Final Report

The mobile phase in coals: Its nature and modes of release: Final report: Part 1, Structural inferences from dry catalytic hydrogenation of a subbituminous coal

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THE MOBILE PHASE IN COALS: ITS NATURE AND MODES OF RELEASE

Frank Derbyshire, Principal Investigator

Final Report - Part 1

STRUCTURAL INFERENCES FROM DRY CATALYTIC HYDROGENATION OF A SUBBITUMINOUS COAL

by

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Date Published December 1986

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OVERVIEW

The objectives of this three-year program have been to examine a concept of coal structure in which coal is considered to consist of an insoluble macromolecular cross-linked network which accomodates materials of relatively low molecular weight. The low molecular weight materials have been referred to as the mobile or molecular component.

The term "mobile" arises because pulsed free-induction-decay $^1\text{Hnmr}$ studies have shown the presence in coals of populations of radically different rotational mobility. It is inferred that these populations are contained in component species differing in molecular size and mode of association; the mobile phase is the component containing the protons of highest mobility.

The general concept of a two- or multi-component model has been proposed in various forms since about the turn of the century. It has been recently revived with some vigor in an attempt to provide a model which is more realistic than the average structural models of the past and which offers the potential for reconciling measurable coal parameters with coal behavior.

Some of the mobile phase can be removed by extraction in solvents at their boiling points, when the yield is a function of solvent composition and coal rank. Other constituents of the mobile phase were thought to be liberated only upon extraction for greatly extended periods, after thermal pretreatment or upon liquefaction. Thus the mobile phase may be contained in open or close porosity or be bonded in some manner to the macromolecular network.

The specific aims of this program were to elucidate and develop these structural concepts and to investigate their importance to the mechanisms

and kinetics of coal liquefaction. These objectives have remained unaltered although the experimental techniques have necessarily evolved and changed during the course of the program.

Two complementary approaches were originally adopted. The first was a two-year study under the direction of Dr. Peter Given, in which it was intended to follow the manner of release of the mobile phase, using markers such as polycyclic alkanes and long-chain alkyl aromatics, by reaction under conditions of varying severity, ranging from Soxhlet extraction to liquefaction.

As will be described below, the concept of a mobile phase has undergone some development since the research discussed here was first proposed. A considerably body of new information on the subject has been generated, with partial support from this project and the co-operation of workers in other laboratories. The new information comes from tandem M.S. analyses of products obtained from a coal under conditions of increasing severity, and from application of the free-induction-decay nmr technique to a much larger suite of coals, following with each a wider range of relaxation times than in previous work. Accordingly, some revision of the experimental strategy has been necessary, as will be seen.

The second approach, which was conducted over a three-year period under the direction of Dr. Frank Derbyshire, adopted the procedure of dry (no solvent) catalytic hydrogenation as a probe technique by which to pursue the program objectives. In the absence of solvent, it is possible to observe directly changes in the composition of the coal and the coal soluble products.

Using an impregnated molybdenum catalyst, coals were reacted under mild conditions (below 400°C and 7 MPa hydrogen pressure) when condensation and cracking reactions are minimized and the derived products should be

reasonably representative of those structures present in the parent coal. The changes in yield and composition of the gaseous, liquid and solid products have been followed as a function of reaction time and temperature using a variety of analytical techniques. Six coals, ranging in rank from a lignite to an hvA bituminous coal, have been examined, although most attention has been given to a subbituminous B coal (Anderson seam, Wyoming) and an hvA bituminous coal (Lower Kittanning seam, Ohio).

The first two parts of the final report will deal respectively with the studies performed on these two coals and the implications of the results to the coal structural model and to the mechanisms of liquefaction. The third part will contain an account of Dr. Given's findings, the results of the dry catalytic hydrogenation of the other subject coals and a comparative and summary assessment of the overall achievements of the project.

ABSTRACT

In a study to provide insight into the two component structural model of coal and the mechanisms of coal liquefaction, an approach was adopted in which a subbituminous coal was reacted with hydrogen in the presence of an impregnated molybdenum sulphide catalyst and in the absence of solvent. Reactions were conducted at temperatures between 300 and 400°C and for reaction times up to 180 min. The composition and yields of gaseous products, chloroform-soluble liquids and insoluble residues were followed as a function of the reaction conditions by means of different analytical and characterization techniques: gas chromatography; ^1H NMR; elemental analysis; FTIR; solvent swelling in pyridine.

It was found that the liquefaction process was divided into two distinct regimes typified by low and high liquid yields (<ca. 10% and > ca. 20%, respectively). At low yields (realized at 300°C), there was little production of $\text{C}_1\text{-C}_4$ hydrocarbons, and the gases were mostly composed of CO and CO_2 . There was a sharp increase in the aliphatic hydrogen content of the liquids which was attributed to the liberation of long chain alkanes and paraffinic substituents to aromatic rings.

These materials were apparently contained within the coal structure by weak bonding and physical entrapment and were released by mild thermal reaction. The presence of the catalyst did not significantly influence the production of liquids at this temperature. It is probable that the catalyst was instrumental in promoting hydrogenation reactions such as aromatic saturation and the cleavage

and stabilization of oxygen linkages, neither of which need necessarily increase the extract yield.

There was a 25 % increase in the swelling ratio in pyridine of the chloroform extracted residues over that of the parent coal. Two explanations, or a combination of them, are proposed to account for this phenomenon; improved access of pyridine upon removal of the more readily liberated liquids and/or an increase in hydrogen bonding through catalytic hydrogenation of oxygen crosslinks.

At high yields, the rate of C_1 - C_4 production increased and the aliphatic hydrogen content of the liquids was reduced concomitant with a reduction in hydrogen content and an increase in the concentration of asphaltenes.

It is believed that these liquids were substantially derived from the coal network and that the abrupt change in properties between low and high yields is representative of a boundary, based upon behavioral characteristics, between the mobile and network phases.

Under these conditions, the catalyst was highly active in promoting the conversion to liquids. The mechanism appears to involve thermolytic bond cleavage supported by catalytic hydrogenation.

There was a large reduction in the coal swelling properties at high conversions, due to a decrease in the concentration of reactive macerals and in the extent of hydrogen bonding upon the elimination of oxygen functionalities. The latter had the greater influence and it is concluded that a large proportion of the intra-network cross-linking in this coal involves hydrogen bonding.

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Chapter 1

INTRODUCTION

The principal objectives of the present study are to investigate the two-component concept of coal structure and the mechanisms of coal liquefaction, through low-temperature catalytic hydrogenation in the absence of a solvent.

A specific aim of this research is to examine the concept of coal structure, in which coal is considered to comprise a three-dimensional macromolecular network which accommodates lower molecular weight species (the so-called mobile phase or molecular phase) in open and closed porosity and by chemical bonding.

A basic knowledge of coal structure is fundamental to the development of coal liquefaction. While coal liquefaction is currently uneconomical, there will probably be some future need to develop an efficient means to convert coal to liquid fuels and chemicals, since the eventual depletion of oil reserves is inevitable. In order to develop more efficient routes to coal liquids an improved understanding of liquefaction mechanisms is necessary.

The development of a coal structural model which allows a capability for assessing coal behavior is essential to all coal utilization technologies and would provide a sound basis for developing a more specific understanding of the structure of coals. It is considered that the two-component, or possibly multi-component, concept of coal structure, is the only model which takes into account coal behavioral aspects and the presence of the smaller molecules in

coals. The latter are ignored in most models and yet their presence is integrally related to various coal properties.

The two-component model, while having validity, is not clearly developed or defined. The nature and extent of the mobile phase, its origins, its interaction with the network and the composition of the network itself are by no means understood. Similarly, there is no clear account of the reactions and interactions of these constituents during coal liquefaction. The intention of the current research is to provide information which can contribute to clarifying these questions.

The scope of the research has been limited to a study of a single subbituminous coal. Some comparative information on the behavior of a bituminous coal has been provided by the analyses of samples produced in a related project (P.G. Stansberry; research in progress).

Dry (solvent-free) catalytic hydrogenation was originally developed by researchers at the United States Bureau of Mines (Weller and Pelipetz, 1951). Their objective was to study the liquefaction of coals while avoiding complications in data interpretation due to the presence of solvent. Most of this research was conducted at temperatures of 450°C and higher.

The technique has been adopted in the present study, using an impregnated molybdenum catalyst. Molybdenum compounds have been shown to be highly effective in liquefaction catalysis (Weller, 1982). However, for the purposes of this research much lower temperatures were used than in the original work in order to minimize the extent of condensation and cracking reactions.

By following the changes in yield and composition of the liquefaction products at the temperatures of 300-400°C and reaction times up to 180 min, it was intended to derive information on the liquefaction process and the structural make-up of the parent coal.

Chapter 2

LITERATURE REVIEW

The objectives of the research described in this report were to investigate the utility of using dry (no solvent) catalytic hydrogenation of a subbituminous coal to provide insight into the coal structure and the mechanisms of liquefaction. The literature reviewed in this chapter is concerned principally with these topics.

2.1 Coal Liquefaction

Although the mechanisms of coal liquefaction are not firmly established, there is a general consensus that, in the substantial absence of an active catalyst, conversion can be considered to occur via free radicals generated through thermal bond cleavage. This is assumed to involve the breaking of (principally) covalent bonds and the liberation of lower molecular weight radical species from the reactive maceral components of the coal (Van Krevelen, 1961; Berkowitz, 1979). To qualify this statement, there is a growing belief that a considerable part of the coal structure involves weaker, non-covalent bonds, such as hydrogen-bonds (Larsen, 1983) and that the species which are extractable in solvents and liberated by mild thermal treatment may play an important role in liquefaction (Brown and Waters, 1966a). Furthermore, covalent bond cleavage can be initiated not only by thermolysis but also by the action of radicals such as H. and HS. (Stenberg et al., 1982; Vernon, 1980). However, for the purposes of this discussion it will be assumed that the greater part of the generated radicals are of thermal origin.

Ideally, each free radical is stabilized by the addition of a hydrogen atom leading to the production of low molecular weight, stable products. Hydrogen stabilization involves hydrogen transfer between hydrogen-rich and hydrogen-poor entities in the liquefaction system (Whitehurst et al., 1977). The hydrogen is supplied by hydrogen transfer from the liquefaction solvent, from hydrogen gas and by internal hydrogen rearrangement within the coal structure.

2.1.1 Liquefaction Solvent

The liquefaction solvent serves as a means to introduce the coal feed into the system, as a medium for heat and mass transfer, and is directly involved in the liquefaction process, promoting the dispersion, dissolution and stabilization of the coal products. Consequently, the extent of coal conversion and the distribution of products are strongly dependent upon the chemical and physical properties of the solvent.

2.1.1.1 Hydrogen Donors

The most effective sources of transferable hydrogen are partially hydrogenated condensed aromatics (hydroaromatics) containing labile hydrogen which can be abstracted to stabilize free radicals. These compounds are referred as H-donors. Examples of such compounds are tetrahydronaphthalene, 9,10-dihydrophenanthrene, and dihydropyrene. Such structures are present in the coal itself and are important components of liquefaction solvents.

Donor effectiveness is strongly dependent upon the chemical structure of the donor compound (Obara et al., 1983; Curran et al.,

1967), and is related to the degree of saturation and to the number of condensed rings. Complete saturation provides stable naphthenes (e.g., decalin) which are poor H-donors in comparison to partially saturated compounds, examples of which are given in the preceding paragraph.

The ease of hydrogen abstraction increases with increasing ring condensation; for example, 9,10-dihydrophenanthrene has been shown to be a more effective H-donor than tetralin. The greater the number of aromatic rings per molecule, the more readily the hydrogen can be donated (Whitehurst et al., 1980b).

2.1.1.2 Hydrogen Shuttlers

It has been suggested that certain aromatic compounds can be instrumental in redistributing hydrogen between different parts of the coal-solvent system (so-called hydrogen shuttling). Heredy and Fugassi (1966) noted that polyaromatic compounds such as naphthalene, and phenanthrene can promote the solubilization of bituminous coals with no apparent hydrogen consumption, which they concluded was due to their ability to reversibly accept and donate hydrogen. The necessary hydrogen was supplied from the coal which was the only available source.

Derbyshire and Whitehurst (1981) found that in an inert atmosphere and using pyrene as a solvent, a small quantity of dihydropyrene was produced during coal liquefaction. Since the hydrogen could only originate from the coal, these results supported the concept of hydrogen shuttling (H-shuttling). They further found that in a hydrogen atmosphere, higher concentrations of dihydropyrene were produced and coal conversion increased. Under these conditions,

it was assumed that most of the dihydropyrene was formed by reaction with hydrogen gas and was probably catalysed by coal mineral matter.

Polycondensed aromatic compounds have been found to produce synergistic effects in coal conversion when mixed with lower-boiling H-donors (e.g. pyrene with tetralin). Mixtures containing low concentrations of tetralin produced conversions similar to that obtained in pure tetralin. The result was attributed to the transfer of hydrogen from tetralin to pyrene, creating more active donors (Derbyshire et al., 1982).

Other studies have confirmed that the addition of high-boiling and non-distillable solvent components can improve liquefaction. Experience in continuous pilot plants has shown that the recycle of heavy ends (bottoms recycle) increases conversion and produces higher distillate yields (Derbyshire et al., 1982). The reasons for these effects are attributed to improved H-transfer due to the presence of polycondensed aromatics in the heavy liquids, and to the selectively extended residence time of the heavy ends and to improved solvation of the dissolving coal (Derbyshire and Whitehurst, 1981).

2.1:1.3 Physical Properties

As indicated above, physical properties, such as the ability of a solvent to disperse the coal products, can be as important as chemical reactivity. The effectiveness of pyrene during coal conversion has been attributed not only to its ability to promote H-transfer but also to its ability to solubilise and disperse the coal decomposition products. Effective dispersion can reduce the rate of second order
C retrogressive reactions.

The importance of physical solvation in coal liquefaction has been discussed by Whitehurst et al. (1980b) and Davies et al. (1977). For example, although tetralin is a reasonably good hydrogen donor, it has been found that when cooling a reaction mixture of this solvent and coal, a large proportion of the liquefied products can be precipitated (Clarke et al., 1980), illustrating that tetralin is not a good solvent for the liquefied coal products. Therefore, both the chemical and physical properties of a solvent determine its effectiveness in coal conversion.

2.1.1.4 Solvent Side Reactions

Solvents components can also undergo side reactions during liquefaction. These include isomerization, cracking, alkylation, polymerization, and the formation of adducts with coal which ultimately degrades the solvent quality. For example, rearrangement can occur in donor solvent molecules which leads to the loss of regenerable donor capability, e.g. the isomerization of tetralin to methyl indan (Curran et al., 1967).

Nitrogen-containing solvent components provide a particularly good illustration of solvent adduction/polymerization.

Tetrahydroquinoline has been found to be an effective liquefaction solvent giving high coal conversions under mild conditions. However, due to its chemical interaction with coal, there is extensive incorporation of this compound in the high molecular weight liquefaction products (Hausigk et al., 1969; Derbyshire et al., 1984).

Cronauer et al. (1978) found that, for pure tetralin and other compounds adduction can still occur even in the presence of a high

concentration of a donor. Whitehurst et al. (1980b) found that the extent of solvent side reactions is inversely proportional to the donor concentration.

2.1.2 Coal

The coal itself is a potential source of stabilizing hydrogen. Neavel (1976) noted that the liquefaction of a bituminous coal in non-donor vehicles, such as naphthalene and decalin, gave high conversions to benzene solubles at short reaction times (less than 5 minutes). These results indicated that coals contain their own source of donatable hydrogen which can cap the thermally generated free radicals (autostabilization). This source of hydrogen is probably present in hydroaromatic structures.

The internal hydrogen donating capacity of coals is obviously limited and continued reaction in the absence of an effective H-donor agent leads to condensation reactions and a reduction in conversion.

The conversion attainable in the absence of an external hydrogen source is rank dependent. Maximum conversions are realised for coals with a carbon content of approximately 85 % (Whitehurst, 1980a; Clarke et al., 1980; Derbyshire and Whitehurst, 1981). Coals with over 89% carbon content are effectively inert in liquefaction and low-rank coals require external hydrogen sources to attain high conversion levels.

Brown and Waters (1966a) proposed that the relatively low molecular weight, hydrogen-rich bitumens in bituminous coals were of hydroaromatic character, and could serve as solvating and hydrogen-donating agencies during thermal decomposition.

2.1.3 Hydrogen Gas

The presence of hydrogen gas can promote coal liquefaction and can overcome constraints due to solvent quality (Furlong et al., 1976). As stated earlier, direct hydrogenation of solvent components can lead to the in-situ production of H-donors, e.g. the reduction of pyrene to dihydropyrene (Derbyshire and Whitehurst, 1981).

In addition, hydrogen can react directly with coal. Vernon (1980) using model compounds, showed that molecular hydrogen can participate directly in free radical reactions under the conditions typically used in liquefaction and can compete with hydrogen donors for radical stabilization. Hydrogen radicals can cleave C-C bonds that are too strong to break thermally.

Although it is possible for molecular hydrogen to stabilize free radicals in the absence of a catalyst or donor solvent, the reaction rate is slow and compares unfavorably with the rate of recombination of radicals (Speight, 1983). The direct interaction between hydrogen gas and coal is considered to take place mainly by means of catalytic reactions.

2.2 Kinetics of Liquefaction

The conversion of coal to gases and solvent-soluble liquids can be considered to take place in two stages: in the first, part of the coal is rapidly converted with low hydrogen consumption, and in the second, conversion proceeds more slowly with higher hydrogen consumption.

In the first stage, the extent of conversion is dependent on the structure of coal as well as on the composition and concentration of H-donors. Whitehurst et al. (1980b) showed that at short residence times (3 min), when there is relatively little hydrogen consumption, intermediate rank coals (80-88 %C maf) were most reactive. This result is similar to that described in section 2.1.2.

The low hydrogen consumption in the first stage is attributed to limited bond cleavage (Curran et al., 1967) as evidenced by the low yields of hydrocarbon gases produced at short reaction times (Whitehurst et al., 1980b).

In the second stage, conversion proceeds more slowly and is more dependent upon the H-donor concentration. If the hydrogen donor capacity of the system is limited, the free radicals will tend to undergo recombination reactions, resulting ultimately in the formation of char (coke) (Whitehurst, 1980a; Neavel, 1976).

Since retrogressive reactions reduce the liquefaction yields, and adversely affect the product distribution, the presence of an effective source of hydrogen is crucial. In general, the demand for hydrogen can be considered to be equivalent to the need for radical stabilization (Curran et al., 1967). The higher consumption of hydrogen associated with the second stage is related to reactions involving molecular weight reduction and heteroatom removal.

2.3 Catalytic Liquefaction

The use of catalysts in liquefaction can improve coal conversion, liquid yields, and product quality. In addition, they can lead to reductions in reaction severity and hydrogen consumption. The desired

catalyst functions are hydrogenation, molecular weight reduction and the removal of heteroatoms.

Liquefaction catalysts are usually employed in the form of highly dispersed materials, often impregnated on the coal, or as supported (heterogeneous) catalysts. Notable exceptions are the molten halide catalysts, which will not be considered here (Olah et al., 1984).

Both forms of catalysts have been used in single stage processes to promote both coal dissolution and a certain degree of upgrading to distillates. Examples of the use of dispersed catalysts are the I. G. Farben process (Romey et al., 1981) and the DOW process (Moll and Quarderer, 1979) and, for heterogeneous catalysts, the H-Coal process (Alpert and Wolk, 1981). The SRC-II process is an example of a nominally thermal single stage process. The solid liquefaction products, which consist of both inorganic and organic materials, are referred to as reactor solids. The inorganic components derive from the coal mineral matter, although the composition of the original constituents may have been altered during reaction. The solid organic material (insoluble organic material or IOM) may consist of undissolved coal and the products of regressive reactions.

The reactor solids possess some catalytic activity and their inclusion in the SRC-II recycle stream was believed to promote liquefaction (Alpert and Wolk, 1981).

In the modern concept of two-stage processing, in which coal dissolution and coal liquids upgrading are conducted successively in separate reactors, the reaction sequence can be thermal/catalytic or catalytic/catalytic. The second stage invariably employs a heterogeneous catalyst while in the first stage, both dispersed and

heterogeneous catalysts have been investigated (Derbyshire et al., 1986b; Neuworth and Moroni, 1984). The following discussion is principally concerned with catalysed dissolution.

It is probable that heterogeneous catalysts promote coal dissolution indirectly, through the hydrogenation of solvent molecules and coal liquids (Gorin, 1981). The role of dispersed catalysts is less clear and there is evidence to indicate that they may interact directly with the coal structure (Derbyshire, 1986a).

The problems of catalyst recovery, essentially require dispersed catalysts to be disposable. That is, they must be sufficiently cheap or used in very low concentrations to make them economical.

Certain coal mineral matter constituents have been shown to be active in coal liquefaction and these materials are usually grouped with dispersed catalysts. One of the objectives of research in coal mineral matter catalysis has been to identify possible sources of cheap disposable catalysts.

Catalysis by coal mineral matter has been demonstrated to improve product quality and selectivity during coal liquefaction (Guin et al., 1979). In particular, pyrite has been shown to be one of the most catalytically active materials commonly encountered in coals. The addition of pyrite can catalyse liquefaction promoting solvent reactions, such as hydrogenation, the removal of functional groups, increased conversion and the production of oils (Granoff and Montano, 1981).

The clays kaolinite and montmorillonite, which make up the greater part of the mineral content of most coals, have also been claimed to enhance coal conversion (Mukherjee and Choudhury, 1976).

However, since the content and composition of mineral components can vary widely, the majority of processes do not rely on mineral matter effects but employ added catalysts.

The development of coal conversion catalysts began in Germany prior to and during World War II (Weller, 1982). Bergius originally employed dispersed iron catalysts for coal conversion, while a dispersed molybdenum oxide catalyst was used at Leuna for the liquefaction of German brown coal during the period 1927 to 1934.

Since then, a wide range of metals including Ni, Pt, Mo, Fe, Sn, W, and other transition metals have been tested as supported and unsupported catalysts in coal conversion. Sulphide catalysts have been found to be among the most active (Weller, 1982).

Molybdenum compounds can be highly active catalysts for the hydroliquefaction of coal, as well as for the upgrading of coal derived-liquids. When molybdenum is employed as a once-through catalyst, molybdenum based compounds have been found to be effective at concentrations as low as 100-200 ppm, as employed in the DOW process (Weller, 1982).

The effectiveness of disposable catalysts is dependent upon their dispersion. Weller and Pelipetz, (1951) examined the influence of the mode of catalyst addition on dry (solvent-free) coal liquefaction. They found that, except for SnCl_2 which was highly effective regardless of the mode of addition, added catalysts (NiCl_2 , FeSO_4 , and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) were much more effective when impregnated on the coal than when physically admixed. The mode of catalyst addition appears to be less critical when a solvent is present (Schlesinger et al., 1962).

A number of studies of catalysed liquefaction have been conducted in the absence of solvent (Hawk and Hiteshue (1965); Weller and Pelipetz (1951); Weller (1982)) to simplify the interpretation of data since the liquefaction products are necessarily derived from coal. In addition, solvent-free or dry hydrogenation demonstrates that added solvent is not necessary to liquefy coal. As the reaction proceeds, the coal effectively provides its own solvent.

2.4 Coal Composition and Liquefaction

2.4.1 Coal Rank

Coal characteristics significantly influence the process of liquefaction (Whitehurst et al., 1980b; Given et al., 1975a, 1975b). However, due to the heterogeneity of coal and lack of understanding of coal structure, attempts to correlate fundamental properties and liquefaction behavior have not been very successful.

Yarzab and co-workers (Yarzab et al., 1980), after studying a wide range of coals, concluded that it was not possible to distinguish a single parameter or group of parameters which would predict the behavior of coal in liquefaction.

However, there is a general relationship between liquefaction behavior and coal rank: mid-rank coals (75-85% maf C approx.) liquefy most readily; higher rank coals are almost inert. Low-rank coals liquefy more slowly than bituminous coals and require more hydrogen in order to attain high conversion levels (Whitehurst et al., 1980b).

In general, high rank coals (> 89% C) show very little reactivity towards liquefaction. This is attributed to their highly condensed,

strongly bonded structures. It has been reported that low-rank coals convert more slowly than bituminous coals, requiring higher severity conditions to attain high conversions (Neavel, 1981). However, research conducted in this laboratory has shown that low-rank coals appear to convert more readily than bituminous coals in the presence of a catalyst and under mild conditions (Derbyshire et al., 1986a).

This apparent discrepancy appears to be related to the intrinsically low thermal stability of subbituminous coals and lignites. It has been proposed that some of the oxygen functionalities in low-rank coals can readily form cross links on mild thermal input (Neavel, 1982). Thus, the coals would be rendered less amenable to liquefaction and would require more severe conditions and higher hydrogen availability to redress these adverse effects. These comments are consistent with the observed behavior of low-rank coals in processes where the feed coal is rapidly elevated to temperatures in excess of 400°C (Neavel, 1981). In the presence of an active hydrogenation catalyst and at low severity, thermally initiated cross-linking would be inhibited allowing the coal to be more readily liquefied.

For bituminous coals there appears to be a correlation between the reactivity of these coals in liquefaction and their coking properties (Marsh and Neavel, 1980). Coking is the ability of some coals to become fluid on heat treatment, forming an agglomerated mass which in turn, resolidifies and converts into coke (Neavel, 1982).

It has been shown that the chloroform-soluble material in coals correlates with fluid properties, and that, the removal of these materials can destroy the fluid behavior and reduce the liquefaction

conversion yield (Van Krevelen, 1961; Larsen et al., 1980). Brown and Waters (1966a) showed that the yield of the chloroform extractables reaches a maximum between 85-90 % maf carbon. They suggested that the presence of these low-molecular weight, hydrogen rich materials can serve as H-donors during thermal decomposition which would account, in part, for the high reactivity of bituminous coals in liquefaction.

It is known that mild oxidation reduces both the fluid properties and the conversion of bituminous coals. This phenomenon has been attributed to the formation of cross-links (Cronauer et al., 1983). Low-rank coals may form such links on mild thermal treatment which prevents plastic development (Neavel, 1982).

2.4.2 Functional Groups

The most common functional groups in coals contain oxygen. They include phenols, alcohols, carboxylic acids, ethers and carbonyl groups. In bituminous coals oxygen has been reported to be present primarily in phenolic and ether groups, with few carbonyl and carboxylic groups (Blom et al., 1957; Whitehurst et al., 1980a); however, Pitt (1979) indicates the possibility that the majority of oxygen in bituminous coals is in carbonyl and hydroxyl groups with the remainder being in ether and carboxyl groups.

Low-rank coals have a distinctly different organic chemistry from that of higher rank coals. They have much higher oxygen contents (20-30%) (Francis, 1961) most of which is in the form of phenolic and carboxylic groups. The carboxylic groups can participate in ion exchange and chelation reactions, usually with metals. Carboxyl groups have been shown to be present as salts, where the protons have been

replaced by metal cations, principally Ca^{2+} and Na^+ . Low-rank coals can contain up to about 3 % by weight of exchangeable cations (Ca, Mg, Na) (Wakeley et al., 1979). Decomposition of the carboxylates during liquefaction can lead to the formation of calcium carbonate deposits (calcite and vaterite). The growth and agglomeration of such deposits can cause problems in continuous process units (Wakeley et al., 1979).

During liquefaction, it seems that ether linkages are cleaved first and the loss of hydroxyl groups occurs more slowly (Whitehurst et al., 1980b). Whitehurst et al. (1977) concluded that the cleavage of ether bonds contributes to the initial fast dissolution of coals.

Organic sulfur is present in coals as thiophenes, sulfides, disulfides, and thiols. Oxidative techniques used to identify sulfur groups in coals, indicated that about 60-80% of the organic sulfur in bituminous coals is in the form of dibenzothiophene or related structures (Shah, 1981).

The predominant nitrogen functional groups are heterocyclic rings such as pyridine or pyrrole derivatives.

It has been shown that the ease of removal of heteroatoms during hydrogenation decreases in the order: sulphur (organic), oxygen, nitrogen (Fisher and Eisner, 1937).

2.5 Coal Structure

The available literature on coal structure and structural models is very extensive. A comprehensive review of this subject up to 1982 has been given by Davidson (1982). In relation to the present study, a brief presentation of the more conventional approaches to describe

coal structure will be given together with a description of the latest proposed models.

2.5.1 Early Theories of Coal Structure

The fact that coal is a heterogeneous solid has been a major problem in providing direct information on its chemical structure. Many investigations have attempted to infer structural information indirectly by studying the interactions of coal with solvents including solvent extraction and liquefaction.

Dryden (1952), based upon the results of solvent extraction experiments, proposed a model which involved an insoluble matrix, consisting of large and strongly linked micelles (an association or aggregate of molecules) in intimate association with smaller, weaker micelles. The smaller micelles could only be extracted if the coal was swollen by an appropriate solvent. Thus, the process of extraction involves the diffusion of the small micelles through the swollen pores of the matrix. It was interpreted that the solvent is imbibed between the larger units which constitute the insoluble residue. Nevertheless, this proposal did not explain how micelles in the insoluble portion were interlinked.

Brown and Waters (1966a, 1966b), considered the substance of coking coal (mainly vitrinite) to be a molecular aggregate or an association of molecules of widely varying shape and size, which were described as follows:

- A) -oily and solid "bitumens" of low molecular weight (less than 600),

B1) -"humins" of colloidal dimensions (molecular weight larger than 600), and

B2) -"humins" of macromolecular dimensions composing the insoluble portion of the coal

These authors believed that the micelles and macromolecules, B1 and B2 were linked by hydrogen bonding and weaker van der Waals/London forces into a rigid gel structure, while trapping the bitumens, A, in its pores, as "guest" molecules.

Their conclusions were based on studies of coal fluidity and extractions in chloroform. They suggested, that hydrogen bonds provide the main forces of adhesion between molecules in low-rank coking coals, and thus, the extent of bonding depends on the available number of hydroxyl, carbonyl and other polar groups. These bonds are replaced by van der Waals forces as rank increases, because of the progressive elimination of functional groups during coalification.

In low-rank coking coals, it was proposed that, the molecules were rigidly held together in a gel structure of hydrogen bonds, made possible by the high concentration of polar groups. The mechanical rigidity of the gel, and its ability to take up polar solvents and thereby swell, were considered to depend to a considerable extent on the concentration of polar groups engaged in hydrogen bonding.

In comparison, "as hydrogen bonding is progressively eliminated with increase in rank, the gel structure of coking coals tend to degenerate into a sol type of structure with some degree of orientation and better packing of molecules becomes possible under the

influence of dispersion forces and external pressure" (Brown and Waters 1966b, p. 45).

The model was intended to explain qualitatively the mechanisms of thermal softening and the role of chloroform extractable material.

Other models have tried to describe the structure of coal by employing the concept of an average or representative structure which embodies the available analytical information. Such models have been developed by Wiser, Pitt, Ladner, Given, and others (Davidson, 1982).

The supporting ideas for the postulation of Given's model were based on infrared analysis performed by Brown (1955) and X-ray scattering studies by Hirsch (1954) on bituminous coals of approximately 82-83 % C (maf) content. These studies led to several conclusions:

- the greater part of the hydrogen in coals is attached to aliphatic carbons
- the degree of substitution in aromatic systems is very high
- the greater part of the carbon in coals is contained in aromatic systems

Given's model attempted to reconcile these conclusions and also account for various other coal properties. The model incorporates several features encountered in other molecular structures which have been proposed for high-volatile bituminous coals (Given, 1960); all contain relatively small condensed aromatic systems; the non-aromatic part of the structure consists mostly of cycloparaffinic and

hydroaromatic ring systems and there are few alkyl (methyl) groups. In addition, the model is three dimensional.

However, in a chapter written in Francis' book (Francis, 1961), Given later emphasized the limitations of the model. He pointed out that it is only possible to talk about coal structure if the material is reasonably homogeneous. He restated that in order to consider a structure for coal it must be restricted to vitrinite, since it is the most abundant component of the majority of bituminous coals and there is a large body of available information on this maceral group.

2.5.2 Two-component Models

Several authors (Van Krevelen, 1965; Brown and Waters, 1966a; Vahrman, 1972; Dryden, 1952; Given, 1984a; Wheeler, 1913) have developed models which have tried to account for the fact that a certain proportion of coals is extractable while the bulk of the coal is insoluble, thus suggesting the idea of a two-component (or more generally, multi-component) system. These models include some of the earlier theories described in the previous section (2.5.1).

2.5.2.1 The Mobile Phase

In current terminology, the smaller molecules contained within the coal structure are referred to as the mobile or molecular phase while the insoluble portion is considered to consist of a three dimensional macromolecular network.

The model introduced by Vahrman (1972) considered coal to consist of an insoluble three-dimensional matrix of large molecules, and a potentially soluble, lower molecular weight portion. Most of the small

molecules were assumed to be present in the micropores (or spaces between sheets of molecules). The idea was based upon the results of extraction experiments which showed that the majority of the smaller molecules are only extracted with difficulty under mild conditions, compared to the larger yields obtainable by more severe treatment (Palmer and Vahrman, 1972).

With prolonged solvent extraction, higher yields were obtained. It was concluded that much of this material was in pores too narrow to permit easy access by the extracting solvent, and that many of them are present in clathrates (molecular cages) in the macromolecular structure.

The yield of extractable liquids can be increased by heating prior to solvent extraction. It has been shown that the amount of chloroform-soluble material in bituminous coals can be increased several fold by pre-heating to temperatures of 400-440°C (Dryden and Pankhurst, 1955; Lazarov and Angelova, 1976; Brown and Waters, 1966a; Illingworth, 1920). It was assumed that heat treatment made the extractable materials more accessible to solvent by alteration of the pore structure. Brown and Waters (1966a) and Dryden and Joy (1961) believed that such materials were trapped or held physically in coal.

However, a debate exists concerning the proportion of these materials and the manner in which they are occluded in the macromolecular matrix.

Recent spectroscopic work has been interpreted to show that a significant proportion of the mobile phase is physically trapped inside the coal structure (Bodzek and Marzec, 1981). Approximately half of the molecular components found in the solvent extracts of a

high-volatile bituminous coal were also found to be present in low temperature tars. This suggested that molecular components of coal can be evaporated during carbonization and can survive carbonization temperatures; thus, the material appeared to be physically trapped in the coal structure.

Youtcheff (1983) observed that the yield of alkanes present in the liquefaction products of three bituminous coals was six to eight times greater than could be obtained by Soxhlet extraction, and consisted mostly of n-alkanes, C_{12} - C_{35} . It was concluded that the alkanes released during liquefaction had been physically trapped in the coal matrix and were mostly not extractable by solvents at lower temperatures.

Mudamburi (1983) reported that the hexane soluble fractions of liquefaction products from a bituminous coal contained long-chain alkylnaphthalenes with C_1 - C_{15} or C_1 - C_{20} side chains. The author concluded that the homologous series released during liquefaction had been trapped in the network and were part of the mobile phase, since it was difficult to conceive a macromolecular network that could release such compounds by pyrolysis. The total yield of alkanes and alkyl-aromatics were in the range 2-18 % of dmmf coal.

Snape et al. (1985) have also shown evidence which suggests that coal liquids contain long alkyl chains joined to aromatic rings. However, the authors suggested that these materials may be formed during coalification from algal and lignin-derived materials and that some of them may be an integral part of the network structure. Contrary to Mudamburi's view, the authors concluded that it is likely that some alkanes are trapped within the coals, but a certain portion

of the long alkyl chains are bound to more condensed aromatic structures in both bituminous and lignitic coals.

Bodzec and Marzec (1981) suggested that the proportion of molecules difficult to remove by solvent extraction, were bound to macromolecules by means of electron-donor-acceptor interactions. The presence of functional groups in solvent extracts was interpreted to imply the existence of electron-donor and electron-acceptor complexes between molecules and macromolecules and between the molecules themselves.

The concept of electron-donor-acceptor complexes was also applied by Jurkiewicz et al. (1982). These authors measured the ^1H NMR free induction decay signals from a swollen coal (high-volatile bituminous) and its corresponding extracts using different types of solvents. It was found that the mobile hydrogen content of the coal, when swollen with nucleophilic solvents (pyridine, dimethylformamide, and dimethylsulphoxide) was significantly greater than in the solvent extract (<15% vs. >20%). The results were interpreted to mean that the immobile phase (cross-linked network) includes a portion of smaller molecules (200-600 amu) which are attached to the macromolecules by electron donor-acceptor interactions. It was concluded that macromolecules constitute no more than 60% wt of the coal.

Such an interpretation has been debated by Lynch and Barton (Given et al., 1986) who contend that the disruption of some of the polar bonds by nucleophilic solvents would increase the molecular mobility within the coal not only through the detachment of molecules from the network, but also by decreasing the density of polar

cross-links allowing greater mobility of macromolecular chain segments.

In summary, the available information indicates that the mobile component is contained within the coal by both physical constraints and by chemical bonding. Obviously, this description does not provide a convenient boundary between the mobile phase and the network. A more precise definition of the mobile phase and the proportion of the coal it constitutes is lacking.

2.5.2.2 The Macromolecular Network

Other research has focused upon elucidating the nature of the insoluble (network) portion of the coal.

Green and co-workers (1982) inferred from the results of solvent swelling experiments performed by Brenner (Green et al., 1982) that the macromolecular network will absorb solvents and swell without dissolving, and that the amount of swelling is controlled by the cross-link density and interactions between the solvent and the network. It was suggested that coal is composed of macromolecular chains, containing a variety of subunits, which are interconnected by cross-links, hydrogen-bonds (the greater proportion) and covalent bonds. The macromolecular chains become flexible after swelling and reorient themselves within the matrix, causing a deformation of the structure, while the presence of cross linkages prevents dissolution of the structure.

The cause of coal swelling in solvents is considered to be due to the reorientation of macromolecular chains located between (primarily)

non-covalent cross-links, such as hydrogen bonds, where the cross-links are weakened by solvent interactions (Green et al., 1982).

In the coal model proposed by Larsen (1983), cross-links composed of hydrogen bonds are considered to play a significant role in the physical properties of coals. During swelling, a coal-coal hydrogen bond will be replaced by a coal-solvent hydrogen bond if the new bond is stronger than the original. Thus, the stronger the bonds formed by a solvent, the more coal-coal hydrogen bonds can be broken and the more the coal will swell.

Green and co-workers (1982) postulated that when swelling is reduced it is indicative of the matrix becoming less flexible. For example, strong (covalent) cross-links such as those produced by condensation reactions upon thermal treatment can lower the extent of swelling (Suuberg et al., 1985).

The nature of bonding in the network has been often assumed to be predominantly covalent. However recently, Larsen (1985) presented a structural model based on a bituminous coal, Illinois No.6, whose significant feature is the large number of cross-links attributed to hydrogen bonds relative to covalent bonds. In this model, based upon data derived from swelling experiments, hydrogen bond cross-links exceed covalent ones by a factor of four. There are strong similarities between this model and the earlier ones by Dryden (1952) and Brown and Waters (1966a) where hydrogen bonding was also assumed to play an important role in intramatrix bonding.

In his essay of "The Organic Geochemistry of coal" (Given, 1984b), Given reviewed the latest concepts and main ideas proposed about coal structure. The focus of this work is centered on the

two-component model consisting of a macromolecular network and a lower molecular weight mobile phase.

Three basic points are related to the concept of the network. Nelson (1979) by studying the swelling of coals showed that the size and/or flexibility of chain segments between cross-links passes through a maximum at 75% C and is dependent upon rank. This phenomenon was regarded as supporting evidence for coal showing viscoelastic properties.

The second point is the geochemical origin of the macromolecular structure. Given maintains that the input to coalification is already polymeric, contrary to Van Krevelen's belief, which pictures the coalification process as a condensation-polymerization of smaller molecules (humic acids) formed by the earlier degradation of biological macromolecules (Van Krevelen, 1965).

Given's ideas are supported by some recent studies by Larsen and co-workers, who proposed that coalification is not a condensation-polymerization process, after studying the molecular weight distribution of the pyridine extracts of two bituminous coals (Larsen et al., 1984). They found that the distribution was biased towards the higher molecular weights. This is the opposite trend that would be expected if coalification were a condensation polymerization process according to the change in the distribution of monomers and of gel with the extent of reaction as predicted by Flory's distribution (Flory, 1946). The authors concluded that if the insoluble portion of a coal is regarded as a cross-linked-gel and the extractable soluble molecules constitute the sol, the condensation-polymerization theory can not be applied to the process of coalification.

Finally, the analogy between coal and polymeric materials and the application of the Flory-Rehner Model (1943) of cross linked polymers is debatable. The number average molecular weight between cross-links, M_c , is a measure of the extent of cross-linking in polymers which relates to stiffness and swelling characteristics. However, such a model assumes among other things, a non-porous solid. In most cases, corrections are not made for solvent uptake and the data obtained from solvent swelling of coals by different workers (Hsieh, 1984; Larsen et al., 1983) shows little correspondence. The applicability of this model (and the parameter M_c) to coals is questionable.

In summary, the concept of a two phase or two component model, which has been advocated in a number of forms by researchers over a long period appears to be gaining more general acceptance. The model is not, however, clearly defined in terms of the origin, composition and extent of the mobile phase, the interaction between the mobile phase and the network, and the structure and bonding within the network itself.

Given (1984b) supports the concept of coal as a cross-linked macromolecular solid and that the cross-links are composed of ether groups and short methylene chains. The network is considered to be of a porous nature and contains a variety of polar functional groups and polycyclic aromatic and hydroaromatic rings. Larsen (1985), however, has proposed a different conformation for the network, which is envisaged to contain a significant proportion of hydrogen bond cross-links.

The mobile phase, may originate from small molecules that were trapped or retained in the peat matrix during the coalification

process. The alternative suggested by Van Krevelen's proposals is that the mobile phase is residual "monomer."

The material extractable by solvents at their boiling points does not necessarily represent the whole assembly of small molecules in coal, since they can be present in inaccessible pores or contained in clathrates (molecular cages) in the macromolecular structure (Bodzec and Marzec, 1981).

Other evidence suggests that part of the mobile phase is bonded to the network and may even form a part of the integral structure (Snape et al., 1985).

Chapter 3

EXPERIMENTAL PROCEDURE

In this chapter are described the procedures and techniques used for coal sample preparation and storage, liquefaction reactions and product work-up, and the analytical techniques employed for coal and coal product characterization.

3.1 Sample Preparation and Storage

The coals selected for this study were obtained from the Penn State Coal Sample Bank. Their characteristics are shown in Table 3.1. The selection of the coals was based on their high vitrinite content (between 82-91 %). Petrographic analyses of the coals were supplied by The Penn State Coal Sample Bank.

The following analyses were conducted in order to better characterize the coals; the determination of moisture content; elemental composition; mineral matter content (by low-temperature ashing); Fourier transform infrared spectroscopy (FTIR).

The moisture content of the coals was determined by the standard test ASTM D3173, and is reported in Table 3.1. Samples of approximately 1 g were placed in an oven at 104°C, under a flowing stream of dry nitrogen for 1 hr, after which, the samples (in duplicate) were removed and their moisture content determined.

The mineral matter content was determined by low temperature ashing (LTA) following the procedure described by Jenkins and Walker (1978). This method has been considered to provide satisfactory

Table 3.1 Coal Characteristics

<u>Penn State Sample Bank</u>	<u>PSOC 1403-P</u>	<u>PSOC 1266</u>
Seam	Anderson	L Kittanning
County	Campbell	Mehoning
State	Wyoming	Ohio
Province	N. Great Plains	Eastern
ASTM rank class	Subbit. B	HVA
Moisture content (% wt)	23.3	3.4
Mineral Matter *	11.9	6.1

(%wt dry coal)

*by Low Temperature Ashing

Elemental composition (%dmmf)

C	72.9	83.2
H	4.5	5.0
N	1.2	2.1
S (org)	0.9	0.5
O (By difference)	20.4	8.6

Maceral Analysis (%vol)

Vitrinite	87.5	91.2
Exinite	1.7	2.6
Inertinite	10.8	6.2

oxidizes the organic constituents of coal with reportedly minimal changes to the mineral matter.

However, since low rank coals contain a high proportion of carboxyl groups which are associated with calcium, sodium and other metals, a certain amount of the generated ash is derived from the cations in these salts rather than from minerals. To eliminate this interference in the mineral matter determination, it was necessary first to wash out the cations from the subbituminous coal using the procedure by Given and Miller (1971). The ion-exchangeable cations were removed using a 1N solution of ammonium acetate before proceeding with the LTA of the low rank coal. The coal was slurried with the ammonium acetate solution at room temperature for two hours, and filtered. The residue was then washed with a further 20-30 ml of the solution and then rinsed with an excess of distilled water. The washing procedure, using first ammonium acetate solution and then water, was repeated until the ammoniacal odor had disappeared. The sample was then slurried in deionized water, filtered, and dried in a vacuum oven overnight at 60°C before proceeding to the LTA determination.

Elemental analyses of the samples were determined by Galbraith Laboratories Inc., Knoxville, Tenn.

3.2 Catalytic Liquefaction

3.2.1 Catalyst Impregnation

The coals were impregnated with molybdenum catalyst to a loading of 1% wt Mo (dry mineral matter free), using an aqueous solution of a

water-soluble molybdenum salt. In order to introduce the catalyst in its most active form (MoS_2) (Anderson and Bockrath, 1984; Weller, 1982), an aqueous solution of ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (supplied by Climax International Co.), was used to produce the thiosalt, $(\text{NH}_4)_2\text{MoS}_4$, by reaction with H_2S . The thiosalt decomposes to form MoS_2 upon mild heating (Naumann et al., 1982).

The procedure consisted of dissolving the requisite quantity of ammonium heptamolybdate in an amount of distilled water which would give an approximate weight ratio of water to coal of 1.5:1, which gives ease of handling without using excess of water. For instance, to impregnate 35 g of dmmf coal, 0.74 g of ammonium heptamolybdate was dissolved in about 53 g of distilled water.

Once the salt was completely dissolved, a stream of hydrogen sulfide was bubbled through the solution for a period of 30 min at room temperature to effect conversion to the thiosalt. The conversion takes place rapidly and is marked by the solution changing from colorless to orange and then dark red.

The coal was then added to the solution and the mixture was continuously stirred for 30 min to form a slurry. The slurry was then dried under vacuum at 120°C or, in some cases, at 0°C to remove excess water. The batch of impregnated coal was stored in a vacuum desiccator containing anhydrous calcium sulfate (W.A. Hammond Drierite Co).

The residual moisture in the impregnated coal was determined by drying a sample at 104°C , in an oven under a stream of flowing nitrogen (ASTM D3173).

3.2.2 Liquefaction Reactions

The liquefaction reactions were performed in tubing bomb reactors, details of which have been previously described (Yarzac et al., 1980). The system consists of a reaction bomb with a gas-tight valve, a fluidized sand bath heater, an oscillator assembly and a gas-tight manifold. The reactors of about 23 cc capacity were made of 10 cm long stainless steel tubing, 16 mm inner diameter, with two Swagelok end fittings capped by two Swagelok plugs. A length of stainless steel tubing 33 cm long, of 2.1 mm inner diameter, was welded to the reactor and connected to a shut-off valve and a pressure gauge (13.8 MPa maximum pressure). Fig.3.1 shows the assembly of a tubing bomb mounted in the reactor holder.

Reactions were conducted at temperatures between 300°C and 400°C for residence times between 5 and 180 min. The bombs were loaded with approximately 3.5-4.5 g of impregnated coal and 0.02 cm³ of CS₂ to ensure that the molybdenum was maintained in the fully sulphided form.

The loaded reactors were purged three times with nitrogen, and flushed twice with hydrogen prior to pressurizing them to 7 MPa with hydrogen. Before pressurizing the reactors with hydrogen, a check was made to ensure that reactors were leak-tight. After pressurizing with nitrogen, the reactor was immersed in a water bath. Leakages around the valves were tested using soap-solution. If no pressure drop or leaks were detected, the reactors were flushed and pressurized with hydrogen, and firmly secured in the oscillation assembly. Then the bombs were heated rapidly to the reaction temperature by immersion in

ASSEMBLY OF TUBING BOMB AND HOLDER

FIG. 3.1

the pre-heated fluidized sand bath. Previous work has shown that the internal temperature of the reactor reaches the bath temperature within 2 min (Szladow and Given, 1981).

Agitation was provided by oscillating the reactors through a displacement of 2.5 cm at a frequency of 50 min⁻¹. It was established in earlier studies (Szladow and Given, 1981) that these conditions provided a adequate degree of mixing of the reactor contents. After reaction, the bombs were removed from the sand bath and were quenched to room temperature by immersion in cold water.

3.2.3 Product Work-up

3.2.3.1 Gas Analysis

The gaseous products from the reactors were vented at room temperature into a gas-trap of known volume, from which samples were removed for analysis by gas chromatography.

A gas chromatograph, Varian model 3700, was used for gas analysis. Two sets of columns were employed for the separation of gaseous components: the first was a Porapak Q column (180 cm of 80/100 mesh) in series with a Porapak R column (15 cm of 80/100 mesh) which separated CO₂ and C₁ to C₄ hydrocarbons; the second was a Molecular Sieve 5A column (180 cm) for CO determination. A manually operated 10 port multi-functional sampling valve (Valco Instruments) allowed the sample to be switched into the different columns. Helium was used as the carrier gas.

A thermal conductivity detector provided the output signal which was transformed into digital form by an ADALAB A/D converter and fed

into an Apple IIe computer. Data collection and integration were controlled by software developed by Interactive Microware, Inc.

Response factors were determined by injecting samples of pure gases, thus allowing the concentrations and yields of gaseous products to be calculated.

3.2.3.2 Solvent Extraction

After venting the gases, the products remaining in the reactor were, in some cases, transferred into a glass vial and sealed under a nitrogen atmosphere for later analysis by infrared spectroscopy and optical microscopy.

For most of the experiments, the reactor contents were washed out with chloroform (Fisher Scientific, technical grade) and transferred into a dry, pre-weighed ceramic thimble. The thimble was then placed in a Soxhlet apparatus, and the contents were extracted with chloroform for a period of 12 h or until the solvent was colorless. Extraction was conducted under a blanket of flowing nitrogen.

After extraction, the chloroform-soluble material was filtered through a Whatman #42 filter paper. The solvent was removed from the filtrate in a rotary evaporator at 40 to 50°C under reduced pressure and was then further dried for 3 h in a vacuum oven at 100°C. The chloroform-insoluble product remaining in the ceramic thimble was dried under vacuum at 100°C for 12 h prior to weighing.

The chloroform-soluble materials were further separated into oil and asphaltene fractions by extraction with hexane (Fisher Scientific, technical grade). The fractionation involved first adding a small quantity of chloroform (5-10 ml) back to the extract to dissolve it

and then adding about 125 ml of hexane. The flask containing the mixture was placed in a ultrasonic bath to promote dispersion in the hexane. Once the material was removed from the walls of the flask and the extract was well dispersed, the mixture was refluxed under nitrogen for about 24 h.

The oil fraction (soluble in hexane) was separated by filtering through a Durapore filter (Millipore, membrane of 47 mm, .22 u). The solvent was removed from the filtrate in a rotary evaporator at 50°C under reduced pressure. The hexane-soluble fraction, was then dried in a vacuum oven at 100°C for about 3 h.

The asphaltenes (hexane-insolubles) were washed several times with hexane and then dried in a vacuum oven for 12 h at 100°C.

3.2.3.3 Calculations

It is important to mention that there are several factors which influenced the experimentally determined product yields. Volatile materials were undoubtedly lost when venting the gaseous products and during the removal of solvents. In addition, the water generated during liquefaction could not be quantified. To compensate for such losses the yield of liquids was calculated from the recovered residue and the amount of gas produced. The formulae employed for these calculations are:

$$\% \text{ Chloroform-solubles yield} = 100\% - \% \text{ gas} - \% \text{ residue}$$

$$\% \text{ Oils} = 100\% - \% \text{ asphaltenes} - \% \text{ residue} - \% \text{ gas}$$

where the percentages of residue, gas, and asphaltenes were experimentally determined.

Because of the method of calculation, any water produced is reported as part of the oil yield.

3.3 Sample Analysis

Several techniques were used to characterize the coals and their reaction products.

3.3.1 Elemental Analysis

The carbon, hydrogen, nitrogen and sulphur contents of coals and chloroform-soluble extracts were determined by elemental analysis (Galbraith Laboratories, Inc.). Samples of approximately 200 mg were sealed under nitrogen in glass vials for shipment.

3.3.2 ^1H NMR Analysis

Proton nuclear magnetic resonance spectrometry (^1H NMR) was used to obtain proton type distributions for the chloroform-soluble materials.

Samples of approximately 40-50 mg of extract were dissolved in 1 ml of D-Chloroform (99.8 Atom % D, from Aldrich Chemical Co). The solution was filtered through a glass-wool plug and placed in spectral grade glass tubes of 4 mm i.d. for analysis. D-Chloroform is a useful solvent for ^1H NMR since the isotopic impurities cause less interference with the signals from the samples than other solvents. The samples were run in a Bruker WP200 instrument using FT- ^1H NMR at 200 MHz.

The typical resonance frequencies of hydrogen types distinguishable by ^1H NMR in coal and coal derivatives are given as shifts downfield from tetramethylsilane (TMS) which is used as an internal reference. Table 3.2 shows the chemical shift (ppm) assignments for the different types of protons (Karr, 1978).

The proton type distribution was determined from the NMR spectra by measuring the individual areas using an APPLE II-e computer supplied with a software package for graphic applications, Apple-Graphics, and a graphic tablet.

3.3.3 Infrared Spectroscopy

The coals and liquefaction products were analyzed by Fourier transform infrared spectroscopy (FTIR), which has been shown to be an useful tool for the analysis of coal and coal products (Painter and Coleman, 1979). FTIR analysis offers information concerning the types of functional groups which are present, while a comparison of the absorption intensities between different spectra can indicate changes in the relative abundance of these groups.

Samples of 1.2-1.3 mg were mixed with 300 mg of KBr (99 + %, infrared grade, from Aldrich Chemical, Co) in a Wigg-L-Bug to prepare pellets for spectroscopic analysis (after the procedure described by Painter and co-workers; Painter et al., 1981). KBr is used as a binder and has the advantage over some other materials of having no specific absorption bands in the mid-infrared region. Its major disadvantage is that it is hygroscopic, which masks the OH absorptions at 3300 cm^{-1} .

Spectra were recorded on a Digilab model FTS 15/B Fourier Transform Infrared Spectrometer. Four hundred scans (interferograms)

Table 3.2 Typical Resonance Frequencies in ^1H NMR

^1H shift ppm Downfield from TMS	Hydrogen Type
5.5 - 9.0	Aromatic and Phenolic
2.0 - 3.3	Methylene groups alpha to ring
1.6 - 2.0	Methylene other than alpha to ring Naphthenic methylene and methine
1.0 - 1.6	Methylene groups beta or more from ring Methyl groups beta to ring
0.5 - 1.0	Methyl groups gamma or further from ring

of the sample at 2 cm^{-1} resolution were co-added to obtain each spectrum, and recorded in the absorbance mode.

Because the sample weights were different, it was necessary to normalize the spectra before they could be compared. Spectra were normalized to a sample weight of 1 mg using the scaling factor given in the following equation (Kuehn, 1983):

$$K = \frac{1}{\frac{\text{wt of pellet}}{\text{weight of coal} \times (300 + \text{weight of coal})}}$$

In order to examine the absorptions due to hydroxyl groups, without interference caused by the presence of water, samples were derivatized by acetylation with acetic anhydride. The reaction was carried out for 48 hours using the method of Blom and co-workers (1957), followed by the usual procedure for pellet preparation. Aromatic and aliphatic -OH groups in coal are converted to acetate groups -COO-CH₃, which absorb at 1770 and 1740 cm^{-1} and are well separated from the absorption bands of water (3400 - 3300 cm^{-1}).

Typical absorption frequencies in the infrared are shown in Table 3.3 (Painter et al., 1982).

3.3.4 Coal Swelling Experiments

The volumetric swelling procedure developed by Liotta and co-workers (1983) was applied to the chloroform-insoluble portions of parent coal and liquefaction products using pyridine as the swelling agent. It has been shown that volumetric swelling methods give the

Table 3.3 Band Assignments for the Infrared Spectra of Coals

Wave Number, cm^{-1}	Band Assignment
3300	OH groups
3100-3000	Aromatic C-H stretch
2956	Aliphatic CH_3 asymmetric stretch
2921	Aliphatic CH_2+CH_3 asymmetric stretch
2853	Aliphatic CH_2 and CH_3 symmetric stretch
1835	$\text{C}=\text{O}$, anhydride
1775-1765	$\text{C}=\text{O}$, ester with electron withdrawing group attached to single bonded oxygen, $\text{Ar}-\text{O}-\underset{\text{O}}{\text{C}}-\text{R}$
1740	$\text{C}=\text{O}$ ester, $\text{R}-\underset{\text{O}}{\text{C}}-\text{O}-\text{R}'$
1720-1690	$\text{C}=\text{O}$, ketone, aldehyde, carboxylic acid
1650-1630	$\text{C}=\text{O}$, highly conjugated
1600	Aromatic ring stretch
1590-1560	Carboxyl group in salt form $-\text{COO}^-$
1490	Aromatic ring stretch
1450	CH_2-CH_3 bend, possible some aromatic ring modes
1375	CH_3 groups
1330-1110	C-O stretch and OH bend in phenoxy structures and ether
1110-1000	Alcohols, aliphatic ether
900-700	C-H aromatic out-of-plane bending modes

same results as gravimetric procedures and, furthermore, the former has the advantage that no correction for coal pore volume is necessary since what is measured is the increase in size of the coal particle (Green et al., 1984).

The procedure employed was as follows:

400-600 mg of chloroform-extracted coal sample was placed in a glass tube (8 mm o.d.), centrifuged at 1700 r.p.m. for 5 min in a centrifuge (International Equipment Company). The height of the coal column was measured (h_1). About 3-4 ml of pyridine (Fisher Scientific, reagent grade) was then added and the tube was shaken to ensure complete mixing. The tube was again centrifuged and the height (h_2) measured. The mixing and centrifuging was repeated until a constant value of h_2 was reached. Measurement of h_2 was made on the day of sample preparation, 5 days later, and 30 days later. In general, the last two measurements produced very close values.

The volumetric swelling is defined as (Green et al., 1984):

$$Q = \frac{h_2}{h_1} = \frac{V_c + V_s}{V_c}$$

where V_c = Volume of coal

V_s = Volume of solvent absorbed

Chapter 4

RESULTS AND DISCUSSION

The main theme of the research concerns a study of the catalytic hydrogenation of a subbituminous coal in the absence of added vehicle. In addition, some of the research involves a comparison of the behavior of the subbituminous coal (PSOC-1403P) and a bituminous coal (PSOC-1266).

4.1 Characterization of Coals

4.1.1 Properties of Parent Coals

Some properties of the parent coals used in this research are summarized in Table 3.1. Coal samples were supplied by the Penn State Coal Sample Bank, as were the petrographic analyses.

The results of analyses to determine moisture content, elemental composition, and ash content (by low-temperature ashing; LTA) have been reported in Table 3.1.

4.1.2 Analysis of Coals by Fourier Transform Infrared Spectroscopy

The parent coals were analysed by Fourier Transform infrared spectroscopy (FTIR). A brief discussion of the spectral features of these two coals will be given as these are germane to later results and discussions.

The FTIR spectrum of the subbituminous coal (PSOC-1403P) (A) and the coal mineral matter (B) (obtained by LTA) are shown in Fig.4.1. The most intense absorption bands in spectrum (A) are those located in the region $3000-2750\text{ cm}^{-1}$ which correspond to the absorption of aliphatic C-H groups (Refer to Table 3.3). A second prominent band is centered at 1600 cm^{-1} which has been attributed to the C-C aromatic ring vibration (Painter et al., 1981). The next significant band is located near 1440 cm^{-1} , and is believed to be due to the bending modes of CH_3 and CH_2 groups (Painter et al., 1981). Finally, some of the bands located between $1200-600\text{ cm}^{-1}$ are due to mineral matter contributions, as can be inferred from spectrum (B).

The more evident absorption bands in (B) are attributed to gypsum (1100 cm^{-1}), kaolinite (1010 and 1035 cm^{-1}), and illite and montmorillonite (530 and 470 cm^{-1}) (Painter et al., 1978). The band located near 3400 cm^{-1} in spectrum (B) is probably due to OH absorption caused by water uptake during sample preparation.

The spectra of the bituminous coal (PSOC-1266) and its coal mineral matter are shown in Fig.4.2. As above, the bands located at frequencies lower than 1200 cm^{-1} mainly represent absorptions by mineral matter components.

Comparing spectra (B) in figures 4.1 and 4.2, it appears that similar mineral matter constituents are present in both coals although, presumably, their relative concentrations and individual stoichiometry are different.

The spectrum of the bituminous coal, Fig.4.2 (A), possesses the same general features as exhibited by the subbituminous coal, Fig.4.1(A). However, a comparison of the two coals in Fig.4.3, shows

FTIR SPECTRUM OF THE
SUBBITUMINOUS COAL (PSOC-1403P) (A)
AND MINERAL MATTER SPECTRUM (B)

FIG. 4.1

FTIR SPECTRUM OF
BITUMINOUS COAL (PSOC-1266) (A)
AND MINERAL MATTER SPECTRUM (B)

FIG. 4.2

FTIR SPECTRA OF THE
SUBBITUMINOUS COAL (PSOC-1403P) (A)
AND BITUMINOUS COAL (PSOC-1266) (B)

FIG. 4.3

that there are significant differences in the relative intensities of the absorption bands.

The aromatic C-H stretching mode ($3100-3000\text{ cm}^{-1}$) is much larger and better defined for the bituminous coal than for the subbituminous coal. The aromatic C-H out of plane absorption band ($900-700\text{ cm}^{-1}$) which is assigned to substituted aromatic rings (Colthup, 1981) is also more pronounced in the bituminous coal spectrum. Similarly, the aliphatic C-H absorption band between $3000-2750\text{ cm}^{-1}$ is much sharper for the subbituminous coal. These observations are, not surprisingly, consistent with the expected increase in coal aromaticity with rank.

Another notable difference between the spectra is the incipient band around $1700-1680\text{ cm}^{-1}$ for the subbituminous coal, which has been attributed to the presence of carbonyl bearing compounds such as ketones and carboxylic acids, (Painter et al., 1981). This band is characteristic of low-rank coals Given (1984b) and is not apparent in the bituminous coal spectrum.

4.1.3 Chloroform Extraction of Parent Coals

Soxhlet extraction of the parent coals in chloroform gave yields (%dmf) of 2.0 % for the bituminous coal and 4.4 % for the subbituminous coal. In general, low-rank coals contain more readily extractable chloroform-soluble material than high-rank coals, which has been attributed to their higher porosity, facilitating the access of solvent into the coal structure (Brown and Waters, 1966a).

The chloroform soluble extracts were analyzed by FTIR, Fig.4.4. In general, the spectral differences between the extracts of these

FTIR SPECTRA OF THE CHLOROFORM-SOLUBLE
EXTRACTS FROM
SUBBITUMINOUS COAL (PSOC-1403P) (A)
AND BITUMINOUS COAL (PSOC-1266) (B)

FIG. 4.4

coals are similar to those observed for the whole coals (Fig 4.3), although a number of features can be more clearly distinguished.

The intensity of the aromatic C-H band (located between 3100-3000 cm^{-1}) is prominent for the bituminous coal and almost negligible for the subbituminous coal. The greater aromatic C-H content of the bituminous coal extract, relative to that of the subbituminous coal, is also reflected in the bands assigned to aromatic C-H out-of-plane stretching between 900 and 700 cm^{-1} .

The absorption band due to aliphatic C-H groups (3000-2700 cm^{-1}) is much more intense in subbituminous coal spectrum. The pronounced aliphatic character of this extract is substantiated by the presence of a small band located around 724 cm^{-1} in spectrum (A). This absorption arises from the interaction between paraffinic chains containing at least four $-\text{CH}_2-$ groups and is frequently encountered in low rank coal extracts. The splitting of the bands at 730 cm^{-1} and 720 cm^{-1} occurs when paraffin chains form an ordered (crystal-like) arrangement (Sobkowiak et al., 1984); methylene chains of sufficient length and regularity must be present to allow the formation of ordered domains.

The carbonyl absorption band, centred at approximately 1700 cm^{-1} , is a distinctive feature of the subbituminous coal extract and is much more clearly resolved than in the spectrum for the whole coal (figures 4.1 and 4.2). The presence of this band is consistent with the higher content of carboxylic groups and carbonyl containing species found in low rank coals and further shows that there is an appreciable concentration of these functionalities in the extractable coal liquids.

To supplement the FTIR analyses, the chloroform-solubles from the parent coals were examined by ^1H NMR. The chemical shift (ppm) assignments for the different types of protons are given in Table 3.2, (chapter 3, section 3.3.2) as downfield shifts from tetramethylsilane, which was used as an internal reference. Corrections were made, when necessary, to compensate for interference with the signal caused by solvent impurities.

The distribution of proton types for the parent coal extracts is given in Table 4.1. It can be seen that there is a higher total content of aliphatic protons (H_α , H_β , and H_γ) for the subbituminous coal extract, as would be expected.

Elemental analyses of the coal extracts, Table 4.2, shows that in both cases, the H contents and H/C atomic ratios are significantly higher for the extracts than for the whole coals, consistent with the findings of Brown and Waters (1966a).

The extracts evidently contain relatively hydrogen-rich soluble species. The high hydrogen content of the subbituminous coal extract is attributed to its high aliphatic content.

4.2 Catalytic Hydrogenation of the Subbituminous Coal (PSOC 1403-P)

4.2.1 Influence of Gas Atmosphere and Catalyst Addition

Some preliminary experiments were conducted to compare the effects of catalytic and non-catalytic liquefaction on the conversion and product distribution of the subbituminous coal (PSOC-1403P). The results of non-catalytic experiments conducted in hydrogen and nitrogen atmospheres are reported in Tables 4.3 and Table 4.4.

Table 4.1 ¹Hnmr Distribution of Chloroform-soluble
Extracts from Parent Coals (%)

Coal	H α	H β	H γ	H α +OH
Subbituminous(PSOC-1403P)	15.2	48.8	27.4	8.6
Bituminous (PSOC-1266)	17.4	48.0	13.1	21.5

Table 4.2 Elemental Analysis of Parent Coals and their
Chloroform-soluble Extracts (% dmmf)

Sample	C	H	N	H/C atomic
Subbituminous coal (PSOC-1403P)	72.9	4.5	1.2	0.7
Bituminous coal (PSOC-1266)	83.2	5.0	2.1	0.7
Subbituminous Extract*	79.9	9.5	0.6	1.4
Bituminous Extract*	77.2	6.5	n.d.	1.0

n.d - not determined

* chloroform soluble

Table 4.3 Product Yields (% dmmf) from by Non-catalytic Reaction

(Subbituminous coal(PSOC-1403P);60 min reaction;7MPa,cold)

Atmosphere	N ₂		H ₂	
T (°C)	%C.S.*	%Total gas	%C.S.*	%Total gas
300	4.8	5.4	6.4	4.6
350	7.0	11.4	10.7	11.2
400	2.6	9.1	7.7	10.3

* C.S- Chloroform Soluble Extract

Table 4.4 Gas Yields (%dmmf) from Non-catalytic Reaction

(Subbituminous coal(PSOC-1403P);60 min reaction;7MPa,cold)

Atmosphere	N ₂			H ₂		
T (°C)	%CO	%CO ₂	%C ₁ -C ₄	%CO	%CO ₂	%C ₁ -C ₄
300	.13	5.22	--	.14	4.44	--
350	.31	10.29	.81	.38	9.59	.79
400	.25	8.25	.63	.69	8.82	.78

Note: Yield of chloroform-solubles for unreacted coal

is 4.4% dmmf

In nitrogen, the liquids yield was increased by reaction at 300 and 350°C to 4.8 and 7.0 % dmmf respectively (compared to 4.4% for the unreacted coal). On going to 400°C, there was a subsequent decrease in extract yield.

An increase in chloroform-soluble yield, upon pre-heating coals in inert atmospheres to temperatures similar to and above those used here, has been reported a number of times (Illingworth, 1920; Dryden and Pankhurst, 1955; Brown and Waters, 1966a, 1966b; Dormans and Van Krevelen, 1960). Brown and Waters (1966a), and Dormans and Van Krevelen (1960) noted that, the extract yields increased to a maximum at a certain preheating temperature beyond which the yields were reduced. This suggested that at higher temperatures condensation/polymerization reactions reduce the extract yields.

The extract yields were higher for reaction in hydrogen, which is consistent with the results of previous studies (Stansberry et al., 1984). It was proposed that hydrogenation, possibly promoted by mineral matter catalysis, reduced the tendency to condensation resulting in higher yields. However, even in hydrogen, there was a reduction in yield on increasing the reaction temperature to 400°C, indicating that condensation reactions begin to predominate at higher temperatures.

The gas atmosphere did not appear to influence the yields or composition of the product gases. In all cases, the gases consisted mainly of CO₂ with smaller proportions of CO and C₁-C₄ hydrocarbon gases. At 350 and 400°C, the gas yields were significantly higher than those obtained at 300°C, most of the increase being due to the production of CO₂.

The gas analysis does not include H_2S . Although the production of this gas was detected by gas chromatographic analysis, the concentration was negligible relative to the other components. In general, H_2S yields were an order of magnitude lower than those of the $\text{C}_1\text{-C}_4$ gases.

The results of non-catalytic and catalytic reactions are compared in Table 4.5. The procedure for catalyst impregnation was described in the previous chapter (section 3.2.1). At 300°C in hydrogen, there was no apparent influence of the catalyst on extract yield. However, at 350 and 400°C , the catalyst was evidently highly active in promoting the yield of liquids. No significant differences in total gas yields were found for catalytic and non-catalytic hydrogenation. Similarly, the formation of CO and CO_2 appeared to be independent of the presence of the catalyst in the system.

If the catalyst function is primarily hydrogenative and thereby promotes the stabilization of thermally generated free radicals, this could explain the apparent low catalytic activity towards liquid formation at 300°C when the rate of thermal bond cleavage will be low.

This is not to state that the catalyst is inactive at 300°C but simply that the changes brought about in the presence of the catalyst are not apparent in terms of increasing the yield of liquids. Research in catalytic coal liquefaction, where the process was conducted in sequential low ($250\text{-}400^\circ\text{C}$) and high temperature reactions ($>400^\circ\text{C}$) has shown that low temperature hydrogenation can strongly influence the overall conversion and product selectivity; oils being produced in preference to asphaltenes and light hydrocarbon gases (Derbyshire et al., 1986b).

Table 4.5 Effect of Catalyst Addition on Chloroform-solubleYields (%dmmf) in Hydrogen

(Subbituminous coal(PSOC-1403P);60 min reaction;7 MPa cold)

System	Temperature		
	300 °C	350 °C	400 °C
H ₂	6.4	10.7	7.7
H ₂ / MoS ₂	6.5	34.7	60.7

It is possible that at low temperatures (in the region of 300°C) the catalyst is instrumental in saturating aromatic rings, which would facilitate bond cleavage at higher temperatures, and in breaking and stabilising weaker linkages, such as ether bridges. Breaking such bonds would not necessarily be sufficient to liberate extractable low molecular weight species since they may be connected to the coal network at several points of attachment.

4.2.2 Influence of Catalyst Impregnation Technique

Related studies have shown that the conditions used to dry the slurry of the coal and the aqueous solution of tetrathiomolybdate can affect catalyst activity. It is believed that the drying conditions affect dispersion. Impregnated coal samples were analysed by colleagues at the Free University of Brussels using dispersive x-ray analysis (EDAX). Samples which were vacuum freeze dried gave a more uniform molybdenum dispersion than those which were dried at 120°C in vacuum (Derbyshire et al., 1986a). Similarly, the conversion to chloroform-solubles of a bituminous coal, PSOC-1266, increased from 35.8 to 44.2 % when the coal-catalyst slurry was oven-dried and freeze-dried respectively (reaction for 60 min, at 400°C in hydrogen).

The effect of drying conditions upon liquefaction behavior was tested further in this research. Samples of the impregnated subbituminous coal were dried in vacuum at either 0°C or 100°C and then reacted for different times at 400°C.

In contrast to the earlier data, it appears that the conditions used for drying did not have any significant effect on the extract yields for this coal, Fig.4.5.

**CONVERSION TO CHLOROFORM-SOLUBLES AT 400°C
AS A FUNCTION OF DRYING TECHNIQUE**

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPa H₂,
COLD; 1% WT Mo)

FIG. 4.5

The apparent insensitivity of the subbituminous coal to the drying technique may be related to the mode of impregnation. The molybdenum salt was introduced from aqueous solution which would be expected to produce a comparatively strong interaction with the more polar subbituminous coal. A relatively weaker interaction would be anticipated for the more hydrophobic bituminous coal. The strength of the interaction could influence the degree of dispersion and the resistance to sintering at drying temperatures.

Since the choice of drying conditions did not appear to be critical with this coal and because faster drying was of practical expedience, high temperature drying (100°C) was used in the remainder of the research. Unless otherwise noted, all of the impregnated coals were dried at 100°C in vacuum.

4.3 Product Distribution

4.3.1 Yields of Chloroform-soluble Extract

In the following tables and figures, the yield of chloroform-solubles were calculated as described in chapter 3, section 3.2.3.3.

The effects of reaction temperature and residence time on the yield of chloroform-solubles produced by dry catalytic hydrogenation is shown in Fig.4.6. Repeated experiments showed these data to be reproducible to within ± 3 %. There is no apparent reason for the somewhat more scattered data obtained at 350°C.

In general, the extract yields increased with increasing residence time and reaction temperature. At 300°C, the production of chloroform-solubles was low, and even after extended reaction the

**CHLOROFORM-SOLUBLE YIELD VS. TEMPERATURE
AND REACTION TIME**

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPa H₂,
COLD; 1% WT Mo)

FIG. 4.6

yield was not much higher than that obtained by Soxhlet extraction of the parent coal (4.4 % dmmf). It was noted in section 4.2.1 that at this temperature the catalyst exhibited low apparent activity in terms of liquids production.

Much higher yields of extract were measured at 350 and 400°C.

- After 180 min at 400°C the extract yield was about 65 %. Taken together with the gas yield (see below) this means that almost 80 % of the coal was converted to gaseous and soluble liquid products under these mild reaction conditions.

In relation to the mobile phase/network concept of coal structure this implies that, at these high yields, the chloroform-soluble extract contains a large proportion of materials derived from the network, which is not wholly consistent with recent high estimates of the mobile phase content of coals (Jurkiewicz et al., 1982; Bodzek and Marzec, 1981).

The reduction in rate at extended reaction times may be partly due to the fall in hydrogen partial pressure as hydrogen is consumed by reaction. From a knowledge of the product gas composition and the initial and final (cold) pressures in the tubing bomb reactors, it has been possible to calculate the change in hydrogen partial pressure with reaction time, Fig.4.7. At high extract yields, the partial pressure had fallen to about 4.3 MPa, when it is possible that condensation reactions would begin to prevail over hydrogenation reactions. The overall change in hydrogen partial pressure corresponds to a hydrogen consumption of about 2 % wt dmmf coal.

HYDROGEN PRESSURE (MPa) VS. CHLOROFORM-SOLUBLE YIELD

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPa H₂, COLD; 1% WT Mo)

FIG. 4.7

However, these results can also be explained if the conversion of the coal to liquids and gases is first order with respect to the unconverted coal. An analysis of coal conversion kinetics will be contained in the second part of this final report.

It was found that, in this system, the effects of residence time and reaction temperature were, to some extent, interchangeable with respect to liquid yields. For instance, at 350°C and 30 min conversion the extract yield was similar to that obtained at 400°C and 15 min; similar yields were obtained at 300°C for 60 min and at 350°C for 5 min.

It was also observed that extract yields between 8 and 20 % ~~dnmf~~ were not obtained in any of the experiments with this coal, although some experiments were specifically designed to try and produce intermediate yields. This observation may simply reflect a random hiatus in the data or it may have greater significance. That is, the lower yields (4-8 %) may represent the limit of more easily liberated liquids and the higher yields (> 20 %) may mark the onset of substantial depolymerization of the bulk coal structure. This hypothesis is not without foundation since, as will be shown, other properties change sharply in going from < 8 % to > 20 % yields. In this context, the maximum yield of extracts produced by non-catalytic reaction was 7.0 % in nitrogen and 10.7 % in hydrogen.

Because of the lack of data between low and high yields, the anticipated change in properties between 10-20 % liquids yield is presented as a discontinuous curve in many of the following graphs. It should also be made clear that the data obtained at low yields are considered to be more reliable than that at higher levels of

conversion; the mass balances were typically 94% compared to almost 100% at liquid yields below 10 %.

At high yields, the increased production of volatiles will contribute to losses in the liquid products. Consequently, the reported analyses of the recovered liquids do not represent the composition of the whole liquid product. For these reasons, the scatter in analytical data will increase with increasing conversion.

4.3.2 Oil and Asphaltene Yields

The chloroform-soluble extracts were further characterized by solvent fractionation into oils (hexane-soluble) and asphaltenes (hexane-insoluble). The distribution of these product fractions are shown as a function of temperature and reaction time in Fig.4.8. The overall change in oil/asphaltene distribution is more clearly expressed by plotting the oils to asphaltene ratio as a function of extract yield, Fig.4.9.

At low yields (below 10 %), there was a sharp increase in the oil to asphaltene ratio (by more than a factor of 16). This increase was followed by an equally steep decline as the yield increased to over 20%. On going to higher yields, the ratio appeared to pass through a minimum and then gradually increase.

As proposed earlier, an extract yield of about 8% may correspond to the limit of easily (thermally) liberated liquids. These liquids evidently have a low asphaltene content.

As will be discussed in the following sections, at these low yields the extractable liquids are highly aliphatic. These materials (presumably representative of the so-called mobile phase) are

YIELD OF OILS AND ASPHALTENES AS A FUNCTION OF TEMPERATURE AND REACTION TIME

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPa H₂, COLD; 1% WT MO)

FIG. 4.8

OIL TO ASPHALTENE RATIO OF CHLOROFORM-SOLUBLES AS A FUNCTION OF YIELD

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPa H₂, COLD; 1% WT MO)

FIG. 4.9

differentiated, at least by their solubility characteristics, from the more asphaltenic materials which are produced at higher yields. The latter are probably derived from the breakdown of the macromolecular structure. Above about 20% extract yield, the gradual increase in the oil to asphaltene ratio suggests that the catalyst is effective in converting asphaltenes to oils, perhaps through the elimination of functional groups.

From the fact that the presence of the catalyst does not appear to be particularly active in the production of the low yield (300°C) products, it is possible that the generation of additional liquids is dependent upon a combination of both thermal and catalytic reactions. An increase in extractable liquids upon the thermal pretreatment of coals has been noted by numerous authors, as reviewed in chapter 2. What is not, however, clear is the extent and mechanism of liberation of these liquids. This topic is relevant to defining what constitutes the mobile phase.

Calkins (1983) studied the low temperature pyrolysis of coals and concluded that the low molecular weight aliphatic hydrocarbons produced by flash pyrolysis below 700°C result primarily from the cracking of long methylene chains which are chemically combined in the coal structure or physically trapped within it.

Jurkiewicz et al. (1982) claimed that the proportion of the smaller molecules of a high-volatile bituminous coal can compose up to about 40 % of the coal structure, some of these liquids being attached to the network by electron-donor-acceptor interactions. From the results of ^1H NMR studies of swollen coals, Marzec in Given et al. (1986) considered that the content of extractable liquids can amount

to 25-35% for high-volatile bituminous coals and 35-45% for lower rank coals. It was proposed that a large number of relatively small molecules are readily extractable (20-150°C with common solvents) while others are extracted with difficulty due to binding interactions with the network and to being physically trapped within closed porosity.

Vahrman (1972) obtained high yields of liquids by extracting for very long periods with a benzene-ethanol solvent mixture, which suggests that a large proportion of the liquids are not bonded and that the rate of removal is diffusion limited. In summary, from the available evidence it appears probable that the more easily extracted smaller molecules are contained within the network both by weak bonding and by physical entrapment.

4.3.3 Yields of Product Gases

The yields and composition of gases corresponding to the liquid yields presented in Fig 4.6 are given in Table 4.6 and are plotted against liquid yield in Fig.4.10. The data are more scattered than the extract yields, one obvious source of error being leaks from the tubing bombs.

The yields of carbon monoxide and light hydrocarbons both increased with reaction time and temperature; the CO₂ yield also increased with temperature but there is some suggestion that it passed through a maximum with increasing residence time. The ratio of CO₂ to CO is high (typically ranging between 5 and 10) as would be expected for a coal of this rank (Calkins, 1983; Whitehurst et al., 1980b).

Table 4.6 Gas Composition and Yield (%dmnf)
 (Subbituminous coal (PSOC-1403P); 7 MPa H₂, cold; 1% wt Mo)

<u>Reaction (T,t)</u>	<u>%CO</u>	<u>%CO₂</u>	<u>%C₁-C₄</u>	<u>%Total gas</u>
<u>T= 300°C</u>				
<u>Time (min)</u>				
5	-nd-	0.84	-nd-	0.84
15	.14	2.03	0.02	2.19
30	.10	2.67	0.08	2.85
60	.12	1.66	0.06	1.84
180	.20	1.78	0.19	2.17
<u>T= 350°C</u>				
<u>Time (min)</u>				
5	0.01	3.85	0.08	3.94
15	0.35	5.90	0.45	6.70
30	0.85	9.55	2.24	12.64
60	0.33	6.75	0.59	7.67
180	0.19	0.71	1.23	2.13
<u>T= 400°C</u>				
<u>Time (min)</u>				
5	0.71	11.27	2.03	14.01
15	0.92	7.68	2.43	11.21
30	1.11	5.23	2.11	8.45
60	1.35	9.38	4.04	14.77
180	1.49	0.86	4.68	6.93

n.d- Not detected

YIELD OF GASEOUS PRODUCTS VS. CHLOROFORM-SOLUBLE YIELDS

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPa H₂,
COLD; 1% WT Mo)

FIG. 4.10

Despite the scatter in the data, there is evidently a strong correlation between the yields of these gases and the formation of liquids, Fig.4.10. There was little production of light hydrocarbons at low extract yields (< 8%), indicating that there was relatively little cracking at 300°C. The yields of these gases increased with increasing conversion (commensurate with higher reaction temperature).

The rate of production of CO_x was highest at low extract yields. The high evolution of these gases, even under mild conditions, reflects the low stability and rapid rates of decomposition of the carboxylic acid groups (Whitehurst et al., 1977).

4.4 Composition of Chloroform-soluble Extracts

4.4.1 Elemental Analysis

Elemental analyses of the chloroform-soluble extracts produced by dry catalytic hydrogenation are shown in Table 4.7. The change in H/C atomic ratio with yields is plotted in Fig.4.11. At low yields, the extracts were richer in hydrogen than the parent coal extract. It will be recalled that these products possessed a high oil content, figure 4.9. However at high yields, the H/C atomic ratio was lower, and appeared to decrease with increasing reaction temperature. The higher rates of cracking and dehydrogenation at higher temperatures will contribute to the reduced hydrogen content and it can not be assumed that the coal structures rendered soluble at high yields contain less hydrogen than those formed earlier.

Ross et al. (1985) were able to obtain different levels of conversion of a bituminous coal at the same reaction severity. The

Table 4.7 Elemental Analysis and H/C Atomic Ratio of
Chloroform-soluble Extracts (% dmmf)

(Subbituminous coal(PSOC-1403P);7MPa H₂,cold;1%wt Mo)

	Extract yield*	C	H	N	H/C
Parent coal	4.4	79.92	9.53	0.67	1.43

T= 300 °C

Time (min)					
15	6.6	78.89	10.54	0.24	1.60
60	6.5	-----	8.63	0.38	---
180	8.4	82.56	10.98	0.44	1.59

T= 350 °C

Time (min)					
5	5.4	79.52	9.72	0.70	1.47
15	29.7	80.71	7.95	1.15	1.18
30	43.9	78.29	7.60	1.08	1.16
60	34.7	81.25	8.72	1.00	1.28
180	55.2	83.17	8.45	1.13	1.22

T= 400 °C

Time (min)					
5	34.6	81.76	7.82	1.16	1.14
15	44.5	82.50	7.69	1.29	1.12
30	50.9	83.47	7.65	1.27	1.10
60	60.7	85.12	7.64	1.36	1.07
180	69.3	87.44	8.15	1.01	1.12

* Chloroform-soluble extract

--- not determined

H/C ATOMIC RATIO VS. CHLOROFORM-SOLUBLES YIELD

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPA H_2 ,
COLD; 1% WT MO)

FIG. 4.11

system they used was the base-catalysed liquefaction of Illinois No.6 coal in CO/H₂O. By adjusting the pH, different degrees of conversion can be obtained under the same reaction conditions.

Consequently, they were able to analyse liquefaction products as a function of conversion while avoiding any artifacts introduced by the necessity of increasing the reaction severity. They found that the products obtained at 29% and 60% conversion were remarkably similar in composition and distribution. From their results it appears that liquefaction is limited by the rate of chemical bond breaking and involves the progressive production of similar materials. This contrasts to the observations of Whitehurst et al. (1978) where it was found that product character changes with degree of conversion; liquid yields increased with increasing reaction severity and they became progressively more aromatic. The results obtained by these workers suggest a process which proceeds with increasing difficulty.

As Ross and co-workers observed, increased reaction time and temperature will result in increased condensation and aromatization of the products and can result in fallacious deductions about the composition of the original coal structural units.

The foregoing illustrates the problems in deriving unequivocal inferences about coal structure and liquefaction mechanisms, since the technique used to derive information will inevitably bring about changes which permit ambiguous interpretations.

Referring to figures 4.9 and 4.11, it is apparent that, on going from low to high yield, there is a change in liquids composition. It has been suggested that the low-yield products are relatively easily liberated and are representative of the so-called mobile-phase. At

high yields, the liquids are suggested to derive from the macromolecular network; they have a lower hydrogen content are more asphaltenic and (as will be shown in sections 4.4.2 and 4.4.3) are more aromatic in character than the low-yield liquids. Consequently, the sharp changes in oil to asphaltene ratio and H/C atomic ratio on going from < 8% to > 20% yield can be attributed to a dilution effect. The subsequent changes in composition on going to higher yields are accompanied by increasing reaction severity and thus, as in the discussion above, it is not possible to make unqualified conclusions about the composition of coal structural units which contribute to the liquid products at high conversion. However, judging from the gradual nature of the changes in compositional parameters which occur above 20% yield (under conditions where the rates of aromatization and dehydrogenation will be moderate), the results tend to support Ross's contention that there is a degree of uniformity in coal structure.

From the elemental analyses of the parent coal (Table 4.2), the chloroform-soluble extracts (Table 4.7) and the gaseous products (Table 4.6) it is possible to estimate the elemental composition of the insoluble residue at any level of conversion. The calculations do not however account for any addition to the residue of hydrogen from the gas phase.

Following the liberation of ca. 10% chloroform-soluble liquids, which have a relatively high hydrogen content ($H/C = 1.60$), the residue hydrogen to carbon atomic ratio is calculated to be about 0.63, compared to 0.7 for the parent coal. For comparison, the H/C atomic ratio for pyrene is 0.625.

The implication from these calculations is that the average structure of the residue, after conversion to 10% chloroform-soluble liquids consists of 4 condensed aromatic rings. This suggestion is not of course, in keeping with the generally accepted view that the cyclic structural units in coals of this rank contain 2-3 rings (Given, 1984b) and it must be stressed that the calculation provides only an estimate. Nonetheless, this numerical exercise illustrates that, for this coal, the mobile phase (here identified as hydrogen-rich, readily liberated liquids) cannot account for much more than 10% of the parent coal. For the coal to contain a greater proportion of the mobile phase, constituents with much lower hydrogen contents must be included and these appear to be indistinguishable from materials derived by degradation of the network.

From Table 4.7, it can be seen that the nitrogen content of the chloroform extractables increased with increasing liquid yield; the nitrogen concentration was 0.67 % in the parent coal extract and 1.15 % in the products after hydrogenation at 400°C and 180 min. Evidently, with increasing yield, a higher concentration of nitrogen containing compounds are rendered soluble. However, there was no evidence to indicate that there was any significant denitrogenation under these conditions. It is known that the ease of heteroatom removal decreases in the order of S > O > N (Whitehurst et al., 1980b).

4.4.2 ¹H NMR Analysis

The chloroform soluble extracts were subjected to ¹H NMR spectroscopic analysis, in order to determine the distribution of

proton types: H_{α} , H_{β} , H_{γ} , and H_{Ar+OH} ; the protons β were further divided into subcategories β_1 and β_2 , where:

α are protons attached to a carbon adjacent to the ring
(benzylic carbons)

β_1 are CH_2 protons conjugated with or close to carbonyl groups or benzene rings

β_2 are polymethylene protons

γ are protons on methyl groups

H_{Ar+OH} are protons attached to aromatic carbons and hydroxyl groups

The results of 1H NMR analysis of the chloroform soluble extracts obtained at 300, 350 and 400°C are shown in Table 4.8. There will inevitably be some scatter in these data as there are variable losses of volatile liquids due to solvent stripping of the extracts (see section 3.2.3.3., chapter 3). The lost materials will generally be richer in hydrogen than the remaining extract and will thus introduce some errors into the determination of the extract hydrogen contents and proton type distributions. Nonetheless, as these losses did not exceed 2-3 %wt, the general trends shown by these data should not be greatly distorted.

The concentrations of hydrogen in the chloroform-soluble extracts, corresponding to the different proton types, were calculated from the elemental analyses (Table 4.7) and the 1H NMR distributions (Tables 4.8).

The total aliphatic hydrogen content (H_{α} , H_{β} , and H_{γ}) is plotted against extract yield in Fig.4.12 where it can be seen that at low yields there was a sharp increase in the aliphatic hydrogen

Table 4.8 Hydrogen-type Distribution of Chloroform-soluble Extracts (%)(Subbituminous coal(PSOC-1403P);7MPa H₂,cold;1%wt Mo)

	Extract yield*	H _α	H _β	H _γ	H _{Ar+OH}
Parent coal	4.4	15.2	48.8	27.4	8.6

T= 300 °C

Time (min)					
5	3.4	10.2	55.2	26.83	7.2
15	6.6	11.4	73.2	11.84	3.5
30	4.4	6.1	81.9	7.69	4.5
60	6.5	8.7	69.7	10.63	11.0
180	8.4	12.1	63.9	17.66	6.2

T= 350 °C

Time (min)					
5	5.4	15.4	56.4	22.6	5.4
15	29.7	26.6	43.4	17.4	12.6
30	43.9	30.6	40.9	13.2	15.3
60	34.7	23.8	50.1	16.3	9.8
180	55.2	28.4	41.5	12.4	17.7

T= 400 °C

Time (min)					
5	34.6	29.8	36.3	12.4	21.4
15	44.5	36.6	37.4	11.1	15.9
30	50.1	24.5	52.3	9.9	13.2
60	60.7	31.5	36.0	9.8	22.7
180	69.3	29.3	41.8	13.5	15.4

*- Chloroform-soluble extract

TOTAL ALIPHATIC HYDROGEN VS. CHLOROFORM-SOLUBLES YIELD

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPA H_2 , COLD; 1% Mo)

FIG. 4.12

content of the chloroform-soluble liquids over that in the parent coal extract (from 8.7 to 10.3 % wt). This increase corresponds to the increase in total hydrogen content which was observed over the same range of yields, Fig.4.11. At yields above about 10%, the aliphatic hydrogen fell to a lower and essentially constant value of about 6.6 % wt (that is, approximately 80 % of the hydrogen contained in the extracts was present in aliphatic structures).

The changes in hydrogen type distribution with extract yield can be seen more clearly in Fig 4.13. With increasing yield, the alpha hydrogen content appeared to progressively increase to a higher constant value (the increase may be due to the saturation of aromatic rings, the scission of C-C benzylic bonds, and also from ring-opening reactions); the combined aromatic and hydroxyl content behaved similarly although, unfortunately, it is not possible from these data to see how these proton types changed individually. It seems probable that there would be an increase in phenolic -OH since in other work (Stansberry et al., 1984) it was shown that monoaromatic phenols are produced during dry catalytic hydrogenation.

The gamma hydrogen content steadily decreased with increasing extract yield. It is evident that the initial increase in the total hydrogen content and in the aliphatic hydrogen was due to an increase in hydrogen atoms in the beta position. The distribution of $H\beta$ between β_1 (methylene and methine groups other than β to ring) and β_2 (methylene groups β or more from ring) is shown in Fig.4.14. As can be seen, the whole of the increase in $H\beta_1 + \beta_2$ is due to an increase in $H\beta_2$, which is consistent with there being a sudden increase in the concentration of long paraffinic chains. These results

VARIATION OF HYDROGEN TYPE DISTRIBUTION AS A FUNCTION OF CHLOROFORM-SOLUBLES YIELD

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPa H_2 , COLD; 1% WT MO)

FIG. 4.13

VARIATION OF H_β VS. CHLOROFORM-SOLUBLES YIELD

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPa H_2 ,
COLD; 1% WT MO)

FIG. 4.14

are consistent with those of other workers who have reported the liberation of long chain aliphatics upon liquefaction (Youtcheff, 1983) or during low temperature pyrolysis (Calkins, 1983).

It has been shown that low-rank coals can contain large proportions of aliphatic materials, primarily in the form of polymethylene moities which are destroyed during coalification and are essentially absent in the anthracite coals (Given, 1984b).

As discussed more generally in section 4.3.2, it is not clear whether these paraffinic materials are trapped within or chemically bonded to the macromolecular network. Snape et al. (1985) have presented evidence to suggest that some of the long alkyl chains are joined to aromatic structures. These workers found long alkyl chains in the aromatic fractions of pyrolysis tars and supercritical gas extracts, while such structures were virtually absent in extracts obtained under less severe conditions. Such findings are contrary to the view that long alkyl chains and aromatic groups are completely separated. The authors also found that when reaction conditions were more severe, the concentration of long alkyl chains in the aromatic fraction decreased. This result was attributed to thermal breakdown of the long paraffinic side chains.

4.4.3 Fourier Transform Infrared Spectroscopy of Chloroform-soluble Extracts

All of the chloroform-soluble extracts were examined by infrared spectroscopy. The change in spectral characteristics with increasing conversion (equivalent to increasing reaction time at a given

temperature) are accurately represented by the selected spectra (A) to (E) in Fig.4.15.

At low conversions, (B), there was an increase in the intensity of the C-H aliphatic band ($3000-2750\text{ cm}^{-1}$) and of the specific band corresponding to the CH_2 symmetric stretch (2850 cm^{-1}) over that of the extract from the parent coal (A).

In addition, the absorption bands located at $720-730\text{ cm}^{-1}$ in spectrum (A), indicating the presence of aliphatic chains of four or more $-\text{CH}_2-$ units (Sobkowiak et al., 1984), were slightly sharper in spectrum (B), and disappeared at higher yields. These changes correspond to the liberation of alkanes from the coal matrix as evidenced by the results in the previous sections.

Appart from the increase in paraffinic species, there are no significant differences between the composition of the parent coal extract and the extracts produced at low conversion yields. In neither spectrum (A) or (B) was there any detectable absorption of the C-H aromatic band ($3100-3000\text{ cm}^{-1}$).

At higher conversions, the intensities of the C-H aliphatic bands were substantially reduced, (C)-(E). The intensity of the CH_2 symmetric stretch (2850 cm^{-1}) also decreased and the asymmetric CH_3 (2956 cm^{-1}) stretch increased with increasing conversion. The reduction of CH_2 groups relative to CH_3 may be related to the increase in C_1-C_4 gas production; cracking of paraffinic chains would reduce their length and increase the proportion of terminal CH_3 groups.

There is a notable change in the carbonyl absorptions ($1800-1650\text{ cm}^{-1}$), attributed to ketones, and carboxylates, which disappears at high conversions and temperatures above 300°C . Whitehurst and

FIG. 4.15 FTIR SPECTRA OF CHLOROFORM-SOLUBLE EXTRACTS OBTAINED AT DIFFERENT LEVELS OF CONVERSION OF SUBBITUMINOUS COAL

(A) PARENT COAL (B) 6.6% (DMMF) (C) 29.7% (DMMF)
(D) 44.5% (DMMF) (E) 60.6% (DMMF)

co-workers (1977) established that carbonyl-containing compounds, such as esters and carboxylates are reactive functionalities which can cleave under thermal treatment to produce CO, CO₂, and phenols. The authors concluded that the evolution of those gases during coal liquefaction could be attributed to the decomposition of esters and carboxylates.

Since the coal used for this study is of low rank, the presence of substantial amounts of carboxylic acid groups and carbonyl bearing compounds is anticipated, as well as a significant evolution of CO and CO₂ gases.

Another relevant difference observed with increasing extract yield is the development of the C-H aromatic band located at 3100-3000 cm⁻¹. While this band is not perceptible in spectrum (A), it begins to be noticeable when conversion yields are above about 20%. Parallel to the appearance of this band, is the appearance of the out-of-plane aromatic C-H absorption (900-700 cm⁻¹) which also becomes more pronounced at higher yields. The increasing intensity of bands attributed to substituted aromatic rings (880-860, 815, and 750 cm⁻¹) indicates that more aromatic structures have been incorporated into the chloroform-soluble products. This increase in aromaticity, which was not seen readily by ¹H NMR spectroscopy because of the masking effect of the OH protons, is small but distinct. It appears, therefore, that the coal network is comprised of more aromatic structures than the liquids produced at low yields.

Consequently, the aromaticity of the total extract would be expected to increase with increasing yield. However, there is also the consideration that, as the reaction proceeds, dehydrogenation

reactions may contribute to the increase of the aromaticity in the chloroform solubles. At high temperatures, extended reaction times and reduced hydrogen partial pressure, it is quite possible that the liquids are catalytically dehydrogenated.

Because of these possible effects, as discussed in section 4.4.1, it cannot be assumed that, with increasing conversion, the coal structures which are rendered chloroform soluble are more aromatic. However, even if aromatization, due to the increase in reaction severity, were insignificant and the composition of the coal and the structural units was independent of conversion level, there would still be an observed increase in aromaticity with yield due simply to the progressive dilution of the earlier liberated aliphatic materials.

4.4.4 Fourier Transform Infrared Spectroscopy of Asphaltenes

Infrared spectroscopic analysis of the asphaltene fractions of the chloroform-soluble extracts showed generally similar changes to those described for the whole extracts. For this reason, the spectra have not been shown. There was an increase in the aliphatic C-H bands at low conversion yields which then, start to decreased at higher yields. The increase in aliphatic absorption in the asphaltenes suggests that a portion of the long paraffinic chains released at low yields are present as substituent groups, in agreement with the results of Snape et al. (1985).

As was mentioned earlier, increasing severity of reaction can cause a decrease in the concentration of such structures due to the scission of alkyl-aryl chains.

A reduction in the absorption of the carbonyl stretching band with increasing yields was also observed in these spectra.

4.5 Fourier Transform Infrared Spectroscopy of Chloroform-insoluble Residues

4.5.1 Subbituminous Coal, PSOC-1403P

Infrared spectroscopic studies of the acetylated chloroform-insoluble residues show that at low conversions, there is apparent little change in the concentration of OH groups, spectra (A) and (B), Fig.4.16. The contributions of ester groups produced by acetylation of aromatic and aliphatic OH functionalities can be seen in the absorption bands at 1770 and 1740 cm^{-1} . At higher conversions, the intensities of these bands decrease sharply, spectra (C) and (D). The OH groups may be removed in the solubilized products or, through hydrogen consumption, form water. It is also possible that some phenols are eliminated by condensation reactions (Whitehurst et al., 1977).

It would be of interest to ascertain the effect of the catalyst on OH removal. However, it was not possible to compare the residues from catalytic and non-catalytic reactions at similar levels of conversion.

4.5.2 Comparison between Subbituminous and Bituminous Coals

Although the bulk of the data for this work was obtained using a subbituminous coal (PSOC-1403P), analyses were also made of the products obtained from the catalytic hydrogenation of a bituminous

FIG. 4.16 FTIR SPECTRA OF ACETYLATED CHLOROFORM-INSOLUBLE RESIDUES OBTAINED AT DIFFERENT LEVELS OF CONVERSION OF SUBBITUMINOUS COAL PSOC-1403P

(A) PARENT COAL (B) 6.6% (DMMF) (C) 29.7% (DMMF)
(D) 60.6% (DMMF)

coal (PSOC-1266) under similar conditions, provided by Peter G. Stansberry (Fuel Science Program, The Pennsylvania State University).

Some comparisons of the behavior of these two coals have already been made.

It was found that the initial rate of conversion was higher for the low-rank coal at low temperatures which suggests that the activation energy for the formation of extractable liquids is lower for this coal than for the bituminous coal (Derbyshire et al., 1986a). An alternative explanation may be that there was a higher dispersion of catalyst on the low-rank coal, as discussed in section 4.2.2. However, it seems more probable that the presence of the catalyst and the reaction conditions used in this study were more favorable to control the rupture of the weaker linkages in the subbituminous coal structure leading to a higher rate of liquids production.

It was also found that the liquid products from the two coals differed in chemical composition. The extractable liquids from the low-rank coal were less asphaltenic, richer in hydrogen, and more aliphatic than the bituminous coal extract (Derbyshire et al., 1986a).

For the subbituminous coal it was shown in section 4.5.1 that the disappearance of OH groups from the chloroform-insoluble residue corresponded closely to an increase in the production of liquids. The FTIR spectra of acetylated samples of the insoluble residues from the bituminous coal, catalytically hydrotreated at 400°C and for different reaction times, are shown in Fig.4.17. There is an evident reduction in the absorption of the ester bands (1770 and 1740 cm^{-1}), corresponding to phenolic and aliphatic OH, with increasing residence time and conversion.

FTIR SPECTRA OF ACETYLATED CHLOROFORM-
INSOLUBLE RESIDUES OF BITUMINOUS COAL (PSOC-
1266) OBTAINED AT 400°C FOR DIFFERENT
REACTION TIMES (A) PARENT COAL
(B) 15 MIN (C) 30 MIN (D) 60 MIN

FIG. 4.17

Comparing these spectra to those for the subbituminous coal in figures 4.16 or 4.18, it can be seen that at high conversion, there appears to be a higher concentration of OH groups remaining in the bituminous coal residues.

These observations suggest that OH groups in the bituminous coal are more stable and less readily removed during liquefaction. The majority of the oxygen in low-rank coals is considered to be contained in carbonyl, carboxyl and phenolic hydroxyl groups whereas in bituminous coals the oxygen is principally present as carbonyl and phenolic hydroxyl groups (Pitt, 1979). The carbonyl and carboxylic groups will be eliminated readily upon thermal treatment, as shown by the high rate of CO_x production at low conversions for the subbituminous coal, Fig.4.10. The phenolic OH groups are presumably attached to more condensed aromatic systems in the bituminous coal than in the low-rank coal, which may account for their higher stability. Yao and Kamiya (1979) found that naphthols are very stable to thermal treatment, while other alcohols and ketones were hydrogenated.

4.6 Solvent Swelling of Chloroform-insoluble Residues

The extent of swelling in pyridine has been used as a means to try and characterize the changes in the chloroform-extracted residues with progressive hydrogenation.

The change in the swelling ratio of the residues with increasing conversion to chloroform-soluble liquids is shown in Fig.4.19. In parallel with the changes in extract composition in going from low to high conversion (as seen by the results of elemental analysis, ^1H NMR,

FTIR SPECTRA OF ACETYLATED CHLOROFORM-INSOLUBLE RESIDUES OF SUBBITUMINOUS COAL (PSOC-1403P) OBTAINED AT 400°C FOR DIFFERENT REACTION TIMES (A) PARENT COAL (B) 15 MIN (C) 30 MIN (D) 60 MIN

FIG. 4.18

**VARIATION OF THE SWELLING RATIO IN PYRIDINE OF
CHLOROFORM-EXTRACTED RESIDUES WITH
CHLOROFORM-SOLUBLE YIELDS**

(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPA H_2 ,
COLD; 1% WT MO)

FIG. 4.19

oil/asphaltene ratio and FTIR) the swelling ratio increased sharply at low conversion, passed through a maximum and fell to much lower values at conversions greater than 20 %. Duplicate experiments confirmed that these data were reproducible.

At low conversions, the reaction severity may not have been sufficient to appreciably disrupt the coal structure. The FTIR analyses of the residues showed that, under these conditions, there did not appear to be any appreciable change in the OH content compared to that of the parent coal. Thus, there should be little change in the extent of hydrogen bonding and, hence, swelling behavior. The fact that the swelling ratio increased over that of the parent coal may simply be due to improved access of the swelling solvent upon removal of the more readily liberated chloroform-soluble liquids.

Jenkins and Mitchell (1978) have shown that the solvent extraction of coal liquids leads to an increase in the pore volume and surface area of the insoluble residue.

An alternative explanation is that, under these reaction conditions, there was an increase in the extent of hydrogen bonding. As discussed in section 4.2.1, the presence of the catalyst did not significantly affect the yield of extractable liquids. Other evidence indicates that the catalyst is not inactive at temperatures of ca. 300°C and is probably involved in promoting hydrogenation reactions and the cleavage and the stabilization of weaker bonds, such as ether bridges. Such reactions would not necessarily lead to an increase in the content of extractable liquids. However, the breaking and stabilization of oxygen linkages would be expected to generate hydroxyl groups which could participate in hydrogen bonding. The

replacement of covalent linkages by hydrogen bonds could account for the observed increase in swelling.

At higher conversions, two factors probably contribute to the reduced swelling of the residues; the removal of polar groups will reduce the extent of hydrogen bonding; the progressive liquefaction of vitrinite will lower its concentration in the residue and hence reduce the swelling ratio.

Petrographic analyses of the chloroform insoluble residues were performed by R. Lin (Coal Research Section, The Pennsylvania State University) to determine the change in concentration of vitrinite macerals with increasing conversion. Table 4.9 shows the variation in percentage of the maceral components in the chloroform-insoluble residue with chloroform-solubles yield.

From this information, it was possible to calculate the theoretical change in volumetric swelling ratio which would be caused simply by the reduction in vitrinite concentration, assuming that the unconverted vitrinite has a similar composition to that in the parent coal. The predicted behavior is shown as the theoretical curve in Fig.4.19.

A comparison of the two curves shows that, in the absence of compositional changes, the predicted swelling ratios are much higher than those determined experimentally and that the predicted values only begin to decrease significantly at yields above about 35%. FTIR analyses of the chloroform-insoluble residues, Fig.4.16, showed that there was a sharp decrease in OH concentration at conversions greater than about 10%. In view of these considerations, it seems that the observed sharp reduction in swelling with increasing conversion is

Table 4.9 Petrographic Analyses of Chloroform-insoluble Residues

Chloroform-solubles yields	% Inertinite	%Vitrinite + Liptinite
8.5	7	93
34.7	9	91
44.5	37	63
50.0	45	55
60.7	59	41

mainly attributable to the elimination of functional groups and, hence, hydrogen bonding.

The swelling ratios measured for the parent coal, and for the residues at low conversions, are much higher than those reported in the literature, where values of ca. 2 are more common. There are three possible explanations for these differences. First, the majority of swelling studies have been conducted on bituminous coals, which swell to a lesser extent than low-rank coals (Peppas et al., 1983). Second, it is common practice to extract coals in pyridine prior to swelling in this same solvent. It is also well established that, following extraction in pyridine, it is extremely difficult, if not impossible, to completely remove this solvent. Thus, it seems probable that the extraction process itself will result in coal swelling which is to some extent irreversible. Consequently, the subsequent swelling of the extracted coals in pyridine will not produce the volume change which would be anticipated for the unextracted coal or for coal extracted in a less nucleophilic solvent (such as the chloroform used in this research). Thirdly, it is also common practice to dry coals before extraction and swelling. Mild thermal treatment may induce covalent cross-linking (especially for low-rank coals) and eliminate hydrogen bonds whose presence is related to the swelling properties. The coals in this research were always dried to a residual moisture content of a few percent.

Chapter 5

SUMMARY AND CONCLUSIONS

The technique of dry catalytic hydrogenation, using sulphided molybdenum as a catalyst, has been used as a probe for investigating some aspects of the structure and the liquefaction mechanisms of a subbituminous coal.

The changes in yield and composition of gas, chloroform-soluble liquids and residual products, over a range of reaction times and temperatures, have been followed by a number of techniques.

It was found that two regimes of liquefaction can be distinguished. At low conversions (up to about 10% liquid yields) liquids and gases are apparently liberated either through the release of physically trapped materials or through the rupture of weak linkages by which these species are attached to the insoluble coal network. Under the reaction conditions used, it appears that the process involves mild thermal reactions and the presence of the catalyst does not significantly affect the product yields; the conversion to soluble liquids at 300°C in the presence of catalyst was similar to the maximum yields attained in a non-catalytic reaction.

However, it seems probable that the catalyst was involved in promoting reactions such as aromatic hydrogenation and the cleavage and stabilisation of oxygen linkages. It is proposed that the liquid yield of about 10% dmwf corresponds to the limit of the more readily liberated liquids for this coal.

As has been shown, at these low conversion levels, there were high rates of production of CO and CO₂ but only small quantities of C₁-C₄ hydrocarbons were generated. The extractable liquids were much more paraffinic than the parent coal extract or the liquids produced at higher levels of conversion, as manifest by ¹H NMR and FTIR analyses. The early release of paraffinic material, usually as n-alkanes and as long chain substituents to aromatic structures, upon mild pyrolysis or upon liquefaction has been observed by other workers (Youtcheff, 1983; Snape et al., 1985).

As this stage there did not seem to be any significant change in the functional group concentration in the extracted residues (as evidenced by qualitative assessment of the -OH concentration from FTIR spectra) or in the extracts (carbonyl group concentration). In turn, this would indicate that there would be little change in the extent of hydrogen bonding in the residue and therefore, there should be little change in residue swelling properties.

In fact, the swelling ratio was found to be about 25% higher than for the chloroform-extracted parent coal. The increase in swelling may be due to easier access of the swelling solvent (pyridine) upon removal of the more readily extracted liquids, to an increase in the extent of hydrogen bonding caused by catalytic stabilization of oxygen linkages or to a combination of these factors.

At higher conversions (above about 20% liquid yields) there were several significant changes; the paraffinic character and C=O content of the extracts decreased, the C₁-C₄ yield increased, the oil to asphaltene ratio in the extracts was greatly reduced, and the swelling ratio of the residue also decreased concomitant with a fall in the

concentration of -OH groups. Relative to the liquids obtained at low yields, the products obtained at high conversions had a lower hydrogen content, were more aromatic and contained higher concentrations of asphaltenes.

The study of a single coal, or even a small number of coals, precludes the derivation of firm conclusions pertaining to the properties and behavior of coals in general. Nevertheless, these studies have important applications to the structure of coal and the process of coal liquefaction. These implications are discussed in some detail below although further research is obviously necessary to examine their validity on a broader basis.

Significance to Coal Structure

Evidently there is a sharp demarcation between the events which take place at low and at high conversions. In the context of the mobile phase/network concept of coal structure, it can be argued that, for the coal studied here, the observed boundary represents a practical limit of the mobile phase, beyond which additional products derive from the substantial breakdown of the network. Although this definition would lead to the extent of the mobile phase being much less than that suggested by Given et al. (1986) and Jurkiewicz et al. (1982), it would seem to have validity in terms of the experimental data and the phenomenological behavior of this coal.

A part of the problem in defining what constitutes the so-called mobile phase is the mode of its attachment to the network and whether this simply involves the physical entrapment of the smaller molecules or whether they are bonded to the macromolecular structure. According

to some researchers, such materials are not really free and trapped within the structure, but rather, they are attached to aromatic structures, and probably weakly bonded to the network (Snape et al., 1985).

Logically, it is to be expected there will be a gradation in the manner in which smaller molecules are associated with the network. This may involve both physical and chemical forces such as surface tension; physical entrapment; dispersion forces; hydrogen bonding; weak and strong covalent bonds. It is doubtful whether any single technique can clearly distinguish between these different modes of attachment. Even with the boundary described above, in which the mobile phase is considered to consist of those materials easily liberated at 300°C, when these effects of thermal reaction are small, it is most probable that diverse types of bonding have been disrupted. Therefore, it is reasonable to define the mobile phase / network with respect to behavioral characteristics rather than purely theoretical considerations. Further, it is apparent that, at least for the subject coal of this research, the boundary between these "phases" is defined clearly by the measured changes in properties with increasing conversion.

It also appears from this study, and from the swelling results in particular, that, for this subbituminous coal, a considerable proportion of the cross-links between network structures must involve non-covalent bonds such as hydrogen bonds. The high oxygen content and functionality of this coal is obviously a significant factor in the formation of such bonds.

Significance to Liquefaction

The liquefaction experiments have shown that, in the presence of an active hydrogenation catalyst, the subbituminous coal was readily converted to liquid products at low temperatures and pressures.

A low yield (up to 10%) of liquid products was obtained by mild thermal reaction (300°C). It appears that those liquids were held in the structure by weak bonds and by physical entrapment. The production of liquids did not appear to be significantly influenced by the presence of the sulphided molybdenum catalyst; there was little difference in the yields obtained in thermal and catalysed reactions. The catalyst is probably involved in promoting hydrogenation reactions which do not directly lead to increasing the content of extractable liquids.

Conversions greater than 20% were attained by increasing the reaction temperature from 300°C to 350 or 400°C. Under these conditions, the presence of the catalyst was found to have a strong influence in promoting the liquid yields. The increase in liquids production was accompanied by an increase in the rate of formation of C1-C4 gases. A reasonable explanation of these observations is that the catalyst provides a primarily hydrogenative function and that the driving force for degradation of the network is thermolysis. With respect to defining the attributes of coal dissolution catalyst, it would be more desirable, to catalyse bond cleavage at low temperatures in addition to providing hydrogenation activity. In this way, the selectivity to liquids would be enhanced at the expense of the production of light hydrocarbons. More efficient use of hydrogen and

reduced reaction severity are essential to improving the viability of coal liquefaction.

In comparison to the products obtained at low yields, the liquids obtained at high conversions were more aromatic and asphaltenic in character. Since those liquids represent the greater proportion of the products, a more detailed study of their composition is warranted in order to ascertain the most effective routes for subsequent refining and upgrading. Although the asphaltene concentration is between 30-50%, the total liquids have a reasonably high hydrogen content (in the range 7.6-9.7%), most of which is contained in paraffinic structures. Consequently, it is supposed that hydroprocessing these liquids to produce an all distillate product would be quite straight forward.

BIBLIOGRAPHY

- Alpert, S.B., and Wolk, R.H., in "Chemistry of Coal Utilization", Edited M.A. Elliot, John Wiley and Sons, New York, 1981.
- Anderson, R.R., and Bockrath, B.C., Fuel, 63, 329, 1984.
- Berkowitz, N. "An introduction to coal technology", Academic Press, New York, 1979.
- Blom, L., Edelhauser, L., and Van Krevelen, D.W., Fuel, 36, 135, 1957.
- Bodzek, D. and Marzec, A., Fuel, 60, 47, 1981.
- Brown, J.K., J. Chem Soc. , 744, 752, 1955.
- Brown, H.R. and Waters, P.L., Fuel, 45, 17, 1966a.
- Brown, H.R. and Waters, P.L., Fuel, 45, 41, 1966b.
- Calkins, W.H., ACS Div. of Fuel Chem., preprints, 28, No.5, 85, 1983.
- Clarke, J.W., Kimber, G.M, Rantell, T.D., and Shipley, D.E., in "Coal Liquefaction Fundamentals", ACS Symposium Series No.139, 1980.
- Colthup, N.B, Daly., L.H., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1981.
- Cronauer, D.C., Jewell, D.M., Shah, Y.T., and Kuesser, K.A., Ind. Eng. Chem. Fundam., 17, 291, 1978.
- Cronauer, D.C., Ruberto, R.G., Silver, R.S., Jenkins, R.G., Ismail, I.M.K., and Schlyer, D., Fuel, 62, 1116, 1983.
- Curran, G.P., Struck, R.T., and Gorin, E., Ind. Eng. Chem. Proc. Des. Dev., 6, 166, 1967.
- Davidson, R.M., in "Coal Science", Vol 1, edited by M. L. Gorbaty, J. W. Larsen and I. Wender, Academic Press, New York, 1982.
- Davies, G.O., Derbyshire, F.J., and Price, R.J., J. Inst. of Fuel, 50, 121, 1977.
- Derbyshire, F.J. and Whitehurst, D.D., Fuel, 60, 655, 1981.
- Derbyshire, F.J., Odoerfer, G.A., Varghese, P., and Whitehurst, D.D., Fuel, 61, 899, 1982.
- Derbyshire, F.J., Odoerfer, G.A., and Whitehurst, D.D., Fuel, 63, 56, 1984.

- Derbyshire, F.J., Davis, A., Lin, R., Stansberry, P.G. and Terrer, M.T., Fuel Proc. Tech., 12, 127, 1986a.
- Derbyshire, F.J., Davis, A., Epstein, M., and Stansberry, P.G., Fuel, 65, 1233, 1986b.
- Dormans, H.N.M., and Van Krevelen, D.W., Fuel, 40, 473, London, 1960.
- Dryden, I.G.C., Fuel, 31, 176, 1952.
- Dryden, I.G.C., and Pankhurst, K.S., Fuel, 34, 363, 1955.
- Dryden, I.G.C. and Joy, W.K., Fuel, 40, 473, London, 1961.
- Fisher, C.H. and Eisner, A. Ind. and Eng. Chem., 29, 1371, 1937.
- Flory, P.J., Chem. Rev., 39, 137, 1946.
- Flory, P.J. and Rehner, J.J., J. Chem. Phys., 11, 512, 1943.
- Francis, W., "Coal: Its Formation and Composition", Edward Arnold (Publishers), London, 1961.
- Furlong, L.E., Effron, E., Vernon, L.W., and Wilson, E.L. Chem. Eng. Prog., 72, 71, 1976.
- Given, P.H., Fuel, 39, 147, 1960.
- Given, P.H. and Miller, R.N., Annu. Meet. Geol. Soc. Am., Abstract Programs, 3 (7), 580, 1971.
- Given, P.H., Cronauer, D.C., Spackman, W., Lovell, H.L., Davis, A., and Biswas, B., Fuel, 54, 34, 1975a.
- Given, P.H., Cronauer, D.C., Spackman, W., Lovell, H.L., Davis, A., and Biswas, B., Fuel, 54, 40, 1975b.
- Given, P.H., Prog. Energy Combust. Sci., 10, 149, 1984a.
- Given, P.H., in "Coal Science", Vol 3, edited by M. L. Gorbaty, J.L. Larsen, and I. Wender, Academic Press, New York, 1984b.
- Given, P.H., Marzec, A., Barton, W.A., Lynch, L.J., and Gerstein, B.C., Fuel, 65, 155, 1986.
- Gorin, E. in "Chemistry of Coal Utilization", Second Suppl. Vol., edited by M. A. Elliot, John Willey and Sons, 1981.
- Granoff, G., and Montano, P.A., in "Chemistry and Physics of Coal Utilization-1980, AIP Conference Proceedings, edited by B.R. Cooper and L. Petrakis, American Institute of Physics, 1981.

- Green, T., Kovac, J., Brenner, D., and Larsen, J.W. in "Coal Structure", edited by R.A. Meyers, Academic Press, New York, 1982.
- Green, T.K., Kovac, J. and Larsen, J.W., Fuel, 63, 35, 1984.
- Guin, J.A., Tarrer, A.R., Lee, J.M., Lo, L. and Curtis, C.W., Ind. Eng. Chem. Proc. Des. Dev., 18, 371, 1979.
- Hausigk, D., Koelling, G., and Ziegler, F., Brennstoff-Chem, 50, 8, 1969.
- Hawk, C.O., and Hiteshue, R.W., U.S. Bureau of Mines Bulletin 662, 1965.
- Heredy, L.A. and Fugassi, P., "Coal Science", Am. Chem. Soc. Monograph No. 55, 448, 1988.
- Hirsch, P.B., Proc. Roy. Soc. London, A226, 143, 1954.
- Hsieh, S.T., Ph. D. thesis, The Pennsylvania State University, 1984.
- Illingworth, S.R., J.Soc. Chem. Ind., 39, 111, 1920.
- Jenkins, R.G. and Mitchell, S.C., Fuel, 57, 394, 1978.
- Jenkins, R.G. and Walker, P.L. in "Analytical Methods for Coal and Coal Products", edited by C. Karr, Vol II, 265, Academic Press, New York, 1978.
- Jurkiewicz, A., Marzec, A., and Pislewski, N., Fuel, 61, 647, 1982.
- Kuehn, D.W., Ph. D. thesis, The Pennsylvania State University, 1983.
- Larsen, J.W., Sams, T.L., and Rodgers, B.R., Fuel, 59, 666, 1980.
- Larsen, J.W., Green, T.K., and Chiri, I., Proc. Int. Conf. on Coal Science, Pittsburgh, p. 277, 1983.
- Larsen, J.W., Mohammadi, M., Yiginsu, I., and Kovac, J., Geochimica et Cosmochimica Acta, 48, 135, 1984.
- Larsen, J.W., ACS Div. of Fuel Chem., Preprints, Vol 30, No 4, 444, 1985.
- Lazerov, L. and Angelova, G., Fuel 50, 338, 1971.
- Liotta, R., Brons, G., and Isaacs, J., Fuel, 62, 781, 1983.
- Lucht, L.M. and Peppas, N.A., ACS Symposium Series No. 169, 1981.
- Marsh, H. and Neavel, R.C., Fuel, 59, 511, 1980.

- Moll, N.G. and Quarderer, G.J., Chem. Eng. Prog., 75, No 11, 46, 1979.
- Mudamburi, Z., Ph. D. thesis, The Pennsylvania State University, 1983.
- Mukherjee, D.K., and Choudhury, P.B., Fuel, 55, 4, 1976.
- Naumann, A.W., Behan, A.S., Thorsteinson, E.N., Proc. Climax Fourth International Conference on the Chemistry and Uses of Molybdenum, edited by H.F. Barry and P.C. Mitchell, Climax Molybdenum Co., Ann Harbor, Michigan, p 313-318, 1981.
- Neavel, R.C., Fuel, 55, 263, 1976.
- Neavel, R.C., Phil. Trans. R.Soc. Lond., A300, 141, 1981.
- Neavel, R.C., in "Coal Science", Vol 1, edited by M. L. Gorbaty, J. W. Larsen, and I. Wender, Academic Press, New York, 1982.
- Nelson, J.R., Ph.D. thesis, The Pennsylvania State University, 1979.
- Neuworth, M.B. and Moroni, E.C., Fuel Proc. Technol., 8, 231, 1984.
- Obara, T., Yokono, T., and Sanada, Y., Fuel, 62, 813, 1983.
- Olah, G.A., Bruce, M.R., Edelson, E.H., and Husain, A., Fuel, 63, 1130, 1984.
- Painter, P.C., Coleman, M.C., Jenkins, R.G., Whang, P.W., and Walker, P.L., Fuel, 57, 337, 1978.
- Painter, P.C. and Coleman, M.C., Fuel, 58, 301, 1979.
- Painter, P.C., Snyder, R.W., Starsinic, M., Coleman, M.M., Kuehn, D.W., and Davis, A., Applied Spectroscopy, 35, 475, 1981.
- Painter, P.C., Snyder, R.W., Starsinic, M., Coleman, M.H., Kuehn, D.W., and Davis, A., ACS Symposium Series No. 205, 1982.
- Palmer, T.J., and Varhman, M., Fuel, 51, 22, 1972.
- Peppas, N.A., Lucht, L.M., Hill-lievense, M.E., and Hooker, D.T., Final Technical Report for DOE, DE-FG22-80PC30222, 1983.
- Schlesinger, M.D., Frank, L.V., and Hiteshue, R.W., U.S. Bureau of Mines, Report of Investigations 6021, 1962.
- Pitt, G.J., in "Coal and Modern Coal Processing: An Introduction", edited by G.J. Pitt and G.R. Millward, Academic Press, New York, 1979.
- Romey, I., Friedrich, F. and Stroble, B., ACS Fuel Div. of Chem., preprints 26, No.1, 76, 1981.

Ross, D.S., Laine, R.M., Green, T.K., Hirschon, A.S., and Hum, G.P., Fuel, 64, 1323, 1985.

Shah, Y.T., and Gray, J.A., in "Reaction Engineering in Direct Coal Liquefaction", Energy Science and Technology, Addison-Wesley Publishing Company, 1981.

Snape, C.E., Ladner, W., and Bartle, K.D., Fuel, 64, 1394, 1985.

Sobkowiak, M., Reisser, E., Given, P., and Painter, P.C. Fuel, 63, 1245, 1984.

Speight, J.G., "The Chemistry and Technology of Coal", Chemical Industries Series, Vol. 12, Marcel Dekker, Inc., New York, 1983.

Stansberry, P.G., Terrer, M.T., Derbyshire, F.J., and Finseth, D.H, ACS Div. of Fuel Chem., preprints, 29, No 5, 67, 1984.

Stenberg, V.I., Baltisberger, R.J., Ogawa, T., Raman, K., and Woolsey, N.F., ACS Div. of Fuel Chem., preprints, 27, No 3-4, 1982.

Suuberg, E.M., Lee, D., and Larsen, J.W., Fuel, 64, 1668, 1985.

Szladow, A.J., and Given, P.H., Ind. Eng. Chem. Process Des. Dev., 20, 27, 1981.

Vahrman, M., Chemistry in Britain, 8, 16, 1972.

Van Krevelen, D.W. "Coal: Typology, Chemistry, Physics, Constitution", Elsevier publishing company, Amsterdam, 1961.

Van Krevelen, D.W., Fuel, 44, 229, 1965.

Vernon, L.W., Fuel, 59, 102, 1980.

Wakeley, L.D., Davis, A., Jenkins, R.G., Mitchell, G.D., and Walker, P.L. Jr, Fuel, 58, 379, 1979.

Weller, S., and Pelipetz, M.G., Proc. of the Third World Petroleum Congress, edited by Brill, Netherlands, p.91, 1951.

Weller, S.W., Proc. of the Fourth International Conference on Chemistry and Uses of Molybdenum, edited by H.F. Barry and P.C.H. Mitchell, 1982, p.179.

Wheeler, R.V., J.Chem. Soc., 103, 1715, 1913.

Whitehurst, D.D., in "Organic Chemistry of Coal", edited by J. W. Larsen, ACS Symposium Series No 71, 1978.

Whitehurst, D.D., Farcasiu, M., Mitchell, T., and Dickert Jr, J.J.
"The nature and origin of asphaltenes in Processed coals", EPRI Report
AF-480, July, 1977.

Whitehurst, D.D., in "Coal Liquefaction Fundamentals", edited by D.D.
Whitehurst, ACS Symposium Series No 139, 1980a.

Whitehurst, D.D., Mitchell, T.O., and Farcasiu, M., "Coal
Liquefaction: the chemistry and technology of thermal processes",
Academic Press, New York, 1980b.

Yao, T. and Kamiya, Y., Bull. Chem. Soc. Jpn., 52, 492, 1979.

Yarzab, R.F., Given, P.H., Spackman, W., and Davis, A., Fuel, 59, 81,
1980.

Youtcheff, J.S., Given, P.H., Baset, Z., and Sundaram, M.S., Org.
Geochem., 5, 157, 1983.

Youtcheff, J.S., Ph. D. thesis, The Pennsylvania State University,
1983.

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THE MOBILE PHASE IN COALS: ITS NATURE AND MODES OF RELEASE

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