is primarily the result of the increased coal-solvent interactions. The presence of ionic crosslinks is not absolutely

Q_{rel} VALUES OBTAINED FROM THE CITRIC ACID WASHED
AND O-ACETYLATED RAWHIDE COAL, TEXAS
LIGNITE AND BIG BROWN LIGNITE

Solvent	Q_{rel}		
	Rawhide	Texas Lignite	Big Brown Lignite
Pyridine	1.5	1.4	1.6
N-methyl-2-pyrrolidone	1.4	0.9	1.4
Tetrahydrofuran	1.2	-	1.2
Nitrobenzene	0.9	0.9	0.7
Ethanol	1.2	1.1	1.1

eliminated, but their effect on the macromolecular structure of the coal is overshadowed by the coal-solvent interactions. Thus, the attempt to separate the changes in the coal network structure resulting from the removal of ionic bonds and the effect of increased coal-solvent interactions was unsuccessful. The same logic could also be used with the non-polar solvents, but these solvents cannot disrupt hydrogen bonds thus a comparison of the CAW and O-acetylated coals would be meaningless.

The solvent swelling ratios are not quantitative measures of changes in the crosslink density of the coal. The determination of the number average molecular weight between crosslinks, $\overline{M}_c$, and subsequent calculation of the crosslink density, ρ_x , provides a quantitative answer to the question of whether the ionic bonds do play a role in the macromolecular structure of the coal. To satisfy the requirements of regular solution theory, only the data from the non-polar solvents may be used in the $\overline{M}_c$ calculations. $\overline{M}_c$ values for the Rawhide coal were calculated using the Flory-Rehner equation for comparative purposes (Equation 14) and are presented in Table XLIX. This treatment is not as adequate for coals as is the Kovac equation, however. A density of 1.3 g/ml was assumed in all calculations. Only $\overline{M}_c$ values for the Rawhide coal are presented. The $\overline{M}_c$ values mirror the solvent swelling ratios. The dry, native and CAW coal have nearly the same $\overline{M}_c$ value. The demineralized coal has an average $\overline{M}_c$ value which is larger than that of the dry coal but not significantly. The three $\overline{M}_c$ values are statistically the same; the values all fall within one standard deviation. The Flory-Rehner $\overline{M}_c$ values are, however,

TABLE XLIX

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF
 DRY, CITRIC ACID WASHED AND DEMINERALIZED RAWHIDE
 COAL USING THE FLORY-REHNER EQUATION

Solvent	Dry	$\bar{M}_c$	
		CAW ^a	DEM ^b
o-Xylene	132	219	219
Toluene	186	186	265
Carbon Disulfide	142	142	142
Chlorobenzene	235	235	235
Tetralin	222	138	222
Benzene	92	144	209
Cyclohexane	-	-	139
Average	168	177	204

^aCAW = Citric Acid Washed.

^bDEM = Demineralized.

unrealistically low. Thus the Kovac equation (Equation 15) which is more appropriate for application to coals was applied to the solvent swelling data. N was varied from 0.5 to 4.0. The results are presented in Table L. The trends are the same as those observed with the Flory-Rehner equation but the $\overline{M}_c$ values are larger. The $\overline{M}_c$ values of the dried and CAW samples are approximately the same. The demineralized coal has an $\overline{M}_c$ value that is somewhat larger than the $\overline{M}_c$ of the dried coal. Again the dry, CAW and demineralized coal $\overline{M}_c$ values are within the standard deviation of the calculated values. Obviously, the $\overline{M}_c$ of the coal is not changing after the citric acid wash and demineralization treatment. Since the $\overline{M}_c$ values do not vary significantly, no change in the crosslink density is expected.

The focus of the work presented in this section was to investigate the effect of organically bound cations on the macromolecular structure of the low rank coals and to investigate the possibility of the demineralization process producing changes in the coal structure. The solvent swelling experiments do not reveal whether ionic crosslinks are present. The attempt to distinguish between changes in the coal network and increased coal-solvent interactions after removal of ionic bonds was not entirely successful. The solvent swelling results do show that if ionic crosslinks are present, they are replaced by hydrogen bonds when they are removed. In addition, the solvent swelling experiments also indicated little change in the coal network after demineralization.

TABLE L

THE NUMBER AVERAGE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF
RAWHIDE COAL USING THE KOVAC EQUATION

		$\bar{M}_c$					
Dry	N	0.5	0.75	1.0	2.0	3.0	4.0
o-Xylene		413	319	272	202	179	167
Toluene		605	464	395	290	256	238
Benzene		287	221	189	140	124	116
Carbon Disulfide		620	506	451	366	338	324
Tetralin		724	557	474	348	306	285
Average		530	414	356	269	241	226
$\bar{M}_o$		1059	552	356	135	80	57
Citric Acid							
Washed	N	0.5	0.75	1.0	2.0	3.0	4.0
o-Xylene		712	545	465	342	301	280
Toluene		605	464	395	290	256	238
Benzene		479	366	311	228	200	186
Carbon Disulfide		620	506	451	366	338	324
Tetralin		432	334	285	212	187	175
Average		570	444	285	288	256	241
$\bar{M}_o$		1139	592	382	144	85	60
Demineralized N							
		0.5	0.75	1.0	2.0	3.0	4.0
Cyclohexane		436	337	288	213	189	176
o-Xylene		712	547	465	342	301	280
Toluene		897	685	581	423	370	344
Benzene		706	540	458	333	292	271
Carbon Disulfide		620	506	451	366	338	324
Tetralin		724	557	474	348	306	285
Average		682	529	453	338	299	280
$\bar{M}_o$		1365	705	453	169	100	70

H. Solvent Extractions

Solvent extraction is a common technique used to study the chemical properties of coals. It is often assumed the material extracted from the coal accurately reflects the original coal. Clearly some solvents will be more efficient in extracting soluble material from coal than others. The chemical and physical properties of a solvent determines the effectiveness of the solvent in coal extraction. Dryden¹⁴⁰ showed that solvents possessing a heteroatom, such as nitrogen or oxygen, with an unshared pair of electrons were very efficient in coal extraction. The extraction efficiency was attributed to the enhanced nucleophilicity of the solvent due to the unshared pair of electrons on the heteroatom. The physical properties of the solvent also play an important role. Several physical properties such as cohesive energy density, dielectric constant, surface tension, and electron donor-acceptor properties have been studied.^{52,74} Obviously the choice of solvent is important in maximizing the extraction of the coal. The approach used here to select a solvent for coal extraction is based on regular solution theory. In essence, regular solution theory embodies the old chemical adage "like dissolves like". In more specific terms, if the solubility parameter of the solvent equals the solubility parameter of the extractable material, maximum extraction will be observed. Previous work⁶ indicates that bituminous coals have solubility parameters of approximately $9.5 \text{ (cal/cm}^3)^{1/2}$ in non-polar solvents. Considering all solvents, non-polar and polar, the effective coal solubility parameter is approximately $10.5 \text{ (cal/cm}^3)^{1/2}$. Thus

solvents with solubility parameters near $10.5 (\text{cal/cm}^3)^{1/2}$ which are also good hydrogen bond acceptors should be ideal candidates for coal extractions. To illustrate the point that the combination of a solubility parameter and good hydrogen bond acceptance is important, five coals were Soxhlet extracted with 1,2-dichloroethane which has a solubility parameter equal to $9.8(\text{cal/cm}^3)^{1/2}$, but is a poor hydrogen bond acceptor. The extraction results are presented in Table LI. Little material is extracted from the coal. Thus the value of the solubility parameter is important, but does not ensure the effectiveness of the solvent for coal extractions.

By application of regular solution theory and recognition of the importance of the presence of hydrogen bonding N-methyl-2-pyrrolidone ($\delta = 11.0 (\text{cal/cm}^3)^{1/2}$) (NMP) was chosen as a solvent for coal extraction studies. Other studies have confirmed the potential of NMP as a coal extraction solvent: NMP is a better solvent for coal than dimethylsulfoxide.¹⁴¹

The results of the NMP extractions are presented in Table LII. Also included in Table LII is the percent of extraction of Illinois #6 with pyridine. NMP is a high boiling solvent (202 °C) and is difficult to remove by ordinary vacuum drying. To remove the residual NMP from the insoluble residue after NMP extraction, the insoluble residue was extracted with either THF(tetrahydrofuran), methanol, or water for one week in a Soxhlet extractor. The elemental analyses of the coal and coal extracts are listed in Table LIII. From the elemental analyses, the insoluble residue washed with methanol has the smallest percent nitrogen, indicating methanol is the most efficient

TABLE LI

EXHAUSTIVE EXTRACTION YIELDS USING 1,2-DICHLOROETHANE AS THE
SOLVENT FOR VARIOUS COALS

Coal	% Extraction ^a
Rawhide	5.42
Illinois #6	1.30
Bruceton	1.40
Big Brown Lignite	0.95
Texas Lignite	0.91

^aBased on yield of extract obtained.

TABLE LII

WEIGHT PERCENT OF ILLINOIS #6 COAL EXTRACTED^a BY
EXHAUSTIVE SOXHLET EXTRACTION WITH N-METHYL-
2-PYRROLIDONE (NMP) AND PYRIDINE

Solvent	% Extraction
NMP/THF wash ^b	28.30
NMP/CH ₃ OH ^b	33.27
NMP/H ₂ O ^b	35.29
Pyridine	17.17

^aBased on insoluble residue.

^bExtracted with NMP then washed with specified solvent as described in text.

TABLE LIII

ELEMENTAL ANALYSES (WEIGHT PERCENT) OF UNEXTRACTED AND EXTRACTED
ILLINOIS #6 COALS

Coal	%C	%H	%N	%S	%O ^a	%ASH
Illinois #6						
Parent	70.82	4.37	1.67	1.57	11.09	10.48
Pyridine extracted	71.56	4.51	3.82		12.44 ^b	7.67
NMP/THF ^{c,d}	67.11	4.49	1.81	2.24	10.22	14.13
Extract	76.74	5.96	4.62	0.62	11.29	0.77
NMP/CH ₃ OH ^{c,d}	67.89	4.44	1.64	1.99	9.82	14.22
Extract	75.14	6.13	4.80	0.47	12.73	0.73
NMP/H ₂ O ^{c,d}	70.43	4.87	2.68	1.149	3.01	17.52
Extract	74.61	6.15	5.37	0.57	12.36	0.94

^a By difference.

^b O+S by difference.

^c NMP = N-methyl-2-pyrrolidone.

^d Insoluble residue; extracted with NMP then washed with specified solvent.

solvent for removing residual NMP. Examination of the results contained in Table LII indicate NMP is a better solvent for coal extraction than pyridine. The percent extraction reported for the NMP extractions varies from 8-11% greater than that reported for pyridine.

The large differences observed in the percent extractability when pyridine and NMP are used as coal extraction solvents is surprising. Pyridine and NMP have similar solubility parameters (10.7 and 11.0 $(\text{cal}/\text{cm}^3)^{1/2}$, respectively) and both are capable of accepting hydrogen bonds. Volumetric solvent swelling experiments (Table LIV) indicate that NMP is as effective as pyridine in swelling coal. It is possible that NMP is interacting with the coal via bond formation or bond breakage. To investigate these possibilities, attention was focused on the NMP coal extract and insoluble residue.

If bond breakage is occurring during the NMP extraction, it is likely that the number average molecular weight, ($\overline{M}_n$), of the extracts would be smaller than the $\overline{M}_n$ observed for pyridine extracts of the same coal. Thus $\overline{M}_n$ of the NMP and pyridine coal extracts was measured by vapor pressure osmometry. One point easily overlooked is that the NMP extracts contain residual NMP which will directly influence the $\overline{M}_n$ measured. If the $\overline{M}_n$ is corrected to account for the residual NMP, the $\overline{M}_n$ value becomes unrealistically high. Therefore the $\overline{M}_n$ value measured for the NMP extract by vapor pressure osmometry are meaningless and can provide no information concerning degradative processes which may be occurring during the NMP extraction.

If the extraction of the coal with NMP is breaking bonds, it is not unreasonable to anticipate changes in the insoluble coal matrix.

TABLE LIV

VOLUMETRIC SWELLING RATIOS, $Q_{v,dry}$, OF VARIOUS COALS SWOLLEN
WITH N-METHYL-2-PYRROLIDONE AND PYRIDINE

Coal	$Q_{v,dry}$	
	Pyridine	NMP ^a
Rawhide, Dry ^b	2.4	2.3
Rawhide, PEXT ^c	2.0	2.2
Big Brown, Dry	2.0	1.9
Big Brown, PEXT	2.2	-
Texas Lignite, Dry	2.2	2.1
Texas Lignite, PEXT	2.0	2.1
S. Beulah, Dry	1.8	1.5
S. Beulah, PEXT	1.7	1.9

^aNMP = N-methyl-2-pyrrolidone.

^bDried at 110°C under vacuum overnight.

^cPEXT = Pyridine extracted.

The key experiment used to monitor changes in the macromolecular structure of coal is solvent swelling. The Illinois #6 coal extracted with NMP was swollen volumetrically with pyridine and NMP. The swelling ratios were compared with the volumetric swelling ratios obtained after extracting Illinois #6 coal with pyridine. The results are presented in Table LV. The NMP is more efficient at swelling the NMP-extracted coal than pyridine. The pyridine results indicate little if any change in the macromolecular structure of the coal after extraction with NMP. When NMP is used as the swelling solvent, larger $Q_{v,dry}$ values are obtained.

The NMP extraction yield is up to 11% greater than that of the pyridine extraction yield. The most reasonable explanation for the increased extractibility is some bond breaking, but this is contradicted by the swelling experiments. Either selective bond breaking is occurring or the extraction process is very specific and poorly understood. Recent work¹⁴² indicated that NMP is covalently incorporated into the coal liquefaction extract of a subbituminous coal. This conclusion was based on Fast Ionization Mass Spectrometry and the increase in the nitrogen content of the coal extract. The increase in nitrogen content was also observed with the Illinois #6 coal (see Table LII). The amount of NMP incorporated into the Illinois #6 coal extract, based on the increase in the nitrogen content, and assuming the NMP was merely trapped in the coal extract, was calculated to vary between 24 and 29%. One striking feature in the elemental analyses of the coal extracts and residues is the reduction of the percent sulfur in the extract. The sulfur reduction

TABLE LV

VOLUMETRIC SWELLING RATIOS, $Q_{v,dry}$, OF N-METHYL-2-PYRROLIDONE
AND PYRIDINE EXTRACTED ILLINOIS #6 COAL

Coal	Pyridine	$Q_{v,dry}$
		NMP ^a
NMP/CH ₃ OH ^b	2.4	2.7
NMP/H ₂ O ^b	2.4	2.8
NMP/THF ^b	2.4	2.8
Pyridine extracted	2.3	-

^aNMP = N-methyl-2-pyrrolidone.

^bExtracted with NMP then washed with specified solvent as described in text.

implies the NMP extraction may be selectively breaking bonds in the coal. One difference in the pyridine and NMP extraction procedure is the temperature of the extraction. The temperature of the coal during a pyridine Soxhlet extraction is 85 °C. NMP extractions run at approximately 165 °C. Whether the extraction temperature does have an effect on the extraction yield is uncertain.

CHAPTER V

SUMMARY AND SUGGESTIONS FOR FURTHER WORK

The purpose of the work performed in this dissertation was twofold. First, it was necessary to determine whether the solvent swelling approach could be applied to the lower rank coals and used to characterize the macromolecular structure of the lower rank coals. Second, the possible structural role of ionic bonds in low rank coals was examined. Three coals were examined in detail in the study: two lignite samples and one bituminous coal. A summary of the results of the work performed is now presented:

1. The extension of the solvent swelling technique to the lower rank coals was only moderately successful. The native subbituminous coal indicated regular solution theory behavior, but the two native lignite samples did not. As the rank of the coal decreases, the regular solution theory behavior degenerates. Considering regular solution theory was developed for non-polar systems, where specific interactions such as hydrogen bonding are not allowed, this result is not necessarily surprising; the lower rank coals are more polar than the bituminous coals.

2. Hydrogen bonds play an active role in the macromolecular structure of the lower rank coals.

3. Regular solution theory and solvent swelling techniques were used to calculate the $\overline{M}_c$ and crosslink density of the lower rank coals.

4. Solvent swelling experiments indicate that the removal of ionic crosslinks has little effect on the macromolecular structure of the lower rank coals. The use of non-polar solvents in the solvent swelling experiments was unsuccessful primarily due to the replacement of the ionic bonds with hydrogen bonds. It is also possible so few ionic crosslinks exist their presence has little effect on the coal network structure. The solvent swelling results with polar solvents indicated that coal-solvent interactions were increased after ionic bond removal.

5. In solvent extractions, the importance of choosing a solvent which has a solubility parameter near that of the coal and is also a good hydrogen bond acceptor was demonstrated.

While much information has been gained concerning the macromolecular structure of the lower rank coals and coal-solvent interactions, additional research in the following areas deserves attention:

1. Hydrated coals. The role of water in coals is poorly understood. Whether or not the presence of water has an effect on the macromolecular structure of coals has not been determined and is worthy of investigation.

2. Presence of Mineral Matter in Coals. Coals are heterogeneous materials consisting of inorganic and organic fractions. While it has been shown the presence of ionic bonds has little effect on the macromolecular structure of the lower rank coals, it is not clear whether the mineral matter is effecting the swelling process.

Application of the solvent swelling technique to macerals should provide some insight as to whether the presence of mineral matter affects the swelling process.

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VITA

Susan E. Shawver was born in Beckley, WV on October 21, 1958. She graduated from Woodrow Wilson High School in June of 1976 and received a B.S. in Chemistry from West Virginia Wesleyan College in 1980. In the fall of 1980 she entered the University of Tennessee.

The author is a member of the American Chemical Society.