

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 increase 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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