Solvent extraction of coal with dimethylsulfoxide and other solvent blends at low temperatures
by I-Hsing Tsao

A thesis submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in Chemical Engineering
Montana State University
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Abstract:
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In general, extraction yield is affected by type of coal, the composition of the solvent, extraction temperature, the number of consecutive extractions, and the particle size of coal.

The solvent extraction of coal can be hypothesized as a three-stage process which includes penetration of solvent, swelling of the coal by solvent and solvation and removal of coal fragments from the coal matrix. A rationale for this hypothesis is presented and compared to present experimental results and literature results.

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of

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Solvent extraction of coal with dimethylsulfoxide (DMSO) and solvent blends such as DMSO/tetralin and DMSO/carbon disulfide (CS_2) was performed at atmospheric pressure under the boiling point of solvents. Extract and solvent were separated from coal residue by filtration. Residue and extract were then analyzed.

Experimental data show that DMSO is an active solvent which can extract about 30 wt% of Kittaning coal at 320°F. Tetralin and carbon disulfide alone are not active solvents. However when blended with DMSO, they increase the extraction yield. Over 45 wt% of Bakerstown coal was extracted by DMSO/tetralin (1:4 vol) in six consecutive extractions at 320°F. About 25 wt% of Bakerstown coal was extracted by DMSO/CS_2 (1:1 vol) at room temperature. The presence of additives, such as cumene, quinone, and hydroquinone, drastically reduces the extraction yield due to the interactions between the additives and the active solvents. In general, extraction yield is affected by type of coal, the composition of the solvent, extraction temperature, the number of consecutive extractions, and the particle size of coal.

The solvent extraction of coal can be hypothesized as a three-stage process which includes penetration of solvent, swelling of the coal by solvent and solvation and removal of coal fragments from the coal matrix. A rationale for this hypothesis is presented and compared to present experimental results and literature results.

CHAPTER 1

INTRODUCTION

Energy and material are essential to the progress of civilization. Coal can provide both energy and raw material. It has been used as one of the most important energy resources since the seventh century A.D. After the discovery of petroleum and later nuclear power, the importance of coal in its energy aspect has declined. The vast reserve of coal seems to be overlooked while petroleum has served as the primary resource of synthetic materials and as fuel for automobiles and machinery. Coal lay quiet and unnoticed for many decades and became important again when the world was shocked by the oil embargo in 1973 and came to realize how limited are the oil reserves that we have.

In searching for alternatives we have begun to pay more attention to the centuries old resource, coal. Besides burning it as it is in power plants we try to liquefy, gasify, or just dissolve coal chunks into more manageable form. With the hope that one day all the cars and machines may run on coal-derived liquids, that clothing and plastics will be manufactured from organic materials extracted from coal, the need to study coal becomes more and more pressing.

Since the mid seventies, several coal liquefaction and gasification pilot plants have been in operation. The high conversion rate of those processes was encouraging, but their high energy consumption was not. Low-temperature processes such as the one proposed by Sears [1982] promise in terms of energy consumption an

economical way of coal utilization. This thesis forms part of that research work.

Coal

Origin of Coal

Coal is an aggregate of heterogeneous substances composed of organic and inorganic materials. The organic materials are derived mainly from plant remains which have undergone various degrees of decomposition as well as physical and chemical alteration after burial in peat swamps [Ting 1982]. The inorganic materials in coal consist for the most part of mineral matter: chiefly clay minerals, quartz, carbonates, sulfides, and sulfates, as well as many other substances in very small quantities [Elliott 1981, chap. 7, p. 415]. Mineral matters in coal derive from many sources, such as transportation by water or air, direct precipitation from solution, precipitation by organic metabolism, and secondary precipitation from groundwater.

An optically homogeneous discrete organic material in coal is called a maceral. There are three major groups of macerals: the vitrinite, liptinite (exinite), and inertinite groups. Just as rocks consist of mixtures of minerals, coal contains mixtures of macerals. In contrast to minerals, however, macerals do not have a well-defined chemical composition. Instead, these distinct components appear to reflect different plant origins.

Geologists generally agree that the original raw material for coal was humic matter - plant remains that had been decomposed by the action of bacteria and fungi. According to most theories, the slow

conversion to coal involved heating the humus at high temperatures -in the region of 750°F (400°C). However, according to Winans and his research group [Research & Development 1984] at the Argonne National Laboratory near Chicago, IL, such high temperatures are rare in geological deposits. The Argonne team made simple coals at 300°F (150°C), a temperature that is fairly common in geological formations. The group heated undecomposed lignin, the substance that holds plant cells together, in the presence of montmorillite or illite clay. The process led to simple coals, whose rank depended on the length of exposure to the 300°F temperature. Although these experiments did not fully reproduce conditions found in nature, they do suggest how natural coal could have formed.

Because of different plant origins and coalification conditions, there are different types of coals.

Classification

In the United States, coals are classified into various ranks according to the ASTM Standard of Classification of Coals by Rank [ASTM 1979]. Basically, two parameters, fixed carbon and calorific value, are used for this classification. The former is used for classifying high-rank coals and the latter is used for low-rank coals with overlapping at the high volatile A bituminous coal rank. As a reference, the ranges of percent carbon, percent volatile (both on moisture ash free basis), calorific value, moisture content, and reflectance in oil for coals of various ranks are given in Table 1. [Tsai 1982, p.3]

Table 1. Coal properties of various ranks
[Parks 1956, Hirst 1940, ASTM 1979]

Rank	Volatile (Wt%, maf)	Carbon Content (Wt%, maf)	Calorific value (Btu/lb, mmmf)	Moisture (Wt%)	Reflectance (% in Oil)
Lignite	69-44	76-62	8,300-6,300	52-30	0.25-0.4
Sub	52-40	80-71	11,500-8,300	30-12	0.4 -0.65
Hvb B,C	50-29	86-76	13,000-10,500	15-2	0.4 -0.75
Hvb A	49-31	88-78	>14,000	5-1	0.75-1.1
Mvb	31-22	91-86	--	5-1	1.1 -2.0
Lvb	22-14	91-86	--	5-1	1.1 -2.0
Anthracite	14-2	99-91	--	--	>2.1

Sub : Subbituminous
Hvb : High volatile bituminous
Mvb : Medium volatile bituminous
Lvb : Low volatile bituminous
maf : moisture ash free
mmmf: moisture mineral matter free

In coal petrography, the rank of coal is measured by the reflectance of vitrinite since vitrinite is the most abundant maceral group. The rank of coal increases as the reflectance of vitrinite increases.

Coal Structure

Coal is a physically heterogeneous and chemically complex solid [Tsai 1982]. It was once thought to consist of sheets of carbon atoms arranged in a pattern of six-sided rings, laid out neatly like tiles on a floor. Hydrogen, nitrogen and oxygen atoms were randomly scattered throughout this graphite-like structure.

The newly emerging molecular picture of many coals is of a three-dimensional network of units, each consisting of several carbon atoms. These units are linked by methylene (CH_2) chains of oxygen, sulfur, nitrogen and hydrogen atoms. In fact, coals typically contain a mixture of these gigantic "molecules," with one molecule sometimes caught in the web of another [Peterson 1983].

Coal Models

Historically, the models for coal evolved from solvent extraction studies. Coals of any rank up to anthracite are partially soluble in certain solvents. Depending on the character of both the coal and the solvent, the resulting solution is either largely molecular or largely colloidal.

One view of coal structure is that it consists of a mixture of molecules of a very broad range of sizes associated by hydrogen

bonding and van der Waals interactions. A good example of this structure is that proposed by Sternberg [1971, 1974]. He suggested that coal is composed of a mixture of molecules whose molecular weights run from the low hundreds to about 65,000. However, there were fundamental objections to models which treated coals as associated molecules of moderate size, say molecular weight less than 100,000. If the molecules are held together by noncovalent interactions, any solvent whose interactions with coal rival the energetics of the coal-coal interactions will dissolve it. This has not been observed to occur. Even over very long periods of time, coals swell but do not dissolve. Coal structures which involve association only by noncovalent interactions are not satisfactory as models. Therefore, many other scientists [Kovac 1977; Larsen 1978] consider coal to consist of an insoluble, highly crosslinked matrix.

A different view of coal structure is given by micelle models. Early investigators believed that the solutions obtained from low-temperature extractions were colloidal in nature. Recent work has cast doubt on some of these beliefs. Evidence now exists for a similarity in chemical composition between the solubles and the parent coal [Biggs 1936; Dryden 1950, 1952 (Fuel); Rybicka 1959; Brown 1959; Dormans 1960]. This has led several investigators to hypothesize that the insoluble coal matrix also consists of micellar units. Dryden's coal model [Dryden 1951] is one that includes an insoluble matrix consisting of large and strongly linked micelles in intimate association with smaller, less strongly linked micelles. The smaller micelles can only be extracted if the coal matrix is first swollen by

an appropriate solvent. The extraction process then involves the diffusion of the individual micelles throughout the swollen pores of the matrix. Evidence for such a model comes from extraction studies of coal with the specific amine solvent, ethylenediamine [Dryden 1951 (Fuel)]. The question arises as to what kind of forces keep the micelles in the insoluble portion from dispersing during extraction. Brown and Waters [1966] believed that the micelles in the solid state were interlinked by hydrogen bonds and weaker van der Waals forces. The hydrogen bonding is superseded by van der Waals forces as rank increases because oxygen-containing groups are progressively eliminated during coalification. The micelles of the lower-rank coals are therefore held together in a relatively open structure. With increasing rank, cross-linking is less extensive, permitting greater freedom of movement of the micelles; the rigid gel structure degenerates into a sol type of structure accompanied by better packing of micelles. Although this model can be used to explain the mechanism of thermal softening and numerous other properties of coal, many scientists are not convinced that crosslinks without chemical bonds are strong enough to prevent solvation from making the matrix soluble.

The evidence in direct support of micellar structures is at best weak: For instance, the treatment of coal with ethylenediamine gives a colloidal suspension of rather large particles [Dryden 1952 (Fuel)]. If the ethylenediamine treatment can break a few chemical bonds, then the particles may be just large pieces of the matrix which have been cleaved off.

It has also been shown that the infrared spectra of the

solvent-extracted materials bear a striking resemblance to those of the original coal and also to those of the insoluble extraction residue. This similarity has been taken as an indication of a polymeric character. Studies on coal genesis and various methods of chemical coal degradation also suggest that coal has a macromolecular structure.

There are several properties of coals which, when taken together, provide conclusive evidence for the macromolecular nature of coals. They are as follows: 1. coals are not completely soluble; 2. coals swell; and 3. coals are viscoelastic. There is also evidence from chemical studies for the macromolecular nature of coals (Specific evidence will be discussed in Chapter 3). This argument was first made by van Krevelen [1961] then elaborated by Green et al. [1982]. Dryden [1963] and Given [1961] have also provided thorough explanations of the coal constitution of coal developed from their work on bituminous coals.

Vahrman [1970] saw coal as consisting of both an insoluble three-dimensional matrix of large molecules and a potentially soluble portion consisting of smaller molecules. The smaller molecules are inclusions in a macro-micro pore system that penetrates the coal matrix [Spence 1970; Rahman 1970]. A considerable portion of these molecules are absorbed in pores of molecular size. It is assumed that all molecules not equally accessible; rather, some reside in pores of narrow diameter and others lie "loose" in pores of larger diameter. The Vahrman model, however, does not offer information about what constitutes the nature of the forces that hold the larger molecules

together. Nonetheless two important ideas concerning coal structure have emerged from Vahrman's work. First, we can state with some confidence that coal consists primarily of an insoluble matrix or residue along with a substantial portion of smaller molecules. Secondly, we can say that the smaller molecules lie in the macro-micro pore system of the coal. It appears that much of this material is located in pores too narrow to permit easy access by the extraction solvent.

That coal is an insoluble matrix with substantial amounts of smaller molecules is a point of general agreement. It is the second generalization that remains open to question. One may well ask: Do all the smaller molecules necessarily lie initially in the pore system, or are they trapped in the coal matrix itself rather than the pores?

In a study related to such questions, Van Krevelen [1965] compared coal to a polymer that had been formed by trifunctional stepwise polycondensation. A characteristic feature of the three-dimensional polycondensation reaction is the occurrence of insoluble "gels" at a certain stage of the condensation. The number-average molecular weight of the still-soluble part reaches a maximum at the gel point; beyond this point the average molecular weight of still-soluble part decreases. Generally speaking then in applying the theory of three-dimensional polycondensation of coal genesis, one can assume that the "gel point" has been reached and exceeded at the end of the lignite stage. Bituminous coal can then be represented as a three-dimensional polymeric network with a certain amount of soluble

fraction of low degree of condensation entrapped in the interstices of the polymeric network.

Building on the work of Vahrman and Van Krevelen, Larsen and Kovac [1978] developed a model of bituminous coal structure which consists of two essential elements: (1) a cross-linked, three-dimensional, macromolecular network and (2) substances filling pores of a network.

Later Green et al. [1982] presented a somewhat detailed structural model developed from examining a variety of coal models proposed up to 1980. The existence of largely aromatic and hydroaromatic "clusters", as suggested by many x-ray and chemical degradation studies, is accepted. These clusters are thought to have a molecular weight distribution covering the low hundreds. They are extensively bonded internally, so that they can be freed from the coal matrix more easily than they can themselves be chemically degraded. These clusters are then linked together covalently to form a network. Since each cluster is polyvalent, the potential for extensive cross-linking exists. There is chemical evidence that the links between clusters are short methylene chains and various types of ether linkages. Not all clusters are bonded to the network, but some are dissolved in it. These dissolved clusters are extractable with a good solvent.

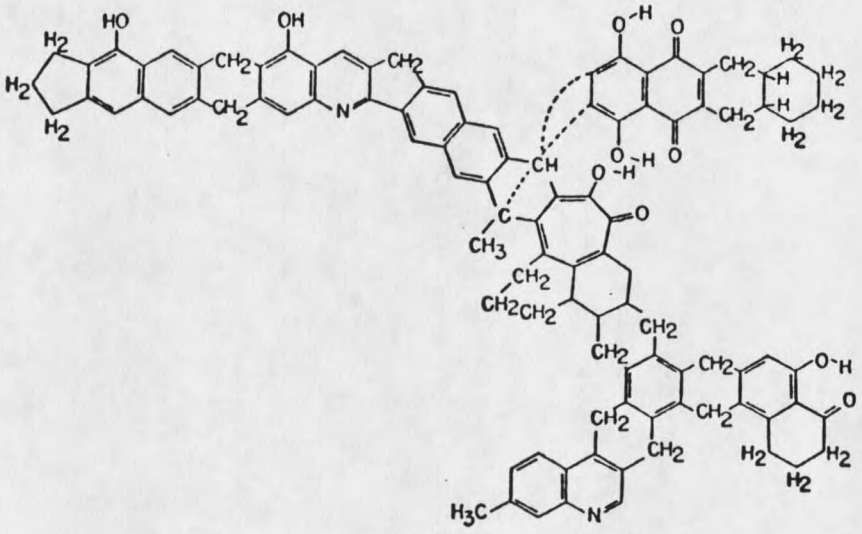
Some coal scientists prefer to ascribe the entanglement of macromolecules to the cross-linking of macromolecules. The polar bonds (which include hydrogen bonds and those in charge transfer complexes) not only are the means by which smaller molecules are attached to the macromolecular structure [Marzec 1979] but they also stabilize parts of the macromolecular network [Szeliga 1983] and thus,

in conjunction with covalent cross-links, help to determine the macromolecular conformation of the coal.

Hombach [1981], Liotta [1981] and Larsen [1983] are in agreement that hydrogen bonding is the dominant non-covalent crosslink in coals, while Marzec [Szeliga 1983] argues for the dominant importance of donor-acceptor interactions. Since hydrogen bonding is one form of donor-acceptor interaction, there is not necessarily any conflict here.

Because the macromolecular structure of coal resembles that of a tridimensional polymeric network, with a sizable amount of extractable, low molecular weight material being contained within the network, some "basic unit" structures of coal have been proposed. Van Krevelen proposed formulas for the aromatic part of the structure of coals at different stages of coalification. Given [1960] (Figure 1), Wiser [1973], and Gibson [1978] have also proposed model molecule structures for high-volatile bituminous coals of approximately 82-83% carbon content (maf). Despite significant differences among these proposals, several of their basic features are similar. They propose that the basic structure of bituminous coal is an aromatic/hydroaromatic system. The average number of condensed aromatic rings is two to four, and phenanthrene and fluorene types predominate. The non-aromatic part of the molecule consists mostly of cyclo-paraffinic and hydroaromatic ring systems, and there are few alkyl (mainly methyl) groups. The aromatic rings in the aromatic/hydroaromatic structure form lamellae. These aromatic lamellae, in groups of two or

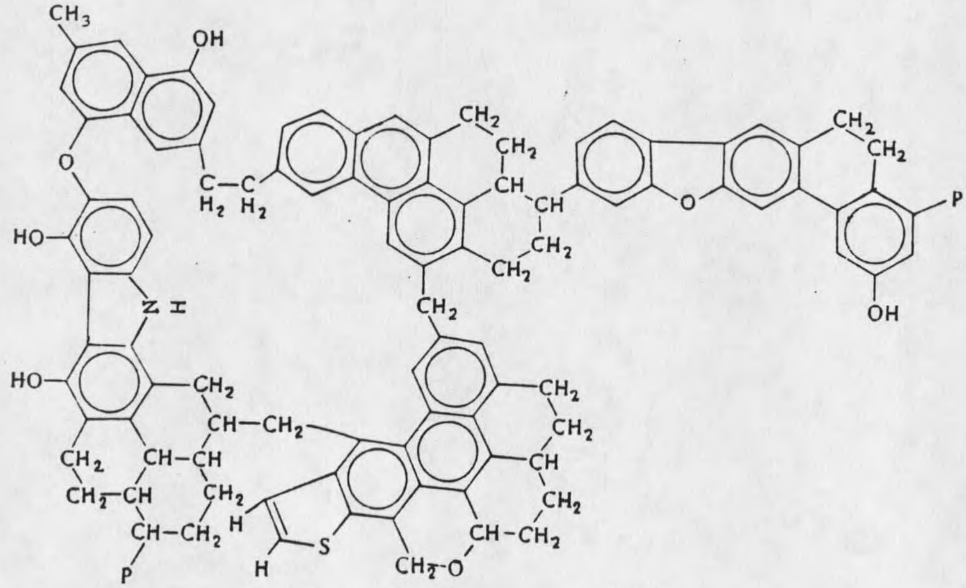
Figure 1. Given's idealized molecular structure of vitrinite in bituminous coal. (a) molecular unit or layer (top view); (b) composite alignment of layers (side view). [Given 1960].



more, are stacked and form larger, imperfect sheets or ring clusters. The sheets or clusters are buckled due to the presence of hydroaromatic or five-membered rings.

Heredy and Wender [1980] have proposed a formula for the coal molecule. Their general formula $C_{100}H_{79}O_7NS$, for an arbitrary "molecular" size, was derived for a high-volatile, vitrinite-rich bituminous coal of 83% carbon content (Figure 2).

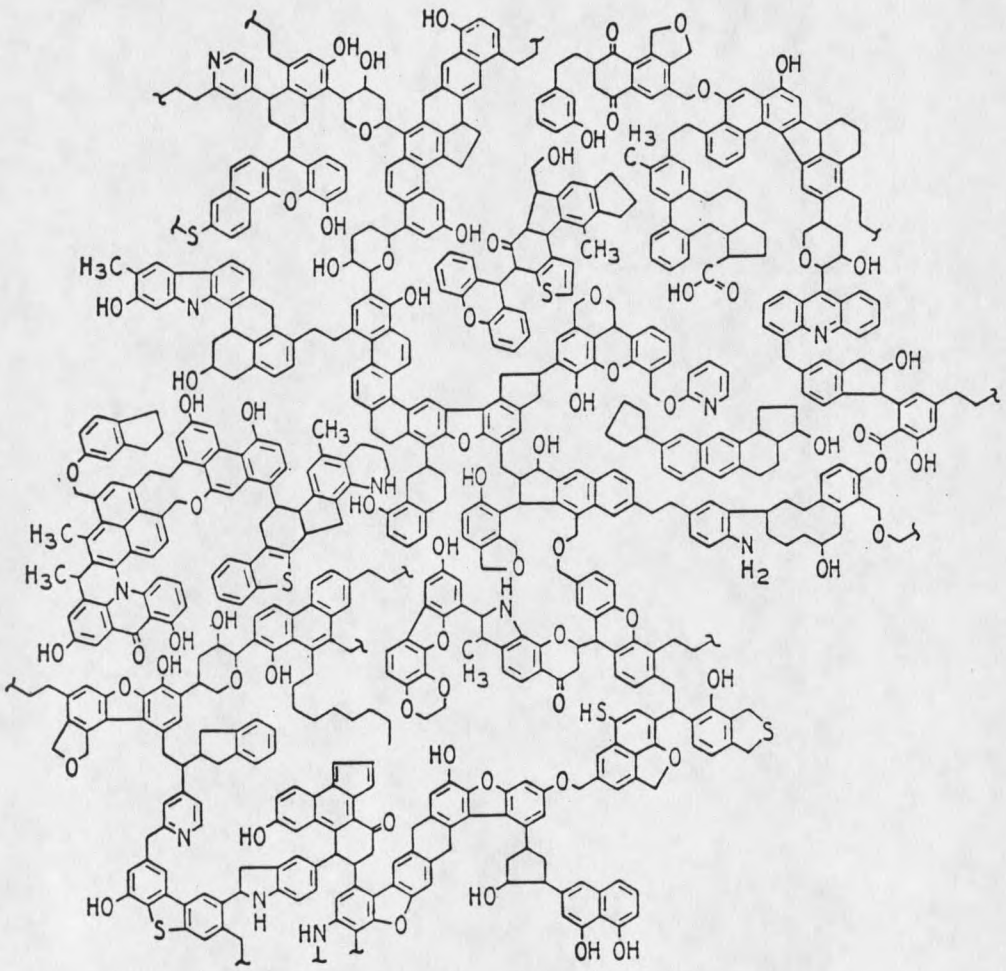
Figure 2. Structure of the coal model molecule proposed by Heredy and Wender. [Heredy and Wender 1980]



Recent evidence derived from liquefaction studies as well as the development of new analytical techniques have provided substantial amounts of new information about several important aspects of coal structure. Shinn [1984] has produced a model which adequately reflects current concepts (Figure 3). The distribution of atoms in the coal model was determined to be $C_{661}H_{561}O_{74}N_{11}S_6$ to represent vitrinite-rich high-volatile bituminous coals. In this model, portions of coal can be removed at mild conditions under which few if any covalent bonds will be broken. Exhaustive extraction of the model coal would yield about 20 wt% of the organic matter in the extract. Given [1983] has referred to such materials as mobile phase. Although Shinn [1984] believes 40-60 wt% of the coal may be "mobile", his model considers only those materials liberated by low-temperature solvent extraction to be truly mobile. Marzec et al. [1979, 1983] state that the mobile phase may include up to 40 wt% of the coal and can be partly immobilized in the absence of imbibed solvents by binding to the network (immobile phase) through hydrogen bonding or as electron donor/acceptor complexes. Yokono and Sanada [1978] have found that the quantity of mobile component present in one sample of Japanese coal was 41 wt% at room temperature. This mobile phase is equivalent to the small molecules trapped or occluded in the micropores of coal discussed earlier [Vahrman 1972].

In brief, whether or not coals contain a substantial fraction of relatively small molecules clathrated within the macromolecular network which for extraction require a long time or extra thermal energy for release remains a topic still subject to considerable debate.

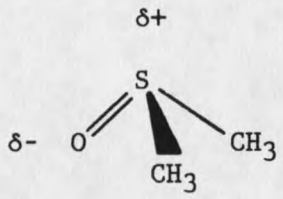
Figure 3. Model of bituminous coal structure proposed by Shinn. [Shinn 1984]



Solvents and Coal Extraction

Dimethylsulfoxide (DMSO)

The DMSO molecule is a pyramidal structure with sulfur, oxygen and carbon atoms at the corners [Bastiansen 1948].



Bond length		Bond angle	
C—H	1.08 Å	CSC	100°±5°
C—S	1.82 Å	CSO	107°±5°
S—O	1.47 Å		

The sulfur-oxygen bond is quite polar so that the liquid has a high dielectric constant of 46.7 and a high dipole moment (μ = 3.9 debyes). This polarity and geometry lead to considerable organization in the liquid state in which DMSO molecules are associated into chains by dipole attraction [MacGregor 1966]. The dielectric constant is high enough to permit easy charge separation and hence good solubility for a variety of ionic, polar, and polarizable molecules.

Since the sulfur atom is the positive atom of the dipole, one might expect the positive charge to activate the hydrogen atoms of the methyl groups of DMSO making them more acidic. However, this effect is very weak. The acidity constant for DMSO is about 10^{-31} which makes it about 0.001 as acidic as diphenylmethane [Steiner 1965].

The basicity of DMSO, which results from the enhanced electron density at the oxygen atom, is slightly greater than that of water. DMSO is particularly prone to participate as the acceptor molecule in hydrogen bonding. Lindberg [1961] has estimated that the hydrogen bond between DMSO and water is 4/3 times as strong as that between

water and water. This ability of DMSO to compete effectively for hydrogen donor molecules is an important factor in the effect of DMSO on some reaction rates [Parker 1962].

Related Work in Solvent Extraction of Coal

Solvent extraction is one of the oldest and most commonly used tools in coal structural studies. A liquid which produces a high degree of swelling in coal is often referred as a "solvent" for coal even though the coal matrix does not dissolve in the liquid.

The long history of solvent extraction of coal dates back to 1860s since the work of De Marsilly [1862]. Fremy [1861] recognized that pyridine is an effective solvent for coal even at room temperature. The earlier workers did their investigation more or less in an empirical way. They subjected coal to solvent action at elevated temperature and pressure and then fractionated the extract thus obtained in a series of solvents and ascribed specific properties to the fractions thus separated. Unfortunately, the many apparently contradictory ideas which resulted from these studies stood in the way of conceiving a common model as a basis for the solvent extraction of coal.

Dryden [1963] has presented a comprehensive review of the work on the solvent extraction of coal accomplished up to the late 1950s. Another useful early review on coal extraction is available in van Krevelen's book on coal chemistry [1961]. According to van Krevelen, coal extraction methods can be classified into four groups: (1) extractive disintegration, (2) extractive chemical disintegration, (3)

nonspecific extraction, and (4) specific extraction.

(1) The operation of extractive disintegration is carried out at rather high temperature (>200°C) and may lead to very high extract yields. Extraction with phenanthrene at its boiling point is a typical example. It has been demonstrated that two chemical interactions, hydrogen exchange and incorporation of phenanthrene into coal, take place between phenanthrene and coal [Heredy 1966]. The formation of the coal extract can be interpreted as a free radical chain reaction resulting in the breaking of certain bonds of coal and aromatization of some hydroaromatic structures. It appears that phenanthrene plays the role of a chain carrier in this process.

(2) The operating temperature of extractive chemical disintegration is also high, about 300-400°C. Hydrogen donors, such as tetralin and hydrophenanthrenes, are usually used. Their chemical composition, as well as the composition of the extract, is significantly changed during the process. Neavel [1976] has investigated the high-temperature extraction of a high-volatile bituminous coal (78% C, maf). Heating coal to 400°C in tetralin converts ≈90% of the ash-free coal to pyridine soluble material within two minutes. He suggests a free radical mechanism: the macromolecular coal structures are pyrolyticly decomposed, followed by the stabilization of free radicals through internal hydrogen disproportionation.

Although disintegration processes usually give higher extraction yields due to chemical bonding breakage, these processes are less favorable as the cost of energy increases with temperature and reaction.

(3) Unlike the disintegration process, nonspecific extraction only extracts a small amount, a small percentage, of the coal. The operation is preferably at low or moderate temperatures. Many common solvents, hydrocarbons, chlorinated hydrocarbons, and alcohols have been used at temperatures up to 150°C. (4) Most specific extraction methods extract between 15 and 40% of the parent coal at temperatures below 200°C. The most effective solvents have electron donor capacities and, in consequence, are nucleophilic. Pyridine is a typical example and has been extensively studied [Friedel 1968; Yokoyama 1973; Vecerikova 1975; Lino 1983; Green 1984; van Bodegom 1985]. Since pyridine is a nucleophilic solvent, possessing an unshared pair of electrons, it behaves as an electron donor and will interact with electron-deficient centers (e.g. aromatic structures with delocalized unpaired electrons, protons in heteroatom groups) in the vitrinite structure [van Krevelen 1961; Marzec 1979]. Consequently, the pyridine molecules are able to disrupt existing donor-acceptor bonds, not only detaching smaller molecules from the macromolecular network as suggested by Jurkiewicz et al. [1981, 1982] but also possibly increasing the flexibility of the macromolecular structure and molecular fragments. In addition, the tendency for pyridine molecules to concentrate around electron-deficient centers in the macromolecular network attenuates the interactions that lead to bonding between these centers and neighboring constituent groups and thereby allows greater segmental mobility of these parts of the vitrinite structure [Barton 1984].

Dipolar aprotic solvents are a class of solvents which can be used

for specific extractions. Roy, Banerjee, and Singh [1976] studied the action of dipolar aprotic solvents, including dimethylsulphoxide (DMSO) as a representative member, on coal. The results obtained show that the solvent capacity of DMSO is comparable to that of any other good solvent, such as pyridine or ethylenediamine. The effect of particle size on the extraction capability is evident from their experimental data. About 12% of coal was extracted by DMSO at room temperature. Soxhlet extraction gave higher yields with DMSO (22.7%), pyridine (23%), and N-methyl-2-pyrrolidone (35.3%). They reported hexamethylphosphoramide (HMPA), a dipolar aprotic solvent, as a weak solvent for coal. This result contradicts the findings of Sears [1982] who observed the strong interaction between HMPA and coals but also noticed the difficulty of separating coal residue from extracted material in HMPA. The effectiveness of mixed solvent was suggested by Hombach [1980] and an ethanol-benzene mixture is known to be good solvent for the extraction of brown coal. Lino and Matsuda [1983] found that a carbon disulphide-pyridine mixture is an efficient solvent for the extraction of bituminous coals at room temperature. They reported a large amount of extract yield (41.5%) with five successive extractions at room temperature. The extraction yields obtained are considerably higher than those for pyridine alone, except for brown coal. There is an interesting finding revealed by the nuclear magnetic resonance (nmr) study: the extract from the 1:1 pyridine-carbon disulphide mixture is similar to the pyridine extract, but not the carbon disulphide extract. Other carbon disulphide-organic solvent mixtures have been studied [Lino and Matsuda 1983] and dimethylformamide (DMF), HMPA

and DMSO are found to be good co-solvents with carbon disulphide. On the other hand, benzene, carbon tetrachloride and tetrachloroethylene show no synergistic effect in a mixture with carbon disulphide. Van Bodegom et al. [1985] studied the dissolution behavior of three medium-rank (80.5-86.6% Carbon content) and three high-rank (89.5-93.3% Carbon content) coals in aliphatic amines and pyridine. Dissolution of medium-rank coals does not depend on temperature in the 120-180°C temperature range and not involve the breaking of chemical bonds. A maximum extract yield of ≈50% appears to exist and is approximately constant over the bituminous range.

Efforts to Predict the Solvent Power

A number of theoretical approaches have attempted to correlate solvent effectiveness with chemical and physical properties of the solvent [van Krevelen 1965; Dryden 1952 (Chem. and Ind.); Marzec 1979]. The properties that make a solvent a good one for coal have been thought to be, in chemical terms, the availability of a lone electron pair, a large electron-donor number (DN) and a small electron-acceptor number (AN) and, in physical terms, a solubility parameter comparable with that of coal.

The concept of "solubility parameter", developed for polymeric systems, has been applied to the solubility of coal macromolecules in the process of solvent extraction. The Hildebrand solubility parameter [Hildebrand 1962], a measure of cohesive forces, is defined as the positive root of the cohesive energy density:

$$\delta = (U_{vap}/V_m)^{1/2} \qquad (1)$$

where U_{vap} = the molar heat of vaporization and V_m = the molar volume. The dimensions of the solubility parameter in cgs units are $cal^{0.5}/cm^{1.5}$ or "hildebrands". In SI units the nearest equivalent is $MPa^{0.5}$ or $J^{0.5}/cm^{1.5}$. To convert from hildebrands to $MPa^{0.5}$ multiply by $(4.187)^{0.5} = 2.046$.

Based on the theory of swelling of crosslinked polymers and the thermodynamics of regular solutions, the enthalpy of interaction between a solvent and coal is given by:

$$H = kTn_sV_sv_s(\delta_{coal}-\delta_s)^2 \qquad (2)$$

where v_s = the volume fraction of the solvent at equilibrium swelling, V_s = the molar volume, n_s = the number of moles of solvent, and δ = solubility parameter. The most favorable interaction is 0 kcal/mole; therefore a maximum in coal-solvent interaction and hence in solubility should occur when the solubility parameters of solvent and coal are identical.

In order to select solvents which match the coal in solubility parameter, the solubility parameter of coal was investigated. Van Krevelen [1965] calculated theoretical values of δ for coals as a function of rank by summing the energy density contributions of atoms and constitutional characteristics. The calculated δ for the high rank coals (85-90% Carbon content, maf) are in the range of 11.9 to 10.6. Kirov et al. [1967] determined solubility parameters from swelling

experiments in various solvents and Hombach [1980] determined solubility parameters for coals of different rank by measuring the spectrophotometric absorbance of extracts obtained by treating the coals with binary solvent mixtures. The parameters ranged from ≈9.9 to 11.2 hildebrands and showed little dependence on the chemical nature of the solvents in the mixture. Several researchers examined the relation of solvent parameters to the extractability and swelling of coal and the dissolvability of coal liquids [ref. 1-13 in Jones 1985]. Van Krevelen was able to predict that both ethylenediamine (12.4 hildebrands) and pyridine (10.6 hildebrands) are suitable solvents for high rank coals. However, many solvents with compatible solubility parameter, such as 1-propanol (12 hildebrands), are poor solvents for the same kind of coal. This failure of prediction should come as no surprise, because the Hildebrand solubility parameter describes only non-specific van der Waals interactions; it includes no specific interactions such as hydrogen bonds and donor-acceptor complexes. Since the interactions of coals with most good solvents are exothermic [Green 1984], it is clear that regular solution theory should not apply. In regular solution theory it is assumed that mixing is random and the change of entropy (ΔS) is calculated on this basis. The existence of any specific complexes invalidates this assumption and for coal-solvent systems, the existence of specific interactions has been demonstrated.

A regular solution theory has been extended to systems involving specific interactions by splitting the solubility parameter into contributions from the various specific interactions. While this

approach exceeds the limits of the theory and is, strictly speaking, invalid, it does work in a number of cases. It probably works because of compensation between enthalpy and entropy. The formation of a specific complex has an unfavorable entropy which is compensated for by the favorable enthalpy of complexation. Hombach has used these complex solubility parameters to isolate hydrogen bonding as an important internal associative force in coals. Furthermore, he has suggested that a mixture of poor solvents for coal can act as a better solvent when chosen with respect to the solubility parameter [Hombach 1980].

Hansen [1967] proposed a three-dimensional solubility parameter which consists of three major intermolecular forces that affect solubility: dispersion, dipole, and hydrogen bonding interactions. Ward [1984] found that the three-component solubility parameter concept showed some promise for correlating effectiveness of solvents and solvent mixtures on coal. He also noted that the hydrogen bonding component appeared to be especially important. Roy et al. [1976] studied the extractability of coal at 35°C as a function of the dielectric constant (ε) of dipolar aprotic solvents. The results, however were ambiguous: dimethylsulphoxide (ε = 46.6) was comparable with pyridine (ε = 12.3) and better than ethylenediamine (ε = 14.2).

In order to evaluate the solvent power for coals, Dryden [1952 Chem. and Ind.] tested about one hundred solvents and found that the solvent activity could not be accounted for by internal pressure, surface tension, dielectric constant, or dipole moment of the solvent. He observed that:

- The degree of solvent power depends on the availability of an unshared pair of electrons in the solvent.
- Participation of the lone pair in resonance of the molecular skeleton reduces solvent power.
- Hydrogen-bonding in the liquid phase tends to reduce solvent power.
- Large molecular size and high viscosity reduce solvent power.

He termed those solvents, which are very active in swelling and dissolution of coal, as specific. In his study, Dryden found most primary aliphatic amines (e.g. ethylenediamine) to be specific solvents. However, some coal scientists argue that such strong solvent power of primary aliphatic amines is due to chemical reaction [Bodzek 1981].

A different approach to the quantification of solvent properties is to measure the ability of the solvent to interact with specific substances. Gutmann [1976] has developed the scales of donor number (DN) and acceptor number (AN) to characterize a solvent's ability to donate electron density to electron-deficient centers and to accept electron density from electron-rich centers. (These interactions are of the Lewis acid-base type.) The donor number of a base is simply the calorimetrically determined enthalpy of adduct formation between the base and antimony pentachloride ($SbCl_5$), measured at high dilution in 1,2-dichloroethane. The acceptor number is defined as the ^{31}P nmr chemical shift observed for the reference base $(C_2H_5)_3PO$ when dissolved in the solvent in question, relative to the chemical shift observed in the solvent hexane.

By examining the extraction yield of 18 solvents at ambient

temperature, Marzec et al. [1979] found that we can expect high extraction yield from a group of solvents with high electron-donor number (DN > 19) and low electron-acceptor number (AN < 21). Attempts were made to correlate the extract yields versus solvent parameters, namely: Gutmann's electron-donor and acceptor numbers (DN, AN), Hildebrand's solubility parameters, Snyder's [1974] solvent selectivities, and Dryden's [1963] internal pressure (δ^2). The results suggested that the electron-donor as well as acceptor properties of the solvents do influence the coal extraction process while polarity of the solvents, their internal pressure, and their ability to interact via London forces and via dipole interaction do not reflect the effectiveness of the solvents in coal extraction, similar to what Dryden had concluded earlier.

The possible correlations of solvent acceptor and donor numbers with extractability and swelling of hvb coal at ambient temperatures were investigated. Both the extract yield and the swelling ratio increased with the increased in the DN or DN-AN values of solvents [Marzec 1979; Pajak 1985; Marzec 1983]. Jones [1985] considered that the value of the ratio DN/AN for solvents is more reliable as a predictor of solvent effectiveness for coal extractability or coal swelling than are DN, DN-AN, net hydrogen-bonding index or Hildebrand solubility parameter. However his correlation diagram still shows significant scatter.

Mechanism of Solvent Extraction of Coal at Low Temperature

Various models have been proposed from time to time to explain the

mechanism of solvent extraction of coal. The model proposed by Dryden [1963], also termed as "micellar sieve extraction mechanism", can encompass a broad field of experimental observations, in comparison with that proposed earlier by coal scientists [Agde and Hubertus 1936; Kreulen 1945]. Two classes of intimately connected micelles were recognized. The matrix of larger and most strongly linked micelles can be partly and progressively dispersed in a suitable solvent by increasing the temperature. The second kind of micelles which are less strongly bonded are entrapped within the matrix unless it is first swollen by the solvent. The micelles, assumed to be rigid and comparatively indestructible (valid if below 300°C, [Hill 1966]), are extractable as individual units by the penetration of solvent molecules into the swollen portion of the matrix.

How are the second kind of micelles released? How is the matrix swollen by solvent molecules? Dryden did not answer these key questions specifically. However, he did try to shed some light on the problem by considering the possible types of interaction between coal and solvent molecules with lone-pair electrons [Dryden 1952 Chem. and Ind.]. The formation of a hydrogen bridge between coal and solvent molecules was strongly suggested as the possible swelling mechanism. It leads to the broader donor-acceptor approach, which includes hydrogen-bonded, coordinate, charge transfer or even weaker complexes in molecular interaction.

A model for coal extraction, based on the assumption that donor-acceptor bonds occur in coal and are responsible for binding together macromolecular network and extractable substances filling the

pores of a network has been worked out by Marzec et al. [1979, 1983]. Extraction is in principle a substitution reaction: pore substances are replaced by a solvent molecule in their $Donor_{network}$ $\longrightarrow$ $Acceptor_{pore\ substance}$ or $Donor_{pore\ substance}$ $\longrightarrow$ $Acceptor_{network}$ bonds that bind together structural elements of an original coal. Released pore substances are withdrawn by a solvent. If the extractable substances are trapped in the coal matrix instead of filling the pores, the coal is swelled by the extraction solvent due to the donor-acceptor interaction between coal matrix and solvent. While the matrix is expanded, the trapped materials might be released and diffused out. In Marzec's view, any dissolution of a coal network seems to be negligible, as no example is known wherein carbon-carbon bonds of a network skeleton can be destroyed by the activity of the applied solvents at ambient temperature. According to the donor-acceptor mechanism, effective solvents, (i.e., solvents capable of substitution) are characterized by specific DN and AN values that fulfil the requirement that donor-acceptor bonds formed between solvent and coal are of higher energy than donor-acceptor bonds present in the original coal or in the solvent itself. If Marzec's mechanism is valid, there should be good correlations between the effectiveness and the AN and/or DN of extraction solvents.

The correlation of extraction of yield with DN and AN is not as high as the correlation of swelling ratio with DN and AN [Szeliga 1983; Marzec 1979]. It implies that Marzec's mechanism may only work for the swelling stage, but does not consider other stages involved in solvent extraction of coal. A better correlation of the

dissolvability of coal preasphaltene with DN/AN has been reported [Jones 1985]. Preasphaltene is defined as the toluene-insoluble, tetrahydrofuran (THF) soluble fraction of coal liquefaction sample. Therefore, there is little crosslinked network in preasphaltenes. It implies that the concept of correlation with DN and AN works better when there are no network restrictions.

Research Objective

Since dimethylsulfoxide (DMSO) has the characteristic of an active solvent: high electron donor number, and has been recognized as a good solvent for coal extraction at low temperatures [Roy 1976], and since it is less toxic and cheaper than tetramethylurea and hexamethylphosphormide, both of which were reported as active solvents for coal in solvent blends [Sears 1982; Ward 1984; Ichioka 1985], it is logical to study the role of DMSO in solvent extraction of coal.

This research has been undertaken in order to study the action of solvents, mainly dimethylsulfoxide, and solvent blends, such as DMSO/tetralin and DMSO/carbon disulfide, on bituminous coals under atmospheric pressure and temperatures below the boiling points of the solvents. Various combinations of factors, such as composition of solvent, extraction temperature, number of consecutive extractions, and particle size of coal, are investigated to increase the solvent extraction yield of coal. Extraction experiments and residue and extract analysis are conducted to gain the understanding of the extraction processes.

CHAPTER 2

METHODOLOGY

The major experiments conducted in this research consisted of extraction experiments with coal under a variety of operating conditions: atmospheric pressure and at temperatures below boiling point of solvents; and with the use of solvents. Several analyses were performed on the obtained residues and extracts, and the yields measured.

Materials

The bituminous coals used in this study are listed in Table 2, together with their elemental properties, moisture and ash free basis, and handling conditions since reception. Kittaning and Bakerstown coals were selected based on their high extraction yields with tetramethylurea (TMU) and hexamethylphosphoramide (HMPA) [Sears 1982; Ward 1984; Ichioka 1985]. Results from this research could be used to compare with those of previous researches.

Dimethylsulfoxide was extensively used in this study as an extracting agent. It was purchased from Aldrich Chemical Company and used without further purification. Tetralin was used as a major blending solvent in mixture with DMSO. The physical properties of DMSO are listed in Table 3. The sources and grade of other solvents used are listed in Table 4. Other chemicals used in this research are listed in Table 5.

Table 2. Analysis of coals used

Coal	Kittaning	Bakerstown			
Batch	Chunk#3	Chunk#1	Chunk#2	Bag#1	Bag#2
Ash (wt%)	13.0	9.6	7.5	10.2	10.2
Moisture (wt%)	0.7	0.27	1.56		
Nitrogen (wt%)	1.2	1.2	1.8	1.8	1.7
Carbon (wt%)	83.0	85.3	87.9	86.3	86.2
Hydrogen (wt%)	5.3	5.5	5.8	5.4	5.4
Sulphur (wt%)	4.0	4.8	3.2	3.5	3.8
Handling in	air	air	N_2	N_2	air
Grinding	ballmill	hand	hand	hand	ballmill
Sieving		hand	hand	hand	machine
Storing in	air	air	N_2	N_2	N_2

Table 3. Physical properties of DMSO [MacGregor 1967]

Property	Value
Freezing point, °C	18.55
Boiling point at atm., °C	189.0
Enthalpy of vaporization, kcal/mole at 25°C	12.64
Density, g/ml at 25°C	1.0958
Refractive index, at 25°C	1.4773
Dielectric constant, at 25°C	46.7
Dipole moment, at 20°C	4.3
pKa	31.3
Surface tension, dyne/cm at 25°C	42.86
Viscosity, c.p. at 25°C	1.99

Table 4. Other solvents used in the study

Solvent	Source	Grade
Carbon disulphide	Baker	Baker Analyzed
Cumene		Lab
Limonene (1)	Fritzsche	Lab
Methylene dichloride	MCB	Reagent, A.C.S.
N-Methyl-2-pyrrolidinone	Baker	Lab
Pyridine	Baker	Baker Analyzed
Tetralin	Aldrich	99%

Table 5. Chemicals used

Chemical	Sources	Grade
Acetone		Lab
Benzyl benzoate	Aldrich	99+%
Cumene hydroperoxide	Lucidol	
Diphenylmethane	Aldrich	99%
Ethanol		95%
Hydrogen peroxide, 30%	Baker	Lab
Hydroquinone	Diamond	Photo
2-Hydroxydiphenylmethane	Aldrich	99%
Isopropanol		Lab
Lupersol 130	Lucidol	
Phenyl benzoate	Aldrich	99%
Quinone	Aldrich	98%

Extraction Procedure

The solvent extraction was performed in a 500 ml glass flask heated by a hot plate with magnetic stirring. A condenser was set on the top of flask to condense the solvent vapor. Extraction experiments were carried out under nitrogen atmosphere by either purging the flask with nitrogen or by operating inside a glove box. A glove box was used for most extractions to provide a purer nitrogen environment so that the whole operation might never be exposed to air. Usually the solvent or solvent mixture was first heated up to the desired temperature, then a preweighed coal sample was added. After digesting in the flask, the coal solution/dispersion was suction filtered with Whatman No. 1 filter paper designed to retain crystalline precipitates larger than 11 microns. The filtration residue was washed with non-active solvents (e.g. acetone, isopropanol, or ethanol) then dried in a desiccator under vacuum. The

apparent extraction yield is calculated as

$$\text{apparent extraction yield} = \frac{\text{coal weight - residue weight}}{\text{coal weight}} \quad (3)$$

Analytical Procedures

Analysis of Coal and Residue

(1) Elemental analysis — Elemental carbon, nitrogen, hydrogen and sulphur contents of coal samples and residues of extraction experiments were determined with a Carlo Erba Model 1100 Elemental Analyzer. Elemental C, N, H or S was catalytically oxidized to CO_2, NO_2, H_2O or SO_2, then analyzed by a built-in gas chromatograph with a Carlo Erba DP110 integrator. An on-line Osborne I microcomputer was used to store data, and calculate the weight percentage of each element in the samples. The accuracy of elemental analyses was approximately ±1.1% of measured value for carbon, ±2.1% of measured value for hydrogen, ±1.5% of measured value for nitrogen and ±2.0% of measured value for sulfur, based on standard deviations of measured values from theoretical values for numerous standard compounds run.

(2) Ash content determination — Ground coal samples were ashed in an air-available oven at 700-750°C for approximately 10 hours. In order to avoid flames during ashing, the oven temperature was adjusted to rise from room temperature to 700-750°C gradually at the rate of 50°C/hour. The residue weight percentage of ashing was taken as the ash content of the coal sample. The coefficient of variation was less than 0.5% based on several duplicated

measurements.

(3) Moisture content determination — Ground coal samples were dried in an air-available dryer at 105°C till a constant weight was reached. The weight loss from drying was taken as the moisture content. Although the moisture content of coal would vary according to the humidity of surrounding atmosphere, the accuracy of result reported in dry-basis should not be much affected due to the very low moisture content (less than 2 wt%) measured in all the coal samples.

(4) Swelling ratio measurement — The volumetric swelling procedure developed by Liotta et al. [1983] was applied to both Kittaning and Bakerstown coals. The volumetric procedure was chosen because it is convenient and proven to give the same results as the more common gravimetric procedure [Green 1984, p.935]. Approximately 0.5-0.55 gram of coal (150/200 Tyler mesh) was placed in an 8 mm o.d. Pyrex tube and centrifuged for 5 minutes in an International Equipment Co. (IEC) Model HT centrifuge at 1750 rev/min. The height of coal was measured as h_1. Excess solvent (DMSO 2 ml) was added and the tube was vigorously shaken with a mechanical shaker to ensure complete mixing. The coal was again centrifuged and the height was measured. The mixing and centrifuging were repeated until a constant height of coal, h_2, was reached. The volumetric swelling ratio on a dry basis, $Q_{v,dry}$ is defined as

$$Q_{v,dry} = \frac{h_2}{h_1} = \frac{V_{c,dry} + V_s}{V_{c,dry}} \qquad (4)$$

where V_s = volume of solvent absorbed by a unit volume of dry coal, $V_{c,dry}$. The coefficient of variation of swelling ratio was less than 2.6% based on the results of duplicated measurements.

(5) Estimation of coal/residue particle density — The density was estimated by the following steps:

(a) Pack the particles in a glass tube of uniform thickness of 0.764 cm (3/10 inches) i.d., tap the tube till the height of filled particles is constant. The height is H and the filled particles weight, W.

(b) If the packing porosity, ε, is known, the density of particle can be calculated as

$$d = \frac{W}{\pi r^2 H(1-\varepsilon)} \tag{5}$$

where r is the radius of tube, r = (i.d.)/2

(c) The porosity of particles was estimated with a sphericity correlation [Brown 1950]. The sphericity in turn was estimated with roundness which was measured by image analysis. The roundness was defined as

$$\text{roundness} = \frac{1000 * \text{perimeter}^2}{4\pi * \text{area}} \tag{6}$$

where the perimeter and area of particles were measured in image analysis.

(6) Image analysis — The image analysis system included an Olympus

BHS microscope with phase contrast objectives, a Plumicon high sensitivity, black and white Video camera, and an Cambridge / Olympus Q10 image analyzer. The resolution is 0.37 micron per pixel. The measurements were mainly the size (area, length, width in microns) and shape (roundness factor) of the particles or flocs in solutions/dispersions.

Analysis of Extract Solution

(1) Constituent identification — The gas chromatograph / Mass spectrometer (GC/MS) was used to identify constituents in solution or coal extract. The Varian 3700 GC was equipped with a DB-5 capillary column, the Vacuum Generators VG 7070E-HF double focusing mass spectrometer has mass range 4-2600 a.m.u. and maximum resolution 25,000. In case of separation difficulties, coal extract was fractionated into hexane, benzene, methylene chloride, and pyridine-soluble fractions before feeding into the GC/MS.

(2) Viscosity measurement — A Cannon-Fenske Viscometer was used to measure the kinematic viscosity of solvents and solutions /dispersions. The temperature was maintained at 40°C by placing viscometer in a water bath. Five or more measurements were taken for each solvent or solution. The coefficient of variation was less than 1.7%.

(3) Light scattering — A Brice Phoenix PP1 Universal Light Scattering Photometer Series 2000 was used to estimate the particle size in very dilute solutions/dispersions.

(4) Ultracentrifugation —

(a) The solution/dispersion was first put in the Dupont Sorvall RC-5B Superspeed Centrifuge which was operated at 10,000 rpm, 10 min, at 20°C.

(b) The upper portion of the centrifuged solution/dispersion was again put in Dupont Sorvall Ultracentrifuge at 45,000 rpm, 10 micron vacuum, 20°C for 15 hours.

(c) The upper and lower portions of solution/dispersion from (b) were then subjected to image analysis.

CHAPTER 3

RESULTS AND DISCUSSION

Seventy-six extraction experiments were conducted under a variety of operating conditions (Appendix A). The factors believed to influence extraction yields were composition of solvent, extraction temperature, number of consecutive extractions, and particle size of coal. The effect of solvent-to-coal ratio and oxidation of coal was also investigated.

In order to aid the reader in following the presentations of this chapter, mnemonics will be used to label all extraction runs. Each mnemonic contains the following information: type and particle size of coal sample, extraction temperature, solvents/additives in the solvent mixture, and the original run number. The naming scheme of mnemonics is the following:

TYPE	SIZE	TEMP
K - Kittaning	L - 35/100 mesh	3 - above 300°F
B - Bakerstown	M - 100/150 mesh	2 - 200°F to 300°F
r - residue	S - 150/200 mesh	1 - room temp

SOLVENTS / ADDITIVES

D - dimethylsulfoxide (DMSO)		P - pyridine
H - hexamethylphosphoramide (HMPA)		T - tetramethylurea (TMU)
N - N-methyl-2-pyrrolidinone (NMP)		
cm - cumene	hq - hydroquinone	nb - n-butanol
cs - carbon disulphide	ip - isopropanol	qu - quinone
de - decalin	lm - limonene	sb - s-butanol
dm - dichloromethane	mr - myrcene	t - tetralin
dp - dipentene	na - naphthalene	

For example, BL2tDcm_115 is the mnemonic name of RUN 115. In that experiment Bakerstown coal (B), 35/100 mesh size (L), was extracted at 273±7°F (2) with 1.18 moles tetralin (t), 0.56 mole DMSO (D) , and 0.07 mole cumene (cm). Solvents are listed in the descending order of molar concentration.

Because one of the objectives of this research is to study factors that affect extraction yield, the first part of this chapter will present the findings that relate to extraction yield.

Results Based on the Analysis of Residue

Composition of Solvent

A. Extraction with DMSO

Dimethylsulphoxide (DMSO) has been regarded as an active solvent in coal extraction [Roy 1976]. In this study, DMSO was used extensively as a major extraction agent. Table 6 lists seven extraction experiments that used DMSO as the sole solvent. By itself, DMSO extracted about 30% of Kittaning coal or about 14% of Bakerstown coal (bag#2) at 320°F. However, DMSO was not effective at lower temperatures as can be observed in BM1D_164 and BM2D_172.

High reproducibility is observed in Runs BL3D_149 and BL3D_150 (coefficient of variation = 3.4%), and in Runs BS3D_173 and BS3D_180 (coefficient of variation = 0.3%) if the same type of coal is used in the extractions.

Table 6. Extraction with DMSO

RUN	Coal	Temperature (°F)	Yield (%)
KS3D_105	Kittaning c#3	320-350	29.6
BL3D_149	Bakerstown b#1	300-335	12.1
BL3D_150	Bakerstown b#1	318-340	11.3
BM1D_164	Bakerstown b#1	room temp	1.1
BS2D_172	Bakerstown b#2	175-240	0.9
BS3D_173	Bakerstown b#2	300-324	13.8
BS3D_180	Bakerstown b#2	310-330	13.9

B. Extraction with DMSO/tetralin Blends

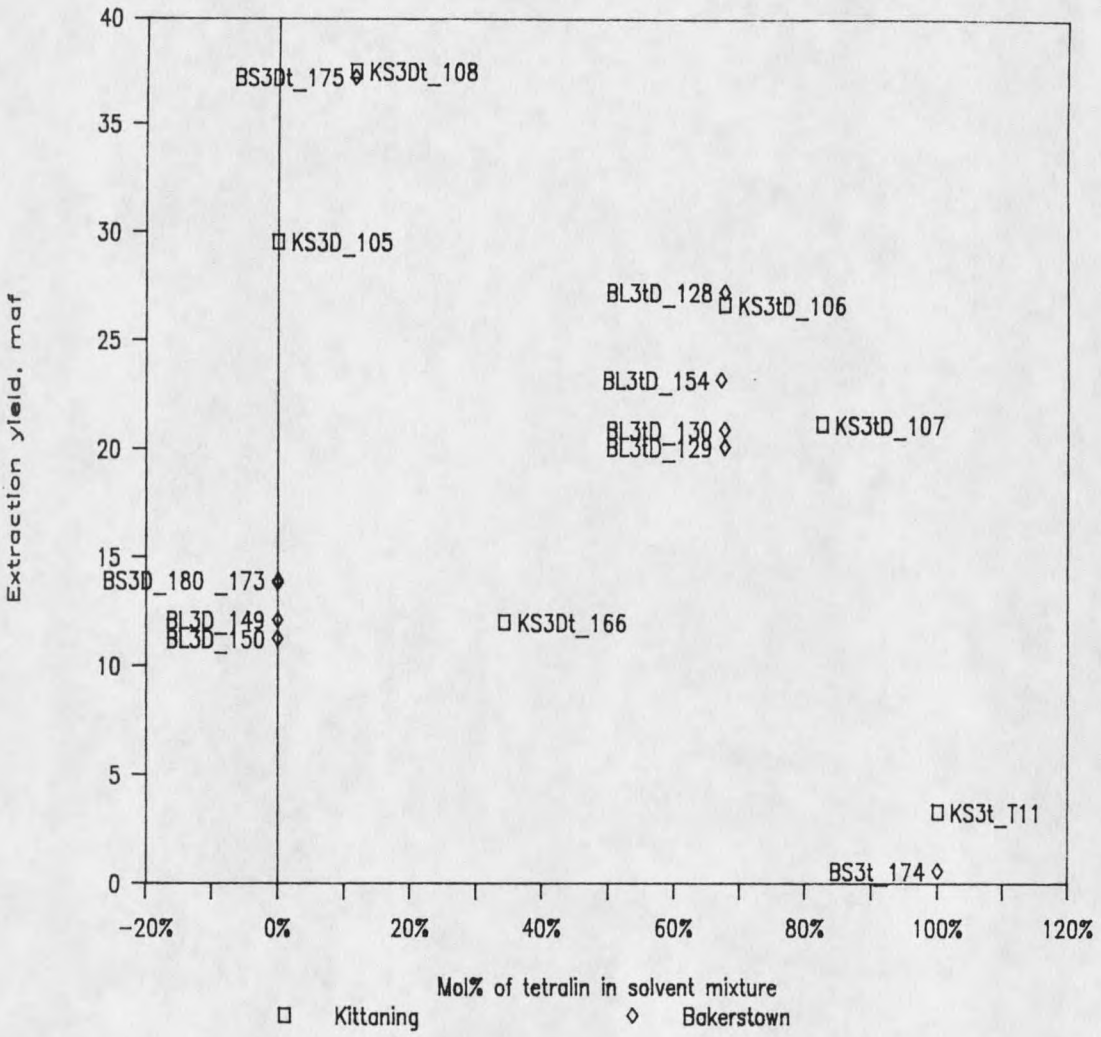
Tetralin by itself is not an active solvent in extracting coals. BS3t_174 extracted merely 0.6% of Bakerstown coal with 150 ml tetralin. However, when blended with active solvents, it may enhance the extraction yield as noted in previous studies [Ward 1984]. Five runs were conducted to examine the effect of tetralin in DMSO/tetralin blends on Kittaning coals. Another ten runs were performed on Bakerstown coals. The results of those runs are plotted in Figure 4.

With 12 mol% of tetralin, KS3Dt_108 yielded a value of 37.5%; clearly higher than the 29.6% of KS3D_105 extracted with DMSO alone. Even with 68 mol% of tetralin, i.e. there were more tetralin molecules than DMSO molecules in the blend, KS3tD_106 still yielded a comparable 26.7%.

For Bakerstown coals, 68 mol% tetralin blends extracted yields of 20.1 to 27.3%, that were twice as much as the pure DMSO runs did. Moreover the yield increased almost threefold when there was 12 mol% tetralin present.

Trying to achieve even higher extraction yield, the author mixed 100 ml DMSO with 100 ml tetralin (34.2 mol% tetralin) in KS3Dt_166.

Figure 4. Effect of tetralin on extraction yield. Balance of the solvent mixture is DMSO.



However, it resulted in an unfilterable colloidal mixture. After adding 400 ml cool tetralin in the mixture, a yield of 12% was accounted for. It is more likely to be the expected yield of a run with 100 ml DMSO and 500 ml tetralin (72.4 mol% tetralin) at a lower temperature.

There are other non-active solvents, such as, carbon disulphide and naphthalene which may also enhance the extraction yield. This enhancement effect will be discussed later.

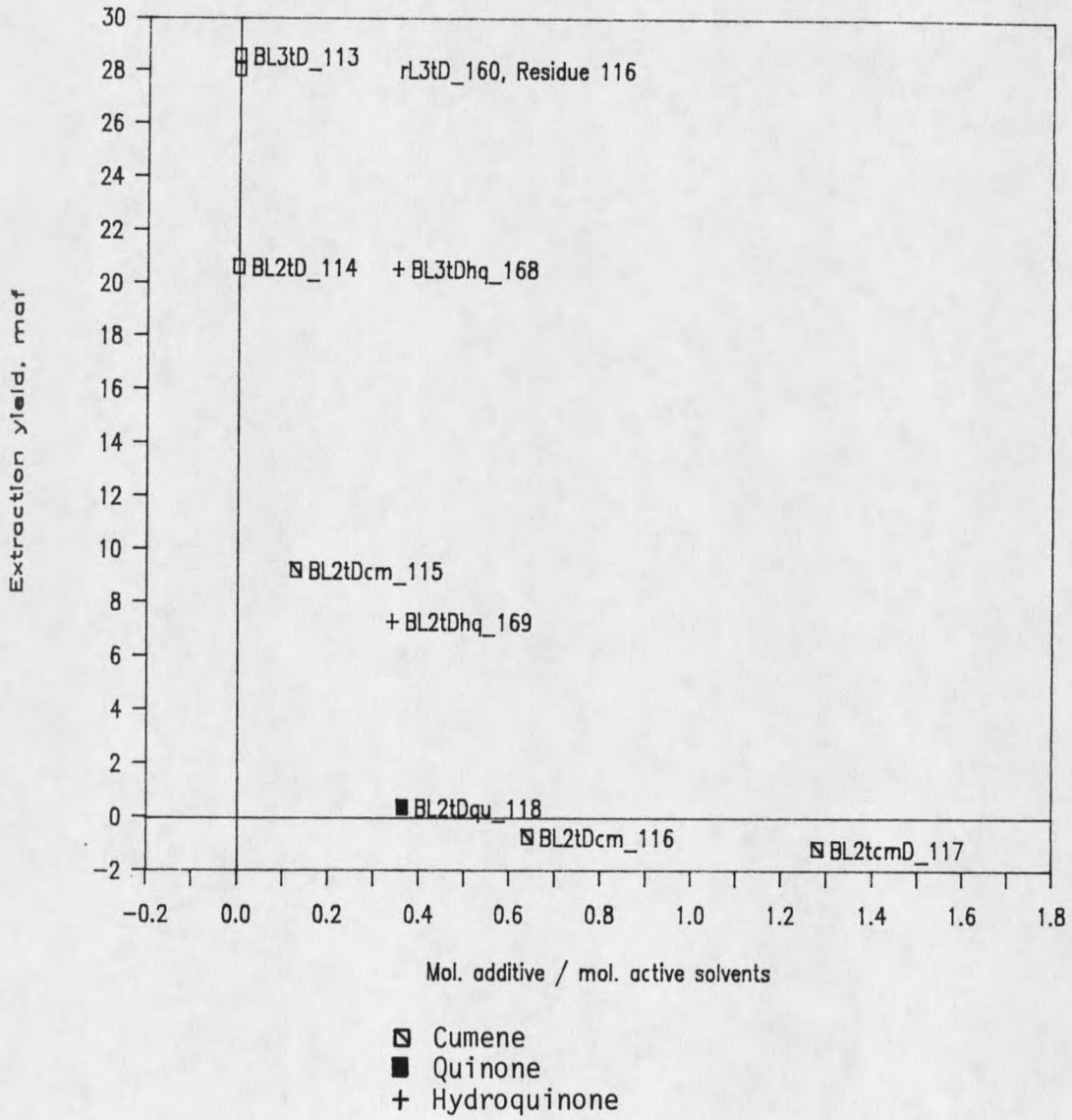
C. Effect of Cumene, Quinone and Hydroquinone in Solvent Blends

Cumene, quinone, or hydroquinone were used in addition to 200 ml DMSO/tetralin solvent blends in several extraction experiments. Extraction yields were reduced drastically in those runs in comparisons with runs using DMSO/tetralin as only solvents. Results of those runs are shown in Figure 5.

In BL2tD_114, DMSO/tetralin (1:4 vol) extracted 20.6% of coal at 265±5°F. With 0.07 mole of cumene present in the solvent blend, the extraction yield of BL2tDcm_115 dropped to 9.2%. Figure 5 indicates that extraction yield decreased as the molar ratio of cumene to DMSO increased.

The inhibition effect of cumene was not permanent. In BL2tDcm_116, no material could be extracted from coal while 50 ml cumene was present in the solution. However, in rL3tD_160, a 28.1% yield was obtained by extracting the residue of BL2tDcm_116 with DMSO/tetralin only. It is about the same yield as BL3tD_113, in which fresh coal was used. Apparently the cumene molecules did not alter

Figure 5. Effect of cumene, quinone and hydroquinone on extraction yield. Active solvent is DMSO.



coal structure or tie up active sites of residue after the washing and drying process which was applied between extractions.

It was once thought that the solvent extraction processes involve free radicals [Neavel 1982]. Cumene and quinone were used because they were known free radical traps [Lowry 1981].

With 0.2 mole of quinone in the solvent blend, yield was only 0.4%. Quinone was originally a yellow powder. When it dissolved in DMSO/tetralin (1:4 vol) solvent mixture, the color of the solution changed from yellow to reddish violet at low temperatures, 100-150°F. It indicated the formation of donor-acceptor complex possibly between DMSO and quinone [Sur 1972]. The white powder hydroquinone did not dissolve in DMSO/tetralin solution easily below 200°F, but it was well dissolved at 250°F. The color of the solution changed to bright brown as the hydroquinone dissolved and DMSO-hydroquinone donor-acceptor complex developed. The presence of hydroquinone also reduced extraction yields, but not as much as quinone did. Probably this is due to the reported accepting capacity of hydroquinone being lower than that of quinone. Consequently, BL2tDhq_169 had 64.5 per cent yield drop, while BL2tDqu_118 had a more stunning 98.2 per cent loss in yield.

D. Effect of Carbon Disulfide in Solvent Blends

Carbon disulfide has been reported as a non-active solvent in extracting coals. However, it enhanced the extraction whenever it was present with an active solvent [Lino 1983]. Several known active solvents were mixed with carbon disulfide to extract Bakerstown coal at room temperature. The results appear in Table 7.

Table 7. Effect of carbon disulfide on extraction yield[a]

RUN	Solvent[b]	Yield (wt%, maf)
BM1D_164	DMSO	1.1
BM1csD_162	DMSO/Carbon disulfide	20.9
BM1P_165	Pyridine	2.8
BM1csP_163	Pyridine/Carbon disulfide	12.8
BM1N_179	NMP[c]	1.5
BM1csN_181	NMP/Carbon disulfide	-[d]
BM1csdm_178	CH_2Cl_2/Carbon disulfide	0.2

[a] Bakerstown coal 100/150 mesh in 100 ml of solvent at room temperature for 60 minutes

[b] 1:1 mixture by volume

[c] N-Methyl-2-pyrrolidinone

[d] The solution/dispersion was like thick paste. It could not be filtered. Filtration became possible only after the solution was diluted with 200 ml acetone. Calculated yield would be -5.2%

BM1D_164 and BM1P_165 showed that DMSO and pyridine were not effective at room temperature. If carbon disulfide was blended with DMSO or pyridine, the extraction yields jumped ten per cent. The consecutive extraction of DMSO/carbon disulfide gave about 27.1% cumulative yield. Considering the low temperature, it was very effective. N-Methyl-2-pyrrolidinone (NMP) was reported as an active solvent for low rank coals [Roy 1976], but the mixture of NMP and carbon disulfide was not effective at all. The failure of carbon disulfide to enhance extraction in this case might be attributable to filtration problems. The solution/dispersion of BM1csN_181 was paste-like and could not be filtered. The filtering difficulty might

be caused by the strong interaction between coal and solvent mixtures. Dichloromethane is not an active solvent. The presence of carbon disulfide did not improve the extraction as we would predict from BM1csdm_178. This result is in agreement with that of Lino and Matsuda [1983] who first reported the effect of carbon disulfide in a mixture containing pyridine.

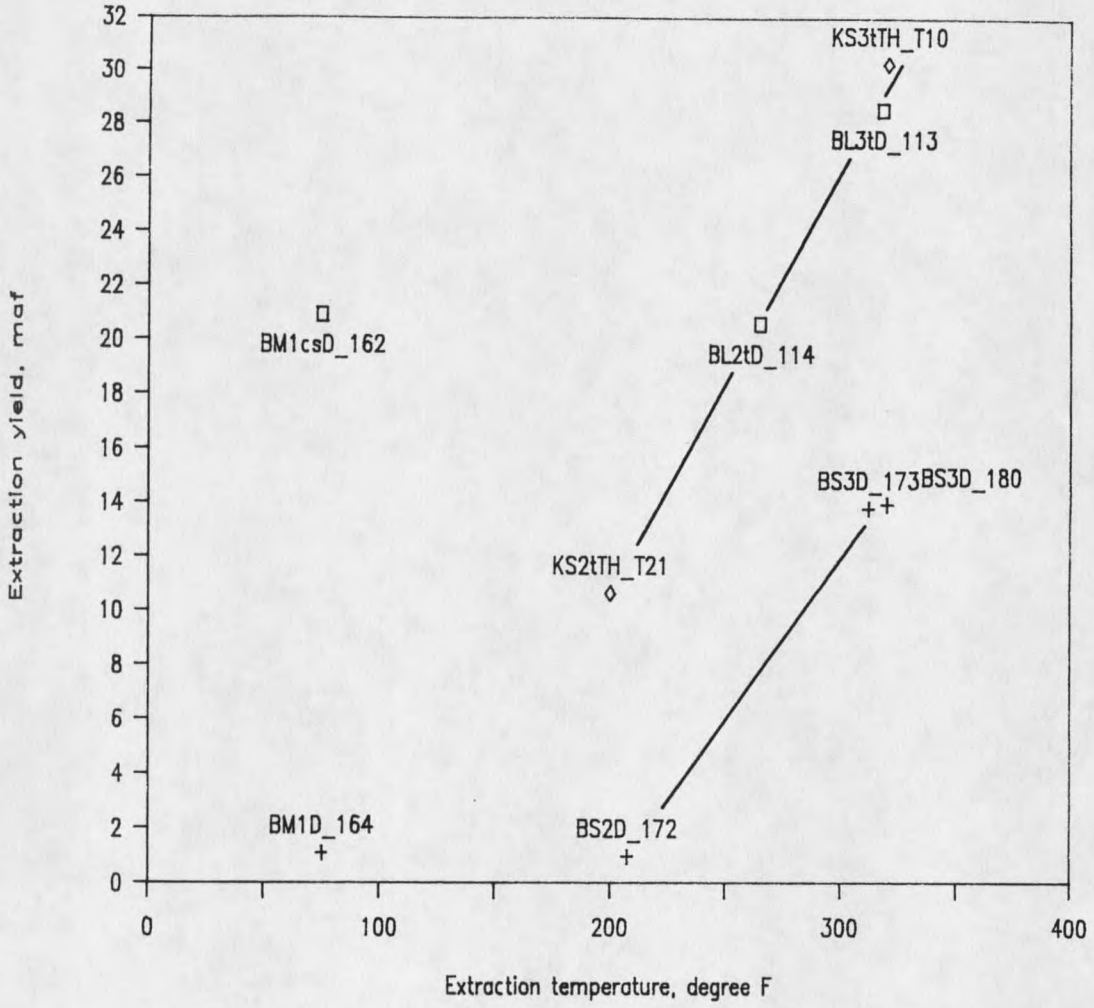
Extraction Temperature

In Figure 6 BM1D_164 and BS2D_172 had very low yields when DMSO was the only solvent and the extraction temperatures were below 240°F. At a higher temperature, 320°F, BS3D_173 and BS3D_180 were able to extract about 14% of coal. For experiments using DMSO/tetralin (1:4 vol) as the solvent blend, BL3tD_113 at 320°F also had larger yield than BL2tD_114 at 270°F. There is almost a linear correlation between the extraction yield and the extraction temperature when 80 vol% of tetralin was used in the solvent blend with either DMSO or TMU/HMPA as the active solvent. However, at room temperature, BM1csD_162 gave 20.9% yield with a DMSO/CS_2 solvent mixture. On the other hand, tetralin, known as a non-active solvent, only extracted 0.6% of coal by itself even at 320°F. It suggests that greater yield can be achieved with a higher extraction temperature and a proper solvent blending.

Number of Consecutive Extractions

Several extractions were performed on the residues of previous extraction runs.

Figure 6. Effect of temperature on extraction yield.
Runs KS3tTH_T10 and KS2tTH_T21 were done by a co-worker.
[Ward 1984]



In Figure 7 the results from three sets of runs were plotted. KS3tD_107 extracted 21.2% of Kittaning 150/200 mesh coal with DMSO/tetralin (1:9 vol). The residue of this run was extracted again with the same kind of solvent blend and only 0.2% was yielded in rS3tD_111. It appeared that this solvent blend could not extract any more material out of the coal. The results indicated that the extractable portion was almost exhausted for the same kind of solvent blend after one extraction.

In KS3Dt_108, DMSO/tetralin (4:1 vol) extracted 37.5% of coal, later DMSO/tetralin (1:9 vol) was able to extract 6.7% from its residue. In Figure 4, we noted DMSO/tetralin (1:9 vol, or 82.5 mol% tetralin) was a weaker solvent blend than DMSO/tetralin (4:1 vol, or 11.5 mol% tetralin). This suggests that a different composition of solvent blends might extract different portions of coal. Similar results were observed in KS3D_105 and rS3tD_110.

A Bakerstown coal was extracted consecutively several times till the coal was exhausted, i.e. no more material could be extracted from the coal under same conditions. Figure 8 demonstrates a general trend: The more number of extractions done on the coal, the lower was the yield. As we observed earlier in Kittaning coals, possibly less extractable material was left in the coal after each extraction.

After three or four extractions, some chemicals were introduced into the process in the hope of increasing the yield of the nearly exhausted coal. Aromatic cumene hydroperoxide and aliphatic Lupersol-130 [Product Bulletin, Lucidol Pennwalt] were used because they are known free radical initiators.

Figure 7. Two consecutive extractions with various solvent blend compositions in the second extraction. Extraction temperature is ≈320°F.

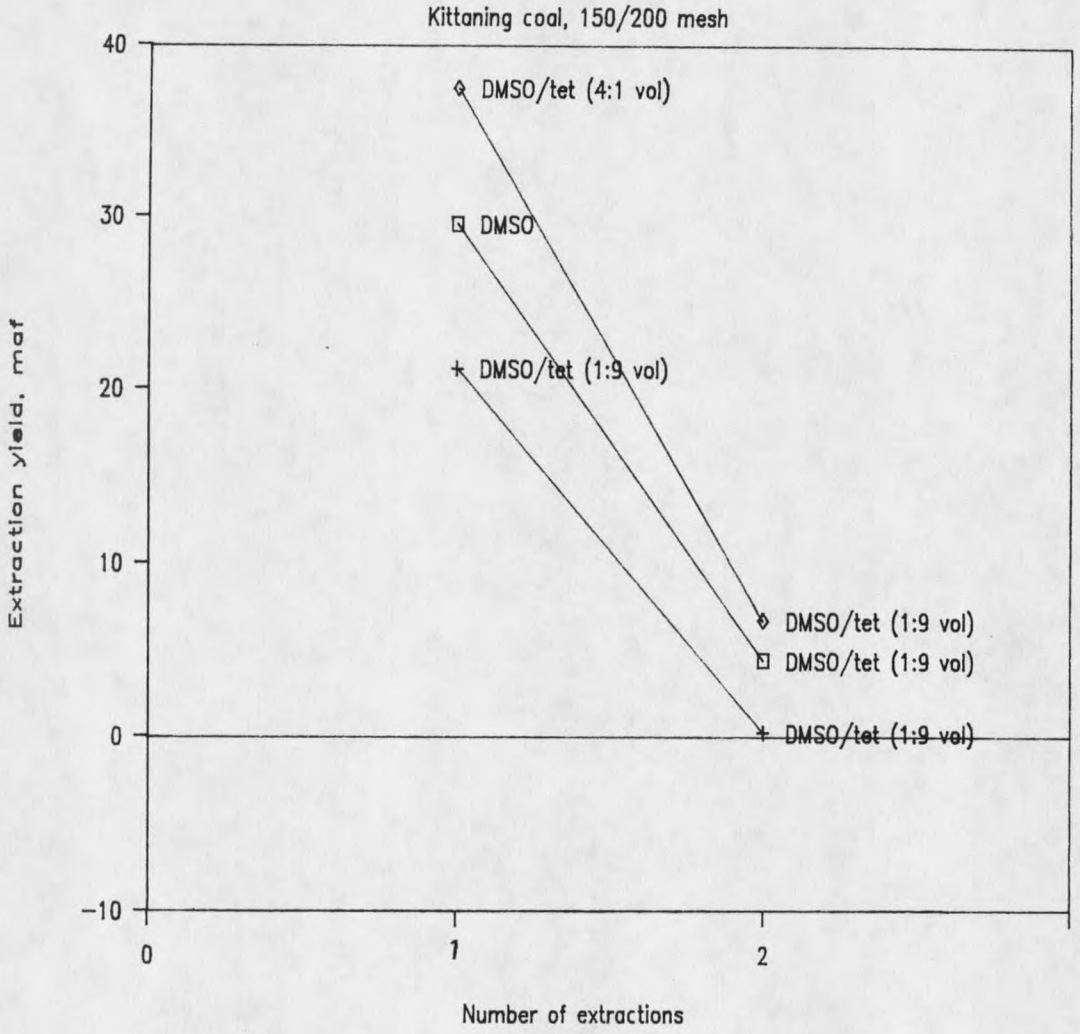
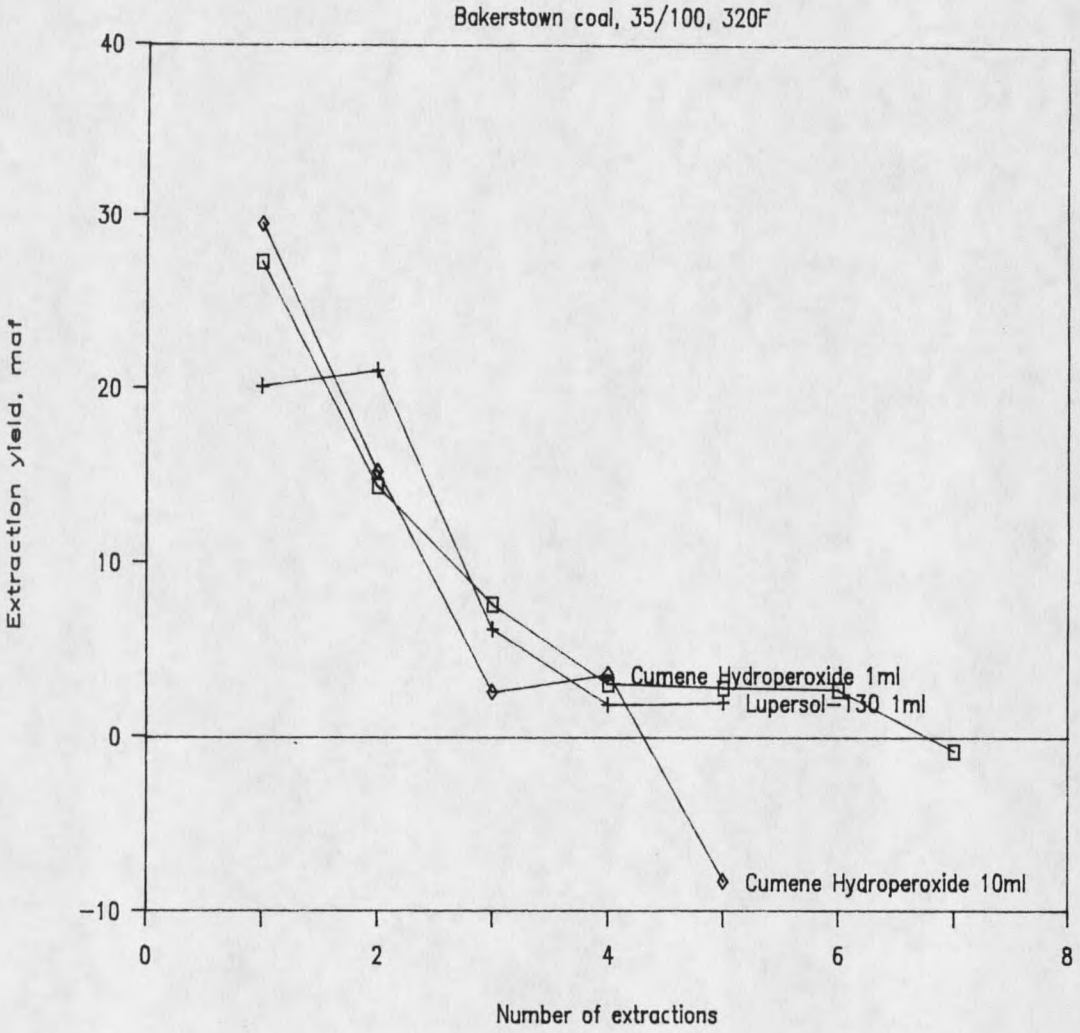
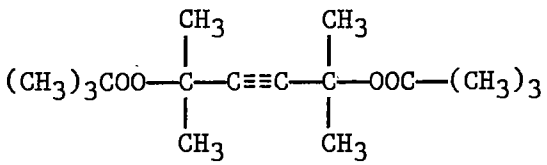


Figure 8. Yield with several consecutive extractions. Coal samples are extracted repeatedly till exhaustion. Various free radical initiators are tested in the hope of reviving exhausted residues.



Lupersol-130 is the trade name of

2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3.



Mixing one milliliter of Lupersol-130 with DMSO/tetralin (1:4 vol) in rL3tD_144, the author extracted two per cent from the residue of rL3tD_141 which had a yield of 1.8 per cent. The effect of Lupersol-130 was negligible and the yield was comparable with the 2.8% of a parallel run, rL3tD_143, which used no Lupersol-130.

In another experiment rL3D_151 with 1 ml cumene hydroperoxide had a 3.6% yield which was similar to the yield of its preceding run, rL3tD_147. The residue of rL3D_151 was mixed with 10 ml cumene hydroperoxide then extracted again in rL3tD_156. There were gas bubbles evolved during the extraction. A noticable weight gain in residue resulted in a negative yield. Cumene hydroperoxide possibly decomposed in the solution and produced ca. 0.2 grams residue which was counted as part of the coal residue. The assumptions and calculations are detailed in the Appendix B.

So far it has been noted that neither Lupersol-130 nor cumene hydroperoxide enhanced the extraction yield of nearly exhausted pre-extracted coals. To investigate their possible effect in earlier stages of consecutive extractions, residue of BL3tD_130 were extracted in rL3tD_131 and rL3tD_132, one with Lupersol-130 and one without.

The difference in yields, displayed in Figure 9, was insignificant between these two runs. One milliliter of Lupersol-130 was used in BL3tD_148 and 2 ml cumene hydroperoxide were added in BL3tD_154. BL3tD_148 yielded 29.5% and BL3tD_154 had 23.2% extraction. Both are comparable with the yields of runs without free radical initiators. It indicates that both free radical initiators do not enhance the extraction yield of fresh coals. Figure 10 shows the results of two parallel experiments, one with cumene hydroperoxide and one without. First the coal was extracted with 200 ml DMSO then the residue was extracted by DMSO/tetralin (1:4 vol). The higher yield in the second extractions was expected because the presence of tetralin made a stronger solvent blend for Bakerstown coal as illustrated in Figure 4. Because of the apparent decomposition of cumene hydroperoxide, rL3tD_152, with 5 ml cumene hydroperoxide, had a notable lower yield than rL3tD_153.

Cumulative yields were calculated for consecutive extractions (Appendix C). It was assumed that 1) only the non-mineral portion of coal can be extracted, and 2) there is no solvent incorporation in the residue after washing and drying. In addition the ash content of residue was assumed to be the same as the ash content in the coal sample before extraction. Figure 11 shows that the cumulative yield for Bakerstown coal ascended steeply in the first two to three extractions, then gradually reached a plateau. It agrees with results found by most coal scientists in that there is an upper bound on the amount of material that can be extracted from coals at low temperatures; the primary, covalent bondings in a coal network would not be broken below

Figure 9. Effect of Lupersol-130 on extraction yield.
Bakerstown coal, 35/100 mesh, DMSO/tetralin (1:4 vol).
Extraction temperature ≈ 320°F.

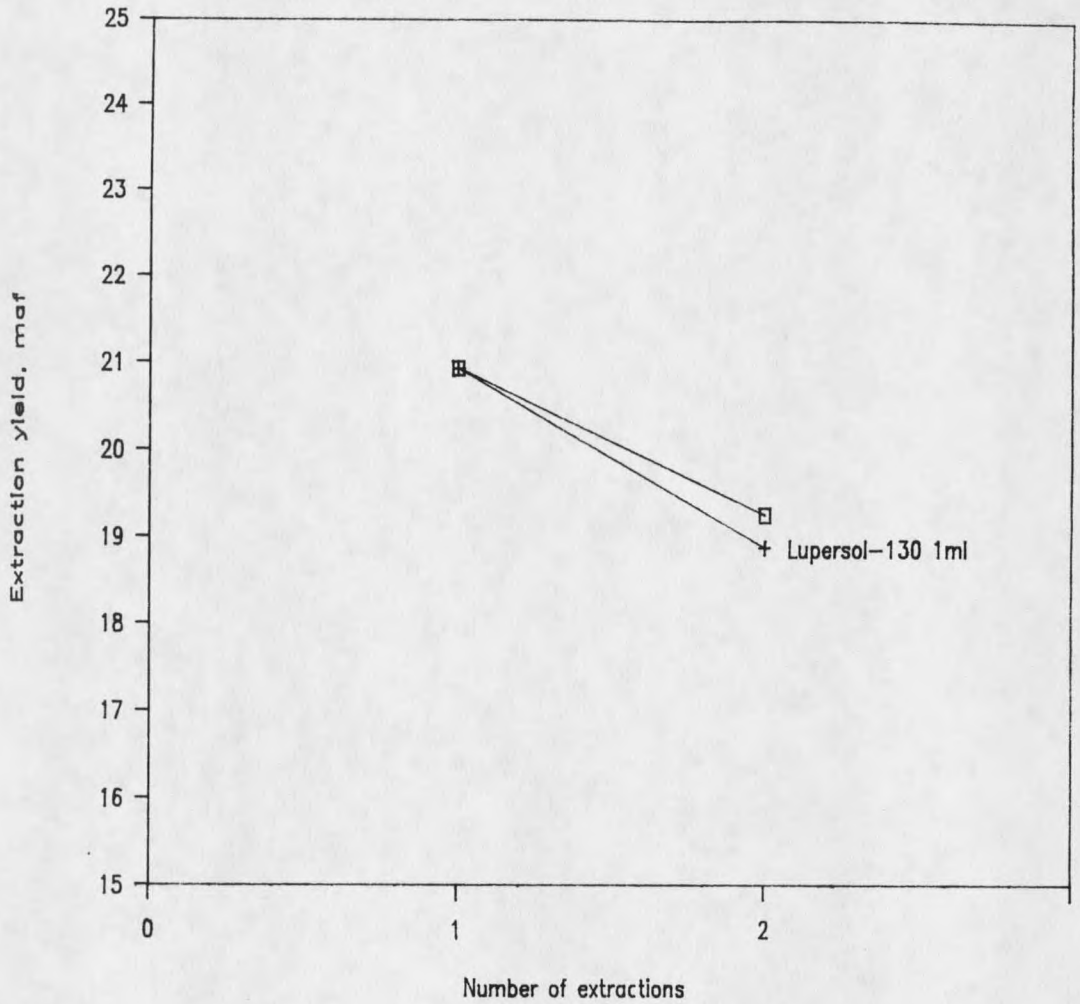


Figure 10. Effect of cumene hydroperoxide on extraction yield.
Bakerstown coal, 35/100 mesh. Temperature ≈ 320°F.
First extraction: DMSO.
Second extraction: DMSO/tetralin (1:4 vol).

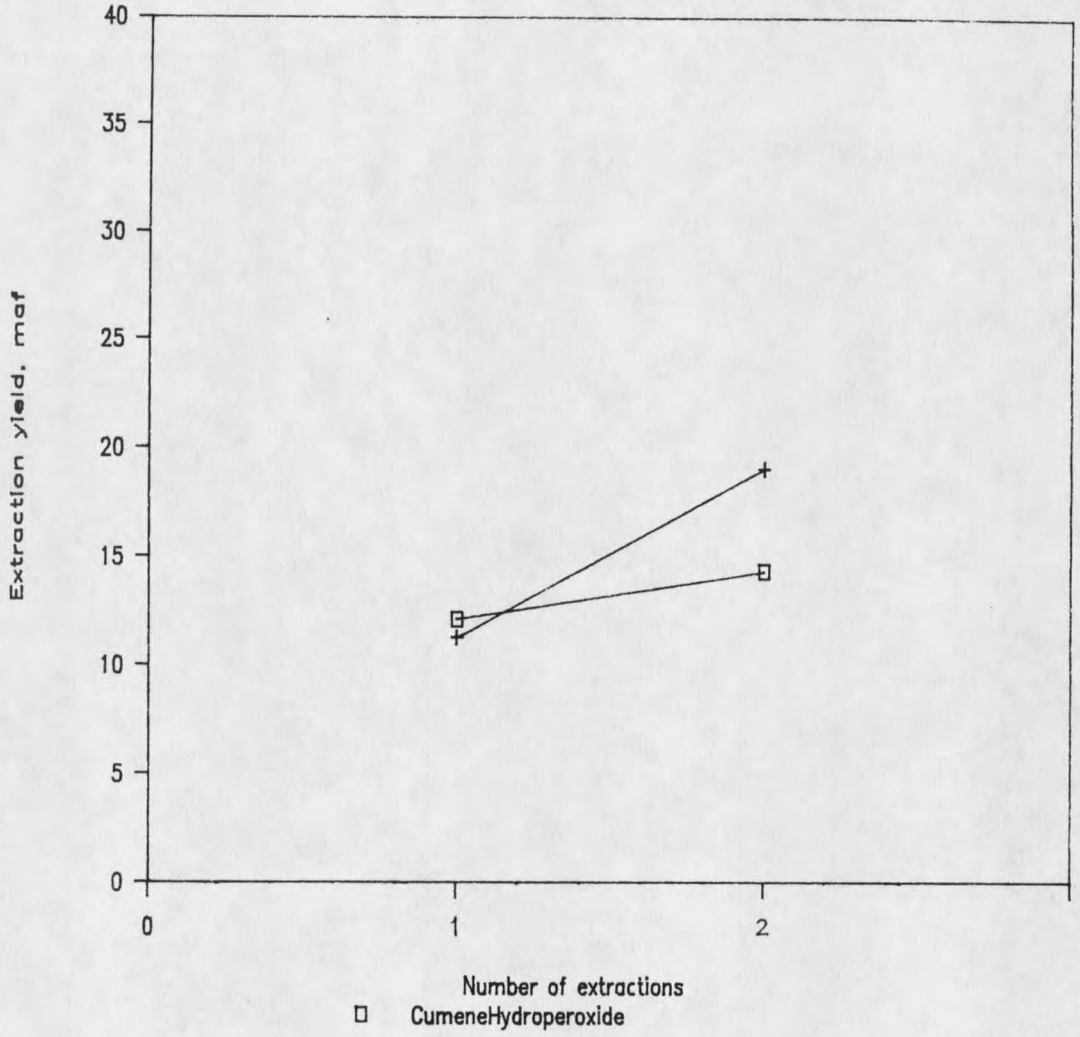
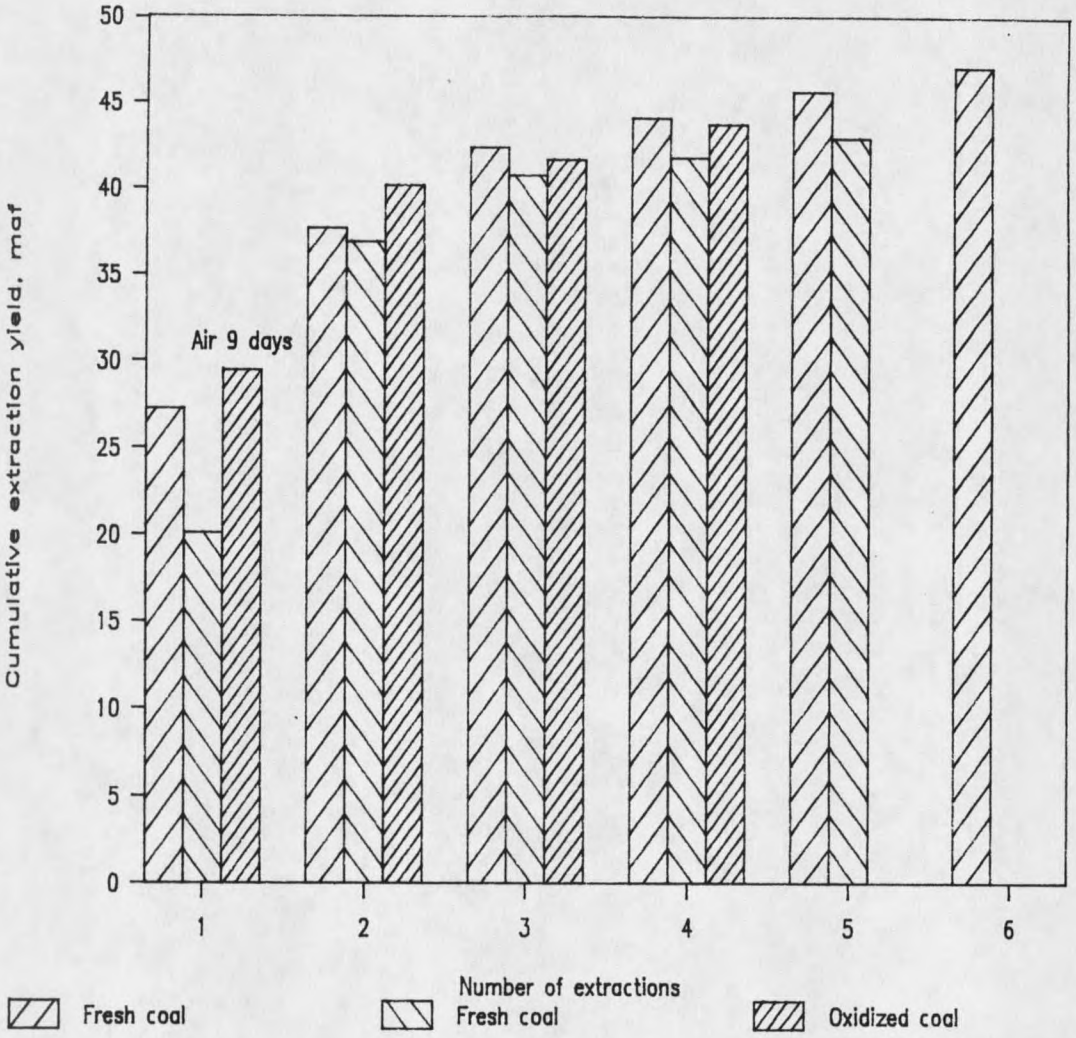


Figure 11. Cumulative yield of consecutive extractions. Bakerstown coal, 35/100 mesh. Temperature ≈ 320°F. DMSO/tetralin (1:4 vol).



400°F [Neavel 1982; Given 1986]. Therefore, only a limited amount of material, which is bonded by secondary bondings or trapped in coal network, may be extracted.

Particle Size of Coal

Three particle sizes, 35/100, 100/150, and 150/200 meshes, were studied. As evident in Figure 12, it took six to seven consecutive extractions to exhaust a 35/100 mesh Bakerstown coal; it took three extractions for the 100/150 mesh coal, and only two extractions to exhaust a 150/200 mesh sample. Previous studies have shown that the major portion of the ultimately attainable extraction occurs within the first five minutes for 150/200 mesh Kittaning coals [Ward 1984].

One possible explanation is that diffusion is the key to the particle size effect: the larger the particle size, the more difficult for solvent to penetrate into the coal networks. During an extraction, the outer pores of coal particles may become saturated with extractable materials in solution, consequently fresh solvent molecules have little access to inner pores. Washing and drying procedures between extractions remove most extractable material and solvent molecules from the outer pores. The extractable materials which are trapped deep inside the pores can now be accessed by the solvent in the next extraction.

Diffusion Hypothesis

Bakerstown 35/100 coal and residue of BL3tD_148 were subjected to image analysis. Figure 13 shows that the size distributions of

Figure 12. Effect of coal particle size on extraction yield.

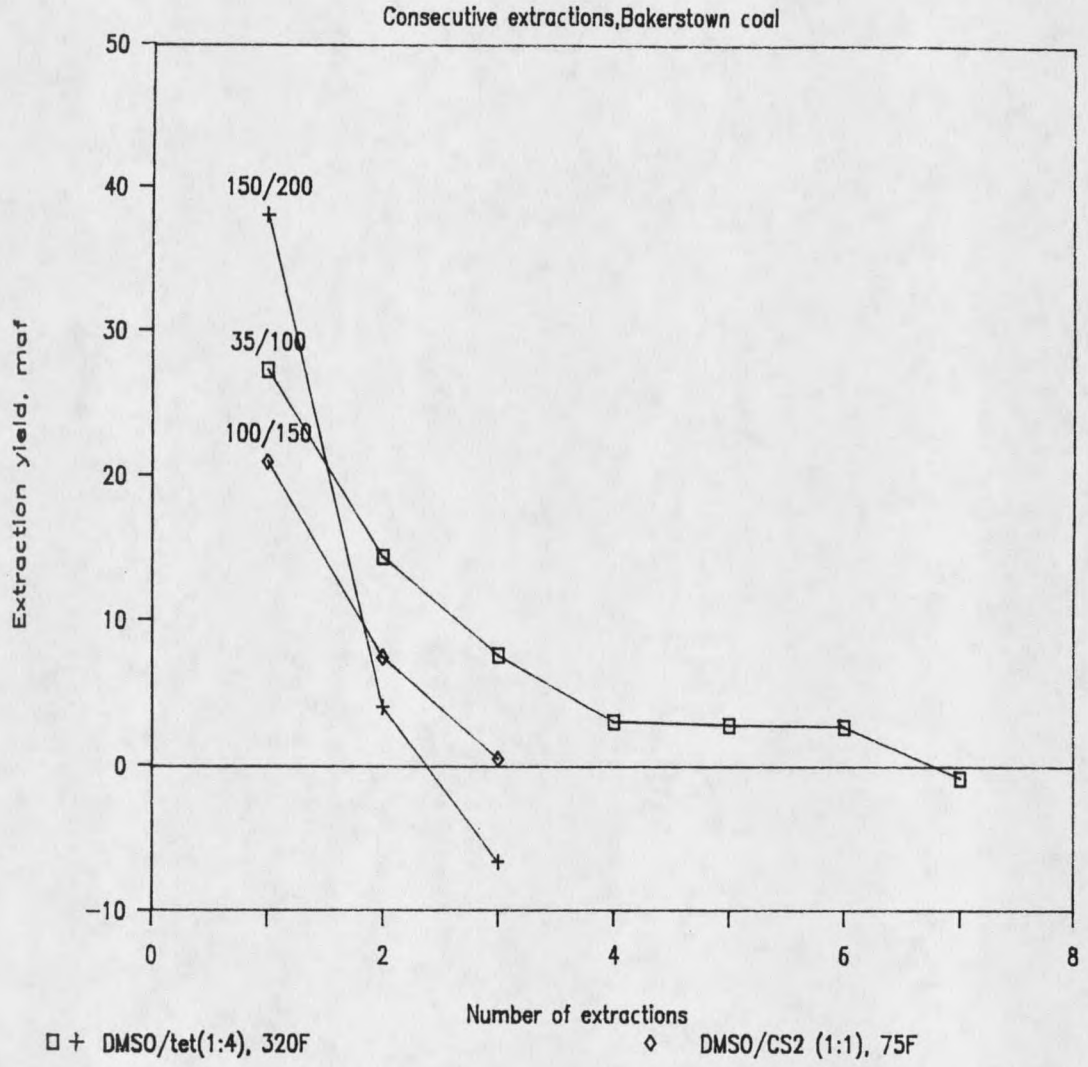
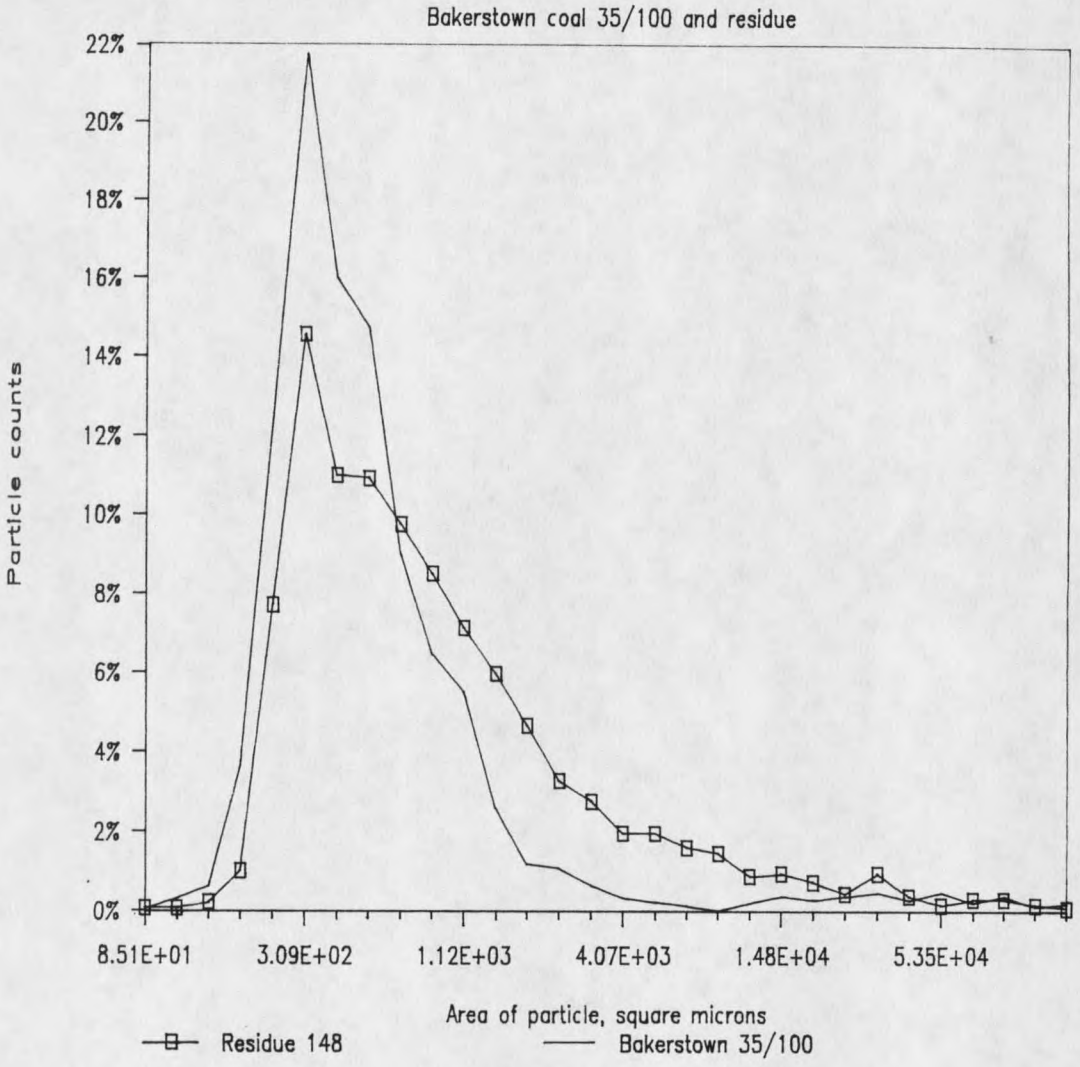


Figure 13. Particle size distribution of coal and residue.



unextracted and extracted coal particles were similar. It indicates that solvent extraction does not "chew away" the outer shells of coal particles. Otherwise, the distribution curve of residues would have been shifted to the lower size dimensions. The extracted material, which was 29.5% of coal, should have come out of pores in the coal. The total weight distribution in Figure 14 and 15 shows that the weight of coal particles is concentrated on larger particles, consequently the weight loss and extraction yields are mainly contributed by larger coal particles. This line of reasoning was investigated in further detail. The densities of Bakerstown 35/100 and residue of BL3tD_148 were estimated by using methods stated in Chapter 2. The detailed calculations are in the Appendix D. The density of Bakerstown coal is 1.388 when porosity is estimated at 0.35. The density of residue of BL3tD_148 is 0.967. The resulting extraction yield should be 30.3% based on the density difference. Inspection of Appendix A indicates an empirical result of 29.5% which is very close to that estimate.

Figure 12 reveals that the particle size did affect the consecutive extraction yield. Three different particle sizes were used in the consecutive extraction studies. The sizes were:

Tylor mesh	Screen opening (microns)	Median (microns)
35/100	147 - 495	321
100/150	106 - 147	126.5
150/200	75 - 106	90.5

Figure 14. Weight distribution of coal particles.

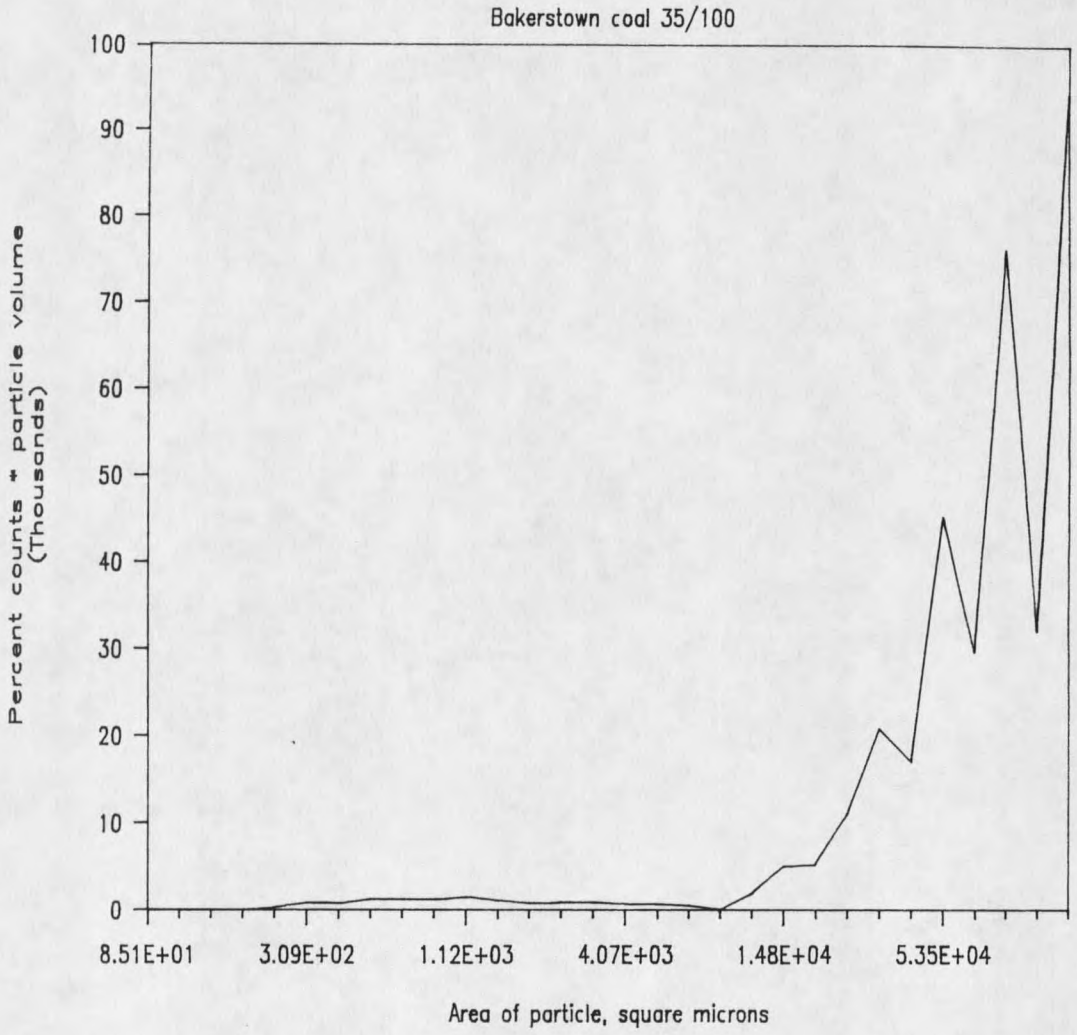
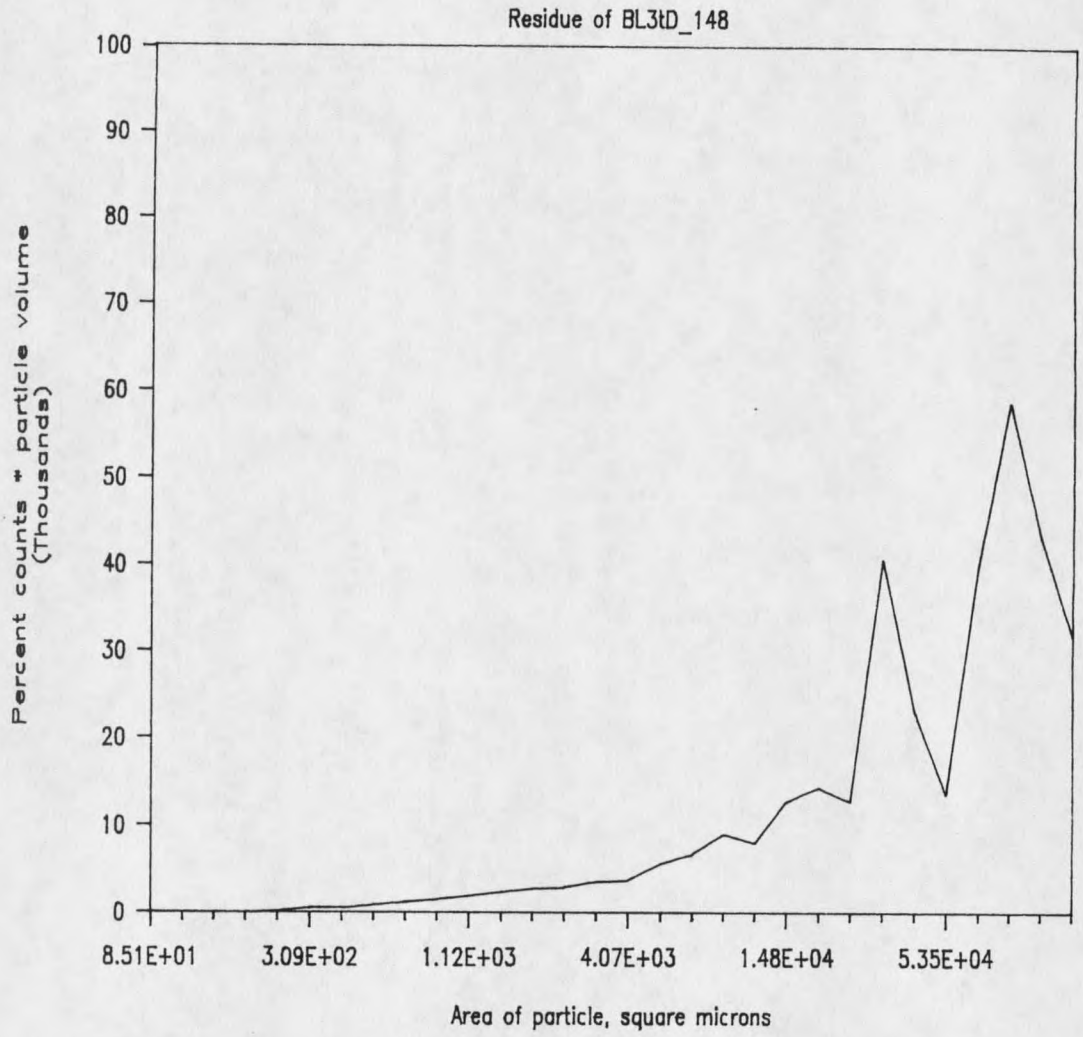


Figure 15. Weight distribution of residue particles.



A simple diffusion model is constructed to explain this effect. In theory, the penetration of solvent molecules into pores is controlled by the concentration gradient of solvent and extractable materials, the operating conditions, and the steric hindrance of solvents in coal. For simplicity, it was assumed that cylindrical pores were radially uniform and the depth of penetration was constant. Other basic assumptions for this diffusion model are:

1. coal particles are spherical,
2. pore volume and pore size are uniformly distributed, as are extractable materials,
3. with the same extraction time and mixing condition, the solvent may diffuse into coal pores to the same depth (45 microns was assumed; because the 150/200 mesh, median radius ≈ 90 microns, coal particles were exhausted in two consecutive extractions), and
4. after washing and drying, the outer pores of the pre-extracted residue is opened up due to the removal of extractable materials. Solvent molecules now may penetrate deeper into pores. The yield of n^{th} extraction is calculated as

$$\text{Yield},n = 4/3 * \pi P * [(r - (n-1)d)^3 - (r - nd)^3] \qquad (7)$$

Where r = median radius of coal particles,

d = diffusion depth,

P = extractable portion of coal

$$= \frac{\text{total yield from experimental date}}{\text{total volume of coal particles}}$$

Figure 16 shows that the extraction yields based on this simple diffusion model did fit experimental data quite well. Note that the runs with 100/150 particles were performed at room temperature. This implies that the temperature did not affect the penetration depth because sufficient extraction time allowed concentration equilibria to be reached.

Solvent-to-coal Ratio

Extraction experiments were performed using high solvent-to-coal ratio to ensure sufficient solvent molecules for carrying out the extraction/dissolution processes. Figure 17 and Figure 18 well demonstrate the irrelevance of extraction yield and solvent-to-coal ratio since the ratios are high. The small value of solvent-to-coal ratio in this study was 0.174 moles of solvent blends per gram of coal in BL3tD_129 and BL3tD_130 (20 ml solvent/gram coal). In other words, there were 0.118 moles of tetralin and 0.056 moles of DMSO used as the solvent blends for one gram of Bakerstown coal. If the average "molecular" weight of extractable coal fragments was 200, then there were roughly 24 tetralin molecules and 11 DMSO molecules against one coal fragment "molecule." Apparently there were always sufficent solvent molecules around in the extractions.

Oxidation of Coal

The majority of the experiments in this study were performed in a nitrogen environment using fresh coal samples that had limited contact with air. Several coal samples were exposed to air at different

Figure 16. Predicted extraction yield vs. number of extractions according to the diffusion hypothesis.

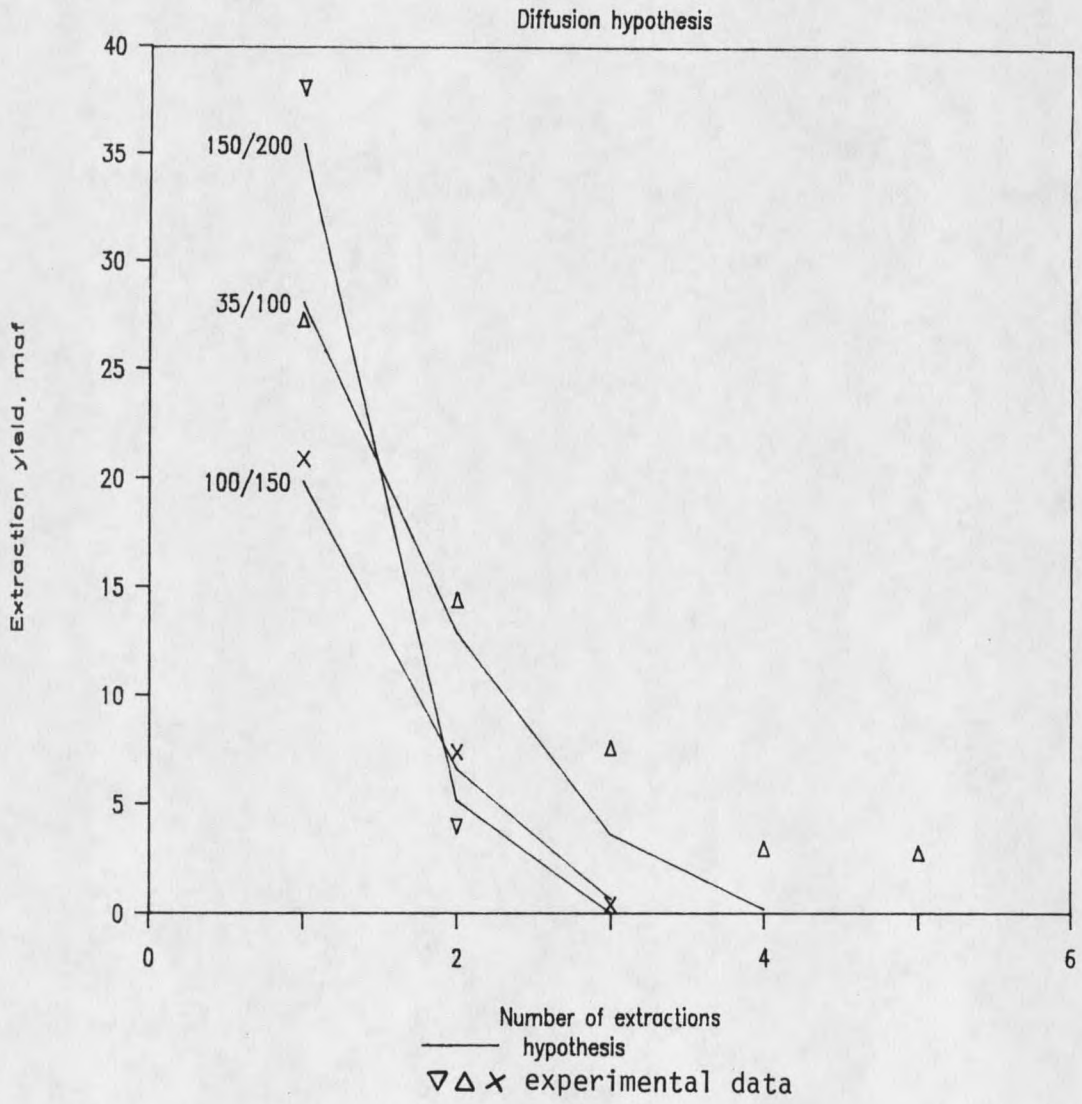


Figure 17. Effect of solvent-to-coal ratio on extraction yield. All the coal samples were not pre-extracted.

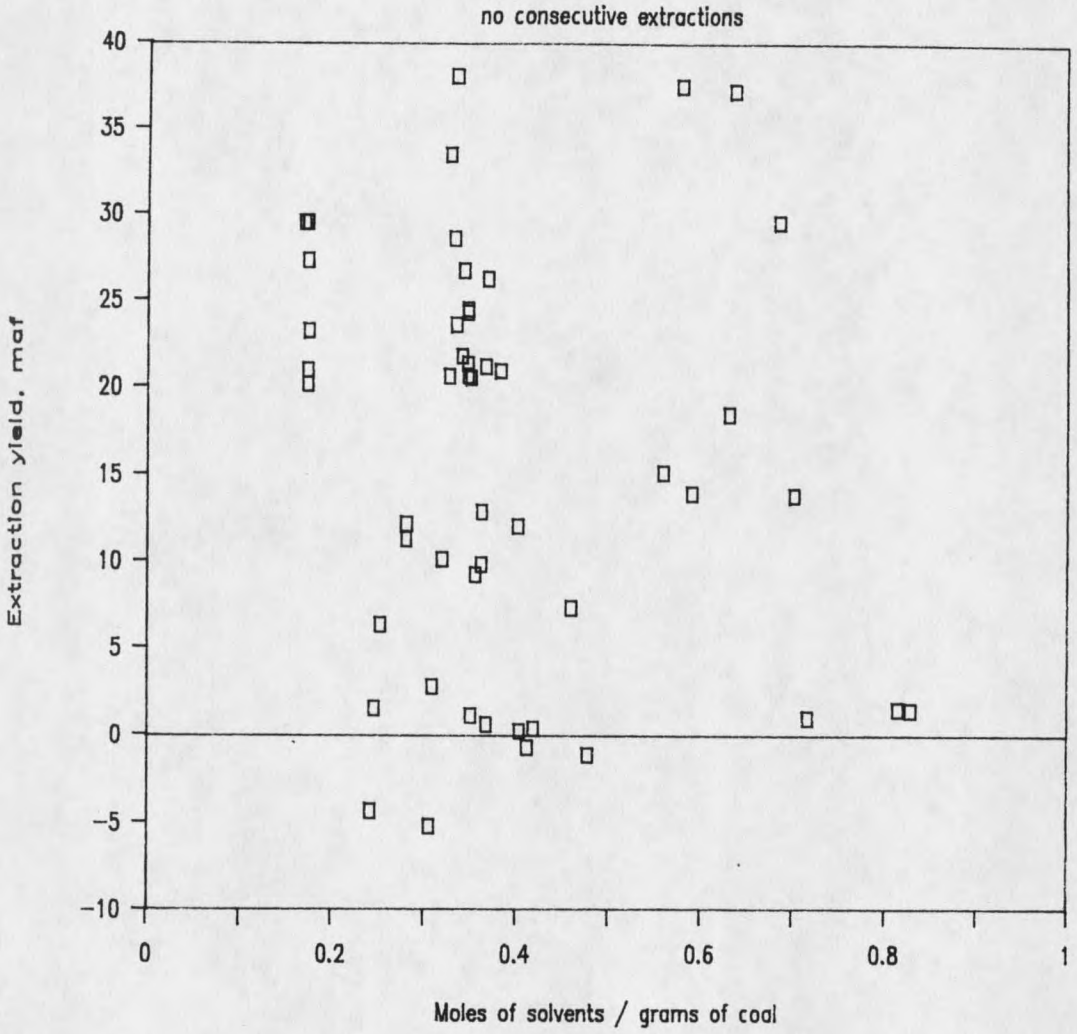
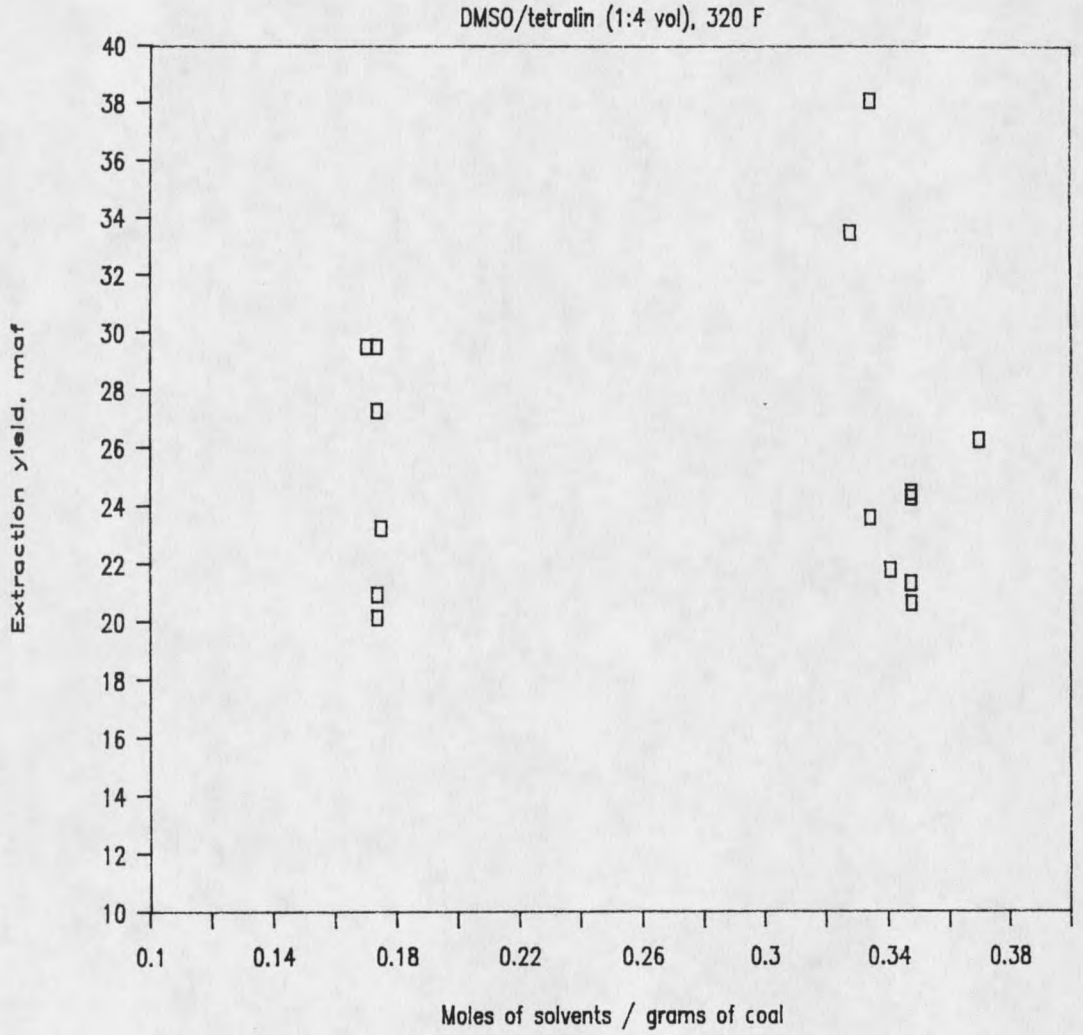


Figure 18. Effect of solvent-to-coal ratio with DMSO/tetralin as the solvent blend on extraction yield.



temperatures for various length of time. Table 8 summarizes the condition of the coal samples and corresponding extraction yields.

Table 8. Extraction experiments of oxidized coals

RUN	batch	Oxidation treatment	Yield (%)
BL3tD_119	c#3	none[a]	33.5
BL3tD_120	c#3	45 days at room temp.[b]	21.3
BL3tD_121	c#3	45 days at room temp. 30 min at 150°C[c]	23.6
BL3tD_122	c#3	45 days at room temp. 60 min at 150°C	24.3
BL3tD_135	c#3	45 days at room temp. 3 hours at 150°C 47 hours at 105°C	26.3
BL3tD_136	c#3	45 days at room temp. 3 hours at 150°C 144 hours at 105°C	20.6
BL3tD_123	c#3	50 days at room temp.	24.5
BL3tD_124	c#3	50 days at room temp. 30 min at 150°C	21.8
BL3tD_128	b#1	none	27.3 (47.2)[d]
BL3tD_129	b#1	none	20.1 (43.1)
BL3tD_137	b#1	9 days at room temp.	29.5 (43.9)

[a] Coal was kept in a tightly capped bottle under nitrogen
[b] Coal was exposed to air at 1 atmosphere
[c] Coal was heated in a dryer without forced air flow
[d] Cumulative yield from consecutive extractions are in parenthesis.

Exposing coal samples to air for nine days did not reduce yield in BL3tD_137 and the consecutive extraction runs gave cumulative yield

comparable to fresh coals. In general, coals with extended air contact gave slightly lower yields than fresh coals. However, oxidation at 105°F or 150°F did not affect the yield so as to reveal any significant trend. Thus on the basis of this set of runs the effect of air oxidation upon coal is indeterminate.

It has been shown [Heard 1984] that the organic part of coal can ultimately be oxidized to carbon dioxide and water by repeatly adding a 30% solution of hydrogen peroxide over a period of six weeks at temperatures up to 80°C. Bituminous coal is generally believed to be composed of structural units of several fused aromatic rings connected with alkyl chain bridges into which a variety of functional groups have been substituted. These groups can be oxided and the alkyl chains severed with relative ease. A 30% of solution of hydrogen peroxide (pH = 3.67) was used to oxidize a residue which has been extracted six times. The oxidation was vigorous and evolved a great amount of gas, presumably mostly oxygen with some carbon dioxide present. The residue treated with hydrogen peroxide was then used in the seventh extraction, rL3tD_146. With this H_2O_2 treatment, there was no increase in extraction yield.

Incorporation of Solvent in Residue

Solvent incorporation has been reported in most solvent extraction experiments [Roy 1976, Narain 1983, Ward 1984, Van Bodegom 1985, Ichioka 1985]. Solvent incorporation is typically indicated by an increase of sulfur content after extraction, as the sulfur containing solvent, DMSO, was retained in the residue. However one should note

that sulfur content increases can also result from the retention of the inorganic sulfur compounds in the residue after extraction, in which case solvent incorporation needs to be verified by some other method.

Examining the correlation between change of %S in coal samples and yield of extraction experiments with DMSO in the solvent blend, the trend shown in Figure 19 is weak in general: the per cent incorporated sulfur appears to increase as extraction yield increases. The stronger interactions between coal and DMSO may have resulted in higher yields. DMSO would replace the extracted material at the center of interaction, the acidic site in coal network. However, there were many runs having high extraction yields but negative sulfur incorporation, i.e. a decrease in sulfur content. All of those were experiments using pre-extracted coals. No particular trend is found in Figure 20 for those runs.

Sulfur increase was observed in most runs with fresh (never extracted) Bakerstown coals as shown in Figure 21. Two runs with DMSO/tetralin (1:4 vol) as the solvent blend, BL2tDcm_116 and BL2tcmD_117, had a decrease in sulfur contents and negative extraction yields. Possible explanations for these results include:

1) very little DMSO-coal interaction resulted in very little DMSO retention; or
2) the retention of co-solvent, such as tetralin, reduced the sulfur content which was reported as the weight percentage of residue; or
3) there was a loss of inorganic sulfur.

Figure 19. Change of sulfur content with extractions using DMSO as an active solvent.

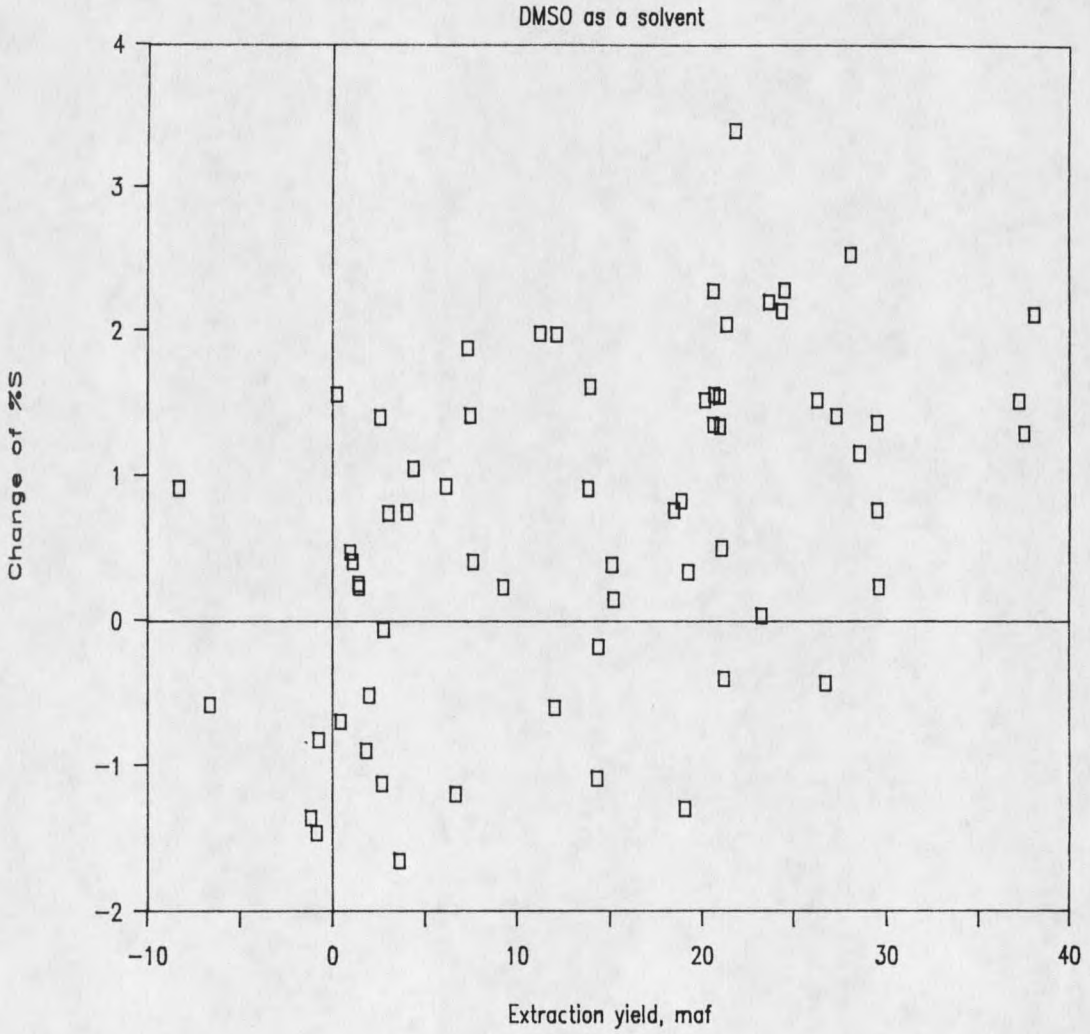


Figure 20. Change of sulfur content with extractions of pre-extracted coal using DMSO as an active solvent.

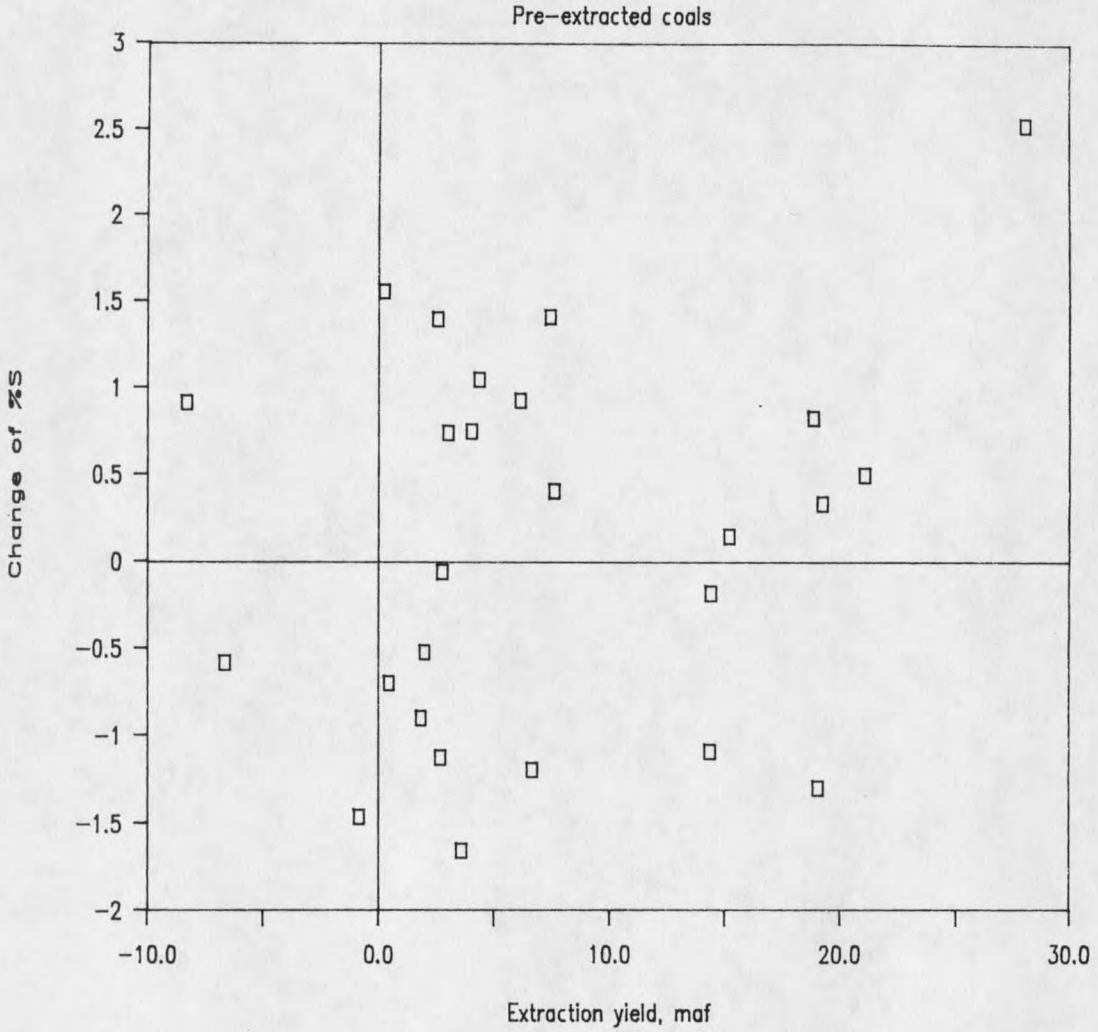
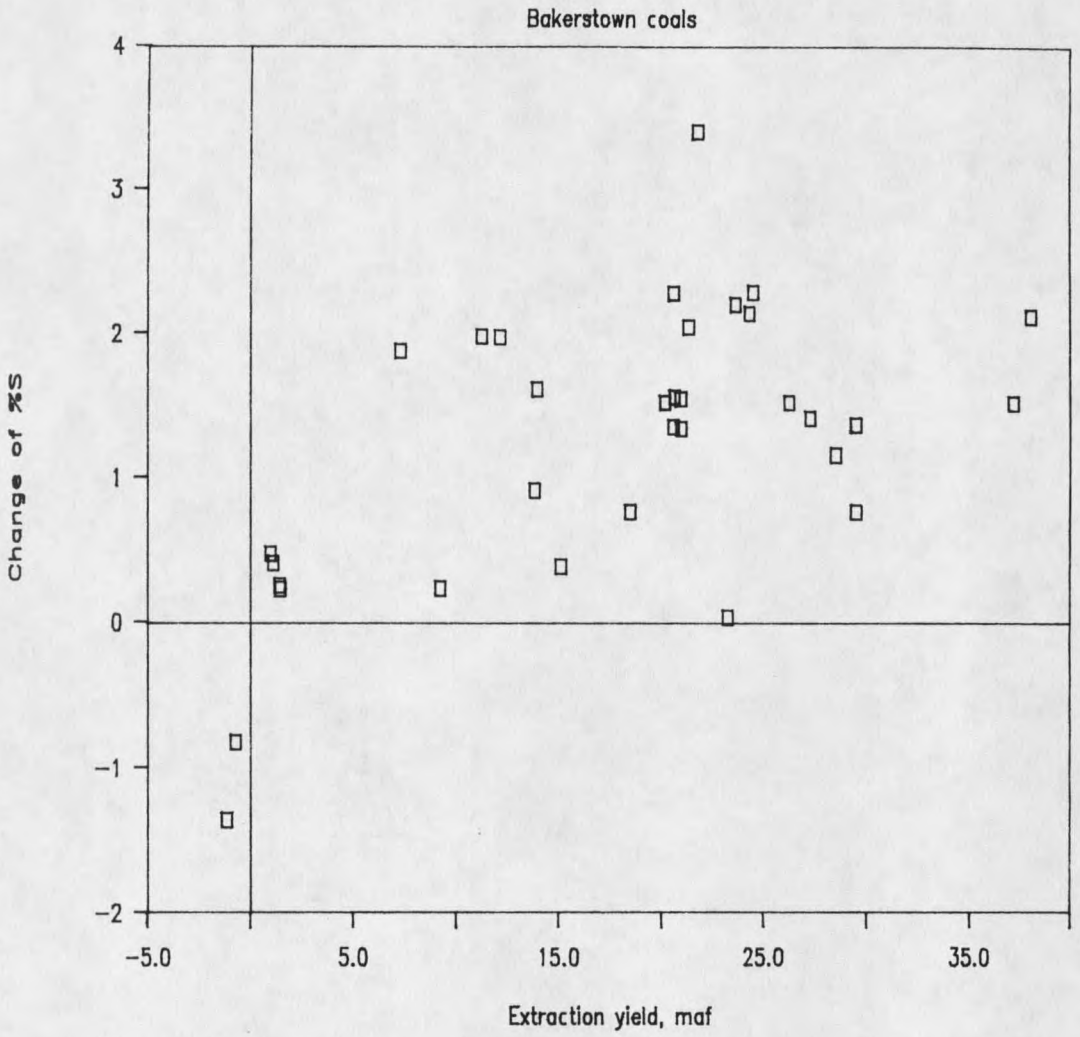


Figure 21. Change of sulfur content with extractions of fresh coal using DMSO as an active solvent.



A closer examination of the change of sulfur content is shown in Figure 22 for the consecutive extractions. A relatively good coefficient of determination ($r^2 = 0.5$) was observed to exist between the number of extractions and the change of %S. The percentage of sulfur in residue decreases as the number of extractions increases. That may be because the inorganic sulfur, mainly pyrite, is removed from the graduately loosened coal matrix after several extractions. A weak trend can also be noticed in Figure 23 for the extraction yield versus the change of %S. It implies that maybe more sulfur-containing solvent is incorporated into the coal network as the coal-solvent interaction increases. The extraction yield, measured from the weight differences between coal and residue, may be a deviation from the actual yield.

It has been suggested that a way to "correct" the calculation of yield is to assume that the %S or %N increase is solely caused by the incorporation of sulfur or nitrogen-containing solvent molecules [Roy 1976, Ward 1984, Van Bodegom 1985, Ichioka 1985]. However this correction scheme neglects to consider the following:

1) organic sulfur, or nitrogen, -containing fragments may be extracted from coal structures;
2) inorganic sulfur may, or may not be, retained in the residue; it is not controlled by the effectiveness of the extraction solvent;
3) the retention of a non-sulfur or non-nitrogen containing solvent may reduce the %S or %N obtained from elemental analysis which is based on the weight of analytical samples.

Figure 22. Change of sulfur content vs. number of extractions in consecutive extractions.

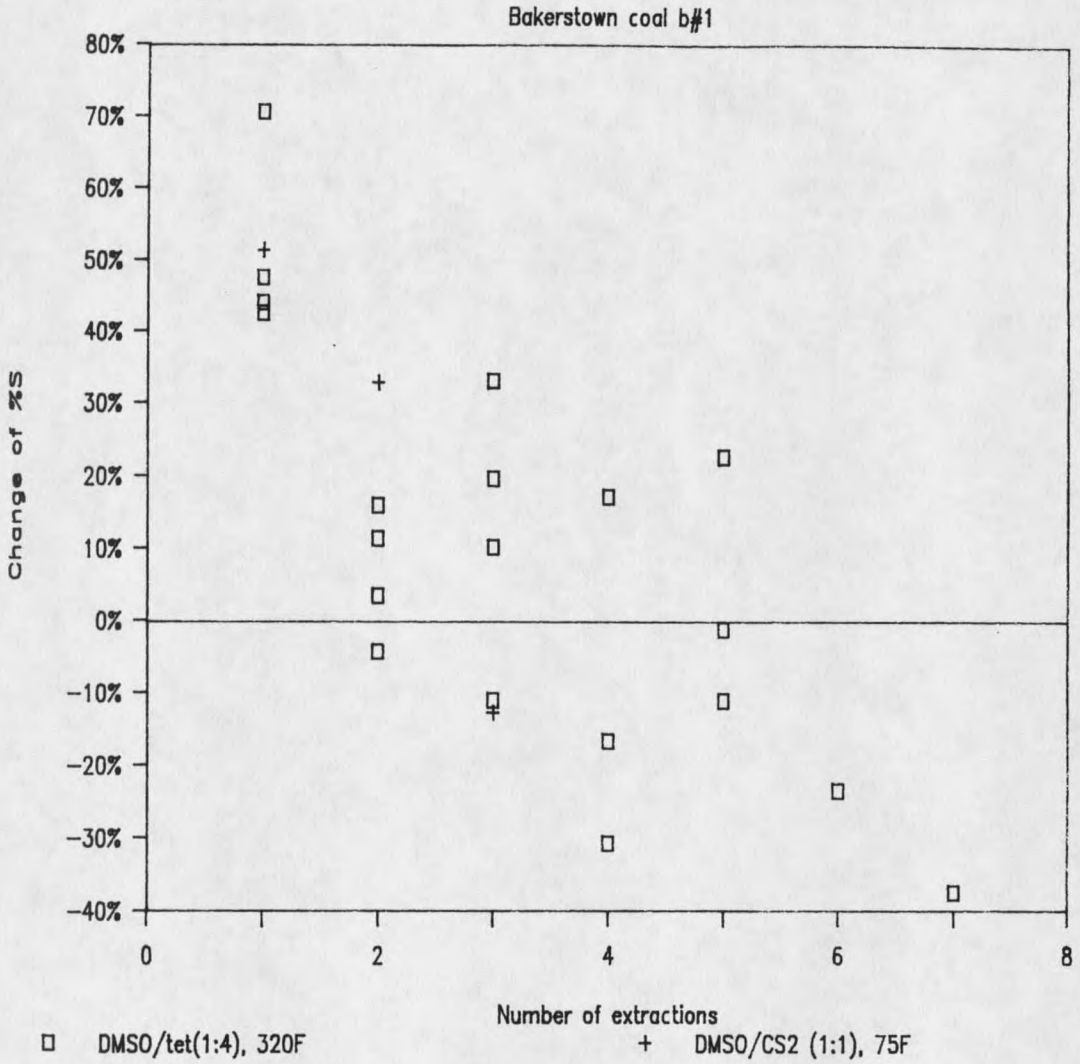
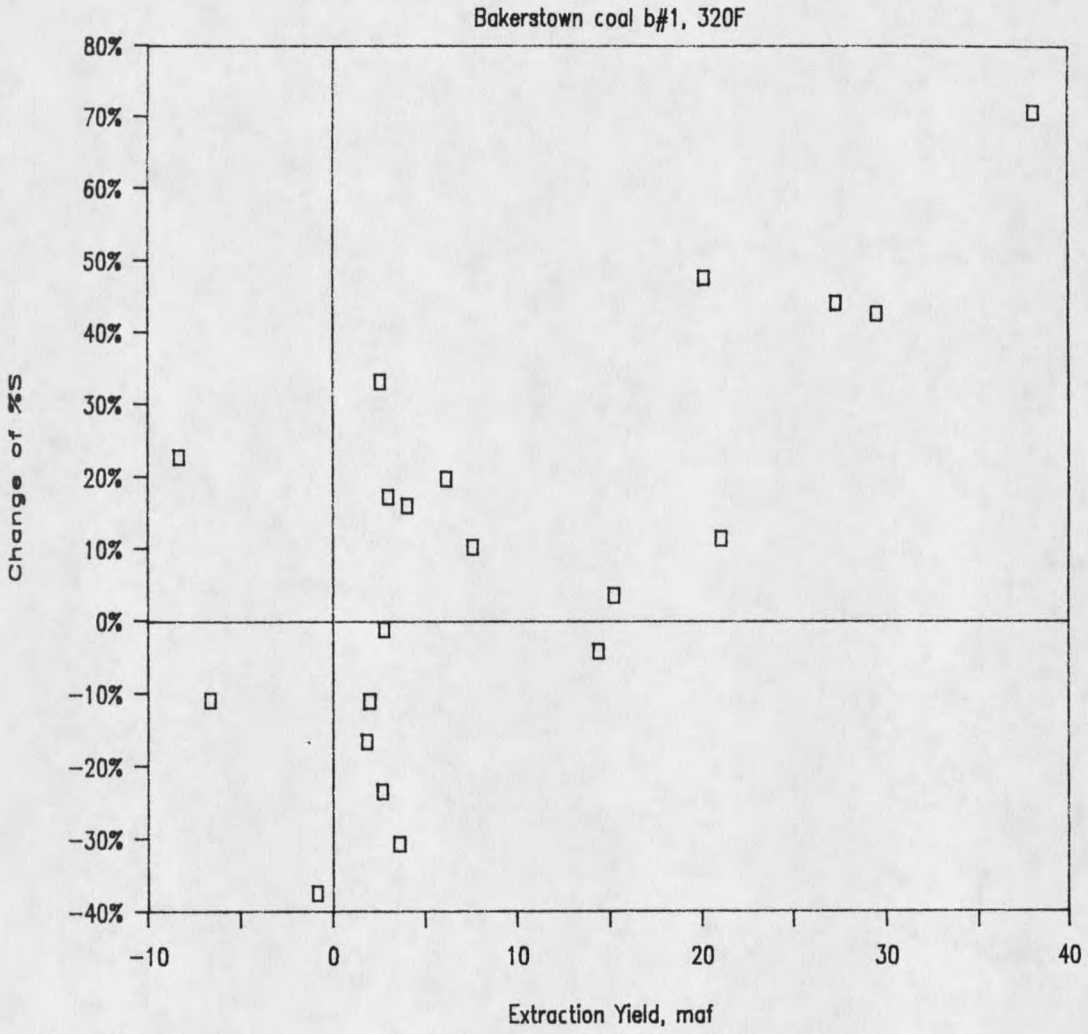


Figure 23. Change of sulfur content vs. extraction yield in consecutive extractions.



Therefore, it is very difficult to determine with accuracy the amount of solvent retained in the residue. Extraction yields reported in this thesis are not "corrected" for possible solvent incorporation. Because almost all extraction runs had a change in sulfur content less than 2 wt% of coal, it is relatively small comparing with 10 to 30 wt% of extraction yields obtained in most runs.

In order to examine the possible solvents retained in the residue, four residues were mixed with twice as much isopropanol in a flask and vigorously shaken for thirty minutes, then filtered. The filtrate was analyzed by GC/MS. Results are tabulated in Tables 9 and 10.

Table 9. Compounds retained in residues of extraction

RUN	Solvent	Compounds identified Major	Trace
rL3tD_153	DMSO/tetalin	tetralin	C_4H_9NO, pyridine, $C_6H_{10}O$, C_4H_7NS, Naphthalene, $C_{10}H_{10}O$
BS3tT_3[a]	TMU/tetralin	tetralin	TMU, HMPA[b]
BM1csD_162	DMSO/CS_2	DMSO	C_4H_9NO, $C_6H_{10}O$, tetralin, $C_2H_6O_2S$
BM1csP_163	pyridine/CS_2	Pyridine	C_4H_9NO, $C_6H_{10}O$

[a] experiment conducted by coworker E. Chilcote
[b] The solvent blend might have been contaminated by TMU/HMPA mixture which was used extensively at the time.

Table 10. Elemental analysis of runs in Table 9.

RUN	Yield	%N,diff[a]	%S,diff	C/H,diff
rL3tD_153	19.1%	-0.5	-1.3	0.136
BS3tT_3	3.5%	-0.1	NA	0.010
BM1csD_162	20.9%	-0.6	1.5	0.056
BM1csP_163	12.8%	-0.3	1.2	0.035

[a] diff = after extraction - before extraction

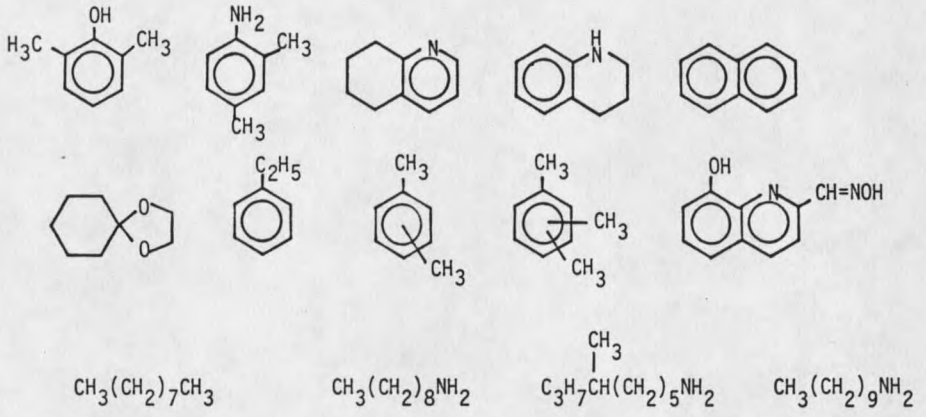
Tetralin was the major solvent retained in tests at higher temperature (320°F), while an active solvent, such as DMSO or pyridine, was largely retained in residue at room temperature extraction experiments. Active solvents might also have been retained in residues at higher temperature, but the bonding (possibly electron donor-acceptor bonds) established at high temperature between active solvents and coal was strong enough to avoid being washed out by isopropanol (i.e. replacement by isopropanol).

Results Based on the Analysis of Extract Compounds Extracted from Coal by DMSO and Tetralin

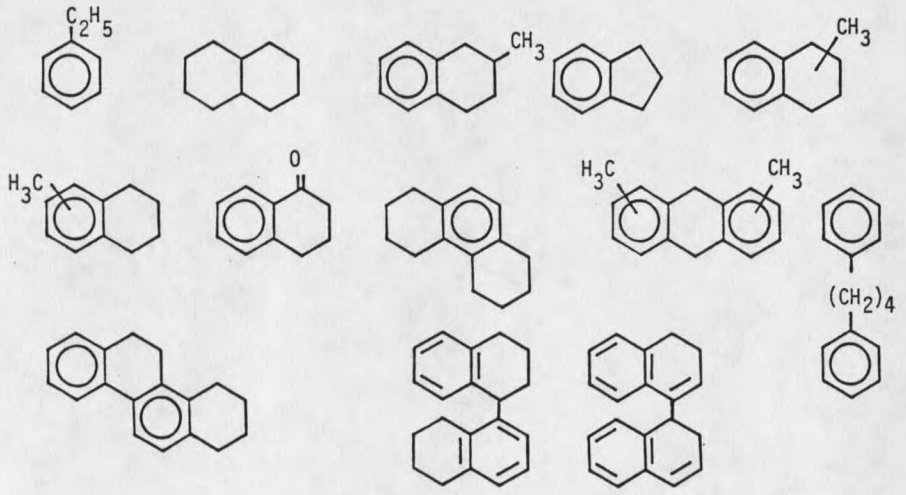
Extracts of Run BS3D_173 (yield = 13.8%), in which DMSO was the solvent, and Run BS3t_174 (yield = 0.6%), in which tetralin was the solvent, were analyzed by GC/MS to identify organic material in the extracts (Figure 24). The gas chromatograms of those runs are included in Appendix E. According to mass spectrum analysis, compounds in DMSO extract might be as heavy as 2000 a.m.u. However only those compounds with lower mass (≤260 a.m.u.) were identified.

Organic compounds extracted by DMSO included such functional groups as hydroxyl, amino, or ethyl; however aromatic and aliphatic hydrocarbons were also found in the extract. On the other hand tetralin extracted mostly aromatic, cyclic, and aliphatic hydrocarbons. The results suggest that tetralin, which is not nuclearphilic, cannot attack polar sites and is unable to extract fragments that are bonded to a coal network with secondary interactions. Consequently BS3t_174 had a much lower extraction yield than BS3D_173.

Figure 24. Chemical compounds in extract identified with GC/MS. (a) Compounds present in DMSO extract. (b) Compounds present in tetralin extract.



(a)



(b)

Extract Solution as a Colloidal System

Coal-derived liquids from coal liquefaction processes [Briggs 1982, Kalliat 1984] and extracts from solvent extraction of coals [Roy 1972, van Bodegom 1985] have been described as colloidal systems. Several solutions of coal extracts in this study underwent various analyses to gain an understanding of their colloidal nature.

The GC/MS furnished the information about the chemical species present in the coal extract. For the tetralin extract (Run BS3t_174) with the molecular weight of extracted materials ranging from 106 to 258, the dimensions of the larger particles could be as long as 10 Å. For the DMSO extract (Run BS3D_173), the molecular weight may range from 100 up to 2000 based on the mass spectrum analysis. The dimension of most particles in DMSO extract may be 10-20 Å.

A colloidal particle is a particle composed of about 1000 up to 1,000,000,000 atoms. The diameter of such particles, when they are symmetric units, is between 10 Å and 10,000 Å. By this definition, most coal extract particles are in the size range of colloidal particles. They can be classified as macromolecular colloids. Many other coal chemists also found the existence of the macromolecules in coal extracts (Table 11).

These findings indicate that the extractable material, or the mobile phase, in the coal structure is in the size range of collodial particles. However the size of macromolecular colloids in coal extract solutions is much larger than the extractable material trapped in the coal network, most likely because the aggregation of extractable material occurred in the bulk solution. Colloidal-size

particles may form from the attraction and association of asphaltene and preasphaltene molecules through π-π and hydrogen bonding [Briggs 1982]. Asphaltenes, which are portions of coal-liquids, are the pentane or hexane insoluble, but are soluble in benzene or toluene; but preasphaltenes are benzene or toluene insoluble, and THF or pyridine soluble.

Table 11. Macromolecules in coal extracts

Coal scientists	Findings
Kann [1951]	Ultramicroscope study of the ethylenediamine extract indicates the size of colloidal particles may be upto 100-400 Å.
Van Krevelen [1965]	Number average molecular weight (M_n) in the pyridine extract is 400-1210.
Shinn [1984]	In a bituminous model, the low-temperature extractable fragments have mass 306, 503, and 1182. The size of these fragments is 10-20 Å.
Van Bodegom, Van Veen, Van Kessel, Sinnige-Nijssen, Stuiver [1985]	Electron micrographs of spray-dried extracts show that a substantial amount of colloidal matter (particle sizes up to 0.1 micron) is extracted from medium-rank coals. The colloidal particles should not be thought of as being hard spheres but rather as polymer-like clusters, since small (30 nm) carbon black particles, even when extensively oxidized so as to contain many phenolic and carboxylic groups, are but poorly solubilized.
Given, Marzec, Barton, Lynch, Gerstein [1986]	Low-temperature extractable material has M_n 400-4000. Field Ionization Mass Spectroscopy shows 75-80 wt% has molecular weight 70-800 a.m.u. and 20-25 wt% has molecular weight greater than 1200 a.m.u.

The coal extract solution is a colloidal, but not a suspension, system because suspended particles can be easily removed by

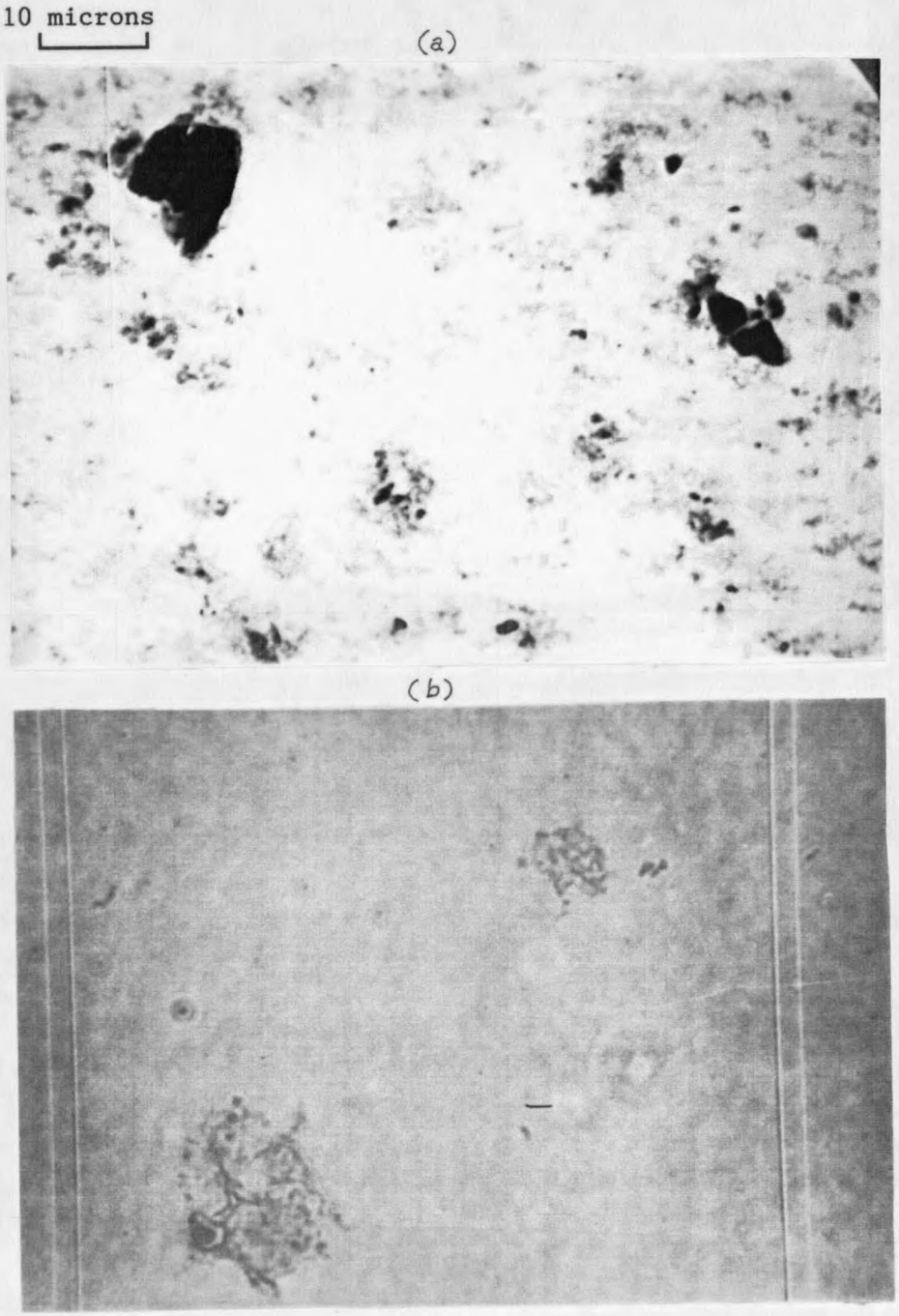
centrifugation. Here coal extract solutions (Runs 173-177) had little separation after 10,000 rpm centrifugation. Colloidal particles are clearly visible in pictures taken from image analysis (Figure 25).

One may ask if coal colloids are micelles. The typical micelle is aggregated from many small molecules bound together by secondary bonds or cohesive forces. Thus micelles can be formed only from substances whose molecules have both a hydrophobic part and a relatively small, polar "head". Moreover, micelles are formed only above a certain critical concentration at a certain temperature. In a tetralin extract, extracted particles are non-polar; therefore they are not good candidates for forming micelles. In a DMSO extract, there are polar molecules as well as non-polar molecules. Although macromolecules may associate into larger and more complex entities which may be called supermicelles, there is yet insufficient data to determine whether they form micelles in the coal extract solution or not. A very dilute (0.00496 gm/l) DMSO extract solution was examined by a light-scattering photometer. The scattering dissymmetry indicated that there were no particles in the dilute solution larger than 200 Å. This result implies that there is no large aggregation in the dilute solution.

Viscosities of extract solutions (Runs 173-177) were measured with Cannon-Fenske Viscometers as described in Chapter 2. Data of the viscosity measurements are in Appendix F. The specific viscosity, η_{sp}, was calculated as

$$\eta_{sp} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}} \qquad (8)$$

Figure 25. Magnified pictures of coal extract. (1500 X) (a) Extract of Run BS3tD_175. (b) Extract of Run BS3tD_176.

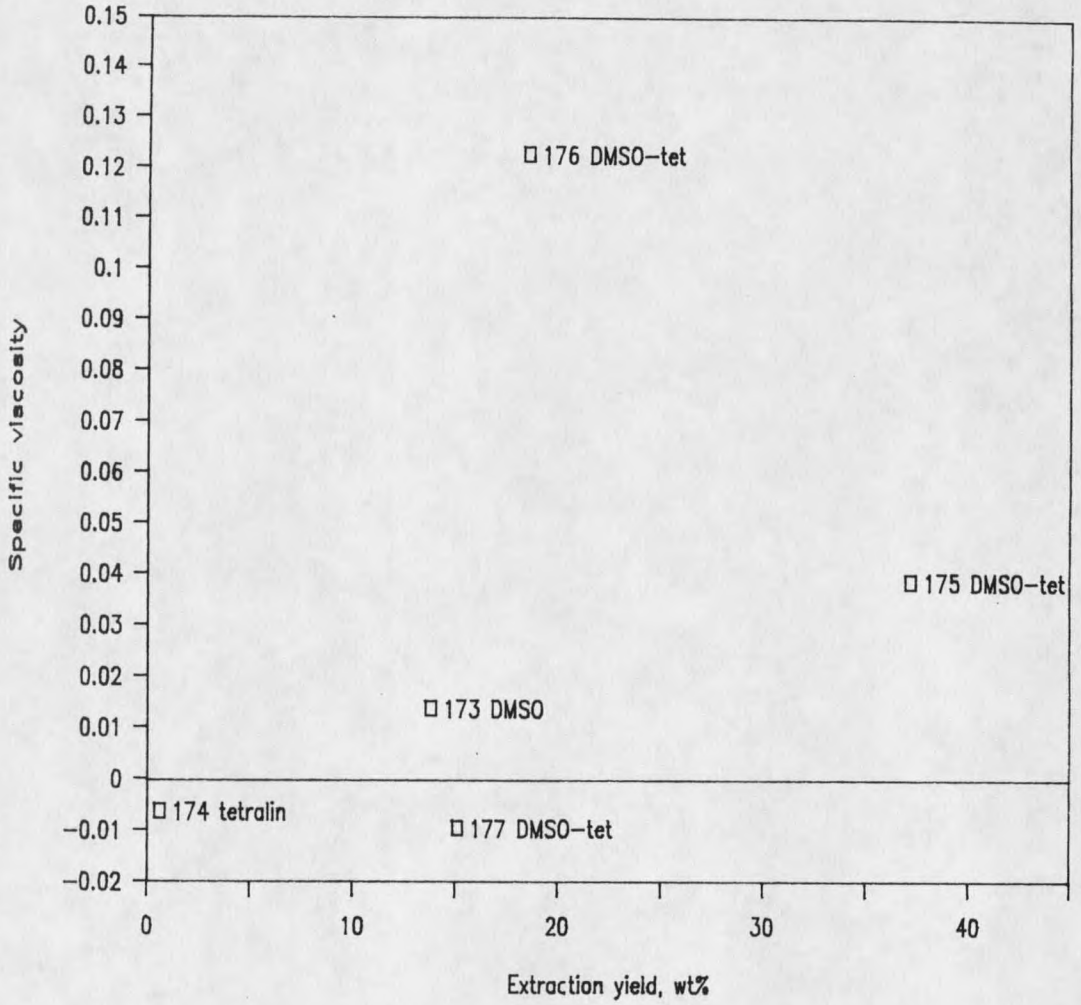


In Figure 26, the specific viscosity of extract solution BS3D_173 is about 1.4 percent higher than that of DMSO. The formation of colloids is most likely responsible for the viscosity increase [Maron 1974, Kalliat 1984]. The viscosity of BS3tD_175 extract solution was increased ≈3.9% because of a high concentration of extract in the solution. The greatest increase in viscosity came from Run BS3tD_176 in which the extraction solution was not filtered until it cooled down to room temperature. With a low concentration of extract (0.33 gm/100 ml), the relatively small number of colloids influenced a much larger volume of the coal liquid. One possible explanation is that the relatively small number of colloids entrap or hold relatively large quantities of coal liquid. The high viscosity would then be the result of the formation of flocs (See Figure 25) in which movement of the liquid is restricted by the large colloids.

To further confirm the colloidal nature of coal extract, flocculation of extract solution was investigated. It is known that flocculation will occur in a colloidal system when proper flocculating agents are added [Hermans 1949, Jirgensons 1958].

Flocculation, or precipitation, can be achieved by adding certain liquids which are non-solvents for the particular solute, and which are miscible with the solvent. By adding the non-solvent, the solvent is deteriorated, and the macromolecules will be pushed out of the solution. The amount of the non-solvent needed for flocculation depends on the following factors: chemical properties of all the components involved, concentration of the solute, molecular weight of the solute, and temperature.

Figure 26. Specific viscosity of extract solution vs. extraction yield.

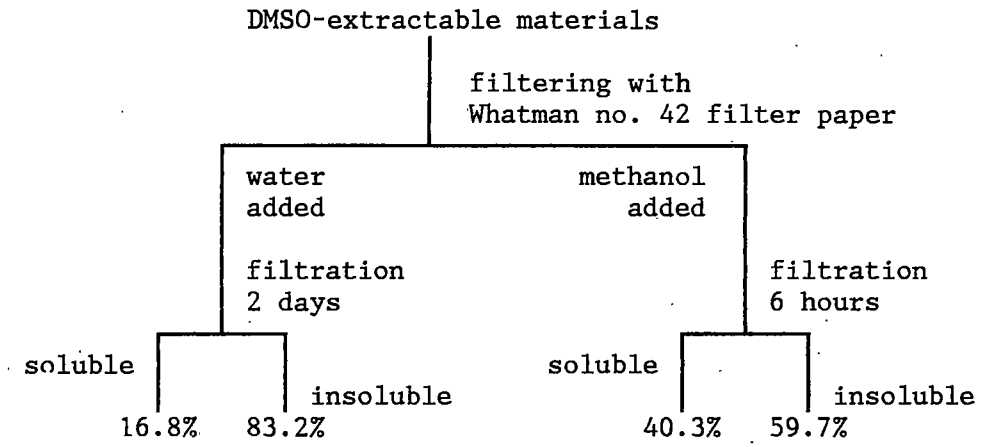


BS3D_173 : Extracted coal with DMSO.
BS3t_174 : Extracted coal with tetralin.
BS3Dt_175 : Extracted coal with DMSO/tetralin (4:1 vol), filtered extract solution immediately after extraction.
BS3Dt_176 : Extracted coal with DMSO/tetralin (4:1 vol), extract solution was not filtered until it cooled down to room temperature.
BS3D_177 : Extracted coal with DMSO (120 ml), 30 ml tetralin was added to the solution after extraction.

Regarding chemical properties: the more the precipitant differs in polarity from the solute the more powerful a flocculant it is. Flocculation experiments are usually carried out in a series of test tubes. Equal amounts of a colloidal solution are introduced into each tube, and equal volumes of a flocculating agent are added, the concentration of the latter being varied stepwise from one tube to the next. After thorough mixing, the series is left alone, and the flocculation is observed after definite time intervals. The classical method for determining the flocculating value of an electrolyte has been to estimate the minimum concentration able to produce turbidity, or precipitation, in the series under the same conditions.

Due to the dark color of coal extract solution, it is difficult to observe the occurrence of turbidity. Therefore a different approach was taken to determine the effect of the addition of non-solvent. Bakerstown coal, 150/200 mesh, was extracted with DMSO at 320°F, then filtered with Whatman no. 1 filter paper (pore opening = 11 microns). The apparent yield was 14%. There was an additional 9.2% of the DMSO-extractable material removed after filtering the extract solution with Whatman no. 42 filter paper which is designed to pass particles smaller than 2.5 microns. Clearly the DMSO extract contains much particulate material of very high molecular weight. These particulate material probably are the fine particles in the original coal samples (see Figure 13). The twice-filtered extract solution was then subjected to the addition of non-solvents, distilled water and methanol. Equal amounts of extract solution and non-solvent were mixed and stirred for 10 minutes, then filtered with Whatman no. 42

filter paper. The very slow filtration indicates the colloidal nature of the solution. The following diagram depicts the results:



Obviously water is a better flocculant. Because water (δ_p = 7.8) has a higher polarity than methanol (δ_p = 6.0), the DMSO-extractable material seems to have a low polarity. Temperature increased from 75 to 115°F during the mixing of DMSO and water, and only a 5°F change was observed for methanol. The large heat of mixing in the water-DMSO system is caused by the super-strong interaction between DMSO and water.

Hypothesis of Solvent Extraction of Coal Process

After examining these experimental results and after a review of the literature on solvent extraction of coal (see Chapter 1), this investigator proposes the following hypothesis in an attempt to explain the solvent extraction of coal process.

There are three stages postulated to be involved in solvent extraction of coal:

1. Penetration -- solvent molecules diffuse into coal pores.
2. Swelling -- solvent molecules interrupt the bonding between extractable materials and coal matrix, enlarge the pore openings, and free the trapped mobile phase.
3. Solvation -- extractable materials surrounded by solvent molecules are removed from coal particles and solvated in bulk solvents.

Penetration

In a previous section — particle size of coal (p. 55) — it is noted that extracts come out of the pores rather than from the outer shells of the coal particles. Therefore, solvents have to penetrate into the pores of coal first in the extraction process.

The three-dimensional macromolecular networks of coal create a system of pores. If one assumes cross-linking via large fragments, meso-and macropores can be expected to occur in the network. In fact, pores in bituminous coals have a very wide range of diameters and entrance sizes. Recent data [Given 1982] indicate that coals exhibit a trimodel distribution of pore sizes, which comprise macropores larger than 50 nm in diameter, mesopores with diameters from 1.6 to 6 nm and micropores of smaller dimensions. Solvent molecules such as DMSO and tetralin are smaller than 0.4 nm (4 Å). The driving forces for the penetration are the concentration gradient between the solvent and the coal (entropic) and all favourable non-covalent interactions between the solvent and the coal (enthalpic) [Green 1984].

There are significant steric effects on the penetration of organic molecules in coals. Bituminous coals have little tolerance to

branched, bulky groups. They behave as if extensive parallel packing of structures occurs. Often, they can accept very large planar groups but have a low capacity for branched groups [Larsen 1985].

Table 12 clearly demonstrates the steric effect of non-active solvents. Limonene molecules are the most branching molecules tested, and consequently have limited access to pores. Because of the high non-active to active solvent ratio, active solvent molecules has little access to the pore entrances.

Table 12. Effect of non-active solvents in solvent blends

Non-active Solvent	Molar ratio[a]	Yield change	Reference Run numbers
CS_2	1.1857	+1800.0%	BM1csD_162, BM1D_164
Naphthalene	5.1071	+6.0%	KS3naTH_T12, KS3TH_T19
Tetralin	4.7143	-28.4%	KS3tD_107, KS3D_105
Decalin	3.6429	-69.4%	KS3deTH_T28, KS3TH_T19
Limonene	3.5357	-72.4%	KS3lmTH_102, KS3TH_T19

[a] The ratio of moles of non-active solvent to moles of active solvent

Swelling

Once solvents have penetrated into the pores of coal particles, the second stage of the extraction process, swelling, takes place.

Coals do not dissolve in solvents, but absorb them and swell [Green 1982]. The swelling is opposed by an elastic response of the coal network which depends on its crosslink density. The crosslinks are both covalent and non-covalent interactions which hold together different parts of the network. As the non-covalent crosslinks are destroyed by stronger coal-solvent interactions, the swelling increases [Green 1984].

Swelling is a mildly exothermic process [Hermans 1949]. This indicates that at a lower temperature more solvent will be bound than at a higher temperature. The rate of swelling, however, increases considerably with increasing temperature, since the molecular movements increase in intensity at high temperatures. Nonetheless, more of the solvent will remain bound in the network after the equilibrium is reached at a lower temperature than at a higher one. The rate of swelling likewise is greatest at the beginning, and decreases as the uptake of the solvent proceeds [Breitenbach 1945].

In the case of coals swelling in DMSO, two kinds of bound DMSO can be considered: tightly bound DMSO by hydrogen-bonding and DMSO bound by cohesion.

Some pores contain small coal molecules, or a trapped mobile phase. Irrespective of their width the pore entrances can be much more easily passed by solvent molecules than by large coal molecules. Therefore, an osmotic-like pressure should be expected in the pores due to the higher concentration of coal molecule solutions inside the pores than outside [Marzec 1983]. The intrapore osmotic pressure, or the mechanical stresses resulted from uneven swelling [Brenner 1983], should be considered to be the source of forces that can loosen the original packing of coal matter, pull apart macromolecules, flatten their conformation and even bring about spontaneous fracture of coal grains as far as covalent cross-linking will allow. All these phenomena result in swelling.

The swelling power of DMSO was examined by determining the swelling ratio of Kittaning and Bakerstown coal samples in DMSO (Table

13). The volumetric measurement method of swelling ratio was described in Chapter 2. Kittaning coal has a higher swelling ratio in DMSO than Bakerstown coal. The extraction yield of Kittaning coal (Run KS3D_105) is also higher than Bakerstown coal (Runs BS3D_173 and BS3D_180) with DMSO as the solvent. The result is consistent with the generalization that the swelling stage is most significant in solvent extraction of coal.

Table 13. Swelling ratio of coal in DMSO

Coal sample	h_1	h_2	Swelling ratio
Kittaning Chunk #3	0.6	0.9	1.5
	0.55	0.87	1.58
Bakerstown Chunk #2	0.7	0.84	1.2
	0.7	0.86	1.23
Bakerstown Bag #1	0.6	0.76	1.27
	0.6	0.75	1.25

Solvation

Although the term solvation is generally used to describe the overall dissolving process, this investigator only uses it to describe the third stage of solvent extraction of coal. Solvation is the process whereby coal molecules are first surrounded by solvents, and then removed from the coal structure. Like the penetration process, solvation is controlled mainly by the concentration gradient and favorable non-covalent interactions. Because the coal network has been swollen by the solvent, solvated fragments are no longer trapped in the coal matrix. Active solvents such as DMSO (δ_d = 9.0) and

pyridine (δ_d = 9.3) are not as good solvation agents as are some non-active solvents such as carbon disulfide (δ_d = 10.0) or tetralin (δ_d = 9.6). The criteria of good solvation agents are believed to be little steric hindrance, high dispersion solubility parameter (high Van der waal force) and low polarity.

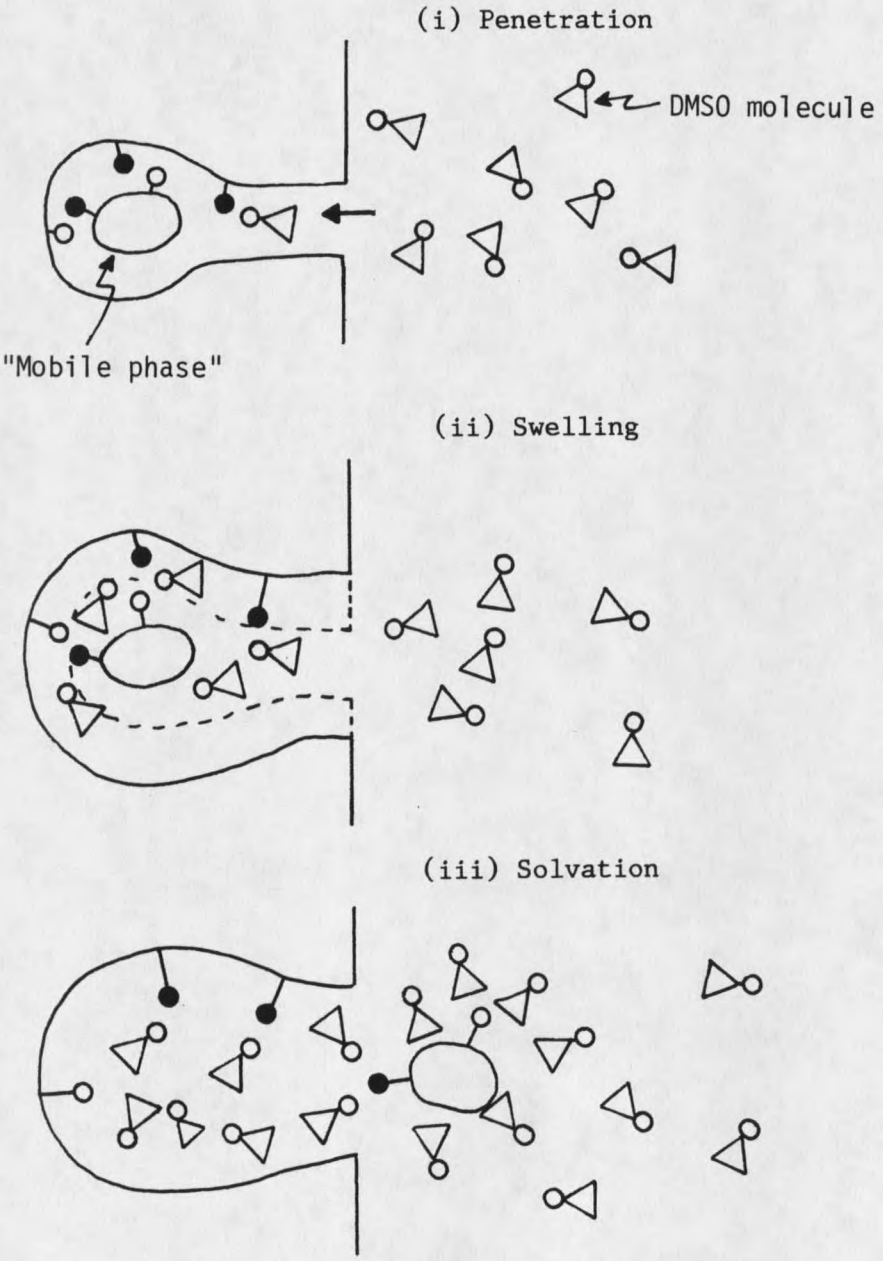
Hypothetical Extraction Scenario

Figure 27 illustrates a solvent extraction of coal process. DMSO molecules, with the dimensions less than 4 Å, can easily penetrate into pores in coal particles then interact with acidic centers (electron acceptors) of coal network (i). Because DMSO is an excellent electron donor, it may replace the "molecules" of mobile phase to form electron donor-acceptor bonds with the coal network(ii). Then the mobile phase is "dissolved" in DMSO (iii). Because of this favorable interaction between DMSO and active centers in the pores, as well as the concentration gradient of solute (the molecules of mobile phase), more DMSO molecules will diffuse into and swell the pores of coal particles. With Brownian motion, the dissolved mobile phase then diffuses out of pores with DMSO.

Implications of the Hypothesis of Solvent Extract of Coal Process

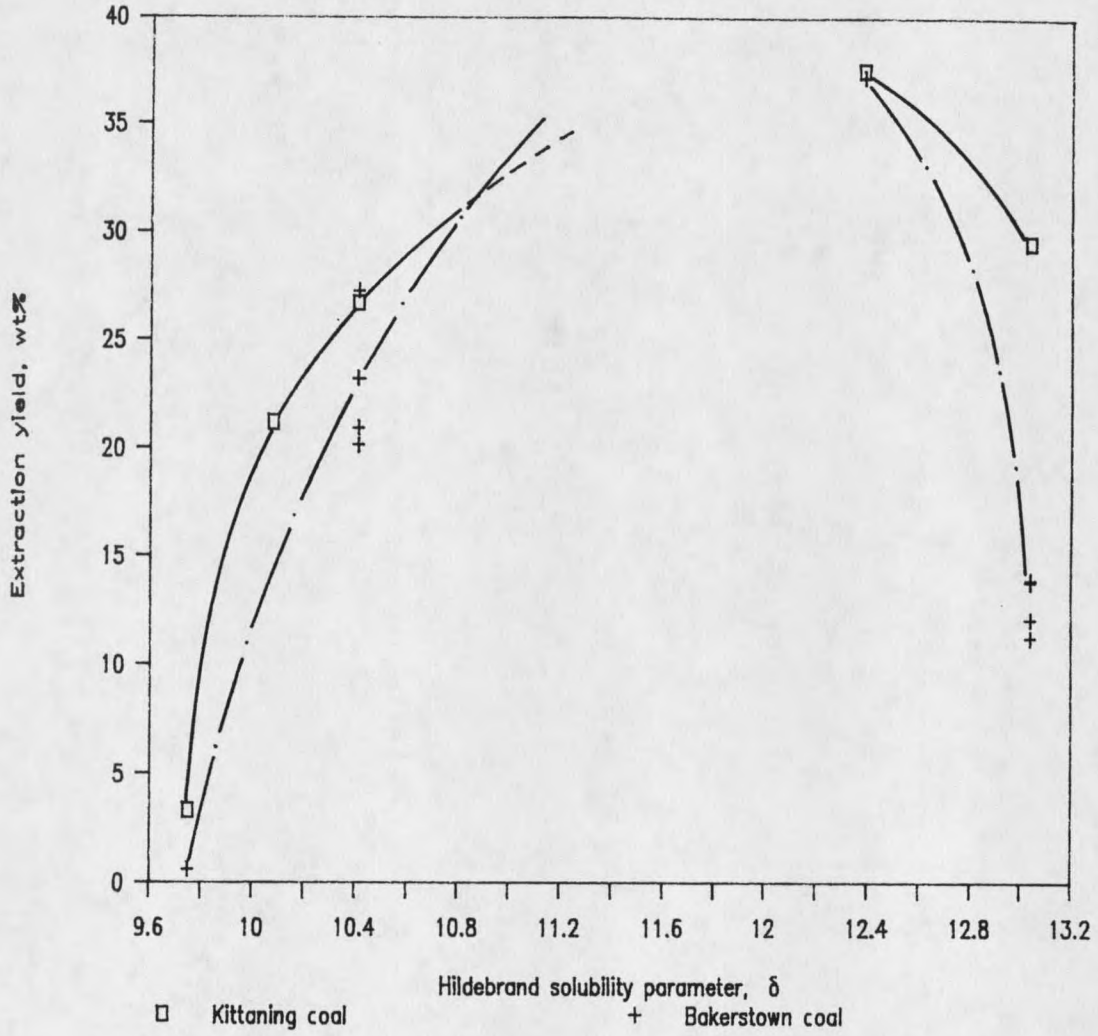
The effectiveness of solvents or solvent blends has been predicted with solubility parameters (δ) or electron donor/acceptor numbers (DN, AN) by most coal scientists without using the three-step extraction hypothesis.

Figure 27. Illustration of a solvent extraction of coal process. (Hypothetical)
—o electron donor or hydrogen bond acceptor
—● electron acceptor or hydrogen bond donor



However, these parameters cannot consistently predict or explain results obtained in many experimental studies, especially for extractions using more than one solvent such as was done in the experiments conducted in this research. For example, the solubility parameter (δ) of Kittaning coal (83% carbon content) is estimated in the range from 11.6 to 12.4 [van Krevelen]. According to the regular solution theory (see Chapter 1, equation 2), the most favorable interaction occurs when solvent and coal have identical values. A solvent blend of DMSO and tetralin with δ between 11.6 and 12.4 should give the highest yield. Such a yield can be projected from the obtained experimental data (Figure 28). The calculation of solubility parameters for solvent blends is described in Appendix G. For Bakerstown coal (≈86% carbon content), the estimated solubility parameter is in the range from 11 to 11.7. The most powerful DMSO-tetralin solvent blend is expected to have a similar solubility parameter. This too is consistent with experimental data (Figure 28). Several coal scientists have reported successful predictions of solvent power by comparing δ_{coal} and $\delta_{solvent}$ [Hombach 1980, Green and Larsen 1984, Weinberg and Yen 1980]. However, the prediction of solubility parameter is not reliable for many solvent blends. For example, DMSO-tetralin (1:4 vol, δ = 10.41) blend extracted 20.6 wt% (Run BL2tD_114) of Bakerstown coal while DMSO-tetralin-cumene (1:4:0.25 vol) with a similar solubility parameter (δ = 10.31) only yielded 9.2 wt% (Run BL2tDcm_115) at 270°F. Solubility parameters also failed to explain why pyridine (δ = 10.65) had a mere 2.8 wt% yield (Run BM1P_165) but pyridine-CS_2 (1:1 vol, δ = 10.33) extracted 12.8

Figure 28. Extraction yield vs. Hildebrand solubility parameter (δ). DMSO and tetralin are used in the solvent blends.



wt% of Bakerstown coal at room temperature. This failure of prediction results from the fact that Hildebrand solubility parameters describe only non-specific van der Waals interactions, but not specific interactions such as hydrogen bonds and donor-acceptor complexes.

Instead of solubility parameters, several scientists have used Gutmann's electron-donor or acceptor numbers in predicting solvent power in coal extraction [Marzec 1979, Pajak 1985, Jones 1985] . It is reported that solvents with large DN and small AN are active solvents [Marzec 1979]. However poor results were observed in the attempts to correlate extraction yield with DN-AN or DN/AN [Marzec 1979, Jones 1985]. The prediction of solvent power with DN is especially unsuccessful in extractions with solvent blends. For example, DMSO (DN = 29.8) extracted 1.1 wt% of coal while DMSO-CS_2 (1:1 vol), which should have lower overall DN due to the weak electron donating ability of CS_2, extracted 20.9 wt%. Similar phenomena have been observed in all extractions with tetralin or carbon disulfide as co-solvent in the solvent blend: DMSO-tetralin or DMSO-CS_2 with a lower DN generally is more effective than DMSO alone in extractions. This anomaly cannot be explained using a single-stage extraction process, because solvent blends with larger DN (higher electron donating power) should have stronger coal-solvent interactions in disrupting bondings between coal network and pore substances which should result in more pore substances extracted out of coal. In fact a good correlation had been observed between swelling ratio and DN [Szeliga 1983].

In the three-stage extraction hypothesis, swelling is a significant, but not the only, stage that affects extraction yield: penetration and solvation are also important. Tetralin and carbon disulfide are solvents with low steric hindrance and should not have negative effects in the penetration stage. During the swelling stage, there are sufficient amounts of DMSO molecules to interact with acidic centers of coal network and pore substances, because a high solvent to coal ratio was used in all extraction experiments. Tetralin or carbon disulfide may ease the self-association of DMSO molecules and enhance the interaction between DMSO and coal. Once the pore substance is detached from the coal network, tetralin (δ_d = 9.6, dispersion parameter) and carbon disulfide (δ_d = 10) would have stronger solvation power than DMSO (δ_d = 9.0) because electron donor/acceptor centers are a small portion of the pore substance structures. Based on the three-stage hypothesis, the effect of non-active solvents in solvent blends can be predicted (Table 12). Carbon disulfide and naphthalene (δ_d = 9.4) can enhance extraction yield because of their higher solvation power. Carbon disulfide is most effective due to its high δ_d and small size. Naphthalene is more effective than tetralin because it is less bulky and it has higher hydrogen parameters (δ_h = 2.9 for naphthalene, δ_h = 1.4 for tetralin) so it may be able to solvate the electron donor/acceptor portion of pore substances. With 80 vol% of tetralin in the solvent blend, there may be insufficient DMSO molecules to cover electron donor/acceptor portions of pore substance. As a result, there should be and there was a drop in the yield. Table 12 indicates that decalin (δ_d = 9.0, δ_h = 0) and

limonene (δ_d = 8.1, δ_h = 0) did not enhance extraction yield due to their low solvating power and large steric hindrance.

In conclusion, a good solvent blend should include (1) an active solvent which has large DN and (2) effective co-solvents that have high δ_d and small molecular size. Co-solvents with a moderate δ_h may be desirable, but large δ_h should be avoided because it will result in a hydrogen-bonding interaction between the active solvent and non-active co-solvents.

CHAPTER 4

SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

The research objective specified earlier in Chapter 1 is addressed by the statements based on experimental data and hypothetical reasoning which appear under the appropriate heading below. The order of presentation merely reflects the order of appearance in the research objective section.

Composition of the Solvent

1. Dimethylsulfoxide (DMSO) is an active solvent for coal extraction. It extracted about 30 wt% of Kittaning coal and about 14 wt% of Bakerstown coal at 320°F. At temperatures below 250°F DMSO alone is much less effective.
2. Tetralin and carbon disulfide (CS_2) are non-active solvents. However the solvent blend of DMSO/tetralin and DMSO/CS_2 demonstrated stronger extraction power than pure DMSO in the extraction of coal. The enhancement effect of tetralin and CS_2 is attributed to their solvation/dispersion ability and small steric hindrance.
3. Interactions between additives, such as cumene, quinone, and hydroquinone, and the active solvent, DMSO, reduce extraction yields dramatically. This negative effect does not inhibit subsequent extractions using solvents without these additives.

Extraction Temperature

4. Higher extraction temperatures (not greater than the boiling point of solvent) and proper composition of solvents can achieve higher extraction yields.

Number of Consecutive Extractions and the Particle Size of Coal

5. There is limited amount of material that can be extracted from coal at low temperatures. The limit for Bakerstown coal is about 48 wt%, which can be obtained through consecutive extractions.

The number of consecutive extractions required to exhaust coal samples depends on the particle size of coal.

6. Extraction solvents do not dissolve the outer shell of coal particles but remove macromolecules from the pores of the coal network.

Analysis of Extracts

7. Organic compounds extracted by DMSO, an active and specific solvent, included such functional groups as hydroxyl and amino, but aromatic and aliphatic hydrocarbons were also present in the extract. Tetralin, a non-active solvent, extracted for the most part aromatic, cyclic, and aliphatic hydrocarbons. These results imply that an active solvent has the capacity to interrupt the electron donor/acceptor interactions between functional groups of the pore substance and those of the coal network.

8. The extract solution of coal is a colloidal system.

Understanding of the Extraction Process

9. Solvent extraction of coal can be hypothesized as a three-stage process which includes penetration, swelling and solvation.

10. A good solvent blend for extracting coal should include an active solvent and effective co-solvents that have good solvation power and little steric hindrance.

This study has explored the process of coal extraction using diverse solvents. The results obtained hopefully will clarify some of the issues involved in this important process. The implications of these results lead to the recommendations that follow:

1. Search for optimal solvent blends for coal extractions at low temperature by selecting active solvents with strong electron donating power and one or more effective co-solvents.
2. Study solvent recovery techniques in order to make solvent extraction of coal process commercially attractive.
3. Study the retention of DMSO in the extraction residue with low sulfur coals.
4. Study pore structures of coal, and the possible restricted diffusion phenomena in solvent penetration and solvation stages because the dimension of solvent molecules is compatible with that of micropore openings.
5. Study ways to verify the three-stage hypothesis of solvent extraction of coal.

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APPENDICES

APPENDIX A

EXTRACTION EXPERIMENT DATA

Table 14. Extraction experimental data

Mnemonic	Run	Coal Type	Size	%Ash	Res %ash	Temp (F)	Solvent 1
KS3mrTH	101	Kittaning c#3	150/200	13.0	12.5	305	TMU 20
KS31mTH	102	Kittaning c#3	150/200	13.0	14.3	320	TMU 20
KS3dpTH	103	Kittaning c#3	150/200	13.0	13.8	320	TMU 20
KS3D	105	Kittaning c#3	150/200	13.0	17.5	320-350	DMSO 200
KS3tD	106	Kittaning c#3	150/200	13.0	16.9	308-330	DMSO 40
KS3tD	107	Kittaning c#3	150/200	13.0	15.9	310-336	DMSO 20
KS3Dt	108	Kittaning c#3	150/200	13.0	19.3	320-338	DMSO 160
rS3tD	110	Res 105	150/200	17.5	18.2	308-330	DMSO 20
rS3tD	111	Res 107	150/200	15.9	16.0	294-328	DMSO 20
rS3tD	112	Res 108	150/200	19.3	20.4	308-330	DMSO 20
BL3tD	113	Bakerstown c#1	35/100	9.6	12.9	302-334	DMSO 40
BL2tD	114	Bakerstown c#1	35/100	9.6	11.8	260-270	DMSO 40
BL2tDcm	115	Bakerstown c#1	35/100	9.6	10.5	266-280	DMSO 40
BL2tDcm	116	Bakerstown c#1	35/100	9.6	9.5	270-280	DMSO 40
BL2tcmD	117	Bakerstown c#1	35/100	9.6	9.5	262-272	DMSO 40
BL2tDqu	118	Bakerstown c#1	35/100	9.6	9.6	262-270	DMSO 40
BL3tD	119	Bakerstown c#2	35/100	7.5	10.8	320-335	DMSO 40
BL3tD	120	Bakerstown c#2	35/100	7.5	9.3	310-325	DMSO 40
BL3tD	121	Bakerstown c#2	35/100	7.5	9.5	295-315	DMSO 40
BL3tD	122	Bakerstown c#2	35/100	7.5	9.6	295-320	DMSO 40
BL3tD	123	Bakerstown c#2	35/100	7.5	9.6	340-355	DMSO 40
BL3tD	124	Bakerstown c#2	35/100	7.5	9.3	315-350	DMSO 40
BL3tD	128	Bakerstown b#1	35/100	10.2	13.6	320-340	DMSO 40
BL3tD	129	Bakerstown b#1	35/100	10.2	12.5	310-340	DMSO 40
BL3tD	130	Bakerstown b#1	35/100	10.2	12.6	290-325	DMSO 40
rL3tD	131	Res 130	35/100	12.6	15.2	320-335	DMSO 40
rL3tD	132	Res 130	35/100	12.6	15.1	275-345	DMSO 40
rL3tD	133	Res 128	35/100	13.6	15.5	305-325	DMSO 40
rL3tD	134	Res 129	35/100	12.5	15.3	315-330	DMSO 40
BL3tD	135	Bakerstown c#2	35/100	7.5	9.8	315-335	DMSO 40
BL3tD	136	Bakerstown c#2	35/100	7.5	9.2	325-350	DMSO 40
BL3tD	137	Bakerstown b#1	35/100	10.2	13.9	315-335	DMSO 40
rL3tD	138	Res 133	35/100	15.5	16.5	315-345	DMSO 40
rL3tD	139	Res 134	35/100	15.3	16.2	310-325	DMSO 40
rL3tD	140	Res 138	35/100	16.5	17.0	315-330	DMSO 40
rL3tD	141	Res 139	35/100	16.2	16.4	325-345	DMSO 40
rL3tD	142	Res 137	35/100	13.9	16.0	315-335	DMSO 40
rL3tD	143	Res 140	35/100	17.0	17.4	300-340	DMSO 40
rL3tD	144	Res 141	35/100	16.4	16.7	307-330	DMSO 40
rL3tD	145	Res 143	35/100	17.4	17.7	325-345	DMSO 40
rL3tD	146	Res 145	35/100	17.7	17.6	325-350	DMSO 40
rL3tD	147	Res 142	35/100	16.0	16.4	305-325	DMSO 40

Table 14 (continued)

Mnemonic	Run	Coal Type	Size	%Ash	Res %ash	Temp (F)	Solvent 1
BL3tD	148	Bakerstown b#1	35/100	10.2	13.9	300-345	DMSO 40
BL3D	149	Bakerstown b#1	35/100	10.2	11.5	300-335	DMSO 200
BL3D	150	Bakerstown b#1	35/100	10.2	11.4	318-340	DMSO 200
rL3D	151	Res 147	35/100	16.4	16.9	320-335	DMSO 200
rL3tD	152	Res 149	35/100	11.5	13.2	315-350	DMSO 40
rL3tD	153	Res 150	35/100	11.4	13.7	315-345	DMSO 40
BL3tD	154	Bakerstown b#1	35/100	10.2	12.9	300-335	DMSO 40
rL3tD	156	Res 151	35/100	16.9	15.8	315-325	DMSO 40
3tD	157	none		0.0	0.0	300-335	DMSO 40
BS3tD	158	Bakerstown b#1	150/200	10.2	15.6	300-345	DMSO 40
rS3tD	159	Res 158	150/200	15.6	16.1	305-345	DMSO 40
rL3tD	160	Res 116	35/100	9.5	12.8	290-320	DMSO 40
BM1csP	161	Bakerstown b#1	100/150	10.2	11.2	room	Pyridine 50
BM1csD	162	Bakerstown b#1	100/150	10.2	12.6	room	DMSO 50
BM1csP	163	Bakerstown b#1	100/150	10.2	11.6	room	Pyridine 50
BM1D	164	Bakerstown b#1	100/150	10.2	10.3	room	DMSO 100
BM1P	165	Bakerstown b#1	100/150	10.2	10.5	room	Pyridine 100
KS3Dt	166	Kittaning c#3	150/200	13.0	14.5	309-340	DMSO 100
rS3tD	167	Res 159	150/200	16.1	15.3	300-340	DMSO 40
BL3tDhq	168	Bakerstown c#1	35/100	9.6	11.8	307-335	DMSO 40
BL2tDhq	169	Bakerstown c#1	35/100	9.6	10.3	270-300	DMSO 40
BS2Dnb	170	Bakerstown b#2	150/200	10.2	10.3	215-235	DMSO 100
BS2Dsb	171	Bakerstown b#2	150/200	10.2	10.3	185-240	DMSO 100
BS2D	172	Bakerstown b#2	150/200	10.2	10.3	175-240	DMSO 150
BS3D	173	Bakerstown b#2	150/200	10.2	11.6	300-324	DMSO 150
BS3t	174	Bakerstown b#2	150/200	10.2	10.3	290-320	Tetralin 150
BS3Dt	175	Bakerstown b#2	150/200	10.2	15.3	300-340	DMSO 120
BS3Dt	176	Bakerstown b#2	150/200	10.2	12.2	315-340	DMSO 120
BS3D	177	Bakerstown b#2	150/200	10.2	11.8	315-330	DMSO 120
BM1csdm	178	Bakerstown b#1	100/150	10.2	10.3	room	CH2C12 50
BM1N	179	Bakerstown b#1	100/150	10.2	10.4	room	NMP 100
BS3D	180	Bakerstown b#2	150/200	10.2	11.7	310-330	DMSO 200
BM1csN	181	Bakerstown b#1	100/150	10.2	9.8	room	NMP 50
rM1csD	182	Res 162	100/150	12.6	13.5	room	DMSO 50
rM1csD	183	Res 182	100/150	13.5	13.5	room	DMSO 50

Table 14 (continued)

Mnemonic	Run	Solvent 2	Solvent/Additive 3	Time	Yield appar	Yield maf
KS3mrTH	101	HMPA 20	Myrcene 160	60	-3.8	-4.4
KS3lmTH	102	HMPA 20	Limonene 160	60	8.8	10.1
KS3dpTH	103	HMPA 20	Dipentene 160	60	5.5	6.3
KS3D	105			60	25.7	29.6
KS3tD	106	Tetralin 160		60	23.3	26.7
KS3tD	107	Tetralin 180		60	18.4	21.2
KS3Dt	108	Tetralin 40		60	32.7	37.5
rS3tD	110	Tetralin 180		30	3.6	4.4
rS3tD	111	Tetralin 180		30	0.2	0.2
rS3tD	112	Tetralin 180		30	5.4	6.7
BL3tD	113	Tetralin 160		20	25.8	28.6
BL2tD	114	Tetralin 160		20	18.6	20.6
BL2tDcm	115	Tetralin 160	Cumene 10	20	8.3	9.2
BL2tDcm	116	Tetralin 160	Cumene 50	20	-0.7	-0.7
BL2tcmD	117	Tetralin 160	Cumene 100	20	-1.0	-1.2
BL2tDqu	118	Tetralin 160	Quinone 22 gm	20	0.3	0.4
BL3tD	119	Tetralin 160		20	31.0	33.5
BL3tD	120	Tetralin 160		20	19.7	21.3
BL3tD	121	Tetralin 160		20	21.9	23.6
BL3tD	122	Tetralin 160		20	22.5	24.3
BL3tD	123	Tetralin 160		20	22.7	24.5
BL3tD	124	Tetralin 160		20	20.2	21.8
BL3tD	128	Tetralin 160		20	24.5	27.3
BL3tD	129	Tetralin 160		20	18.1	20.1
BL3tD	130	Tetralin 160		20	18.8	20.9
rL3tD	131	Tetralin 160		20	16.8	19.3
rL3tD	132	Tetralin 160	Lupersol-130 1	20	16.5	18.9
rL3tD	133	Tetralin 160		20	12.4	14.4
rL3tD	134	Tetralin 160		20	18.4	21.1
BL3tD	135	Tetralin 160		20	24.3	26.3
BL3tD	136	Tetralin 160		20	19.1	20.6
BL3tD	137	Tetralin 160		20	26.5	29.5
rL3tD	138	Tetralin 160		20	6.4	7.6
rL3tD	139	Tetralin 160		20	5.2	6.1
rL3tD	140	Tetralin 160		20	2.5	3.0
rL3tD	141	Tetralin 160		20	1.5	1.8
rL3tD	142	Tetralin 160		20	13.1	15.2
rL3tD	143	Tetralin 160		20	2.3	2.8
rL3tD	144	Tetralin 160	Lupersol-130 1	20	1.7	2.0
rL3tD	145	Tetralin 160		20	2.2	2.7
rL3tD	146	Tetralin 160		20	-0.7	-0.9
rL3tD	147	Tetralin 160		20	2.1	2.5

Table 14 (continued)

Mnemonic	Run	Solvent 2	Solvent/Additive 3	Time	Yield appar	Yield maf
BL3tD	148	Tetralin 160	Lupersol-130 1	20	26.5	29.5
BL3D	149		Cumene Hydroperoxide 1	20	10.9	12.1
BL3D	150			20	10.1	11.3
rL3D	151		Cumene Hydroperoxide 1	20	3.0	3.6
rL3tD	152	Tetralin 160	Cumene Hydroperoxide 5	20	12.7	14.3
rL3tD	153	Tetralin 160		20	16.9	19.1
BL3tD	154	Tetralin 160	Cumene Hydroperoxide 2	20	20.9	23.2
rL3tD	156	Tetralin 160	Cumene Hydroperoxide 10	20	-6.9	-8.3
3tD	157	Tetralin 160	Cumene Hydroperoxide 10	20		
BS3tD	158	Tetralin 160		20	34.2	38.1
rS3tD	159	Tetralin 160		20	3.4	4.0
rL3tD	160	Tetralin 160		20	25.4	28.1
BM1csP	161	Carbon disulfide 50		60	8.8	9.8
BM1csD	162	Carbon disulfide 50		60	18.8	20.9
BM1csP	163	Carbon disulfide 50		60	11.5	12.8
BM1D	164			60	1.0	1.1
BM1P	165			60	2.5	2.8
KS3Dt	166	Tetralin 100		60	10.5	12.0
rS3tD	167	Tetralin 160		20	-5.6	-6.6
BL3tDhq	168	Tetralin 160	Hydroquinone 21.6 gm	20	18.6	20.6
BL2tDhq	169	Tetralin 160	Hydroquinone 21.03 gm	20	6.6	7.3
BS2Dnb	170	n-Butanol 50		20	1.3	1.4
BS2Dsb	171	s-Butanol 50		20	1.3	1.4
BS2D	172			20	0.9	0.9
BS3D	173			20	12.4	13.8
BS3t	174			20	0.5	0.6
BS3Dt	175	Tetralin 30		20	33.4	37.2
BS3Dt	176	Tetralin 30		20	16.6	18.5
BS3D	177			20	13.6	15.1
BM1csdm	178	Carbon disulfide 50		60	0.2	0.2
BM1N	179			60	1.4	1.5
BS3D	180			20	12.5	13.9
BM1csN	181	Carbon disulfide 50		60	-4.7	-5.2
rM1csD	182	Carbon disulfide 50		60	6.5	7.4
rM1csD	183	Carbon disulfide 50		60	0.4	0.4

Table 14 (continued)

Mnemonic	Run	%N	%C	%H	%S	%N	%C	%H	%S	C/H	Res
		<	Residue		>	<maf	residue			maf>	wt.
KS3mrTH	101	1.5	76.4	5.5	3.9	1.7	87.3	6.3	4.4	1.15	5.4455
KS3lmTH	102	2.0	76.9	5.1	2.1	2.4	89.7	6.0	2.5	1.25	3.6185
KS3dpTH	103	2.1	77.3	5.1	1.9	2.4	89.7	5.9	2.2	1.25	4.7530
KS3D	105	1.0	74.7	4.7	3.5	1.2	90.6	5.7	4.2	1.31	3.0385
KS3tD	106	1.0	73.4	4.6	2.9	1.2	88.3	5.6	3.5	1.32	3.8928
KS3tD	107	1.3	74.0	4.8	3.0	1.5	88.0	5.7	3.6	1.29	3.5635
KS3Dt	108	1.1	70.6	4.7	4.3	1.4	87.5	5.8	5.3	1.26	2.9528
rS3tD	110	1.2	71.5	4.7	4.3	1.5	87.3	5.7	5.3	1.27	2.3075
rS3tD	111	1.3	71.2	4.7	4.3	1.6	84.7	5.6	5.1	1.26	2.8921
rS3tD	112	1.3	71.0	4.8	3.2	1.7	89.2	6.0	4.1	1.24	2.3805
BL3tD	113	1.0	70.6	4.7	5.2	1.2	81.1	5.4	6.0	1.25	3.8784
BL2tD	114	1.1	73.0	4.9	6.3	1.3	82.8	5.5	7.1	1.24	4.3231
BL2tDcm	115	1.1	75.1	5.0	4.5	1.2	83.9	5.6	5.1	1.25	4.6561
BL2tDcm	116	1.0	78.7	5.1	3.6	1.1	87.0	5.6	4.0	1.29	5.1119
BL2tcmD	117	1.0	77.4	5.0	3.2	1.1	85.5	5.5	3.5	1.30	5.1862
BL2tDqu	118										4.6167
BL3tD	119										3.6570
BL3tD	120	1.8	74.3	4.9	4.8	2.0	81.9	5.4	5.3	1.25	4.0135
BL3tD	121	1.8	73.6	4.9	4.9	1.9	81.4	5.4	5.4	1.26	4.0638
BL3tD	122	1.7	74.4	4.9	4.9	1.9	82.3	5.4	5.4	1.25	3.8755
BL3tD	123	1.6	73.6	4.7	5.0	1.8	81.4	5.2	5.5	1.29	3.8670
BL3tD	124	1.6	70.2	4.5	6.0	1.7	77.4	4.9	6.7	1.30	4.0718
BL3tD	128	1.5	76.7	4.8	4.3	1.7	88.7	5.5	5.0	1.34	7.5500
BL3tD	129	1.4	69.5	4.4	4.4	1.6	79.5	5.1	5.1	1.31	8.1920
BL3tD	130	1.4	74.9	4.6	4.3	1.6	85.7	5.3	4.9	1.35	8.1200
rL3tD	131	1.4	65.9	4.2	4.4	1.7	77.7	4.9	5.2	1.31	1.7882
rL3tD	132	1.6	74.1	4.6	4.8	1.9	87.3	5.5	5.7	1.33	3.2649
rL3tD	133	1.6	76.4	4.6	4.0	1.9	90.4	5.4	4.8	1.38	5.6745
rL3tD	134	1.5	71.5	4.3	4.7	1.8	84.4	5.1	5.6	1.37	5.3259
BL3tD	135	1.5	74.6	4.7	4.3	1.7	82.7	5.2	4.8	1.32	3.5579
BL3tD	136	1.6	75.7	4.8	4.4	1.7	83.4	5.3	4.8	1.31	4.0450
BL3tD	137	1.5	75.9	4.7	4.2	1.7	88.2	5.4	4.9	1.35	7.4970
rL3tD	138	1.3	73.2	4.4	4.3	1.6	87.7	5.2	5.2	1.40	5.0533
rL3tD	139	1.3	74.0	4.5	5.4	1.5	88.3	5.3	6.5	1.38	4.8348
rL3tD	140	1.3	74.3	4.5	4.9	1.5	89.5	5.5	5.9	1.36	4.7288
rL3tD	141	1.1	73.0	4.4	4.7	1.3	87.3	5.2	5.6	1.39	4.5690
rL3tD	142	1.3	75.2	4.7	4.2	1.5	89.6	5.6	5.0	1.33	6.4306
rL3tD	143	1.1	73.3	4.6	4.8	1.3	88.6	5.6	5.9	1.32	4.2988
rL3tD	144	1.2	74.0	4.6	4.2	1.4	88.9	5.5	5.1	1.34	4.3958
rL3tD	145	1.2	74.1	4.8	3.9	1.4	90.1	5.8	4.7	1.28	3.6262
rL3tD	146	1.1	72.3	4.4	2.7	1.3	87.7	5.3	3.3	1.37	3.2769
rL3tD	147	1.1	73.7	4.5	5.4	1.4	88.2	5.4	6.4	1.35	6.1877

Table 14 (continued)

Mnemonic	Run	%N	%C	%H	%S	%N	%C	%H	%S	C/H	Res
		<	Residue		>	<maf		residue		maf>	wt.
BL3tD	148	1.2	75.8	4.6	3.7	1.3	88.0	5.3	4.3	1.38	7.3500
BL3D	149	1.4	76.0	4.9	4.9	1.6	85.9	5.5	5.5	1.29	8.9100
BL3D	150	1.4	75.5	4.8	4.9	1.6	85.1	5.5	5.5	1.29	8.9900
rL3D	151	1.4	73.7	4.4	4.0	1.7	88.6	5.3	4.8	1.38	5.9211
rL3tD	152	1.0	72.2	4.3	3.8	1.2	83.1	5.0	4.4	1.39	7.6766
rL3tD	153	1.0	66.7	3.9	3.6	1.1	77.3	4.5	4.2	1.43	7.3959
BL3tD	154	1.0	75.7	4.6	3.1	1.2	87.0	5.2	3.6	1.38	7.9150
rL3tD	156	1.0	67.9	4.2	4.8	1.2	80.7	5.0	5.7	1.34	6.2198
3tD	157										0.0073
BS3tD	158	1.2	66.1	3.9	4.7	1.4	78.3	4.6	5.5	1.42	3.4216
rS3tD	159	1.4	65.5	4.0	5.3	1.6	78.1	4.7	6.3	1.38	3.1408
rL3tD	160	1.5	72.8	4.6	5.7	1.7	83.4	5.3	6.5	1.32	3.5868
BM1csP	161	1.2	73.1	4.4	2.9	1.3	82.3	5.0	3.3	1.37	3.6476
BM1csD	162	0.9	68.0	4.1	4.3	1.1	77.8	4.7	4.9	1.38	3.2480
BM1csP	163	1.2	73.4	4.5	4.1	1.3	83.0	5.1	4.6	1.36	3.5392
BM1D	164	1.1	73.9	4.6	3.4	1.2	82.5	5.1	3.8	1.34	3.9610
BM1P	165	1.2	78.2	4.8	3.3	1.3	87.3	5.4	3.7	1.35	3.9000
KS3Dt	166	1.0	72.1	4.8	2.9	1.1	84.3	5.6	3.4	1.25	4.7531
rS3tD	167	1.0	67.8	4.1	4.8	1.2	80.0	4.8	5.7	1.37	3.2559
BL3tDhq	168	1.2	75.2	4.7	5.5	1.4	85.2	5.3	6.2	1.34	4.4903
BL2tDhq	169	1.0	71.7	4.4	6.0	1.1	79.9	4.9	6.7	1.36	3.9110
BS2Dnb	170	1.2	74.9	4.7	3.6	1.3	83.6	5.2	4.0	1.33	2.3232
BS2Dsb	171	1.1	73.4	4.6	3.6	1.2	81.8	5.1	4.0	1.34	2.3588
BS2D	172	1.1	73.7	4.6	3.8	1.3	82.2	5.1	4.2	1.33	2.9094
BS3D	173	1.1	74.5	4.7	4.1	1.3	84.4	5.3	4.7	1.32	2.6258
BS3t	174	1.3	75.5	4.9	3.7	1.5	84.1	5.5	4.1	1.28	2.9805
BS3Dt	175	1.1	72.0	4.6	4.5	1.3	85.0	5.4	5.3	1.30	1.9903
BS3Dt	176	1.1	73.3	4.6	4.0	1.3	83.6	5.2	4.5	1.33	2.5154
BS3D	177	1.6	75.4	4.6	3.7	1.8	85.5	5.2	4.2	1.36	2.6015
BM1csdm	178	1.5	75.4	4.8	3.4	1.6	84.0	5.3	3.8	1.30	3.9924
BM1N	179	1.5	77.8	4.8	3.4	1.7	86.9	5.4	3.8	1.34	4.1529
BS3D	180				4.8				5.4		4.1534
BM1csN	181				4.8				5.3		4.6355
rM1csD	182				5.5				6.3		2.7688
rM1csD	183				4.9				5.6		2.6120

Table 14 (continued)

Mnemonic	Run	Coal wt.	%N <<	%C Coal	%H	%S >>	%N <<maf	%C	%H Coal	%S	C/H maf>>
KS3mrTH	101	5.2461	1.0	72.3	4.6	3.5	1.2	83.0	5.3	4.0	1.3
KS3lmTH	102	3.9676	1.0	72.3	4.6	3.5	1.2	83.0	5.3	4.0	1.3
KS3dpTH	103	5.0296	1.0	72.3	4.6	3.5	1.2	83.0	5.3	4.0	1.3
KS3D	105	4.0906	1.0	72.3	4.6	3.5	1.2	83.0	5.3	4.0	1.3
KS3tD	106	5.0721	1.0	72.3	4.6	3.5	1.2	83.0	5.3	4.0	1.3
KS3tD	107	4.3687	1.0	72.3	4.6	3.5	1.2	83.0	5.3	4.0	1.3
KS3Dt	108	4.3843	1.0	72.3	4.6	3.5	1.2	83.0	5.3	4.0	1.3
rS3tD	110	2.3939	1.0	74.7	4.7	3.5	1.2	90.6	5.7	4.2	1.3
rS3tD	111	2.8979	1.3	74.0	4.8	3.0	1.5	88.0	5.7	3.6	1.3
rS3tD	112	2.5161	1.1	70.6	4.7	4.3	1.4	87.5	5.8	5.3	1.3
BL3tD	113	5.2283	1.1	77.1	4.9	4.4	1.2	85.3	5.5	4.8	1.3
BL2tD	114	5.3136	1.1	77.1	4.9	4.4	1.2	85.3	5.5	4.8	1.3
BL2tDcm	115	5.0798	1.1	77.1	4.9	4.4	1.2	85.3	5.5	4.8	1.3
BL2tDcm	116	5.0784	1.1	77.1	4.9	4.4	1.2	85.3	5.5	4.8	1.3
BL2tcmD	117	5.1328	1.1	77.1	4.9	4.4	1.2	85.3	5.5	4.8	1.3
BL2tDqu	118	4.6320	1.1	77.1	4.9	4.4	1.2	85.3	5.5	4.8	1.3
BL3tD	119	5.3	1.6	81.4	5.4	3.0	1.8	87.9	5.8	3.2	1.3
BL3tD	120	5.0	1.6	81.4	5.4	3.0	1.8	87.9	5.8	3.2	1.3
BL3tD	121	5.2	1.6	81.4	5.4	3.0	1.8	87.9	5.8	3.2	1.3
BL3tD	122	5.0	1.6	81.4	5.4	3.0	1.8	87.9	5.8	3.2	1.3
BL3tD	123	5.0	1.6	81.4	5.4	3.0	1.8	87.9	5.8	3.2	1.3
BL3tD	124	5.1	1.6	81.4	5.4	3.0	1.8	87.9	5.8	3.2	1.3
BL3tD	128	10.0	1.6	77.5	4.9	3.2	1.8	86.3	5.4	3.5	1.3
BL3tD	129	10.0	1.6	77.5	4.9	3.2	1.8	86.3	5.4	3.5	1.3
BL3tD	130	10.0	1.6	77.5	4.9	3.2	1.8	86.3	5.4	3.5	1.3
rL3tD	131	2.15	1.4	74.9	4.6	4.3	1.6	85.7	5.3	4.9	1.4
rL3tD	132	3.91	1.4	74.9	4.6	4.3	1.6	85.7	5.3	4.9	1.4
rL3tD	133	6.48	1.5	76.7	4.8	4.3	1.7	88.7	5.5	5.0	1.3
rL3tD	134	6.53	1.4	69.5	4.4	4.4	1.6	79.5	5.1	5.1	1.3
BL3tD	135	4.7	1.6	81.4	5.4	3.0	1.8	87.9	5.8	3.2	1.3
BL3tD	136	5.0	1.6	81.4	5.4	3.0	1.8	87.9	5.8	3.2	1.3
BL3tD	137	10.2	1.6	77.5	4.9	3.2	1.8	86.3	5.4	3.5	1.3
rL3tD	138	5.4	1.6	76.4	4.6	4.0	1.9	90.3	5.4	4.8	1.4
rL3tD	139	5.1	1.5	71.5	4.3	4.7	1.8	84.4	5.1	5.6	1.4
rL3tD	140	4.85	1.3	73.2	4.4	4.3	1.6	87.7	5.2	5.2	1.4
rL3tD	141	4.64	1.3	74.0	4.5	5.4	1.5	88.3	5.3	6.5	1.4
rL3tD	142	7.4	1.5	75.9	4.7	4.2	1.7	88.1	5.4	4.9	1.4
rL3tD	143	4.4	1.3	74.3	4.5	4.9	1.5	89.5	5.5	5.9	1.4
rL3tD	144	4.47	1.1	73.0	4.4	4.7	1.3	87.3	5.2	5.6	1.4
rL3tD	145	3.7081	1.1	73.3	4.6	4.8	1.3	88.6	5.6	5.9	1.3
rL3tD	146	3.2541	1.2	74.1	4.8	3.9	1.4	90.1	5.8	4.7	1.3
rL3tD	147	6.3230	1.3	75.2	4.7	4.2	1.5	89.6	5.6	5.0	1.3

Table 14 (continued)

Mnemonic	Run	Coal wt.	%N << Coal	%C	%H	%S >>	%N <<maf	%C	%H Coal	%S	C/H maf>>
BL3tD	148	10.0	1.6	77.5	4.9	3.2	1.8	86.3	5.4	3.5	1.3
BL3D	149	10.0	1.6	77.5	4.9	3.2	1.8	86.3	5.4	3.5	1.3
BL3D	150	10.0	1.6	77.5	4.9	3.2	1.8	86.3	5.4	3.5	1.3
rL3D	151	6.1042	1.1	73.7	4.5	5.4	1.4	88.2	5.4	6.4	1.4
rL3tD	152	8.7933	1.4	76.0	4.9	4.9	1.6	85.9	5.5	5.5	1.3
rL3tD	153	8.9	1.4	75.5	4.8	4.9	1.6	85.1	5.5	5.5	1.3
BL3tD	154	10.0	1.6	77.5	4.9	3.2	1.8	86.3	5.4	3.5	1.3
rL3tD	156	5.8183	1.4	73.7	4.4	4.0	1.7	88.6	5.3	4.8	1.4
3tD	157	0.0000									
BS3tD	158	5.2	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
rS3tD	159	3.2513	1.2	66.1	3.9	4.7	1.4	78.3	4.6	5.5	1.4
rL3tD	160	4.8080	1.0	78.7	5.1	3.6	1.1	87.0	5.6	4.0	1.3
BM1csP	161	4.0	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
BM1csD	162	4.0	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
BM1csP	163	4.0	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
BM1D	164	4.0	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
BM1P	165	4.0	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
KS3Dt	166	5.3084	1.0	72.3	4.6	3.5	1.2	83.0	5.3	4.0	1.3
rS3tD	167	3.0841	1.4	65.5	4.0	5.3	1.6	78.1	4.7	6.3	1.4
BL3tDhq	168	5.5163	1.1	77.1	4.9	4.4	1.2	85.3	5.5	4.8	1.3
BL2tDhq	169	4.1878	1.1	77.1	4.9	4.4	1.2	85.3	5.5	4.8	1.3
BS2Dnb	170	2.3531	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BS2Dsb	171	2.3899	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BS2D	172	2.9343	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BS3D	173	2.9978	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BS3t	174	2.9961	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BS3Dt	175	2.9903	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BS3Dt	176	3.0153	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BS3D	177	3.0099	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BM1csdm	178	3.9996	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
BM1N	179	4.2102	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
BS3D	180	4.7478	1.5	77.4	4.8	3.4	1.7	86.2	5.4	3.8	1.3
BM1csN	181	4.4278	1.5	77.4	4.8	3.0	1.7	86.2	5.4	3.4	1.3
rM1csD	182	2.9610	0.9	68.0	4.1	4.3	1.1	77.8	4.7	4.9	1.4
rM1csD	183	2.6220				5.5				6.3	

Table 14 (continued)

Mnemonic	Run	C/H diff	%S diff	%N,maf diff	%C,maf diff	%H,maf diff	%S,maf diff
KS3mrTH	101	-0.16	0.43	0.58	4.29	1.05	0.47
KS3lmTH	102	-0.06	-1.33	1.19	6.66	0.68	-1.49
KS3dpTH	103	-0.06	-1.57	1.22	6.61	0.67	-1.79
KS3D	105	0.01	0.01	0.08	7.51	0.45	0.23
KS3tD	106	0.01	-0.52	0.06	5.30	0.30	-0.44
KS3tD	107	-0.02	-0.46	0.33	4.95	0.39	-0.41
KS3Dt	108	-0.05	0.79	0.23	4.45	0.50	1.29
rS3tD	110	-0.04	0.83	0.22	-3.21	-0.02	1.05
rS3tD	111	-0.03	1.31	0.07	-3.24	-0.09	1.56
rS3tD	112	-0.02	-1.01	0.30	1.75	0.21	-1.20
BL3tD	113	-0.05	0.84	-0.03	-4.19	-0.07	1.16
BL2tD	114	-0.05	1.91	0.09	-2.47	0.07	2.28
BL2tDcm	115	-0.04	0.17	0.05	-1.38	0.09	0.23
BL2tDcm	116	-0.01	-0.75	-0.11	1.70	0.15	-0.83
BL2tcmD	117	0.00	-1.23	-0.09	0.26	0.01	-1.36
BL2tDqu	118						
BL3tD	119						
BL3tD	120	0.00	1.79	0.26	-5.97	-0.40	2.04
BL3tD	121	0.01	1.92	0.17	-6.51	-0.48	2.20
BL3tD	122	0.01	1.87	0.13	-5.61	-0.40	2.14
BL3tD	123	0.04	1.99	0.05	-6.47	-0.60	2.29
BL3tD	124	0.06	3.03	-0.05	-10.48	-0.92	3.40
BL3tD	128	0.01	1.10	-0.08	2.42	0.10	1.41
BL3tD	129	-0.02	1.25	-0.18	-6.88	-0.35	1.52
BL3tD	130	0.03	1.08	-0.21	-0.60	-0.14	1.34
rL3tD	131	-0.04	0.16	0.09	-8.08	-0.34	0.34
rL3tD	132	-0.02	0.58	0.28	1.57	0.19	0.83
rL3tD	133	0.04	-0.25	0.20	1.61	-0.08	-0.18
rL3tD	134	0.06	0.28	0.16	4.94	0.06	0.50
BL3tD	135	0.07	1.29	-0.08	-5.19	-0.63	1.52
BL3tD	136	0.06	1.36	-0.03	-4.52	-0.56	1.56
BL3tD	137	0.02	1.04	-0.11	1.82	0.02	1.36
rL3tD	138	0.02	0.29	-0.32	-2.62	-0.22	0.41
rL3tD	139	0.00	0.73	-0.26	3.91	0.22	0.93
rL3tD	140	-0.04	0.59	-0.09	1.76	0.26	0.74
rL3tD	141	0.01	-0.77	-0.19	-1.01	-0.10	-0.90
rL3tD	142	-0.02	0.02	-0.20	1.42	0.17	0.15
rL3tD	143	-0.04	-0.07	-0.19	-0.83	0.12	-0.06
rL3tD	144	-0.04	-0.45	0.04	1.57	0.27	-0.52
rL3tD	145	-0.04	-0.95	0.10	1.43	0.25	-1.13
rL3tD	146	0.09	-1.20	-0.12	-2.32	-0.53	-1.46
rL3tD	147	0.03	1.15	-0.15	-1.39	-0.19	1.40

Table 14 (continued)

Mnemonic	Run	C/H diff	%S diff	%N,maf diff	%C,maf diff	%H,maf diff	%S,maf diff
BL3tD	148	0.05	0.52	-0.46	1.72	-0.09	0.76
BL3D	149	-0.03	1.70	-0.25	-0.44	0.11	1.97
BL3D	150	-0.03	1.71	-0.25	-1.18	0.06	1.98
rL3D	151	0.03	-1.41	0.32	0.45	-0.08	-1.66
rL3tD	152	0.10	-1.04	-0.37	-2.78	-0.56	-1.09
rL3tD	153	0.14	-1.25	-0.46	-7.88	-0.98	-1.30
BL3tD	154	0.05	-0.07	-0.61	0.63	-0.15	0.03
rL3tD	156	-0.04	0.82	-0.52	-7.95	-0.33	0.91
3tD	157						
BS3tD	158	0.09	1.61	-0.25	-7.96	-0.81	2.12
rS3tD	159	-0.04	0.60	0.20	-0.17	0.13	0.75
rL3tD	160	0.03	2.08	0.58	-3.54	-0.36	2.53
BM1csP	161	0.04	-0.13	-0.32	-3.91	-0.39	-0.11
BM1csD	162	0.06	1.27	-0.58	-8.39	-0.72	1.55
BM1csP	163	0.04	1.02	-0.31	-3.25	-0.34	1.20
BM1D	164	0.02	0.36	-0.46	-3.77	-0.30	0.41
BM1P	165	0.02	0.29	-0.34	1.08	-0.01	0.33
KS3Dt	166	-0.05	-0.58	-0.05	1.30	0.32	-0.61
rS3tD	167	-0.01	-0.44	-0.43	1.85	0.14	-0.58
BL3tDhq	168	0.05	1.09	0.17	-0.06	-0.19	1.35
BL2tDhq	169	0.07	1.66	-0.12	-5.33	-0.59	1.88
BS2Dnb	170	0.00	0.22	-0.32	-2.64	-0.17	0.25
BS2Dsb	171	0.01	0.20	-0.48	-4.40	-0.32	0.23
BS2D	172	0.00	0.42	-0.39	-4.01	-0.26	0.47
BS3D	173	-0.01	0.75	-0.38	-1.85	-0.08	0.91
BS3t	174	-0.05	0.28	-0.21	-2.12	0.06	0.31
BS3Dt	175	-0.03	1.09	-0.36	-1.17	0.05	1.52
BS3Dt	176	0.00	0.59	-0.38	-2.65	-0.18	0.76
BS3D	177	0.04	0.28	0.10	-0.75	-0.19	0.39
BM1csdm	178	-0.02	0.38	-0.01	-2.28	-0.04	0.42
BM1N	179	0.01	0.38	0.00	0.62	-0.01	0.43
BS3D	180		1.37				1.61
BM1csN	181		1.72				1.88
rM1csD	182		1.18				1.41
rM1csD	183		-0.61				-0.70

Table 14 (continued)

Mnemonic	Run	Comments
KS3mrTH	101	Wash w/ ETOH, Acetone
KS31mTH	102	
KS3dpTH	103	
KS3D	105	
KS3tD	106	
KS3tD	107	
KS3Dt	108	Overnight filtration
rS3tD	110	Wash w/ DMSO, ETOH, Acetone
rS3tD	111	
rS3tD	112	
BL3tD	113	
BL2tD	114	
BL2tDcm	115	
BL2tDcm	116	
BL2tcmD	117	
BL2tDqu	118	
BL3tD	119	No air contact
BL3tD	120	Air 45 days -- coal
BL3tD	121	Air 45 days + 150 C 30 min
BL3tD	122	Air 45 days + 150 C 60 min
BL3tD	123	Air 50 days
BL3tD	124	Air 50 days + 150 C 30 min
BL3tD	128	
BL3tD	129	
BL3tD	130	
rL3tD	131	
rL3tD	132	Add Lupersol w/ coal
rL3tD	133	
rL3tD	134	
BL3tD	135	Air 45d + 150C 3h + 105C 47h
BL3tD	136	Air 45d + 150C 3h + 105C 144h
BL3tD	137	Air 9 days
rL3tD	138	
rL3tD	139	
rL3tD	140	
rL3tD	141	
rL3tD	142	
rL3tD	143	
rL3tD	144	
rL3tD	145	
rL3tD	146	H2O2 treat coal
rL3tD	147	

Table 14 (continued)

Mnemonic	Run	Comments
BL3tD	148	
BL3D	149	
BL3D	150	
rL3D	151	
rL3tD	152	Heat Cumene Hydroperoxide w/solvent
rL3tD	153	
BL3tD	154	
rL3tD	156	Mix Cumene Hydroperoxide w/coal
3tD	157	Correction for Cum Hyd incorporation
BS3tD	158	
rS3tD	159	
rL3tD	160	
BM1csP	161	
BM1csD	162	DMSO-CS2 2 phases
BM1csP	163	Wash ETOH, Acetone
BM1D	164	
BM1P	165	
KS3Dt	166	Dilute w/400 ml Tetralin
rS3tD	167	
BL3tDhq	168	
BL2tDhq	169	
BS2Dnb	170	
BS2Dsb	171	
BS2D	172	
BS3D	173	Wash Acetone, isopropanol
BS3t	174	Wash Acetone, isopropanol
BS3Dt	175	
BS3Dt	176	
BS3D	177	Filter hot
BM1csdm	178	Filter room temperature
BM1N	179	Add Tetralin 30 ml after extraction
BS3D	180	
BM1csN	181	Can't filter, add Actone 200 ml
rM1csD	182	
rM1csD	183	

APPENDIX B

DECOMPOSITION OF CUMENE HYDROPEROXIDE

According to the Pennwalt Product Bulletin [Lucidol 1983], 0.1 moles of cumene hydroperoxide decomposed at 140°C yielded the following products (expressed in mole percent):

Methane	30.0
Oxygen	0.0
Acetophenone	20.0
Cumyyl Alcohol	54.0
Phenol	0.7
Acetone	0.7
Residue	6.8 grams

At 160°C (320°F), the extraction temperature, the half-life of cumene hydroperoxide is c.a. 10 hours. The decay law constant may be calculated as 0.0693. In RUN rL3tD_156, 10 ml (0.0678 mole) cumene hydroperoxide at 320°F for 40 minutes would produce 0.208 gram of residue.

APPENDIX C

CUMULATIVE YIELD

Cumulative yields of consecutive extractions are calculated based on the following assumptions

1. only the organic portion of coal may be extracted, and
2. no solvent is retained in residue after the washing and drying process applied between each consecutive extraction.

The cumulative yield can be expressed as

$$CY_n = (W_{coal} - W_{residue,n}) / W_{coal} \qquad (9)$$

where CY_n is the cumulative yield after n consecutive extractions; W_{coal} is the weight of coal sample before any extraction; $W_{residue,n}$ is the weight of residue after n consecutive extractions. $W_{residue,n}$ is defined as

$$\text{for } n = 1 \qquad W_{residue,1} = W_{coal} * (1 - Y_1) \qquad (10)$$

$$\text{for } n > 1 \qquad W_{residue,n} = W_{residue,n-1} * (1 - Y_n) \qquad (11)$$

Where Y_n is the yield of n^{th} extraction which is obtained from experiments.

This recurrence relationship is solved with iteration techniques to get

$$W_{residue,n} = W_{coal} * (1 - Y_1)(1 - Y_2) \cdots (1 - Y_n) \qquad (12)$$

Therefore

$$CY_n = 1 - (1 - Y_1)(1 - Y_2) \cdots (1 - Y_n) \qquad (13)$$

APPENDIX D

DENSITY ESTIMATION FOR COAL PARTICLES

Density estimation was performed for Bakerstown Bag #1 35/100 coal and residue of BL3tD_148.

Bakerstown coal h = 8.65 cm, w = 3.5773 gm
add 2 ml toluene (s.g. = 0.810 measured)
h_1 = 4.8 cm, w = 1.98222 gm
h_2 = 7.5 cm, with toluene
cross-section area of tube = 0.4584 cm^2

If toluene does not enter pores of coal particles
2 ml / 0.4584 cm^2 - (7.5 - 4.8) cm = 1.6627 cm
1.6627 cm / 4.8 cm = 0.346 = porosity

Residue BL3tD_148 h = 8.5 cm, w = 2.45072 gm
add 2 ml toluene
h_1 = 4.15 cm, w = 1.19188 gm
h_2 = 6.4 cm, with toluene

If toluene does not enter pores of residue particles
2 ml / 0.4584 cm^2 - (6.4 - 4.15) cm = 2.113 cm
2.113 cm / 4.15 cm = 0.509 = porosity

However the roundness of both particles are very similar:
Bakerstown coal mean = 1604, std dev = 416.13
Residue mean = 1525, std dev = 386.52

The porosity (ε) of two samples should be very similar. Because the residue has been extracted, toluene may penetrate into the pores. Assume that the porosity is 0.35 for both samples. From the following formula

$$d = \frac{w}{0.4854 * h * (1 - \varepsilon)} \qquad (14)$$

Density of Bakerstown coal Bag #1 35/100 is 1.388 and density of residue of BL3tD_148 is 0.967.

APPENDIX E

GC SPECTRA OF EXTRACTS

Figure 29. GC spectrum of hexane-soluble fraction of DMSO extract (BS3D_173).

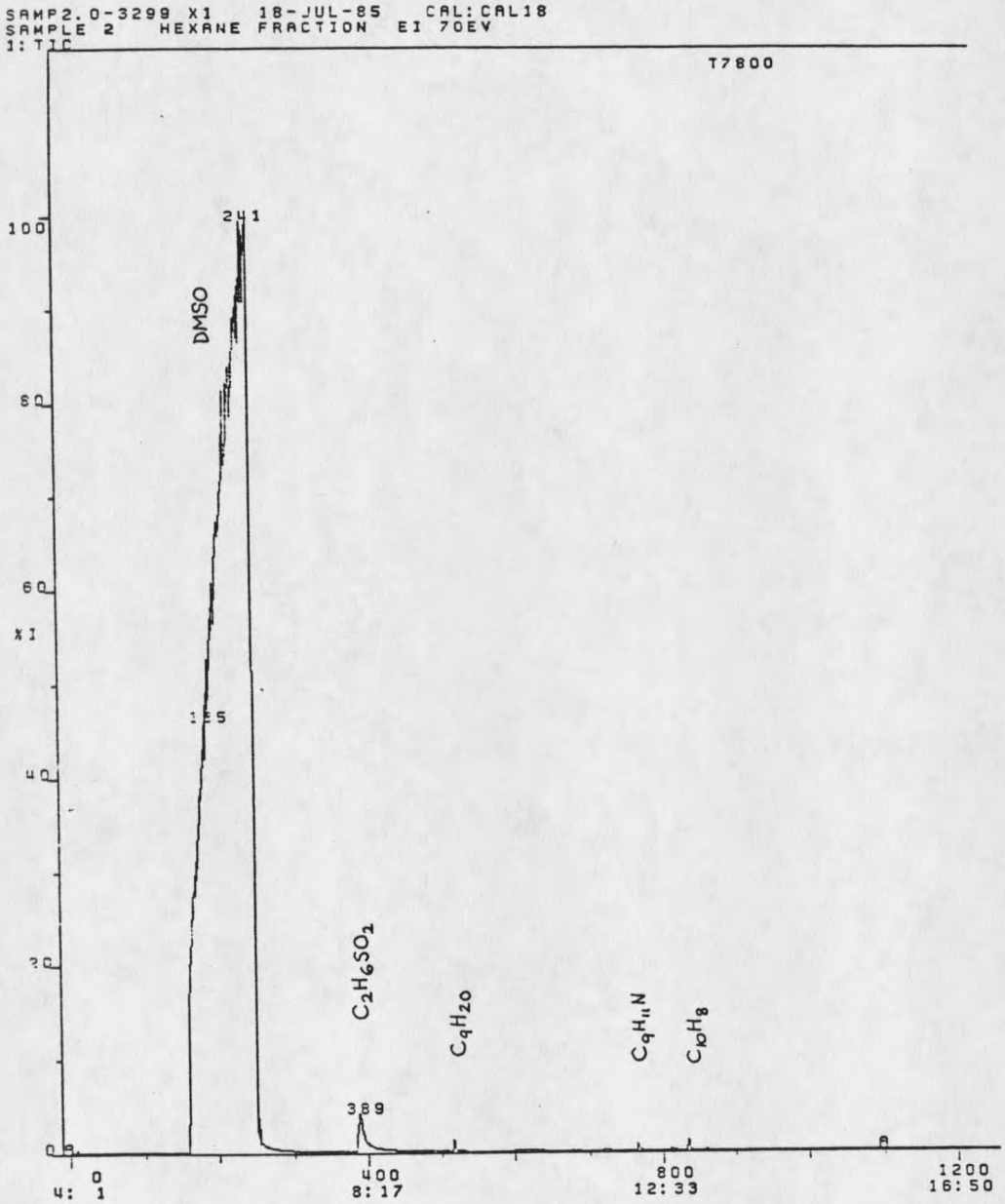


Figure 30. GC spectrum of methylene chloride-soluble fraction of DMSO extract (BS3D_173).

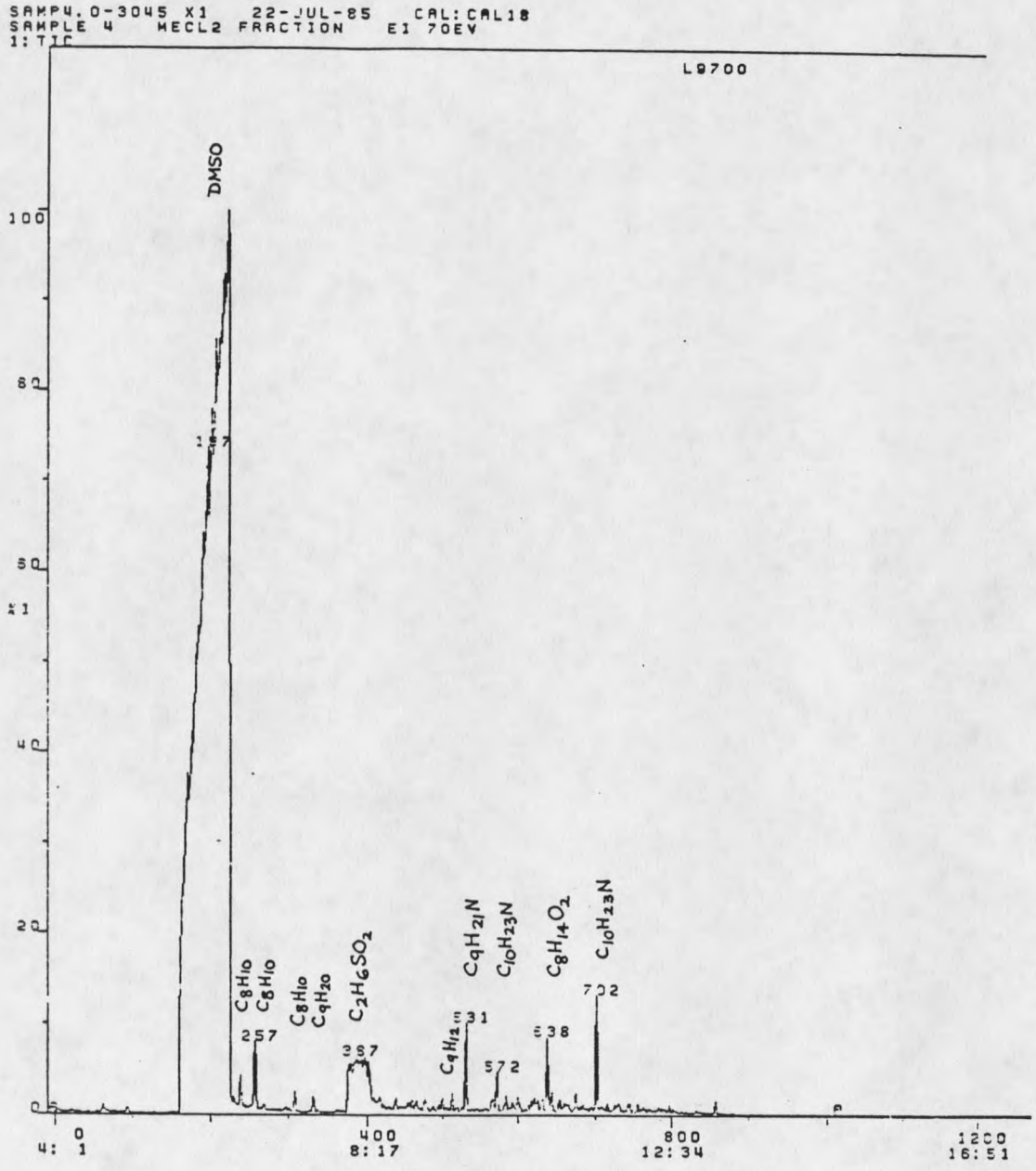


Figure 31. GC spectrum of benzene-soluble fraction of DMSO extract (BS3D_173).

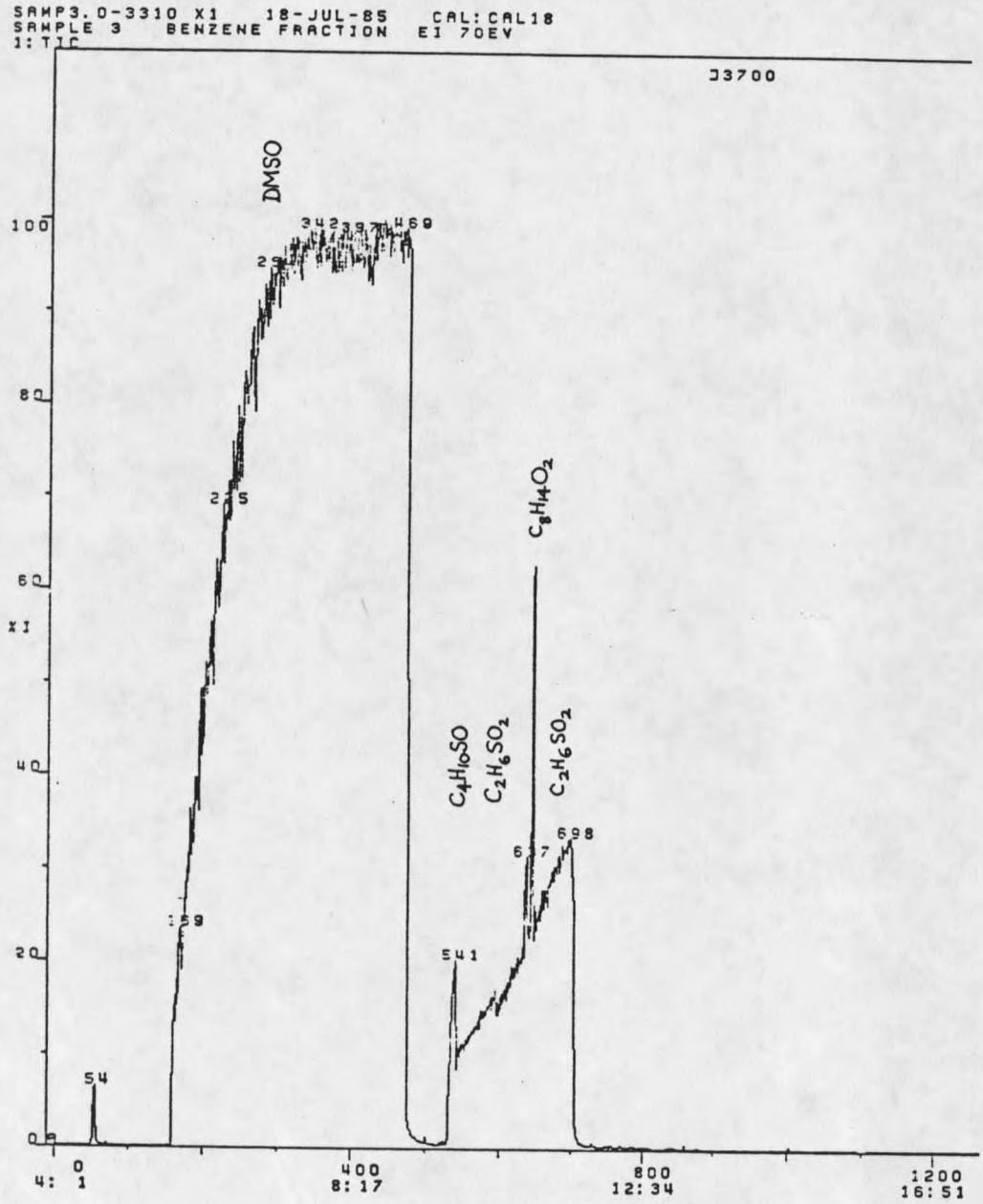


Figure 32. GC spectrum of pyridine-soluble fraction of DMSO extract (BS3D_173).

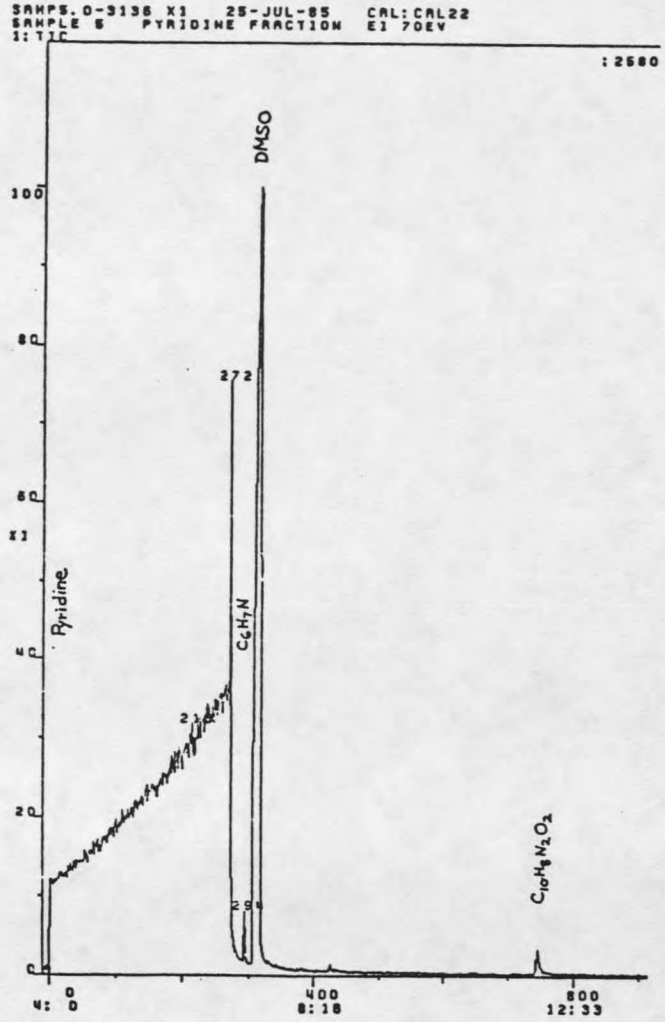


Figure 33. GC spectrum of DMSO-soluble fraction of DMSO extract (BS3D_173).

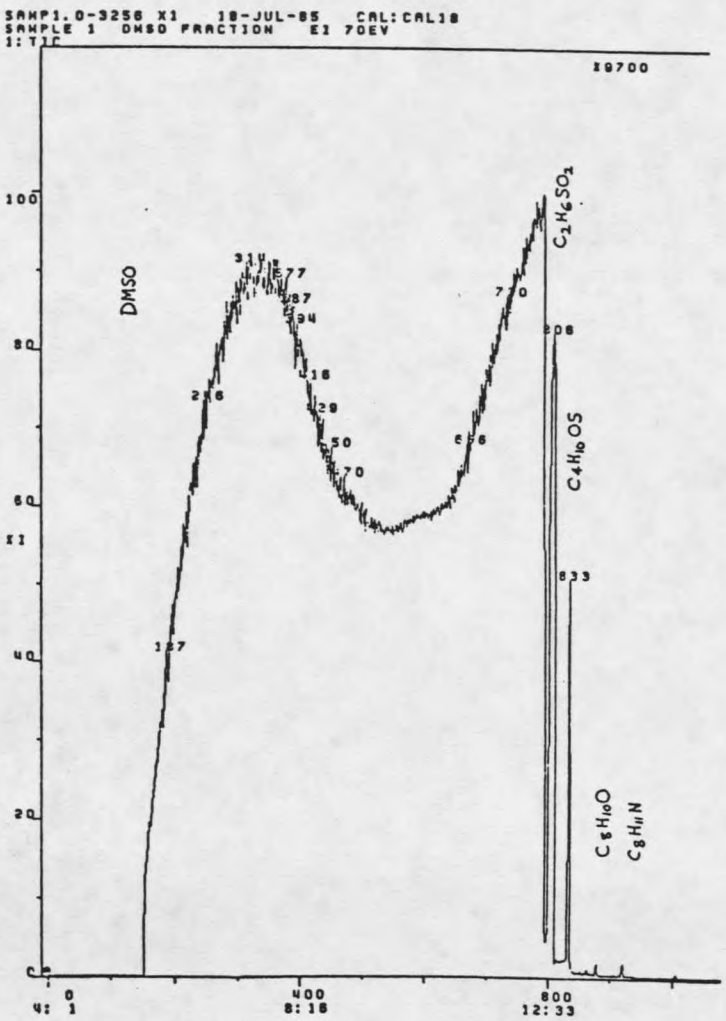


Figure 34. GC spectrum of tetralin extract (BS3t_174).

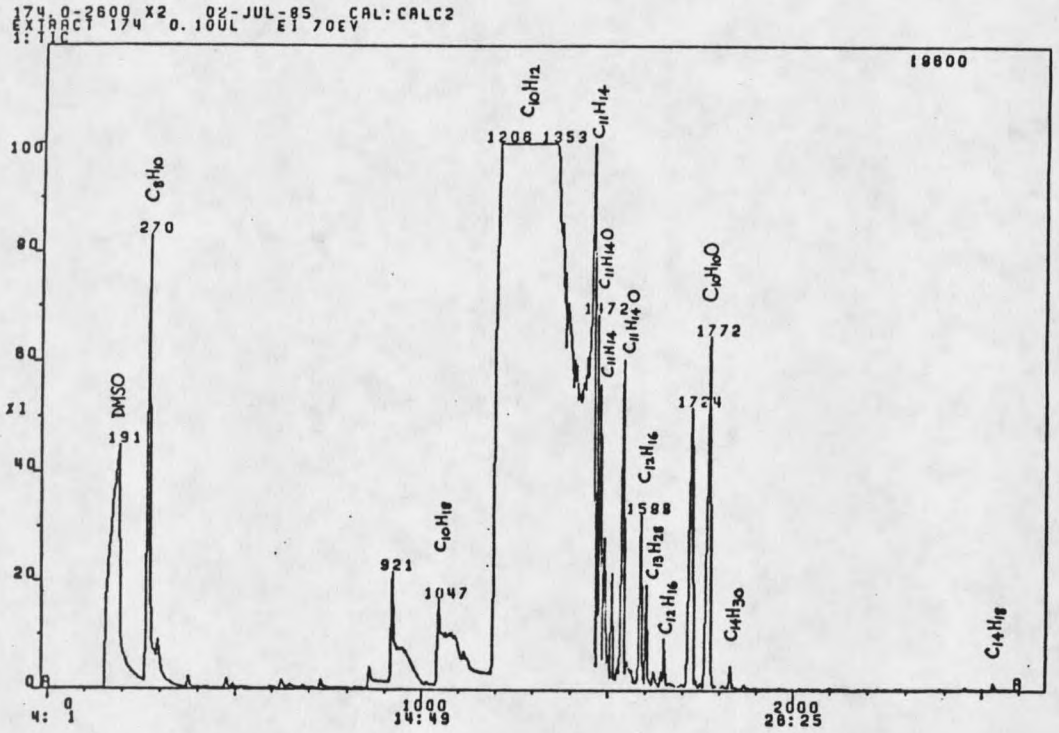
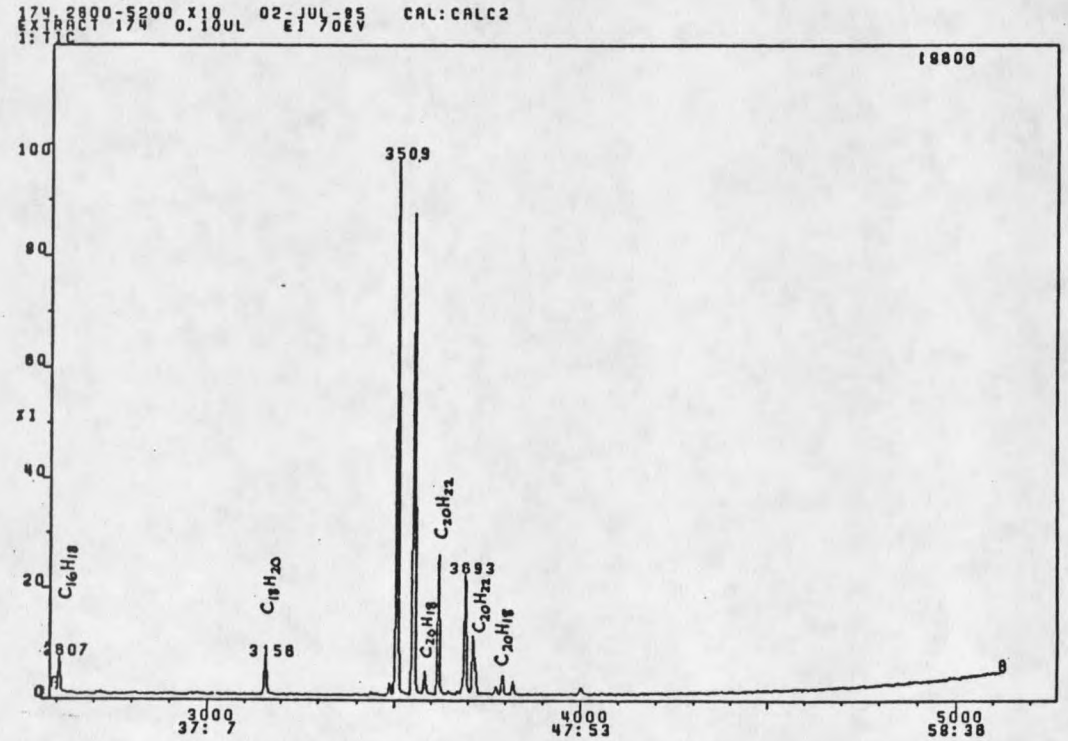


Figure 34 (continued)



APPENDIX F

VISCOSITY MEASUREMENT DATA

Table 15. Viscosity measurement data.

Label	efflux (sec)	density (g/ml)	mu (cstoke)	eta (cp)	eta,sp	conc. (g/100ml)
DMSO	396.09	1.101	1.40215	1.54377		
tetralin	449.20	0.975	1.59016	1.55041		
DMSO-tet	417.84	1.076	1.47915	1.59156		
173 DMSO	401.58	1.101	1.42159	1.56517	0.01386	0.2480
174 tetralin	446.40	0.975	1.58025	1.54074	-0.00623	0.0104
175 DMSO-tet	434.04	1.076	1.53650	1.65327	0.03877	0.6666
176 DMSO-tet	469.09	1.076	1.66057	1.78678	0.12265	0.3333
177 DMSO-tet	413.89	1.076	1.46517	1.57652	-0.00945	0.2723

efflux time is an average of several measurements

Table 15 (continued)

Label	eta,sp / conc	yield maf	Comment
DMSO			
tetralin			
DMSO-tet			
173 DMSO	0.0559	13.8	
174 tetralin	-0.5994	0.6	
175 DMSO-tet	0.0582	37.2	
176 DMSO-tet	0.3680	18.5	filter cold
177 DMSO-tet	-0.0347	15.1	tetralin added later

APPENDIX G

CALCULATION OF SOLUBILITY PARAMETERS FOR SOLVENT BLENDS

The solubility parameter of a solvent mixture can be calculated in one of the following two ways:

1. $\delta_{mix} = \Sigma\ \varphi_i \delta_i$ (15)

2. $\delta_{mix} = \Sigma\ x_i \delta_i$ (16)

where δ = solubility parameter

φ = volumetric fraction

x = molar fraction

In this study, equation 16 is used.

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