

THE STRUCTURE AND REACTIVITY OF HEAVY HYDROCARBONS

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ABSTRACT

The identification of the molecular constituents of coal is an exceptionally formidable, if not impossible, task. And yet, significant advances have been made recently in bringing about an understanding of the molecular nature of coal. As always, there are, and will be, serious questions about the need for such an understanding, relative to the use of coal, but the knowledge gained can often help offset a difficult-to-understand aspect of a processing sequence.

Thus, it can be argued (often successfully with some degree of conviction but not ad nauseam) that understanding of the chemical nature of coal constituents is, just like an understanding of the chemical and thermal behavior of coal, a valuable part of projecting the successful use of coal for conversion and/or utilization processes or as a source of chemicals. Thus the derivations of hypothetical and representative models are of some value.

It is, therefore, the purpose of this article to present some indication of the methods that allow coal to be defined in terms of structural entities and also to include an assessment of the various *molecular* structures proposed for coal.

INTRODUCTION

The structure and reactivity of the so-called *heavy hydrocarbons* is a complex field of endeavor. However, before entering this area a definition is necessary.

By definition, *a hydrocarbon contains carbon and hydrogen only* (Morrison and Boyd, 1973; Fessenden and Fessenden, 1990). On the other hand, *if an organic compound contains nitrogen, and/or sulfur, and/or oxygen, and/or metals it is a heteroatomic compound and not a hydrocarbon*. Organic compounds containing heteroelements (elements such as nitrogen, oxygen, and sulfur), in addition to carbon and hydrogen, are defined in terms of the locations of these heteroelements within the molecule and it is the heteroatomic function that determines the chemical and physical reactivity of the heteroatomic compounds (Morrison and Boyd, 1973; Fessenden and Fessenden, 1990). And, the chemical and physical reactivity of the heteroatomic compounds is quite different from the chemical and physical reactivity of the hydrocarbons.

More correctly, coal is a *hydrocarbonaceous* material insofar as it contains carbon and hydrogen but also other elements that add to the complexity of its composition and behavior. In fact, coal is an *organic rock* that is composed of a complex mix of high molecular weight heteroatomic compounds that requires high temperatures for decomposition (through bond rupture) to produce hydrocarbons. It is not a naturally occurring hydrocarbon, although there are small amounts of occluded low molecular weight hydrocarbons that occur within coal as an integral part of coal.

Acceptance of this simple, but correct, scientific premise will assist in the identification of the molecular composition of coal as well as in coal utilization.

The determination of the properties of coal as a means of coal evaluation and with the goal of predicting behavior during utilization is well documented (Hessley, 1990; Berkowitz, 1979; Speight, 1994). However, there is another area of coal characterization that has been at least equally well documented, but perhaps less well recognized as a means of evaluation, which involves studies of the molecular constituents of coal.

In fact, the heterogeneous chemical structures of the wide range of plant chemicals which formed the starting material for coal promise, but do not guarantee, an almost unlimited range of chemical structures within the various types of coal. Thus, it is perhaps best to consider coal as a variety of chemical entities that virtually dictate coal reactivity under specific conditions.

Coal itself (with the exception of the extractable material) may simply be looked upon as a conglomeration of high molecular weight species that may, or may not, be covalently bonded (or, for example, hydrogen-bonded) together to form a complex *macromolecule*. But, in terms of coal science, nothing is simple and the term *macromolecule* is used here very loosely and it is not used with the object of defining any coal as a *single* molecular entity.

A similar line of thinking has been applied to the search for the structures that exist in the higher molecular weight fractions of petroleum that are particularly prone to produce coke and/or reduce catalyst activity during the processing of these materials (Speight, 1999). In the present context, such studies have been more often over the past two decades since coal has, once again, come into increased popularity as a potential source of gaseous and liquid fuels.

It is often argued (often successfully with some degree of conviction but not *ad nauseam*) that understanding of the chemical nature of coal constituents is, just like an understanding of the chemical and thermal behavior of coal, a valuable part of projecting the successful use of coal for

conversion and/or utilization processes or as a source of chemicals. Statements relating to the derivation of hypothetical and representative models are of some value. In fact, the value of any structural model of a complex molecular entity lies in its use as a means of not only understanding process chemistry and physics but also in its use as a means by which processes can be understood and predictions (perhaps tongue-in-cheek and hopefully near to reality) can be made. Of course, such visions are always subject to the willingness of the chemical modeler to learn from experience and also to subject the model to the necessary changes to render it workable (Speight, 1999).

As an aside, but certainly worthy of note, the identification of many of the constituents of petroleum have been achieved as a result of the volatility of these constituents and subsequent application of methods such as gas-liquid chromatography and mass spectroscopy. But in the case of petroleum residua, identification of the individual constituents is much more difficult and heavy reliance has to be put on identification by molecular type (Speight, 1999). The same is essentially true for coal.

Identification of the constituents of complex mixtures (such as petroleum residua and coal) by molecular type may proceed in a variety of ways but generally can be classified into three methods: (1) spectroscopic techniques, (2) chemical techniques, and (3) physical property methods whereby various structural parameters are derived from a particular property by a sequence of mathematical manipulations. It is difficult to completely separate these three methods of structural elucidation and there must, by virtue of need and relationship be some overlap.

The end results of these methods are *indications* of the *structural types* present in the material (Stadelhofer et al., 1981). However, there is the unfortunate tendency of researchers to then attempt to interrelate these structural types into a so-called *average structure*. But the pronounced heterogeneity of coal makes the construction of *average structures* extremely futile and, perhaps, misleading.

ASSESSMENT OF COAL STRUCTURE

As already noted, the origin of coal dictates that it be a very complex organic material product, having little volatility and containing various molecules which are of different chemical origins and, hence, of different size and chemical structure (Haenel, 1992). Indeed, it must always be emphasized that coal, because of the complexity of its origins, cannot exist as a single molecular entity. Indeed, coal and petroleum, irrespective of their different phases (i.e. solid vs. liquid) might be considered as similar entities, albeit formed from different mixes of the precursors and under different conditions. And no one would ever accuse petroleum of being a single molecular entity and the era of claiming asphaltenes (from petroleum) as being single molecular entities is, hopefully, over.

In fact, coal should be considered (on a molecular scale) as a complex heterogeneous organic rock and it is impossible to represent such a material by any single organic structure. What we obtain from oxidation studies (and for that matter from any other of the so-called structural studies) is a series of structural or functional types that occur in coal, subject of course to the above constraint. This must not be construed as a criticism that should bring an end to studies focused on the structural nature of coal but the limitations must be recognized in order to continue meaningful scientific endeavors that will aid in understanding the chemical and physical nature of coal.

Coal structure can be subdivided into two categories (1) the physical structure and (2) the chemical structure. Coal contains extractable smaller molecules that are an integral part of coal and bear a physical and chemical relationship to the non-extractable material. In contrast to many earlier studies of coal *structure*, both are an essential part of any consideration of the structural types in coal and one cannot exist without the other.

Therefore, in terms of physical structure, it is appropriate to note that coal is considered to be a two-component system, a mobile phase and a macromolecular network (Given, 1984a, 1984b; Given et al., 1986) that consists of aromatic ring clusters linked by bridges (Solomon et al., 1992). Thus, lower molecular weight species, the identifiable components of the mobile system, must also be given attention. How they exist in conjunction with the main body of the coal is another issue. They have been variously referred to as *guest molecules* (Redlich et al., 1985), *clathrates* (Given et al., 1986), and (perhaps even less correctly) as *bitumen* (Kreulen, 1948; Grint et al., 1985; Pickel and Gotz, 1991).

Recent work has used the yield of the chloroform extract of coal as an indication of the extent of the mobile phase (Derbyshire et al., 1991). In untreated coals, only a portion of the mobile phase appears to be removable but after *mild* preheating there are sharp increases in the yield of the extract. Perhaps to no one's surprise, that there is an increase in the yield of chloroform-extractable material with treatment temperature. This has been interpreted to mean that there is a gradation in the manner in which the smaller molecules are associated with the network. Thermal studies also tell us that the thermal chemistry of chemical bonds can also vary with temperature.

The results of such work, as mentioned here (and there are many other examples), may provide strong evidence that the *thermal extraction* (perhaps *thermal decomposition* is a more appropriate term) of coal produces evidence for the molecular species that constitute the mobile phase, but, the *thermal chemistry* of coal is much more complex than these data would suggest! In other words, the pertinent issue relates to the quantity of the mobile phase that exists within coal and under prevailing ambient conditions. In addition, it must also be recognized that a quantity of the mobile phase is generated by the application of thermal conditions that exceed the thermal decomposition threshold of the molecular species in coal. These issues might be resolved by a thorough understanding of the plastic properties of coal (Grimes, 1982).

That coal contains low molecular weight extractable species is a fact. That these species may form a mobile phase within the macromolecular network of coal is effective in explaining some of the many facets of coal behavior, including physical phenomena such as porosity and solvent diffusion (Rodriguez and Marsh, 1987; Hall et al., 1992). However, that the constituents of this network can be extracted (unchanged) by *thermal means* or by solvent treatment after exposure of the coal to high temperatures where the stability of many organic species is suspect and that only the *weak* bonds are broken, is open to question.

In the chemical sense, it should never be forgotten that coal (like petroleum is a natural product and, as such, must be considered to contain vestiges (perhaps somewhat changed from the original!) of the plant material. But to an extent, the nature of the coal must be influenced by the nature of the original material (Given, 1984b; Derbyshire et al., 1989). Studies of the maceral type and content of coal show this to be, at least true in principle but these are physical signs of the coal constitution. Whether these vestiges remain as largely unchanged entities or whether they be completely different from their original form is another question.

An examination of the solubility of coal in a variety of solvents and examination of the infrared spectra of the extracts indicated that coal consists of structures of basically similar chemical type and suggested the coals closely related in rank may be homogeneous in chemical structure. Indeed, there are numerous examples cited in the literature which support this view and it is not surprising that material extracted from coal has been employed as being representative of that particular rank for structural determinations and differences exist predominantly in the molecular weights (i.e. degree of polymerization) of the structural entities.

Caution is advised in interpretations of this nature because the pyridine extracts of coal may, other claims to the contrary because of the complex nature of coal, differ substantially with increasing extraction time and different constituents predominate at different stages of the extractions.

Nevertheless, the major drawback to the investigation of coal structure has been the incomplete solubility of the material, which has in many cases dictated that structural determinations are carried out on extracted material. Even then, the answer may not be complete. For example, coal structure is often considered to analogous to humic acid structure; humic acids are considered to be soluble molecular entities that are produced during the formation of coal. However, humic acid structure is not at all well known and has been, in the past, represented as involving large condensed nuclear systems.

In addition, an aspect of coal science that is often carried in the minds of those whose goal is structural elucidation is the thermal decomposition of coal to coke.

Briefly, it has been assumed, on the basis of the behavior of the thermal decomposition of polynuclear aromatic systems, that coal must also consist of large polynuclear aromatic systems. Be that as it may, such assumptions are highly speculative and, to say the least, somewhat lacking in caution. As an example, similar lines of thinking have been applied to structural assumptions about petroleum asphaltene when it is known from other pyrolysis studies that smaller, but polar systems, can produce as much thermal coke as the larger nonpolar highly condensed systems (Speight, 1999). Indeed, it is now recognized, on the basis of other studies (Winans et al., 1988) that coal structure (especially the structure of non-anthracitic coals) is not necessarily dominated by polycyclic/polynuclear aromatic species.

Thus, concepts of coal structure must also satisfy any of the relevant data from the variety of chemical manipulations of coal that have been described in a previous section and add positive knowledge about the nature of coal. In addition, a consensus of the aromaticity values reported would be that there appears to be a definite increase with rank.

Indeed, the issue of reality or perception has run amok in recent years in petroleum science where workers have laid claim to be the first with a particular structural postulate when their results were based on (at the time believable but proven and acknowledged since then to be) faulty laboratory techniques which produced erroneous, and essentially fictitious, data! And yet we are asked to believe..... But the ethics of such claims leads to other issues! Back to the present issue.

Obviously, on a molecular basis and because of its complexity coal has been viewed as having many forms, only a few of which are noted here. The argument for any particular structure can sway back and forth but the concept of a *chemical structure* of coal or even a simple, repetitive unit cannot really be justified given the extensive heterogeneity of coals.

Application of computer modeling techniques to the issue of coal structure (Carlson and Granoff, 1991; Carlson, 1992) coupled with the potential of synthesizing a model of acceptable behavioral characteristics (Gunderman et al., 1989) might prove to be quite revealing but it should always be remembered that the computer is not a magician but can only feed upon the data in a somewhat limited (usually non-thinking) form. A sound diet of nutritional data could, however, prove to be quite revealing!

There are also indications that coal may be a system of peri-condensed polymeric structures in contrast to the suggestion of coal being predominantly kata-condensed. The occurrence of anthracene in the thermal products of coal processing has, on many occasions, been cited as evidence for the predominantly condensed nature of the aromatic systems in coal. Be that as it may, and there is some degree of truth to this supposition, there is also the distinct possibility that such anthracene systems in the thermal products are, to a degree, thermal artifacts that are formed by various dehydrocyclization reactions.

On a natural product basis, the occurrence of anthracene-type systems in nature and the occurrence of systems that could conceivably form anthracene are not unknown (Weiss and Edwards, 1980). However, the occurrence of phenanthrene systems (the analogous peri-system to anthracene) is also well documented (Fieser and Fieser, 1949) but has often been ignored in terms of structural entities in coal. On the other hand, the phenanthrene system may be (or, at least, appears to be) prevalent in petroleum (Speight, 1999). Thus, the differences in precursor types and maturation paths notwithstanding, there is the distinct possibility of phenanthrene systems occurring in coal to an extent not previously recognized.

Furthermore, it is somewhat interesting to speculate on the similarity, or dissimilarity, between the structural types that are believed to exist in coal and those found in (or speculated to be in the higher molecular weight fractions of) petroleum.

To date, there have not been any serious efforts to match the two. Nor were there any reasons to do this. Nevertheless, the concept of similarity is intriguing! Perhaps the reasons for the lack of comparison has been the complete differences in character of the two materials as well as the, apparently, overwhelming desire of coal to produce coke on heating. Indeed, the propensity for coal to form high yields of coke in thermal reactions has been a cause of question and puzzlement since the very early days of coal technology.

However, it is the obvious physical differences between coal and petroleum that can raise questions when similarities are considered. Perhaps the most convenient approach is to consider the differences in dimension and space between the two. The properties of coal are very suggestive of a three-dimensional network. This is much less obvious in petroleum (asphaltenes) and may only occur to a very minor extent. Such a difference in spatial arrangement would certainly account for some, if not all, of the differences between the two. Serious consideration of such a proposition would aid physical/chemical/structural studies in both fields. And would, hopefully, induce a more constructive thinking in terms of coal/petroleum behavior.

But more than anything, the structural studies of coal are limited by the continued insistence that one molecule of unlimited size can be constructed which will explain all of the properties of coal. And there appears to be a more distinctive, and recent, trend to the belief that the representation of coal by an *average molecular structure* is inappropriate insofar as it does not reflect the molecular diversity of the components of coal and their is an over riding tendency to ignore the known diversity of coal which is evident from petrographic studies.

An alternate choice is the representation of coal as a two-component system, thereby abandoning the concept of individual structures (Haenel, 1992). Obviously during the use of such a model, the details of any chemical transactions may be missing (but they should always be borne in mind and diminished or ignored) and the model might be convenient to explain many, if not all, of the physicochemical aspects of coal behavior. A very worthy accomplishment, indeed!

The fact that coals are heterogeneous as a group and, indeed, heterogeneous individually does not mean that there cannot be a concept of a macromolecular structure. But such a concept should include a variety of molecular types, perhaps in a manner analogous to the formulation of the structural types in petroleum asphaltenes (Long, 1979; Speight, 1999). There would need to be provisions made for the three-dimensional aspect of coal structure as well as for the presence of the lower molecular weight constituents.

Acceptance of these premises would presumably (or, at least, hopefully) facilitate a better understanding of the concepts of coal behavior in during utilization, such as in beneficiation, combustion, and gasification processes as well as in liquefaction processes.

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THROUGH THE LOOKING GLASS: UNRAVELING THE NETWORK STRUCTURE OF COAL

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ABSTRACT

Numerous swelling parameters measured by magnetic resonance microscopy (MRM) are found to correlate with cross-link density of the polymer network under investigation. Use of these parameters to assess the three-dimensional network structure of coal is discussed.

KEYWORDS: coal, swelling, network structure, magnetic resonance microscopy

INTRODUCTION

Since the original idea by Sanada and Honda¹ of treating coal as a three-dimensional cross-linked network, coal structure has been probed by monitoring ingress of solvents using traditional volumetric or gravimetric methods. However, using these techniques has allowed only an indirect observation of the swelling process. More recently, we have developed magnetic resonance microscopy (MRM) approaches for studying solvent ingress in polymeric systems, about which fundamental aspects of the swelling process can be deduced directly and quantitatively^{2,5}. The aim of our work is to utilize solvent transport and network response parameters obtained from these methods to assess fundamental properties of the system under investigation. Polymer and coal samples have been studied to date.

Previous work in our laboratory^{4,5} had demonstrated that MRM is clearly capable of distinguishing between Fickian and Case II diffusion, which represent two extremes of solvent transport in macromolecular systems. Fickian transport was characterized in rubbery samples as a smooth solvent concentration profile increasing with the square root of time. This process was typical for samples that did not undergo a change in physical state as a result of solvent ingress. By contrast, Case II transport processes were found in glassy polymers and coals that underwent a glass-to-rubber transition during swelling. Transport was characterized by a sharp solvent front moving linearly with time, and network relaxation occurred on a time frame that was fast compared to diffusion of the solvent through the network.

It has long been observed that many polymer systems exhibit what is termed anomalous transport behavior. As in Case II transport, the solvent modifies the physical state of the polymer; however, the transition of state occurs on a time scale comparable to diffusion.

Recent MRM studies have shown direct evidence for the latter process, and has allowed a direct observation of network response with relation to cross link density of the network. To perform these measurements, we took advantage of "contrast" imaging protocols, using protonated and deuterated solvents, and thereby observed physical changes in rubber samples imbibed with solvent. Using contrast-imaging techniques, i.e., employing diffusion weighting or T_2 weighting, we were able to obtain additional information on the polymer network directly. We studied four cross-linked isobutylene/*p*-methylstyrene rubber samples and showed that several NMR parameters correlate directly with cross-link density.

RESULTS AND DISCUSSION

Imaging of Protonated Solvent

Time-resolved MRM experiments monitoring ingress of cyclohexane in several rubbers has suggested anomalous swelling behavior. Consistent with this, the region in the center of the samples was completely devoid of solvent throughout the swelling process. Although the cyclohexane front retained the original object shape throughout, the solvent front was not completely sharp as would be expected for pure Case II behavior.

The velocity of the solvent front correlated well with cross-link density. The velocity of the front was greatest in samples with lower cross-link density. This result is expected in light of the diffusion coefficient measurements, which showed that cyclohexane diffuses faster in samples with a lower cross-link density.

Although we attained reasonably good fits to the data with a linear function of position of the solvent front (x) vs. time (t), this approach is only completely accurate in those cases where swelling is purely Case II. Instead, the data were fit to a generalized function:

$$x = k + v \cdot t^n, \quad (3)$$

where k = constant and v = front velocity. For the entire suite of rubbers, the average value calculated for exponent n ranged from 0.75 - 0.87, which implied the dynamics of swelling are intermediate between Fickian ($n=0.5$) and Case II ($n=1$).

MRM images of cyclohexane swelling of a rubber specimen are shown in Figure 3; a diffusion filter was applied prior to imaging for the images on the right. Because the diffusion coefficient of cyclohexane imbibed in the rubber is substantially less than in the bulk, signal from the faster diffusing bulk solvent is suppressed. In the diffusion-weighted images, however, the intensity of imbibed solvent is greatest immediately behind the solvent front. This is in contrast to the unfiltered images, where the signal intensity is fairly uniform throughout the swollen part of the sample. Thus, there is a direct correlation between intensity of pixels in the diffusion-weighted image and absolute magnitude of the diffusion coefficients. Bright regions indicate solvent with correspondingly lower diffusion coefficients.

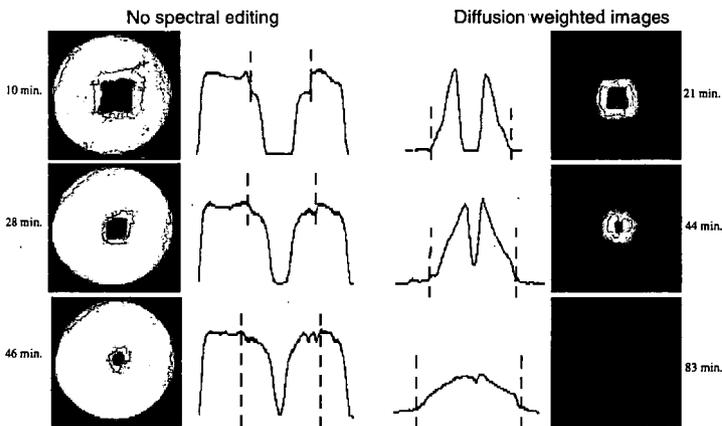


Figure 3. Spin-echo (left) and diffusion-weighted (right) MRM images of rubber specimens.

Moreover, gradations in diffusion coefficients across the swollen samples are perceptible in the filtered images. These effects are most clearly seen and measured in the 1D profiles. Because the diffusion coefficient is a measure of mean free path of a solvent molecule, this distance is shortest for solvent molecules near the solvent front and gradually increases with distance behind the front. This implies that the polymer network continues to expand well after its voids have been filled with solvent.

Imaging in Deuterated Solvent

By acquiring proton images of the rubber samples during a swelling experiment with d_{12} -cyclohexane, we were able to observe changes in the properties of the polymer directly. During swelling, conventional spin-echo MRM indicated that the greatest density of polymer occurs near the solvent front. Behind the front, the density of polymer gradually falls off, consistent with previous results from diffusion-weighted imaging.

Distributional T_2 maps created from the data show a gradation in T_2 values, again with the shortest T_2 's occurring near the solvent front. This parameter reflects changes in polymer chain motion, i.e. the frequency of motion of the polymer chains increases gradually with increasing distance from the solvent front.

We also monitored changes in T_2 vs. swelling time for an area of polymer at a constant distance from the outside edge of the sample. The data fit well to a simple exponential function. The 'rate' of change in T_2 for protons in the polymer correlates with cross-link density of the rubber; the rate is slower for samples with higher cross-link density. Final T_2 values show the same trend; samples with a higher degree of cross linking exhibit a lower final T_2 value.

Relation to Mechanical Models

As we have shown, diffusion coefficients of the solvent and polymer T_2 values parallel one another and reflect the segmental motions of the polymer chains. These changes take place on a time scale comparable to the diffusion process and are characterized by a single rate constant. At this point it is tempting to try to find analogies between the swelling process that we observe and the mechanical processes commonly measured in polymer systems⁴. We draw an analogy between changes in the motional correlation times of the network and strain relaxation in stress-strain experiments.

In a stress-strain experiment, a constant mechanical stress is applied, and the strain required is measured. In a swelling experiment, a constant osmotic stress is exerted by the solvent

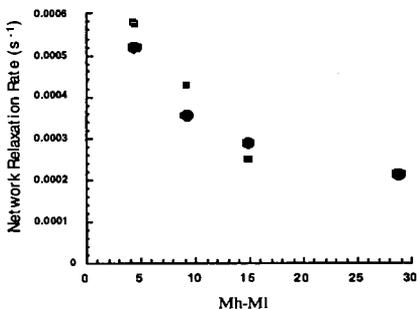


Figure 4. Changes in strain rate from T_2 (circles) and diffusion-weighted (squares) images with cross-link density (Mh-Ml) from rheometry torque measurements.

at and beyond the solvent front. In this case, segmental motion of the polymer chains is measured. In both cases, the strain decreases, or relaxes, over time. In the simple Maxwell model, the relaxation rate is given by a single exponential function. As shown in Figure 4, network relaxation rates, as represented by the experimental T_2 relaxation times and solvent diffusion coefficients, decrease with higher cross-link density of the polymer network.

Preliminary Studies on Coal

MRM images depicting *in situ* swelling of a selected specimen of Pittsburgh No. 8 (APCS 4) vitrain with pyridine are shown in Figure 5. The swelling behavior of this coal is highly anisotropic, and is characterized by the solvent moving fastest in a direction perpendicular to the bedding plane. Diffusion of pyridine in this coal is purely Case II: the solvent front is extremely sharp, moves at a constant velocity, is linear with time, and has an exponential factor close to unity. Furthermore, bright regions are not observed near the solvent front in diffusion-weighted images, suggesting that network relaxation occurs on a time scale that is considerably faster than solvent diffusion.



Figure 5. Time-resolved MRM of swelling of Pittsburgh No. 8 vitrain in pyridine.

Back to the Future

It is without question that unraveling the three-dimensional architecture of coal will be key in advancing our understanding of coal behavior and reactivity. In attempts to realize this objective, many researchers in the past have performed systematic swelling studies on coals of different rank. Recently, Suuberg and coworkers⁶ have explored thermodynamic aspects of solvent-coal interactions by monitoring swelling kinetics as a function of solvent type and temperature. Trends in the observed activation energies were consistent with those expected on the basis of size effects of the solvent molecules and by disruption of donor-acceptor and/or hydrogen bonding interactions. Painter and his coworkers^{7,8} also have explored the intricate balance of thermodynamic forces in various hydrogen bonded systems and have developed good mathematical approaches to model the influence of strong intermolecular interactions on polymer properties. There is little question that theoretical treatment of solvent/solute thermodynamics holds the answer to understanding coal behavior, albeit heretofore difficult to realize.

Our previous work⁴ has allowed an estimate of strain rates from solvent front velocities and network relaxation rates, assuming coal/solvent systems exhibit pure Newtonian viscous behavior. To a first-order approximation, the strain rate can be related to the osmotic stress imparted by the solvent, i.e., the chemical potential of the solvent in equilibrium with the polymer. By applying Flory-Rehner (F-R) theory, parameters such as the number-averaged molecular weight between cross links may be estimated.

Assuming stress is purely osmotic in nature, $\sigma = \Pi$, it follows that for a Newtonian fluid the strain rate

$$d\epsilon/dt = RT/v_s \eta \cdot \ln a_s \quad (4)$$

Using classical F-R theory, we can determine Π at v_2^* , by defining the chemical potential of a solvent in equilibrium with the polymer

$$\ln a_s = [\ln(1-v_2) + v_2 + \chi v_2] + \{Z(v_2^{1/3} + v_2/2)\} \quad (5)$$

solvent terms

entropic constraint

where $Z = \rho v_s / \langle M_c \rangle$, ρ is the dry density of the polymer, v_s is the molar volume of the solvent, and $\langle M_c \rangle$ is the number-averaged molecular weight between cross links. In the past, numerous simplifying assumptions had to be made in order to apply F-R theory to coal systems, e.g. ignoring the non-Gaussian behavior of dense coal networks, hydrogen bonding effects and changing solvent affinities during swelling.

The problem with applying a statistical mechanics treatment to coals as densely cross-linked networks has now been solved using Painter's recently published approach.⁹ Furthermore, any contributions from hydrogen-bonding equilibria to the chemical potential can be dealt with by considering hydrogen bonding effects globally as part of the interaction enthalpy term, and a resolution of this issue soon will be at hand⁸ for coal systems. Moreover, in order to compute the osmotic pressure at v_2^* , one must assume that solvent χ parameter is independent of concentration. Although this is certainly not true, it is unlikely that χ will vary significantly with concentration (the 3rd term in equation 5).

Moreover, MRM is now capable of providing us with a number of key parameters which can be related to cross-link density of the network. We are able to accurately monitor propagation of the solvent through the network, and can obtain important parameters such as the rate of solvent transport, the kinetic order of transport (from Fickian, through anomalous, to Case II), spatial distributions of the solvent diffusion coefficients, and are capable of determining the concentration profile of the solvent front. We have been able to relate these solvent properties to strain rate. Employing deuterated solvents, we additionally are able to monitor changes of the macromolecular network *in situ* during the swelling process. We are able to observe directly mechanical relaxation of the network on the time scale of the swelling experiment, and to determine concomitant changes in microscopic expansion and mobility of the polymer chains.

There are however several relevant issues that need to be resolved first regarding treatment of the MRM data. Can we infer intrinsic strain rates from swelling experiments, in which the stress forces are exerted by solvent at the front under non-equilibrium solvent-solute conditions? Furthermore, is it possible to derive strict relationships of experimental data that are free of assumption yet adequately define fundamental thermodynamic properties of the system? Can parameters such as the T_g and $T_{1\rho}$ relaxation times and the NMR second moments be used to evaluate cross-link densities directly? Finally, would it be possible to systematically vary solvent and temperature conditions of swelling measurements (cf.

Otake and Suuberg⁶) in such a way that influences the kinetic order of transport, thus allowing a direct observation of network relaxation on a time scale appropriate for imaging?

Although the treatment and analysis of MRM data has until now been only approximate, linking network parameters from MRM with new statistical modeling approaches holds exceptional promise in the future for assessing the three-dimensional structure of coal.

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QUANTIFYING FLUIDITY DEVELOPMENT AND MOBILITY IN COALS BY IN-SITU ^1H NMR

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Keywords: Broadline ^1H NMR, mobile and rigid hydrogen, fluidity, coal tar, polyurethanes.

ABSTRACT

After briefly reviewing the information that has been obtained to date using ^1H NMR to rationalise various phenomena associated with fluidity development, the improvements that can be achieved with various additives for poor coking coals will be described from both a practical and a fundamental standpoint. Trapping neutral oils from coal tar within briquettes prepared with phenolic binders enhances the mobility of the semi-fluid material for poor coking coal without significantly increasing the concentration. In terms of polymer additives, polyurethanes are unique in having a fluidity range that overlaps those of coals. Again, their addition vastly enhances the mobility of the semi-fluid material generated from poor coking coals but, unlike pitches, they do not dissolve any additional coal due to the high volatile losses. However, flexible foams have the ability to act as a plasticiser for much of the macromolecular structure in bituminous coals at relatively low temperatures (200-300°C). For high volatile coking coals, the addition of a petroleum coker feed (vacuum resid) can virtually render them completely fluid which accounts for the high yield of mesophase obtained in the resultant semi-cokes.

INTRODUCTION

In-situ broadline ^1H NMR has proved to be a highly successful technique for investigating the molecular motion in coals and pitches during carbonisation⁽¹⁻¹³⁾. There are usually two contributions to free induction decays of coals arising from mobile (faster relaxing) and rigid (slower relaxing) components that display Lorentzian and Gaussian decays, respectively. Coal, as a cross-linked macromolecular network, gives rise to a substantial inert component that does not soften and this produces a broad Gaussian peak in the NMR spectrum with a much narrower Lorentzian peak from the mobile material superimposed. The peak width is inversely proportional to the spin-spin relaxation time (T_2) of the fluid phase and is highly responsive to changes in mobility and this behaviour can be monitored as a function of temperature. It is fitting to describe recent work at the University of Strathclyde on the use of in-situ ^1H NMR to quantify phenomena associated with fluidity development in carbonisation on two counts. Firstly, Professor Sanada's own pioneering contribution to the development of in-situ ^1H NMR which dates back to the late 1970s⁽¹⁾. Secondly, fluidity development is inexorably linked to the thermal breakdown of the network structures existing in bituminous coals. After summarising the information that has been obtained to date using ^1H NMR to rationalise various phenomena associated with fluidity development, the improvements that can be achieved with additives in the behaviour of poor coking coals will be described from both a practical and a fundamental standpoint.

OVERVIEW OF EARLIER WORK

After the technique was first used by Sanada in the late 70s⁽¹⁾ to identify fluid material from coal and pitch at the early stages of carbonisation, Lynch, Sakurovs and co-workers, from the early 80s onwards⁽³⁻⁹⁾, detected both the rigid and fluid phases using a bench top spectrometer and have referred to their approach as Proton Magnetic Resonance Thermal Analysis (PMRTA). They have used mainly the empirical parameter, M_{2T16} , corresponding to the second moment integration limited at a width of 16 kHz, for gauging the reductions in fluidity as a function of oxidation and solvent extraction and the increases due to pitch/model compound addition. Of particular note is the quantification of interactive effects between different components in blends with both pitch and decacyclene being found to have a much greater effect than predicted on improving fluidity⁽⁷⁾. More recently, the issue of synergism between coals in coking blends has been addressed by Sakurovs⁽⁹⁾. In the majority of the binary coal blends investigated, both positive and negative interactions in terms of fluidity enhancement occurred. Positive interactions were generally greatest for blends of high and low volatile bituminous coals while semi-anthracite merely acted as a diluent to suppress fluidity.

Using both the amount and the T_2 of the mobile hydrogen, work at Strathclyde has established that, at maximum fluidity, the mobile phase accounts for 35-50% of the hydrogen remaining for good coking coals with both its concentration and mobility increasing up to this temperature, T_{2s} at maximum fluidity being *ca.* 100 μ s. In contrast, coals that exhibit no softening in the Gieseler generate *ca.* 20% semi-fluid hydrogen with a T_2 of 60-70 μ s⁽¹⁰⁾. Like PMRTA⁽⁶⁾, measurements at Strathclyde have established that some high volatile bituminous coals that display little plasticity development in the Gieseler can generate appreciable fluidity, probably due to volatiles (potential metaplast) escaping at lower temperatures in the Gieseler. Reducing the particle size below *ca.* 150 μ m suppresses plasticity through a reduction in the mobility of the fluid phase with the concentration of rigid material remaining constant. This effect was considerably more pronounced with slow than fast heating (3-4 *cf.* 30°C min⁻¹). In contrast, suppressing the fluidity by mild oxidation reduced primarily the concentration of the fluid phase. Isothermal treatments gave rise to a loss of fluidity due to reductions in both the proportion and mobility of the fluid component. However, the in-situ measurements have confirmed that plasticity development is a reversible phenomenon provided that relatively fast quenching rates (*ca.* 75°C min⁻¹) are used.

As early as 1860, de Marsilly showed that removing solvent extractable material destroys the fluid properties of coking coals⁽¹⁴⁾ as later detected by standard methods, including Gieseler plastometry and dilatation^(15,16). However, it was not possible from standard tests to resolve quantitatively the contributions from the extractable material in coal and the metaplast generated thermally to the overall concentration of fluid material generated. High temperature ¹H NMR measurements were thus carried out on a suite of bituminous coals and their pyridine extracts and residues⁽¹¹⁾. Between one-third and a half of the mobile phase at maximum fluidity is metaplast for good coking coals. Further, taking the separate contributions from the pyridine extracts and residues, the predicted proportions and spin-spin relaxation times of the total hydrogen in the fluid phase at maximum fluidity were in close agreement with those observed for the whole coals. Thus, the pyridine-extractables do not appear to increase the amount of metaplast generated and serve mainly to increase the mobility of the fluid phase.

To help ascertain the contribution semifusinite makes to plasticity development during carbonisation, vitrinite and semifusinite concentrates with purities over 90% were separated by density gradient centrifugation from a medium volatile Australian bituminous coal⁽¹²⁾. For the vitrinite concentrates, the increases in reflectance and the degree of aromatic ring condensation with density correlate with the decreasing mobility of the fluid material. For the coal investigated, the overall contribution of the reactive semifusinite to the fluid phase at maximum fluidity is estimated to be 15 % (*ca.* 4 of the 30 % mobile hydrogen observed). Although interactions between maceral groups may take place in the original coal matrix, mixtures of the vitrinite and semifusinite concentrates did not reveal any synergism.

Hydrogen-donor ability has been ascribed as one of the factors responsible for the stabilisation of the plastic phase during coal carbonisation^(17,18) and to investigate this quantitatively, the interactions of a poor coking bituminous coal with a heat-treated coal tar pitch (CTP) and with a hydrogen-donor pitch (HDP, >450°C residue) obtained from a two-stage coal liquefaction process were compared⁽¹³⁾. When the CTP was added to the coal (25% w/w, 150-250 μ m), the amount of fluid material increased by nearly 20% more than that predicted at maximum fluidity. However, an even larger synergistic effect was observed with the HDP as a result of hydrogen transfer. By 400°C, 90% of the fluid phase concentration observed at 450°C had already been generated, corresponding to an enhancement of 50% over that predicted. However, particle size had a major impact with no enhancement in fluidity was detected below 45 μ m. Other possible approaches to the well-established use of coal tar pitch to enhance fluidity that have been investigated by in-situ ¹H NMR will now be described. The three avenues that have been investigated here are:

- (i) the use of polyurethanes since, in terms of common polymers, these are unique in having a fluidity range that overlaps those of coals;
- (ii) trapping coal tar within briquettes prepared with cold cure phenolic binders prepared from coal tar acids; and
- (iii) the use of a coker feed vacuum resid (VR) to prepare coke rich in mesophase.

EXPERIMENTAL

All the NMR measurements were conducted using a Bruker MSL100 spectrometer equipped with a ¹H high temperature Doty NMR probe, as previously described⁽¹⁰⁻¹³⁾. Approximately 50 mg of sample was packed lightly into a zirconia container and heated with an average heating rate of 4°C min⁻¹ from 25°C up to 550°C in a nitrogen atmosphere. Spectra were obtained at a number of different temperatures and transferred from the spectrometer to a PC for

Fourier transformation and the resultant spectra were fitted to a Lorentzian (narrower peak, fluid material) and a Gaussian (broader peak, rigid material) component.

For the experiments with polyurethane, a rigid and a flexible foam (20% w/w of the foams in the coal blends) were used in co-carbonisation tests with a poor coking coal (the same low volatile bituminous coal (designated AUS-4) as used in the earlier study with pitches⁽¹³⁾). Cold cure briquettes from a similar coal (designated CAN-1) were prepared with a phenolic resole prepared using the acids from low temperature coal tar as described elsewhere⁽¹⁹⁾. However, a resole was also prepared using the whole tar and this also cured successively, effectively trapping the neutral aromatics from the tar within the briquettes. High temperature ¹H NMR experiments were carried out on segments cut from the two types of briquettes and on a physical mixture of the coal with the tar acid resole (85:15 blend). A mass ratio of the VR to Powellton coal of 2:1 was used to replicate the published work of Schobert *et al.*⁽²⁰⁾ where coke with high mesophase content was prepared.

RESULTS AND DISCUSSION

Polyurethane co-carbonisation

Figure 1 shows the ¹H NMR spectra for the 80:20 blends of poor coking coal with the flexible and rigid foams at 450°C. Figures 2 and 3 present the variations with temperature in the proportion and T₂ of the mobile phase, respectively, for the poor coking coal and the blends of this coal with the flexible and rigid foams. The two foams differ in that methyldiisocyanate (MDI) moieties account for 35% of the carbon in the flexible foam compared to 75% in the rigid foam. Further, as well as isocyanate linkages, the rigid foam contains polyisocyanurate (PIR) moieties that confer considerable thermal stability. Thus, whilst the rigid foam is not liquefied fully to temperatures approaching 400°C by which time the volatile losses are high, the flexible foam is liquefied virtually completely by 200°C. This results in approximately 75% of the hydrogen being mobile (Figure 2) which corresponds approximately to 55% of the coal hydrogen, indicating a considerable plasticising effect by the aromatic diamines and diols that result from the cleavage of the isocyanate linkages. This is akin to the effect of polar solvents, such as pyridine, at ambient temperatures^(21,22), although the effect here is larger considering the non-swelling nature of the coal and the related low pyridine extraction yield⁽¹¹⁾. The T₂ of the flexible foam blend at ambient temperatures is high (*ca.* 250 μs, Figure 3) due to the highly flexible chains and it increases to over 500 μs due to the foam being liquefied as the urethane linkages are cleaved. Both the proportion and T₂ of the mobile phase decrease markedly as the flexible foam decomposes until 425°C when the metaplast is generated in significant quantities from the coal⁽¹¹⁾. For the rigid foam, the initial decrease in T₂ can be ascribed to the loss of water. However, as expected, the plasticising effect of the rigid foam is much less pronounced than that of the flexible foam with virtually all the mobile hydrogen below 350°C, which represents the onset of metaplast generation⁽¹¹⁾, being generated from the thermal decomposition of the foam.

By 450°C, the residue yields from both foams are small which means that virtually all of the fluid phase remaining is coal-derived. For this reason, the action of neither of the foams (within experimental error) results in an increase the proportion of mobile hydrogen close to maximum fluidity. However, the rigid foam in particular, for which the residue yield is greater than for the flexible foam, gives rise to a vast increase in T₂ of the mainly coal-derived fluid phase. Thus, the foam residue whilst displaying no appreciable solvent action in terms of increasing the proportion of mobile hydrogen, acts mainly to mobilise the semi-fluid phase to a much greater extent than found for the fluid phase in prime coals (*cf.* T₂ at 450°C of 200 μs for the blend with that of *ca.* 100 μs for good coking coals, albeit the latter contain much more mobile hydrogen). This action is essentially the same as that provided by the pyridine-solubles on the thermally generated metaplast (from the pyridine-insolubles) for good coking coals⁽¹¹⁾.

Coal tar addition to briquettes

It has been found that the enhanced fluidity obtained by trapping the neutral oils from low temperature tar within a cold cure briquette prepared in a laboratory press gives rise to a volumetric increase of 31% for the semi-coke briquette obtained at 600°C compared to only 9% for the normal tar acid resole formulation. Therefore, this initial study suggests that the resole made from whole coal oil can enhance the swelling properties of poor swelling coals considerably. Figures 4 and 5 show the variations with temperature in the proportion and T₂ of the mobile phase hydrogen, respectively, for the whole tar and normal tar acid resole cured briquettes, the green (non-cured) briquette for the whole tar resole and the coal itself. Although for the non-cured briquette, the neutral oils and constituents arising from the thermal decomposition of the binder give rise to an increase in the proportion and the T₂ of the mobile hydrogen at low temperatures, they volatilise below 350°C, resulting in little change in the fluidity characteristics between 400 and 500°C compared to the initial coal (Figures 4 and 5). Above 200-250°C once excess moisture have been removed, such increases in the proportion and

T_2 of the mobile hydrogen have largely been suppressed for the cured resin briquettes, suggesting that, in the case of the whole tar acid resole, the neutral oils have essentially been immobilised. However, for both the cured briquettes, there is an increase in T_2 for the fluid phase hydrogen from 60 to 80-120 μ s between 450 and 500°C (Figure 5), due to the later release of volatiles. The fact that the proportion of fluid hydrogen does not change appreciably indicates that most of the volatiles have been lost from the briquette section used for ^1H NMR and that, unlike CTP, the neutral oils and resin breakdown products are not liquefying the coal. Thus, the swelling action of these constituents in the cured briquettes can be attributed to their ability to mobilise the semi-fluid metaplast generated from the poor coking coal, much in the same way as the rigid polyurethane foam.

Vacuum resid liquefaction

Figure 6 shows the ^1H NMR spectrum obtained at 450°C from the blend of VR and Powellton coal. The rigid phase accounts for less than 4% of the total hydrogen and this proportion corresponds to over 80% of the coal hydrogen being liquefied. This observation, which represents the first full liquefaction experiment conducted by in-situ ^1H NMR, indicates that virtually all of the pre-asphaltenes (THF-insolubles, ca. 40% yield) obtained in the ex-situ liquefaction experiments⁽²⁰⁾ must soften in-situ. Above 450°C, the fluid phase forms semi-coke which, ex-situ, comprises high concentrations of mesophase that can be attributed to the extremely high fluidity observed here. However, unlike petroleum and coal tar pitch where two distinct mesophase types have been resolved with T_{2S} of ca. 20 and 70 μ s with the one having the longer disappearing as more mesophase is formed⁽²³⁾, only one solid phase with the shorter T_2 of 20 μ s is evident here for the VR/coal semi-coke. Thus, the intermediate phase considered to be attributable to gel-like material does not appear to form in significant proportions and the resulting signal is a composite from mesophase spheres and isotropic domains.

CONCLUSIONS

The description of the fluid phase in terms of the concentration and the T_2 of the mobile phase has enabled the effects of various additives during carbonisation to be rationalised in terms of whether they merely solvate the fluid phase as observed for the polyurethanes and the coal tar neutral aromatics within the briquette or, like the VR, dissolve additional coal.

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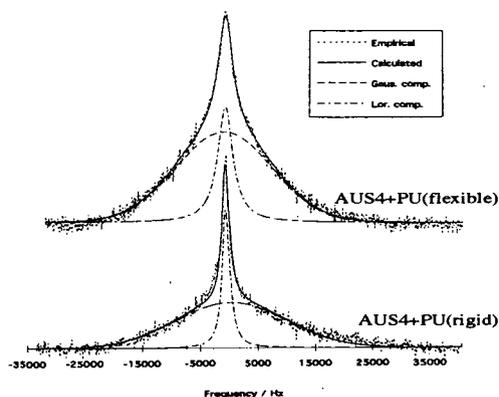


Figure 1 Comparison of ^1H NMR spectra for the blend of poor coking coal with flexible and rigid foams at 450°C

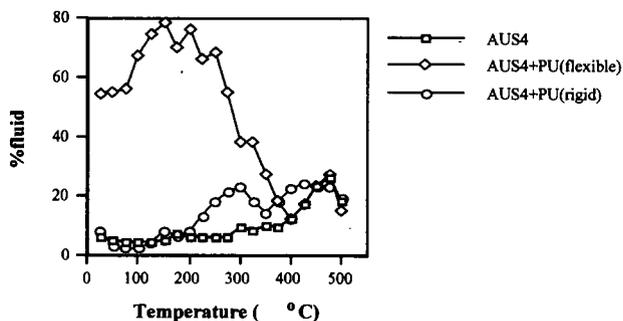


Figure 2 Variation with temperature in the proportion of the mobile phase hydrogen for the poor coking coal and the blends with the flexible and rigid foams (4:1)

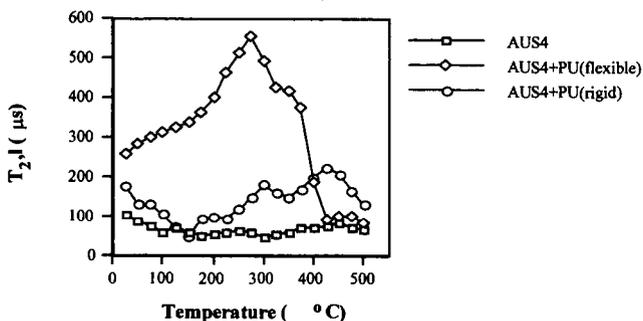


Figure 3 Variation with temperature in the T_2 of the mobile phase hydrogen for the poor coking coal and the blends with the flexible and rigid foams (4:1)

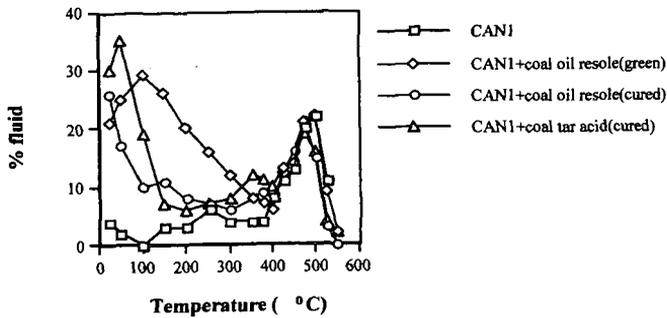


Figure 4 Variation with temperature in the proportion of the mobile phase hydrogen for the normal and neutral oil-containing cold cure briquettes and for the physical mixture of the coal (designated CAN 1) and low temperature coal tar

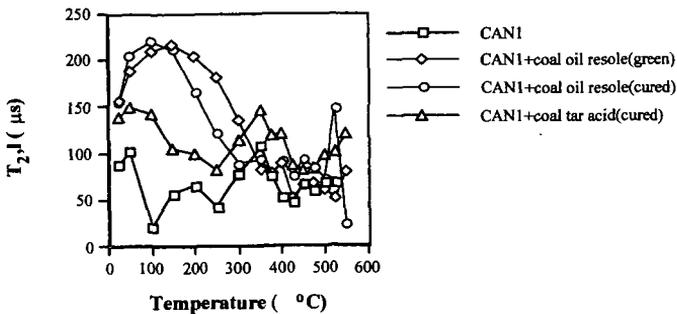


Figure 5 Variation with temperature in the T₂ of the mobile phase hydrogen for the normal and neutral oil-containing cold cure briquettes and for the physical mixture of the coal (designated CAN 1) and low temperature coal tar

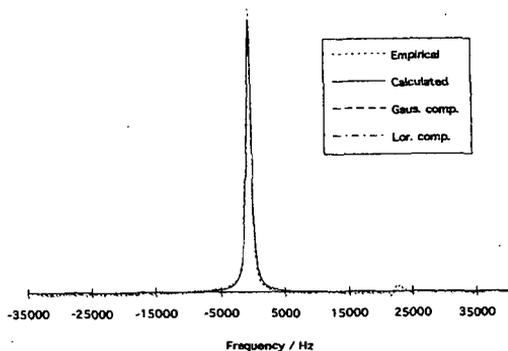


Figure 6 ¹H NMR spectrum obtained at 450°C for the blend of the vacuum resid and Powellton coal (2:1 w/w).

KEROGEN MACROMOLECULAR STRUCTURE

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ABSTRACT

The macromolecular structures of a Bituminous Coal (Illinois No. 6), a Type I kerogen (Green River) and a Type II kerogen (Torcian Shale, Paris Basin) are compared by using solvent swelling measurements. The swelling of Types I and II kerogen roughly follow Regular Solution Theory and show no specific solvent effects. The coal follows Regular Solution Theory for non-polar solvents but shows highly specific interactions with basic molecules. Immature Type I kerogen is much less cross linked than is immature Type II kerogen. Both Type I and Type II kerogen becomes more cross linked during maturation while coals appear to depolymerize during maturation. Only coals are strained. Alkanes dissolve in Types I and II kerogens but not in untreated coals.

RESULTS AND DISCUSSION

Quantitative studies of coal macromolecular structure began with the paper from Sanada and Honda in which they studied the swelling of coals by organic liquids and used the Flory-Rehner equation to calculate the cross-link densities of those coals.¹ The utility of this approach went unappreciated for many years, but it has since become a standard tool of coal science. Coals are Type III kerogens. Types I and II kerogens have long been known to be three dimensionally cross-linked macromolecular solids,² but only recently has systematic study of their macromolecular structure and properties been initiated. It is now possible to compare and contrast some of the macromolecular properties of all three kerogens.

The place to begin is with cross-link densities. All three materials have been studied by solvent swelling and the results are easy to compare. Ironically, the material that was studied first, coal, shows the most complex behavior. Type I kerogen has been selected as the standard to which the others will be compared. Numerous theoretical issues are involved in calculating cross-link densities from swelling measurements.³ Rather than enter the theoretical underbrush, the maximum solvent swelling observed will be taken as a qualitative measure of cross-link density. The solubility parameters of all three kerogens are surprisingly close permitting use of this simplification. The solvent swelling of Green River kerogen is typical of the Type I kerogens so far studied and is shown in Fig. 1. Swelling is reversible and all solvents (non-polar, polar, and hydrogen bonding) fall on the same curve. That curve roughly follows Regular Solution Theory.⁴ The Type II kerogen from Paris Basin Torcian Shale swells much less than does the Type I kerogen and all solvents behave similarly (see Fig. 2). Both kerogens show no specific interactions with the solvents used. The Type II kerogen is much more highly cross linked than Type I. Coals are different (see Fig. 3). First, they swell much more in hydrogen bonding solvents than in non-polar solvents. Two different explanations have been offered for this.^{6,7} For non-polar solvents, the swelling and therefore the cross-link density of pyridine extracted Illinois No. 6 coal is similar to that of the Type I and Type II kerogen used here. The similarity is not general. Green River kerogen swelling varies greatly with its maturation.¹³ But there are also some puzzling aspects to coal swelling that have not yet been considered adequately. For example, if one swells untreated Illinois No. 6 coal with aromatic solvents, the swellings are quite small on the order of 10% to 20%. Part of this is because some of the coal is extracted into the solvent lowering the solvent activity and thus decreasing swelling, but this is probably not the major effect. The same coal after exhaustive extraction with pyridine in these same solvents now swells by 40% to 50%. The changes that cause this difference have not yet been adequately explained. The first swelling of coals is irreversible demonstrating that coals are strained.⁸ This behavior seems to be general and has not been observed with either Type I or II kerogen.

Types I and II kerogen are well behaved showing reversible swelling, no specific solvents effects, and roughly following Regular Solution Theory. Type II is highly cross-linked while Type I is not. Coals are very different. Initial swelling are irreversible and basic solvents interact specifically.

The three kerogens differ in the way the macromolecular structure changes during maturation. The single Type I kerogen studied in detail shows a sharp increase in cross-link density early and late in the maturation process, but in the middle a broad region of constant cross-link density (see Fig. 4). The macromolecular structure changes occurring during the maturation of only one Type I kerogen has been studied, and only three samples of that kerogen. The swelling changes are shown in Fig. 2. They show little beyond increasing cross-linking during maturation. The differences in cross-link density between the Type I and II kerogen will translate into greater capacity of immature Type I kerogen for hydrocarbons and more rapid diffusion from the Type I, other things being equal.

A survey of coal swelling reveals confusing dependence of swelling on rank.⁹ An analysis of the amount and molecular weight distribution of coal extracts led to the conclusion that coalification was a net depolymerization.^{10,11} This is opposite to the behavior of the Types I and II kerogen so far studied. Whether the chemical processes are the same or different, they have opposite effects on the cross-link density of the material.

The capacity of the kerogen to dissolve hydrocarbons has a great effect in the expulsion of petroleum from source rocks. A full discussion of this issue is deferred, but some interesting observations are noted here. The capacity of native coals for alkanes is approximately 0. They do not swell in alkanes. Regular Solution Theory predicts that the enthalpy of coal-alkane interactions will be endothermic compared to coal-coal and alkane-alkane interactions. Native coals will not dissolve saturated hydrocarbons. Such hydrocarbons may be diffusionally trapped in coals. Saturated hydrocarbons swell Type I kerogen by as much as 10-15% in spite of unfavorable thermodynamics. We offer a speculative explanation. If the kerogen structure is inhomogenous and contains regions rich in aliphatic materials, aliphatic liquids might dissolve in these regions. Type II has a very low, but measurable, capacity for alkanes. Perhaps this situation is similar to that of Type I kerogens. These results and conclusions should not be translated to source rocks in petroleum kitchens because pressure effects on polymer structure (e.g. Tg) and mobilities may be significant.

ACKNOWLEDGMENTS

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Table 1. The identity of the swelling solvents in the Figures.*

No.	Solvent	$\delta(\text{cal/cm}^3)^{1/2}$		
1.	n-pentane	7.0	16.	acetonitrile 11.9
2.	n-heptane	7.4	17.	nitromethane 12.7
3.	methylcyclohexane	7.8	18.	pyridine 10.7
4.	cyclohexane	8.2	19.	tetrahydrofuran 9.1
5.	o-xylene	8.8	20.	2-propanol 11.5
6.	toluene	8.9	21.	ethanol 12.7
7.	benzene	9.2	22.	acetone 9.9
8.	tetralin	9.5	23.	dimethyl sulfoxide 12.0
9.	chlorobenzene	9.5	24.	o-dichlorobenzene 10.0
10.	1-methylnaphthalene	9.9	25.	chloroacetonitrile 12.6
11.	carbon disulfide	10.0	26.	carbon tetrachloride 8.1
12.	nitrobenzene	10.0	27.	1,2-trichloroethane 9.6
13.	biphenyl	10.6	28.	1,2-dibromoethane 10.4
14.	propionitrile	10.8	29.	methylene chloride 9.9
15.	nitroethane	11.1	30.	1-butanol 11.4
			31.	1-propanol 11.9

*Brandrup, J. and Immergut, E. H., *Polymer Handbook, 3rd ed.* John Wiley & Sons., 1989.

Figure 1. Swelling ratio of Green River kerogen as a function of swelling solvent solubility parameter. (\square) nonpolar solvents, (\blacksquare) polar solvents, (\diamond) H-bonding solvents. The solid line was calculated using the Flory-Rehner equation: assuming $\delta_p=9.75$, $M=242$, and $V_e=95 \text{ cm}^3/\text{mol}$. This figure is from Ref. 14. See Table 1 for solvent identification.

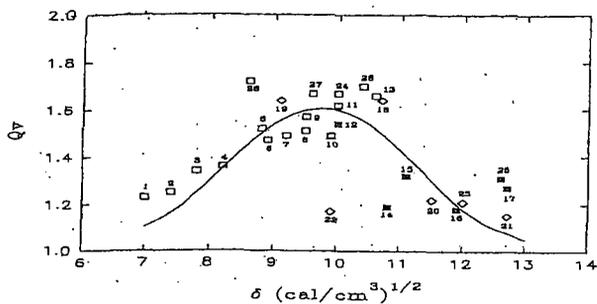


Figure 2. Swelling Ratios of Immature (\square) fully mature (\circ) Paris Basin Type II kerogen. See Table 1 for solvent identification.

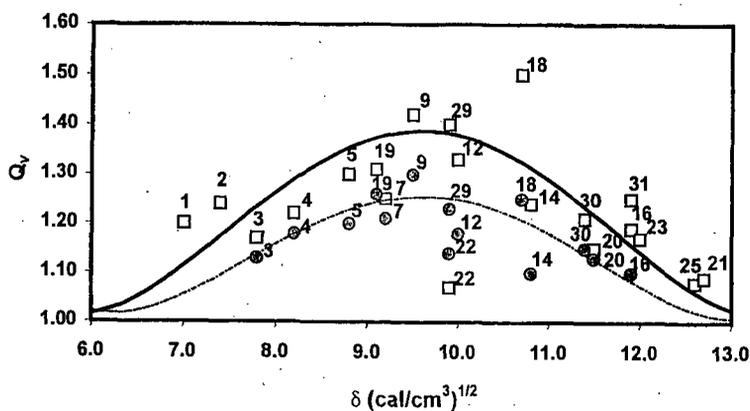


Figure 3. Swelling ratio of Illinois No. 6 coal as a function of swelling solvent solubility parameter (\square) nonpolar solvents, (\blacksquare) polar solvents, (\diamond) H-bonding solvents. See Table 1 for solvent identification. Non-polar solvents are plotted using their non-polar solubility parameters. This figure is from Ref. 12.

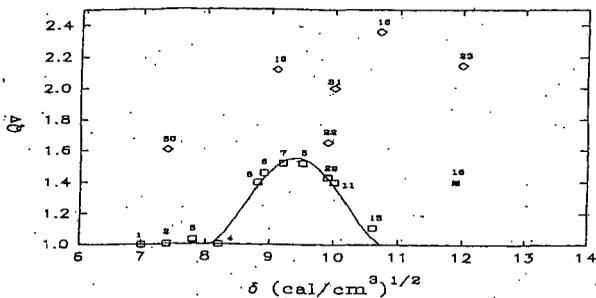
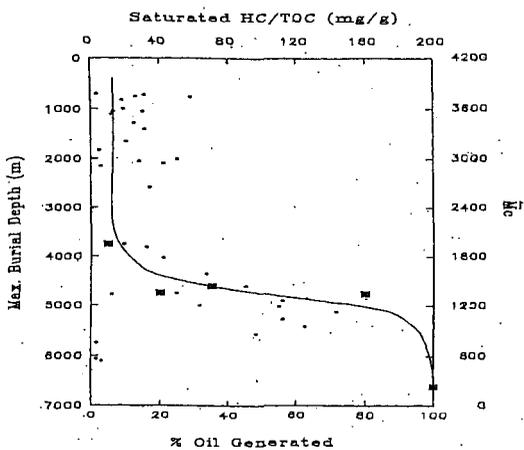


Figure 4. Change in Number Average Molecular Weight Between Cross Links (M_c) as a factor of Maturation for Green River (Type I) kerogen figure from Ref. 13.



MOLECULAR ASSOCIATION AND NETWORK STRUCTURE OF COAL

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Keywords: coal, network structure, molecular association

Introduction

More than three decades ago, Sanada and Honda have treated coal as a three-dimensional network comprised of macromolecular arrays. Since that time, the concept has been followed by many investigators with various approaches as a gauge of coal macromolecular structure. In this paper, a brief overview of our works on macromolecular network structure of coal has been made.

The recent investigations about molecular and network structure by interactions of coal and electron acceptors have been described.

Hardness, Young's Modulus and Mechanical Properties of Coal [1-3]

The Vickers and Knoop indentation hardness and microstrength of coals of every rank have been determined. The hardness number increases with rank, and reaches a maximum at about 80 per cent carbon content. Hardness then decreases with rank for bituminous coal, shows a minimum at about 90 per cent carbon content, and thereafter suddenly increases again for anthracite as shown in Figure 1. Approximate values of Young's modulus (static) of coals are deduced from the hardness numbers and are order of 10^{9-10} dyne/cm².

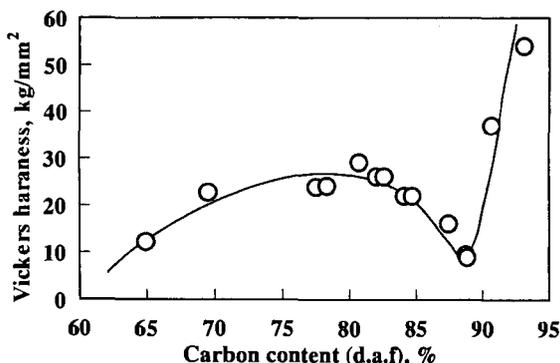


Fig. 1 Relation between Vickers hardness number and rank of coal

The Shore dynamic hardness of coals has also been determined. The relation between Shore hardness and rank of coal shows a maximum at about 80 per cent carbon and a minimum at about 90 per cent carbon content like that static indentation hardness number and rank of coal. The fraction of elasticity and plasticity of coals is deduced from the impact and rebound energies of the free drop indenter. Approximate values of Young's modulus (dynamic) of coals are deduced as well. The calculated dynamic modulus is larger than the static one. The facts imply that coal is one of viscoelastic materials like synthetic high polymer. It is suggested that the mechanical deformation occurred during hardness measurements is mostly governed by non-covalent bonding in the coal structure.

The change of microstrength index versus rank of coal is similar to those of Vickers hardness number and the deduced Young's modulus. The almost similar relationship between the spin-lattice relaxation time derived nuclear magnetic resonance spectroscopy and rank of coal was found as shown in Figure 2.

Temperature Dependence of Knoop Hardness and Glass Transition [4-7]

When amorphous polymers are heated, in general, they show a minimum of indentation hardness,

a maximum of logarithmic decrease of the pendulum, and a change of slope of volume-temperature curve at the glass transition point or zone. We have attempted that the glass transition like phenomena for coal by various measurements, that is, temperature dependence of indentation hardness, decrease of pendulum and volume change method together with wide line NMR at lower temperature range, where there are not occurring any remarkable chemical reactions.

The relation between the Knoop hardness number, H_k , of air-dried coals and temperature is shown in Figure 3. For both brown and bituminous coals, H_k decreases with temperature increase to a minimum at about 50°C and 100°C, respectively and increases with temperature up to 160°C. A small hump is observed at about 80°C for brown coal.

The specimens heated to 160°C were allowed to cool in an ordinary atmosphere, then hardness was again measured at room temperature (closed circle in Figure 3). Bituminous coals and anthracite showed almost similar values to the original specimens. This implies the process is reversible step up to 160°C. On the other hand, the H_k value of brown coal became clearly high. The irreversible step is due to moisture release resulting the structure changes. We conclude that the characteristic points thus obtained with the various methods are brought by glass transition of coal.

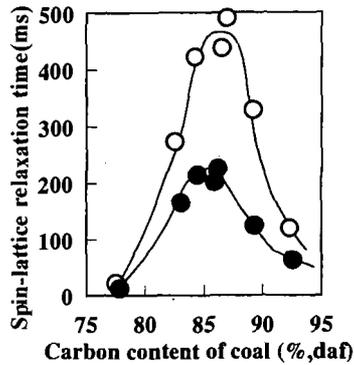


Fig. 2 Relation between ^1H -spin-lattice relaxation time and rank of coal. ● in air; ○ in vacuo

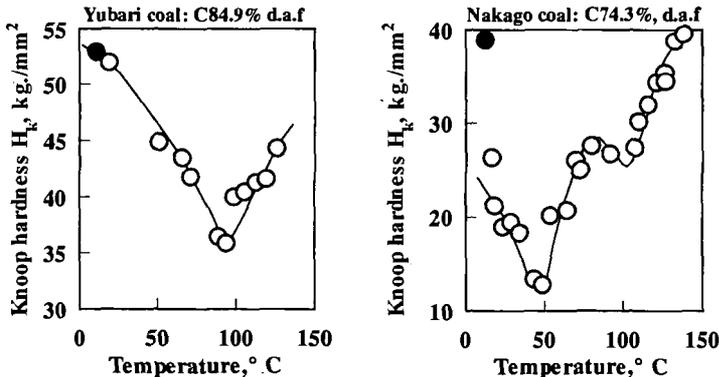


Fig. 3 Temperature dependence of Knoop hardness of coals

Swelling Equilibrium and Three-Dimensional Network composed of Macromolecular Arrays [8-10]

Through the investigations above mentioned, a concept is motivated that coal as a three-dimensional network comprised of macromolecular arrays. Since that time, the concept has fostered into the thermodynamics governing solvent swelling as a gauge of coal macromolecules.

The swelling equilibrium of coal by pyridine at 25.0°C was investigated. The molecular weight per crosslinked unit, M_c , of coal was estimated by applying the equation of Flory-Rehner. [Miss calculations were appeared in the original paper. These are corrected by the experiments separately [11, 12]. The results are summarized and shown in Figure 4. The value of M_c of coal over the range 65 to 80 per cent carbon content (d.a.f.) is almost constant. For bituminous coal, M_c increases suddenly with rank to a maximum at about 85 per cent for Japanese coal, then decreases with increase of rank. This relation coincides well with that between maximum fluidity,

measured by Gieseler plastometer, and rank of coal, as shown in Figure 5. It is suggested that the degree of crosslinking is an important factor in determining the thermal properties of coal.

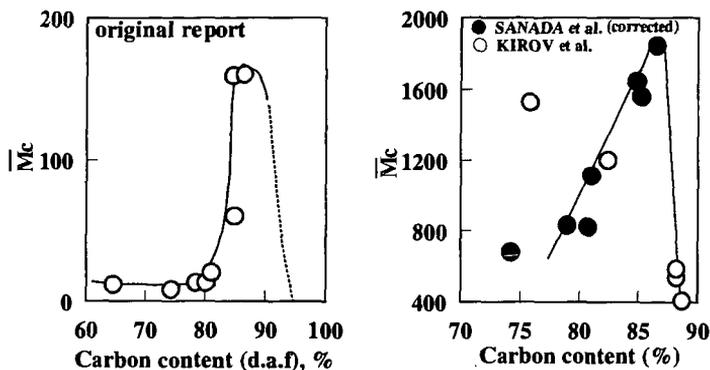


Fig. 4 Relation between molecular weight per crosslinked unit and rank of coal

The equilibrium swelling of coal by various solvents has also been investigated. For brown coal and bituminous coals, the equilibrium swelling degree, Q , increases with increase of the solubility parameter, δ , of the solvent, reaches a maximum at about $\delta = 10.8$, and then decreases with increase of δ as shown in Figure 6. Applying the theory of regular solution, it is estimated that the cohesive energy density of coals over the range from 65 to 87 per cent carbon content is the values between 100 and 140 cal/cm³ ($\delta = 10$ to 12).

In polar solvents the equilibrium swelling degree of coal is almost constant over the range from 65 to 87 per cent carbon content and decreases suddenly with further increase of rank. In non- or slightly- polar solvents, on the other hand, Q increases gradually with increases of rank up to a maximum at about 87 per cent carbon and then decreases. The value of Q for polar solvents increases remarkably with the increase of temperature. Polar solvents form 'coal-solvent' contacts readily by breaking and

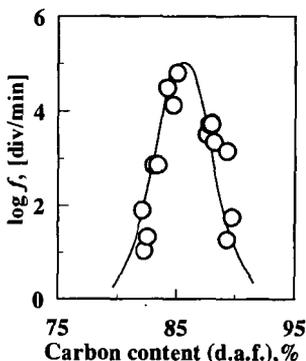


Fig.5 Changes of Gieseler maximum fluidity as a function of coal rank

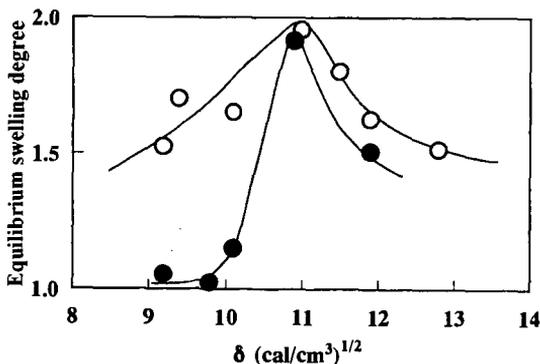


Fig. 6 Relation between equilibrium swelling degree of bituminous coal and solubility parameters of solvents at 25.0°C, ○, (C81.1%); ●, lignite(C65.1%)

/or relaxing the hydrogen bonds in coal. It appears that cohesive forces in coals show a distinct minimum at about 85 to 87 per cent carbon content.

Interactions of coal with various solvents are investigated by means of solvent extraction at the boiling points as well as hardness of solvent-immersed coal. Conclusion obtained is similar to that of swelling measurements.

Molecular Association [12,13]

The thermodynamic behavior of coal is, of course, a macroscopic property. The macroscopic approach examines energy changes in systems with no regard to molecular structure. On the other hand, the microscopic approach examines the molecular structure of coal and related intermolecular interactions.

Interaction energies between molecules are the functions of (1) permanent dipole, (2) induced dipole and (3) dispersion forces. Ionization potential, I , polarizability, α , dipole moment, μ , and distance between the molecules, r , are the most fundamental properties. Figure 7 shows the changes of polarizability and dipole moment together with hydrogen bond energy versus coal rank. Contributions of dipole moment and hydrogen bonding are dominant at the low rank of coal, while polarizability developed by condensed aromatic rings in the structure for high rank coal is important for $\pi-\pi$ interactions. The contributions of polarizability, hydrogen bonding and dipole moment for medium rank coal are less important. The relationships between grindability and thermal fluidity of coal and rank are able to explain from the trends with rank as shown in Figure 7.

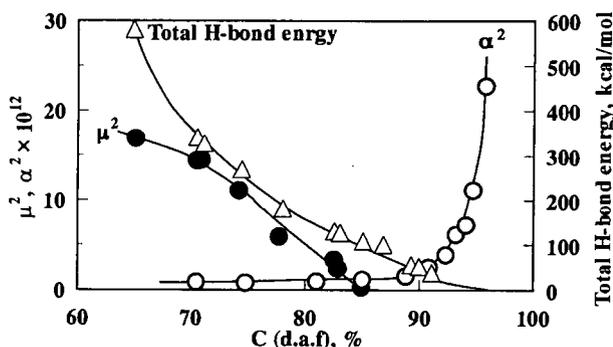


Fig. 7 Relation between molecular association factors and rank of coal

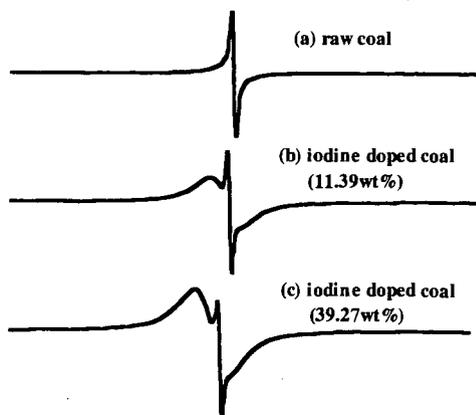


Fig. 8 ESR spectra of raw and iodine doped Upper Freeport(UF) coal

Charge Transfer Complex [15-19]

Coal is consisting with various molecules. It is likely that some of coal molecules behave electron deficient and others sufficient in nature at the solid state. The fact suggests that charge and/or electron transfer are generating between the both. This causes perhaps one of molecular association forces.

Condensed aromatic ring compounds with iodine show a broad e.s.r. signal due to charge transfer. The e.s.r. intensities of them correlate to their ionization potential values. Our investigations for coal have been concentrating the area by means of e.s.r. spectroscopy. Broad e.s.r signal was separated from sharp one by curve deconvolution. Peak intensity of the broad component is increasing with the iodine content as shown in Figures 8 and 9. The intermolecular behaviors of coal have been discussed through the evidences above.

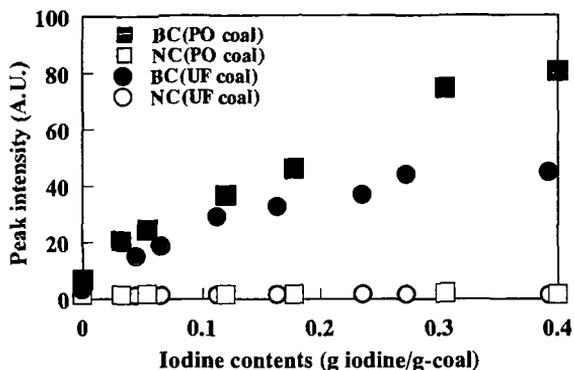


Fig. 9 Changes in peak intensity of iodine doped UF and PO coals ; BC: broad component, NC: narrow component

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