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THE DEPENDENCE OF LIQUEFACTION BEHAVIOR ON COAL CHARACTERISTICS

Final Technical Report for the Period March 1981—February 1984

Part VI: Relationship of Liquefaction Behavior of a Set of High Sulfur Coals to Chemical Structural Characteristics

By
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Part VI: Relationship of Liquefaction Behavior of a Set of
High Sulfur Coals to Chemical Structural Characteristics

by
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FOREWORD

1. Objectives and Scope

The principal objective of this program has been to deepen understanding of the ways in which yields of products and product distributions in liquefaction are determined by the chemical, petrographic, mineralogical and geochemical characteristics of coals. In particular, it is desired to provide a scientific basis for correlations previously established empirically. The following studies are included:

(i) Attempts to induce coals to generate their own hydrogen donor solvent during a repeated series of batch runs. It is very desirable to be able to characterize and compare coals in terms of the quality of the solvent they can generate. A possible way to achieve this ability is to use the products of one run to provide part of the solvent for the next run with the same coal, and repeat this until coal product has replaced the initial tetralin.

(ii) Tests for synergistic effects when mixtures of coals are liquefied. Effects could be due to superior donor solvent or catalytic minerals contributed by one component of the mixture. Quantitative analyses of mineral distributions and some degree of product analysis are obtained when effects are found.

(iii) Aspects of the phenomenology of liquefaction, and in particular rates of loss of O and S functions in the early stages. Can thioether cleavage be an efficient chain initiator in coals of high organic sulfur content?

(iv) The relevance to liquefaction behavior of recent literature concepts of coal as a macromolecular network containing physically trapped molecules. Does liquefaction consist to a significant extent merely of the release of molecules already present inside imperfections in the network? What is the structural character of the network?

(v) An in-depth study of product yields and distributions in the liquefaction of a homogeneous, selected, set of 25 high sulfur, medium rank coals, whose organic chemical structure has been well characterized by means of FTIR, ^{13}C nmr, and analyses of product distributions from oxidation with pertrifluoroacetic acid (Deno reaction). The mass of data is to be examined statistically.

(vi) Exploit the pertrifluoroacetic acid oxidation to characterize asphaltenes and compare them with their parent coals. Asphaltenes are difficult to fractionate chromatographically, and so, like others, we seek average information for unfractionated material.

(vii) Compare the liquefaction behavior of sets of maceral concentrates, including vitrinites, liptinites and semifusinites. Detailed product analyses have been made.

(viii) Exploit computerized GC/MS techniques, particularly regeneration of single ion chromatograms, for identifying key characteristics of the distribution of products in the hexane-soluble oil from a set of coals. Single ion chromatography is specially valuable for detecting and identifying structural types all of which give a common ion under electron impact; alkanes and many homologous series of alkyl aromatics have this feature.

2. Some Comments on this Phase of the Research

This, and the one further experimental part of this Final Report still to be published, attempt to relate liquefaction behavior, including some aspects of product composition, to features of the organic chemical structure of coals. Earlier work led to useful empirical correlations of conversion with basic compositional data. Here, in the final phases of the study, we seek a more scientific, rational, basis for correlations.

ABSTRACT

The initial aim of this research project was to use empirical mathematical relationships to formulate a better understanding of the processes involved in the liquefaction of a set of medium rank high sulfur coals. These coals were chosen due to the fact that previous work had shown that similar samples tended to exhibit high liquefaction yields. Additionally it appeared that rank, organic and pyritic sulfur were important structural parameters in that liquefaction process.

In all, just over 50 structural parameters and yields of product classes were determined. The structural parameters included distribution of acids produced by oxidation with trifluoroperoxyacetic acid (TFPA), aromaticity as determined by CP/MAS ^{13}C nmr spectroscopy, intensity of aliphatic and aromatic C-H absorptions measured by FTIR, infrared absorption due to carbonyl in acetylated coals, and the high and low temperature ash yields. The product classes determined included total conversion, conversion to asphaltenes, oils, and gases. The gases were further analyzed by gas chromatography for hydrocarbons, CO, CO_2, H_2S and hydrocarbons, and the hexane-soluble oils were separated into saturate, aromatic and polar fractions by HPLC. The ratio of tetralin to naphthalene was also determined and the amount of hydrogen transferred was calculated.

In order to gain a more complete understanding of the empirical relationships between the various properties, a number of relatively complex statistical procedures and tests were applied to the data, mostly selected from the field of multivariate analysis. These can

be broken down into two groups. The first group included grouping techniques such as non-linear mapping, hierarchical and tree clustering, and linear discriminant analyses. These techniques were utilized in determining if more than one statistical population was present in the data set; it was concluded that there was not. The second group of techniques included factor analysis and stepwise multivariate linear regressions which were applied in order to gain a better understanding of how chemical properties of the coal affect the yields of various product classes.

Linear discriminant analyses were able to show that five distinct groups of coals were represented in the data set. However only seven of the properties seemed to follow this trend. The chemical property that appeared to follow the trend most closely was the aromaticity, where a series of five parallel straight lines was observed for a plot of f_a versus carbon content. This type of behavior is somewhat surprising in that it was originally believed that the sample set was homogeneous in nature.

The factor patterns for each of the product classes indicated that although each of the individual classes tended to load on factors defined by specific chemical properties, the yields of the broader product classes, such as total conversion to liquids + gases and conversion to asphaltenes, tended to load largely on factors defined by rank. The variance explained and the communalities tended to be relatively low.

Evidently important sources of variance have still to be found. These may include the presence of a diversity of types of vitrinite in any one sample, and the distribution of structural forms of organic

sulfur. It is suggested that the diversity of sulfur forms in high-sulfur coals is primarily responsible for the surprising degree of heterogeneity displayed by the sample set.

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CHAPTER I

INTRODUCTION AND REVIEW OF COAL STRUCTURE
AND LIQUEFACTION PROCESSES

A. INTRODUCTION

Over the last thirty or so years, there has been an extensive num-
ber of papers reporting on the structure of coal, and on its behavior
under liquefaction conditions. Few, however, have sought to relate
organic chemical structure to behavior, and fewer still have used stat-
istical methods to establish relationships or have employed relatively
large sample sets. If one takes into account the wide range of prop-
erties (e.g. calorific value, contents of carbon, hydrogen and oxygen,
petrographic composition, volatile matter yield, aromaticity, and con-
tents of functional groups) that coals from various provinces and seams
exhibit, the use of the   statistical techniques should be of great
importance in elucidating the factors involved in liquefaction and give
significant information about the role of the structures of the coals.

This thesis deals with the use of a variety of methods to gain
structural information on a series of medium rank high-sulfur coals,
in relation to a detailed analysis of their liquefaction products. The
techniques used to investigate the coal's structure include Fourier
transform infrared spectroscopy (FTIR), cross-polarization magic-angle-
spinning nuclear magnetic resonance spectroscopy (CP-MAS), and peroxy-
trifluoroacetic acid (PTFA) oxidations. High performance liquid chroma-
tography (HPLC), FTIR, gas chromatography (GC), and gas chromatography/mass

spectroscopy (GC/MS) have been employed to separate and analyse the liquefaction products. The results from each of the techniques, while informative in their own right, have been further analysed by statistical methods to obtain a clearer understanding of the inter-relationships between the various structural parameters and the product composition.

Thus, the express aim of this study is to formulate a better understanding of the processes involved in coal liquefaction for this specific set of high-sulfur medium rank coals. Of special interest is the role of various coal structural parameters, especially the sulfur content, on the liquefaction product yield and distribution. Of no less importance, but of secondary interest in this study, is the insight gained into the differences in structure of the original coals, and the composition of the liquefaction products.

B. JUSTIFICATION FOR RESEARCH

In 1970 American domestic oil production peaked at 11.3 million barrels per day while usage continued to rise (Stabaugh and Yergin, 1979). By 1979 over 47 percent of the oil consumed in the U. S. had to be imported from external sources. This placed the country in a precarious position, subject to various economic and political pressures, while increasing the danger of U. S. involvement in the political affairs of oil-producing nations. Although estimates vary as to the severity of the problem, and in the early 1980's a sharp reduction in world energy usage brought on by an economic downturn has produced a surplus in productive capacity, it is certain that, over

the long term, instability in the world oil market will be a recur-
ring problem.

It is obvious that a shift in energy utilization away from oil,
towards a more balanced system, is needed if economic and political sta-
bility are to be achieved. Many alternative energy sources have been
proposed, including the development of fusion, and the increased util-
ization of nuclear fission, solar radiation, oil shale, tar sands, and
coal. The direct utilization of coal as an energy source presents many
problems that could be overcome at least in part if the coal could be
converted efficiently to a liquid.

Solid coal is relatively difficult to transport, whereas a liquid
can be distributed through pipelines with existing technology. Solids
do not lend themselves to use as a transportation fuel, because of pro-
blems associated with loading, storage and handling. Coal tends to have
a lower calorific value than commonly used liquid fuels, which further
increases the cost of transportation and calls for larger storage areas.
Liquids produced from coal may have a lower sulfur content, which reduces
the amount of sulfur dioxide released into the atmosphere on combustion.
Finally, the liquids produced from the coal might in the course of time
find use as replacement petrochemical feedstocks.

Previous work has shown that rank (Yarzab et al., 1980; Senftle and
Davis, 1982), petrographic composition, inorganic constituents, and
geologic history can affect the behavior of coals under liquefaction
conditions (Given et al., 1975, 1980). The fact that the chemical com-
position of the liquefaction products is also affected has been demon-
strated by Mudamburi (1983), who observed significant differences in

the quantities of specific classes of compounds such as alkyl deritives of naphthalene furan, phenol, and indanol, in the hexane soluble-fraction separated after the liquefaction of several U. S. and British coals and coal maceral concentrates.

The ramifications of this dependence of liquefaction product composition on the characteristics of the coal from which it was formed will be of great importance to any commercial direct liquefaction process. As coal liquefaction processes develop, feed coals will have to be chosen that produce not only the greatest yield of products, but also product compositions that are most advantageous. If our understanding of the processes involved in liquefaction can be developed to the point where specific coals can be chosen to produce maximum yields of commercially desirable products, the economic feasibility of the overall technology can be significantly enhanced. In addition, an increase in knowledge of coal structure and liquefaction reactions should allow new methods of liquefaction to be proposed and more efficient conditions to be developed for technologies that are already available.

C. LIQUEFACTION PROCESSES

There are two distinct classes of processes currently under development for the conversion of solid coal to a liquid product. With indirect liquefaction, coal is gasified to carbon monoxide and hydrogen, and this so-called synthesis gas is subsequently converted to a liquid fuel with the use of a Fischer-Tropsch catalyst. Indirect liquefaction has the advantage of being able to afford a product distribution that can be altered to meet market demands, particularly if new and more selective

catalysts can be developed. In addition the process is technolog-
ically more advanced, with production facilities that have been in oper-
ation for many years (Lee, 1982).

Direct liquefaction converts coal to liquid products at relatively
low temperatures with the aid of a donor solvent, hydrogen, and in some
cases a catalyst. Direct processes are not at the present being util-
ized on a commercial basis, but it is thought that they will compare
favorably economically with indirect liquefaction when development
reaches the commercial stage. Several direct processes have been in-
vestigated at the pilot plant stage, including the Solvent-Refined Coal
process, the Exxon Donor Solvent process, and the H-Coal process (Spen-
cer and Alpert, 1979).

A somewhat newer process integrates the advantages of the earlier
methods in Two Stage liquefaction. This process involves a non-cata-
lytic, rapid dissolution of the coal (Wiser, 1968; Hill, 1966; White-
hurst et al., 1976) to a viscous but soluble liquid. This primary liquid
product is then catalytically upgraded to the desired product in the
second stage of the process after the mineral matter and heavy ends have
been removed. By dividing the overall process into two stages hydrogen
consumption can be reduced, catalyst lifetime can be extended, and a
better quality product can be obtained.

D. DEPENDENCE OF LIQUEFACTION ON COAL CHARACTERISTICS

   a. General Characteristics

Recently, Given (1983) has critically reviewed the literature per-
taining to the dependence of liquefaction behavior on coal characteristics.

The review also included a discussion of the mechanism of donor solvent liquefaction, emphasizing the role of both organic and inorganic sulfur. Due to the scope and depth of this review only a very brief overview of the work in this area will be given here. However, the literature pertaining to the role of sulfur in the liquefaction process will be discussed in further detail because of its importance to this report.

In general both rank and geological history are important in determining how a coal will react under liquefaction conditions. The work undertaken by Yarzab and coworkers (1980), Given and coworkers (1980a), and Given and Sood (1982) in both batch and continuous flow reactors, showed that the coals could be statistically divided into groups; the principal differences between the groups were the ranges of carbon and total sulfur contents. Assignment to a group had some dependence on geological province of origin. Other aspects of geological history, in addition to rank, may have to be considered when working with a large sample set having a wide representation. For example, many Australian and Western Canadian coals contain considerable amounts of "inertinite" macerals which are in fact fairly reactive under liquefaction conditions (Durie, 1980; Pearson, 1982).

The generally accepted theory of the mechanism of coal liquefaction involves an initial thermal decomposition to form free radicals which are then "capped" by hydrogen donated by the solvent (Neavel, 1976). The involvement of free radicals has been confirmed by esr (electron spin resonance) studies (Petrakis et al., 1981, 1982; Petrakis and Grandy, 1981; Retcofsky, 1978); however, the precise mode of participation of the donor solvent has not been studied in depth. Thus, it is difficult to

propose an exact pathway or mechanism by which the donor solvent migrates through the coal to the thermally formed radicals.

The main mineral matter components of most coals are clays. Clays are polymeric aluminosilicate structures, with acidic OH groups attached to the aluminum and silicon atoms. These OH groups have the ability to catalyze reactions *via* a carbonium ion mechanism if the hydrogen has not been substituted with a cation through a anion exchange reaction (Given, 1983). Although only a small amount of work has been performed to promote understanding the effects of clays during liquefaction, Given and coworkers (1974) have shown that the rate of hydrogen transfer from tetralin to phenanthrene and hydrogenated phenanthrene to naphthalene can be increased through the addition of clays. Both clays and pyrite also appear to catalyze rearrangement and coupling of the donor solvent (Sundaram and Given, 1983).

b. Pyritic and Organic Sulfur

Group 2 coals similar to those choosen for investigation in this work have been found to produce the highest yield of products and possess the highest total sulfur content (Yarzab et al., 1980). Thus, it is commonly believed that one of the factors contributing to the liquefaction yield is promotion by sulfur. The exact role of sulfur is not well understood; however, several theories do exist and will be discussed here. In addition several reviews of the reactions and chemistry of sulfur can be found in the literature which the reader may find helpful (Given and Wyss, 1961; Horton and Randall, 1947; Brooks, 1956; Wandless, 1959).

Several workers have shown that conversion of coals of low sulfur content can be increased by from 5 to 18 percent through the addition

of pyrite (Appel et al., 1979 Granoff and Montano, 1980; Bockrath and Schroeder, 1981; Alexander and Anderson, 1982). It has also been observed that there is a leveling off of the increase of conversion with the addition of more than about ten percent pyrite (Granoff et al., 1978) and the addition of pyrite to a coal already possessing high levels is also ineffective in increasing conversion (Granoff et al., 1978; Neavel, 1981). The effect of pyrite addition is also dependent on the coal from which the pyrite has been isolated (Given et al., 1982), and its particle size (Guin et al., 1979),but appears to be independent of surface area (Stohl, 1983).

There are two theories that attempt to explain these effects. The traditional theory proposes that the iron sulfides (pyrite and pyrrohotite)present in the coal act as catalysts for the rehydrogenation of the donor solvent (Guin et al., 1978), or for other important reactions.

It has been observed that during liquefaction pyrite is reduced to pyrrohotite and hydrogen sulfide at roughly the same rate as the organic matter is converted to liquid products (Given, 1983), pyrrohotite being a non-stoichiometric mineral which can be represented by the formula FeS_x where $x = 1.00 - 1.22$. The value of x appears to be dependent mainly on the activity of sulfur when it is released from organic and inorganic combination (Lambert et al., 1980). Thus coals containing high proportions of organic and pyritic sulfur will tend to form pyrrhotites with a high level of iron vacancies (Bommannavar and Montano, 1982), which appear to promote liquefaction (Montano and Granoff, 1980).

More recent work has led Lambert (1982) and Thomas and coworkers (1982) to reject this theory and propose that the actual promoting

agent is hydrogen sulfide generated by the pyrite-to-pyrrohotite trans-
formation, since neither pyrite or pyrrohotite is capable of dissoci-
ative chemisorption of hydrogen (Cyprès et al., 1981). Thus, the hydro-
gen sulfide produced by the reduction of pyrite must be acting as the
catalyst or promoter. The hydrogen sulfide is thought to act as both a
free radical chain initiate and a hydrogen donor (free radical chain
propagator or terminator), as shown below (Thomas et al., 1982).

$$FeS_2 \rightarrow FeSx + 1-xS: \quad (1.00 < x < 1.22)$$

$$S: + Solvent \ (or \ H_2) \rightarrow HS: + Solvent: \ (or \ H:)$$

$$HS: + H_2 \rightarrow H_2S + H:$$

$$HS: \ (or \ H:) + coal \rightarrow coal: + H_2S \ (or \ H_2)$$

$$coal: + H_2S \rightarrow coal \ H + HS:$$

[HS: etc., refer to free radical species]
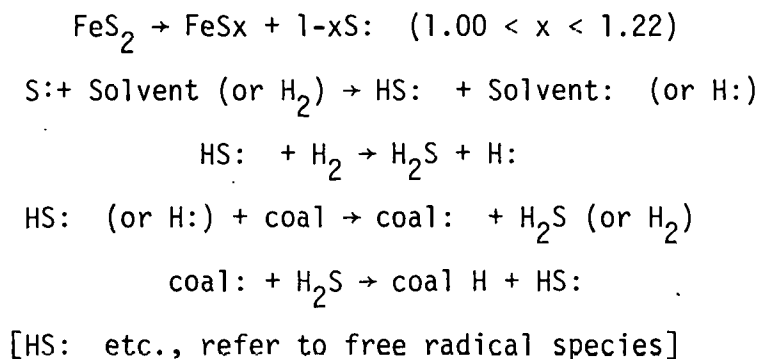
The theory is supported by the fact that H_2S does promote the
generation of free radicals (Srinivasan and Seehra, 1982) and liquefac-
tion (Given et al., 1981; Youtcheff and Given, 1982; Baker et al., 1982;
Sondreal et al., 1982).

The same ideas might be applied to the beneficial effect of organic
sulfur. It was observed that the addition of certain organic sulfur
compounds promoted the transfer of hydrogen between tetralin-d_{12} and
known compounds, and also between the labelled tetralin and a coal,
though the effect was small. It was suggested that certain thiols,
thioethers and disulfides readily dissociate to radicals, which act as
initiators. Thus, sulfide structures in one part of a coal could promote
reactions in other parts (Huang and Stock, 1982).

E. COAL FORMATION

The biochemical stages of coal formation occurred in peat swamps or marshes, which were probably somewhat similar to the Okefenokee Swamp in Georgia and the Everglades in Florida (Spackman et al., 1976 ; Given and Dickinson, 1975; Given, 1972). In most aerobic habitats such as forests and meadows, discarded plant organs are completely degraded by microorganisms to CO_2, H_2O, $SO_4^=$, NH_3, etc. However in water-logged environments a small fraction of the organic material (10%?; Given and Dickinson, 1975) may escape complete degradation, although it will be altered somewhat chemically. These altered materials, consisting of various degraded and repolymerized materials constituted peat, which under favorable conditions may be the precursor of coal.

There is always some degree of water flow into or through the peat-forming areas of a swamp or marsh, capable of transporting suspended mineral grains and dissolved ionic species. Peat swamps tend to be efficient traps for both kinds of inorganic input. The suspended particles settle at the reduced velocity as the water spreads out over the swamp basin and ions can be trapped by ion exchange on the carboxylic acid groups or form chelated coordination complexes with adjacent pairs of functional groups in the peat (Miller, 1977).

Although not totally understood or even very comprehensively studied, chemical or biochemical transformations of the inorganic material occur apparently throughout the peat-forming stage. Organic acids leach K from illite and convert it to kaolinite, and leach Fe from ilmenite, leaving the TiO_2, as anatase, and aerobic growth can induce precipitation of carbonates. If the water is saline, anaerobic bacteria can reduce

sulfate ion to H_2S, a process that most likely leads to the formation of both pyrite and organic sulfur compounds. Most of the mineral matter found in coal is thought to be in place by the end of the peat-forming stage, although some secondary pyrite and calcite may be deposited in cracks and cleats after the organic sediment has been buried and indurated.

The depositional environment is important not only in determining the makeup of the inorganic portion of the coal but also the organic. In the swamp, tidal rivers, deltas, and lagoons behind shoreline beach barriers all provide microenvironments able to support different plant communities giving rise to distinctive peat types (Cohen and Spackman, 1977). Lateral gradients in salinity may be important in determining the amount of sulfur fixation and perhaps the dominance of differing plant communities.

Once the deposition is complete, the processes involved in coalification change from biochemical to purely chemical and physical. Changes brought about by exposure to elevated temperatures are termed metamorphic. In general as the degree of metamorphism or rank increases the contents of volatile matter, moisture, and oxygen decrease, while that of carbon increases (see figure 1; Techmüller, 1967). The initial rule to explain this process was that of Hilt which stated that in a particular coal series rank or the degree of metamorphism increased with the depth of burial. This theory has been elaborated by many workers and a general consensus has emerged that it is not purely the depth of burial that determines rank, but a complex function of the temperature-time history of the coal.
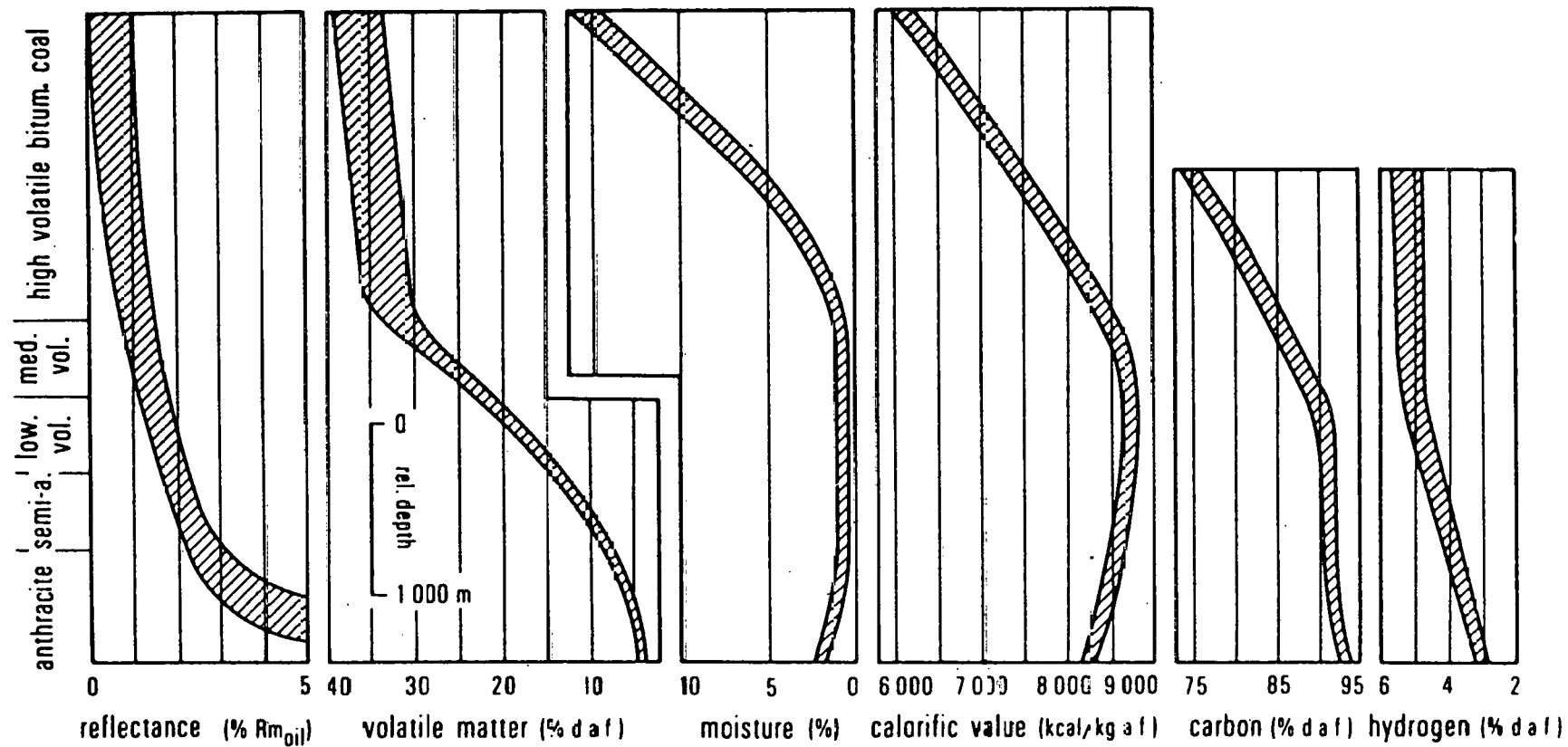
Figure 1. VARIATION OF COAL PROPERTIES WITH DEPTH OF BURIAL
(Teichmüller, 1967)

F. COAL STRUCTURE

Because of the availability of several reviews covering the structure of coal (e.g. Given, 1984; Davidson, 1982; Wender et al., 1980), the material presented here will be limited to a brief overview. However, a more detailed discussion of the forms of organic sulfur will be provided.

a. Physical, Macromolecular and Functional

The fact that coal is an association of organic macerals and inorganic minerals has led Neavel (1979) to describe it as like a fruitcake. It is this extreme heterogeneity that makes coal so difficult to work with and understand. The dominant maceral in most coals is vitrinite, and for this reason when one discusses the structure of coal one is concerned mostly with vitrinite.

It is now widely believed that coal is a cross-linked macromolecular structure (Larsen, 1980), that contains up to about 40% trapped material (Jurkiewicz et al, 1982, and Marzec et al., 1983). The forces holding the structure together appear to be both covalent cross-links and intermolecular hydrogen bonds (Liotta, 1979; Larsen, 1983).

The functional groups present include phenolic hydroxyl (Brown and Wyss, 1955; Friedman et al., 1961; Liotta, 1979, and Yarzab et al., 1979); ethers (Lazarov and Angelova, 1968; Ignasiak and Gawlak, 1977), pyridine-type compounds (Deno et al., 1981a, 1981b, Bodzek and Marzec, 1981; Montgomery and Holly, 1957; Hayatsu et al., 1981), and pyrrole derivatives (Patel et al., 1981).

b. Organic Sulfur

There is at this time no real consensus on either the source or forms of organic sulfur groups found in coal. It is evident that the

sulfur entered initially during the peat stage (Given, 1981). However it is not known how the incorporation of the sulfur into the organic portion of the coal proceeds.

It is fairly certain that at least some of the organic sulfur is present as thiophenic-type compounds. Benzologs of thiophene have been identified in coal liquefaction products (Aczel et al., 1976) and solvent extracts (Aczel et al., 1976; Hayatsu et al., 1978; Bodzek and Marzec, 1981).

The presence of other forms of sulfur is more uncertain. Evidence from methylation reactions with methyl iodide indicates that for a bituminous coal organic sulfides constitute 5-20 present of the organic sulfur. The remaining portion of the organic sulfur was thought to consist of either thiophenic, condensed thiophenic or aryl sulfides, which are unreactive with respect to the methylating agent (Postovski and Harlampovich, 1936; Bogdanova and Boranski, 1961; Prilezhaeva et al., 1963). Depolymerization reactions using Lewis acids led Radianova and Burauskii (1970) to believe that the ratio of sulfides to disulfides does not vary greatly, and thiolic groups do not exist in coals. The Rǎsa coal from Yugoslavia can have organic sulfur contents up to 12 percent. Much of the sulfur can be removed by treatment with alkali metals in various solvents (Given et al., 1958; Ignasiak et al., 1978). This has led to the belief that up to one-third of the sulfur may be present as thioethers.

A second approach that has been used to determine the distribution of organic sulfur groups is the examination of their distribution in liquefaction products or extracts. In addition to the work reported

earlier in this section, Minia and Yanagi (1963) used tetrahydrofuran, dimethylformamide and benzene to show that the extract from Mieke coal contained 3-9 percent of its organic sulfur as thiols, 6 13 percent as disulfides, 28-37 percent as aliphatic thioethers, 7-19 percent thiophenes and aryl sulfides and 30 percent unknown. These results are surprising, since one would not expect the more reactive sulfur groups to survive the coalification process.

A third approach developed by Attar and Dupuis (1978) and Attar and Hendrickson (1982) uses catalytic desulfurization of the coal and detection of the hydrogen sulfide produced. The coal is placed in a cell with a solvent, reducing agent, and catalyst. As the cell is heated the hydrogen sulfide is swept to the detector by a stream of nitrogen. By correlating the temperature at which hydrogen sulfide was released from a coal with that for known sulfur-containing polymers they claimed to be able to distinguish between the various sulfur-containing functional groups. Their results seemed to indicate that the higher the rank the greater the proportion of thiophenic sulfur and that the amount of thioethers remains relatively constant (Attar, 1979).

CHAPTER II

BACKGROUND OF THE ANALYTICAL TECHNIQUES USED

A. INTRODUCTION

In the previous chapter a great deal of information was presented concerning the structure of coal and the processes involved in lique-faction. The work that was performed to gain this knowledge utilized a wide range of techniques, some of which were borrowed from other fields, while others saw their main emphasis for development in studies of coal. This chapter will outline the various methods used in the research des-cribed here, the aim being to give the reader enough information about each technique to understand why it was applied, its limitations, and what information it is capable of providing or has already provided.

B. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

The products of donor solvent liquefaction are a complex mixture of compounds which must be separated further before the results of other analytical techniques such as GC/MS, GC or FTIR can easily be interpreted. The initial fractionation into residue, asphaltenes, gases and oils by boiling point and liquid separation techniques signi-ficantly reduces the complexity of each product; however, these primary fractions are still quite complex. There is a wide range of methods available for performing the secondary separation on each of these initial fractions. This section will give a brief overview of the separation methods which have been applied to the further separation of the oil fraction. The aim is to give the reader some insight into why

a normal phase separation on a bonded amino column was used in this work. In addition a short discussion of the theory of separation utilizing such a column will be given.

a. Theory

Several good reviews of the theory and applications of the various separation techniques are available (Heftmann, 1975; Johnson and Stevenson, 1978; Snyder and Kirkland, 1979). The advantages of high performance liquid chromatography (HPLC) over conventional gravity flow liquid chromatography (LC) include: increased analysis speed; increased resolution between closely spaced compounds; the availability and application of highly sensitive detectors which utilize the change in refractive index or absorption of ultra-violet light to detect elution of a compound from the column; and the availability of reusable columns which do not require repacking after each separation (Johnson and Stevenson, 1978). Other advantages of the application of liquid chromatographic procedures to the separation of coal liquids include: the ability to separate large molecules, which normally exhibit low volatility, and the ease with which the separated sample can be collected for further analysis.

Four types of chromatography are normally possible in HPLC: Liquid/Solid (LSC), which is analogous to a classical gravity flow column separation on silica gel or alumina; partition, in which the mixture to be separated is distributed between the liquid mobile phase and a second liquid coated on or bonded to an inert support; ion exchange, where an acid-base equilibrium exists between the ionic groups on the surface of the support and the ionic components of the mixture, and size exclusion, in which the molecules are separated according to molecular size.

Partition chromatography has been divided into two sub-classes based on the polarity of the stationary and mobile phases; if the mobile phase is more polar than the stationary phase then the method is known as normal phase chromatography and if the reverse is true the system is said to be reverse phase. As a general rule, highly polar samples are more easily separated on a reverse phase column while non-polar samples are best separated under normal phase conditions. Due to the high polarity of many components of coal liquefaction products one would expect to obtain the highest resolution with reverse phase partition chromatography.

Partition chromatography on bonded phase columns has all but replaced the use of coated phase columns because of the elimination of stationary phase solubility in the mobile phase. With a non-bonded stationary phase one must select a phase whose solubility parameter is quite different from that of the mobile phase. With a bonded stationary phase, this requirement is much less important (Locke, 1973). A bonded phase column differs only slightly in retention characteristics from a column coated with the same material (Hogan and Little, 1972). Thus, the same theories that are used to describe behavior on coated columns are normally also applied to bonded phase columns. For more information on the advantages of bonded phase columns, the reader is referred to one of the following reviews: Collin and Guichon (1977); Molnor and Horvath (1977); Scott and Kucera, (1977); Karger and coworkers (1976); Horvath and coworkers (1976); Kirkland (1975); Chang and coworkers (1976); Unger and coworkers (1976); Rehak and Smolkova (1976) and Karch and coworkers (1976).

b. Literature

The most common separation scheme for petroleum and synthetic fuels into less complex fractions that are considerably more amenable to further analysis is known as "SARA" (Saturates, Aromatics, Resins or polars and Asphaltenes fractionation; Jewell et al., 1972). In the SARA scheme the asphaltenes are first removed by liquid-liquid extraction prior to the chromatographic separation into saturates, aromatics and polars. The early methods for performing this separation tended to be time-consuming, required large volumes of solvent and the reactivation of the stationary phase after each separation (Miller, 1982). In order to overcome some of these problems, several workers developed HPLC procedures utilizing activated silica columns (Radke et al., 1980; Selucky et al., 1978; Suatoni and Swab, 1975, 1976). However, several drawbacks were still apparent: an activation step was required, which had to be performed carefully for reproducible results to be obtained; irreversible adsorption was a problem for the most polar components of the oils; large volumes of solvent were still required to elute the samples and to re-equilibrate the column after the separation was complete.

The development of bonded phase columns provided a means of alleviating many of the problems associated with the SARA fractionation using HPLC on activated silica. The bonded phase columns reduced both irreversible adsorption and the amount of solvent needed to equilibrate the column, and eliminated the activation step entirely. The SARA separation has been performed using various groups bonded to silica through alkyl chains: NH_2 (Dark and McGough, 1978; Galya and Suatoni, 1980;

Liphard, 1980; Miller, 1982): CN (Crowley, et al. 1980; Matagunaga and Kusayanagi, 1981; Miller, 1982); mixed NH_2, -CN (Millar et al., 1981; Bollet et al., 1981), and NO_2 (Matagunaga and Kusayanagi, 1981). Both Miller (1982) and Matagunaga and Kusayanagi (1981) have compared the resolution of packings containing the various functional groups, and found that each had specific advantages and disadvantages. However they concluded that the amino-bonded phase was superior in separating phenols and nitrogen containing compounds, but basic and non-basic nitrogen heterocycles were not resolved.

C. CROSS-POLARIZATION MAGIC-ANGLE-SPINNING NMR

With the addition of cross-polarization (CP) and magic-angle spinning (MAS), reliable ^{13}C nmr estimates of the fraction of aromatic carbon f_a became available for the first time. These developments were of great importance in coal science since normal wide line ^{13}C nmr spectra of coal provide little information and the results derived from CP techniques without MAS are somewhat suspect. A complete review of all the literature pertaining to CP-MAS is not possible here; however, the processes involved in CP and MAS will be qualitatively discussed, as will the literature pertaining to coal. In addition, the results from a variation of the CP-MAS technique which utilizes the dephasing time of the ^{13}C nuclei in different environments to resolve different types of aromatic and aliphatic carbons will be discussed.

a. Theory

High resolution nuclear magnetic resonance spectroscopy (nmr) of solids became possible with the development of cross-polarization magic-

angle-spinning nmr (CP-MAS) by Schaefer et al. (1975) using the ideas of Pines et al. (1972). This method combines pulsed nmr with high-speed sample rotation to obtain ^{13}C spectra of solid organic material with line widths as narrow as 2 Hz.

The major source of line broadening in the ^{13}C spectrum of solids is dipolar interactions between the ^{13}C nuclei and closely associated H nuclei causing splitting of the nmr signal. When normal nmr techniques are used with solid samples broad featureless envelopes of unresolved splittings are encountered. These envelopes would be even wider if it were not for the averaging of the dipolar splittings due to spin diffusion of the dipolar-coupled protons.

The proton dipolar broadening could be removed by a high power version of the decoupling technique used in solution nmr; however, sensitivity in solid state ^{13}C spectra is significantly enhanced by proton-carbon cross polarization (CP) which is initiated by spin-locking the protons (Hartmann and Hahn, 1962; Pines et al., 1973). Since the spin-locked protons are decoupled from other nuclei it is very convenient to decouple, simply by spin-locking the protons during the period that the carbon signal is being acquired.

Even after dipolar broadening has been removed, the ^{13}C spectra of solids will appear much broader than a solution spectrum because of asymetric line shapes. These are due to the fact that the chemical shift depends on the orientation of the molecular axes with respect to the external field, and are said to be anisotropic (Haeberlen, 1976). This shift anisotropy can be eliminated while retaining the isotropic shift found in solution through the use of magic angle spinning, where the

sample is rotated rapidly about an axis which makes an angle of 54.7° with the magnetic field (Yannoni, 1982).

b. Applications in Coal Chemistry

The development of the CP technique (Pines et al., 1972, 1973) allowed for the acquisition of ^{13}C nmr spectra of coal that were a significant improvement over those produced by Retcofsky and Friedel (1973) using conventional broad line techniques. The CP technique has been used by VanderHart and Retcofsky (1976a, 1976b, 1978) and Barron and co-workers (1981) to obtain spectra of coals, coal macerals and liquefaction products, whose spectra may be regarded as composed of two overlapping resonances representing the aromatic and aliphatic carbons. In interpreting the spectra it was necessary to assume that the aromatic component of the spectrum was a linearly decreasing function throughout the region of overlap.

In a refinement of the spectrum analysis technique described in the previous paragraph Pines and Wemmer (1978) developed a technique that allowed the CP spectrum to be resolved into four resonance bands, corresponding to simple aromatic carbon atoms, quaternary aromatic, oxygen-bonded aromatic, and aliphatic. This technique was subsequently used by Whitehurst (1978) and Whitehurst and coworkers (1977) to develop f_a values for a series of coals and coal conversion products. However, a plot of H/C versus f_a did not show any correlation making the method somewhat suspect, since Maciel and coworkers (1979) found a smooth curve using CP-MAS.

The addition of magic-angle-spinning to the CP technique significantly increased the resolution between the aliphatic and aromatic

^{13}C resonances (Bartuska et al., 1977). The technique has been used to study several coals (Maciel et al., 1979, and Bartuska et al., 1978a, 1979b), and their variation with rank (Miknis et al. 1982), Maceral concentrates have been investigated by Khan and Schnitzer (1972), Maciel et al. 1982), Pugmire (quoted by Mudamburi, 1983), and Wilson et al. (1984), who found that in general f_a follows the sequence fusinite > vitrinite = micrinite > attrinite > resinite which agrees very well with the results obtained by Retcofsky and VanderHart (1976a) without MAS. Lithotypes separated from Australian coals were investigated by Verheyen (1982), and a variety of ^{13}C nmr techniques, including CP-MAS, were used by Zilm and coworkers (1979) to support a Friedel-Craft mechanism for catalytic hydrogenation with $ZnCl_2$. MacPhee and Nandi (1981) felt that a plot of C_{al}/C_{ar} *versus* oxidation time in air at 105°C indicated that oxidation was occurring at aromatic carbons.

The question of reliability and quantitative accuracy in CP-MAS has been addressed by several workers. Thus Wilson et al. (1980) did not feel that all of the carbons present in coal were observable. Dudley and Fyfe (1982) showed that the CP-MAS signal is independent of recycle time, yet very dependent on contact time; overall they felt that a 90° pulse sequence was best but also recommended calibration with model compounds for true quantitative measurements. Alemany and his coworkers (1983) studied model structures thought to be representative of coal and found that contact times of 2.25ms were needed to obtain the proper atomic ratios. Hagaman and Woody (1981) believe only 50-80% of the carbon in the coal is detected, but on the other hand Pugmire and coworkers (1982) quote work by Wilson showing that f_a values for Solvent Refined Coal were

the same if derived by solution ^1H, solution ^{13}C, or solid state CP-MAS nmr methods.

D. FOURIER TRANSFORM INFRARED SPECTROSCOPY

The use of infrared spectroscopy (IR) has a long history in coal science. Much of the fundamental work using dispersive instruments was performed during the 1950's and 1960's and has been reviewed in several extensive articles (Friedel, 1966; Dryden, 1963; Speight, 1971, 1978). The more recent work, including a majority of the advances realized by the development of FTIR instrumentation, has been reviewed by Painter et al. (1982) and Solomon et al. (1982a). However, a discussion here of some of the controversies in the field is prudent, and a brief review of the specific techniques used in this dissertation is necessary.

a. Theory and Band Assignments

The use of FTIR spectrometers has revolutionized the amount of information that can be extracted from a spectrum. There are several reviews (Griffiths, 1975; Koenig, 1975; and Coleman et al. 1978) that cover the instrumental advantages of the new system. Basically these advantages can be broken down into two categories: those that arise from the use of an interferometer rather than a system of slits and gratings; and those that are realized from the fact that the spectrum is obtained and stored in digital form. The first of these allows for a higher energy through-put espcially in highly absorbing systems such as coal, which allows superior spectra to be taken. The second is probably the most important, since it permits the spectra to be scale-expanded so that subtle features can be investigated, subtracted or used in conjunction with computer programs for curve resolving.

The assignments for most of the characteristic bands in coal are well known (Friedel, 1966; Dryden, 1963; Speight, 1971; Speight, 1978). Table 1 gives a list of most of them. However there is still a great deal of controversy about the assignment of the bands in the region between 1000 and 1350 cm^{-1}. Solomon (1979, 1980) has reported the resolution of several bands in the region and assigned them to ethers. However Painter et al. (1982) believe that firm assignments in this region may not be possible, due to mixing of closely lying vibrational energy levels or even intramolecular mechanical coupling between, for example, adjacent C-C and C-O stretching vibrations in ethers or C-O stretching and O-H bending motions in phenols. They concluded from this that it is highly unlikely that the bands in the region could be assigned to specific groups or motions, but instead were complex, poorly defined, and of mixed character. Thus it seems that if they are correct very little useful information will ever be extracted from this portion of the spectra of coals.

There are two possible assignments for the characteristic band found near 1600 cm^{-1} in coals. It has been alternatively assigned to an aromatic ring-stretching vibration, a chelated carbonyl type structure such as that found in acetylacetone, or to an as yet unknown origin. Although his arguments are rather circumstantial, Painter (1982) convincingly argues that the band can be assigned to the aromatic ring-stretching vibration enhanced by phenolic hydroxyl functionality or linkage of aromatic units by methylene and possibly ether bridges.

b. Spectral Corrections

In order to obtain reliable quantitative information on the functional

Table 1. <u>Band Assignments for the Infrared Spectra of Coals</u>

Wave Number cm^{-1}	Assignment
3030	Aromatic C-H stretching
2950-2850	Aliphatic CH, CH_2, and CH_3 stretching
1600	Most likely aromatic ring stretch (see page 25, in text)
1490	Aromatic ring stretch
1450	CH_2 and CH_3 bend
1375	CH_3 groups
900-700	Aromatic C-H out-of plane bending modes
860	Isolated aromatic H
033	1,4 substituted aromatic groups
815	Isolated H and/or two neighbour H
750	1,2 substituted i.e. neighbouring H
3300	Hydrogen bonded OH
1835	C-O anhydride
1775-1765	C-O, ester with electron withdrawing group attached to single bonded O
1735	C-O ester, other
1690 1720	C-O, ketone, aldehyde, and COOH
1660-1630	C=O highly conjugated
1600	Highly conjugated hydrogen bonded C=O (see page 25 in text)
1560-1590	Carboxyl group as salt, COO^-
1330-1110	C-O stretch and O-H bend in phenoxy structures, ethers
1100-1000	Aliphatic ethers, alcohols

(from Painter et al., 1982)

groups present in coal it is necessary first to account for the mineral matter present. Solomon et al. (1982) reported that the coal spectra could be corrected by subtracting the contributions of kaolinite and illite and scaling the spectra to give the absorbance for 1 mg. of coal on a dry mineral matter free (dmmf) basis. However, Painter et al. (1978a, 1978b) point out that these clays may constitute only 30 to 40% by weight of the mineral matter present in a coal. They therefore suggest that the most accurate method for determining mineral content and adjusting the FTIR spectrum to account for all the mineral matter that may be present is to subtract the spectrum of the low temperature ash (LTA). Occasionally, this procedure is complicated by fixation of organic sulfur and nitrogen as inorganic sulfates and nitrates during the ashing process, but this can be detected and quantitatively measured by FTIR methods (Painter et al., 1978b; Painter et al., 1981).

The second correction to the coal spectrum needed is for the sloping baseline that is encountered. An obvious reason for finding a sloping baseline is scattering of radiation by coal particles. This effect will decrease at an unpredictable rate with decreasing frequency. Dryden (1963) suggested that for higher ranked coals part of the background could be attributed to electronic absorption bands extending into the infrared. One can infer from the discussion that no single (mathematical) function can accurately represent a spectral baseline over any extended range of frequency. Drawing on all of this information, Painter et al. (1982) suggest that if coal spectra are to be accurately curve-resolved or compared, baseline corrections will have to be applied separately to specific regions of the spectrum.

c. <u>Curve Resolving of FTIR Spectra</u>

For the most part coal IR spectra are made up of broad overlapping peaks. Although attempts have been made to integrate absorption intensities over whole regions of a spectrum (Retcofsky, 1977; Durie et al., 1966; Retcofsky and Friedel, 1968), this approach is unreliable due to differences in the extinction coefficients for the contributory bands. It is usually a relatively easy task to curve resolve the region in question into specific bands, but several questions must be addressed if reliable results are to be obtained. The first of these is the peak shape, which is normally assumed to be an empirically determined sum of Gaussian and Lorentzian contributions (Jones, 1969a, 1969b; Jones et al., 1963). The remainder of the problems deal with choosing the proper starting parameter for a least squares optimization procedure (Fraser and Suzuki, 1973). The parameters that must be estimated include the peak positions and heights and the width at half height, all of which can easily be derived from the scale expanded spectrum or its second derivative.

1. <u>C-H Group Determination</u>

There are two regions of the IR spectra of coal that are normally used in investigating the presence of C-H groups. The determination of aromatic groups can utilize the region between 920 and 680 cm^{-1}, which corresponds to the aromatic out-of-plane bending modes while the region between 3000 and 2800 cm^{-1} is used for the aliphatic C-H determinations. In the aliphatic region there is still some controversy as to the exact modes of the five contributing bands; however Painter and coworkers (1982) feel that the band around 2923 cm^{-1} is a composite of the absorptions due

to asymmetrical stretching of CH_2 and CH_3, the band around 2870 and 2956 cm^{-1} to symmetrical CH_3 and CH_2 stretching respectively and that around 2891 cm^{-1} to CH groups. This indicates that if proper extinction coefficients can be derived, a significant amount of information could be derived about the structure of coal.

2. OH Group Determination

A number of attempts have been made to measure directly the OH content of coals by IR spectroscopy (Solomon, 1979; Solomon, 1980; Tschamler and de Ruiter, 1963; and Dryden, 1963), or by measuring the intensities of characteristic bands introduced through chemical reactions (Osawa and Shih, 1971; Friedman et al. 1961; Duffy, 1967; and Durie and Sternhell, 1959). For example, Solomon (1979, 1980) used the relationship between the specific extinction coefficient of the 3450 cm^{-1} absorption band and hydroxyl content developed by Osawa and Shih (1971). However there appears to be a major problem in accounting for the absorption due to water in the pellet. Friedel (1966) has discussed the presence of water in KBr pellets and determined that heating to 175°C was required to remove the last traces, which then reappeared upon cooling. In contrast, Solomon (1979, 1980) has reported complete removal by heating to 110°C overnight. Painter et al. (1978), although not directly addressing whether water could be completely removed, indicated that the coal-KBr mixture provides a good distribution of binding sites, significantly increasing the contribution of water to the intensity of the 3450 cm^{-1} band. In addition broadening of this band due to hydrogen bonding and possible contribution from NH_2 groups makes OH determinations using only FTIR highly suspect.

Durie and Sternhell (1959) were the first to report an IR study of acetylated coal. Although some useful information was obtained, the inability to resolve acetyl bands from those of the original coal made the accurate determination of baselines and measurements of peak intensities impossible. Modern FTIR techniques can easily handle problems such as these simply by subtracting the spectrum of the original from that of the acetylated coal producing well resolved acetyl bands. Once the bands are resolved it is a simple matter to determine baselines and peak areas.

These bands due to C=O in acetyl are found in the region between 1800 and 1600 cm^{-1}. Kuehn and coworkers (1982a,b) have determined that there are five contributory bands in this region. Three are thought to be due to the acetylated OH/NH functionality in the coal, while the remaining two, around 1710 and 1635 cm^{-1}, have been assigned to residual acetic acid from the acetylation procedure and to water in the KBr pellet respectively. The three bands assigned to the C=O of acetates in the coal include that due to phenolic acetates around 1770 cm^{-1}, alcoholic around 1745 cm^{-1}, and acetyl amino NH around 1670 cm^{-1}. It can be concluded that through the use of acetylation and curve resolving it is possible to gain valuable information about the OH functionality present in a coal sample.

Applications of FTIR in coal science include the investigation of the carbonization of solvent refined coal (Painter et al., 1979a), the analysis of fractionated and unfractionated coal liquids (Painter and Coleman, 1979; Solomon and Colket, 1978), investigations of coal oxidation (Painter and Rhoads, 1981; Painter et al., 1980), the modeling of various conversion processes (Solomon, 1979b; Solomon et al., 1981). Overall, the use of FTIR in investigating the structure of coal and its conversion products has contributed a large volume of knowledge and through the use

of curve resolving and other spectral manipulation techniques will continue to do so.

E. LOW TEMPERATURE ASHING

The use of low temperature ashing has found several uses in investigating the mineral matter present in coal. The low temperature ash (LTA) produced by this method closely resembles the original mineral matter in the coal, which makes it the preferred method of directly determining mineral matter and preparing pure samples for the analysis of mineral components by other techniques. Given and Yarzab (1978) have reviewed the literature pertaining to the use of low temperature ashing as a method of directly determining mineral matter, while Jenkins and Walker (1978) discuss the process in relation to separating minerals from the organic portion of the coal.

The LTA is formed by reacting oxygen excited by a radio frequency discharge with the organic portion of the coal at relatively low temperature (80-160°) and pressure (2 torr) (O'Gorman and Walker, 1972; Guilanelli and Williamson, 1982). Miller (1977) has investigated the optimum conditions for performing the ashing to minimize the oxidation of pyrite and ensuring that all of the organic material has been oxidized. His suggestions include an RF power of 50W, stirring the sample three times during the first 8 hours of the initial 24 hour oxidation period to expose new surface, limiting the total oxidation time to 30-36 hours and analyzing for any residual carbon following a 3 N HCl washing.

The low temperature ashing procedure has been suggested as a routine method for the direct determination of a mineral matter (Frazer)

and Belcher, 1973; Miller et al., 1979). However, certain precautions must be taken to ensure that organic sulfur and nitrogen are not fixed and that oxidation of pyrite is minimized (Miller et al., 1979). The problem of sulfur and nitrogen fixation has been investigated by Painter and coworkers (1980), Miller (1978) and O"Gorman and Walker (1971). Although a definitive study of the processes involved is needed, the work already performed indicates that fixation is greatest for low rank coals; however, there are also reports that it may be a problem with oxidized samples of coals in the bituminous rank range. The oxidation of pyrite during the ashing process has been studied by several workers (Huggins and Hoffman, 1978; Miller, 1978; Montano, 1977; Frazer and Belcher, 1973). The general consensus is that oxidation can be mini- mized if care is taken not to have too high an RF power level or allow the ashing to occur for too long a period of time. Other changes that occur during the ashing process include the dehydration of gypsum ($CaSO_4 \cdot 2H_2O$), and rozinite ($FeSO_4 \cdot H_2O$) (Painter et al., 1978b; Frazer and Belcher, 1973), and the oxidation of some Fe^{2+} to Fe^{3+} (Guilianelli and Williamson, 1982; Huggins and Hoffman, 1978).

The LTA's have been utilized by Huggins and Hoffman (1978) in conjunction with Mössbauer spectroscopy to determine that the main pro- ducts of pyrite weathering include hematite (Fe_2O_3), magnetite (Fe_3O_4), and jarosite ($K\ Fe_3(SO_4)_2 \cdot (OH)_6$) as have Rao and Gluskoter (1973) and Walker and coworkers (1975) in quantitative mineral analysis via X-ray diffraction.

Additionally Painter and coworkers in several communications (1978a, 1978b, 1981) have discussed the quantitative analysis of

minerals in the LTA through the use of FTIR. Other workers using the LTA in the quantitative analysis of mineral matter include Gluskoter (1965, 1967), and Estep and coworkers (1968).

Overall the low temperature ashing procedure is the best method for separating mineral matter from the organic substance of coal if care is taken that changes such as oxidation, dehydration, and fixation of nitrogen and sulfur, are minimized. The LTA can then be used for mineralogical analysis by a variety of techniques.

F. TFPA OXIDATIONS

The use of trifluoroperoxyacetic acid as an oxidative degradation method for coal has provided a powerful technique for investigating coal structure. This so-called reverse oxidation, because it tends to oxidize aromatic structures while preserving aliphatic ones, has provided invaluable information concerning the non-aromatic structures found in coal. This information is of special interest since it relates to the linkages between aromatic clusters within the coal.

TFPA was first prepared and investigated by Emmons and Ferris (1953). They found that the peroxyacid could be formed by reacting trifluoroacetic acid with aqueous hydrogen peroxide, the reaction occuring more rapidly than with formic or acetic acids. It was also observed that the peroxyacid exhibited strong oxidizing power.

It is thought that TFPA acts as a source of the electrophilic hydroxyl cation, OH^+, though the cleavage of the O-O bond as shown in Equation 1 (Curry, 1980).

$$CF_3 \cdot \underset{O}{\overset{||}{C}} O \cdot OH \rightarrow CF_3 \cdot \underset{O}{\overset{||}{C}} O^- + OH^+ \text{ - - - - - - - - - - - - - - (1)}$$
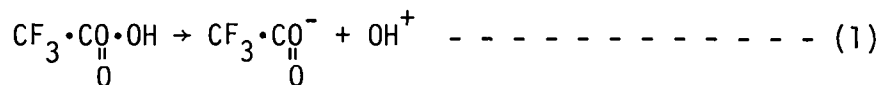
Although the exact mechanism of the oxidation is not known it is thought that the initial step is the direct hydroxylation to the aromatic or aliphatic carbon remote from an electronegative center (Rakitsky, 1980).

A complete review of the non-coal-related literature concerning the uses of TFPA up to 1980 has been given by Rakitsky (1980) and to a lesser extent Curry (1980), so only those papers relating directly to its use in the investigation of coal structure need to be presented here.

The application of TFPA to coal and coal-derived materials has a relatively recent history. Early work by Deno and coworkers (1977) and Greigger (1978) led them to believe that oxidations with TFPA could yield valuable information concerning the structure of coal. Initially four coals and two solvent refined coals were investigated (Deno et al., 1978a, 1978b) along with a number of model compounds. The major product from the whole coals was found to be succinic acid which is thought to be derived from diarylethane and indane-type structures.

Three additional topics of study have come out of this work. The first involves the fate of sulfur and nitrogen-containing functional groups during the oxidation. It appears that both of these groups are oxidized when present as heterocycles, the nitrogen going to the N-oxide and the sulfur to the sulfone. Both of these structures are then thought to be resistant to further attack, due most probably

to the positive nature of the oxidized heteroatom (Venier et al., 1981, and Liotta and Hoff, 1980).

The second topic involves the long-chained aliphatic material present in coal. Product workup conditions utilized by Deno in all of his papers were such that long-chained products were not observed. However other workers have found numerous products in this class by using other procedures (Verheyen, 1982, and Hessley et al., 1982). The lack of these long-chained materials seems to be due to their relative instability under reaction conditions and their limited solubility in the medium.

Liotta and Hoff (1980) have extensively studied the reaction of PTFA with a number of model compounds. The main conclusions were that the production of numerous side products if mild reaction conditions were used makes the analysis of the product difficult.

The inability to obtain a mass balance is due to the mineral-catalyzed decarboxylation of the TPFA reagent. Generally low yields (60-80%) are obtained, which reduces the quantitative accuracy of the data. However, Liotta and Hoff did feel that the reaction shows some promise as a qualitative indication of the alkyl groups present.

G. GAS ANALYSIS

The gases formed during donor solvent liquefaction constitutes a small yet significant portion of the product. A number of workers have investigated this portion of the product, utilizing a wide range of analytical techniques. Most of these techniques were based either totally, or in part, on a gas chromatographic (GC) separation. This section will review the theory of separation for the two techniques used

in this report and present some of the other methods that have been utilized by other workers.

Two variations of gas chromatography were used in this work. The first provided analysis for H_2, H_2S, N_2, O_2, CH_4, and is known as size exclusion or gel chromatography. The second, used in the analysis of all hydrocarbons other than CH_4, is based on the most common variety of GC, gas liquid partition chromatography. Several good reviews of the theory and practice of gas analysis utilizing GC are available (Desty and Goldup, 1975; Jan'ak, 1975), as are various reviews of the general theory of SEC and molecular sieves (Determann and Brewer, 1975) and GLC (Giddings, 1975).

a. Non-hydrocarbon Gases

In pure SEC, separation is obtained because molecules of different sizes enter at different rates the interior of a porous, three-dimensional network. Since large molecules spend less time in the quiescent interior of the network, they are carried through the column more rapidly by the carrier gas than are molecules of smaller size. If there were no interaction between the molecules being separated and the packing material, one would expect a separation to be dependent only on pore size and shape, but this is not normally the case. In a real separation there are interactions between the molecules being analyzed and the surface of the packing (exterior and in pores), which makes the order of elution dependent on the material of which the packing is made as well as on the pore characteristics.

Three types of packing materials are commonly used for the analysis of light non-hydrocarbon gas. The first of these, and probably the most common, is the silica-alumina molecular sieve. However this packing

contains surface OH groups which make highly polar gases such as CO_2 and H_2S difficult to elute. In an attempt to decrease the strong adsorption associated with separations on molecular sieves, packing produced by copolymerization of styrene and ethylvinylbenzene with some divinylbenzene, known under the name "Porapak", presents a viable alternative when highly polar gases must be separated, provided the column is cooled below room temperature to ensure good resolution of less polar gases. The third type of packing is a porous carbon which exhibits intermediate behavior compared to molecular sieves or Porapak. This allows the separation of light gases at just slightly above room temperature yet requires only a moderate rise in temperature to elute the more polar components.

b. Hydrocarbon Gases

A large number of supports and coatings are available for the separation of hydrocarbon gases. Even though these gases are occasionally separated by adsorption or SEC the most common technique utilizes gas liquid chromatography (GLC). Thus, the separation produced is based primarily on the relative volatility of the specific components. There are two forms of packings that can be used in GLC, those in which the stationary phase is coated on the support and those in which the phase is actually chemically bonded. The advantages realized by bonding the stationary phase to the support apply to both HPLC (Section B) and GLC. There is one added constraint in GLC; in HPLC one does not have to worry about the thermal stability of the packings since separation is normally performed at room temperature. However in GLC the samples must be volatilized, which requires temperatures above those encountered in HPLC. Thus, bonded phase GLC columns cannot be used to separate

hydrocarbons which require temperatures greater than 140°C for elution. However, this is a problem not encountered during gas analysis.

H. STATISTICS

The use of statistics in coal research, as in any scientific field, has a long history. The extreme diversity in the structure of various coals, the extreme complexity of a single coal, and the large number of reactions that occur during coal liquefaction, all contribute to making statistics an attractive method of analyzing the complex interrelationships encountered. There are many techniques that can be classifed as statistical. In this section a short discussion of those utilized in analyzing the data acquired in this report will be presented. Of special interest will be discussion of why the techniques were used, their applicability to various types of data, including the limits and precautions in interpreting their results, the type of information that other workers have obtained, and a qualitative description of how the techniques were performed.

The statistics used in this report can be divided into three general categories, descriptive, bivariate, and multivariate. Descriptive techniques encompass those methods which find their use in analysing the data in order to determine its structure and applicability before more complex bivariate and multivariate analysis. Included in this classification are procedures that calculate means, medians, frequency distributions, degrees of skewness and kurtosis, and other interpretations of the shape of the distributions. The main bivariate method is a simple linear least squares regression, which develops the best line through a series of points. This technique is normally used in determining the relationship between two variables, although it also finds use in developing

calibration curves for the various chromatographic methods. Multi-variate techniques in some instances, such as multiple regressions, can be considered as extensions of bivariate techniques, while in other instances perform functions which are totally apart from those encountered in bivariate methods. Two methods utilized in this work fall into this second class. Cluster analysis, which is used to segregate members of a statistical set into subsets based on their characteristics, is the first of these. The second and more heavily used in this work is factor analysis, a grouping of separate techniques all having the function of extracting hypothetical factors from a data matrix which explain a portion of the total variation of the data. These factors can subsequently be interpreted to gain under-standing of how a specific process depends upon a series of other characteristics.

Although a great deal of information can be gained through the use of bivariate methods, the great complexity of the data collected through the number of analytical techniques that can be applied to coal rapidly leads to the utilization of the more complex multivariate methods. In addition, Yarzab and coworkers (1979) have shown that the processes involved in liquefaction are dependent on the interplay of a number of characteristics or variables and therefore require multi-variate techniques for an adequate description. Factor analysis is one of these techniques that has shown great promise in determining the processes involved in coal liquefaction.

Factor analysis is a technique which has as its purpose the anal-ysis of structure within the variance-covariance matrix of a data set.

The initial developmental stages of the method took place during the 1930's and 1940's. It was believed by experimental psychologists of the time that although a single test could not be used to ascertain a person's intelligence, one's score was related to his or her mental ability, along with education, cultural background and environmental circumstances surrounding the test situation. Thus, by utilizing a number of test scores it was thought that factor analysis was capable of extracting an abstract or idealized intelligence factor.

Several of the assumptions used by the early workers in the field of psychology do not lend themselves to the transfer of the technique to other disciplines, and a great deal of the more recent work in the factor analysis area has been devoted to circumventing these problems. The most prominent problem that is encountered in transferring the method is determining the number of factors to be extracted. The early workers had a preconceived idea or model which set the number of factors. In other fields this knowledge does not normally exist and methods have had to be developed such that criteria could be set up for factor retention.

The first problem that is encountered when a factor analysis is performed is whether the data should be standardized. As a general rule whenever the measurements that comprise the data matrix have been made, utilizing different methods, standardization of the variables is required. Although a discussion of the various methods of normalization is beyond the scope of this report, it is important to point out that normalization is necessary for data sets such as the ones utilized here.

CHAPTER III

EXPERIMENTAL PROCEDURES

A. INTRODUCTION

The experimental procedures described in this chapter have been divided into three groups depending on whether they were used in the characterization of the liquefaction products, the determination of coal properties or the statistical analysis of the data. The overall analysis scheme is shown in Figure 2. Although most of the techniques used were not new, many were modified significantly, in ways that will be detailed in the following sections.

B. SAMPLE SELECTION

The sample selection was essentially based on the cluster analysis of Yarzab et al. (1980). All of the coals in the PSU Sample and Data Base, except for those from the Alaskan and Pacific provinces having a PSOC number greater than 349, a mineral matter content less than or equal to 20 percent and being in one of the high volatile bituminous rank classes, were assigned to one of three groups using the equations set up by discriminant analysis (Yarzab et al., 1981). The actual coals to be used in the study were then hand selected from those that had been assigned to group 2 (high sulfur and medium rank) such that their distribution of carbon and sulfur contents and their ratios of pyritic to organic sulfur were as uniform as possible.

C. SAMPLE PREPARATION

The coals selected using the procedure described in the preceding

EXPERIMENTAL METHODS USED IN STUDY OF THE RELATIONSHIP
OF LIQUEFACTION PRODUCTS TO COAL CHARACTERISTICS

COAL

LIQUEFACTION

FTIR
CP-MAS
ACETYLATIONS
PTFA (GC/MS)

GASES
GC
GC/MS

FACTOR ANALYSIS
LINEAR REGRESSIONS

OILS   ASPHALTENES RESIDUE

ALIPHATICS   N COMPOUNDS
        AROMATICS   O COMPOUNDS

GC
GC/MS
FTIR
HPLC
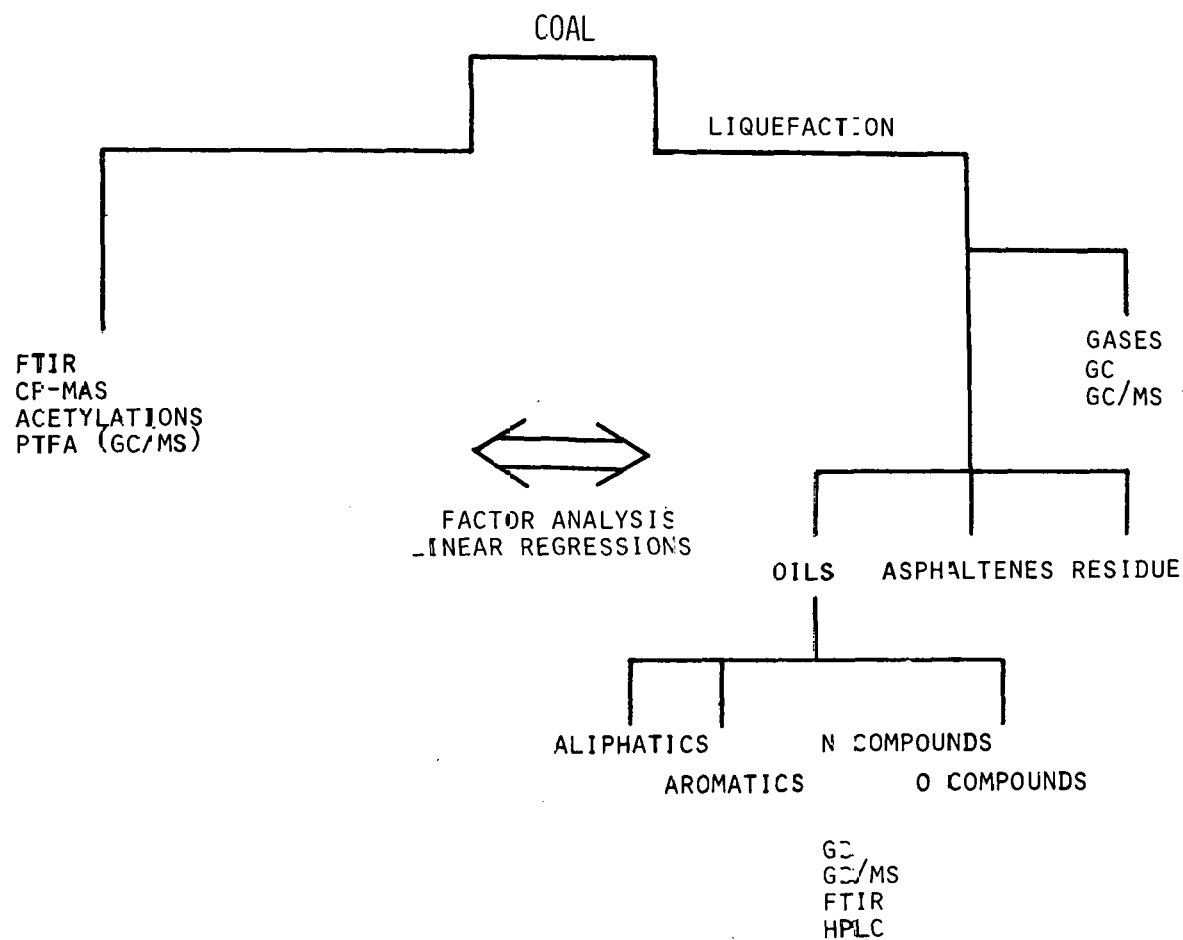
Figure 2. SUMMARY OF EXPERIMENTAL PROCEDURES AND ANALYTICAL METHODS USED

section were obtained from the PSU Sample and Data Base. Fresh cans of coal were used except for PSOC 666 and 773 where they were unavailable. Samples of these two coals were taken from our laboratory stock supply which, although opened, had been throughly purged with nitrogen before storage in a sealed container. Each new can was opened, the contents removed, riffled (ASTM, 1974a), coned and quartered (ASTM, 1974b), into three representative samples. One of these samples was used for the liquefactions, High Temperature Ash (HTA), Low Temperature Ash (LTA), and Fourier Transform Infrared Spectroscopy (FTIR). The second sample was used for the trifluoroperoxyacetic acid (TFPA) oxidations, and the third for the cross-polarization magic-angle-spinning nuclear magnetic resonance spectra (CP-MAS nmr) and sulfate analysis. Each of the samples was fluidized with nitrogen to remove atmospheric oxygen, sealed, and stored in a desiccator until needed.

D. LIQUEFACTIONS

The liquefactions were performed in an apparatus that has been described elsewhere (Szladow, 1979). The system, which is shown schematically in Figure 3, is composed of a reaction bomb with a gas-tight valve, a fluidized bed sand-bath, a shaker or agitator assembly, and a gas-tight manifold. The bombs are made from a stainless steel pipe with Swagelock end fittings and a long-stemmed gas tight valve, to facilitate purging and pressurization (Figure 4).

Each coal (-20 mesh) was dried at 110°C for one hour in a vaccum oven and stored in a desiccator. 2.5 g. of two different coals were weighed out and added to the two bombs. Any of the coal adhering to the weighing paper was rinsed off with 7.5 ml. of tetralin (Fisher Scientific Co., Pittsburgh, Pa.). The bomb was then mounted in the
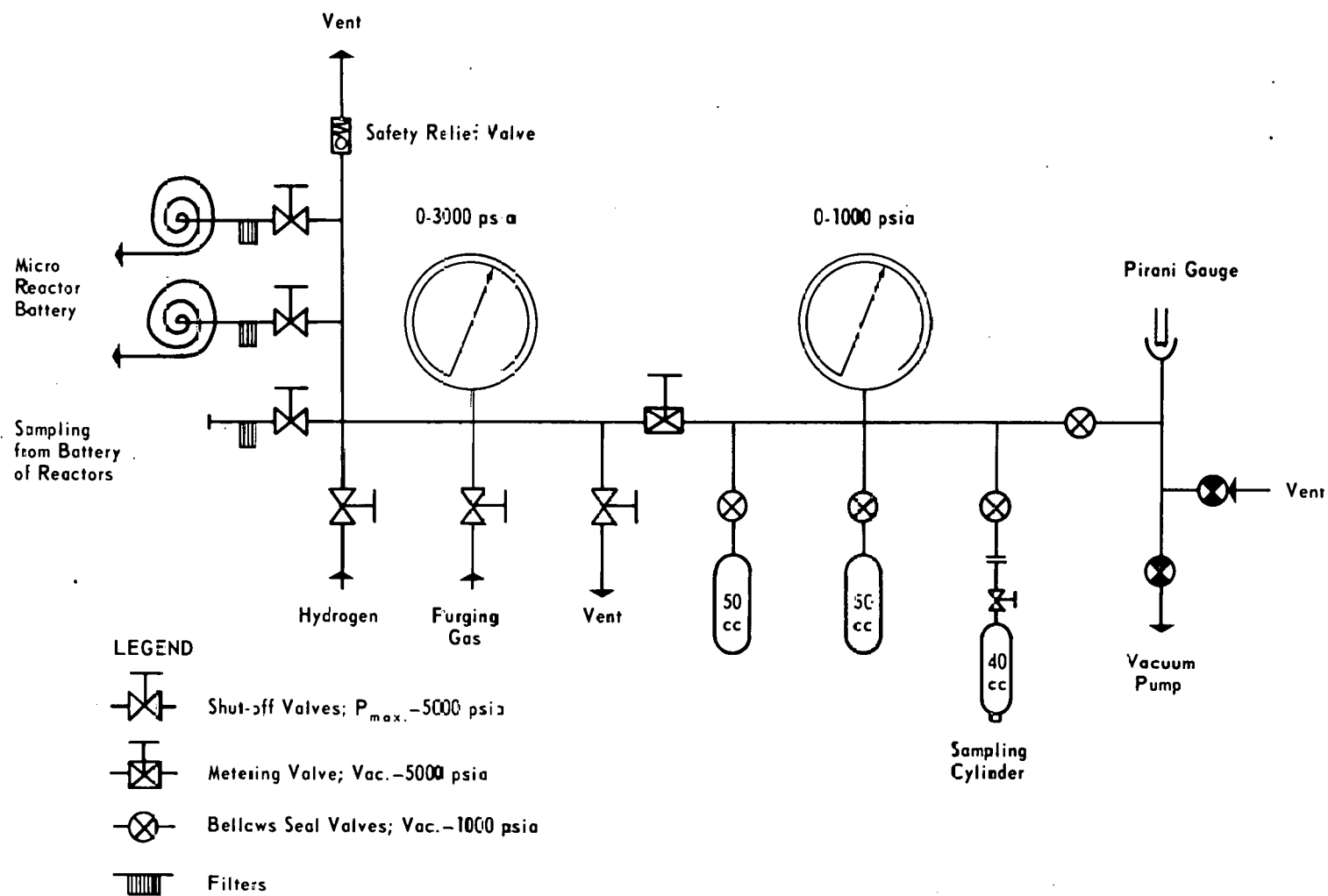
Figure 3. SCHEMATIC DIAGRAM OF LIQUEFACTION APPARATUS
(from Szladow, 1979; pressures are those stated by manufacturers; 1MPa ≡ 145 psi)
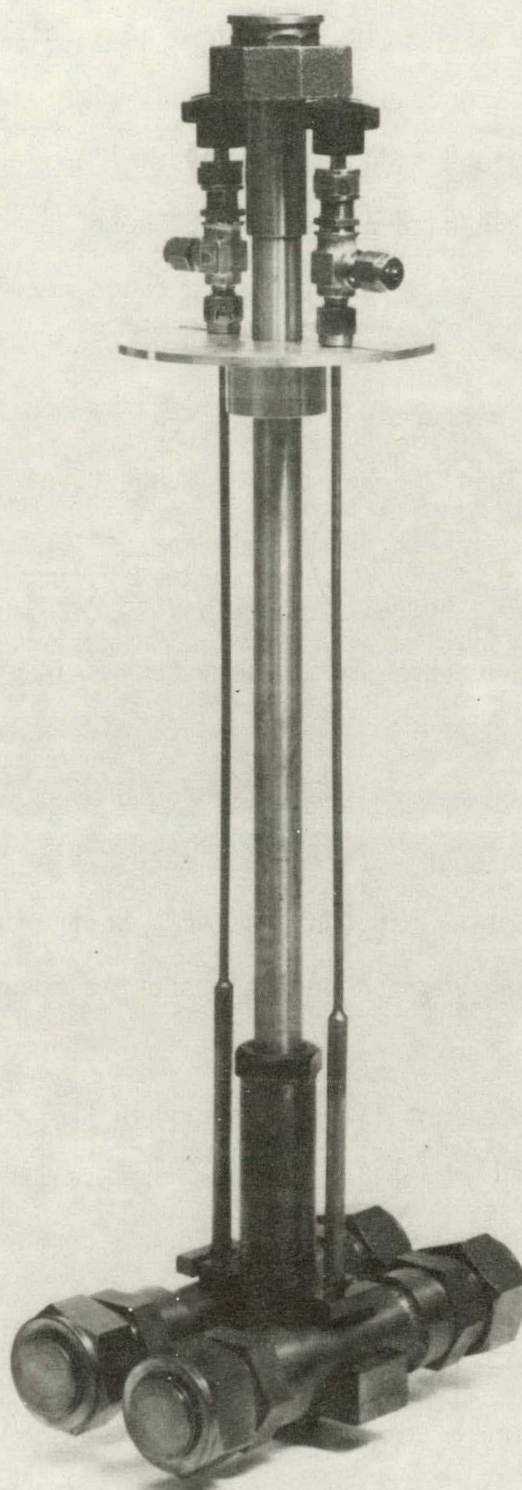
Figure 4. GENERAL VIEW OF MICROREACTOR MOUNTED ON HOLDER (CRADLE)

shaker and gas lines connected. The bombs were purged three times by pressurizing to 1000 psig. with hydrogen, followed by a slow venting. They were pressurized one final time and the hydrogen was turned off on the tank side of the pressure gauge. A period of about 10 minutes was allowed to be sure that there were no leaks, which would be indicated by a drop in the pressure gauge reading.

If no leaks were observed, the valves on the bombs were closed, the shaker set to perform 150 agitations per minute, and the bombs immersed in the fluidized bed bath. Other studies have shown that the reaction vessels reach their maximum temperature within two minutes of being immersed. The bombs were allowed to remain at 425°C for 30 minutes, then removed and immediately cooled in cold water; and the contents were given 30 minutes to equilibrate at room temperature.

The gases were removed from each bomb by allowing small amounts of gas to drain through a three centimeter Tygon tube into a 5 liter Teflon coated sampling bag (Anlabs Inc., North Haven, Conn.). After each portion of the gas had been transferred about 5 minutes were allowed for the material remaining in the bomb to reequilibrate. This process was repeated until the pressure in the bomb was equal to atmospheric . The Teflon sampling bag was then sealed and saved for the analysis of the gases, which was performed as rapidly as possible after sampling.

The material remaining in the bomb was dispersed in ethyl acetate, a process involving a combination of scraping, washing, and sonicating. The material removed from the bomb was then filtered through a tared 30 mm. x 80 mm. alundum extraction thimble. The material remaining in the thimble was extracted with ethyl acetate in a Soxhlet apparatus

under a nitrogen atmosphere for 24 hours. The residue was dried at 100°C in a vacuum pistol for 24 hours, cooled in a desiccator and weighed. The ethyl-acetate-soluble fraction was concentrated by rotary evaporation at 80°C and a pressure of approximately 20 mm. 250 ml. of hexane were then added to the remaining material, the resulting mixture was sonicated for 15 minutes, purged with nitrogen, and allowed to stand for 24 hours. The undissolved material (asphaltenes) was removed by vacuum filtration, dried under vacuum in a drying pistol and weighed. The hexane was removed from the remaining material by rotary evaporation to leave the oils (ethyl-acetate-soluble and hexane-soluble). The oils were then weighed, purged with nitrogen, sealed and stored at reduced temperature in the dark until needed.

The preceding scheme (also see Figure 5) separated the products of liquefaction into four fractions, the gases, or that material in the vapor phase in equilibrium with the product mixture at room temperature and pressure, the asphaltenes, where the materials are soluble in ethyl acetate yet insoluble in hexane, the oils, which are soluble in both ethyl acetate and hexane, and the residue or ethyl-acetate-insoluble material.

E. PRODUCT ANALYSIS

Once the initial separation of the liquefaction products was complete, the gas and oil fractions were further analyzed using the methods described in this section. The analysis of the gases was performed immediately after the liquefactions, but the vacuum distillation determination of the naphthalene/tetralin ratio, and the HPLC deparations, were not begun for several months. During this period the oil fraction, still containing

LIQUEFACTION PRODUCTS

|

——————————— PRESSURE RELEASE

| |

GASES ETHYL ACETATE EXTRACTION ——————————

| |

| RESIDUE

———————— HEXANE PRECIPITATION

| |

| |

ASPHALTENES |

OILS + SOLVENT

|

|

VACUUM DISTILLATION ——————————

| |

| |

| TETRALIN/NAPHTHALENE

OILS MIXTURE

|

|

HPLC

|

|
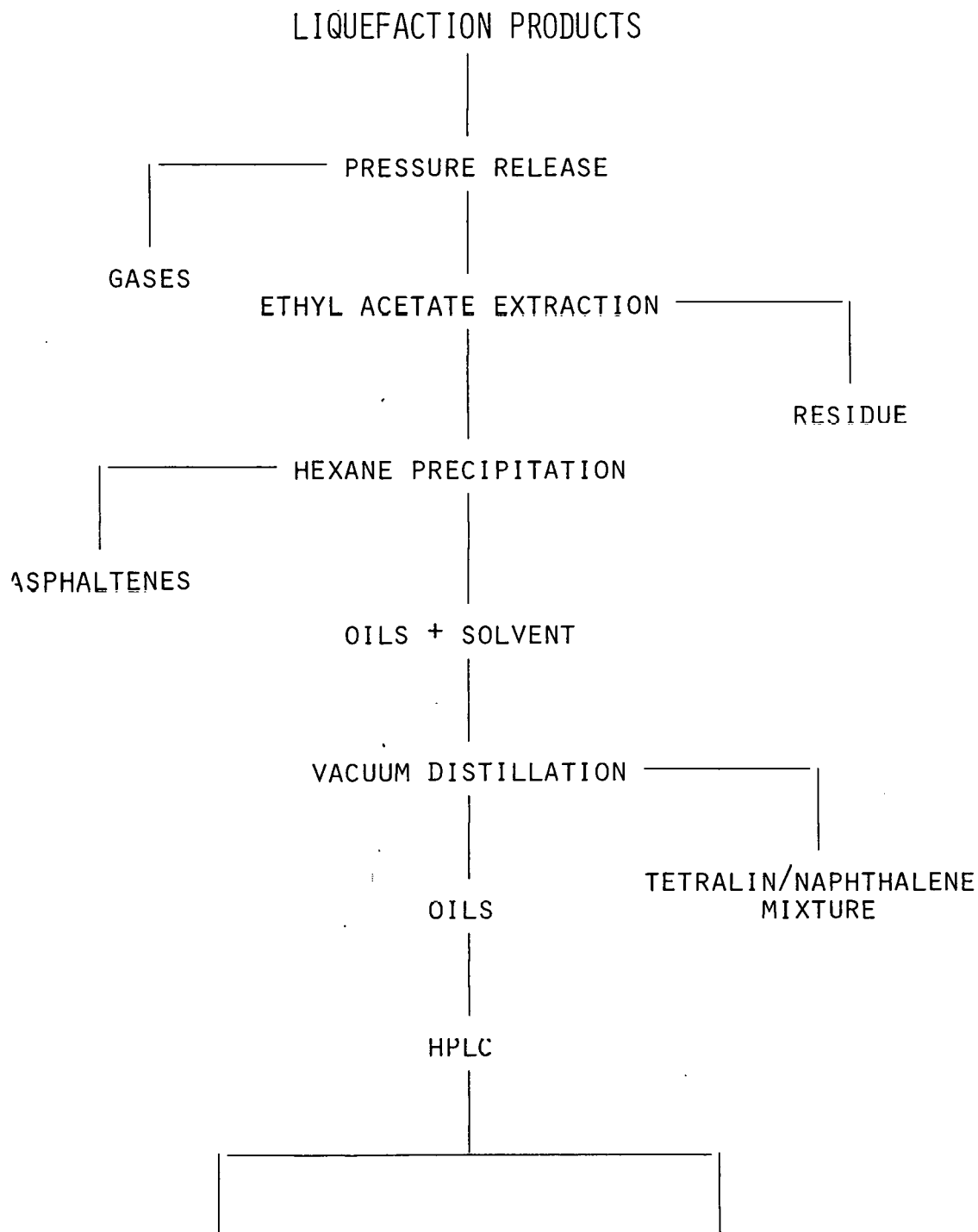
Figure 5. SCHEME USED IN SEPARATION OF LIQUEFACTION PRODUCTS

Table 2. Conditions Used in the Analysis of Gases
Produced During Liquefaction
injector temperature 250° in all cases

Permanent Gases

Column	Carbosieve S (3m)
Detector	TCD (250°C)
Carrier	He (20ml/min)
Temperature Program	35°C for 2 min., 10°C/min to 140°C, 140°C for 5 min.

Hydrocarbon Gases

Column	Duropak (6 ft)
Detector	FID (250°C)
Carrier	HE (20ml/min)
Temperature Program	35°C for 2 min., 10°C/min. to 140°C, 140°C for 5 min.

Hydrogen Gas

Column	Carbosieve S (cm)
Detector	TCD (250°C)
Carrier	Ar (17ml/min)
Temperature	Isothermal at 40°C

Hydrogen Sulfide

Column	Carbosieve (3m)
Detector	TCD (250°C)
Carrier	Ar (20 ml/min)
Temperature	Isothermal at 140°C

the tetralin/naphthalene mixture, was stored in sealed vials, under nitrogen, in a refrigerator in the dark. It was thought that these storage conditions would eliminate the retrogressive reactions that are known to occur during the storage of coal liquids.

a. Gas Analysis

In order to determine the amount of gas produced under liquefaction conditions the composition of the gas was analyzed by gas chromatography (GC) and the volume determined using a wet test meter. By using the composition and volume information the total amount of gas produced could be calculated. The sampling procedure has been described in Section D of this Chapter, so the discussion here will begin with the GC analysis.

The Varian Model 3700 gas chromatograph (Varian Assoc., Palo Alto, Calif.) was configured in such a way that both the flame ionization (FID) and thermal conductivity (TCD) detectors could be used to monitor the effluent from separate columns simultaneously. The FID was used to analyze the hydrocarbon gases (excluding methane) while the TCD was used for H_2, CH_4, CO, CO_2, and H_2S. Two carrier gases were used, argon when hydrogen was being analyzed and helium for all of the remaining gases. The signals from both detectors were recorded on a strip chart recorder (Fisher Model 5000). The columns used included a 180 cm x 3 mm O.D. stainless steel tube packed with GC Durapak n-Octane/Porasil C (Waters Associates, Inc., Milford, Mass.) for the hydrocarbons and a matched pair of 275 cm x 3 mm O.D. stainless steel tubes packed with 60/80 mesh Carbosieve B (Supelco., Inc., Bellefonte, Penna.) for the remaining gases. Table 2 lists the actual conditions under which each gas was analyzed.

Two procedures were used, depending on the number of analyses to be performed simultaneously. If only one analysis was to be performed the conditions on the GC were set to their proper values and allowed to equilabrate. The gas was removed from the sampling bag through its septum, using a locking gas-tight syringe (Hamilton Co., Reno, Nev.) and injected into the proper injection port of the GC. If more than one analysis was to be perfored simultanously each sample was removed from the sampling bag, injected into their respective injectors and the temperature program started.

Quantification of each gas involved the use of standard mixtures (see Figure 6) and, for H_2S, relative response factors, followed by peak integrations using Formula 1. In this formula A is the peak area and h is the height from the baseline and w is the width at half height. Willard et al. (1978) report that this formula accounts for 90 percent of the peak area for normally encountered chromatographic peaks.

$$A = 1/2hw \ldots \ldots \ldots \ldots \quad (1)$$

Complete sets of standards were analyzed and calibration curves generated each week while single standards were run each day to be sure that instrument response factors had not changed.

Once the GC analysis of each sample was complete the volume of gas remaining in the sampling bag was measured by forcing the gas through a wet test meter. This process was accomplished by connecting the valve of the gas sampling bag to the wet test meter with a short (2-3 cm.) piece of Tygon tubing and forcing the gas out of the bag and through the meter. The entire process took less than two minutes, and so dissolution of the gases in the water contained in the meter was assumed to be unimportant. The

Mix Number	Compounds	Amounts ppm by volume	Remarks
1	methane	15.1	±10%, in nitrogen supplied by Supelco Inc.
	ethane	14.6	
	propane	15.6	
	n-butane	15.2	
	n-pentane	15.6	
	n-hexane	15.9	
7	cyclopentane	15.7	±10%, in nitrogen supplied by Supelco Inc.
	methylcyclopentane	16.1	
	cyclopentane	16.7	
	methylcyclohexane	15.9	
32	methane	8.77	±5%, in air, supplied by Supelco Inc.
	ethane	9.42	
	propane	9.59	
	isobutane	9.33	
	n-butane	9.13	
218	methane	0.969	±2%, in nitrogen supplied by Supelco Inc.
	carbon monoxide	0.969	
	carbon monoxide	0.992	
	hydrogen	0.961	
	oxygen	0.997	
19331	ethylene	1000	in helium supplied by Applied Science Laboratories, Inc.
19339	propylene	1000	in helium supplied by Applied Science Laboratories, Inc.

Figure 6. CHART OF STANDARDS USED IN THE ANALYSIS OF GASES
FROM LIQUEFACTION

volume of gas as measured with the wet test meter was then added to that removed for analysis to obtain the total volume of gas produced during the liquefaction.

The amount of each gas produced, V_i, was then calculated by multiplying the percentage of each gas, X_i, by the total volume of gas collected, V_t, (corrected to standard temperature and pressure), using Formula 2.

$$V_i = (X_i/100) \ (V_t) \ \ldots \ldots \ldots \ldots \ldots \ldots \quad (2)$$

The corrected percentages of gas produced could then be calculated, by assuming that all of the nitrogen and hydrogen in the product gas mixture resulted from atmospheric contamination and initial liquefaction atmosphere respectively, using Formula 3.

$$V_i' = V_i \ (V_t/V_x) \ \ \ldots \ldots \ldots \ldots \ldots \ldots \quad (3)$$

Where V_x is the total volume of gas less that attributed to hydrogen and nitrogen.

b. Vacuum Distillations

Each hexane-soluble fraction was distilled at reduced pressure using a spinning band column (B/R Instruments Corp., Pasadena, Maryland) to remove the tetralin and naphthalene. The actual operation of ther distillation column has been described elsewhere (Zoeller, 1984) and so only a brief discussion is needed here.

A spinning band column has a motor driven twisted band whose function is to increase vapor-liquid contact during the distillation. As the band is rotated it brushes the walls of the column, mixing the vapor and liquid. The band is also pitched in such a way as to constantly move the condensate down towards the pot in a given time. The distillation was continued

until the crystallization of naphthalene on the walls of the receiver chamber appeared to be complete.

c. Determination of Tetralin/Naphthalene Ratios

To ascertain the amount of tetralin that had been converted to naphthalene during the liquefactions each hexane-soluble fraction was analyzed by GC prior to vacuum distillation. The analyses were run under the conditions shown in Table 3. The ratios of tetralin to naphthalene were then calculated by measuring the respective peak heights and dividing each by the experimentally determined response factors.

d. High Pressure Liquid Chromatography

Each oil was separated into three fractions using a Waters model ALC/GPC 224 High Pressure Liquid Chromatograph (Waters Associates, Milford, Mass.) equipped with a Model 400 ultra violet (UV) and a Model R401 refractive index (RI) detector. The HPLC was also equipped with two Model 6000A pumps and a Model 660 solvent programmer to allow sol-vent-programmed separations to be performed. Although several different columns were tried, a coupled column configuration consisting of a Direct Connect guard column dry packed with pellicular NH_2 packing, an Adsorbasphere 5µ CN analytical column, and a Spherasorb 5µ NH_2, all supplied by Applied Science (State College, Pa.), was judged to give the best results.

In order to determine the retention times of the various classes of compounds, a series of standards was used (see Table 4). Each stan-dard was injected into the HPLC and the solvent program started at the same time. This program consisted of a logramithmic program from pure hexane to a mixture of methylene chloride with 5% methanol, a 3 minute

Table 3. Conditions for GC Analysis of Tetralin + Naphthalene

Isothermal hold of 30 m. SE30 glass capillary column at 140°C
Flow rate of helium, ca. 1 ml./min.; split ratio (vent/column), 30:1

Table 4. Compounds Used as Standards for Development
of HPLC Separation Procedures

Compound	Supplier
Aliphatic	
Cyclohexane	Fisher
n-Dotriacontane	Supelco
n-Eicosane	"
n-Hexatriacontane	"
n-Triacontane	"
Aromatic	
9,10-Benzophenanthrene	EDCAN Labs
3,4-Benzo-(a)-pyrene	K & K Labs.
9,10-Dihydroanthracene	Aldrich
2,3-Dimethylnaphthalene	EDCAN Labs.
Fluorene	Aldrich
Phenanthrene	Eastman
1-Phenylheptane	Unknown
Naphthalene	Eastman
Phenols	
2-Cyclohexylphenol	Mobil Research
1,2-Dihydroxybenzene	Eastman
2,6-Dihydroxytoluene	Aldrich
2,5-Dimethylphenol	Baker
2,6-Dimethylphenol	Eastman
3,4-Dimethylphenol	Baker
α-Naphthol	Eastman
n-propylphenol	Fisher
2,3,5,6-Tetraethylphenol	Unknown
Basic Nitrogen	
3-Isobutyl-quinoline	Unknown
Quinoline	Unknown
3-4 Benzoquinoline	Unknown
Nonbasic Nitrogen	
Carbazole	Fisher
Piperidine	Unknown
Oxygen Heterocycles	
Dibenzofuran	Aldrich
Xanthene	Aldrich
Xanthone	Aldrich

hold period with the methylene chloride mixture, followed by a step to pure methanol. All solvents were obtained from Fisher Scientific Co. and were filtered through a 5μm filter and sonically degased before each day's use.

The oil samples dissolved in methylene chloride from the vacuum distillation were filtered by forcing them through a 5μm filter with a gas-tight syringe. Once filtered the solvent was evaporated using a stream of dry nitrogen. After the solvent had been removed the sample was weighed and re-dissolved in approximately 1 ml. of methylene chloride. The sample was then injected into the HPLC and the solvent program started.

Three fractions were collected, using tared vials. The solvent was removed from each fraction under dry nitrogen and the remaining material weighed.

F. CHARACTERIZATION OF COALS

In the preceding sections the methods utilized in the separation and analysis of the liquefaction products were described. This section will focus on the analytical techniques utilized in determining the properties of the unreacted coals. Included in this section are high and low temperature ashing, which were used to investigate the amount of mineral matter present in the coal, TFPA oxidations which provide information concerning aliphatic structures, FTIR which when analyzed through the use of curve-resolving and acetylations measure specific functional groups within the coal, and CP/MAS nmr which is able to determine the fraction of aromatic carbon.

a. Ashing

The high temperature ashing (HTA) was performed following ASTM

Method D-3174 (1974). In using this method 16 samples could be ashed simultaneously. More samples could be fitted into the oven, but there appeared to be a large temperature variation between the front and back of the furnace so that only the back half was used. Each coal was ashed in duplicate, and re-ashed if replicate runs did not agree within 0.01 percent.

The method involved drying approximately 2g. of -40 mesh coal under vacuum at 110°C overnight. Two 1g. portions of the dried coal were transferred into tared porcelain crucibles and weighed. The crucibles containing the coals were placed in a cold muffle furnace, and gradually heated to redness. Care was taken to avoid loss of any material as the volatile matter was released. The crucibles were held at 725° until they were at constant weight, cooled to room temperature in a desiccator and reweighed.

The Low Temperature ashings (LTA) were performed following the procedure described by Miller (1977). The LTA was a double chamber unit. Each sample was again ashed in duplicate, and re-done if the duplicates did not agree within 0.1 percent.

Approximately 1.5g. of -80 mesh coal was spread out evenly in a pre-weighed Pyrex Petri dish. The chamber was maintained at about 2 torr, the RF power set at 50w. and the oxygen flow rate to 100ml/min. The samples were stirred three times (every 2 and 1/2 hours) and the oxidation allowed to proceed for an additional 16 1/2 hours. At the end of the 24 hour period the samples were again removed, weighed, stirred and replaced in the asher for two hours. At the end of this period the samples were again removed and weighed. If the loss in weight was not

less than 2mg. the sample was again stirred and replaced in the asher. This process was repeated until the sample had lost less than 2mg. during a two-hour oxidation period. Extreme care was taken to prevent the loss of any of the ash during the stirring process.

b. Trifluoroperoxyacetic Acid Oxidations

Three different methods were used in performing the trifluoroperoxy-acetic acid oxidations. Only the actual oxidation procedure differed in each case, that is, the separations, esterifications, and analyses remained unchanged. The first method was developed initially by Deno et al. (1977), the other two were modifications of this method made in an attempt to preserve long-chained aliphatic materials within the coals but thought to be not stable under the conditions originally used.

The three oxidation procedures will be described initially followed by a description of the separation, esterification and analysis procedures. The first and third oxidation procedures were tested on a sample of PSOC-666 to get some idea of the way the coals reacted under these conditions. The second procedure, which was judged to be superior in preserving any long aliphatic chains, was applied in duplicate to each of the 26 coal samples.

The first procedure involved the production of the oxidizing reagent by mixing 8 ml. of trifluoroacetic acid, 10 ml. of 30% H_2O_2 and 5 ml. of H_2SO_4 in a 50 ml. round bottomed flask. The mixture was then cooled in an ice bath and approximately 0.5 g. of coal added. If the reaction appeared to be occuring too rapidly during the addition, the flask was again cooled in ice water. The reaction mixture was then heated for three hours before cooling in ice water, adding 0.25g. of 5% Pt on

asbestos to decompose any peroxides, and checking with KI paper to be sure that all of the peroxides had been broken down. If a positive KI test was observed, a second 0.125g. portion of the 5% Pt on asbestos was added and the KI test re-done. This process was repeated until a negative KI test was obtained.

The second procedure used an oxidizing reagent produced by mixing 8ml. of trifluoroacetic acid, 10ml. of hydrogen peroxide, 5ml. of sulfuric acid, and 20ml. of chloroform. The two-phase mixture was again cooled in ice water, 0.5g. of coal added, and the mixture refluxed for four hours. At the end of this reflux period the Pt was added and the KI test performed. The process was again repeated until a negative KI test was encountered.

The third procedure used the same amount of coal, hydrogen peroxide, sulfuric acid, and trifluoroacetic acid as the first two, except that the hydrogen peroxide was added dropwise through an addition funnel to the trifluoroacetic acid-sulfuric acid coal mixture. This was accomplished by adding a drop of hydrogen peroxide and alternately placing the reaction vessel in either an oil bath (60°C) or an ice bath in order to keep the temperature as close to 60°C as possible. This addition took approxi mately 45 minutes to complete. After all of the hydrogen peroxide had been added the reaction mixture was heated in the oil bath for four hours. At the end of the reaction period, the vessel was cooled and the remaining peroxides quenched in the same manner as described in the previous two sections.

Once the oxidations were completed, 0.25g. of trimethylacetic acid (Aldrich Chemical Co., Milwaukee, Wis.) was added, and the remaining

solids removed by vacuum filtration. Once removed, the solids were air dried at room temperature before weighing. The filtrate was rotary evaporated at 90°C under vacuum to remove the water and trifluroacetic acid, and a sample of the distillate, dried over $CaSO_4$, was analyzed for acetic acid using ^{1}H nuclear magnetic resonance spectroscopy (nmr). If chloroform had been added to the reaction mixture (procedure 2), it was removed by vacuum rotary evaporation at 30°C, before a sample was taken for nmr analysis. Once the sample had been taken, the material was vacuum rotary evaporated at 90°C to remove the trifluoroacetic acid and water.

From this point on, the carboxylic acid mixtures produced by the three oxidation procedures were treated identically. The acid mixture that remained after the water and trifluoracetic acid had been removed were esterified by adding 5ml. of BF_3 in methanol (Aldrich Chemical Co.) and refluxing for 3 hours. The methyl esters were then extracted with three portions (two of 30ml. one of 40 ml.) of methylene chloride (Aldrich Chemical Co.). The methyl esters in methylene chloride solution were washed with a 100ml. portion of 10% $NaHCO_3$ and two 100ml. portions of saturated NaCl solution. The methylene chloride solution was transfered to a 250ml. boiling flask containing approximately 4g. of anhydrous $CaSO_4$, sealed and allowed to stand for 24 hours. The $CaSO_4$ was removed by vacuum filtration through a fritted glass filter, and the methylene chloride removed by vacuum rotary evaporation at 60°C. The methyl esters were re-dissolved in 10ml. of methylene chloride and stored until needed.

Analysis of the methyl esters was by GC/MS (Finnigan Model 3000), utilizing the Grob injection technique. The purpose of this injection

method is to separate the volatile solvent from the sample. The technique involves volatilizing the sample in the injector, and allowing a 30 second period for the volatilized material to reach the column. The split valve is then opened, so that the volatilized solvent is purged to the atmosphere. The chromatographic separation utilized a 50 m. J&W DB-5 column in an oven programmed to hold for 5 minutes at 50°C and then to heat at 6°C/min to 280°C.

c. Fourier Transform Infrared Spectroscopy

The FTIR spectrum was taken for each LTA sample, acetylated coal and whole coal. The overall procedure involved the same steps for each sample type, so that only one discussion is needed. However, slight differences in the technique as it was applied to the various sample types will be noted in the text. A detailed discussion of the acetylation method is also provided at the end of this section.

1. Determination of Spectra

Exactly 1.3 mg. of the dry sample was mixed with 300 mg. of dry KBr. In the case of the LTA the sample was used as produced, while the coal and acetylated coal samples (-100 mesh) were dried under vacuum for 24 hr. before mixing with the KBr. The KBr was dried in a laboratory oven at 150°C for 48 hours and cooled in a desiccator before mixing. The sample + KBr mixture was ground further with an agate morter and pestle to ensure proper mixing. The mixture was transferred to a Perkin-Elmer Wig-L-Bug, and ground for exactly 30 seconds. The sample was transferred to a pellet press with an evacuable die and pressed at 14,000 psig. Pellets were stored in a vacuum desiccator until the spectra could be recorded.

The spectra were recorded utilizing a Dililab 15B FTS FTIR

spectrometer. Each spectrum was formed by co-adding 400 scans (inter-ferograms) at 2 cm^{-1} resolution. Since the spectrometer was a single beam instrument and the samples were not run under vacuum, a previously col-lected reference spectrum was subtracted from each sample spectrum. Instrumental scheduling considerations normally limited the number of samples per reference to five. Each corrected spectrum was stored on magnetic tape for further analysis.

The spectral analysis techniques used have been discussed in great detail by Painter et al. (1982) and so only a brief discussion is needed here. The initial stage of this procedure involved subtraction, of the LTA spectrum from that of the sample in the region of interest. Although it would have been preferable to have been able to correct the entire spectrum, it was found that differences in the slope of the baseline induced by scattering made this impossible. The second step was to take the second derivative of the spectrum to determine the location of the peak maxima in the region of interest (Kuehn, 1983). This information was needed to ensure that artefact peaks not actually present in the spectrum were not included in the resolved spectrum.

Curve resolving is simply the experimental derivation of calculated curves to match those present in an actual spectrum. The procedure used involves an iterative least squares fitting of a specified number of theoretical curves to match the experimental ones (Kuehn, 1983). In practice the mathematics of the procedure is transparent to the user, requiring only the accurate definition of the number of peaks in the region and an approximation of the width at half height, the area and the relative importance of Gaussian and Lorentzian shapes.

2. Coal Acetylations

In order to determine the amount of OH functionality, each coal was acetylated using a procedure developed by Szladow (1979) and used more recently by Youtcheff (1983). The coal was ground to -80 mesh in a cryogrinder at 90° K in a nitrogen atmosphere before and stored under nitrogen before use. The acetylation procedure was relatively rapid in that 13 samples and 4 standards could be run simultaneously. All of the reagents were used as supplied except for the pyridine, which was distilled and stored over KOH.

Exactly 5.0g. of the coal to be analysed was added to exactly 6 ml. of the reaction reagent, a 1:8 mixture of acetic anhydride (Fisher Scientific Co.) and pyridine (Baker Chemical Co.), and any coal remaining on the weighing paper was washed off with 6 ml. of pyridine. The sealed reaction flasks were placed in an oil bath at 90°C for 24 hours. Each flask was shaken twice during the 24 hour reaction period.

After the reaction was complete the flasks were allowed to cool to room temperature, and the acetylated coal was removed by gravity filtration. The residue was washed with one liter of distilled water, dried at 110°C in a vacuum oven, and removed from the filter paper. The acetylated coal was then stored in a desiccator until the KBr pellet could be made for infrared examination. Acetic acid in the filtrate was titrated, to determine the amount of acetyl consumed.

d. Cross-polymerization Magic-Angle-Spinning ^{14}C Mass Spectrometry

The CP/Mass spectra of each of the whole coal samples were kindly provided by Dr. Gary Maciel at the Colorado Regional NMR Facility. The spectra were recorded on an nmr spectrometer with a contact time of 1 ms

and a repetition time of 0.5 seconds. The number of scans varied from 18000 to 56,000.

G. STATISTICS

Two computer packages were used in the statistical analysis of the data. The SAS package (SAS Institute Inc., Cory, N.C.) was used for the initial factor analysis. Additionally the ARTHUR81 package (Infometrix, Inc., Seattle, WA) was utilized in the grouping analysis and later factor analysis.

CHAPTER IV

RESULTS AND PRELIMINARY DISCUSSION

A. INTRODUCTION

In the previous chapter, the experimental procedures utilized in this work were described. However, very little was stated concerning the logic behind their application or the results they provided. This chapter will present the rationale behind the experimental techniques, and a general discussion of the results. Emphasis will be placed on the development of each method, the characteristics of the data and any limitations such as reproducibility and accuracy. Although a good deal of information will be presented in regard to the structure and composition of the coals and their liquefaction products, the overall interpretation of the data will be for the most part left for the following Chapter where various statistical procedures will be applied. This approach was deemed necessary due to the complexity of the statistical analysis and the need to use data from several techniques at once.

The first two sections of this Chapter will address the question of how well the analysis in the data base represent the sample set as a whole. Of special concern will be the discussion of the possibility of oxidation having occurred since the samples were last tested. This is of interest not only because of the effect on the properties of the coals themselves but also on how they react under liquefaction conditions. The second section will cover the analyses of the various product fractions, including oils, asphaltenes, gases and the subfractions of these classes of products. Finally the last section will cover the analyses of the

structural features of the original coals, by such techniques as Fourier Transform Infrared Spectroscopy (FTIR), Cross-Polarization-Magic-Angle-Spinning Nuclear Magnetic Resonance Spectroscopy (CP/MAS) and trifluoro-peroxyacetic acid oxidations (TFPA)

B. ASH YIELDS AND MINERAL MATTER CONTENTS

High temperature ash yields for all samples are recorded in the Penn State Data Base. They have been re-determined in duplicate on the splits actually used in this study. The two sets of data are compared in Table 5. The mean value of the differences between corresponding pairs of data is 0.048 (omitting the data for PSOC 664 and 768), and the standard deviation around this mean is 0.97. That is, viewed as a set the agreement is very close, but there are a number of quite large individual differences (in 10 cases $|\Delta|>1\%$, where $|\Delta|$ is the numerical value of the difference). Thus in about 50-65% of the cases, the analytical data in the Data Base appear to be well representative of the samples used in this study, and in the remainder moderately so, with the exception of PSOC 664 and 768 where there is a wide divergence. Our experimental values of ash for these coals are evidently not seriously in error for our samples, since the mineral matter content calculated from this ash agrees well with the directly determined values.

The mineral matter contents, needed for converting other data to the dry, mineral-matter-free basis, were determined in duplicate by low temperature ashing, following the procedure of Miller et al. (1979). Also, the high temperature ash yields were combined with pyritic sulfur contents taken from the Data Base to calculate mineral matter

Table 5. High Temperature Ash Yields and Mineral Matter Contents

% of dry coal

Sample PSOC No.	High temp. ash		Mineral matter content	
	Data Base	this Study	calcd, modified Parr	Direct, by LTA
349	10.08	11.21	14.57	14.60
401	10.46	9.37	11.51	12.21
581	10.24	9.82	12.50	13.48
582	13.25	13.35	16.90	17.20
593	10.29	11.58	13.78	13.59
594	12.13	11.41	13.09	14.04
596	10.74	12.03	13.79	14.03
599	15.86	16.10	19.48	19.60
664	12.89	18.28	22.22	22.43
666	16.70	18.99	23.29	22.24
669	12.56	12.37	14.55	14.36
676	16.00	14.59	17.81	18.05
680	12.01	11.38	13.61	13.72
741	14.56	15.08	18.22	18.54
742	16.85	15.76	18.77	18.90
760	12.10	12.38	15.40	15.56
767	6.36	5.26	6.52	6.79
768	20.49	14.62	17.80	18.27
773	7.50	6.84	8.51	9.33
798	12.03	11.32	14.55	14.68
808	4.60	4.75	6.22	6.42
883	16.28	16.27	19.78	20.04
1018	12.16	11.00	13.61	13.83
1082	18.21	14.4	17.63	18.62
1083	7.53	7.24	8.52	8.65
1098	13.67	14.76	17.69	18.01

contents using the modified Parr formula (Given and Yarzab, 1978). Mean values of the direct and calculated mineral matter contents are included in the Table. The standard deviation of the duplicate direct determinations about the means is 0.41%, and the calculated values 0.51%. These values are not quite as good as those Miller et al. (1979) obtained (0.20 and 0.24% respectively). The amounts of unburnt carbon left after LTA were similar to those found by Miller and co-workers.

The data also permit a test of the modified Parr formula. This formula assumes that there is a single constant value for the water of decomposition of clays, that carbonates represent a constant 10% of total mineral matter, ignores sulfate fixation in ash, and assumes no quartz is present (Given and Yarzab, 1978). Yet the agreement here between calculated and directly determined mineral matter contents is remarkably good. The mean value of the differences between corresponding pairs is -0.264±0.418.

Mineral matter contents calculated by means of the modified Parr formula, using the original ash yields, are included in the Data Base printouts. The three sets of mineral matter contents (one direct and two calculated) are compared in histogram form in Figure 7. In all cases the direct determination yielded a value equal to or slightly greater than that calculated from high temperature ash. On the other hand the new calculated mineral matter contents were somewhat less than those reported in the Data Base.

The mineral matter contents used in the remainder of the work will in all cases be the directly determined values.
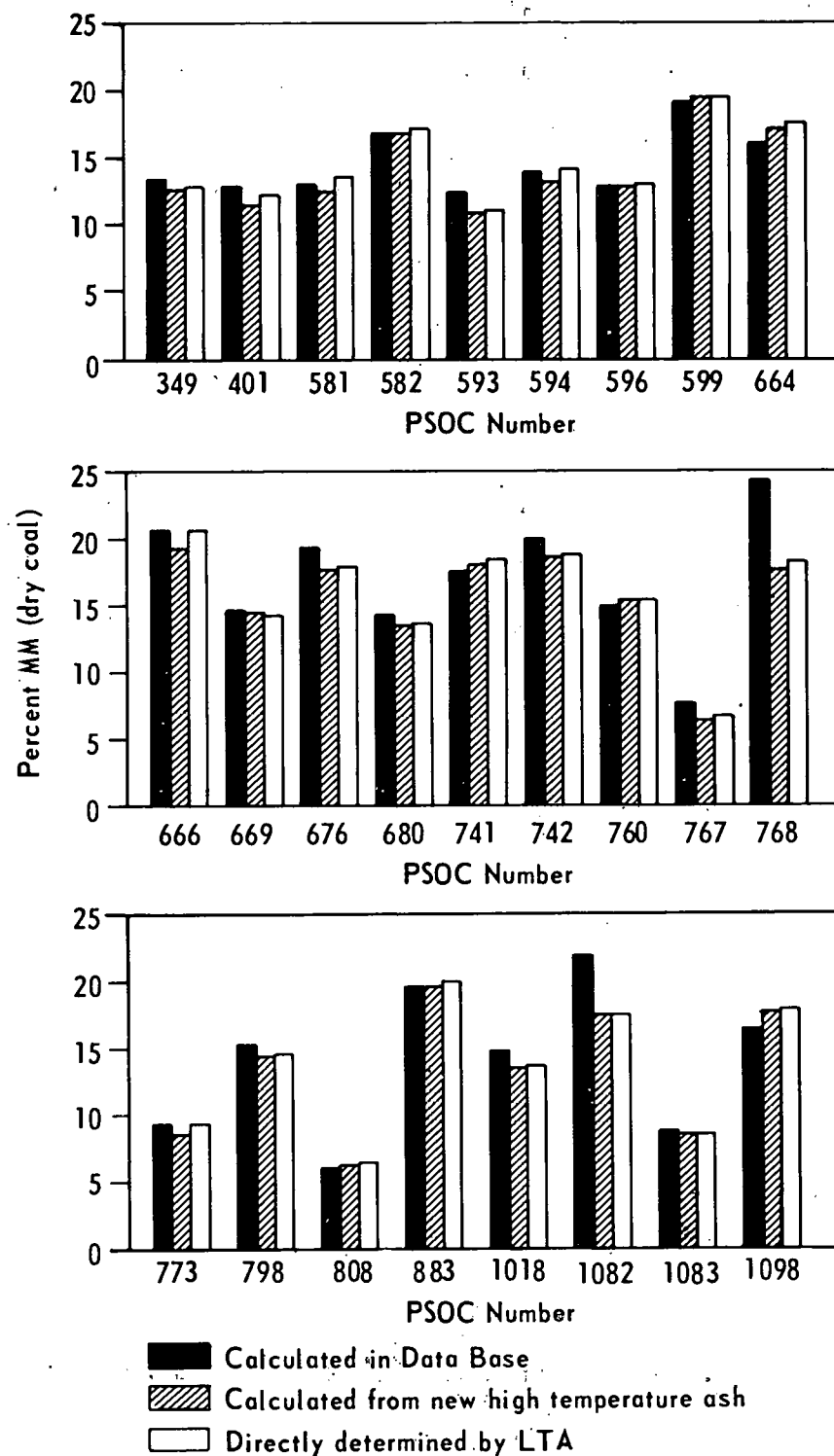
Figure 7. COMPARISON OF CALCULATED AND DIRECTLY DETERMINED MINERAL MATTER CONTENTS

C.   FTIR SPECTRA OF MINERAL MATTER

The infrared spectra of all of the low temperature ash samples were recorded, and an example is shown in Figure 8. Visual examination of the spectra shows that there are differences in the distribution of clay minerals and in the clay/quartz ratios. However, without applying the computerized spectral subtraction procedures of Painter et al. (1981a.), little more can be said. The spectra are available to interested persons from the Fuel Science Program in this College.

D.   CHARACTERISTICS OF COAL USED

The general characteristics of the samples used in this study are given in Table 6. The coals represented two provinces. Four of the coals are from the Appalachian region of the Eastern province while the remaining 22 represented either the Eastern (14) or Western (8) regions of the Interior province. The carbon contents on a dry mineral-matter-free basis (DMMF) range from 76.8 to 87.1 percent, the hydrogen contents (DMMF) from 5.17 to 6.52 percent and the oxygen as determined by difference (DMMF) from 7.21 to 14.35 percent. The ASTM rank classes ranged from HVC to HVA. Nine of the samples were in the higher HVA range, six represented the intermediate HVB range, and eleven were of the HVC class. Thus it can be said that the samples were fairly evenly distributed over the rank range studied. There was no segregation by rank on the basis of province or region, except that none of the coals from the Eastern province could be considered as being HVC.

The total sulfur contents of the samples ranged from a high of 4.26 percent to a low of 1.03 percent. There was no correlation between any of the various sulfur forms. Three of the coals (PSOC 664, 666 and 1082)
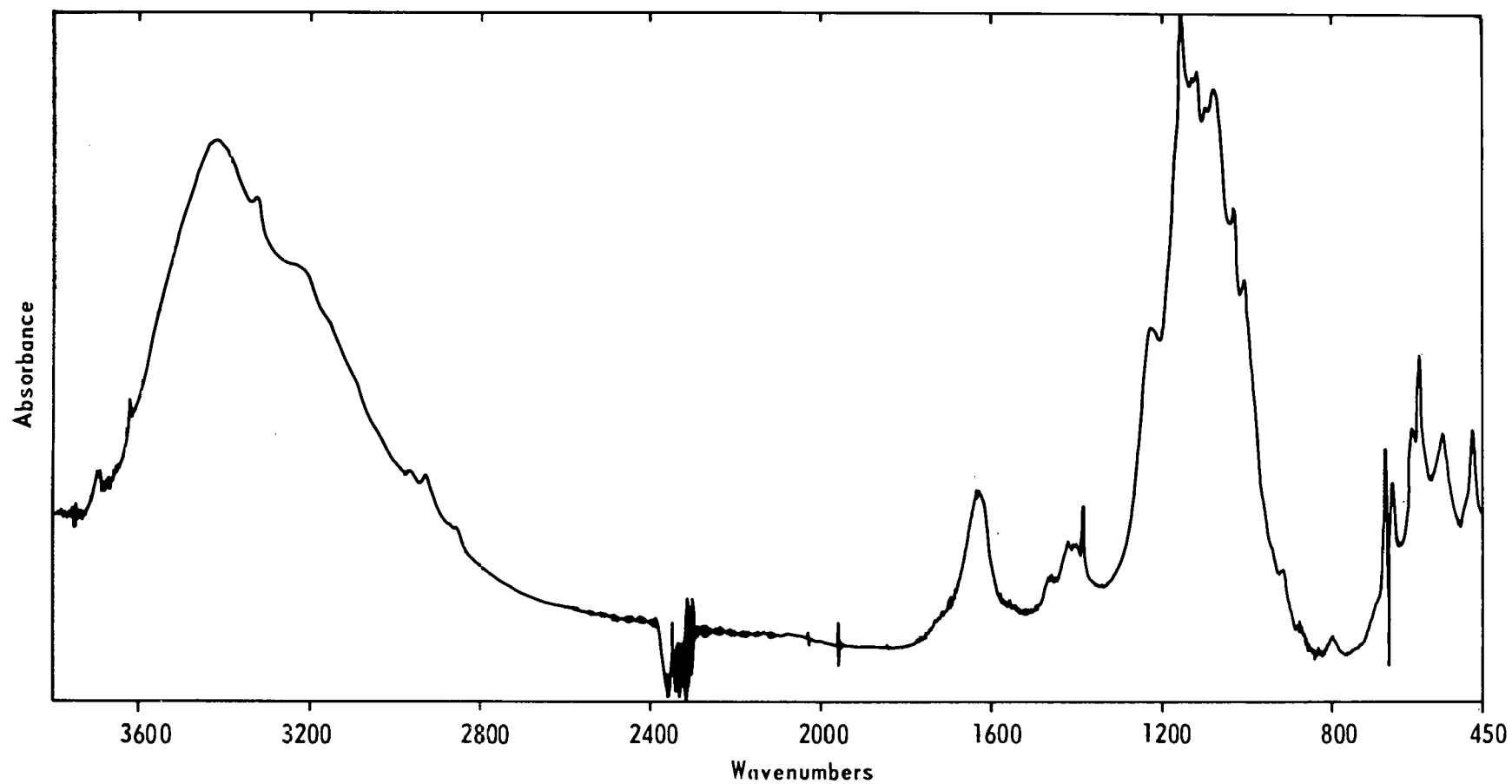
Figure 8. FTIR SPECTRUM OF LOW TEMPERATURE ASH FROM PSOC-666

Table 6. Selected Characteristics of Coals Used in This Study
(a) Sampling Sites and Chemical Analyses

PSOC NUMBER	SEAM NAME	STATE	PROVINCE REGION	ASTM RANK CLASS	DMMF %C	%H	%N	%S	%C	DRY COAL %S PYRITIC	%S SULFATIC	MOTT-SPOONER DIFFERENCE	CV DMMF
349	Lower Clarion	Penna.	East. App.	HVA	84.3	5.80	1.66	1.66	7.21	4.04	0.16	16	15642
401	Mineral	Okla.	Int. W.	HVA	82.6	6.52	1.56	1.38	8.95	1.96	0.18	-26	15576
581	Illinois #5	Ill.	Int. E.	HVB	80.6	5.59	1.14	2.77	7.79	2.98	0.02	48	14770
582	Illinois #5	Ill.	Int. E.	HVB	81.0	5.51	1.26	1.69	9.63	3.85	0.13	117	14844
593	Illinois #5	Ill.	Int. E.	HVC	79.9	5.33	1.47	2.62	11.00	1.47	0.16	100	14420
594	Illinois #5	Ill.	Int. E.	HVC	80.7	5.53	1.29	2.59	8.32	0.42	0.06	-139	14406
596	Indiana #7	Ind.	Int. E.	HVC	81.3	5.46	1.65	1.89	9.40	1.47	0.17	43	14677
599	Indiana #6	Ind.	Int. E.	HVC	81.4	5.17	1.52	2.10	9.35	2.73	0.37	30	14603
664	(Unnamed)	Iowa	Int. W.	HVC	76.8	5.26	1.28	4.26	11.86	3.33	1.25	205	14162
666	(Unnamed)	Iowa	Int. W.	HVC	77.3	5.72	1.30	3.95	10.07	3.90	1.51	-45	14297
669	Illinois #5	Ill.	Int. E.	HVC	79.0	5.37	1.46	2.82	11.17	1.22	0.22	143	14319
676	Indiana #6	Ind.	Int. E.	HVC	79.3	5.38	1.66	2.33	10.90	2.82	0.44	97	14402
680	Indiana #6	Ind.	Int. E.	HVC	79.3	6.25	1.77	1.94	10.31	1.60	0.32	32	14322
741	Kentucky #12	Kenty.	Int. E.	HVB	81.9	5.33	1.51	2.52	9.51	2.50	0.25	92	14900
742	Kentucky #11	Kenty.	Int. E.	HVB	82.7	5.25	1.46	2.51	8.50	2.05	0.11	85	14965
760	Lower Kittanning	Penna.	East. App.	HVB	81.2	5.68	1.25	2.02	9.40	3.01	0.40	-68	14785
767	(Unnamed)	Okla.	Int. W.	HVA	82.1	5.58	1.51	2.46	8.44	1.22	0.10	297	15217
768	Mineral	Okla.	Int. W.	HVA	85.4	5.75	1.46	1.76	7.36	2.73	0.29	-143	15614
773	Ohio #6	Ohio	East. App.	HVB	80.5	5.44	1.40	1.08	11.50	1.67	0.18	264	14640
798	Stigler	Okla.	Int. W.	HVA	87.1	5.28	1.68	1.13	5.30	3.75	0.31	87	15883
808	Croweburg	Okla.	Int. W.	HVA	84.2	5.59	1.77	1.39	7.25	1.82	0.08	-5	15286
883	Drywood	Missouri	Int. W.	HVA	84.9	6.05	1.04	1.30	6.96	2.97	0.44	-109	15687
1018	Lower Kittanning	Penna.	East. App.	HVA	83.5	5.47	1.36	1.59	9.64	2.52	0.22	228	15346
1082	Kentucky #11	Kenty.	Int. E.	HVC	78.6	5.39	1.62	2.91	14.35	2.88	1.04	-44	14201
1083	Kentucky #11	Kenty.	Int. E.	HVC	80.4	5.50	1.32	2.41	10.32	0.71	0.47	-160	14303
1098	Illinois #6	Ill.	Int. E.	HVA	83.0	5.64	1.51	1.91	9.13	2.16	0.27	-196	14967

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Table 6 (continued) Selected Characteristics of Coals Used in This Study
(b) Petrographic Analyses

PSOC Number	% of Dry Coal by Volume								
	Vitrinite	Pseudovitrinite	Fusinite	Semifusinite	Macrinite	Micrinite	Sporonite	Resonite	Cutinite
349	80.6	4.0	1.4	4.3	0.9	3.7	5.0	0.5	0.0
401	82.7	4.8	2.0	3.9	0.2	2.0	4.5	0.0	0.0
581	82.4	4.9	3.4	5.2	0.5	1.6	2.0	0.0	0.0
582	87.3	4.7	5.5	1.4	0.2	0.4	0.5	0.0	0.0
593	89.1	0.0	2.6	7.0	0.4	0.3	0.6	0.0	0.0
594	91.6	0.0	4.8	2.1	0.1	0.5	0.8	0.1	0.0
596	91.8	4.5	0.7	1.8	0.0	0.2	1.0	0.0	0.0
599	90.6	1.2	3.6	3.0	0.4	0.3	0.9	0.0	0.0
664	86.7	1.2	4.5	5.7	0.2	0.6	1.1	0.0	0.0
666	89.8	0.1	4.0	3.5	0.1	1.0	1.5	0.0	0.0
669	89.8	0.0	4.3	2.9	0.0	2.2	0.7	0.1	0.0
676	90.2	1.7	1.4	4.1	0.6	0.9	1.1	0.0	0.0
680	88.4	0.8	3.5	4.9	0.3	0.7	1.2	0.2	0.0
741	94.6	0.4	2.8	1.4	0.2	0.0	0.6	0.0	0.0
742	90.3	2.0	3.4	1.9	0.2	0.6	1.5	0.1	0.0
760	85.1	0.0	1.7	2.5	0.1	5.7	3.7	1.1	0.2
767	89.1	2.4	0.9	2.1	0.1	3.3	1.9	0.2	0.0
768	82.7	1.9	1.9	3.7	0.1	2.2	6.9	0.0	0.4
773	89.4	1.6	1.2	2.7	0.0	1.8	3.3	0.0	0.0
798	83.6	5.0	1.9	8.0	0.2	1.2	0.1	0.0	0.0
808	84.2	5.7	1.0	2.1	0.2	3.2	3.6	0.0	0.0
883	83.0	3.2	2.4	4.0	0.6	2.5	4.0	0.3	0.0
1018	82.2	3.2	3.3	5.6	0.6	1.3	3.7	0.1	0.0
1082	89.6	0.0	2.9	3.6	0.0	1.8	2.1	0.0	0.0
1083	93.3	0.3	1.9	1.7	0.1	1.3	1.3	0.1	0.0
1098	88.6	1.7	2.5	3.5	0.3	1.7	1.4	0.3	0.0

N.B. No sclerotinite or alginite
detected in any sample.

possessed uncharacteristically high sulfatic sulfur contents indicating that oxidation of the pyrite had occurred before the coal samples were collected. It is difficult to speculate what the relationship is between pyrite oxidation and oxidation of the organic portion of the coal. However, one would assume that if a significant amount of pyrite weathering has occurred some oxidation of the organic material has also taken place.

It seems to be true that unweathered coals in the upper part of the high volatile bituminous rank classes do not show absorption in the carbonyl region (1700-1750 cm^{-1}) of their infrared spectra (Given, 1984). The matter has never been clearly demonstrated on an adequate set of coals, but it is possible that unweathered coals of the HVC class from the Interior and Rocky Mountain provinces do show some carbonyl absorption. In the spectra of the coals studied here (to be presented later), most of the HVC coals and those of carbon content less than about 80.5%C (dmmf) do show a rather weak shoulder at about 1720 cm^{-1}, whereas those of higher rank do not (except for PSOC 349). Hence the carbonyl absorption shown by the low rank samples does not necessarily by itself imply weathering. The coals noted above as containing relatively high contents of sulfate are all of the low rank group, and here part of the carbonyl absorption may be due to weathering of the organic matter. Of the higher rank coals, only PSOC 349 (Lower Clarion Seam, Pa.) displays evidence of slight weathering.

Each of the coals can be considered as being vitrinite-rich, with none containing less than 80 volume percent on a mineral-matter-free-basis. The second most abundant maceral type was the inertinite group which tended to comprise less than 10 volume percent of the organic

portion of the coal. The dominant member of the liptinites was sporinite which in PSOC 349 accounted for 5% of the coal. One word of caution must be expressed about the maceral analyses which is that they were performed under white light. This is probably adequate for this set of samples, but it tends to underestimate liptinites when their content is fairly high.

E. STRUCTURAL CHARACTERIZATION OF COALS

   a. Introduction

The results of the various lines of investigation described here throw some light on the structural features of the aromatic and aliphatic parts of coal structure and on the distribution of oxygen-containing functional groups. Unfortunately they provide no information on the distribution of sulfur-containing functional groups, which would be important for this set of coals. The only comprehensive way of obtaining such data that has been described was noted on p. 15 and is that due to Attar (Attar, 1978; Attar and Hendrickson, 1982). It was found in a study of 14 coals that 10 contained thiophenic structures as their major form of organic sulfur (55-80%), while thiols and sulfides predominated in the others (Attar and Hendrickson, 1982).

It is generally accepted that a substantial part of the vitrinite in any coal consists of a cross-linked macromolecular network. It has been argued (Jurkiewicz et al., 1982) that this network contains trapped within itself a substantial fraction of relatively small molecules, not all of which are extractable by solvents. The evidence for this position has been reviewed, and its significance assessed, by Given (1984), who also points out that the trapped phase consists of a very complex mixture

of structural types. One consequence of this two-component model is that any structural information obtained for a vitrinite may represent data averaged for two quite different kinds of material, mixed in poorly known proportions. This should be borne in mind in assessing the information provided below.

It will be recalled that Shadle (1984), in the companion study, has applied the same techniques to the asphaltenes obtained by liquefaction of the same set of coals. Some of his results will be quoted later.

b. Oxidation with Trifluoroperoxyacetic Acid

Trifluoroperoxyacetic acid oxidations were performed on each of the coals in an attempt to investigate the aliphatic structures present. The results from these reactions, although not as reproducible as those of the other techniques utilized in this study, do constitute the first attempt to use TPFA results in a quantitative manner and represent a considerable amount of work in method development, product analysis and data reduction. This section contains an initial discussion of the development of the oxidation method used on the total sample set, and a discussion of the data obtained. This discussion includes the first utilization of statistics in this work.

As discussed in Section F,b of Chapter III, the oxidation technique developed by Deno et al. (1978a, 1978b) was modified significantly in this work. Although providing a great deal of information concerning the aliphatic structures present in coals, a number of problems were found. The most glaring of these was the lack of reproducibility of product yields. Although generalities could be inferred from the yields of the various products, quanitative data of the type needed for a statistical study

were not obtainable. Secondly, long-chained aliphatic material, which
is known to be present in coals, did not appear in the oxidation products.
Hessley et al. (1982) have investigated this problem and found that the
long-chained aliphatic material was insoluble in the reaction mixture or
adsorbed on the Pt/charcoal used to decompose peroxides after reaction,
and much of it could be recovered by extraction with hot chloroform.
Hence the author believes that two processes contribute to the inability
to observe long-chained aliphatic material under the original conditions.
In addition to the solubility problem that Hessley et al. (1982) observed
there is the problem that the long-chained materials are not stable under
vigorous conditions of oxidation.

The initial rationale behind the modified procedure of Shadle (1984)
was to control the reaction temperature during the initial highly
exothermic portion of the reaction, thus increasing both reproducibility
and selectivity. When the reaction was run under the new conditions,
the product mixture was found to be much more complex, indicating that the
selectivity of the reaction had been increased. The reproducibility
was somewhat better under the new conditions.

Although the results of the experiment were favorable, it was felt
that reduction in the reaction temperature was not the only factor that
needed to be considered. PSOC 666 was oxidized under three sets of
conditions: those utilized by Deno, those devloped by Shadle, and a
reaction run without $CHCl_3$ but with the temperature held at the boiling
point of $CHCl_3$ (61°C) by means of a thermostatted waterbath. The results
from the oxidation under a third set of conditions paralleled most closely
those obtained by means of the original Deno method. This leaves two
possibilities: either the temperature inside the reaction flask was in

fact not controlled at 61°C or the $CHCl_3$ phase, when present, was extracting the primary reaction products from the aqueous phase, effectively isolating them from further oxidation.

Although it cannot be absolutely proved, the author believes that the isolating action proposed in the preceding paragraph, and the prevention of losses by adsorption, are the most important factors in improving control of the process. The two main reasons for this belief include the significant decrease in acetic acid yield with a corresponding increase in methyl maleic acid (a known intermediate in the oxidation of aryl methyl groups), and the appearance of long-chained acids, in the products obtained when the chloroform was present.

Identification of components in the methylated oxidation products was mostly by comparison of retention times and mass spectra with those of standards. However, standards and/or reference spectra were not available for all products, and some chromatographic peaks were not identified. All of the identified products, and the unidentified ones with their retention times, for each coal, are listed in the Table in Appendix A, together with the chromatographic peak area of each, expressed as a percentage of total peak area. The larger peaks mostly rose from flat baselines, and so integration presented no problem. To deal with the cases where peaks were incompletely resolved, a computer program was written to integrate the chromatograms. It utilized a two-pass integration method. In the first pass the peaks were detected, by calculating the first derivative of the chromatogram and comparing it to a user-selectable parameter. The beginning and end of the peak were then determined by descending the peak on each side until the absolute value of the derivative

was again below a selected value. In the second pass the peak was integrated by summing all of the scans between the beginning and end of the peak, as defined by the derivative, and subtracting the baseline. The baseline was calculated as a straight line between the start and end of the peak.

The areas for all of the peaks from the TPFA oxidations are tabulated in Appendix A. Because of the large size of this data matrix and the fact that contents of individual acids were not used in any of the statistical analyses it was felt that the summations of product classes presented in Table 7 were considerably more useful.

The largest peak in each chromatogram was oxirane tricarboxylic acid. The second most prominent was phthalic acid. Both products are thought to be derived from aromatic structures. Some hydroaromatic structures, such as 11,12-dihydronaphthacene, afford a certain amount of the oxirane acids on oxidation, but, of known compounds, certain hydroxy-benzoic acids and dihydroxynaphthalenes, give the highest yields (Soboczenski, 1983). The most abundant acyclic aliphatic acids were malonic and glutaric, which were accompanied by lesser amounts of succinic and adipic acids (see Figure 9, in which the mean yields from the 26 coals are plotted). Other major products included oxirane tetracarboxylic maleic and methylmaleic acids.

The structural precursors of the acyclic dicarboxyclic acids are dicussed below.

Examples of the acyclic tricarboxylic acids are propane-1,2,3-tricarboxylic and butane-tricarboxylic acids. They probably originate in various aryl-indane structures (Shadle and Given, 1982). All

Table 7. Relative Concentrations of Classes of Products from TPFA Oxidation of Sample Set

				% of total chromatographic peak area			
PSOC No.	Acyclic diacids	Acyclic triacids	Benzene- Carbox	Oxirane acids	Total methylated	Total ethylated	Total propylated
349	43.4	4.6	10.8	12.5	14.9	6.0	2.3
401	41.9	6.7	14.0	8.6	17.3	4.7	1.60
581	32.7	6.4	17.5	22.4	14.2	2.5	1.59
582	24.3	7.4	18.5	24.6	7.8	4.6	2.26
593	32.3	8.1	12.8	9.6	13.4	2.7	1.84
594	34.7	7.5	13.6	10.8	10.3	2.7	1.71
596	37.1	7.6	13.1	11.2	15.6	2.9	1.26
599	38.5	7.8	12.9	14.6	17.8	2.6	1.40
664	27.9	8.2	18.8	15.7	10.1	2.3	1.27
666	27.3	10.2	17.7	9.7	10.8	1.7	1.02
669	33.4	9.6	12.8	12.3	12.8	3.8	1.96
676	30.4	5.0	16.0	16.4	10.4	2.1	0.60
680	42.2	10.0	10.9	16.0	19.1	1.9	0.73
741	28.8	10.6	13.2	21.2	10.8	3.0	1.31
742	26.2	6.7	19.6	16.7	9.2	2.8	2.17
760	32.7	6.3	14.7	16.7	9.5	3.0	1.78
767	27.7	3.9	25.1	19.2	7.0	2.0	1.79
768	27.7	5.1	15.9	8.4	8.1	1.6	1.54
773	45.5	10.9	10.4	21.7	20.9	1.6	2.08
798	42.3	8.8	25.5	17.9	3.7	3.7	1.07
808	20.8	4.9	18.5	18.4	7.3	1.8	1.59
883	37.5	4.8	17.2	13.3	13.0	4.4	2.04
1018	43.6	10.0	25.0	11.6	21.0	1.8	1.54
1082	28.8	8.6	25.5	9.7	9.4	1.0	1.94
1083	27.6	4.2	19.5	19.2	4.9	2.6	2.12
1098	41.3	4.9	15.5	16.3	17.3	3.3	1.14
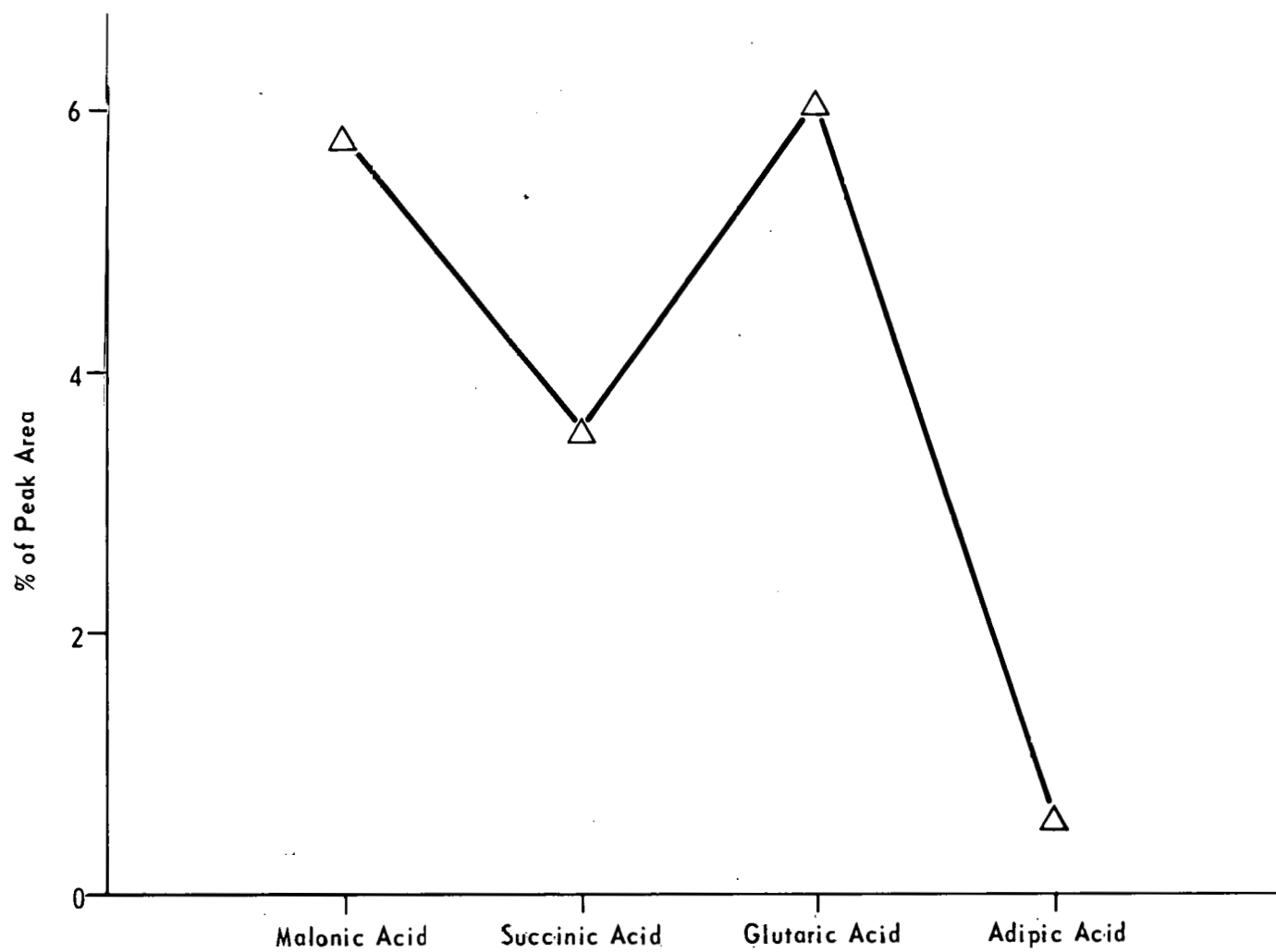
Figure 9. PRODUCTION OF ALIPHATIC DIACIDS IN TFPA OXIDATION

polycyclic aromatic structures give appreciable amounts of phthalic acid, and the benzene polycarboxylic acids probably arise from partly hydrogenated polycyclic structures.

The acetic acid concentration was below the detection limits of the nmr procedure. However, more methyl maleic was observed in the products when chloroform was added to the reaction mixture. Methyl maleic is a known intermediate in the conversion of aryl methyl groups to acetic acid. Thus, it appears that the addition of chloroform has effectively shielded these reactive products. Several chlorinated products were observed in trace amounts in the reaction mixture. However they were present in such low quantities that the contents were normally not measured. The appearance of these products is not surprising since the conditions under which the reaction was run are conducive to the formation of phosgene.

Only two of the prominent acids appear to show any correlation with each other. A plot of the relative peak areas of malonic and succinic acids is presented in Figure 10. The correlation is not good, but even a poor correlation is surprising. Succinic acid is a major product in the oxidation of 1,2-diphenylethane and 9,10-dihydrophenanthrene. It was once thought that malonic acid originated in the oxidation of diphenylmethane and 9,10-dihydroanthracene structures. While these structures do yield some malonic acid, this is not a major product, and the source of the malonic acid produced from coals is still not known (Jones, 1984).

There are a number of products in which a methyl, ethyl or propyl group is substituted in an aliphatic di- or tri- carboxylic acid. Of
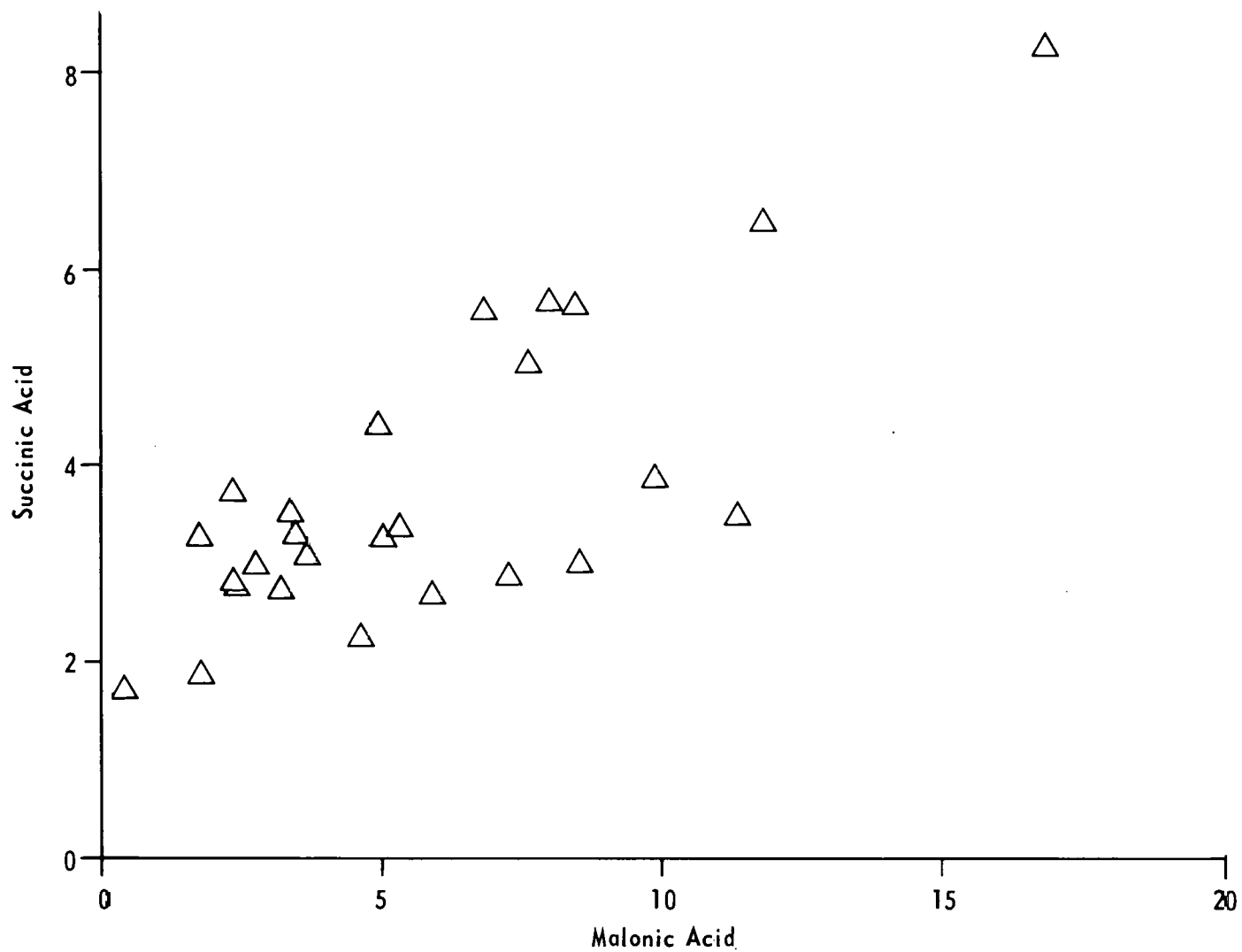
Figure 10. PRODUCTION OF MALONIC AND SUCCINIC ACIDS IN TFPA OXIDATIONS

these, methyl maleic and methyl malonic acids are much the most abundant. At an early stage of this work it was speculated that these substances were the principal source of the hydrocarbon gases formed in lique- faction, and so relative peak areas were computed for the methyl, ethyl and propyl derivatives considered as separate classes (although these classes overlap with the acyclic diacid and triacid classes and probably do not have a common structural source). The relative peak areas due to these classes decrease in the order methyl>>ethyl>propyl (Figure 11). No correlations were in fact found between the yields of hydrocarbon gases and the relative peak areas for the alkyl-substituted acids.

Small quantities of long-chain acids were found. Figure 12 shows the total in current chromatogram for the products from PSOC 760 (Lower Kittanning Seam, Pa.), and under it the regenerated single ion chromato- gram for $m/z = 98$, which is base and characteristic ion for the methyl esters of n. dicarboxylic acids. It is also a marker ion, but not the base peak, for methyl n. carboxylates (for which the base peak is $m/z = 74$, Figure 12c). Presumably these acids were formed from alkanes.

The presentation of the data in Table 7 and the Appendix as percen- tages of the toal chromatographic peak area constitutes a type of internal standardization of the data. This was necessary since the absolute peak areas were poorly reproducible even when scaled with respect to an internal standard. This indicates that the errors associated with the method came in between the oxidation reaction itself and the analysis steps. If either the chromatographic separation or the oxidation were irreproducible one would not expect the internal standardization to help.

The four classes of product discussed include essentially all
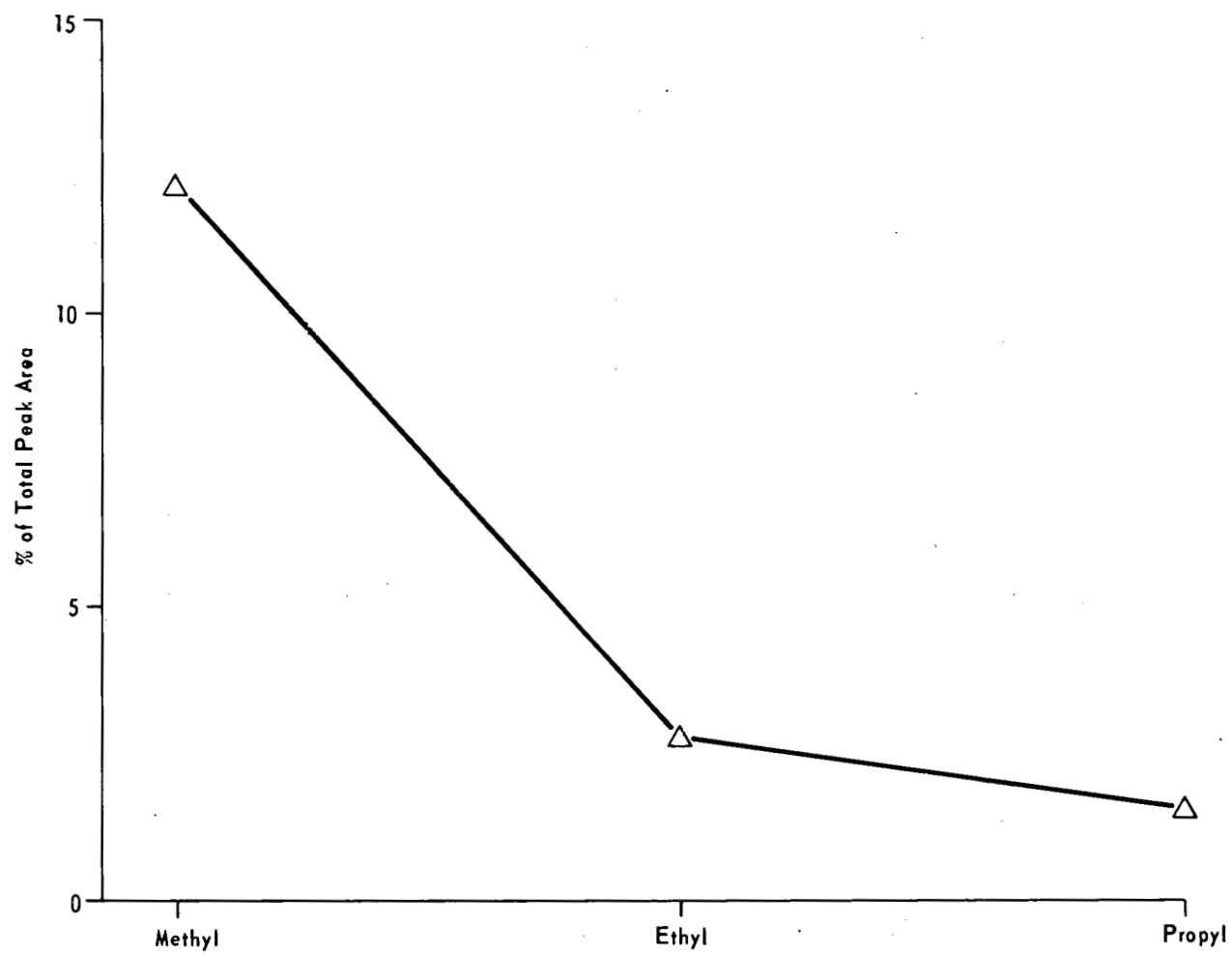
Figure 11. FRACTION OF TOTAL PEAK AREA ACCOUNTED FOR BY ACIDS CONTAINING METHYL, ETHYL AND PROPYL GROUPS
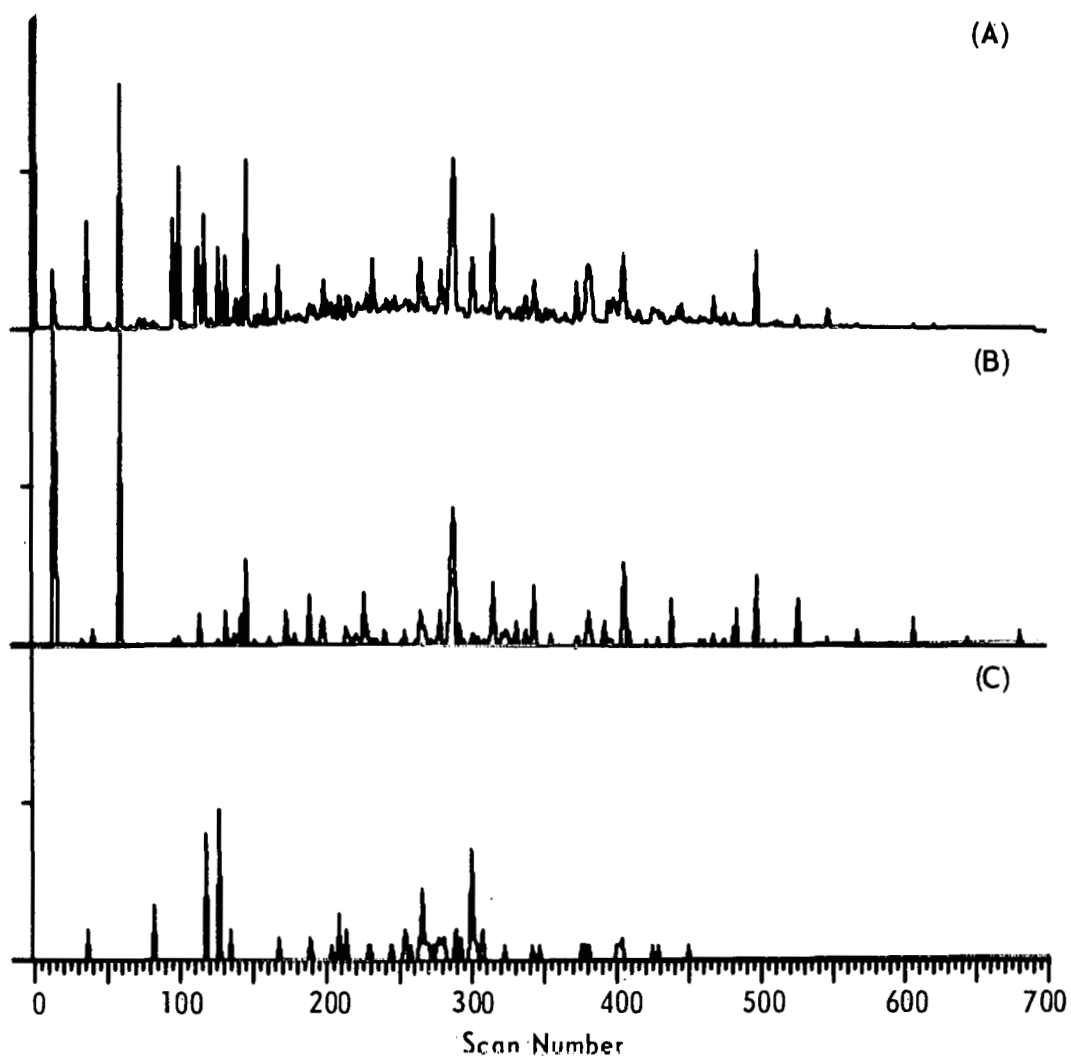
Figure 12. TOTAL ION CURRENT AND REGENERATED SINGLE ION CHROMATOGRAMS
FOR PRODUCTS FROM TFPA OXIDATION OF P.SOC-760
(A) total ion current, (B) m/z 74, (C) m/z 98

products found, and they most probably originate in different structural features of a coal. They might be expected to vary systematically with rank, and to be affected by the distribution of organic sulfur. Accordingly, a factor analysis was performed on the summed relative peak areas of the four classes, together with three basic compositional characteristics of the coals. The results are surprising and are shown in Table 8. The most obviously striking features are the low variance explained, and the low communalities. The communality is the sum of the squares of the loadings of any variable on the various factors; it measures the contribution of that variable to the overall variance explained. Thus we have not found the variables that explain the variance in the yields of the product classes: rank and organic sulfur have almost nothing to do with the variance. The amounts of three of the product classes load moderately (but not impressively) on the same factor. The fourth class, acyclic diacids, seems to vary independently to a large extent.

The reason behind all these negative findings might be that the acids analyzed correspond to fairly small fractions of the carbon and hydrogen in the coal, and are not representative of the major structural features in the coals. Against this view is the fact that the products from coals differ systematically and reproducibly from the products of oxidizing asphaltenes from the same coals; this is unlikely to be so if the products in each case are a small, non-representative, fraction of the structures present in the starting material. Alternatively, we may have encountered another indication that the sample set is much much heterogeneous than had been supposed (see below, p. 94, and further discussion of the point in Chapter V).

Table 8. Rotated Factor Analysis of the Summed Product
          Classes from TPFA Oxidation

Variable	Factor 1	Factor 2	Factor 3	Communality
acyclic diacids	0	-0.21	0.85	0.77
acyclic triacids	-0.24	+0.49	0.30	0.39
benz. carbox. acids	0	0.61	0	0.37
oxirane acids	0	0.59	-0.33	0.47
%C, dmmf	0.60	0	0	0.36
R_o, %	0.56	0	0	0.31
S (org.)	-0.55	0	0	0.30
Variance explained	37.2%	20.2%	15.4%; Σ = 73%	

c. Cross-polarization magic-angle-spinning ^{13}C Nmr

Over the last few years cross-polarization magic-angle-spinning nmr has developed as the easiest, and probably most accurate method of determining the fraction of aromatic carbon in insoluble materials such as coal. CP-MAS spectra were obtained from Colorado State University Regional Nmr Facility, which is under the direction of Dr. Gary Maciel, for each of the coals utilized in this study. The results obtained are in a similar range to those published for other coals (e.g. Havens et al., 1982; Wilson et al., 1984).

The chemical shifts for the aliphatic and aromatic peaks and the fraction of aromatic carbon (f_a) for each of the spectra are reported in Table 9. It was felt that duplicate spectra could not reasonably be requested, and so no indication of reproducibility can be offered. No doubt there are differences in the recorded spectra if the instrument is asked to run the same sample twice, but it is felt that such differences are likely to be small compared with the differences in replicate reading of the aromatic peak areas of any one spectrum. It appears that cutting out and weighing paper records of the peaks is likely to be more accurate than measuring the instrumental integration printed on the recorder chart, and this was done. The standard deviation about the means for duplicate cutting-and-weighing was 3%.

In general the separation between the aromatic and aliphatic regions was very good with no overlap, as can be seen in the example in Figure 13. More importantly, the spinning side bands of the aromatic peak do not overlap the aliphatic absorption, and so no correction to the areas is needed in deriving aromaticity. In using the relation

$$f_a = \Lambda_{ar}/(\Lambda_{ar} + \Lambda_{al}),$$

Table 9. Data from CP-MAS ^{13}C NMR Spectrometry

Sample, PSOC No.	Chemical Shift at Maxima ppm, aromatic	aliphatic	Areas aliph.	Areas arom.	Areas arom. side bands	Aromaticity, f_a
349	130.13	32.19	0.0208	0.0512	0.0084	0.74
401	129.19	32.80	0.0247	0.0648	0.0059	0.74
581	128.41	29.45	0.0536	0.0915	0.0114	0.66
582	128.67	32.30	0.0463	0.0888	0.0273	0.72
593	128.30	32.45	0.0196	0.0395	0.0025	0.69
594	138.90	31.77	0.0245	0.0605	0.0086	0.74
596	125.79	29.66	0.0376	0.0675	0.0091	0.67
599	129.08	31.65	0.963	0.0449	0.0064	0.76
664	132.19	34.77	0.0297	0.0809	0.0094	0.75
666	129.41	32.78	0.0329	0.0717	0.0076	0.71
669	128.16	32.03	0.0275	0.0576	0.0062	0.70
676	128.42	32.31	0.0273	0.0752	0.0074	0.75
680	129.71	32.82	0.172	0.0496	0.0084	0.78
741	126.76	31.67	0.0228	0.0564	0.0053	0.73
742	128.15	31.51	0.0282	0.0795	0.0190	0.78
760	129.71	32.80	0.0253	0.0576	0.0060	0.72
767	128.64	32.79	0.0319	0.0767	0.0051	0.72
768	130.64	31.15	0.067	0.0364	0.0036	0.71
773	126.75	30.38	0.0204	0.0433	0.0030	0.69
798	129.87	30.87	0.0167	0.0578	0.0070	0.80
808	131.01	34.38	0.0240	0.0693	0.0068	0.76
883	127.64	31.51	0.0176	0.0478	0.0056	0.75
1018	130.38	33.73	0.0341	0.0736	0.0058	0.70
1082	129.61	34.26	0.0230	0.0665	0.0068	0.761
1083	132.27	39.25	0.0114	0.0367	0.0070	0.79
1098	129.61	35.29	0.0359	0.0513	0.0045	0.61
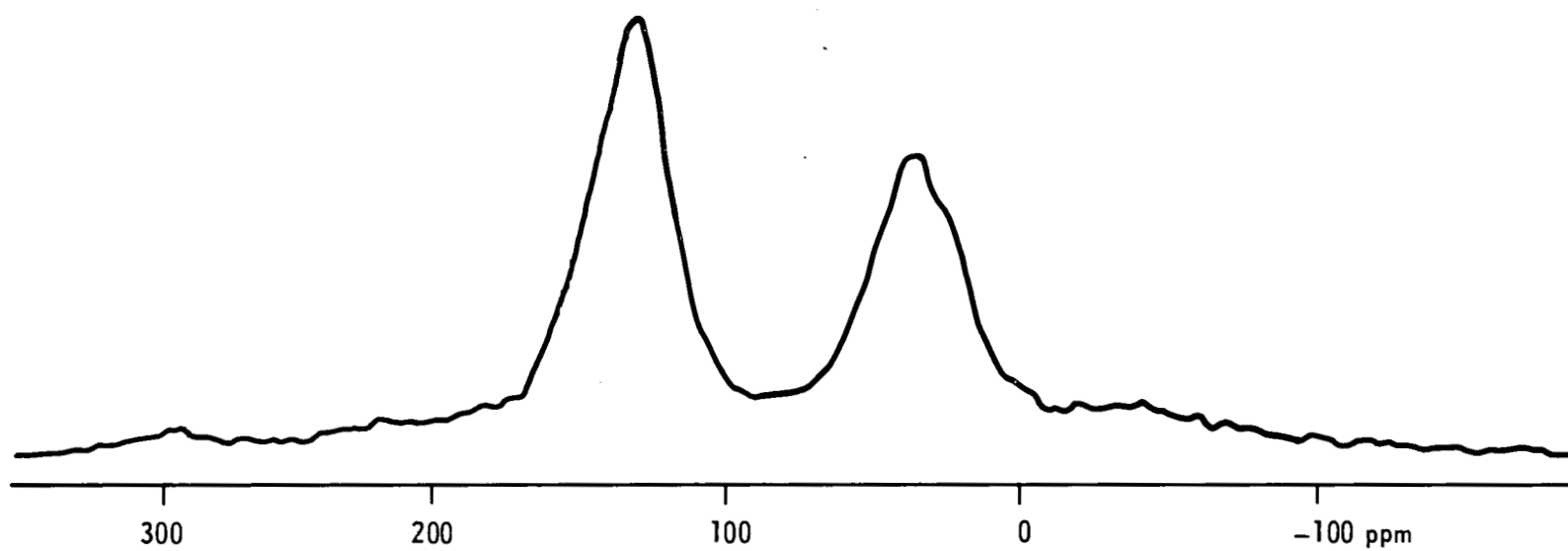
Figure 13. CP–MAS ^{13}C NMR SPECTRUM OF PSOC–1098 COAL
(Illinois No. 6)

where A_{ar} and A_{al} are the areas under the two peaks; the area under the aromatic spinning side bands is included in A_{ar} (the aliphatic peak has no side bands).

All of the f_a values reported in Table 9 appear to be reasonable except for that for PSOC 1098. This is a sample from the Illinois No. 6 seam and is of HVA rank class. It gave a value for f_a of 0.61, which is much too low for a coal of this rank class. It is not clear what caused this anomaly. There appears to have been a problem with the sample, since 64,000 acquisition scans were required to obtain a reasonable spectrum, whereas the normal spectrum required only about half this number. The value of f_a for this sample is excluded from further discussions of the data. A plot of f_a against the carbon content is shown in Figure 14. If one considers the points as belonging to a single population, there is a great deal of scatter, and the variance explained (r^2) by a linear regression is only 3%. This is surprising since similar plots for sets of related coals, using the data of Havens et al. (1983) and Wilson et al. (1984) give linear regressions explaining 50-88% of the variance (Given, 1984). Visual inspection of Figure 14 shows that five nearly parallel lines of differing intercept can be put through the points. The slopes and intercepts of the lines, together with the fractional variance explained by each, are shown in Table 10. It is seen that each line provides an excellent correlation for its set of points. It will be noted from Table 10 that the aromaticity for PSOC 1098 (Illinois No. 6) is anomalous and must be in error. It was felt that there was no choice but to reject it as an outlier from the regressions and from Figure 14.

The significance of the grouping of the coals into five sets was
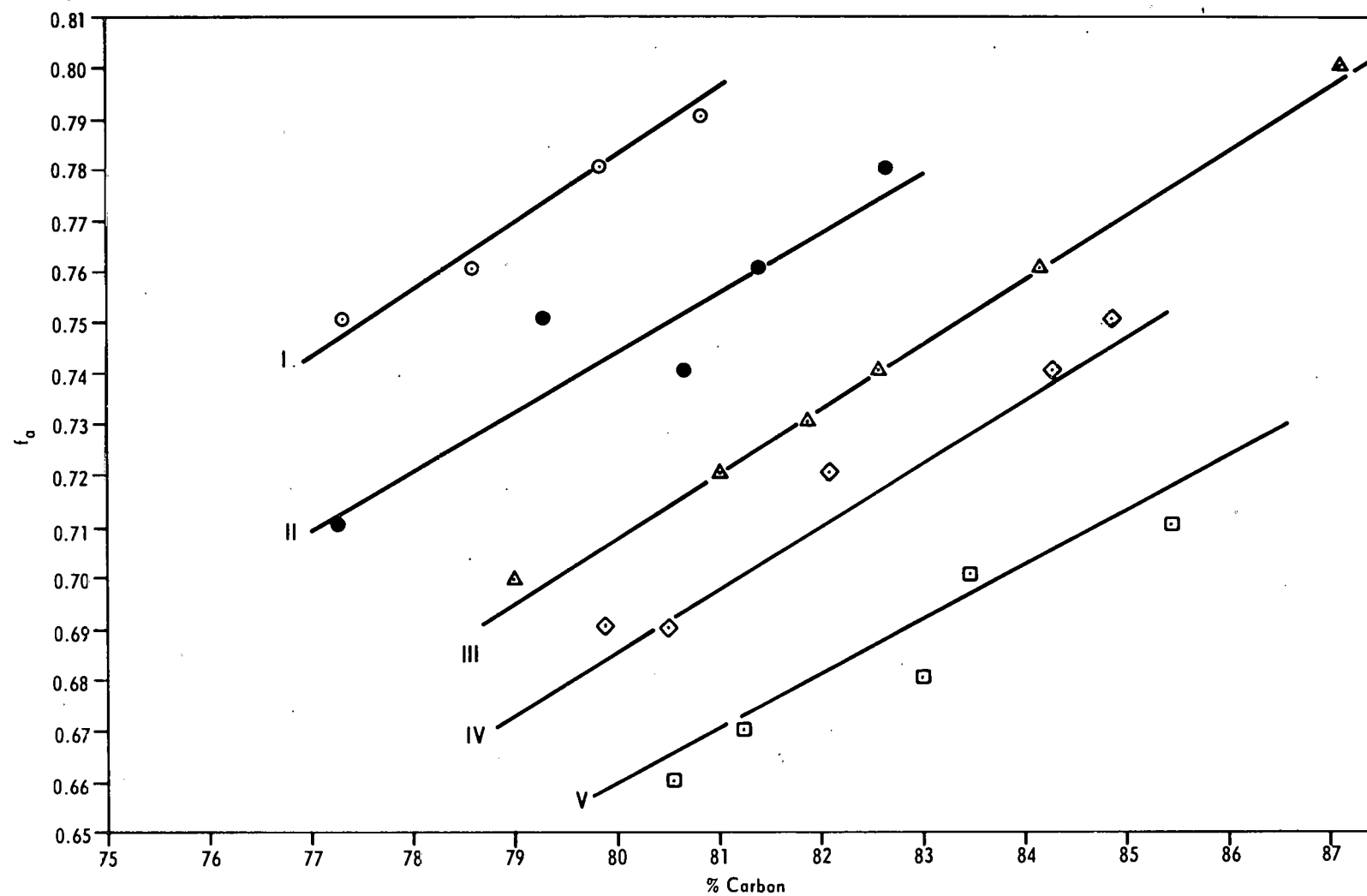
Figure 14. RELATION OF AROMATICITY TO CARBON CONTENT FOR 26 COALS

Table 10. Grouping of Coals into Subsets According to
Levels of Aromaticity

Subset	PSOC No.	%Carbon	f_a	m*	-c*	R^2
I	664	77.3	0.75			
	1082	78.6	0.76	0.0131	0.265	97.0
	680	79.8	0.78			
	1083	80.4	0.79			
II	666	77.3	0.71			
	676	79.3	0.75			
	594	80.7	0.74	0.0116	0.184	86.1
	599	81.4	0.76			
	742	82.7	0.78			
III	669	79.0	0.70			
	582	81.0	0.72			
	760	81.2	0.72			
	741	81.9	0.73	0.0126	0.300	99.3
	401	82.6	0.74			
	808	84.2	0.76			
	798	87.1	0.80			
IV	593	79.9	0.69			
	773	80.5	0.69			
	767	82.1	0.72	0.0123	0.299	98.0
	349	84.3	0.74			
	883	84.9	0.75			
V	581	80.5	0.66			
	596	81.3	0.67			
	1098	83.0	0.68	0.0106	0.188	96.6
	1018	83.5	0.70			
	768	85.4	0.71			

*m = slope, c = intercept

tested by performing a discriminant analysis. This indicates that there is statistically an 85% probability that the coal samples are derived from separate populations. The probability that Groups: 1 and 2 are distinct is 87.5%, groups 2 and 3 is 60%, 3 and 4 is 90%, and 4 and 5 is 90%, when the analysis is provided with the aromaticities, elemental analyses and conversions to the various classes of products. Utilizing only the f_a and elemental analysis the overall probability of the discrete populations being significant falls to 80%. However, the probability that groups 2 and 3 are distinct rises to 70%. The discriminant functions developed and tested in the above discussion are as follows:

Group 1 $-2.27 f_a - 0.40C - 0.54S - 0.41 O + 4.00$

Group 2 $0.99 f_a + 0.15C + 0.12S + 0.14 O + 14.68$

Group 3 $6.20 f_a + 0.43C + 0.46S + 0.38 O + 35.24$

Group 4 $1.98 f_a + 0.14C + 0.30S + 0.14 O + 14.40$

Group 5 $5.49 f_a + 0.33C - 0.23S - 0.24 O + 25.31$

These discriminant functions indicate that when only f_a and the elemental analysis are considered f_a, percent carbon, sulfur and oxygen are important parameters in distinguishing the groups.

There are two possible explanations for these peculiar findings. The first of these is that the samples were not after all selected from a single statistical population. This area will be discussed in detail in the next chapter. The second possibility is that sulfur and oxygen are replacing carbon in the coal as thiophenes and furans thus affecting the fraction of carbon in aromatic systems.

A multivariate least-squares regression for f_a *versus* the contents of carbon, sulfur and oxygen gives the equation below.

$$f_a = 0.0507.C + 0.0803.5 + 0.0023.0$$

However, the variance explained is very low (46 %), showing that with regard to this set of variables, the sample set is far from homogeneous.

Thus the conclusion from this discussion is that what was believed to be a quite homogeneous sample set turns out to be extremely hetero-geneous, and may contain a number of subsets.

d.   Fourier Transform Infrared Spectrometry

The spectrum of each coal in the study was recorded, along with spectra of the low temperature ash and the acetylated coal. The spectra of the LTA's were used in correcting the coal and acetylated coal spectra for absorption due to mineral matter in regions of special interest. No attempt was made to determine mineral matter content from the LTA spectra.

Particular attention has been paid to the aliphatic C-H stretching region (2750-3000 cm^{-1}), the aromatic C-H bending region (700-1000 cm^{-1}), and the carbonyl region (1650-1800 cm^{-1}) of the acetylated coals. First the mineral matter spectrum was subtracted, and drifting baseline re-moved. Then second derivative spectra of the regions of interest were ob-tained, curve resolution performed, the peak frequencies of the resolved bands were noted, and their relative areas obtained by integration in the dedicated computer. At the same time, the computer normalized the peak areas to the basis of 1 mg (dmmf) coal in the sample beam. The integra-tions were performed in duplicate, and the resulting areas agreed to 2% or better.

A similar study has been made of the FTIR spectra of a set of coals from the Lower Kittanning seam in Pennsylvania and Ohio by Kuehn (1983; see also Kuehn et al., 1983), who discusses in some depth the procedures of curve-resolving and gives many examples. The test of the validity

of the curve resolution is to reconstruct the whole spectrum for a region from the deconvoluted peaks, and compare it with the original spectrum. Kuehn shows that the overlap of the two spectra is remarkably close. As an example, the FTIR spectrum of the coal PSOC-1098 (Illinois No. 6) is presented in Figures 15-17. The smoothed second derivative spectrum for the region between 3000 and 2700 cm^{-1} and the curve-resolved component bands are shown in Figure 16, while the regenerated spectrum is compared with the original unresolved spectrum in Figure 17. Applying the curve resolution technique to the aromatic C-H bending region, 750-1000 cm^{-1}, only three bands were resolved, at 750, 800 and 820 cm^{-1}. In her study of vitrinite concentrates from the Lower Kittanning seam, Kuehn (1983) was able to resolve six bands.

The accuracy of the quantitative interpretation of the spectra was somewhat impaired by the difficulty in handling milligram quantities of coals. Two problems are inherent in the procedure utilized and can be traced directly to the 3 mg coal sample required to make up the KBr pellet. The first of these is the difficulty in obtaining a single representative 3 mg sample. The best one can do is to ensure that the sample is as well mixed as possible, before the 3 mg split is taken. The second problem can be traced to losses. Even the slightest wind, or adhesion to the weighing paper, brush or mortar and pestle, could cause a significant percentage of the sample to be lost. The effect of these problems was well illustrated in a determination of the scaling factor needed in the subtraction of the LTA spectrum from that of the coal. As a general rule, the duplication of the factor was found to be approximately ± 20% of the mean. Since one can assume a similar level of replicability in determining spectral intensities for the coal and the LTA, it appears
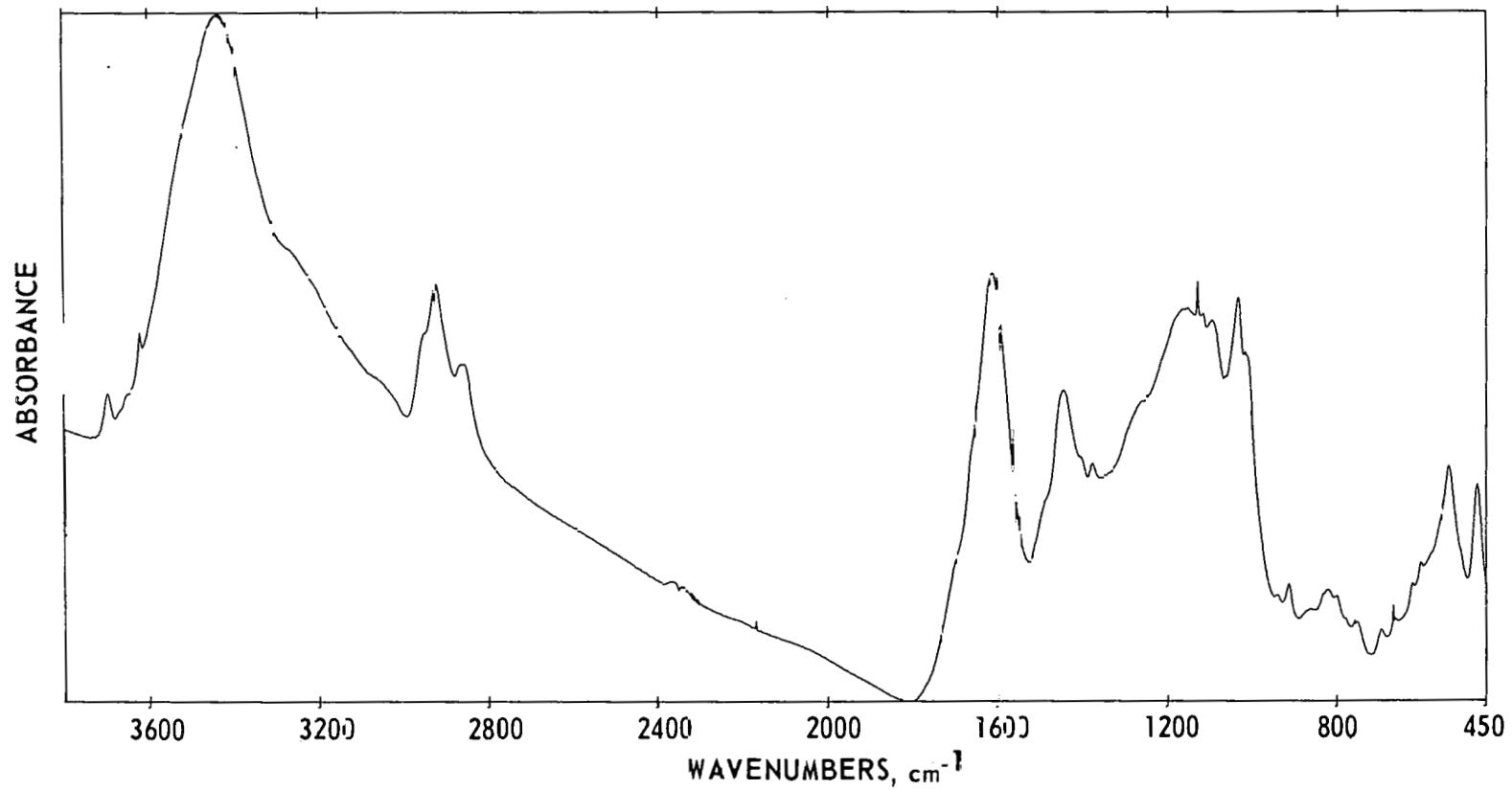
Figure 15. FTIR SPECTRUM OF PSOC–1098 (Illinois No. 6)
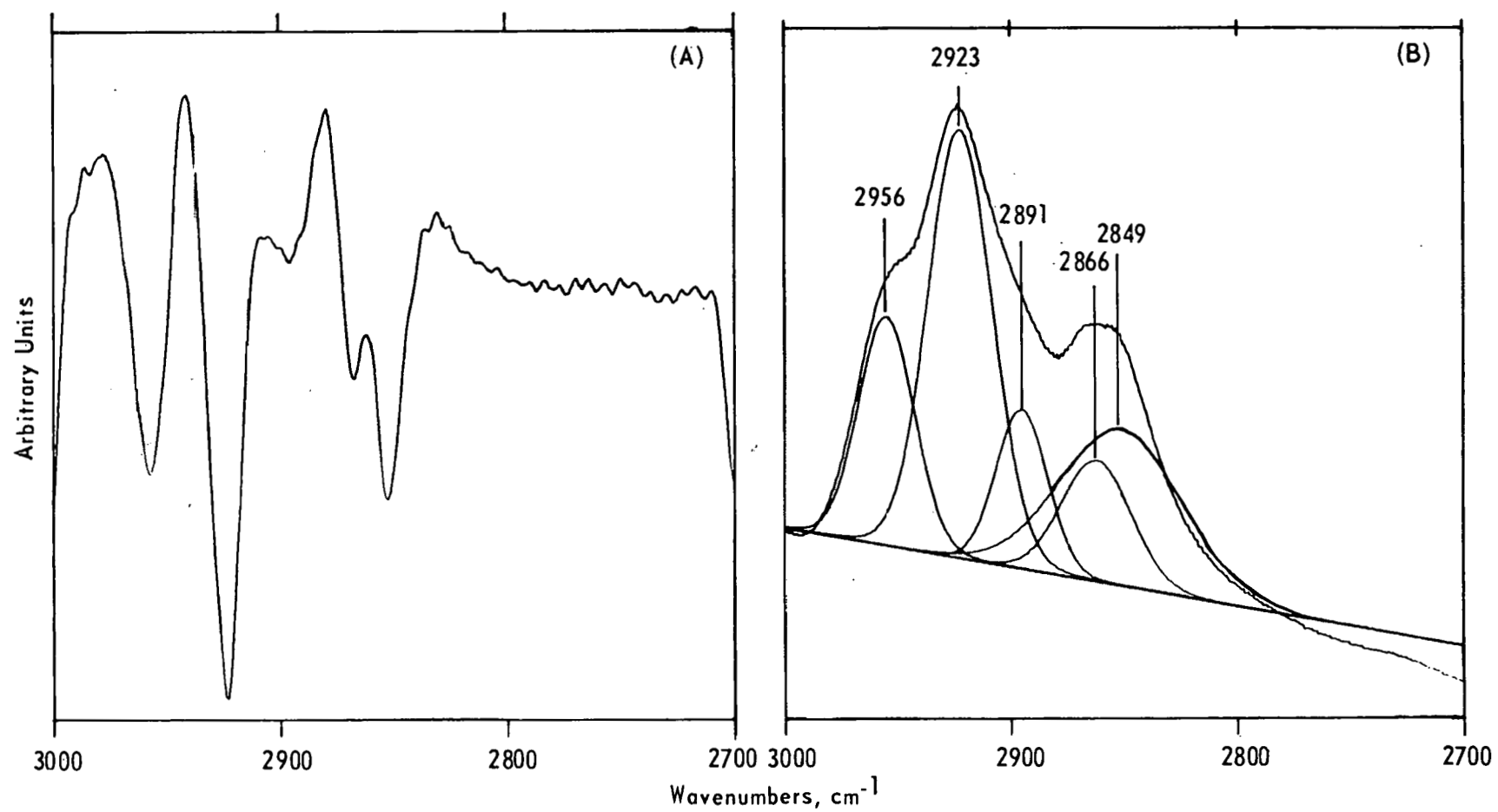
Figure 16. CURVE RESOLUTION FOR ALIPHATIC C–H STRETCHING REGION OF FTIR SPECTRUM
(A) second derivative spectrum, (B) curve-resolved bands
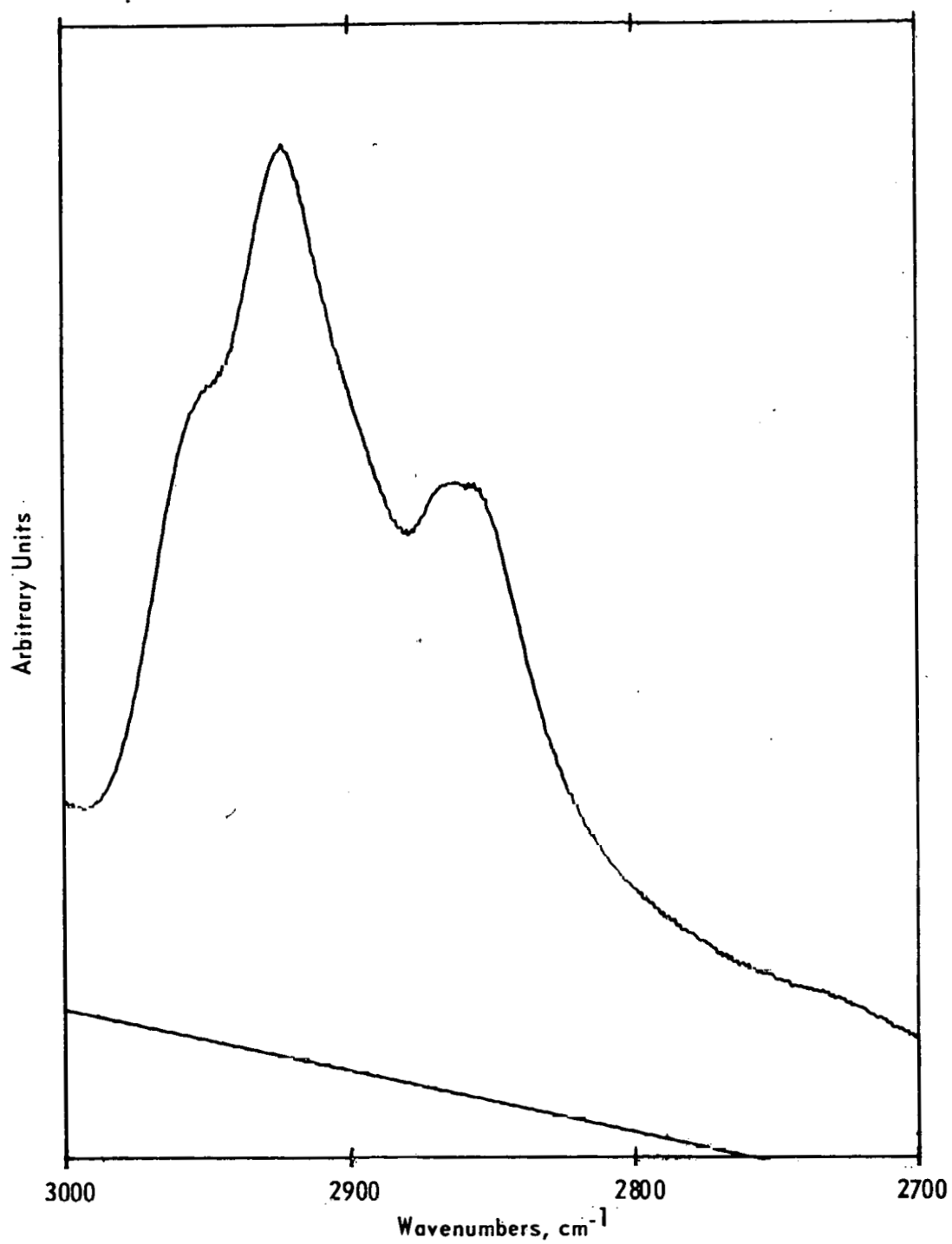
Figure 17. SUPERIMPOSITION OF RECONSTRUCTED SPECTRUM AND ORIGINAL
SPECTRUM OF PSOC-1098, ALIPHATIC C-H REGION

that the intensities in any one spectrum are reproduced to ± 10% or somewhat greater.

The relative peak areas for each of the resolved bands in three regions of interest are shown in Table 11. The complete spectra are shown in Appendix C.

The ratio of the sum of the areas of the resolved aliphatic C-H bands (excluding that at 2923 cm^{-1}) to the sum of the areas of the aromatic C-H bending vibrations was calculated, and might be expected to decrease systematically with increasing rank.

Figure 18 presents a plot of the absorption area assigned to phenolic OH against the oxygen content. There is a considerable amount of scatter present in the data, and the variance explained by the regression is only 0.41%. Two factors probably contribute to the increased scatter in relation to the aliphatic/aromatic C-H absorption data. The most important factor is that the phenolic data are not internally standardized, so that they are extremely sensitive to sampling errors. Also, the accuracy of the oxygen content is somewhat lower than that for carbon, since it is determined by difference and contains all of the errors in the direct determinations; these errors include terms due to approximations in the corrections to ash, carbon and hydrogen for interferences by mineral matter composition.

A plot of the sum of the 1770 and 1745 cm^{-1} absorption bands showed considerably more scatter than the 1770 cm^{-1} band alone. This is opposite to what one would expect and raises questions as to its assignment to alkyl OH. However, Kuehn et al. (1983) found considerably more scatter when the area of the 1740 cm^{-1} band was plotted against vitrinite
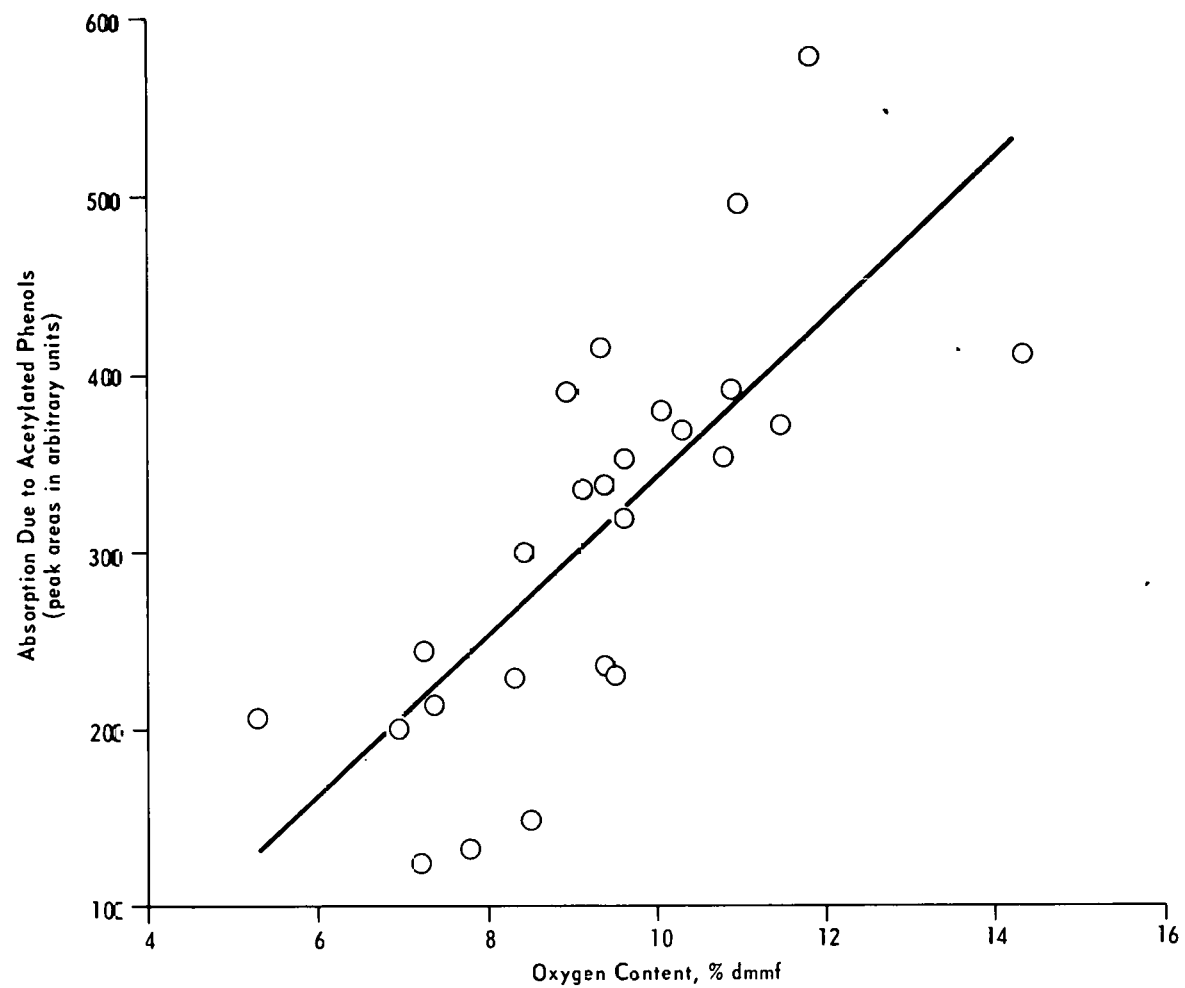
Figure 18. PHENOLIC OXYGEN CONTENT AS RELATED TO TOTAL OXYGEN IN COAL, FROM FTIR DATA

Table 11. Relative Peak Areas for Resolved Components of Certain Regions of the FTIR Spectra

PSOC Number	Aliphatic C-H Stretching Region					Aromatic C-H Bending Region			C=O Region for Acetylated Samples		
	2956	2923	2891	2849	2864	820	800	750	1770	1740	1670
349	283	837	259	141	410	103	357	194	230	195	153
401	353	774	249	224	412	196	417	168	645	501	228
581	256	604	220	173	376	66	262	166	379	56	35
582	282	608	229	172	363	180	296	74	316	299	247
593	278	598	229	173	344	218	217	82	322	313	243
594	281	617	224	182	375	84	237	184	411	320	205
596	217	491	163	174	365	87	198	65	722	359	200
599	254	529	165	169	330	312	378	154	368	151	78
664	213	740	207	183	263	177	112	143	353	239	164
666	315	704	207	185	427	72	127	151	577	112	42
669	311	663	212	191	394	41	88	93	155	75	55
676	260	567	176	173	382	39	116	106	236	203	176
680	263	575	169	166	384	111	173	118	525	332	132
741	300	650	199	190	413	62	163	108	492	495	185
742	201	654	199	186	319	129	109	107	163	155	245
760	253	571	183	187	317	228	128	96	352	187	160
767	354	799	279	272	570	264	253	76	371	301	133
768	358	789	255	242	487	82	195	104	525	318	232
773	208	453	151	234	360	97	170	75	519	334	340
798	373	704	215	202	316	430	289	292	828	334	190
808	277	637	231	207	479	146	194	178	669	364	240
383	428	845	262	243	405	123	292	245	391	180	175
1018	319	656	212	201	394	149	199	80	866	415	453
1082	278	627	172	172	409	97	280	179	412	337	139
1083	286	615	190	189	393	--	161	435	811	359	205
1098	279	605	179	185	416	180	169	171	543	237	176

reflectance than when the 1770 cm^{-1} band was similarly plotted, which is perhaps to be expected since it is much less intense.

It was decided to include the peak areas for all of the 11 bands discussed in a single factor analysis (Table 12). Seven factors were found, accounting for 98% of the variance in the data, but only one or two variables loaded on most of them and so they can hardly be regarded as significant. Most of the values for the aliphatic C-H vibrations loaded on one or both of the first two factors. The area for the 2923 cm^{-1} band asymetrical CH_2 plus CH_3 vibrations provided the sole loading on factor VI, which is perhaps some slight reason for regarding it as different in its trends from the others. Kuehn (1983) performed her factor analyses for the Lower Kittanning samples separately for three regions of the spectrum, and the loadings on factors I and II for the C-H bands are in most respects similar to what she found for her two factors.

The principal conclusion is that there are two sources of the variance in the intensity of the aliphatic C-H vibrations; as a speculation we could suggest that the importance of hydroaromatic rings varies independently of the aliphatic side chains. It is perhaps worth noting that the symmetrical and unsymmetrical CH_2 vibrations (2850 and 2956 cm^{-1}) load most highly on factor I, whereas the CH_3 and C-H vibrations load on factor II. The three acetyl absorption bands load independently of each other and of the aliphatic and aromatic absorptions. The band centred at 1770 cm^{-1}, which is normally assigned to phenolic acetates, appears to load on the same factor as the aromatic absorption around 800 cm^{-1}.

Table 12. Rotated Factor Analysis of Relative Peak Areas of
Resolved Bands in FTIR Spectra of Coal Series

Frequency, cm^{-1}	Factors						
	I	II	III	IV	V	VI	VII
2956	-0.610	-0.387					
2923						0.931	
2891		-0.585					
2849	-0.798	-0.372					
2864		-0.561					
820	0.375	0.632					
800				0.888	0.535		
750	0.610						-0.250
1770							0.883
1745				-0.835			
1670		0.988					

F. DISTRIBUTION OF LIQUEFACTION PRODUCTS

    a. Product Classes

The products from the liquefaction were initially separated into four major classes based on either their boiling point or solubility. Table 13 shows the distribution of the various classes of products for the 26 coals used in this study. The total conversions (original coal-residue) ranged from a high of 78.8 percent for PSOC-582 to a low of 41.4 percent for PSOC-798, while the conversion to asphaltenes (ethyl-acetate-soluble, hexane-insoluble) ranged from a high of 40.9 percent to a low of 19.4 percent for the same two coals. Five of the liquefactions had to be repeated (PSOC 666, 669, 676, 742, and 808) before replication within 1% for the total conversion determination could be obtained.

All measurements were made in duplicate runs, and the mean values are given in the Table. The overall standard deviation about the mean is shown for each class of products except for the lost volatiles, which were determined by difference, as discussed below. It will be noted that the yield of asphaltenes is greater than that of hexane-soluble oils in all cases, the ratio being about 3:2. The oil yields have less absolute accuracy, since complete separation of naphthalene and excess tetralin, with no loss of coal-derived product, is presumably impossible by vacuum distillation. The relative error in the gas yields is very large, probably due to the difficulty of measuring the volume of gas.

The yield of gases is quite low, and much lower than the yields calculated by difference by previous workers (e.g. Mudamburi, 1983). It has always been clear that any products from the coal that condensed with or dissolved in the liquid products and had a normal boiling point

Table 13. Conversion of Coals to Product Classes

(percent d.m.m.f)

Coal PSOC No.	Conversions, % of dmmf coal				
	total liqs. + gases	asphal- tenes	gases	oils	volatile liqs. lost
349	69.4	33.6	2.4	21.8	11.6
401	63.6	33.8	1.8	22.1	5.7
581	77.6	38.2	2.3	27.3	9.9
582	78.7	40.9	2.1	29.0	6.8
593	72.5	32.7	1.3	24.7	13.8
594	69.5	34.5	1.2	24.2	9.6
596	69.2	34.2	1.3	22.4	11.4
599	70.3	35.6	2.2	25.2	7.3
664	79.7	31.6	1.8	29.8	16.5
666	75.2	31.8	2.1	23.8	17.5
669	69.6	35.1	2.5	24.7	7.3
676	69.1	31.4	3.0	23.3	11.4
680	66.2	37.6	2.8	20.6	5.3
741	75.2	35.0	1.9	27.4	11.0
742	69.2	31.9	2.6	22.9	11.8
760	72.3	35.9	2.5	25.3	8.6
767	73.0	35.6	2.0	24.9	10.6
768	65.2	32.8	1.1	22.2	9.2
773	74.4	36.0	1.7	23.0	13.7
798	41.4	19.4	2.9	13.8	5.3
808	55.5	29.9	2.2	22.6	0.8
883	61.9	31.3	1.4	24.3	4.9
1018	64.6	31.5	1.4	30.0	1.8
1082	74.1	34.0	1.7	22.3	16.1
1083	70.5	36.8	3.5	25.7	4.5
1098	67.9	34.7	2.8	26.4	3.9
σ	0.66	1.03	2.01	1.63	—

below about 80°C would be lost when the ethyl acetate was evaporated.
Also, material with a boiling point above that of ethyl acetate but
less than about 220°C would be lost when the tetralin and naphthalene
were removed. The yields of lost volatiles shown in Table 13 were
calculated by difference, and so accumlate the errors in all the direct
determinations. They are mostly in the range 5-10%, though there are a
few values above and below this range, which in any case seems surpris-
ingly high. If the yields of oils and lost volatile material are added
together, the sum approaches the yields of asphaltenes, as shown in
Figure 19, where yields of products in each class are shown in histogram
form. The combination of the volatile products and the oil fraction seems
reasonable, since the volatile fraction is almost certainly composed of
materials related to the oil fraction.

The question that of course arises in relation to the volatile frac-
tion is where it is lost. Gas chromatography of distillates from the
spinning band column showed only slight traces of two isomers of methyl-
indane, which can most probably be considered rearrangement products from
tetralin and should not be considered as part of the coal products. It
must therefore be concluded that the material has been lost prior to this
step, that is, during the evaporation of the ethyl acetate at reduced
pressure. Indeed, the smell of the solvent recovered by evaporation had a
distinct hydrocarbon character. Material evaporated with the ethyl ace-
tate could include some water (though this does not form an azeotrope with
ethyl acetate). The idea that this fraction is related to the oil fraction
is supported by Figure 20 in which conversion to the specific classes are
plotted against total conversion. As can easily be seen the yields of
each fraction except for the gases tends to increase with conversion, while
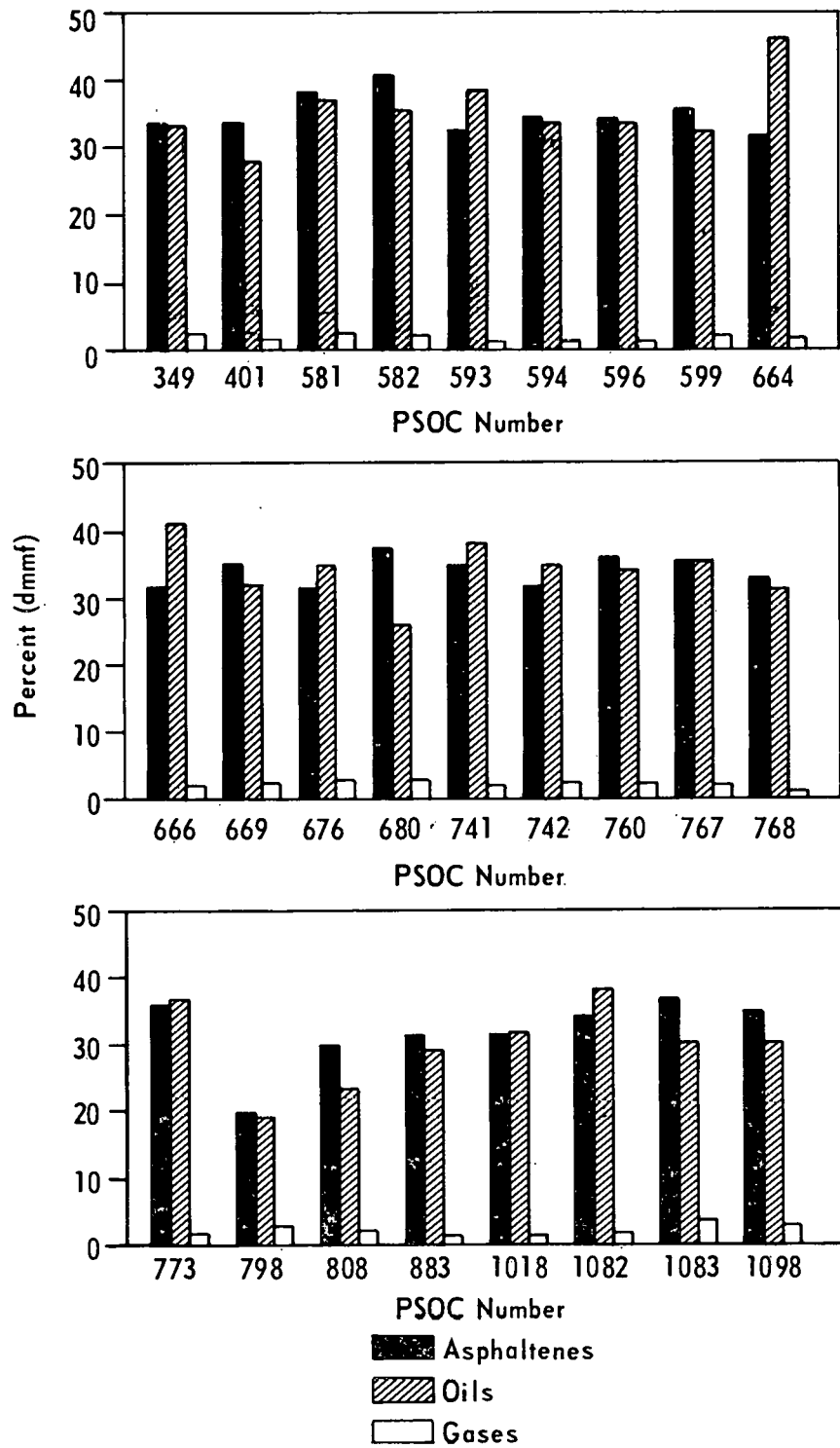
Figure 19. YIELDS OF PRINCIPAL CLASSES OF PRODUCTS FROM LIQUEFACTION
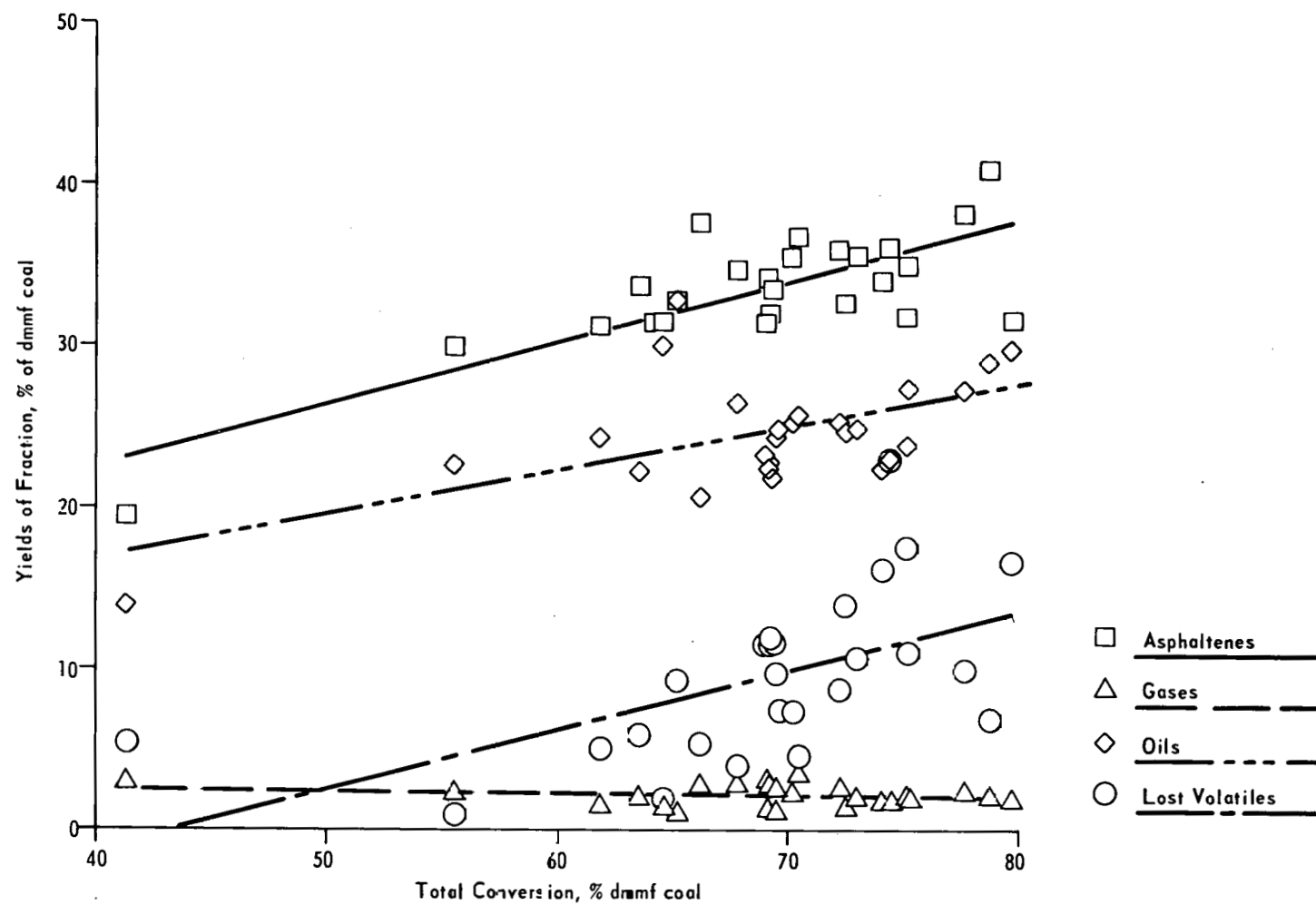
Figure 20. DEPENDENCE OF YIELDS OF PRODUCT CLASSES ON TOTAL CONVERSION

conversion to gas is constant within experimental error. The line for the volatile fraction parallels that of the oils very closely. This supports the idea that the unaccounted for material is more closely related to the oil fraction than to the gases. Time did not permit a more complete analysis of these two distilled fractions. An analysis of this type would be extremely difficult if one considers that, in the best case, the concentration of what is most probably a very complex mixture of compounds would be approximately 125 mg in a liter of solvent. The fact that these materials most probably possess a relatively low boiling point only complicates the analysis. The non-polar components of the ethyl acetate rotary evaporate could possibly be separated by desorption from a silica-alumina column with a slightly polar eluant such as ether; however this process would be difficult and might not account for any polar materials.

In a specially designed experiment, with results shown in Table 14, it was shown that the mass balance can be essentially closed and volatile material recovered. Two coals were each liquefied in duplicate and the products worked up as usual, giving the yields shown in the Table. Two further duplicate runs were performed with each coal, and the products were then rinsed out with a heavy mineral oil instead of ethyl acetate. Very careful distillations in the spinning band column, beginning at atmospheric pressure and slowly reducing the pressure while increasing the pot temperature, were made. The yield of distillate recovered up to an equivalent boiling point of 220° accounted almost completely for the missing mass, as shown in the Table.

b. Gas Analysis

Both the total volume and the composition of the gases were determined. Examples of the chromatographic analyses of the permanent and hydrocarbon

Table 14. Comparison of Product Yields in Normal Runs and
Runs with Heavy Mineral Oil Rinsing of Reactors

	PSOC-760	PSOC-401
(a) Normal Runs		
% Oils	25.29	22.18
% Asphaltenes	35.90	33.70
% Total gases	2.49	1.87
% Lost volatiles	8.61	5.74
(b) Mineral Oil Rinsing		
% Boiling up to 220°/1 atm.	8.65	5.92

gases are shown in Figures 21 and 22. Hydrogen, unlike the other gases, had to be analyzed with argon as a carrier gas, because of the small difference between its thermal conductivity and that of helium which was used as a carrier for all other gases. Sometimes a small peak due to oxygen accompanied the nitrogen peak, respresenting incompletely purged connecting tubing. Nitrogen was present since it was used to purge the gas sampling bag. Although each bag was evacuated before re-use, some gas remained trapped. Because of its mode of entry into the gas mixture the amount of nitrogen tended to be variable, and so also, therefore, was the resolution between O_2 and N_2.

The peaks for the hydrocarbon gases were indentified either by co-injection of standards (ethane, ethylene, propane, propene, isobutane, butane, 2,2-dimethyl propane, 2-methyl butane and cyclopentane) or GC/MS (all of the previous plus butene). Two isomers of butene exist, but they could not be resolved. Resolution, except between ethane and ethylene, was generally very good, though it did tend to decrease for the gases with higher boiling boints. As shown, several changes in attenuation were required in order that the higher boiling gases should be visible on the recorder chart. Absolute yields of the gases are given below, which take account of the various attenuation factors.

H_2S was determined in separate chromatograms on the Carbosieve column mainatined at 140°C, when it gave a well-resolved peak but the permanent gases did not. The first major peak that was resolved was identified as due to hydrogen sulfide by spiking with the pure gas. The second resolved peak was tentatively identified as COS through the use of published retention times (Zweis and Sherma, 1972); no standard could be found to confirm this identification by spiking. The yields of the various gases are

N₂   Permanent Gases from PSOC-808
     Carbosieve Column
     Detector TCD (250 °C)
     Injector (250 °C)
     Carrier He (20ml/min)
     Temperature Program 35 °C,
         2min/10°C/min/140 °C, 5 min
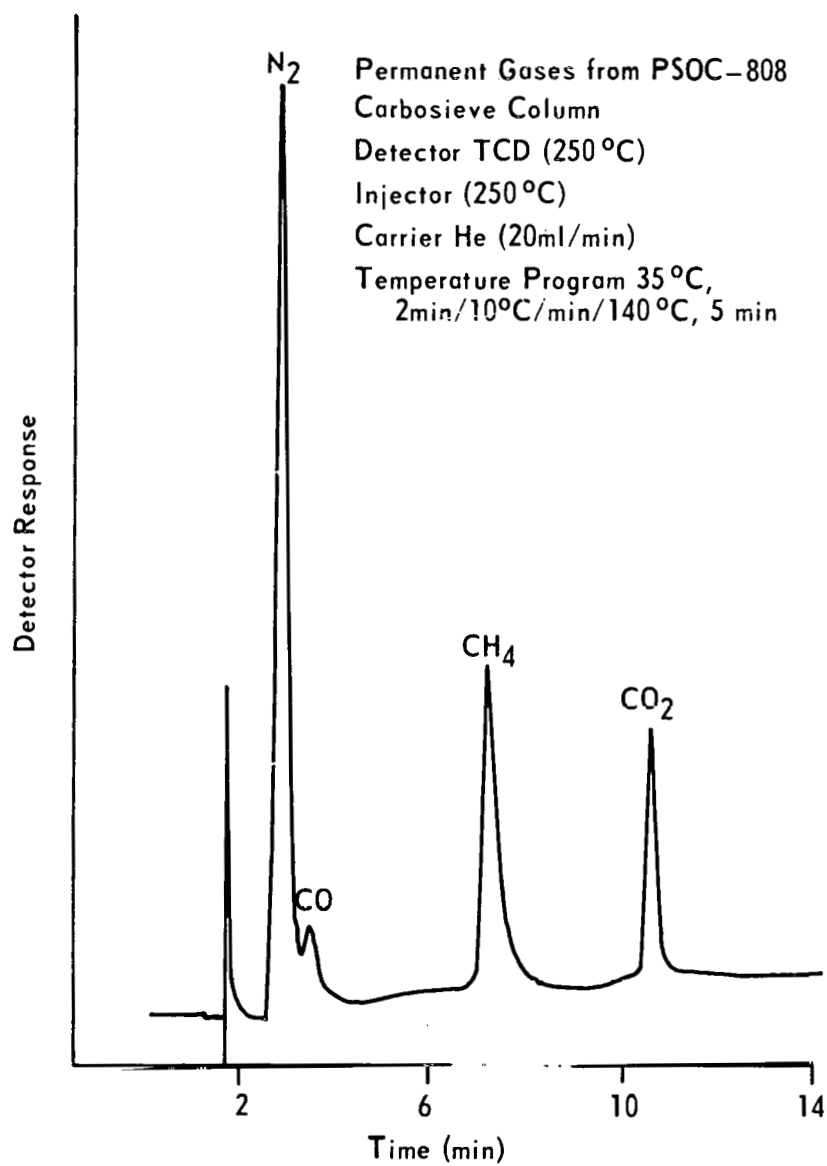
Figure 21. ANALYSIS OF PERMANENT GASES FROM LIQUEFACTION OF
            PSOC-808
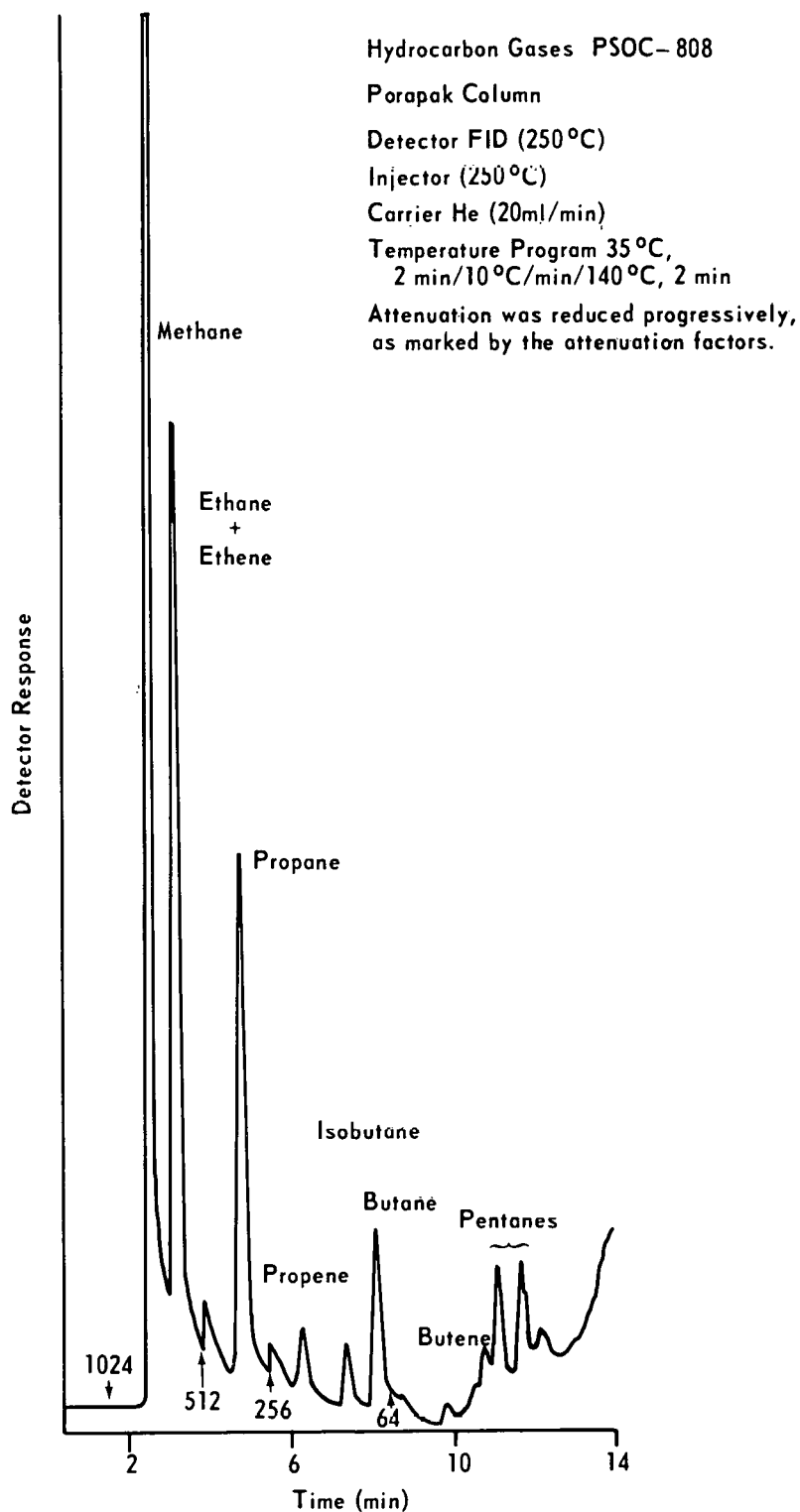
Figure 22. ANALYSIS OF HYDROCARBON GASES FROM LIQUEFACTION
OF PSOC-808

presented in Table 15 as fractions by weights of the organic substance in the original coal. This table also includes the hydrogen content of the gases on the same basis, although it is not a product. Figure 23 shows the yields of classes of gaseous products for each of the coals. These classes are the sulfur-containing (hydrogen sulfide), oxygenated (carbon monoxide and carbon dioxide) and hydrocarbon gases (methane, ethane, ethylene, propane, propene, isobutane, butane, butene, 2,2-dimethyl propane, 1-methyl butane, pentane and cyclopentane).

The conversion to sulfur-containing gases was always less than conversion to hydrocarbon or oxygenated gases. This is in contrast to the results obtained by Longbranch et al. (1978), who found a higher ratio of H_2S to oxygenated species for continuous flow liquefactions at very short contact times (2 min). These workers also found higher hydrocarbons ($>C_2$) by difference to be significantly greater than in this study. However, Whitehurst and coworkers (1976) have found very similar yields of all gases at longer contact times.

It is surprising that the yields of CO_2 are consistently much greater than that of CO. Of 9 coals of carbon content $\leq 80.5\%$, 6 had CO_2 yields $>1\%$, while of coals of $>80.5\%C$, only 2 out of 17 showed CO_2 $>1\%$. Thus the high values of CO_2 yield may be associated with loss of carboxyl groups, but this is far from being the whole story. Among the hydrocarbons, the amounts of n.butane and 2-methyl butane are similar, but, apart from this, the n.alkanes are considerably more abundant than branched chain, cyclic or alkanes. As might be predicted, the yields of hydrocarbons decrease with increasing carbon number. If one sums all the components of the same carbon number, the mean yields for a random selection of 10 coals are:

C_1, 0.628; C_2, 0.138; C_3, 0.129; C_4, 0.019; C_5, 0.0052

Table 15. Yields of Gases as Products from Liquefaction of coals

Percent by weight of dmmf coal

PSOC No.	H_2	H_2S	CO	CO_2	CH_4	C_2H_4 $+C_2H_6$	C_3H_8	C_3H_6 $\times 10^{-2}$	C_4H_{10} $\times 10^{-2}$	iso- C_4H_{10} $\times 10^{-3}$	1+2- C_4H_8 $\times 10^{-4}$	C_5H_{12} $\times 10^{-3}$	2-Me- but. $\times 10^{-3}$	neo- pent. $\times 10^{-4}$	cyclo- pent. $\times 10^{-4}$
349	1.37	0.215	0.063	0.656	0.677	0.178	0.135	1.72	2.37	11.8	19.3	4.52	6.57	10.6	3.93
401	1.47	0.193	0.057	0.392	0.522	0.146	0.107	1.19	2.22	12.9	16.5	5.13	8.85	8.51	7.79
581	1.47	0.342	0.172	0.975	0.552	0.154	0.099	1.21	1.79	9.52	17.6	2.76	4.63	7.05	3.93
582	1.21	0.313	0.120	0.875	0.527	0.141	0.104	1.08	2.11	7.44	6.45	3.88	5.74	4.84	7.22
593	1.28	0.264	0.072	0.542	0.258	0.113	0.070	0.83	1.27	8.07	10.7	2.41	3.70	5.39	4.45
594	1.48	0.175	0.098	0.742	0.207	0.117	0.081	0.69	2.03	5.96	15.5	3.12	5.36	10.1	5.16
596	1.65	0.242	0.068	0.689	0.628	0.146	0.086	3.07	1.65	7.08	8.34	2.83	3.74	7.98	4.92
599	2.21	0.350	0.178	0.799	0.515	0.190	0.274	0.83	1.78	6.35	8.39	0.66	2.86	2.05	1.34
664	1.88	0.413	0.072	1.89	0.232	0.243	0.066	1.70	1.36	6.18	8.46	2.80	2.35	12.3	7.26
666	1.69	0.403	0.178	1.20	0.454	0.231	0.108	0.83	1.66	3.82	8.95	2.22	1.94	8.67	8.39
669	1.77	0.230	0.195	1.41	0.587	0.221	0.096	0.69	1.43	4.75	7.14	2.38	2.37	6.36	8.88
676	1.55	0.314	0.114	1.80	0.812	0.174	0.082	0.45	1.00	2.49	0	0.71	0.56	13.7	1.99
680	1.41	0.263	0.207	1.80	0.702	0.079	0.035	0.17	0.59	2.36	0	0.30	0.27	0	2.78
741	1.74	0.309	0.079	0.591	0.524	0.176	0.102	0.64	1.38	5.03	7.04	2.39	2.15	7.27	6.42
742	1.71	0.325	0.146	1.13	0.657	0.293	0.186	2.74	0	11.3	7.16	3.26	2.82	8.37	11.8
760	2.29	0.316	0.116	0.928	0.694	0.099	0.096	0.43	0.72	1.20	11.0	0.40	0.58	2.17	9.93
767	1.66	0.207	0.053	0.285	0.521	0.171	0.111	1.04	2.32	5.52	11.4	4.58	7.73	4.25	6.99
768	1.79	0.251	0.036	0.220	0.268	0.091	0.092	0.46	7.31	5.04	9.41	2.46	3.63	6.25	4.36
773	1.39	0.132	0.076	0.950	0.380	0.146	0.150	0.90	1.35	4.51	3.23	1.21	3.42	5.78	4.60
798	1.46	0.309	0	0.572	0.963	0.030	0.169	0.047	0.51	0.68	1.05	0.81	0.35	1.03	6.36
808	1.26	0.208	0.065	0.533	0.650	0.079	0.020	0.45	0.92	3.24	4.51	1.24	0.33	8.24	3.81
883	1.38	0.306	0.081	0.227	0.363	0.140	0.067	0.67	0.90	2.04	3.88	1.29	0.44	3.53	3.21
1018	2.08	0.293	0.110	0.240	0.340	0.117	0.070	0.60	1.71	5.55	20.1	1.91	3.10	4.63	3.79
1082	1.65	0.274	0.090	0.741	0.436	0.169	0.056	0.55	1.22	3.02	4.12	1.62	1.45	5.69	3.78
1083	1.48	0.247	0.129	1.30	0.934	0.239	0.016	0.46	1.39	2.52	3.84	1.63	1.56	4.89	4.83
1098	1.09	0.193	0.296	1.12	0.851	0.097	0.056	0.21	0.54	2.16	8.83	0.64	1.07	3.54	3.53

Note: 2-Me-but = 2-methyl butane; neopent. = neopentane; cyclopent. = cyclopentane
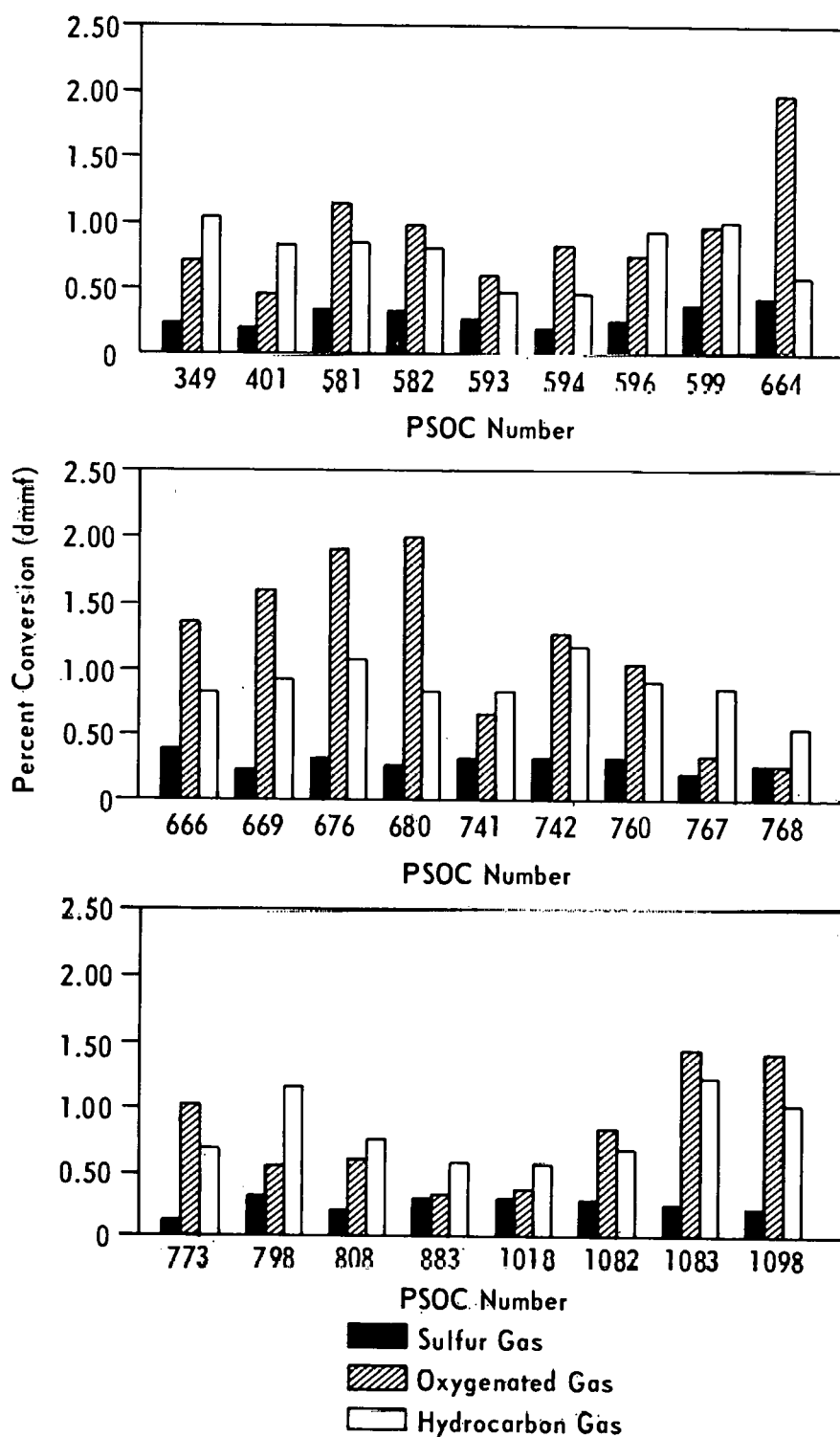
Figure 23. YIELDS OF VARIOUS CLASSES OF GASEOUS PRODUCTS FROM LIQUEFACTION

The near-equality of C_2 and C_3 is unexpected. Presumably hydrocarbons result from thermal cracking of long-chain alkanes or alkylaromatics. In general, thermal cracking of a linear alkane, $C_nH_{2n + 2}$, yields methane, a little ethane, and the first (n-1) alkenes. Under liquefaction conditions alkenes are likely to give alkanes. There are no obvious trends in hydrocarbon distribution with rank.

c. Tetralin/Naphthalene Ratios

The ratio of tetralin to naphthalene was determined by GC to provide information on hydrogen transfer from the solvent to the coal during liquefaction. The vacuum distillate from the spinning band column for each oil fraction was analyzed in duplicate.

The results from the GC separation of the tetralin naphthalen mixture are presented in Table 16, for each sample except PSOC-594, for which no results are available. Reproducibility of the method was generally very good with a standard deviation between duplicates of 1.07%. Since the values are reported as ratios the main source of error in the measurements can be traced to inconsistencies in the vacuum distillation. There were a number of problems associated with this procedure: it was difficult to determine when to stop the distillation, and solidification of the naphthalene in the take-off section of the still tended to cause blockages and stop distillation prematurely.

Table 16 also shows the amount of hydrogen lost by tetralin, calculated from the yield of naphthalene and assuming that all of it is added to the coal (the author is indebted to P. Stansberry for a direct determination of the ratio of molar response factors; 1.04 mole tetralin gives the same peak area as 1 mole naphthalene). Of course, some of the tetralin is converted to such artifacts as methyl indanes and hydrogenated

Table 16. Ratio of Peak Areas in the GC Separation of Tetralin
           and Naphthalene

PSOC No.	Tetralin/ naphthalene	H lost by tetralin*
349	5.9	0.87
401	7.2	0.71
581	5.0	1.02
582	4.5	1.17
593	4.8	1.05
594	-	-
596	5.9	0.86
599	8.8	0.62
664	4.8	1.10
666	7.3	0.74
669	5.1	0.98
676	5.3	1.01
680	5.6	0.74
741	5.9	0.98
742	4.9	1.18
760	6.4	0.81
767	6.7	0.71
768	7.8	0.71
773	4.8	1.00
798	9.7	0.53
808	8.9	0.53
883	10.2	0.53
1018	7.2	0.72
1082	5.5	1.02
1083	5.7	0.84
1098	6.0	0.89

*as gm H per 100 gm. dmmf coal

binaphthyls. The effect of this is to reduce the figures for hydrogen transferred. On the other hand some of the hydrogen lost may have been used in reducing pyrite. There is a tendency for hydrogen consumption to increase with decreasing rank.

The figures in Table 15 included the contents of hydrogen in the gaseous products, and from these the amount of H_2 consumed can be estimated. Unpublished work by J. Zoeller (personal communication) indicates that under conditions used in this work, little naphthalene is rehydrogenated, so that hydrogen gas probably effects little reduction of the organic matter of the coal. However, a correlation was found between hydrogen gas consumed and H_2S generated, so perhaps reduction of pyrite was the main function of the hydrogen. There was also some correlation between H_2S generated and the pyritic sulfur content (the correlation with organic sulfur was less good; see Table 22, below).

Thus the data for the two kinds of hydrogen consumption are offered with some uncertainty about their significance.

d. <u>HPLC Separations</u>

Subsequent to the initial separation of the products of liquefaction into four general classes (gases, oils, asphaltenes and solid residue), the oils were further separated utilizing a semi-preparative scale HPLC separation.

Two different separation techniques were tried and dismissed before the technique described in Chapter III, Section E(d) was settled upon. A series of standard compounds was assembled and utilized in evaluating each of the separation techniques. The results from the separation of a six-component mixture are shown in Table 17 for each of the three

Table 17. <u>Capacity and Separation Factors for Compounds in</u>
<u>Six-Component Mixture Used for Testing Separations</u>

Compound	Pseudo-capacity factor, k	Separation factor, α
Cyclohexane	0.05	
		64.6
Naphthalene	3.23	
		1.41
3,4-Benzo(a)pyrene	4.54	
		1.25
Piperidine	5.67	
		1.18
3-4-Benzoquinoline	6.71	
		1.11
3,4-Dimethylphenol	7.43	

The pseudo-capacity factor, k, is defined as V_r/V_v, where V_r is
the retention volume of one component of a mixture and V_v is the
retention volume of another component that is not adsorbed (that,
V_v is the void volume in the column). The separation factor for
a pair of components is defined as $\alpha = K_1/k_2$, where K_1 and k_2
are the pseudo-capacity factors for the two components as defined
above.

methods. As can easily be seen method 3 gave the best overall results. With method 1, the reverse phase procedure, the separation tended to be determined by the numbers of alkyl group substituents rather than the boiling point. This overshadowed the advantage of having the lowest amount of unaccounted for material; since liquefaction products contain a great deal of alkylated material, this feature seemed undesirable. The two normal phase separations were more or less equivalent in the type of separation that they achieved. However the amino column (which is capable of hydrogen bonding) appeared to perform slightly better in separating the polar and aromatic classes, and was able to resolve nitrogen heterocycles from phenols in this standard mixture. Thus, it was decided that the gradient-eluction normal-phase separation gave the best overall results.

The data presented in Table 17 show that the separation of heterocyclic nitrogen compounds and phenols is possible on an amino column. However, this was not found to be the case with the oil samples. Most of the chromatograms did show some degree of separation of the nitrogen-containing compounds being present, but the resolution between them and the phenolic fractions was so poor that trying to collect separate fractions was deemed useless. The degree of separation of these two classes is shown in Figure 24. This chromatogram represents what would be considered the best case, having been run just after the column had been regenerated. Also shown on the Figure are the times at which the receivers for different fractions were changed, and the approximate times at which the various classes of polar compounds began to dominate the eluate. It is obvious that although the two classes were distinguishable, the overlap was too great to afford any meaningful fractions. Thus,
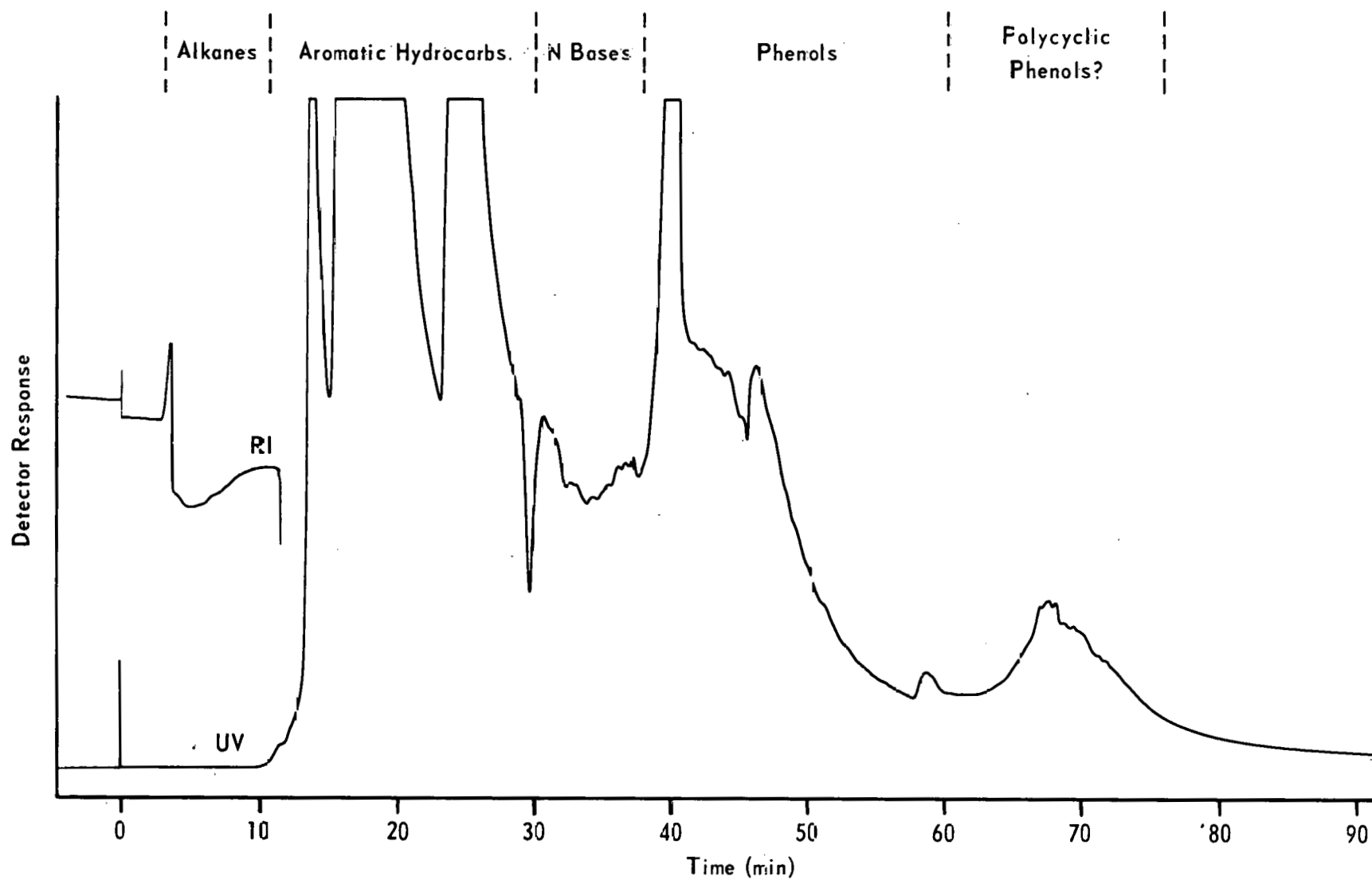
Figure 24. HPLC ANALYSIS OF OIL FROM PSOC-1098

in the results reported in Table 18, the "polar" fraction contains both the nitrogen- and oxygen-containing compounds.

One other problem that should be addressed is the elution of sulfur-containing compounds. Model compounds, such as dibenzothiophene co-eluted with the aromatic hydrocarbon fraction. It appears that the sulfur-containing compounds are not polar enough to separate on any bonded phase HPLC column, and this has also been reported by Uden and co-workers (1981) and others. No doubt ethers, thioethers, and O-heterocycles also eluted with the aromatic hydrocarbons.

Mean values of yields of the compound classes from each coal are reported in Table 18. The material unaccounted for was found to be less than 2% in each case. Reproducibility was relatively good, with a standard deviation of 1.07% for all fractions (material unaccounted for being excluded). It should be remembered that the fraction unaccounted for represents that material which remained on the column after the separation was complete and also any errors in weighing, dilution or injection of the sample. Thus, this fraction can be thought of as having two terms: that which had always a positive value due to irreversible adsorption on the column; and that which was indeterminate and could be either positive or negative. "Unaccounted" represented <0.5% of dmmf coal.

The irreversibly adsorbed material did present a problem during the series of separations. As more and more material collected on the column, resolution deteriorated. Normally only 5-6 separations could be performed before column regeneration was required. Even after regeneration, resolution was still somewhat diminished from that obtained when the column was new.

For the most part, resolution between alkanes, aromatic hydrocarbons

Table 18. Yields of Fractions from HPLC Separations

PSOC No.	Percent of Oil			Pol/Aro.	Percent of Coal (dmmf)		
	Saturates	Aromatics	Polars		Saturates	Aromatics	Polars
349	2.1	31.1	66.8	2.15	0.46	6.79	14.6
401	4.1	27.5	68.4	2.49	0.91	6.10	15.2
581	5.6	27.9	66.5	2.38	1.53	7.61	18.1
582	2.7	29.3	68.0	2.32	0.78	8.50	19.7
593	4.1	26.9	69.0	2.57	1.01	6.64	17.0
594	3.9	26.3	69.3	2.59	0.94	6.49	16.8
596	8.1	26.3	65.6	2.49	1.32	5.90	14.7
599	5.3	26.9	67.8	2.52	1.34	6.78	17.1
664	3.8	26.3	69.9	2.66	1.13	7.82	20.8
666	2.1	28.5	69.4	2.44	0.50	6.78	16.5
669	4.8	27.1	68.1	2.51	1.19	6.70	16.8
676	3.7	26.3	70.0	2.66	0.36	6.12	16.3
680	1.7	27.4	70.9	2.59	0.35	5.64	14.6
741	6.5	27.1	66.4	2.45	1.78	7.42	18.2
742	4.8	28.1	67.1	2.39	1.10	6.43	15.4
760	6.3	27.8	65.9	2.37	1.59	7.03	16.7
767	3.5	29.4	67.1	2.28	0.87	7.31	16.7
768	2.8	34.4	62.8	1.83	0.62	7.62	13.9
773	4.5	31.4	64.1	2.04	1.04	7.23	14.8
798	1.7	37.3	61.0	1.64	0.23	5.13	8.4
808	3.8	26.3	70.0	2.66	0.85	5.94	15.8
883	4.6	32.7	62.7	1.92	1.12	7.94	15.2
1018	6.0	29.7	64.3	2.16	1.80	8.89	19.2
1082	3.4	24.7	71.9	2.91	0.76	5.52	16.1
1083	3.2	28.3	68.5	2.42	0.82	7.27	17.6
1098	2.1	29.4	68.5	2.33	0.56	7.77	18.1

and combined polars appeared to be good. The time between the elution of the aliphatic and aromatic compounds was long enough that no overlap would be expected. This is confirmed by the FTIR spectrum of an alkane fraction shown in Figure 25. This and the spectra shown below were obtained from smears on KBr windows. The fractions were dissolved in a hexane-methylene chloride mixture, and applied dropwise to the window. The window plus smear was left overnight under a gentle stream of nitrogen, and it was then left in a vacuum desiccator for some days.

Absorption in Figure 25 is confined to the 2800-2950, 1375-1450 and 720 cm^{-1} regions, which is characteristic of alkanes. The small doublet band near 720 cm^{-1} is a skeletal vibration of alkyl chains having at least four carbon atoms. The fact that it is a doublet implies that some degree of crystallization has taken place in the smear. Since absorption due to CH_3 is weak, the fraction evidently consists largely of straight chain alkanes.

In the spectrum of the "aromatic fraction", absorption due to methyl is quite large, no sharp alkane skeletal vibration near 720 cm^{-1} is seen, and the pattern of aliphatic C-H stretching vibrations in the region 2800-3000 cm^{-1} is different from that seen in the alkane fraction (Figure 26). Hence it is unlikely that the receiver was changed too soon and some alkane collected with the aromatic fraction. Aromatic absorptions are weak (3030, 1600, 1500, 750-950 cm^{-1}), and aromatic structures are primarily single-ring. The sharp band at 1725 cm^{-1} is striking; it is due to the presence of an aliphatic ketone (or possibly an aliphatic ester). Other vibrations due to C-O and C=O groups are seen between 1050 and 1270 cm^{-1}.

It is really not possible to determine from the spectrum of the
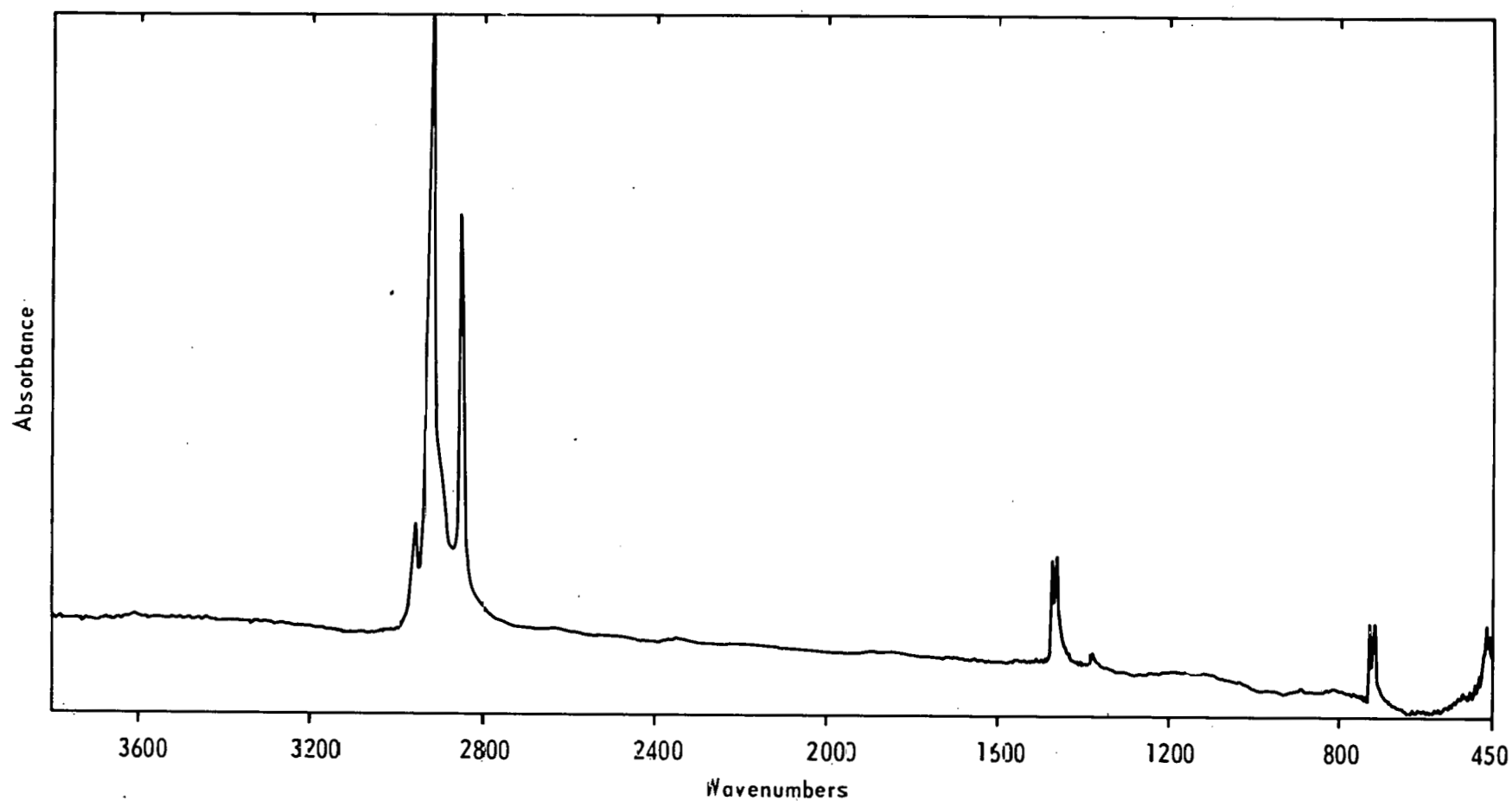
Figure 25. FTIR SPECTRUM OF ALKANES FROM HPLC SEPARATION OF OIL FROM PSOC-666
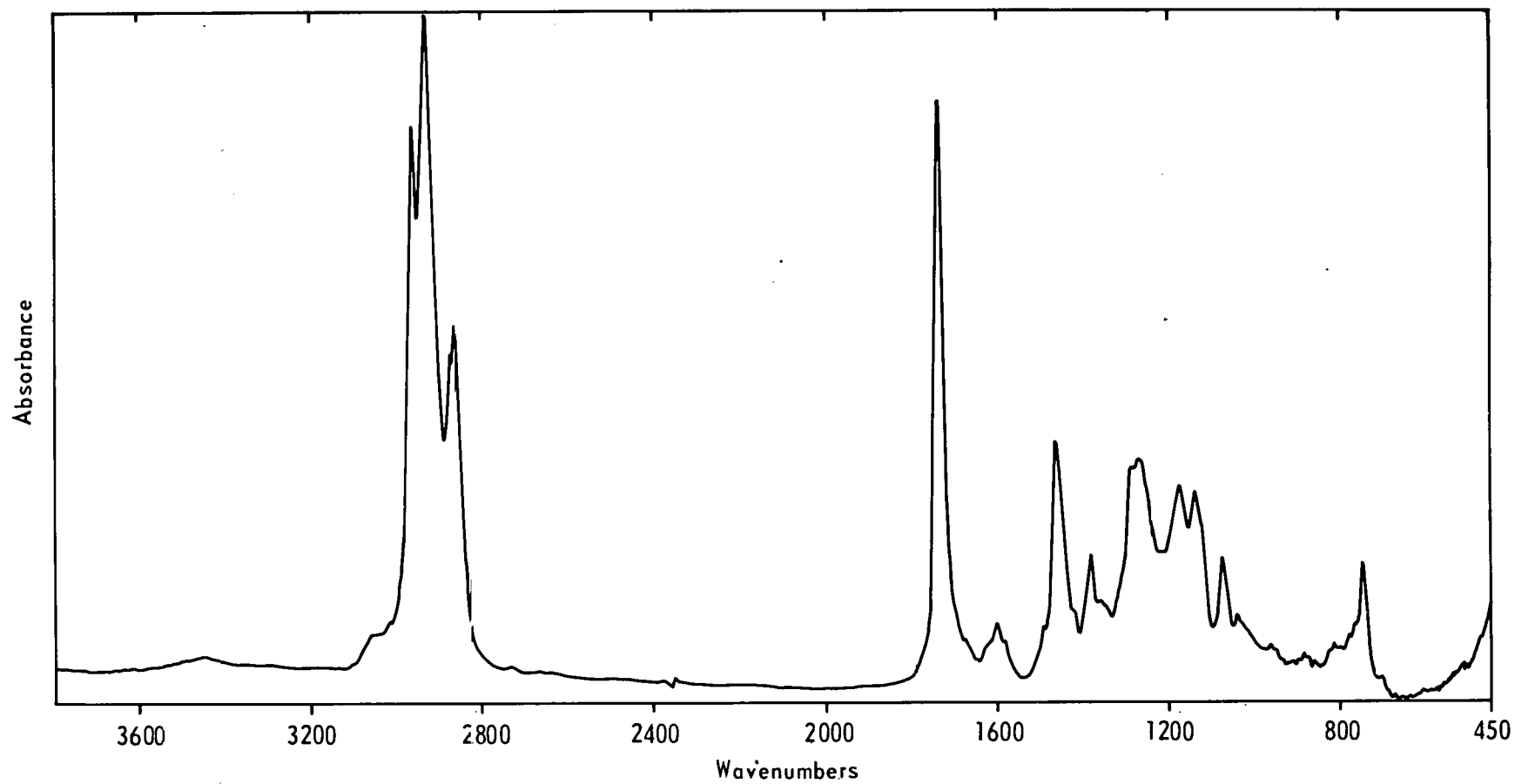
Figure 26. FTIR SPECTRUM OF NON-POLAR AROMATIC FRACTION FROM HPLC SEPARATION OF OIL FROM PSOC-666

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polar fraction (Figure 27) whether some polycylic aromatic hydrocarbons has a pronounced aliphatic character, and methyl absorptions are specially strong (2956, 1375 cm^{-1}). However, aromatic character is more marked than in Figure 26 (1625, 1580, 750-910 cm^{-1}). The region 1550-1800 cm^{-1} is particularly complex. The shoulder at 1760 cm^{-1} must be due to the presence of a phenolic carboxylate ester in small amount, while the band peaking at 1715 cm^{-1} most probably indicates aliphatic ketones. The marked overlapping of bands in this region ensures that the bonds centred at 1675, 1615 and 1575 are not peaking at their normal group frequencies. Aromatic ketones or quinones and olefinic double bands may be present, and the aromatic breathing vibration is certainly present in the complex envelope. The fact that the spectrum was run on a smear and not on a KBr pellet allows us to assume that the OH band centred at 3450 cm^{-1} represents hydrogen-bonded hydroxyl and not water (and that the 1615 cm^{-1} band is not due to water).

Thus the information in the spectra is interesting and contains a number of unexpected features. Unfortunately FTIR spectra were not run on the HPLC fractions from other coals, and nor were ^{1}H nmr spectra obtained.

Judging from the shape of the chromatogram in the region between the non-polar aromatic and polar fractions a small degree of overlap occurred. This degree of resolution between the two fractions was somewhat different for each separation and depended on the condition of the column, the individual sample and how well the cut between the fractions was made. However, it is important to point out that in all cases the degree overlap was small. In Figure 28, the yields of the HPLC
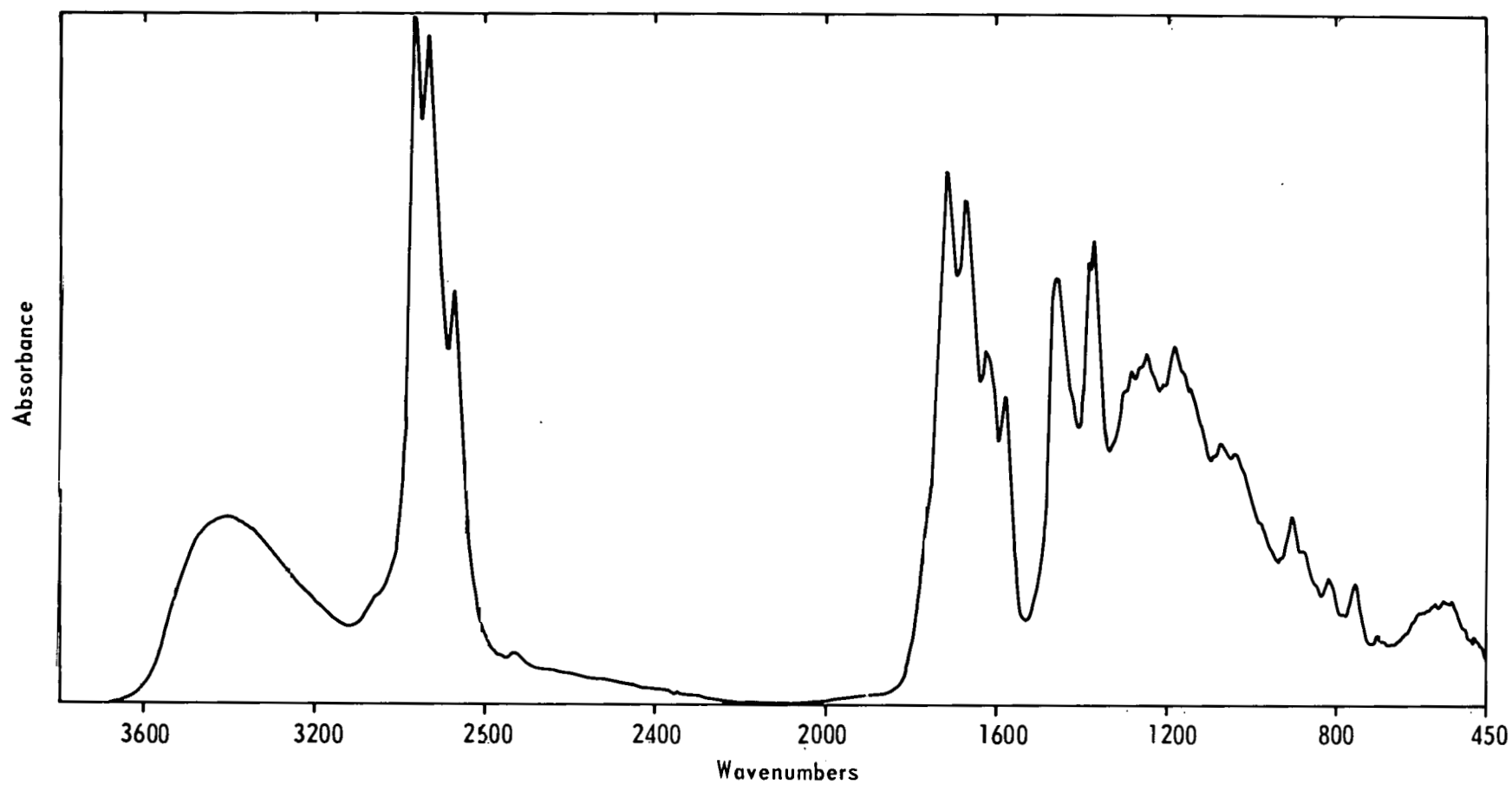
Figure 27. FTIR SPECTRUM OF POLAR FRACTION FROM HPLC SEPARATION OF OIL FROM PSOC—666
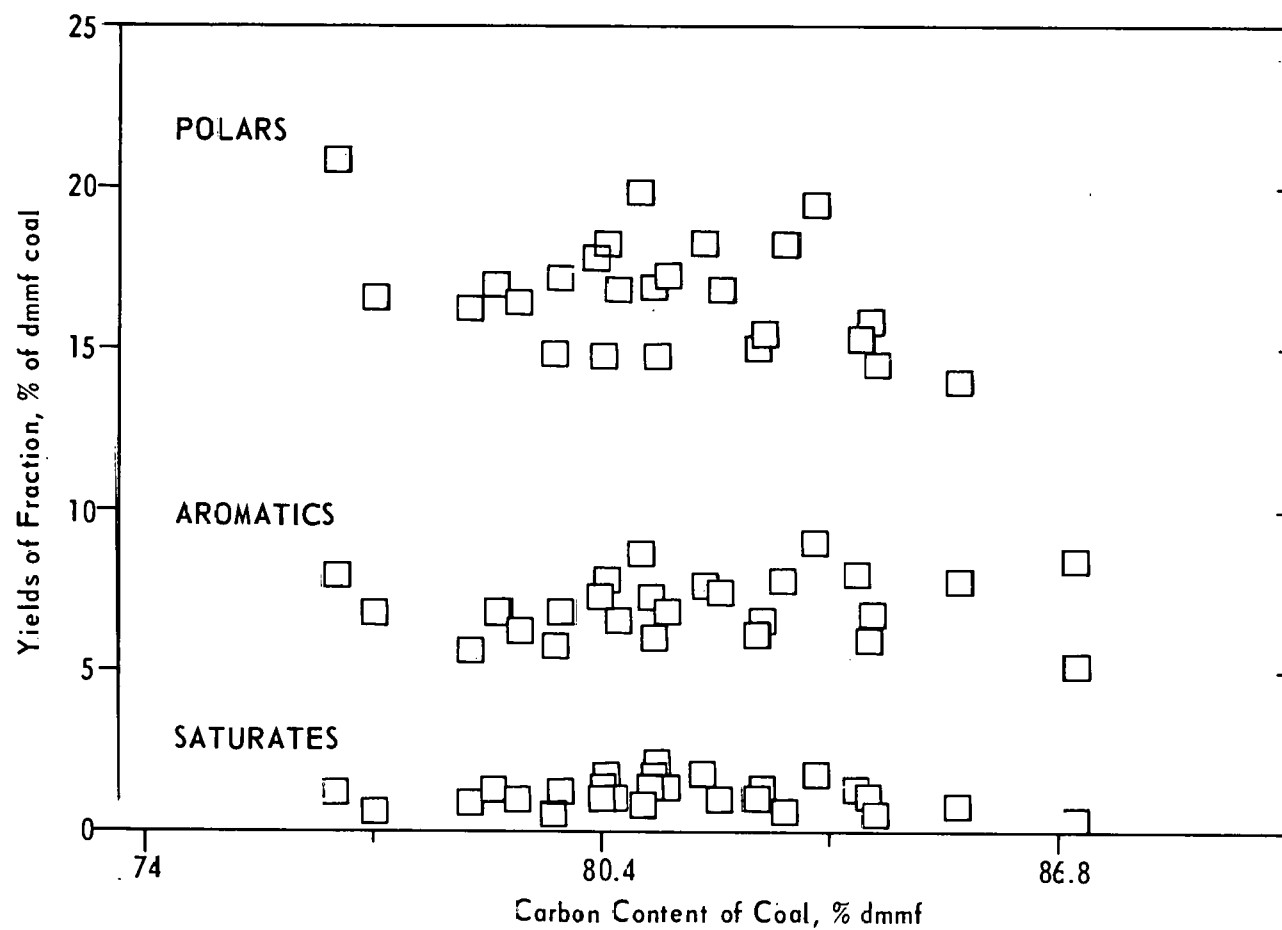
Figure 28. YIELDS OF HPLC FRACTIONS IN RELATION TO RANK

fraction is plotted against the carbon content of the coal. The most striking feature of this figure is the small degree of change with rank. Although a fair amount of scatter is present in the data there may be a real trend of decreasing yield of polars with increasing rank. Since in the rank range covered the O content of the coals decreases markedly, one would have expected a bigger effect.

It should be pointed out that the scatter is somewhat greater for the polar fraction than for the others. This is probably due to a greater degree of irreversible adsorption on the column. It is intuitively obvious that this fraction should be affected by this process to the greatest extent, and one would also expect the magnitude of adsorption to vary with the state of the column. Thus, one would expect to see an increase in irreversible adsorption of the polar fraction in a separation made immediately after the column is regenerated. In this way some apparently random noise will be introduced.

CHAPTER V

STATISTICAL ANALYSES OF DATA

A. INTRODUCTION

In the previous chapter the results of applying a variety of analytical methods to the original coals and their liquefaction products were presented with a minimum of discussion. In this chapter various statistical methods will be used in a search for interrelationships within the very large data matrix. In making this search a number of problems have to be addressed. One important issue to be investigated is the possibility of more than one statistical population being present in the sample set or data set. We must obviously try to solve the problem posed in Chapter I, how are aspects of liquefaction behavior related to features of the structural chemistry of coals? In all statistical studies, one is likely to be confronted with the problem of outliers, that is, individual data points that seem not to fit the general pattern of data points of the same kind.

The total matrix of data points for coal properties and liquefaction behavior is envisaged as being clustered in n-dimensional space; are some data points so remote from their clusters as to be highly anomalous and likely to skew distributions seriously?

A general overview of the statistical analysis scheme is provided in Figure 29. The initial phase involves a preliminary examination of the variables and samples to determine if the variables seem coherent

PRELIMINARY EXAMINATION

1.) Frequency Histograms
2.) Univariate Statistics
    a) means
    b) standard deviations
    c) skewness and kurtosis coefficients
    d) variable - variable plots

Modify

Intractable
Variable

Intractable
Sample

Remove

INITIAL CLUSTERING

1.) Tree Cluster
2.) Hierarchical Clustering
3.) Factor - Factor Plots

More than one
population

One Population

Split Data
Set

MODIFICATION OF DISTRIBUTIONS

Single Populations

STATISTICAL ANALYSIS

a) Bivariate Regressions
b) Factor Analysis
c) Multivariate Regressions

Figure 29. OVERVIEW OF STATISTICAL SCHEME USED

or whether more than one population is present. Also, the scheme is intended to ascertain if any of the samples differ so greatly as to be considered intractable from a statistical point of view (that is, to be outliers). The methods utilized in these procedures include distribution plots (frequency histograms), univariate statistics such as calculation of means, standard deviations, minimum and maximum values of a range, and coefficients of skewness and kurtosis, variable-variable plots, and correlation analysis. The second step involves the use of hierarchical and tree-clustering techniques, and factor-factor plots to partition the sample or data set into more homogeneous populations, if this proves necessary. The data for the subsets are then split up and the initial analysis is repeated. If a sample is found to be totally intractable it would normally be removed before the grouping techniques are applied; however, no totally intractable variables were found in the present study. If it is found necessary to partition the sample set into more homogeneous subsets, further statistical analysis is performed independently on the various subsets. After an initial examination of data structure, factor analysis will be extensively used as an investigative tool in searching for multi-variate relationships.

One further point that should be emphasized is the problem associated with the presence of a non-infinite sample set. Care must be taken to ensure that incorrect interpretations are not made because of the normal scatter of data when a limited number of samples is available.

B. DEFINITION OF THE DATA SET

If one includes all of the FTIR band intensities, the yields of all important products of TFPA oxidation, the basic compositional data for

the coals, and all of the information about product distributions,
including gas analyses, the data matrix becomes of quite unmanageable
size. Obviously a process of selection is necessary, and any selection
will to some extent be arbitrary. It is desirable that the selection
should give some weight to each of (a) rank and environments of deposi-
tion of samples, (b) structural features of the coals, and (c) yields
and product distributions in liquefaction. The parameters selected
and used in most of the statistical studies are listed in Table 19;
thus the practical data matrix consisted of 26 coal samples by 19
properties. For factor analyses several smaller sets had to be chosen.
For the preliminary examination (data structure), some supplementary
parameters were added, as will be shown below (Table 20, p. 142).

For the most part the basis of selection in Table 19 is obvious,
but a few comments are called for. Total gas yields were excluded
because the variability is small and the reproducibility poor. Never-
theless H_2S is included because of the importance of establishing
relationships with hydrogen consumption and forms of sulfur in the coals.
Ratios of gases should be more reproducible and the ratio of lower to
higher hydrocarbons might be related to structural features in the coal
and to yields in TFPA oxidation. The rationale for summing yields of
various groups of products from TFPA oxidation has been given earlier;
here a further simplification is made; "aromatic" acids refers to the sum
of the peak areas of benzene carboxylic and oxirane carboxylic acids.

C. AN EXAMINATION OF DATA STRUCTURE

The initial problem that must be addressed in a statistical analysis
of a large data set is that of initially evaluating the variables that

Table 19. Variables Selected for Study of Interrelationships by Statistical Methods

Property	Associated with	Property	Associated with
%C dmmf H/C O/C R_o, %	rank	f_a S_o phenolic OH ali./arom. C-H CH_2/CH_3 ratio, I.R. arom. acids, TPA acyclic di/tri acids, TPFA	structure
oil yield (oil + lost vols.)/asph. oil + lost vols. + gases polar fractn., HPLC $(C_1 + C_2)/(C_3 - C_5)$ gases tetr./naphth. ratio	products	yield, H_2S, % of coal S_p, % of dry coal	sulfur

have been chosen. The purpose of the initial evaluation is to determine whether these distributions are amenable to further analysis by techniques such as factor analysis. Three separate distribution patterns are possible for a set of variables. Gaussian distribution about a central value, which is the optimum case; a skewed distribution, where more of the samples lie to one side of the maximum value than the other; and a bi- or multi-modal type of distribution, where two or more frequency maxima are encountered.

Examples of each of these distributions are presented in Figure 30. Part a of the figure presents the distribution of fractions of the coal converted to hydrocarbon gases on liquefaction and represents what is most probably a reasonable approximation to Gaussian distribution around the maximum. The possibility that this really represents a bi-modal distribution cannot be excluded, because of the limited size of the sample set. Truly Gaussian patterns are rarely obtained with experimental data, especially when a rather limited number of data points is available. Figure 30b represents what must be considered a skewed distribution. For certain purposes, variables that exhibit distributions of this type need to be transformed by means of some suitable function before other statistical techniques are applied. The final type of distribution, illustrated in Figure 30c, represents a bi-modal distribution, for the yields of the non-polar aromatic fraction from HPLC separation of oils from liquefaction. This type of distribution could possibly be indicative of more than one statistical population being present in the data. This possibility must be checked before the

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(a) Total Yield of Hydrocarbon Gases (Gaussian)

(b) Yield of H_2S Gas (Skewed)

(c) Yield of Non-polar Aromatic Fraction from HPLC (Bi-modal)
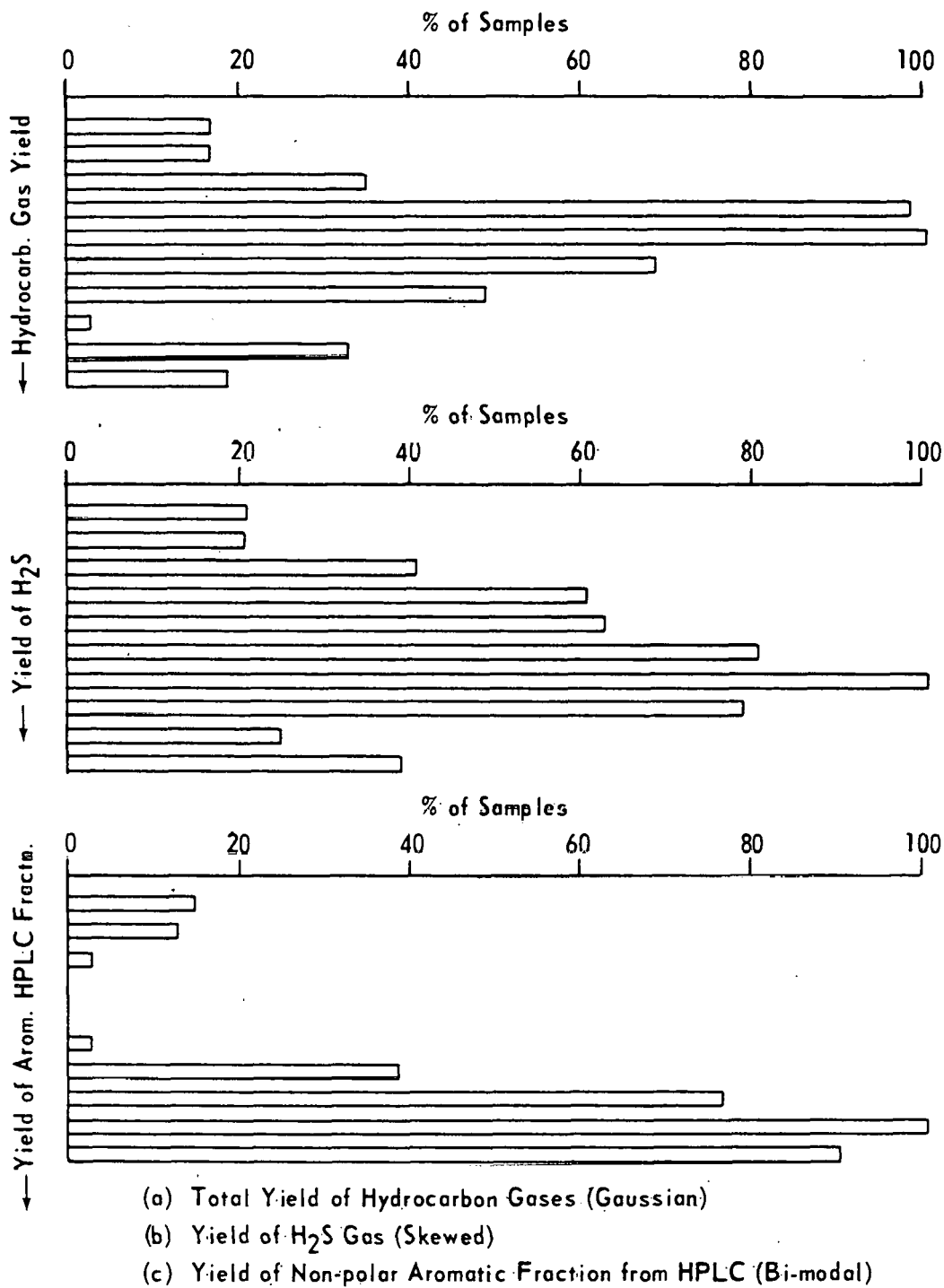
Figure 30. EXAMPLES OF DIFFERENT FREQUENCY DISTRIBUTIONS OF DATA

results from the use of subsequent statistical techniques can be fully trusted.

a. Tests of the Data Set

For the reasons set out in the previous section it is necessary to examine the types of distribution present in the various kinds of data. The summary statistics in Table 20 present the basis for doing this. Included in the table are the means, standard deviation, normalized standard deviation $(S.D./\bar{X})$, minimum and maximum of ranges, coefficient of skewness $[(\alpha_{2,i} = m_{3,i}/(m_{2,i})^{3/2}$ where $m_{3,i} = \sum_{k=1}^{n}(x_{,k} - \bar{X}_i)^3/n$, $m_{2,i} = \sum_{k=1}^{n}(x_{i,k} - \bar{X}_i)^2/n$, n = the number of samples and k is any integer from 1 to n], and the coefficient of kurtosis $[\alpha_{4,i} = m_{4,i}/(m_{2,i})^2$ where $m_{4,i} = \sum_{k=1}^{n}(x_{i,k} - \bar{X}_i)^4/n]$. Although all of the summary statistics in the table are important in describing the data the coefficients of skewness and kurtosis are of special interest. These two values along with the frequency histograms of the type shown in Figure 30 indicate that there is a good possibility of more than one statistical population being represented in the data set. Most of the variables show at least some degree of skewness or kurtosis, with organic sulfur content, tetralin/naphthalene ratio, and conversion to lost volatiles, exhibiting the greatest degree of skewing. The yield of the aromatic HPLC fraction, conversion to asphaltenes, yield of polar HPLC fraction, and total conversion, show the largest coefficients of kurtosis, indicating a bi- or multi-modal distribution.

It may be inferred that if some of the parameters show bi- or multi-modal distributions, then the set of coal samples might be

Table 20. Summary Statistics of the Variables Studied, Including Skewness and Kurtosis

	Variable	Mean	Standard deviation	Normalized stand. dev.	Min. value	Max. value	Range	Skewness	Kurtosis
1.	f_a	0.731	0.037	0.051	0.660	0.800	0.14	-0.0389	2.20
2.	%C	81.5	2.47	0.030	76.8	87.1	10.3	0.227	2.77
3.	%H	5.55	0.30	0.053	5.17	6.52	1.35	1.72	6.28
4.	%S	1.56	0.25	0.16	1.25	2.29	1.04	1.22	4.49
5.	$%S_0$	2.26	0.77	0.35	1.08	4.26	3.18	0.915	3.80
6.	conversion liquids + gases	68.0	9.51	0.14	41.4	79.7	38.3	-1.63	5.47
7.	asphaltene yield	33.0	4.68	0.14	19.4	40.9	2.15	-1.69	6.41
8.	yield of alkanes (HPLC)	1.00	0.44	0.44	0.23	1.82	1.59	-3.69	2.43
9.	neutral aromatic fraction (HPLC)	6.44	1.99	0.31	0.10	8.89	8.79	-2.08	7.24
10.	polar fraction	16.3	2.34	0.14	8.40	20.8	12.4	-1.14	6.45
11.	yield H_2 gas	384	67.3	0.18	256	553	297	0.633	3.46
12.	H_2S yield	3.83	0.87	0.22	2.00	5.65	3.65	0.0127	2.70
13.	CH_4 yield	15.6	6.5	0.39	6.33	30.2	23.8	0.280	2.47
14.	C_2 gas yield	2.46	0.95	0.38	0.49	4.50	4.01	0.241	2.74
15.	$CO+CO_2$ yield	11.4	5.84	0.51	2.85	23.7	20.8	0.479	2.26
16.	hydrocarbon gases	20.5	6.63	0.32	9.49	36.4	26.9	0.240	2.82
17.	C_3 gas yield	1.26	0.58	0.46	0.29	2.93	2.64	0.861	4.01
18.	%O	9.31	2.00	0.21	4.79	11.3	7.05	-0.605	2.41
19.	aliphatic/aromatic C-H ratio	2.12	1.11	0.52	0.01	3.98	3.97	-0.304	2.22
20.	aliphatic OH content	284	128	0.45	24.0	577	553	0.134	2.75
21.	aromatic OH content	393	250	0.64	35.0	866	831	0.484	1.97
22.	acetylatable NH content	245	146	0.60	42.0	728	686	1.48	5.72
23.	mineral matter, %	15.3	4.26	0.28	6.42	22.4	16.0	-3.98	2.65
24.	gas yield	2.11	0.63	0.30	1.07	3.53	2.46	1.96	2.42
25.	oil yield	24.2	3.26	0.13	13.8	29.9	16.2	-8.21	5.50
26.	yield of lost volatiles	9.07	4.42	0.49	0.83	17.5	16.6	0.0891	2.30
27.	tetralin/naphthalene ratio	6.36	1.60	0.25	4.53	10.2	5.67	0.988	3.01
28.	H_2 gas recovered	1.59	0.29	0.18	1.09	2.23	1.19	0.686	3.09
29.	vitrinite content	87.6	3.85	0.044	80.6	94.6	14.0	-0.201	1.95
30.	pyritic S	2.13	1.06	0.49	0.04	3.90	3.86	-0.195	2.13

Notes: (a) the gas yields (items 11-17 inclusive) are expressed as ml(NTP) per gm. dmmf coal (b) the FTIR band intensities (items 19-21) are expressed as areas in arbitrary units (c) item 28 is same as item 11 but is expressed as gm H_2 per 100 gm dmmf coal.

heterogeneous and need to be partitioned into subsets. In this case, the next step is to determine the number of statistically significant groups, and which coals belong in each group. Additionally, one would like to evaluate the confidence that can be placed on the grouping.

b. Is the Sample Set Heterogeneous?

Possibilities of partitioning the data set into clusters were examined first using both hierarchical and tree clustering methods. Hierarchical clustering is a technique based on the similarity of a set of samples in n-dimensional space. The technique as described by Kowalski (1974) involves an initial assumption that there is a single cluster. The distance matrix is then constructed, the data set scanned and the most similar samples clustered. The process is repeated at the next greatest similarity level, until each sample forms an individual cluster. In tree clustering each sample is taken to be the center of a cluster. The distances between it and all other samples are then calculated. The groups are then determined by maximizing the distance over the entire data set. Each of these techniques indicated that the data should perhaps be represented by three clusters, but is not capable of determining which sample should be assigned to which cluster, because it cannot handle the situation where some of the variables are correlated with each other. It is therefore necessary to perform a factor analysis on the total set of data, and rotate the result for the purpose of determining the number of independent factors present. The variance explained by each factor is shown in Figure 31. It appears that after 16 factors have been extracted, further extraction accounts
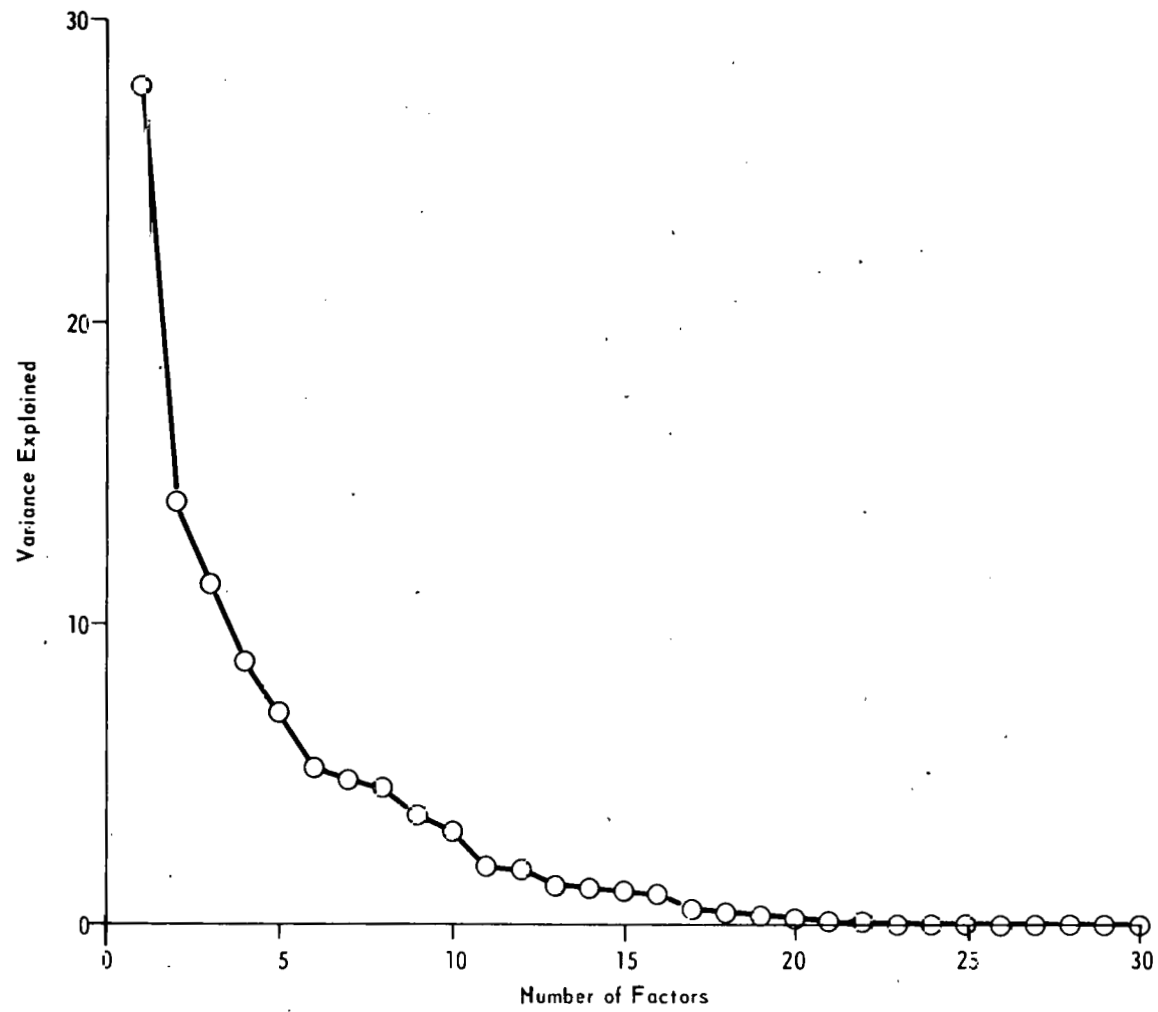
Figure 31. VARIANCE EXPLAINED IN FACTOR ANALYSIS OF TOTAL DATA SET

for a trivial additional amount of the total variance. These operations led to what is known as the reduced, orthogonalized, data matrix; the data have been "decorrelated."

Plots of the eigenvalues corresponding to the second and third factors *versus* the first and the second *versus* the third are presented in parts a and b of Figure 32. As can easily be seen there appears generally good separation between the relatively compact coals groups. The coal samples thus assigned to the three factors are as follows:

Group 1   PSOC   349, 401, 594, 599, 798, and 883
Group 2   PSOC   581, 582, 593, 596, and 1098
Group 3   PSOC   664, 666, 669, 676, 680, 741, 742, 760,
                   767, 768, 773, 808, 1018, 1082, and 1083

It is now possible to perform cluster analyses using the data from the factor analysis. In fact, neither non-linear mapping (Figure 33) nor hierarchical clustering (Figure 34) confirmed this sample structure. Additionally, tree clustering was not able to detect any sample subsets at all. Further analysis of the factor plots (Karhunen-Loeve projection) indicated that Factor 1 had significant loading for only two variables, contents of oxygen and of phenolic groups. Examination of the Karhunen-Loeve projections for factor pairs excluding Factor 1 indicated that the proposed grouping was due mainly to the distribution of oxygen. Removal of the two oxygen-related variables from the data set produced the Karhunen-Loeve projections for the first two factors shown in Figure 35, which do not indicate any particular partitioning into subsets.
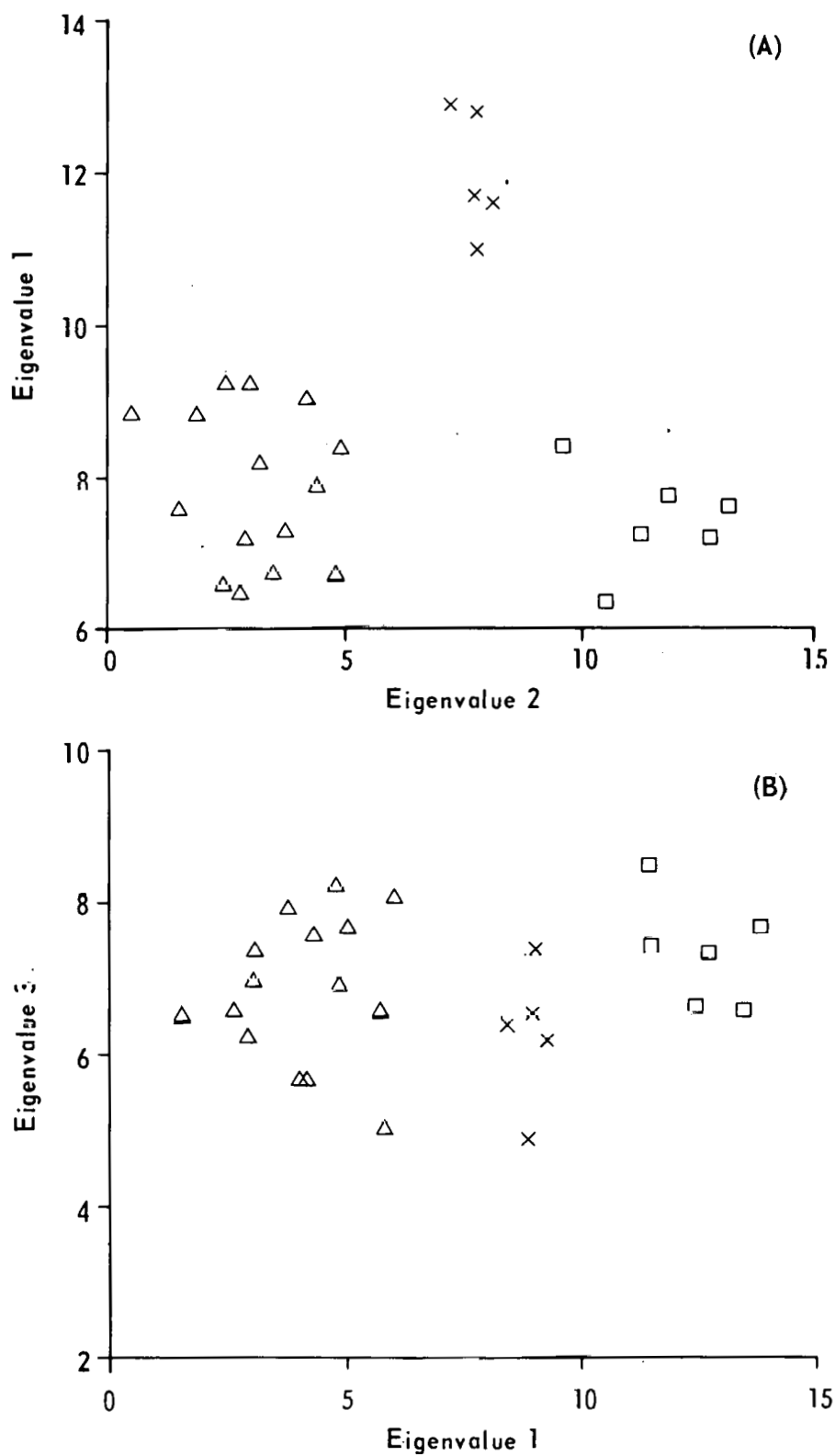
Figure 32. EIGENVALUES FOR FIRST THREE FACTORS IN FACTOR
ANALYSIS OF TOTAL DATA SET
(A) Factors 1 and 2, (B) Factors 1 and 3
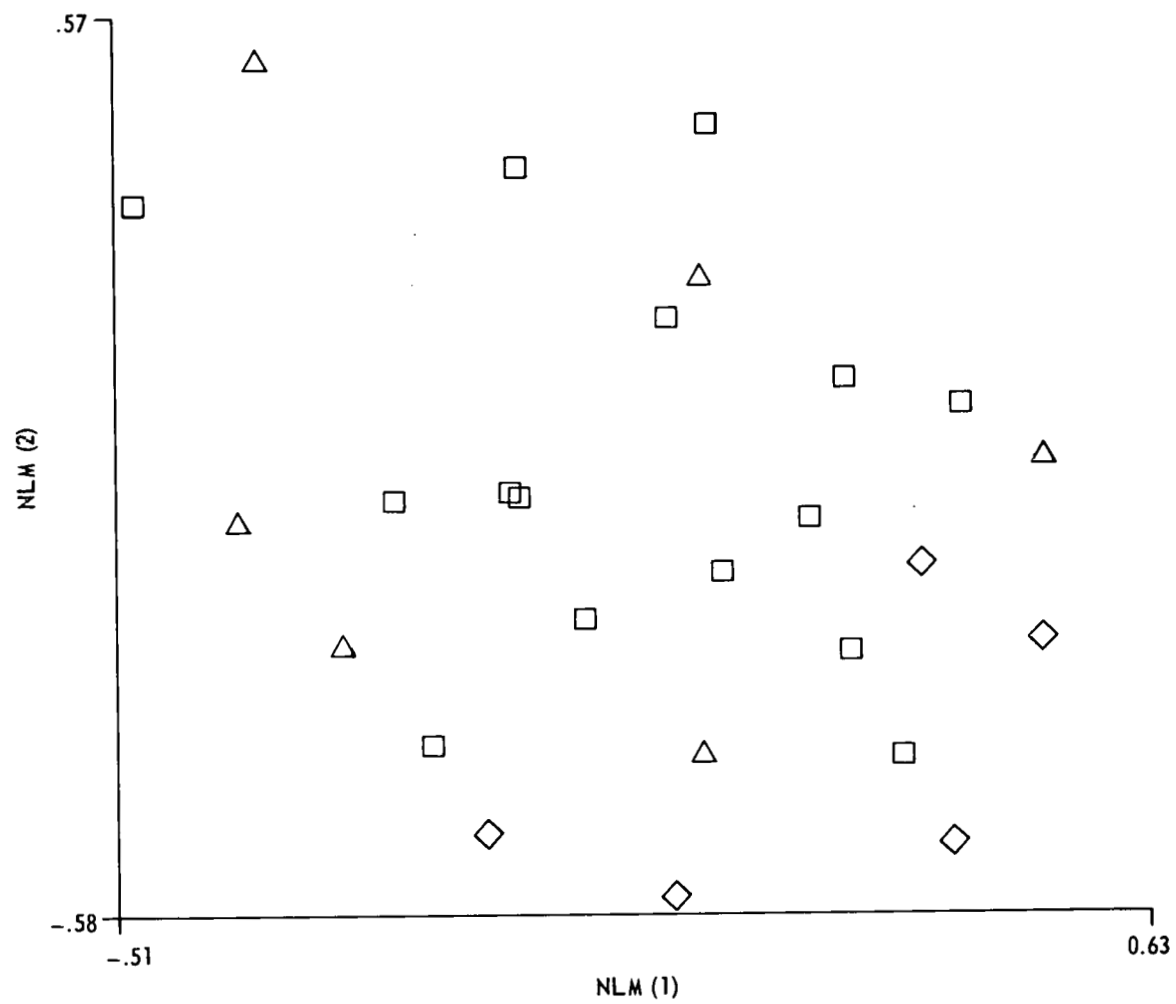
Figure 33. NON-LINEAR MAPPING OF STRUCTURAL PROPERTIES OF COALS
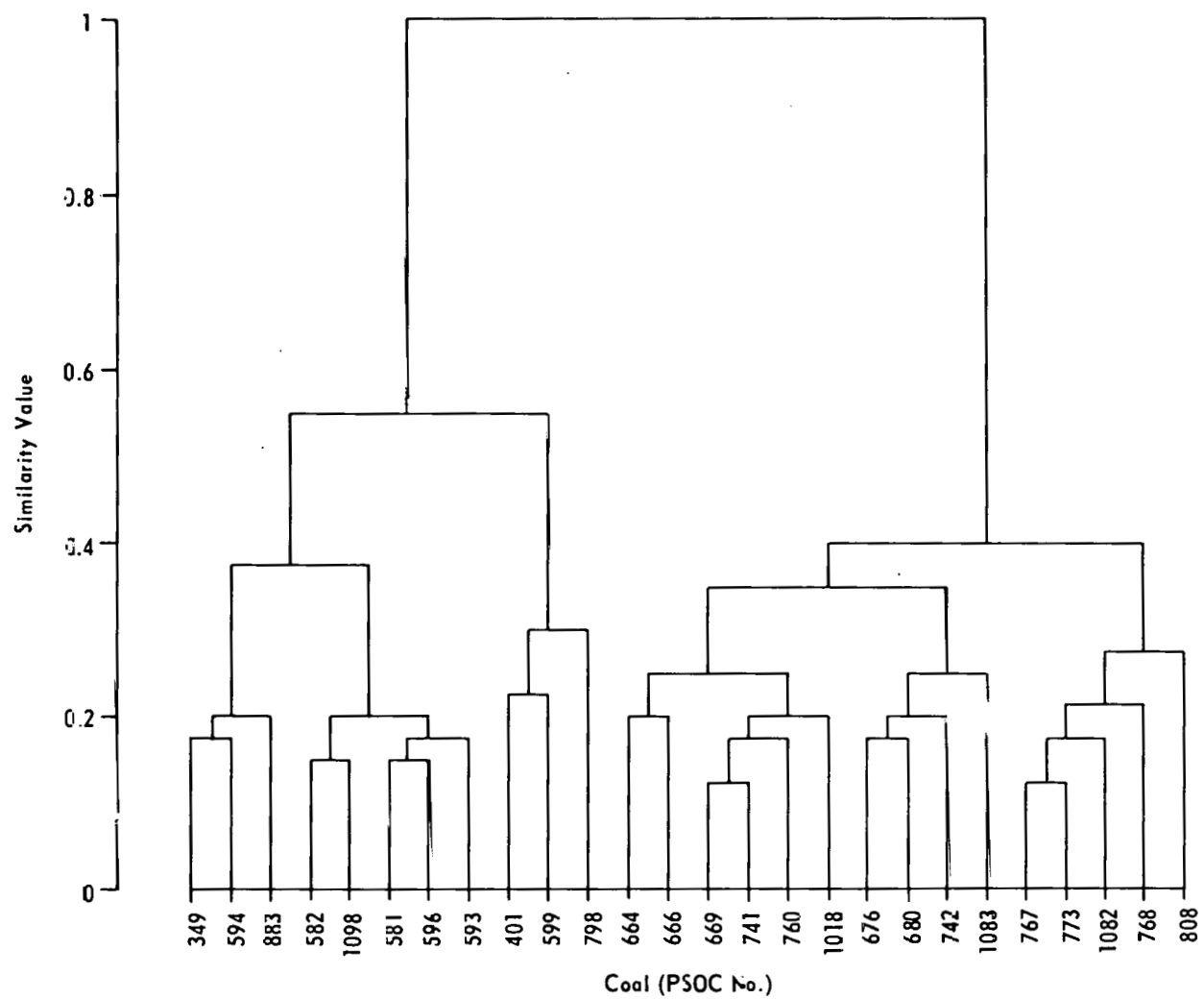
Figure 34. HIERARCHICAL CLUSTERING OF STRUCTURAL PROPERTIES OF COALS
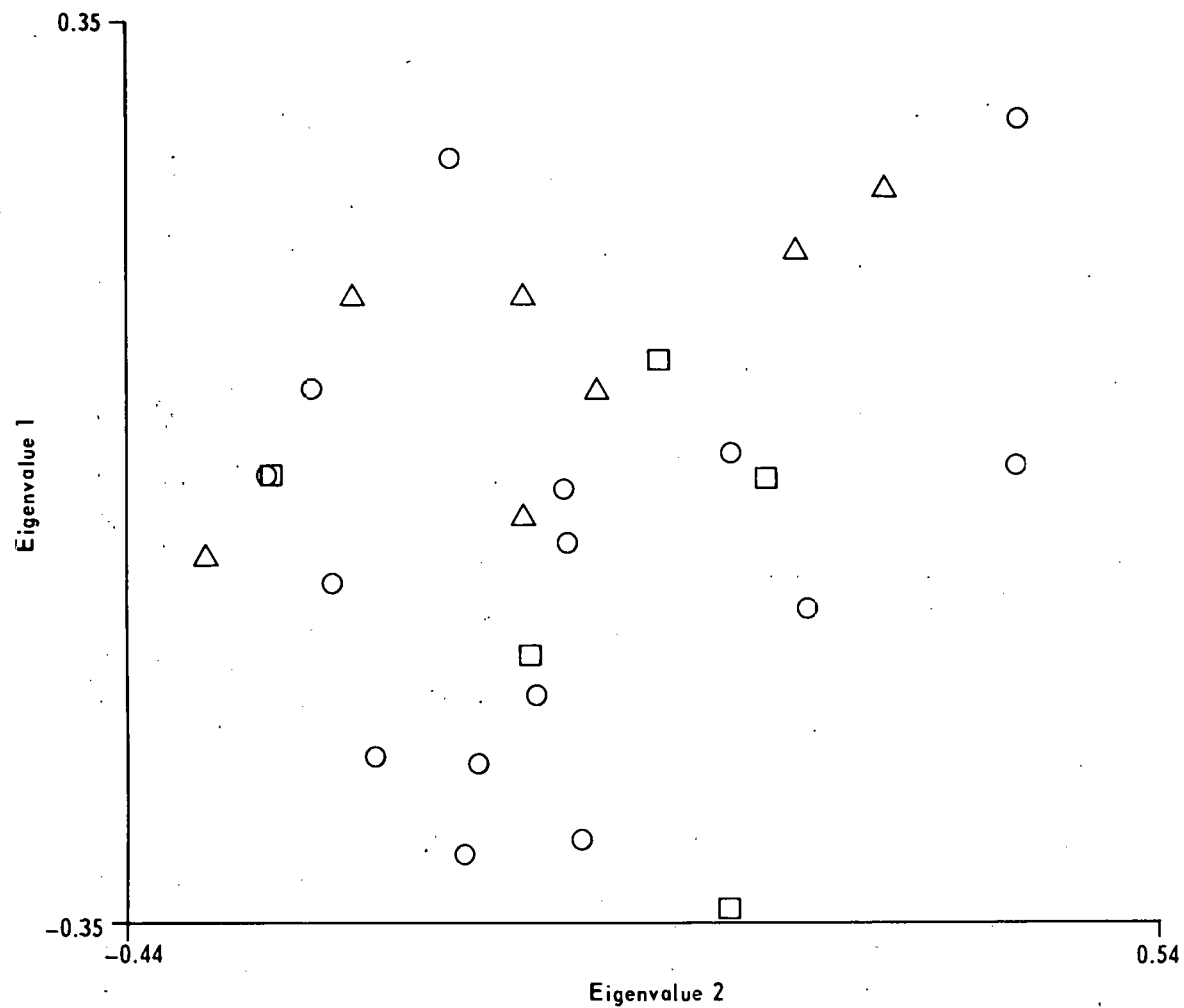
Figure 35. KARHUNEN-LOEVE PROJECTIONS FOR FIRST TWO FACTORS FROM FACTOR ANALYSIS OF COAL PROPERTIES

It appears that although certain variables have skewed and poly-modal distributions, this is apparently not due to the presence of distinguishable subsets of coals. Moreover, where multi-modal distributions occur for any properties, P and Q, the modes are different, and involve different sets of coals, for the two properties.

c. The Special Case of Aromaticity

A particularly striking example of the multi-modal distribution of a structural characteristic was discussed earlier: the aromaticity derived from ^{13}C NMR data. This is surprising since the coal samples were selected as representing what was believed to be a very homogeneous sample set, and reasonable correlations between carbon content and aromaticity can be seen in data in the literature (Wilson et al., 1984, Havens et al., 1983, Boudou, 1982). Yet the five linear regressions in Figure 14 appeared highly significant.

The types of cluster analysis already performed are of no value when the data points segregate into a number of linear relationships. In attempting to find out why the data fell out as they do, the initial step is to examine the plots for those variables selected as having the highest Fisher weights for the solutions of the multi-dimensional, multi-variant regressions (Table 21). An example of this type of plot is presented in Figure 36. As will be seen from Table 21, the Fisher weights show a marked drop between the oxygen content and the yield of propyl-substituted acids in TFPA oxidation, and this was taken as the cut-off point below which segregation into five linear relationships is not significant. The seven properties that do, according to this test, partition into linear relationships are, in descending order of

Table 21. Variance and Fisher Weights of Variables for Solution of Multi-linear Regression Discriminant Analysis

Variables in Original Sequence	Variables Resequenced by Variance Wt.	Variance Weight	Variables Resequenced by Fisher Wts.	Fisher Weight
1. f_a	1. f_a	2.65	1. f_a	2.11
2. %C	15. $CO + CO_2$	1.76	35. ethylated acids	0.742
3. %H	2. %C	1.71	15. $CO + CO_2$	0.736
4. %N	33. O/C	1.66	2. %C	0.724
5. $\%S_o$	20. alc. OH	1.61	33. O/C	0.66
6. total convn.	35. ethylated acids	1.60	20. alc. OH	0.655
7. asph. yield	18. % O	1.60	18. %O	0.652
8. alkanes	37. propylated acids	1.51	37. propylated acids	0.492
9. aroms, HP_C	5. $\%S_o$	1.50	29. % vitr.	0.451
10. polars, HPLC	29. % vitr.	1.48	5. $\%S_o$	0.449
11. H_2 recov.	14. C_2 gas	1.42	14. C_2 gas	0.381
12. H_2S	26. lost vols.	1.37	21. phen. OH	0.372
13. CH_4	21. phen. OH	1.35	26. lost vols.	0.348
14. C_2 gas	17. C_3 gas	1.32	23. m.m.	0.288

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Table 21. Continued

Variables in Original Sequence	Variables Resequenced by Variance Wt.	Variance Weight	Variables Resequenced by Fisher Wts.	Fisher Weight
15. $CO + CO_2$	23. m.m.	1.31	17. C_3 gas	0.283
16. hydrocarbon gas	24. total gas	1.30	24. total gas	0.262
17. C_3 gas	12. H_2S	1.25	12. H_2S	0.220
18. %O	36. methyl acids	1.25	36. methyl acids	0.218
19. al./ar. OH	40. aromatic acids	1.24	9. aroms. HPLC	0.207
20. alc. OH	9. aroms. HPLC	1.22	40. aromatic acids	0.207
21. phen. OH	19. al./ar. OH	1.21	19. al./ar. OH	0.188
22. NH	4. %N	1.21	4. %N	0.179
23. m.m.	8. alkanes	1.20	27. tetr./naphth.	0.172
24. total gas	27. tet./naphth.	1.13	8. alkanes	0.166
25. oil yield	39. total diacids	1.13	39. total diacids	0.152
26. lost vols.	30. $\%S_p$	1.17	30. $\%S_p$	0.151
27. tet./naph.	13. CH_4	1.16	13. CH_4	0.144

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Table 21. <u>Continued</u>

Variables in Original Sequence	Variables Resequenced by Variance Wt.	Variance Weight	Variables Resequenced by Fisher Wts.	Fisher Weight
28. total reactive macs.	32. %S (tot.)	1.16	32. %S (tot.)	0.126
29. % vitr.	28. total reactive macs.	1.14	28. total reactive macs.	0.123
30. %S$_p$	10. polars, HPLC	1.14	10. polars, HPLC	0.117
31. H/C	34. acyclic di+triacids ;	1.14	34. acyclic di+triacids	0.116
32. %S (tot.)	16. hydrocarb. gas	1.12	3. %H	0.109
33. O/C	3. %H	1.12	16. hydrocarb. gas	0.109
34. acyclic di+triacids	6. total convn.	1.11	11. H$_2$ recov.	0.099
35. ethylated acids	11. H$_2$ recov.	1.11	6. total convn.	0.096
36. methylated acids	38. oxirane acids	1.10	38. oxirane acids	0.084
37. propylated acids	25. oil yield	1.10	25. oil yield	0.083
38. oxirane acids	7. asph. yield	1.07	7. asph. yield	0.057
39. total diacids	31. H/C	1.03	31. H/C	0.028
40. aromatic acids	22. NH	1.03	22. NH	0.025

153
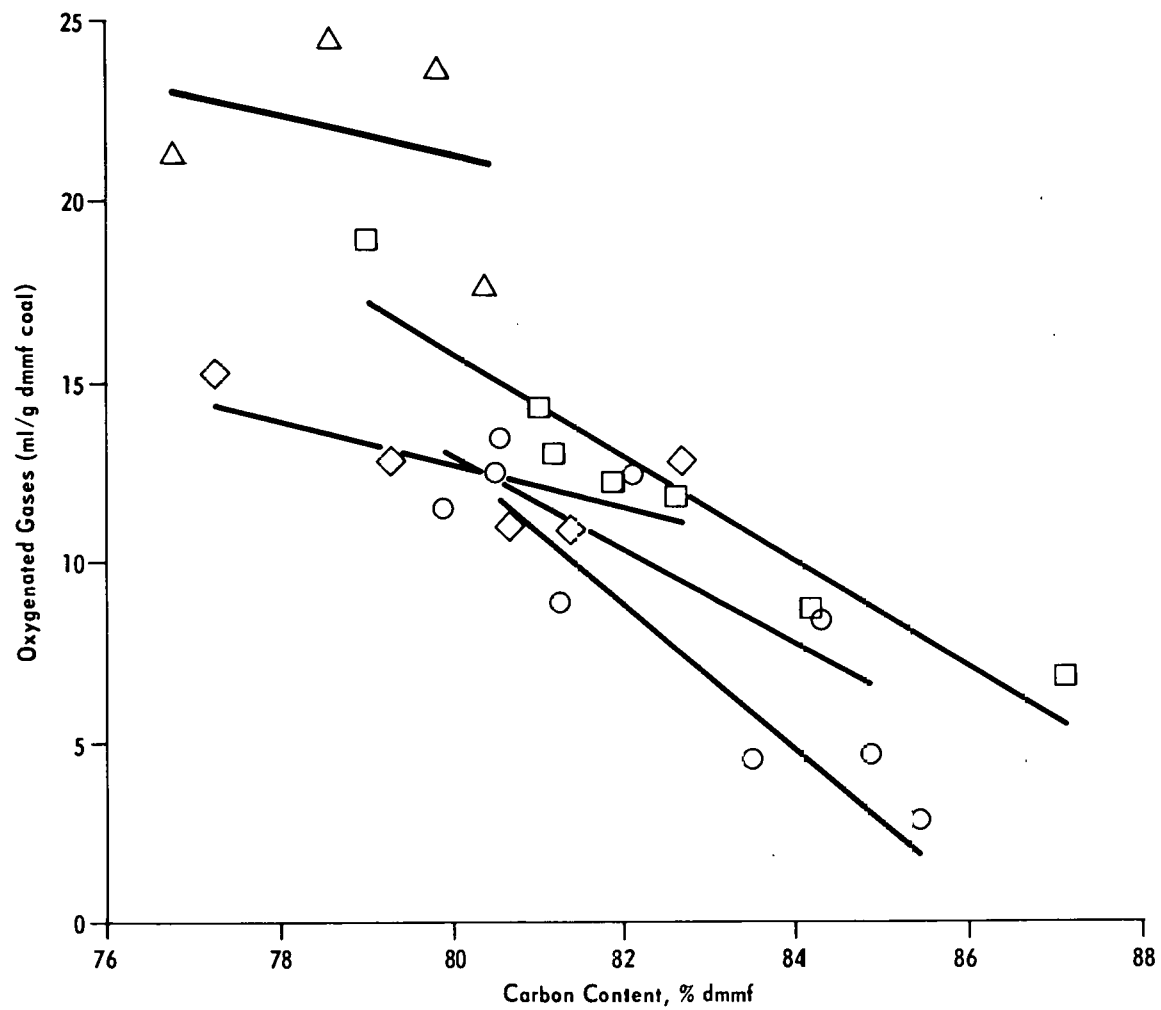
Figure 36. RELATION OF YIELD OF OXYGEN-CONTAINING GASES TO CARBON CONTENT

Fisher weights, f_a, yield of CO_2 + CO, %C, O/C, phenolic OH content from FTIR, yield of ethylated acids from TFPA oxidation and %O. It will be noted that several of these parameters are related to the content of oxygen.

Secondly, a non-linear map was constructed for the above seven properties from the distance matrix as described by Duda and Hart (1973). This technique preserves interpoint distances while projecting the data on to two-dimensional space. A technique such as this is especially useful when the variables in question are practically correlated and the groups in question lie on specific lines. The non-linear map presented in Figure 37 was constructed using only f_a. It clearly shows the structure that was initially observed in the f_a results (Figure 14). Progressive introduction of the variables of lower Fisher weights clearly reduces the fit of the five lines, as indicated by the sharp drops in the Fisher weight.

The next step in the analysis was to generate the multi-linear discriminant functions for each group. Not only does this give an indication of the importance of each of the seven properties or variables in the overall separation problem but also provides a method by which the overall accuracy of the grouping can be evaluated. By removing 20 percent of the members of the sample set into a separate test set, re-performing the analysis and then utilizing the derived discriminate functions, one can get a very good idea of how discrete the groups actually are.

This procedure leads to a set of five discriminant functions which are of the type:
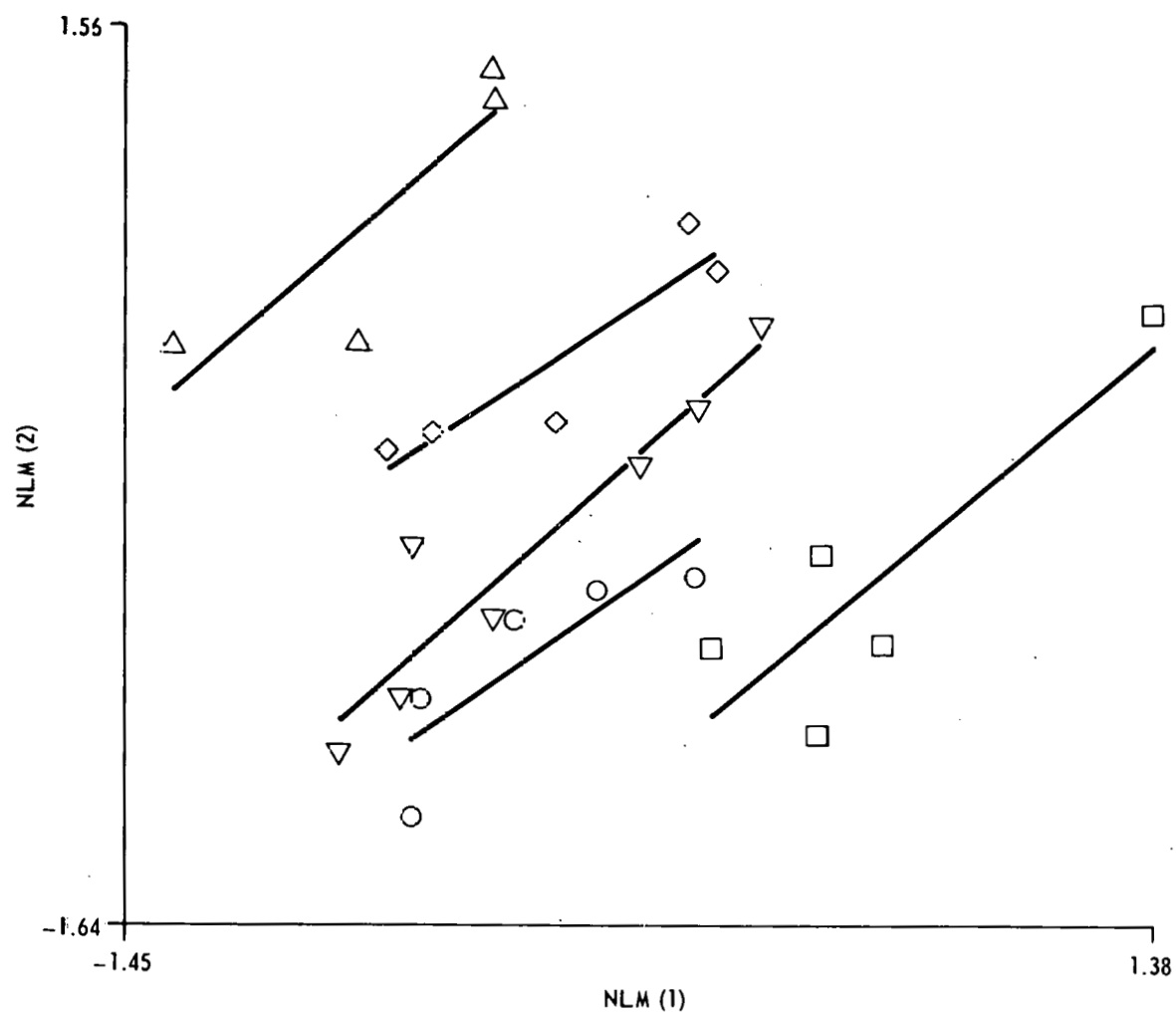
Figure 37. NON-LINEAR MAP SHOWING GROUPING OF COAL PROPERTIES

$$G_1 = \Sigma a_i x_i + b$$

$$G_2 = \Sigma p_i x_i + q$$

$$G_3 = \Sigma p_i x_i + S_1/etc.$$

where x_i is the value of a coal property and a_i is its coefficient, and b, q, etc. are constants. Seven coal properties are included. One substitutes values for the properties of a coal into these equations and determines which equation gives as algebraic sum the largest positive value to the function G. If this were G_3, the sample would be assigned to the third group of coals defined by the aromaticity plot (Figure 14). One then removes 20% of the samples and re-conducts the whole test on this subset. If the assignment to groups is the same as before, as was in fact the case here, then it can be assumed that the groups of coals are quite clearly separated.

d. <u>Concluding Comments on Data Structure</u>

It will be recalled that the coal samples studied in this project were selected from the Penn State Sample and Data Base by means of the discriminant analysis of Yarzab et al. (1980). This analysis purported to assign a coal correctly, in 98 cases out of 100, to the high-sulfur, medium-rank, high-conversion group of coals identified by Yarzab et al. on the basis of cluster analysis of the characteristics of 104 coals from the Eastern, Interior and Rocky Mountain coal provinces. This was the basis for believing that a homogeneous set had been selected. It is true that the original cluster analysis had no information on structural characteristics of the coals.

The surprising nature of the relationship between aromaticity and carbon content obviously raised the questions, do any other properties relate in this fashion, and does it imply that the sample set is after all heterogeneous and needs further partitioning? The second question was also raised by the observed values of kurtosis for several of the variables. An answer has been sought by a variety of approaches; it is clearly negative: further partitioning of the sample set is not called for. It is true, however, that univariate distributions of several of the variables are either skewed or multi-modal, as listed above on p. 142.

The remaining part of this chapter will be mostly concerned with the use of factor analysis in searches for interrelationships between the various kinds of data. For this purpose transformations of variables to achieve approximately Gaussian distributions are not essential unless one wishes to test such hypotheses as that loadings below a certain value are indistinguishable from zero. It appears that for a sample size of the magnitude of that used here this cut-off is probably in the range 0.3-0.4)D. Glick, personal communication, 1984); more precise information than this is not needed for present purposes. Accordingly it was decided not to transform any of the variables. Because of its complex relationships, the aromaticity has been sparingly used in what follows.

D. BIVARIATE TRENDS

Having investigated the data structure in general terms, we can now proceed to use the data in searches for interesting interrelationships. Before entering multivariate analysis, it is necessary to look

at bivariate trends, although with coals these are not particularly informative by themselves (Abdel-Baset, et al., 1978). We shall be seeking here indications of the factors that are especially important in determining the behavior of coals.

A correlation matrix is shown in Table 22, based on the 19 parameters listed in Table 19 (a full correlation matrix covering all of the data is presented in Appendix B).

As will be seen the majority of correlation coefficients are low. There are two variables that show no values of r greater than about 0.4, and these are unlikely to explain any useful fraction of variance: ratio of $(C_1 + C_2)/(C_3 + C_4 + C_5)$ gases, and the ratio of peak areas of CH_2 and CH_3 bands in the C-H stretching region. A number of the high or relatively high values of correlation might be expected, such as those between the variables used in defining rank (%C, O/C, R_o), between H_2S and forms of sulfur, and the moderate inverse correlation between aromaticity and ratio of band areas, (aliphatic C-H)/(aromatic C-H). H/C is normally considered a rank parameter, but here the only moderate correlation it shows is with the ratio, acyclic diacids/ acyclic triacids, from TFPA oxidation, implying that the latter does have some significance in characterizing structure.

A fairly large number of variables showed moderate to high correlations with all three of carbon content, O/C and reflectance, in fact very nearly the same variables in each case: O/C, S_o, %OH, yield of polar HPLC fraction, sum of oil + lost volatiles + gases, and hydrogen consumption from tetralin. It is not obvious why the last

Table 22. Correlation Matrix Between Selected Variables

VARIABLE	1 f_a	2 %C	3 H/C	4 O/C	5 S_o	6 S_p	7 %OH	8 ali/aro C-H	9 arom. acids TFPA	10 oil yield	11 oil + (vols.) aspn.	12 polar HPLC frac.	13 oil + vols. + gases	14 (C_1+C_2)/(C_1-C_5) gases	15 H_2S	16 R_o	17 H-consumpn. (tetr.)	18 acyclic diacids/triacids	19 CH_2/CH_3 bands FTIR
1. f_a	1																		
2. %C	.165	1																	
3. H/C	-.204	-.303	1																
4. O/C	-.201	-.979	.233	1															
5. S_o	-.067	-.724	.238	.678	1														
6. S_p	.008	-.067	.023	.027	.191	1													
7. %OH	.040	-.571	-.099	.569	.431	.331	1												
8. ali./aro. C-H	-.550	-.190	-.032	.220	.243	.004	.044	1											
9. arom. acids TFPA	.060	.027	-.374	.047	-.149	.218	.025	-.145	1										
10. oil yield	-.430	-.416	.207	.474	.394	.113	.332	.235	.222	1									
11. (oil + volatiles)/asph.	-.001	-.373	.021	.286	.611	.323	.442	.207	-.131	.179	1								
12. polar HPLC fract.	-.346	-.562	.250	.516	.510	.070	.415	.170	.189	.958	.236	1							
13. oil + vois. + gases	-.358	-.746	.273	.693	.768	.179	.443	.309	.042	.610	.584	.653	1						
14. (C_1 + C_2)/(C_1 - C_5) gases	.197	.045	-.118	-.043	-.176	-.053	.052	-.145	.179	-.195	-.135	-.077	-.428	1					
15. H_2S	.178	-.298	.012	.221	.553	.716	.321	.033	.117	.247	.435	.254	.375	-.152	1				
16. R_o	.332	.820	-.191	-.812	-.660	.041	-.359	-.382	-.017	-.457	-.149	-.542	-.736	.206	-.202	1			
17. H consump. (tetr.)	.147	-.644	0.010	.627	.502	-.201	.191	.110	.147	.343	.148	.432	.623	-.167	.022	-.687	1		
18. acyclic diacids/triacids	-.167	-.258	.547	.145	.381	.145	.052	.116	-.289	.026	.250	.058	.276	-.061	.216	-.134	-.194	1	
19. CH_2/CH_3 bands FTIR	-.421	-.422	.025	.421	.215	-.158	.236	.227	.096	.442	.095	.438	.562	-.055	-.099	-.362	-.467	.032	1

three should be rank-dependent, but it is interesting that they are.
Lastly, three of the variables seem to be specially interesting because
they each show moderate to high values of correlation coefficient with
several other variables; they are: yield of polar HPLC fraction (-%C,
O/C, S_0, oil yield), yield of oil + lost volatiles + gases (-%C, O/C,
S_0, oil yields,, ratio of oil + lost volatiles to asphaltenes, polar
HPLC fraction), and hydrogen consumption from tetralin (-%C, O/C, S_0,
oil + lost volatiles + gases, and $-R_0$). There is of course some inter-
correlation amongst these, but the observations are interesting and
will help in guiding searches for multivariate correlations.

In order to reduce the data matrix to manageable proportions the
selection of variables (Table 19) had to be severely limited. The
results of TFPA oxidations suffered badly in this process, and so
a ,bivariate correlation relating to these reactions is shown in graph-
ical form in Figure 38, in which the yields of acyclic diacids +
triacids are plotted against the sum of the acids derived from
aromatic structures (benzene carboxylic + oxirane acids). It is of
interest that they tend to be inversely related. The variance
explained by the least squares regression is cx %.

E. MULTIVARIATE ANALYSES

As a foundation for the discussion of multivariate relationships,
it has been thought useful to recapitulate in summary form the kinds
of information available on features of the structure of the coals
(Table 23) and on product distributions (Table 24). The content of
these tables should be borne in mind during the following discussion.
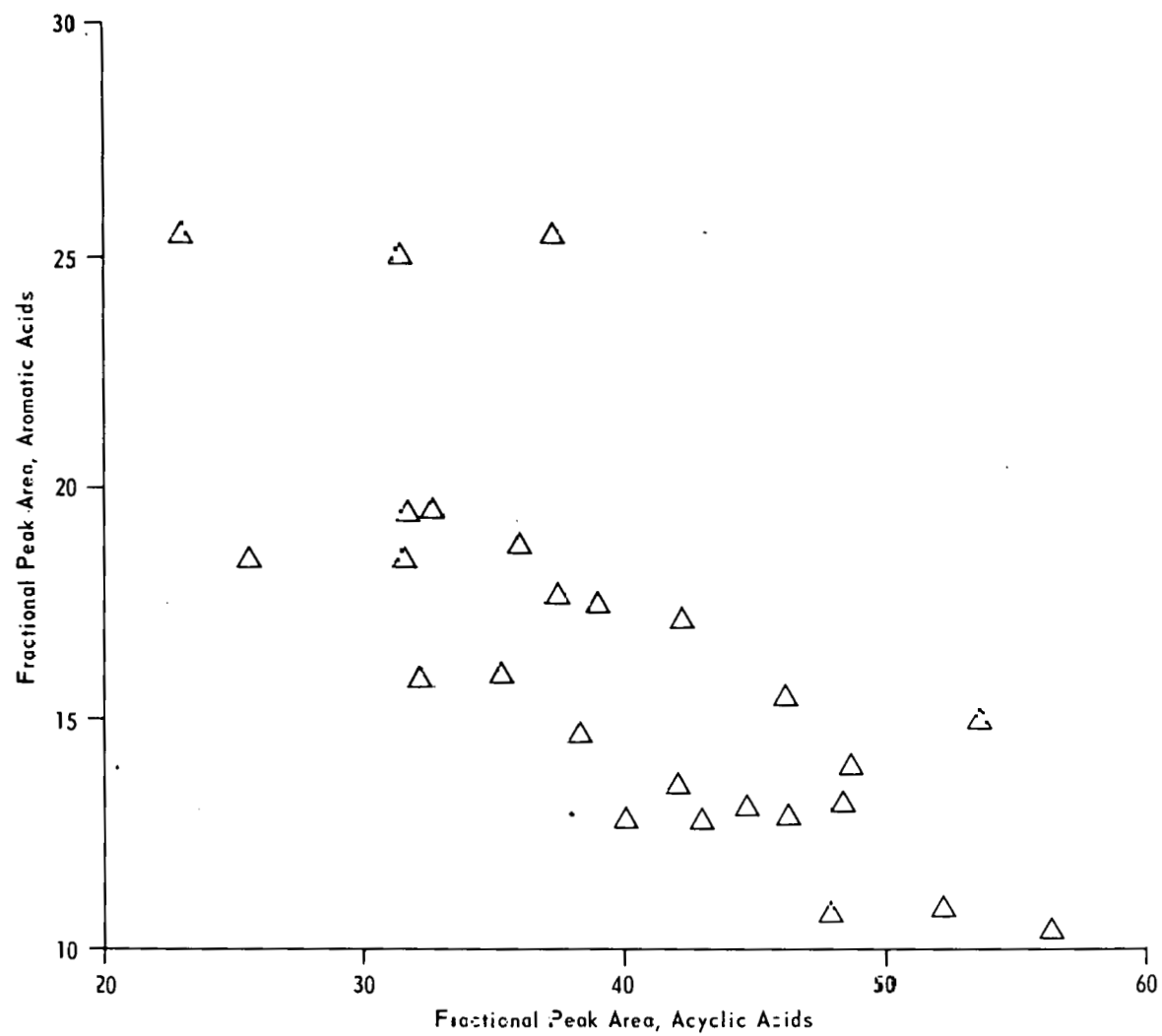
Figure 38. YIELDS OF ACYCLIC AND AROMATIC-DERIVED ACIDS FROM TFPA OXIDATION

Table 23. <u>Recapitulation of Kinds of Structural Information Available</u>

<u>Parameter</u>	<u>Information content</u>	<u>Form Used in statistics</u>
f_a	fraction of aromatic carbon	f_a
C-H (arom.)	relative amounts of aromatic C-H vibrations in variously substituted benzene rings	(a) ali./arom. C-H area (IR)
C-H (ali.)	relative amounts of C-H vibrations in CH_2 and CH_3	(b) CH_2/CH_3 ratio
OH	relative amounts of phenolic and alcoholic OH and acetylatable NH	total OH
TFPA oxid. products	(i) representative (?) fragments of aliphatic structures in coals, (ii) relative importance in parent coal of aliphatic chains and linking groups *versus* certain phenolic and polycyclic aromatic structures.	(a) concn. of arom. acids, (b) ratio of acetic diacids/ triacids.
?	distribution of ether and organic S groups	not
?	degrees of ring fusion and substitution of aromatic systems.	not

Table 24. Recapitulation of Information Available on Product Distributions

Product Fractions	Comments on Significance	Form Used in Statistics
oil	hexane-soluble condensible products; includes all mobile phase of coal	(a) oil
asphaltene	hexane-insoluble; includes (i) larger fragments of coal, (ii) products of retrogressive reactions	(b) oil + vols./asph.
lost volatiles	only available by difference: C_5-C_{10} hydrocarbons, aliphatic and aromatic?	(c) oils + vols. + gas
gases	various sources: forms of S, forms of O, side chains. Small in total amount and in variance. CO_2 small but considerable variance	above, also H_2S and $(C_1+C_2)/(C_3-C_5)$ ratio
HPLC fractions	(i) alkanes very small and no doubt all part of mobile phase, (ii) "aromatic" fraction includes ethers, ketones, O and S heterocycles as well as aromatic hydrocarbons, (iii) polar fraction, quantitatively the largest, includes phenols, N bases, benzologs of pyrrole, quinones (?)	polar fraction

Because of the large number of chemical properties and product fractions that were available, and the limited size of the sample set, a large number of factor analysis were carried out to fully investigate the interrelationships within the data set. Generally, over 85 percent of the total variance was accounted for in each factor pattern. However, the variance explained by any one product class or property (the communality) tended to be significantly less. The variables were chosen so that each represents a distinct source of information; hence there tended to be only a single variable loading highly on any one factor. The discrete sources of information included variables related to rank, the structure of the organic matter, product distribution and the fate of sulfur. It may be that each of these sources is at least indirectly related to rank; however, there is enough variation that discrete factors were normally obtained.

The strategy used in setting up the large number of factor analysis performed was to select one of the eleven variables that relate to some aspect of conversion in liquefaction, and combine this with six or so coal characteristics in the factor pattern. For each product variable, the best factor pattern was selected on the basis of the variance explained and the magnitude of the loadings. The summary in Table 25 relates to the set of best patterns devised and evaluated in this manner. Thus column 2 indicates that the best pattern when H_2S yield was the product parameter selected contained four factors, H_2S had a loading of 0.76 on the second of these factors, and pyrite sulfur also loaded on the same factor with a loading of 0.72. Among

Table 25. Summary of Information Provided by Factor Patterns for the
Individual Product Fractions

Product	No. of factors in best pattern for each product (variance explained)	Identification of factor(s) and loading for stated product	Coal characteristics loading on same factor and loading value
H_2S	4 (92.5	II (0.76)	$\%S_p$ (0.72)
$CO + CO_2$	3 (83.2)	I (0.62)	$\%C$ (-0.51), $\%S_0$ (0.42), O/C (0.51)
		II (0.41)	ali./arom. C-H (-0.87)
hydrocarbogases	4 (89.7)	II (0.65)	ali./arom. C-H (-0.82)
		IV (0.63)	% vitrinite (0.75)
total gas yield	4 (85.0)	I (-0.41)	$\%C$ (0.58), O/C (-0.56), $\%S_0$ (-0.51)
		II (0.70)	ali./arom. C-H (-0.69)
polar HPLC fract.	4 (90.4)	III (-0.31)	O/C (-0.69), phen. OH (-0.49)
		II (-0.35)	% vitr. (-0.66), phen OH (-0.55)
arom. HPLC fract.	4 (91.6)	II (0.61)	% Sp (0.78)
		III (0.4.)	% vitr. (0.81)
alkane HPLC	4 (84.4)	II (0.71)	ali./arom. C-H (0.62)
		IV (-0.3.)	% vitr. (-0.81)

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Table 25. <u>Continued</u>

Product	No. of factors in best pattern for each product (variance explained)	Identification of factor(s) and loading for stated product	Coal characteristics loading on same factor and loading value
oil yield	4 (84.8)	I (0.40)	%C (-0.53), O/C (0.53), %S_0 (0.43), % vitr. (0.47)
		III (0.79)	%C (-0.31), O/C (0.32), %S_0 (0.35), % vitr. (-0.37)
asphaltene yield	4 (81.0)	II (-0.42)	%S (0.51), acyclic acids TFPA (-0.64)
		III (0.45)	arom. acids TFPA (0.82)
lost volatiles	4 (85.7)	I (0.51)	%C (-0.50), O/C (-0.45) %S_0 (0.49)
total conv., liqs + gas	4 (87.4)	I (-0.55)	%C (0.45), %S_0 (-0.59)
		II (-0.41)	%C (0.51), % vitr. (-0.41) %O (-0.70)

the sub-classes of gases, hydrogen sulfide appeared to be most closely related to pyritic sulfur, as might be expected. Oxygenated gases showed significant loadings on two factors; one of these related to rank and the other as to the aliphatic/aromatic character of the coal structure. Hydrocarbon gases also showed significant loadings on two factors, the same aliphatic/aromatic character and, surprisingly, the vitrinite content. Thus it can be easily seen that among the individual sub-classes of gases each loads on a factor that is generally independent of rank, except for the oxygenated gases.

The rotated factor pattern for conversion to gases is examined in more detail in Table 26. This pattern is different in that there is an increased importance of rank (Factor 1), although there is a significant amount of variance explained by other factors. It should be noted that the significant loading on the rank factor was only seen for the total oxygenated gases, not for the sub-classes of gases. This is the first indication that although individual fractions or, in this case, individual groups of gases, appear to load on chemical properties that are only partially correlated with rank, the sum of the individual products is much more closely related to rank.

Returning to Table 25, we see that the polar fraction from the HPLC separation loaded highly on only one of the four factors determined to be significant (see Figure 27 for more detail). The fact that this fraction loaded on the same factor as the phenolic OH content and the O/C ratio is perhaps not surprising, since phenols are more abundant than amines. It will be recalled that this fraction also showed a

Table 26. Rotated Factor Pattern for Conversion to Gases and
Selected Chemical Properties

	Factor				
Property	I	II	III	IV	Communality
Gas yield	-0.44	0.70			0.68
% Carbon	0.53				0.34
O/C Ratio	-0.56				0.31
% S_O	-0.51				0.26
% Vitrinite				-0.84	0.71
% S_P			-0.67		0.45
Aromatic Acids from TFPA			-0.71		0.50
Aliphatic/Aromatic C-H Ratio		-0.67			0.45
Variance per Factor	38.8	21.4	17.0	7.8	
Cumulative Variance	38.8	60.2	77.2	85.0	

Table 27. Rotated Factor Pattern for Yield of Polar HPLC
Fraction and Selected Chemical Properties

Property	Factor				Communality
	I	II	III	IV	
Polar HPLC Fraction	0.24	-0.35	-0.81		0.84
% Carbon	-0.54	0.32	0.28		0.47
% Vitrinite	0.24	-0.66			0.49
Phenolic OH		-0.55	-0.49	0.22	0.59
% S_O	0.58				0.34
% S_P				0.88	0.77
O/C Ratio	0.49	-0.38	-0.69		0.86
Variance by Factor	54.7	17.0	10.7	7.9	
Sum of Variance	54.7	71.8	82.5	90.4	

bivariate correlation with oil yield. The aromatic fraction loaded on two of the four factors in its rotated factor pattern. Of these, pyrite content also loaded on the same factor. Yarzab et al. (1980) found pyrite content to be one of the factors tending to increase total conversion; perhaps its effect is to increase the neutral aromatic products. The second factor on which the aromatic HPLC loaded was dominated by the vitrinite content. The yield of alkanes again had significant loadings on two factors: factor II, which in this case was defined by its relatively high loading for the aliphatic/aromatic C-H ratio, and factor IV which also exhibited a large loading for vitrinite content. It is not easy to know what to make of these loadings, since the alkanes are mostly physically trapped in coals as part of the mobile phase (Youtcheff et al., 1983).

The rotated factor pattern for oil yield is strange in that the main loading for this class of products takes place only on a factor that has no other significant loadings if one takes 0.40 as the cutoff for significance. However, as Table 28 shows, oil yield also loads (rather weakly) on another factor, which contains significant loadings by several coal characteristics mostly related to rank. It is also strange that the aliphatic/aromatic C-H ratio loads very strongly on a factor of its own (IV). These are interesting observations and may indicate that all of the chemical properties when taken as a whole contribute to the formation of this fraction.

Conversion to asphaltenes exhibited a significant loading on two of the four factors deemed significant in its factor pattern. The first

Table 28. <u>Rotated Factor Pattern for Conversion to Oils and Selected Chemical Properties</u>

Property	Factor I	II	III	IV	Communality
Oil yield	0.40		0.79		0.78
% Carbon	-0.53		-0.31		0.38
O/C	0.53		0.32		0.38
% S_O	0.43		0.35		0.31
% Vitrinite	0.47		-0.37		0.36
% S_P		0.70			0.49
Aromatic Acids, TFPA		0.66			0.44
Aliphatic/Aromatic C-H				0.96	0.92
Variance per Factor	41.7	19.5	13.3	9.7	
Cumulative Variance Explained	41.7	61.2	75.0	84.8	

factor also had significant loadings for pyritic sulfur (again a cata-
lytic effect?) and aliphatic TFPA products, while the second factor
could be designated as that factor defined by the high loading due
to aromatic TFPA products. Thus the possibility is present that this
fraction is much more dependent on the nature of the aromatic clusters
in the coal than any of the others examined thus far, perhaps because
of its relatively high molecular weight. Only one factor exhibited
a significant loading for the lost volatiles and various parameters
related to rank load in the same factor (in this sample set, $\%S_0$
appears to be rank-related). This fraction is probably a mixture of
materials from different sources, and contains compounds that are
closely akin to those found in the other fractions. For example it
contains water, lighter hydrocarbons falling between those found in
the gas fraction and those in the saturate fraction, dissolved gases,
and most probably light aromatic liquids. There is no obvious reason
why its yield should decrease systematically with increasing rank.

The rotated factor pattern for total conversion is presented in
detail in Table 29. Four factors were required in accounting for just
over 87 percent of the total variance. Significant loadings for the
overall conversion yield were on two of the factors, in both of which
conversion is inversely related to carbon content, and in one of which
(II) a direct relation with oxygen content is seen. Thus we see a
marked rank dependence. With this sample set, H/C seems to show little
systematic variation in parallel with the other rank parameters. Here
it loads on the same factor as vitrinite content. Once again, the

Table 29. Rotated Factor Pattern for Total Conversion and
           Selected Chemical Properties

| Property | Factor | | | | Communality |
	I	II	III	IV	
Conversion to gases + liqs.	-0.55	-0.41			0.47
Aliphatic/Aromatic C-H				0.97	0.94
% Carbon	0.45	0.51			0.46
H/C Ratio			0.83		0.69
% S_0	-0.59				0.35
% Vitrinite	-0.30	-0.41	0.52		0.53
% Oxygen		-0.70			0.49
Variance per Factor	49.3	17.1	13.6	7.3	
Cumulative Variance Explained	49.3	66.4	80.1	87.4	

aliphatic/aromatic C-H ratio loads highly on Factor IV unaccompanied by any other variable. It seems that this quantity characterizes structure in a unique manner that does not affect liquefaction behavior.

The rotated factor pattern for the whole set of the selected 19 variables described previously is presented in Table 30. The significance of this pattern is somewhat suspect due to the high variable to sample ratio, but the results are interesting nonetheless. Six factors were found to be significant in accounting for just under 80 percent of the total variance. As expected each of the factors exhibited loading for more than one variable, though both the loadings and the communalities tended to be relatively low compared with those found in patterns derived with lesser numbers of variables. Also, the analysis permits investigation of interrelationships not revealed by the previous factor analyses.

The first factor could be best characterized as a rank factor with significant loadings for O/C ratio, carbon content, reflectance, and organic sulfur content (but not H/C). The second contains the variables related to sulfur, but also the ratio of liquids to asphaltenes. This is quite interesting in that it may point to the idea that hydrogen sulfide has some importance as a hydrogen donor during liquefaction. That is, the ratio of lighter products to solids increases with increasing hydrogen sulfide in the reaction vessel and the possibility exists that there is a chemical causality.

The variables characterizing coal structure load mostly on Factors III, IV, and V. Organic sulfur content has little or no parallelism

Table 3C. Rotated Factor Pattern for Nineteen Selected Variables

Property		I	II	III	IV	V	VI	Communality
rank	%C	-0.41						0.17
	H/C				-0.62			0.38
	O/C	0.41						0.17
	R_o, %	-0.36						0.13
structure	f_a			0.27	-0.56			0.39
	S_o	0.37	0.28					0.22
	phenolic OH	0.24	0.29			0.41		0.31
	al./ar. C-H				0.65			0.42
	CH_2/CH_3 ratio				0.31			0.096
	aromatic acids, TPFA			-0.35	0.40			0.28
	acyclic ci/triacids				-0.57			0.32
products	oil yield			-0.56				0.31
	(oil + lost vols.)/asph.		0.41					0.17
	yield, oil + vols. + gas	0.32		0.35			0.31	0.32
	polar fractn, HPLC			-0.52				0.27
	tetr./naphth. ratio	0.37						0.14
	$(C_1 + C_2)/(C_3 - C_5)$ gases						-0.81	0.66
sulfur	yield H_2S		0.52					0.27
	S_F, %		0.51					0.26
% Variance Explained per Factor		35.7	12.7	10.7	8.4	6.7	5.7	
% Variance Explained, Cumulative		35.7	48.4	59.1	67.5	74.2	79.9	

with the structural features. Factor IV is probably related to character-istics of the aliphatic parts of coal, though the increase relation between the aliphatic/aromatic C-H and the CH_2/CH_3 ratios on the one hand, and H/C cn the other, is surprising. So also is the appearance of aromatic acids from TFPA oxidation in this factor, though there may be a structural relation. These acids are inversely related to the ratio of di/tri acyclic acids: the tri-acids probably derive from fairly highly aromatic precursors, such as arylindanes.

Factors III and V seem more concerned with aspects of the aromatic character of the coal; the yields of oil, of oil + volatiles + gases and of the polar HPLC fraction all load also on Factor III, while none of the product classes load on Factors IV or V.

The ratio of C_1-C_2 to C_3-C_5 gases loads highly on Factor VI, accompanied by a rather weak inverse loading of the yield of oil + volatiles + gases. Presumably this implies some degree of dependence of the conversion variable on aliphatic structural characteristics, though it is difficult to specify its nature or significance.

In order to investigate the relationship between conversion and hydrogen consumption from the donor solvent, a number of separate factor patterns were formed. The results from these patterns showed that generally, conversion of tetralin to naphthalene appeared to follow total conversion, conversion to lost volatiles, and to hydrogen sulfide, and pyritic sulfur, most closely. The correlation with lost volatiles is not surprising since this fraction probably contains most of the water produced during the liquefaction, and one would expect a

considerable amount of the donatable hydrogen to be utilized in generating it. However, the relationship with pyritic sulfur and hydrogen sulfide gas indicates that hydrogen is not only being removed from the gas phase by the pyrite but also from the tetralin. Although the hydrogen sulfide gas produced by this reaction appears as if it may be important in increasing conversion to liquid products relative to asphaltenes, one would think that this process would increase the hydrogen consumption from the donor solvent, but this is not supported by the results of the factor analyses.

In this section, a few examples have been selected to illustrate what seems to be a quite general phenomenon. The variance in total conversion and the more inclusive product classes is explained fairly fully by variations in rank. The variance in the narrower product classes tends to require various structural characteristics for adequate explanation. This seems to be a general conclusion of some importance.

Two aspects of coal composition have received inadequate attention in this report: distributions of macerals and minerals. It was shown in Table 20 that the mean vitrinite content of the coals used was 87.6 87.6+3.85%, which seems very satisfactory. The minor macerals are unlikely to have much direct influence on liquefaction, except that quite minor amounts of liptinites might efficiently initiate chain reactions. Also their relative amounts might usefully characterize or classify environments of deposition, which are likely to influence the behavior of coals formed after burial of the peat.

It is standard practice in current petrographic studies to distinguish several different kinds of vitrinite (Teichmüller, 1982). Given (1984) questions whether there may not be, in chemical terms, several distinct vitrinitic materials or a fairly wide continuum of vitrinite characteristics in any one coal.

Thus analyses showing a mean vitrinitic content of 87.6% are not so impressive after all. To have recognized this in the present study would have required the performance of some special analyses and introduction of several more variables; even then the distribution of vitrinitic macerals may have been unsuitable for statistical analysis. As has been seen, total vitrinite was included in a number of the factor analyses and has some significance.

To have paid more attention to the distribution of inorganics would have required quantitative analysis of the FTIR spectra of the low temperature ash samples. It would have been impractical to have entered the full mineral analysis into the statistical analyses, but the ratio of quartz to clay minerals might be a useful datum characterizing enviroments of deposition.

CHAPTER VI

CONCLUDING REMARKS

In the study of the liquefaction behavior of 104 coals from 3 coal provinces of the U.S., Yarzab et al. (1980) could only define the characteristics of coals by means of their basic compositional features, and had only total conversion to liquids plus gases with which to identify liquefaction behavior. Within these limits, they found that of the three groups of coals segregated by a form of cluster analysis, one group, characterized by high sulfur contents, showed the best performance in liquefaction (see also Given and Sood, 1982). Moreover, principal components analysis showed that, for this group, both organic and pyritic sulfur independently appeared to promote liquefaction. Some understanding of the role of pyrite has been reached (Lambert, 1982; Thomas et al., 1982; Stenberg et al., 1982; Baldwin and Vinciguerra, 1983), but the role of organic sulfur, or the nature of its participation in the process, has been little studied.

The broad objectives of this project were stated in Chapter I. More specifically, it would be desirable to find answers to the following questions:

1. In mechanistic terms, what is the role of organic sulfur in the liquefaction of coals?

2. Is there some fundamental structural reason for the good performance of high sulfur coals in liquefaction?

3. Can total conversion to liquids plus gases be predicted more successfully when properties related to structure are available?

4. Can conversion to individual product classes be predicted from a knowledge of basic compositional and chemical structural characteristics of the coals?

It would be too optimistic to expect full answers to the first two questions to have emerged from the present study, since few parameters related to sulfur were available (and it is difficult to see what additional parameters could feasibly have been obtained). Some very ingenious experiments based on new techniques or instrumentation are called for here.

As a basis for answering the third and fourth questions, more than 50 properties of each coal have been measured, if one includes all the components of the gas analyses and all the principal products of TFPA oxidation. The range of techniques used should provide a reasonably comprehensive overview of important structural features of the coals. Directly determined hydroxyl contents and mineralogical analyses (from FTIR) would no doubt have been desirable. Computer-analyzed Curie-point pyrolysis/mass spectra (Meuzelaar et al., 1982) perhaps might have added an important extra dimension to the structural chacterization if it had been available. Even so, what is presented here constitutes the most extensive characterization of a set of coals yet to be published, and this by itself constitutes a notable accomplishment. It was obviously necessary to reduce to manageable proportions the mass of data that is available, since the size of the sample base also had to be severely limited. Nevertheless, we should be in a better position at this point than any previous worker to relate behavior to properties, and in attempting to do this have used a variety of statistical procedures.

Some contribution to solution of the problems under discussion has been made by a statistical study (by Diane Weldon) of results obtained by A. Sood of Gulf Research and Development Co. (reported by Given et al., 1982). The Gulf workers had carried out continuous flow liquefaction runs on 38 of the coals from the Appalachian and Interior provinces that had been in the sample set used by Yarzab et al. (1980). Gas analyses and some degree of product fractionation were performed. One of the parameters measured was the "distillability," which represented the yield of material distillable at 3 torr pressure to a pot temperature of 400°C. A stepwise multiple regression analysis was performed using the program UPREG. This program determines first which single coal property is the best predictor of distillate yield, and computes the variance explained. Other variables are added to the equation one by one. An analysis of variance is performed at each step; any non-significant variable is passed over and the next one considered. For the data obtained in liquefaction runs at 455°C the result was:

$$\text{distillate (\% of dmmf coal)} = 270 - 47.1R_o - 0.76\text{ VM} - 1.7C - 5.6H$$

in which reflectance alone accounted for 77% of the variance explained (r^2), and all of the terms accounted together for 83%. For the data from 440°C runs the regression was:

$$\text{distillate, \%} = 66.3 - 47.6\ R_o - 1.55\ S_t$$
$$(73\%) \qquad (78\%)$$

where the values for variance explained appear in parentheses. Thus some degree of predictability was achieved for the distillability of products from the set of 38 coals of Carboniferous age.

Other product parameters obtained in the Gulf study were yields
of hexane-soluble oils, asphaltenes, C_1 - C_4 hydrocarbons, higher
alkanes, and acid gases (CO_2, CO, H_2S). Factor analyses were performed
on these variables excluding alkane yield but including total conversion
and distillate yield. Most of the variables loaded on the first factor,
indicating that the yields of most of the product classes vary in a
manner parallel to the variation in total conversion. The exceptions
were yields of asphaltenes and C_1 - C_4 gases, each of which loaded
heavily on its own separate factor. The results were interpreted as
not encouraging a search for correlations between individual yield
parameters and coal characteristics.

An answer to the third question above has been sought by perform-
ing a stepwise multiple regression of total conversion observed in
the present study on a number of basic compositional properties and
the structural parameters, using a program in the SAS statistical
package. The result was:

total convn. % = - 10.7 + 102 O/C - 80.2f_a - 5.5N + 0.47 acyclic
                        (47)   (55)   (60)

acids TFPA + 70.2 H/C + 0.67 vitr. + 0.25S_t
 (67)   (70)   (71)   (73)

The numbers in parentheses show the cumulative variance explained after
each variable has been inserted. The regression calls out 7 of the 18
variables provided; these include some rank parameters and some related
to structure, but the obvious rank parameters (%C, R_o, VM) are not
called. It is interesting to recall that the equation developed by
Yarzab et al. (1980), no structural parameters being available, was:

convn. $= 39.0 + 0.86$ VM $- 22.8$ R_o $+ 1.39$ S_t $(r^2 = 79\%)$

A similar multiple regression was performed for the conversion to hexane-soluble oils. The result was:

convn. to oils, $\% = 39.4 - 48.5$ f_a $- 0.74$ S_o $+ 0.12 S_t$ $- 1.6$ N
$\qquad\qquad\qquad\quad$ (18) $\qquad$ (32) $\qquad\qquad\qquad$ (45)

$+ 0.17$ acyclic acids TFPA $+ 0.008$ aliph. OH $- 0.088$ arom. acids TFPA
$\quad$ (50) $\qquad\qquad\qquad\qquad$ (54) $\qquad\qquad\qquad$ (54)

$+ 0.01$ acetylatable NH $- 0.008$ arom. OH $+ 0.31$ MM $+ 16.4$ H/C
$\quad$ (59) $\qquad\qquad\qquad\qquad$ (63) $\qquad$ (67) $\qquad$ (69)

$- 0.06$ VM
$\quad$ (70)

Here 12 variables are called out from a total of 18. This time the volatile matter yield does appear, though explaining little additional variance.

These equations are too cumbersome to be of much practical value for purposes of prediction. Nevertheless, they appear to show that to explain the variance in the conversion data, many characteristics of each coal are needed, and these include structural properties as well as those related to rank. Thus the earlier conclusion is reinforced: we have still not identified the crucial variables that explain much of the variance in coal behavior—if we had identified them, much simpler and more effective multiple regression equations could no doubt be generated.

Performance of multiple regressions for individual product classes was considered, but it was decided not to perform them. The sample set was rather small for this kind of operation, and the results of the

factor analyses (low loadings and communalities) were not encouraging
in this connection. Thus no answer to the fourth question can be
offered at the present time. However, as stated at the end of the
previous chapter, the factor analyses do indicate that explanation
of the variance in the yields of the product classes require the
introduction of structural parameters not directly dependent on rank.

The set of findings just discussed seems to arise from a totally
unexpected degree of heterogeneity of the sample set. The principal
conclusion from the many factor analyses performed really is that impor-
tant sources of variance in the data matrix have still not been
identified. Yarzab et al. (1980) argued that there are several path-
ways or bands of the metamorphic evolution of coals, not just one.
Given (1984) emphasizes the point that rank is not the only source of
variance in coal properties, and the results reported here document
this. The finding that the plot of aromaticity and some other proper-
ties against carbon content partitions into five parallel lines adds
specific detail on the consequences of there being several sources of
variance, but these have still to be identified in geochemical terms.
Why are there five bands of evolution of aromaticity for these coals
(but not for others)? It is probably permissible to infer that the
selection of a set of high sulfur coals, though wise on some grounds,
was on balance unfortunate, in that the high content of forms of sulfur
tends to promote heterogeneity. Probably a greater degree of predictive
ability could be achieved with medium sulfur Appalachian coals or low
sulfur coals of Cretaceous age from the Western provinces of the U.S.

Ignasiak et al. (1978) have drawn attention to the extraordinary
Raša coal of Yugoslavia. This has the carbon content of a lignite but

much less oxygen, and 10-12% organic sulfur. It becomes fluid on heating and forms a strong coke. Ignasiak et al. suggested that much of the sulfur replaces oxygen in ether links, that the thio-ethers are more labile thermally than ethers, and, that the whole balance of competing thermal reactions is thereby upset. This is an interesting idea, and could have some relevance to the structure of the coals studied here. Some of the sulfur is no doubt present in benzologs of thiophene. These tend to be more reactive than homocyclic aromatic compounds, and are less able to form polynuclear condensed systems during metamorphism on heating in the laboratory. In fact, varying distributions of organic structural types may well be an important source of variance in the data.

Thus high sulfur coals may well have important structural features that are not yet understood and cannot be accounted for by the parameters measured here. The finding here of a further degree of heterogeneity of coals, perhaps associated with sulfur, is of considerable interest, and a major part of the contribution made by the research described.

REFERENCES

Adbel-Baset, M. G., Yarzab, R. F., and Given, P. H. (1978), Dependence on liquefaction behaviour on coal characteristics. 3. Statistical correlation of conversion in coal-tetralin interactions, Fuel, 57, 89-94.

Aczel, T., Williams, R. B., Pancirov, R. J., and Karchmer, J. H. (1976), Chemical properties of Synthoil products and feeds, Final Report, Part 1, prepared by Exxon Research and Engineering Company, Baytown, Tex., to U. S. Department of Energy under Contract No. EY-76-C-21-8007, Report No. MERC-8007-1.

Alemany, L. B., Grant, D. M, Alger, T. D., Pugmire, R. G. (1983), Cross-polarization and magic-angle sample spinning NMR spectra: III. effect ^{13}C dipolar interaction on proton-carbon interactions, J. Am. Chem. Soc., 105, 6697-6704.

Alexander, B. F., and Anderson, R. P. (1982), SRC II processing of western coals with added pyrite, Div. Fuel Chem., Amer. Chem. Soc., Prepr., 27(2), p.18-28.

Appell, H. R., Miller, R. D., Illig, E. G., Moroni, E. G. and Steffgen, F. G. (1979), Coal liquefaction with synthesis gas, Report PETC/TR-7911, U. S. Dept. of Energy, Oak Ridge, Tenn.

ASTM (1977a) Standard method of preparing coal samples for analysis, ANSI/ASTM D 2013-72, in 1977 Annual Book of ASTM Standards, Part 26, Gaseous Fuels; Coal and Coke; Atmospheric Analysis, American Society for Testing and Materials, Philadelphia, Penna.

ASTM (1977b) Standard method sampling and fineness test of pulverized coal, ASTM D-197-30, in 1977 Annual Book of ASTM Standards, Part 26, Gaseous Fuels, Coal and Coke; Atmospheric Analysis, American Society for Testing and Materials, Philadelphia, Penna.

Attar, A. (1978), Chemistry, thermodynamics and kinetics of reactions of sulfur in coal-gas reactions: A Review, Fuel, 57, pp. 201-212.

Attar, A. (1979) Sulfur groups and their determinantion, in Analytical Methods for Coal and Coal Products, Vol. 3, ed. C. Karr, Academic Press, N.Y., 1979, pp. 587-624.

Attar, A., and Dupuis, F. (1978), On the distribution of organic sulfur functional groups in coal, Div. Fuel Chem., Amer. Chem. Soc., Prepr., 23(2), 44-50.

Attar, A. and Hendrickson, G. G. (1982), Functional groups and heteroatoms in coal, in Coal Structure, ed. R. A. Meyers, Academic Press, NY, pp. 132-192.

Baker, G. G., Owens, T. C., and Rindt, J. R.(1982), Effect of several disposable catalysts on liquefaction of lignite, *in* Proc. Annual Meeting of American Society of Civil Engineers, New Orleans, Louisiana, 122 pp.

Baldwin, R. M. and Vinciguerra, S.(1983), Coal liquid catalysis: Iron pyrite and hydrogen sulfide, Fuel, 62, 498-501.

Barron, P. F., Stephens, J. F., and Wilson, M. A. (1981), Aromatic and aliphatic composition of the solid and liquid products from hydrogenation of Liddell coal, Fuel, 60, 547-549.

Bartuska, V. J., Maciel, G. E., Schaefer, J., and Stejskal, E. O. (1977), Prospects for carbon-[13]nuclear magnetic resonance analysis of solid fossil-fuel materials, Fuel, 56, 354-358.

Bartuska, V. J., Maciel, G. E., Miknis, F. P. (1978a) ^{13}C nmr studies of coals and oil shales, Div. Fuel Chem., Amer. Chem. Soc., Prepr., 23(2), 19-23.

Bartuska, V. J., Maciel, G. E., and Miknis, F. P. (1978b), Organic structure studies of fossil fuels by nuclear magnetic resonance. Div. Fuel Chem., Amer. Chem. Soc., Prepr., 23(4), 132-137.

Bockrath, B. C. and Schroeder, K. T. (1981), Coal mineral matter in liquefaction *in* New Approaches in Coal Chemistry, eds. B. D. Blaustein, B. C. Bockrath and S. Friedman, Amer. Chem. Soc. Symp. Series 169, pp. 191-200.

Bodzek, D. and Marzec, A. (1981), Molecular components of coal and coal structure, Fuel, 60, 47-51.

Bogdanova, V. A. and Boranski, A. O. (1961), Thio-ether sulfur in some Irkutsk coals, Kratk. Soobsch. Nauchno-Issled. Rabotakh, 2a, sb68 [Chem. Abstr. 63, 17741e (1965)].

Bollet, C., Escalier, J.-C., Souteyiand, C., Caude, M. and Rosset, R. (1981), Rapid separation of heavy petroleum products by high-performance liquid chromatography, J. Chromatogr., 206, 289-300

Bommannavar, A. S. and Montano, P. A. (1982), Mössbauer study of the thermal decomposition of FeS_2 in coal, Fuel, 61, 523-528.

Boudou, J.-P. (1981), Organic diagenesis of deltaic sediments (Mahakam, Indonesia), D.Sc. Thesis, University of Orléans, France.

Brown, J. K. and Wyss, W. F. (1955), Oxygen groups in bright coals, Chem. and Ind., 1955, 1118.

Brooks, J. D. (1956), Organic sulfur in coal, J. Inst. Fuel, 29, 82-85.

Chans, S. H., Gooding, K. M. and Regnier, F. E. (1976), Use of oxiranes in preparation of bonded phase supports, J. Chromatography, 120, 321-333.

Cohen, A. D. and Spackman, W. (1977), Phytogenic organic sediments and sedimentary environments in the Everglades-Mangrove complex - Part II. The origin, description and classification of the peats of southern Florida, Palaeontographica, 162, Abt. B, 71-114.

Coleman, M. M. and Painter, P. C. (1978), Fourier transform infrared studies of polymeric materials, J. Macromol. Sci. Revs. Macromol. Chem., C16, 197-313.

Collin, H. and Guichon, G. (1977), Introduction to reversed-phase high-performance liquid chromatography, J. Chromatogr., 141, 289-312.

Crowley, R. J., Siggia, S. and Uden, P. C. (1980), Class separation and characterization of shale oil by liquid chromatography and capillary column gas chromatography, Anal. Chem., 52, 1224-1228.

Curry, K. W. (1980) A gas chromatography/mass spectrometry study of the aliphatic structures of coal, M.S. Thesis, The Pennsylvania State University, p. 3.

Cypres, R., Ghodsi, M. and Stocq, R. (1981), Behaviour of pyrite durin, hydrogenation of graphite at atmospheric pressure. Fuel, 60, 247-250.

Dark, W. A. and McGough, R. R. (1978), Use of liquid chromatography in the characterization of asphalts, J. Chromatogr. Sci., 16.

Davidson, R. M. (1982), Molecular structure of coal in Coal Science, Vol. 1, eds. M. L. Gorbaty, J. W. Larsen, and I. Wender, Academic Press, NY, 83-160.

Deno, N. C., Greigger, B. A., Messer, L. A., Meyer, M. D. and Stroud, S. G. (1977) The inverse oxidation of alkyl benzenes, Tetrahedron Lett., 1703-1704.

Deno, N. C., Greigger, B. A. and Stroud, S. G. (1978a) The aliphatic structures in coal, Div. Fuel Chem., Amer. Chem. Soc., Prepr., 23(2), 54-57.

Deno, N. C., Greigger, B. A. and Stroud, S. G. (1978b) New method for elucidating the structures of coal, Fuel, 57, 455-459.

Deno, N. C., Curry, K., Jones, A. D., Minard, R., Potter, T., Rakitsky, W., Wagner, K. and Yevak, R. J. (1981a) Low-temperature chemical fragmentation of coal, in Chemistry and Physics of Coal Utilization - 1980, ed. B. R. Cooper and L. Petrakis, Amer. Inst. Phys., NY, pp. 154-156.

Deno, N. C., Curry, K. W., Jones, A. D., Keegan, K. R., Rakitsky, W. G., Richter, C. A. and Minard, R. D. (1981b) Linear alkane chains in coal, Fuel, 60, 210-212.

Desty, D. H. and Goldup, A. (1975) Chromatograpy of hydrocarbons in Chromatography: A Laboratory Handbook of Chromatographic and Electrophoretic Methods, 3rd, ed. E. Heftman, VanNostrand Reinhold Co., NY, pp. 915-948.

Determann, H. and Brewer, J. E. (1975) Gel Chromatography, in Chromatography: A Laboratory Handbook of Chromatographic and Electrophoretic Methods, 3red, ed., E. Heftman, VanNostrand Reinhold Co., NY, pp. 362-389.

Dryden, I. G. G. (1963) Chemical constitution and reactions of coal, in The Chemistry of Coal Utilization, ed. H. H. Lowry, John Wiley and Sons, NY, pp. 232-295.

Duda, R. O. and Hart, P. E. (1973), Pattern classification and scene analysis, Wiley, NY.

Dudley, R. L. and Fyfe, C. A. (1982), Evaluation of the quantitative reliability of the ^{13}C CP-MAS technique for the analysis of coals and related materials, Fuel, 61, 651-657.

Duffy, L. J. (1967), The chemistry of vitrinite macerals from coals in the bituminous range, Ph.D. Thesis, The Pennsylvania State University.

Durie, R. A. (1980), The characteristics of Australian coals and their implications in coal liquefaction, in Coal Liquefaction Fundamentals, ed. D. D. Whitehurst, Amer. Chem. Soc. Symp. Series 139, pp. 53-75.

Durie, R. A. and Sternhell, S. (1959), Some quantitative infra-red absorption studies of coals, pryolysed coals and their acetyl derivatives, Australian J. Chem., 12, 205-217.

Durie, R. A., Shewshyk, Y. and Sternhell, S. (1966), Spectroscopic studies of the hydrogen distribution in the vitrains and their solvent extracts from some Australian bituminous coals, Fuel, 45, 49-113.

Emmons, W. D. and Ferris, A. F. (1953), Oxidation reactions with trifluoroperoxyacetic acid, J. Am. Chem. Soc., 75, 4623-4624.

Estep, P. A., Kovach, J. J. and Karr, C., Jr. (1968), Quantitative infra-red multicomponent determination of minerals occurring in coal, Anal. Chem., 40, 358-363.

Fraser, R. D. B. and Suzuki, E. (1973) The use of least squares in data analysis, in Physical Principles and Techniques of Protein Chemistry, Pt. C., ed. S. J. Leach, Academic Press, NY, pp. 301-355.

Frazer, F. W. and Belcher, C. B. (1973), Quantitative determination of the mineral-matter content of coal by a radio-frequency oxidation technique, Fuel, 52, 41-46.

Friedel, R. A. (1966), Infrared spectroscopy in coal structure research in Applied Infrared Spectroscopy, ed. O. N. Kendall, Reinhold, NY, pp. 312-343.

Friedman, S., Kaufman, M. L., Steiner, W. A. and Wender, I. (1961), Determination of hydroxyl content of vitrains by formation of tri-methylsilyl ethers, Fuel, 40, 33-46.

Galya, L. G. and Suatoni, J. C. (1980), Rapid SARA separations high-performance liquid chromatography, J. Liq. Chromatogr., 3, 229-242.

Gerstein, B. C., Murphy, P. D. and Ryan, L. M. (1982), Aromaticity in coal, in Coal Structure, ed. R. A. Meyers, Academic Press, NY, pp. 87-131.

Giddings, J. C. (1975) Theory of chromatography in Chromatography: a Laboratory Handbook of Chromatographic and Electrophoretic Methods, 3rd, ed., E. Heftman, VonNostrand Reinhold Co., NY, pp. 27-44.

Given, P. H. (1972), Biological aspects of coal origins, in Advances in Organic Geochemistry 1971, eds. H. von Gaertner and H. Wehner, Vieweg und Sohn, Braunschweig, Germany, Pergamon Press, pp. 69-92.

Given, P. H. (1981), Organic geochemistry and chemistry of coal macerals, Text of Short Course on Coal Characteristics and Coal Utilization, The Pennsylvania State University, June, 1981.

Given, P. H. (1983), The dependence of liquefaction behaviour on coal characteristics, Final Technical Report, March 1981-February 1984, Part 1, DOE-407804-FR-1, Contract No. DE-AC22-81-PC-40784.

Given, P. H. (1984), An essay on the organic geochemistry of coal in Coal Science, Vol. 3, eds. M. Gorbaty, J. W. Larsen, and I. Wender, Academic Press, NY, pp. 63-251.

Given, P. H. and Dickinson, C. H. (1975), Biochemistry and microbiology of peats: in Soil Biochemistry, Vol. 3, eds. E. A. Paul and A. D. McLaren, Marcel-Dekker, NY, pp. 123-212.

Given, P. H. and Peover, M. E. (1958), Study of quinone groups in solvent extracts of coals by controlled potential electrolysis, in Proc. Residential Conference, Science in the Use of Coal, Inst. of Fuel, London, pp. A33-A37.

Given, P. H. and Sood, A. (1982), Dependence of coal liquefaction behavior on coal characteristics. 6. Product distribution from coals treated in a continuous flow reactor, Fuel, 61, 968-971.

Given, P. H. and Wyss, W. F. (1961), Chemistry of sulfur in coal, BCURA Monthly Bull., 251-179.

Given, P. H. and Yarzab, R. F. (1978), Analysis of the organic substance.of coals: Problems posed by the presence of mineral matter, in Analytical Methods for Coal and Coal Products, Vol. 2., ed. C. Karr, Academic Press, NY, pp. 3-39.

Given, P. H., Lupton, V. and Peover, M. E. (1958), Ease of reduction of a series of coals and its relation to their structure, Nature, 181, 1059-1060.

Given, P. H., Spackman, W., Walker, P. L. and Lovell, H. L. (1974), Relation of coal characteristics to coal liquefaction behavior, Report No. 2 from Pennsylvania State University to National Science Foundation (RANN Division) under Grant No. GI-38974, pp. 50-52.

Given, P. H., Cronauer, D. C., Spackman, W., Lovell, H. L., Davis, A. and Biswas, B. (1975), Dependence of coal liquefaction behavior on coal characteristics: 2. Role of petrographic composition, Fuel, 54, 40-49.

Given, P. H., Schleppy, R. and Sood, A. (1980a), Dependence of coal liquefaction behavior on coal characteristics. 5. Data from continuous flow reactor, Fuel, 59, 747-750.

Given, P. H., Spackman, W., Davis, A. and Jenkins, R. B. (1980b), Some proved and unproved effects of coal geochemistry on liquefaction behavior with emphasis on U. S. coals, in Coal Liquefaction Fundamentals, ed. D. D. Whitehurst, Amer. Chem. Soc. Symposium Series No. 139, pp. 3-34.

Given, P. H., Spackman, W., Davis, A., Lovell, H. L. and Painter, P. C. (1981), The relation of coal characteristics to liquefaction behavior, Quart. Tech. Progress Report for period March to May 1981 from The Pennsylvania State University to U. S. Department of Energy under Contract No. DE-AC22-81-ET-10587, Report No. DOE-ET/10587-1.

Given, P. H., Spackman, W., Davis, A., Walker, P. L., Lovell, H. L., Coleman, M. and Painter, P. C. (1982), The relations of coal characteristics to liquefaction behavior, Final Rpt. Part III: Mechanistic studies, product distribution and supportive analytical investigations, Prepared for U.S. Dept. of Energy, Rept. No. FE2494-FR-3.

Gluskoter, H. J. (1965), Electronic low-temperature ashing of bituminous coal, Fuel, 44, 285-291.

Gluskoter, H. J. (1967), Clay minerals in Illinois coals, J. Sediment. Petrol., 37, 205-214.

Granoff, B. and Montano, P. A. (1980), Mineral matter effects in coal conversion, in Proc. Conference on Chem. and Physics of Coal Utilization, eds. B. R. Cooper and L. Petrakis, Amer. Inst. Phys., pp. 291-308.

Granoff, B., Baca, P. M., Thomas, M. G. and Noles, G. T. (1978), Chemical studies on the synthoil process, Task 2: Mineral matter effects, Sandia Laboratories Report SAND-78-1113, Alburquerque, New Mexico.

Griffiths, P. R. (1975), Photometric precision in infrared spectra measured by Fourier transform spectroscopy, J. Appl. Spectroscopy, 24, 11-14.

Greigger, B. A. (1978), The aliphatic structure of coal, M.S.Thesis, The Pennsylvania State University.

Guilianelli, J. L. and Williamson, O. L. (1982), Comparison of microwave and radiofrequency low-temperature ashing of coal using iron-57 Mössbauer spectroscopy of sulfur forms, Fuel, 61, 1267-1272.

Guin, J. A., Tarrer, A. R., Prather, J. W., Johnson, D. R. and Lee, J. M. (1978), Effects of coal minerals on the hydrogenation, desulfurization and solvent extraction of coal, Ind. Eng. Chem., Process. Des. Dev., 17, 118-126.

Guin, J. A., Tarrer, A. R., Lee, J. J., Lo, L. and Curtis, C. W. (1979), Further studies of the catalytic activity of coal minerals in coal liquefaction. 1. Verification of catalytic activity of mineral matter by model compound studies, Ind. Eng. Chem., Process. Des. Dev., 18, p. 371-376.

Haeberlen, U. (1976), Advances in magnetic resonance, Suppl. 1, Academic Press, NY, 208 pp.

Hagaman, E. W. and Woody, M. C. (1981), Statistical coal structure analysis by CP/MAS ^{13}C nmr spectrocopy:quantitative evaluation of aromaticity parameters, Proceedings of the Intern. Conf. on Coal Sci., Düsseldorf, 807-811.

Hartmann, S. R. and Hahn, E. L. (1962), Nuclear double resonance in the rotating frame, Phys. Rev., 128, 2042-2053.

Havens, J. R., Koenig, J. L., and Painter, P. C. (1982), Chemical characterization of solid coals through magic-angle carbon-13 nuclear magnetic resonance, Fuel, 61, 393-346.

Havens, J. R., Koenig, J. L., Kuehn, D., Rhoads, C., Davis, A., Painter, P. C. (1983), Characterization of coals and coal oxidation by magic-angle ^{13}C nmr spectroscopy, Fuel, 62, 936-941.

Hayatsu, R., Winans, R. E., Scott, R. G., Moore, L. P., Studier, M. H. (1978), Trapped organic compounds and aromatic units in coals, Fuel, 57, 541-548.

Hayatsu, R., Winans, R. E., Scott, R. G., McBeth, L. and Moore, L. P. (1981), Investigation of aqueous sodium dichromate oxidation for coal structure studies, Fuel, 60, 77-82.

Heftman, E., ed., (1975) Chromatography: A laboratory handbook of chromatographic and electrophoretic methods, 3 ed., vanNostrand Reinhold Co., NY.

Hessley, R. K., Benjamin, B. M. and Larsen, J. W. (1982), Deno oxidation: Insoluble high molecular weight aliphatic material from coals and further model compound studies, Fuel, 61, 1085-1087.

Hill, G. R., Hariri, H., Reed, R. I., Anderson, L. L. (1966), Kinetics and mechanism of solution of high volatile coal in Coal Science, Amer. Chem. Soc. Adv. Chem. Ser. 55, ed. P. H. Given, Washington, D. C.

Horgan, D. F. and Little, J. N. (1972), A comparison of conventionally-coated and chemically-bonded stationary phases in liquid chromatography, J. Chromatogr. Sci., 10, 76-79.

Horton, L. and Randall, R. B. (1947), The occurrence of sulphur and nitrogen in coal, Fuel, 26, 127-132.

Horvath, C., Melander, W. and Molnar, J. (1976), Solvophobic interactions in liquid chromatography with nonpolar stationary phases, J. Chromatogr., 125, 129-156.

Huang, G. B. and Stock, L. M. (1982) On the role of sulfur compounds in coal liquefaction, Div. Fuel Chem., Amer. Chem. Soc., Prepr. 27,' [4], 28-36.

Huggins, R. E. and Huffman, (1978), Mössbauer studies of coal and coke: quantitative phase identification and direct determination of pyritic iron sulfide sulfur content, Fuel, 57, 592-604.

Ignasiak, B. S. and Gawlak, M. (1977), Polymeric structure of coal 1. Role of ether bonds in constitution of high-rank vitrinite, Fuel, 56, 216-222.

Ignasiak, B. S., Fryer, J. F. and Jadernik, P. (1978), Polymeric structure of coal. 2. Structure and thermoplasticity of sulfur-rich Rasa lignite, Fuel, 57, 578-584.

Jan'iak, J. (1975), Chromatography of nonhydrocarbon gases *in* Chromatography: A Laboratory Handbook of Chromatographic and Electrophoretic Methods, 3rd, ed. E. Heftman, van Nostrand Reinhold Co., NY, pp. 882-901.

Jenkins, R. G. and Walker, P. L. (1978), Analysis of mineral matter in coal, *in* Analytical Methods for Coal and Coal Products, ed. C. Karr, Jr., Academic Press, NY, pp. 265-292.

Jewell, D. M., Weber, J. H., Bunger, J. W., Plancher, H. and Latham, D. R. (1972), Ion-exchange coordination and absorption chromatographic separation of heavy-end petroleum distillates, Anal. Chem., 44, 1391-1395.

Johnson, E. L. and Stevenson, R. (1978), Basic liquid chromatography, Varian Associates, Inc., Palo Alto, Calif., pp. 8-9.

Jones, A. D. (1984), The chemical structures of coal as determined by selective oxidative degradation, Ph.D. Thesis, The Pennsylvania State University.

Jones, R. N. (1969a), Computer programs for absorption spectrophometry, Appl. Optics, 8, 597-601.

Jones, R. N. (1969b), The measurement of infrared spectra with digitally recording spectrophotometers, Pure Appl. Chem., 18, 303-322.

Jones, R. N., Seshadri, K. S., Jonathan, N. B. W. and Hopkins, J. W. (1963), A statistical approach to the analysis of infrared band profiles, Can. J. Chem., 41, 750-762.

Jurkiewicz, A., Marzec, A. and Pislewski, N. (1982), Molecular structure of bituminous coal studied with pulse nuclear magnetic resonance, Fuel, 61, 647-650.

Karch, K., Sebestian, I. and Halasz, I. (1976), Preparation and properties of reversed phases, J. Chromatogr., 122, 3-16.

Karger, B. L, Gant, J., Hartkopf, A. and Weiner, P. H. (1976), Hydrophobic effects in reversed-phase liquid chromatography, J. Chromatogr., 128, 65-78.

Khan, S. U. and Schnitzer, M. (1972), Permanganate oxidation of humic acids, fulvic acids, and humins extracted from Ah horizons of a black Chernozem, and a black Solonetz soil, Can. J. Soil Sci., 52, 43-51.

Kirkland, J. J. (1975), Microparticles with bonded hydrocarbon phases for high-performance reverse-phase liquid chromatography, Chromatographia, 8, 661-668.

Kuehn, D. W. (1983), Characterization of the organic structure of the Lower Kittanning coal seam using FTIR spectroscopy and optical properties, Ph.D. Thesis, The Pennsylvania State University.

Kuehn, D. W., Davis, A., Snyder, R. W., Starsinic, M. and Painter, P. C. (1982a), The application of FTIR and solid state ^{13}C nmr to the characterization of a set of vitrinite concentrates, Div. Fuel Chem., Amer. Chem. Soc., Prepr. 27(2), pp. 55-65.

Kuehn, D. W., Snyder, R. W., Davis A. and Painter, P. C. (1982b), Characterization of vitrinite concentrates. 1. Fourier transform infrared studies, Fuel, 61, 682-694.

Kuehn, D. W., Davis, A., and Painter, P. C. (1983), A data base for the analysis of composition and characteristics of coal seams and macerals, Final Report No. 4, Characterization of the organic structure of the Lower Kittanning coal seam using Fourier transform infrared spectroscopy and optical properties, Report to U. S. Dept. of Energy No. DOE-30013-F4 from Coal Research Section, The Pennsylvania State University.

Koenig, J. L. (1975), Applications of Fourier transform infrared spectroscopy to chemical systems, Appl. Spectroscopy, 29, 293-308.

Kowalski, B. R. (1974), Computers in Chemical and Biochemical Research, Vol. 2, Academic Press, NY.

Lambert, J. M., Jr. (1982), Alternative interpretation of coal liquefaction catalysis by pyrite, Fuel, 61, 777-778.

Lambert, J. M., Simkovich, G. and Walker, P. L. (1980), Production of pyrrhotites by pyrite reduction, Fuel, 59, 687-690.

Larsen, J. W. (1980), Coal structure in Chemistry and Physics of Coal Utilization-1980, eds. B. R. Cooper and L. Petrakis, Amer. Inst. of Physics, NY, pp. 1-27.

Lazarov, L. and Angelova, G. (1968), Treatment of coals with sodium in liquid ammonia solution, Fuel, 47, 333-341.

Lee, B. S. (1982), Synfuels from coal, AIChE Monograph Series No. 14, AIChe, NY, 42 p.

Liotta, R. (1979), Selective alkylation of acidic hydroxyl groups in coal, Fuel, 58, 724-728.

Liotta, R. and Hoff, W. S. (1980), Trifluoroperoxyacetic acid oxidation of aromatic rings, J. Org. Chem., 45, 2887-2890.

Liphard, K.-G. (1980), Hydrocarbon Group-type analysis of coal liquids by high-performance liquid chromatography, Chromatographia, 13, 603-606.

Locke, D. F. (1973), Chemically bonded stationary phases for liquid chromatography, J. Chromatogr. Sci., 11, 120-128.

Longanbach, J. R., Droese, J. R. and Chauhan, S. P. (1978) Short residence time coal liquefaction, Final Report Battelle Columbus Laboratories, Report EPRI-AF-780.

Maciel, G. E., Bartuska, V. J., and Miknis, F. P. (1979), Characterization of organic material in coal by proton-decoupled ^{13}C nuclear magnetic resonance with magic-angle spinning, Fuel, 58, 391-394.

Maciel, G. E., Sullivan, M. J., Petrakis, L. and Grandy, D. W. (1982), ^{13}C nuclear magnetic resonance characterization of coal macerals by magic-angle-spinning, Fuel, 61, 411-414.

MacPhee, J. A. and Nandi, B. N. (1981), ^{13}C nmr as a probe for the characterization of the low-temperature oxidation of coal, Fuel, 60, 169-170.

Marzec, A., Jurkiewicz, A. and Pislewski, N. (1983), Application of ^{1}H pulse n.m.r. to the determination of molecular and macromolecular phases in coal, Fuel, 62, 996-1002.

Matsunaga, A. and Kusayanagi, S. (1981), A comparative study of HPLC column packings for the separation of aromatic and polar compounds in fossil fuel liquids, Div. of Fuel Chem., Amer. Chem. Soc., Prepr. 26(2), 59-67.

Meuzelaar, H. L. C., Haverkamp, J. and Hileman, F. D. (1982), Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials, Elsevier. Amsterdam.

Miknis, F. P., Sullivan, M., Bartuska, V. J. and Maciel, G. E. (1982), Cross-polarization magic-angle-spinning ^{13}C nmr spectra of coals of varying rank, Org. Geochem., 3, pp. 19-28.

Millar, R. L., Ogan, K. and Poile, A. F. (1981), Automatic column switching in liquid chromatography, Amer. Lab., 13, 52-62.

Miller, R. (1982), Hydrocarbon class fractionation with bonded-phase liquid chromatography, Anal. Chem., 54, 1742-1746.

Miller, R. N. (1977), A geochemical study of the inorganic constituents of some low-rank coals, Ph.D. Thesis, The Pennsylvania State University.

Miller, R. N. and Given, P. H. (1978), A geochemical study of the inorganic constituents of some low-rank coals, Technical Report 1., Prepared for U. S. Department of Energy under Contract No. EX-76-C-01-2494.

Miller, R. N., Yarzab, R. F. and Given, P. H. (1979), Determination of mineral-matter contents of coals by low temperature ashing, Fuel, 58, 473-476.

Minra, Y. and Yanasi, Y. (1963), The sulfur content of Japanese coals, I. Introduction and distribution of sulfur compounds in coals, Nenryo Kyakai-Shi, 42, 21-24. [Chem. Abstr., 61, 10501 (1964)].

Molnar, J. and Horvath, C. (1977), Separation of amino acids and peptides on non-polar stationary phases by high-performance liquid chromatography, J. Chromatogr., 142, 623-640.

Montano, P. A. (1977), Mössbauer spectroscopy of iron compounds found in West Virginia coals, Fuel, 56, 397-400.

Montano, P. A. and Granoff, B. (1980), Stoichiometry of iron sulfides in liquefaction residues and correlation with conversion, Fuel, 49, 214-216.

Montgomery, R. S. and Holly, E. D. (1957), Studies of the acids obtained by oxidation of bituminous coal - thermal decomposition of copper salts, Fuel, 36, 493-500.

Mudamburi, Z. (1983), A study of the products of liquefaction of some American and British coals, Ph.D. Thesis, The Pennsylvania State University.

Neavel, R. C. (1976), Liquefaction of coal in hydrogen-donor and non-donor vehicles, Fuel, 55, 237-242.

Neavel, R. C. (1979), Coal structure and coal science. Overview and recommendations, Div. Fuel Chem., Amer. Chem. Soc, Prepr. 24(1), 73-77.

Neavel, R. C. (1981), Exxon donor solvent liquefaction process, Phil. Trans. Roy. Soc., A300, 141-156.

O'Gorman, J. V. and Walker, P. L., Jr. (1971), Mineral matter characteristics of some American coals, Fuel, 50, 135-151.

O'Gorman, J. V. and Walker, P. L., Jr. (1972), Mineral matter and trace elements in U. S. coals: Research and Development Rept. No. 2, to Office of Coal Research, U. S. Dept. of Interior, Under Contract No. 14-01-0001-390, 184 pp.

Osawa, Y. and Shih, J. W. (1971), Infra-red spectra of Japanese coal: The absorption at 3450 and 1260 cm^{-1}, Fuel, 50, 53-57.

Painter, P. C. and Coleman, M. M. (1979), Application of Fourier-transform infrared spectroscopy to the characterization of fractionated coal liquids, Fuel, 58, 301-308.

Painter, P. C. and Rhoads, C. (1981), Fourier transform infrared studies of coal oxidations, Div. of Fuel Chem., Amer. Chem. Soc., Prepr., 26(1), pp. 35-41.

Painter, P. C., Coleman, M. M., Jenkins, R. G., Whang, P. W. and Walker, P. L., Jr. (1978a), Fourier transform infrared study of mineral matter in coal. A novel method for quantitative mineralogical analysis, Fuel, 57, 337-344.

Painter, P. C., Coleman, M. M., Jenkins, R. G. and Walker, P. L. Jr. (1978b), Fourier transform infrared study of acid-demineralized coal, Fuel, 57, 125-126.

Painter, P.C., Yamada, Y., Jenkins, R. G., Coleman, M. M. and Walker, P. L., Jr. (1979), Investigation of retrogressive reactions leading to the carbonization of solvent-refined coal, Fuel, 58, 293-297.

Painter, P. C., Snyder, R. W., Pearson, D. W. and Kwong, J. (1980a), Fourier transform infrared study of the variation in the oxidation of a coking coal, Fuel, 59, 282-286.

Painter, P. C., Stepusin, S., Snyder, R. W. and Davis, A. (1981a), A Fourier transform infrared study of mineral matter in coal: The application of least squares curve-fitting program, Appl. Spectrosc., 35, pp. 102-106.

Painter, P. C., Coleman, M. M., Snyder, R. W., Mahajan, O., Kamatsu, M. and Walker, P. L., Jr. (1981b), Low temperature air oxidation of coking coals: Fourier transform infrared studies, Appl. Spectrosc., 35, 106-110.

Painter, P. C., Snyder, R. W., Starsinic, M., Coleman, M. M., Kuehn, D. W. and Davis, A. (1982), Fourier transform IR spectroscopy: Application to the quantitative determination of functional groups in coal, in Coal and Coal Products: Analytical Characterization Techniques, Fuller, E. L., Jr., Amer. Chem. Soc., Symp. Series No. 205, pp. 47-76.

Patel, K., Stenberg, V. I., Baltisberger, R. J., Woolsey, N. F. and Klabunde, K. (1981), Solubility increase of coal-derived liquids by silylation and acetylation: intermolecular hydrogen bonds, Fuel, 59, 449-450.

Pearson, D. E. (1982), Trends in utilization of British Columbia coal, in Coal: Phoenix of the '80s, ed. A. Taweel, CIC Coal Symposium, Halifax, Nova Scotia, Canada, Canadian Society for Chemical Engineering, Vol. 1, pp. 21-22.

Petrakis, L. and Grandy, D. W. (1981), Free radicals in coal and coal conversion. 6. Effects of liquefaction process variables on the in-situ observation of free radicals, Fuel, 60, 1011-1021.

Petrakis, L., Grandy, D. W. and Ruberto, R. G. (1981), Free radicals in coal and coal conversions. 5. Methodology for the in-situ investigation of free radicals in coal depolymerization under SRC-II, Fuel, 60, 1013-1016.

Petrakis, L, Brandy, D. W. and Jones, G. L. (1982), Free radicals in coal and coal conversion. 7. An in-depth experimental investigation and statistical correlative model of the effects of residence time, temperature and solvents, Fuel, 61, 21-28.

Pines, A. and Wemmer, D. E. (1978), Developments of solid state nmr and potential applications to fuel research, Div. Fuel Chem., Amer. Chem. Soc., Prepr. 23(2), 15-18.

Pines, A., Gibby, M. G. and Waugh, J. S. (1972), Proton-enhanced nuclear induction spectroscopy. A method for high resolution nmr of dilute spins in solids, J. Chem. Phys., 56, 1776-1777.

Pines, A., Gibby, M. G. and Waugh, J. S. (1973), Proton-enhanced nmr of dilute spins in solids, J. Chem. Phys., 59, 569-590.

Postovski, J. J. and Harlampovich, A. B. (1936), The presence of thioether sulphur in organically fixed sulphur of coals, Fuel, 15, 229-232.

Prilezhaeva, E. N., Fedorovskaya, N. P., Miesserova, L. V., Domanima, O., and Khaskina, I. M. (1963), Determination of sulphur content of hydrocarbons by Brems-Strahlung absorption measurements, Tr. Inst. Goryuch. Iskop., Moscow, 21( ), pp. 202-[Chem. Abstr. 60, 6215 (1964)].

Pugmire, R. J., Woolfenden, W. R., Mayne, C. L., Karas, J. and Grant, D. M. (1982), Application of 2-D and dipolar dephasing ^{13}C nmr techniques to the study of structural variations in coal macerals, Div. Fuel Chem., Amer. Chem. Soc, Prepr. 28(1), 103-117.

Radke, M., Willsch, H. and Welte, D. H. (1980), Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography, Anal. Chem., 52, 406-411.

Rakitsky, W. G. (1980), Oxidation methods for the study of coal structure, Ph.D. Thesis, The Pennsylvania State University.

Rao, C. P. and Gluskoter, H. J. (1973), Occurrence and distribution of minerals in Illinois coals, Ill. State Geol. Surv. Circ. No. 476, 56 pp.

Rehak, V. and Smolkova, E. (1976), Chemically bonded stationary phases for gas and high performance liquid chromatograph, Chromatographia, 9, 219-229.

Retcofsky, H. L. (1977) Investigation of the chemical structure of coal by nuclear magnetic resonance and infrared spectroscopy, Applied Spectroscopy, 47, 116-121.

Retcofsky, H. L. (1978), Application of spectrometry in studies of coal structure, Scientific Problems of Coal Utilization: CONF-770509 Oak Ridge, Tenn., pp. 79-97.

Retcofsky, H. L. and Friedel, R. A. (1968), Spectral studies of carbon disulphide extract of bituminous coal, Fuel, 47, 487-491.

Retcofsky, H. L. and Friedel, R. A. (1973), Carbon-13 magnetic resonance in diamonds, coals, and graphite, J. Phys. Chem., 77, 68-71.

Retcofsky, H. L. and VanderHart, D. L. (1978), ^{13}C-^{1}H cross-polarization nuclear magnetic resonance spectra of macerals from coal, Fuel, 57, 421-423.

Rodionova, L. E. and Barauskii, A. O. (1970), Active sulfur groups of Irkutsk coals studied by a chemical reaction method, Izv. Nauchro-Issled. Inst. Nefte-Uglekhim. Sint. Irkutsk. Univ., 12, 93-94. [Chem. Abstr., 75, 51229 (1971)].

Schaefer, J., Stejskal, E. O., Buchjahl, R. (1975), High-resolution carbon-13 nuclear magnetic resonance study of some glassy polymers, Macromolecules, 8, 291-296.

Scott, R. P. W. and Kucera, P. (1977), Examination of five commercially available chromatographic reversed phases (including the nature of the solute-solvent-stationary phase interactions associated with them), J. Chromatogr., 142, 213-232.

Selecky, M. L., Ruo, T. C. S. and Strausz, O. P. (1978), High-pressure liquid chromatography fingerprinting of petroleums and petroleum products, Fuel, 57, 585-591.

Senftle, J., and Davis A. (1982), A data base for the analysis of composition and characteristics of coal seams and macerals, Final Rept. I: Thermoplastic properties and liquefaction behavior of coals and vitrinite concentrates from the Lower Kittanning seam, Report to U.S. Dept. of Energy, No. DOE-30013-F1, from Coal Research Section, The Pennsylvania State University.

Shadle, L. J. (1984), A chemical study of asphaltenes from the liquefaction of coal, Ph.D. Thesis, The Pennsylvania State University.

Shadle, L. J. and Given, P. H. (1982), Dependence of coal liquefaction behaviour on coal characteristics. 7. Structural differences between coals of different rank and asphaltenes derived from them, Fuel, 61, 972-979.

Snyder, L. R. and Kirkland, J. J. (1979), Introduction to Modern Liquid Chromatography, 2 ed., John Wiley & Sons, Inc., NY.

Soboczenski, S. (1984), A study of the structure of coal using oxidative degradation with trifluoroperoxyacetic acid, Ph.D. Thesis, The Pennsylvania State University.

Solomon, P. R. (1979), Relation between coal structure and thermal decomposition products, Div. Fuel Chem., Amer. Chem. Soc., Prepr. 24(2), 184-195.

Solomon, P. R. (1979b), Experimental study modeling of coal pyrolysis at high temperatures, Div. Fuel Chem., Amer. Chem. Soc., Prepr. 24(3), 154-159.

Solomon, P. R. (1981), Relation between coal structure and thermal decomposition products, in Coal Structure, eds. M. L. Gorbaty and K. Ouchi, Adv. in Chem. Ser. No. 192, Amer. Chem. Soc., Washington, D.C., pp. 95-112.

Solomon, P. R. and Colket, M. B. (1978), Evaluation of fuel nitrogen in coal devolatilization, Fuel, 57, 749-755.

Solomon, P. R. and Hamblen, D. B. (1980), Fourier transform infrared spectroscopy in Chemistry and Physics of Coal Utilization, eds. B. R. Cooper and L. Petrakis, Amer. Phys. Soc., pp. 121-140.

Solomon, P. R. Hobbs, R. H., Hamblen, D. G., Chin, W., Cura, A. L. and Graff, R. S. (1981), Correlation of coal volatile yield with oxygen and aliphatic hydrogen, Fuel, 60, 342-346.

Solomon, P. R., Hamblen, D. G. and Cavangelo, R. M. (1982), Applications of Fourier transform IR spectroscopy in fuel science, in Coal and Coal Products: Analytical Characteristization Techniques, Fuller, E. L., Jr., Amer. Chem. Soc. Symp. Series No. 205, pp. 77-131.

Sondreal, E. A., Wilson, W. G. and Stenberg, V. I. (1982), Mechanism leading to process improvements in lignite liquefaction using CO and H2S, Fuel, 61, 925-938.

Spackman, W., Cohen, A. D., Given, P. H. and Casagrande, D. J. (1976), The comparative study of the Okefenokee swamp and the Everglades-mangrove swamp-marsh complex of southern Florida, Field guidebook printed for Geol. Soc. Amer. pre-convention field trip, 15-17 Nov. 1974 (subsequently published by Coal Research Section, The Pennsylvania State University.

Speight, J. G. (1971), Application of spectroscopic techniques to the structural analysis of coal and petroleum, Appl. Spectrosc., Rev., 5(2)., 211-264.

Speight, J. B. (1978), Assessment of structures in coal by spectro-scopic techniques, *in* Analytical Methods for Coal and Coal Products, ed. C. Karr, Jr., Vol. 2, Academic Press, NY, pp. 75-101.

Spencer, D. F. and Alpert, S. B. (1979), Liquefaction and gasification: a promising outlook, Coal Min. Process., 16, 44-49.

Srinivasan, G. and Seehra, M. G. (1982), Changes in free radicals in coal-derived pyrites upon heating in N_2, H_2, and vacuum: role of pyrite-pyrrhotite conversion, Fuel, 61, 1249-1253.

Stabaugh, R. and Yergin, D. (1979), Energy future, Random House, NY, 353 p.

Stenberg, V. I., Baltisberger, R. J., Ogawa, T., Raman, K., and Woolsey, N. F. (1982), Hydrogen sulfide catalysis of low rank coal liquefaction, Div. Fuel Chem., Amer. Chem. Soc., Prepr. 27(3), 22-27.

Stohl, F. V. (1983), The effects of iron sulfide surface area vari-ations on coal liquefaction, Fuel, 62, 122-126.

Suatoni, J. C. and Swab, R. E. (1975), Rapid hydrocarbon group-type analysis by high performance liquid chromatography, J. Chromatogr. Sci., 13, 361-366.

Suatoni, J. C. and Swab, R. E. (1976), Preparative hydrocarbon com-pound type analysis by high performance liquid chromatography, J. Chromatogr. Sci., 14, 535-537.

Sundaram, M. S. and Given, P. H. (1983), Characterization of arti-facts produced from tetralin donor vehicle under coal liquefaction conditions, Div. of Fuel Chem., Amer. Chem. Soc., Prepr., 28(5), 26-39.

Szladow, A. J. (1979), Some aspects of the mechanism and kinetics of coal liquefaction, Ph.D. Thesis, The Pennsylvania State University.

Teichmüller, M. (1982), Origin of petrographic constituents of coal, *in* Stach's Textbook of Coal Petrology, eds. E. Stach, M.-Th. Mackowsky, M. Teichmüller, G. H. Taylor, D. Chandra and R. Teichmüller, Gebrüder Borntraeger, Berlin, Third Edition, pp. 219-294.

Teichmüller, M. and Teichmüller, R. (1967), The diagenesis of coal (coalification), *in* Diagenesis of Sediments, eds, G. Larsen and G. V. Chilingar, Elsevier, NY, pp. 391-415.

Thomas, M. G., Padrick, T. D., Stohl, F. V. and Stephens, H. P. (1982), Decomposition of pyrite under coal liquefaction conditions: a kinetic study, Fuel, 61, 761-764.

Tschamler, H. and deRuiter, E. (1963) Physical properties of coals, *in* Chemistry of Coal Utilization: Suppl. Volume, ed. H. H. Lowry, John Wiley & Sons, NY, pp. 35-118.

Uden, P. C., Crowley, R. J., Joyce, W. F. and Siggia, S. (1976), Liquid chromatographic separation and high resolution gas chromatography of shale oil polar compounds, Div. Fuel Chem., Amer. Chem. Soc., Prepr. 26(2), 1981, pp. 82-88.

Unger, K., Becker, V. and Roumeliotis, P. (1976), Recent developments in the evaluation of chemically bonded silica packings for liquid chromatography, J. Chromatogr., 125, 115-127.

VanderHart, D. L., and Retcofsky, H. L. (1976a), Estimation of coal aromaticities by proton-decoupled carbon-13 magnetic resonance spectra of whole coals, Prep. Coal Chem. Workshop, 1976, 202-218.

VanderHart, D. L. and Retcofsky, H. L. (1976b), Analysis of the aromatic content of whole coals by high power proton decoupled ^{13}C nmr, Fuel, 55, 202-204.

Venier, G. G., Squires, T. B., Chen, Y., Shei, J. G., Metzler, R. M. and Smith, B. F. (1981), The fate of sulfur functions on oxidation with trifluoroperoxyacetic acid, Div. of Fuel Chem., Amer. Chem. Soc., Prepr., 26(1), 20-25.

Verheyen, T. V. (1982), Structural characterization of selected Australian coals, Ph.D. Thesis, Univ. of Melbourne, Australia

Wandless, A. M. (1959), Occurrence of sulfur in British coals, J. Inst. Fuel, 32, 258-266.

Wender, I., Heredy, L. A. Neuworth, M. B. and Dryden, I. G. C. (1980), Chemical reactions and constitution of coal, *in* Chemistry of Coal Utilization, ed. M. D. Elliot, Second Supplementary Volume, Wiley, NY, pp. 1825-1832.

Whitehurst, D. D. (1978), Chemistry and constitution of coal, Amer. Chem. Soc. Symposium Series, 71, ed. J. W. Larsen, pp. 1-35.

Whitehurst, D. D., Farcasiu, M. and Mitchell, T. O. (1976), The nature and origin of asphaltenes in processed coals, Annual Report from Mobil Research and Development Corp. to Electric Power Research Institute, Report EPRI-AF-252.

Whitehurst, D. D., Farcasia, M. and Mitchell, T. O. (1977), The nature and origin of asphaltenes in processed coal, EPRI-AF-480. Electric Power Res. Inst.

Willard, H. H., Merritt, L. L. Dean, J. A. (1978), Instrumental methods of analysis, 5th Edn. D. van Nostrand Co., NY.

Wilson, M. A., Pugmire, R. C., Karas, J. Alemany, L. B., Woolfenden, W. R., Grant, D. M., Given, P. H. (1984), Carbon distribution in coals and coal macerals by cross-polarization magic-angle-spinning carbon-13 nuclear magnetic resonance spectrometry, Anal. Chem., 56, 933-943.

Wiser, W. (1968), Kinetic comparison of coal pyrolysis and coal dissolution, Fuel, 47, 575-586.

Yannoni, C. S. (1982), High resolution nmr in solids, Accs. Chem. Res. 15, 201-208.

Yarzab, R. F., Abdel-Baset, Z. and Given, P. H. (1979), Hydroxyl contents of coals:new data and statistical analyses, Geochim. Cosmochim. Acta., 43, 281-287.

Yarzab, R. F., Given, P. H., Davis, A., and Spackman, W. (1980), Dependence of liquefaction behavior on coal characteristics. 4. Cluster analysis for characteristics of 104 coals, Fuel, 54, 81-92.

Youtcheff, J. S. (1983), Contributions to the phenomology of coal liquefaction, Ph.D. Thesis, The Pennsylvania State University.

Youtcheff, J. S. and Given, P. H. (1982), Dependence of coal liquefaction behavior on coal characteristics. 8. Aspects of the phenomenology of the liquefaction of some coals, Fuel, 61, 980-987.

Youtcheff, J. S., Given, P. H., Baset, Z. and Sundaram, M. S. (1983), The mode of association of alkanes with coal, Org. Geochem., 5, 157-164.

Zilm, K. W., Pugmire, R. J., Grant, D. M., Wood, R. E., and Wiser, W. H. (1979), A comparison of the carbon-13 nmr spectra of solid coals and their liquids obtained by catalytic hydrogenation, Fuel, 58, 11-16.

Zoeller, J. H. (1984), Attempts to induce generation of hydrogen donor solvent from coals, M.S. Thesis, The Pennsylvania State University.

Zweig, G. and Sherma, J. (1972), Handbook Series in Chromatography, Vol. 1, CRC Press, Inc., West Palm Beach, Florida, 131 pp.

APPENDIX A

Analyses of Products of Oxidation of Coals with Trifluoroperoxyacetic Acid

Analyzed by GC/MS as Methyl Esters. Data represent percent of total GC area.

Coal, PSOC No.	Butyric	branched pentanoic?	malonic	methyl-malonic	methyl-hexanoic	maleic	succinic	methyl-succinic
349	4.72	1.00	6.9	0.75	0.00	5.6	5.3	3.0
401	3.74	0.42	8.0	0.96	0.22	5.7	4.8	1.1
581	7.05	0.00	7.3	0.61	0.04	2.9	4.5	2.9
582	3.20	0.00	1.8	0.21	0.00	1.9	1.6	2.3
593	2.07	1.59	8.6	0.49	0.07	3.0	4.8	1.7
594	2.17	1.06	5.9	0.62	0.07	2.7	6.5	3.5
596	6.98	1.21	7.7	0.46	0.63	5.5	4.1	2.0
599	9.06	1.67	8.5	0.66	0.57	5.6	4.2	2.1
664	7.15	2.98	3.2	0.34	0.31	2.7	3.2	1.8
666	6.38	2.83	3.7	0.40	0.31	3.1	3.0	1.8
669	2.72	0.36	5.3	0.97	1.27	3.4	2.2	0.9
676	7.49	0.00	2.4	1.02	0.45	3.7	2.2	1.0
680	4.29	0.23	11.4	0.37	0.24	3.5	3.1	3.8
741	6.87	0.29	5.0	0.14	0.29	3.3	2.0	1.0
742	1.99	0.50	4.6	0.06	0.14	2.3	3.6	1.3
760	2.36	0.00	3.4	0.20	0.06	3.5	4.0	5.0
767	1.80	0.00	1.8	0.13	0.23	3.3	2.2	5.4
768	2.88	0.00	3.5	0.15	0.28	3.3	2.0	4.4
773	3.52	1.38	16.9	0.80	0.27	8.3	8.1	1.5
798	2.63	0.01	0.5	0.00	0.00	1.7	0.4	1.4
808	11.08	0.00	2.4	0.32	0.56	2.8	2.0	1.3
883	4.67	0.06	5.0	0.44	0.00	4.4	3.9	3.2
1018	2.63	0.00	11.9	0.57	0.00	6.5	6.2	1.5
1082	5.68	0.00	2.5	1.03	0.48	2.8	2.2	5.4
1083	3.90	0.00	2.8	1.05	0.49	3.0	2.1	5.1
1098	1.99	2.19	9.9	0.75	0.07	3.9	4.5	3.6

Coal, PSOC No.	hydroxyl succinic	methyl maleic	benzoic	(MW 174)	(MW 178)	glutaric	methyl-adipic	(MW 172)	ethyl maleic	(Scan No. 156)
349	2.5	4.0	2.68	0.90	2.84	6.2	0.54	2.28	2.91	3.1
401	2.1	4.7	2.22	3.12	0.02	7.4	0.49	1.58	2.80	1.9
581	3.0	2.1	1.59	0.76	0.43	4.6	0.32	0.64	1.13	1.4
582	1.3	2.8	0.42	0.72	0.72	4.3	0.35	0.81	4.26	0.4
593	1.8	2.1	1.49	0.92	2.00	5.4	0.30	0.93	0.84	1.9
594	1.4	2.3	1.39	1.30	0.00	6.4	0.52	0.85	1.86	0.8
596	2.5	4.0	0.97	0.00	1.47	6.0	0.00	0.64	0.54	2.4
599	2.6	4.5	1.10	0.00	1.38	6.4	0.00	0.73	0.54	2.0
664	2.5	2.2	1.35	0.37	1.31	7.7	0.32	1.02	0.72	1.6
666	2.8	2.0	1.58	0.47	1.31	7.0	0.21	0.83	0.64	1.0
669	2.6	2.2	1.69	0.21	0.41	8.2	1.23	0.00	0.36	3.5
676	3.6	3.2	4.16	1.81	0.48	10.7	0.00	0.00	0.88	1.2
680	4.6	1.8	2.00	1.13	0.00	10.7	0.00	0.20	0.76	1.2
741	1.9	1.7	0.87	0.70	0.21	5.0	0.30	0.87	1.17	1.8
742	1.8	2.1	0.75	0.80	2.05	4.8	0.37	0.93	1.06	1.8
760	3.3	2.2	1.91	0.89	1.30	5.1	0.44	0.48	0.87	2.1
767	2.2	2.3	0.69	0.32	1.54	5.9	0.19	0.59	0.67	1.3
768	2.0	2.3	0.68	0.40	1.40	5.6	0.17	0.58	0.58	1.0
773	2.2	0.5	0.58	0.08	4.87	2.9	0.00	0.59	0.41	1.2
798	0.4	2.5	0.49	0.70	1.82	2.4	0.00	1.26	2.03	1.7
808	0.2	3.6	0.85	1.25	0.41	3.4	0.61	0.00	0.05	1.8
883	3.1	4.1	2.40	1.25	1.79	6.5	0.27	1.37	2.56	1.8
1018	2.8	5.8	2.57	1.40	1.86	4.4	0.00	0.00	0.00	1.8
1082	2.3	2.4	0.79	0.84	1.64	6.1	0.88	0.98	0.99	0.0
1083	0.2	0.3	0.65	0.40	1.03	7.1	0.65	0.10	0.20	2.4
1098	1.7	4.1	2.32	0.98	0.90	7.7	0.24	0.91	1.25	2.1

Coal, PSOC No.	adipic	2-phenyl-acetic	propyl-maleic	propyl-suc-cinic	(Scan No. 190)	dimethyl-adipic	(Scan No. 195)	ethyl-glutaric	(Scan No. 203)	(Scan No. 210)
349	0.33	0.89	1.69	0.69	0.44	0.91	1.58	0.21	0.75	0.73
401	0.34	0.89	0.98	0.62	0.57	0.00	2.06	1.12	0.72	0.81
581	0.26	1.06	0.18	1.41	0.62	0.00	1.62	0.88	0.39	0.81
582	0.72	1.41	1.93	0.33	0.87	0.31	2.11	0.57	0.00	2.34
593	0.20	0.39	1.32	0.52	0.60	0.35	1.29	0.59	0.32	1.00
594	0.53	0.64	1.47	0.24	0.43	0.45	1.11	0.66	0.09	0.82
596	0.82	0.84	0.69	0.57	0.21	0.24	1.71	0.84	0.00	0.00
599	0.82	0.75	0.00	0.44	0.38	0.00	1.68	0.68	0.00	0.00
664	0.37	1.06	0.79	0.48	0.91	1.43	1.64	1.46	0.53	1.53
666	0.50	0.87	0.63	0.39	0.88	1.45	2.53	1.07	0.19	0.53
669	0.65	0.52	1.44	0.52	0.00	0.00	2.38	1.03	0.15	0.44
676	0.00	2.00	0.26	0.40	0.90	0.09	0.90	0.38	0.52	0.07
680	0.32	0.42	0.22	0.51	0.57	0.00	1.25	0.82	0.16	0.64
741	0.04	0.42	1.31	0.00	0.37	0.39	1.58	1.02	0.43	1.31
742	0.31	0.35	1.52	0.65	0.93	0.38	1.72	1.01	0.32	1.02
760	0.29	0.81	1.36	0.42	0.56	0.59	1.39	0.34	0.71	0.63
767	0.53	0.38	1.29	0.50	0.16	0.87	1.40	1.03	0.33	0.27
768	0.50	0.40	1.07	0.47	0.29	0.79	1.39	1.05	0.40	0.26
773	0.65	0.34	1.72	0.36	0.00	0.65	1.05	0.00	0.10	0.00
798	0.31	0.36	1.07	0.00	0.20	0.61	1.36	1.08	0.37	0.31
808	0.72	0.70	1.10	0.49	0.22	0.24	2.21	0.14	0.03	0.28
883	0.21	0.69	1.46	0.58	0.54	0.56	1.16	1.59	0.47	0.80
1018	0.80	0.96	1.54	0.00	0.29	0.00	0.88	0.82	0.00	0.00
1082	0.38	0.83	1.46	0.48	0.56	0.10	1.90	1.38	0.60	0.05
1083	0.79	0.70	1.60	0.52	0.95	0.00	2.90	1.49	0.17	0.06
1098	0.22	0.42	0.76	0.67	0.61	0.20	1.64	0.73	0.35	0.65

Coal, PSOC No.	ethane-tricarb-oxylic	(Scan No. 221)	(Scan No. 230)	(Scan No. 244)	(Scan No. 254	a C_7 diacid	(MW 158)	oxirane-tricarb-oxylic	propane-1,2,3,-trioic
349	2.5	0.74	0.20	3.4	0.39	0.65	2.0	11.5	0.27
401	3.0	1.09	0.79	3.7	0.65	0.57	1.2	7.7	1.17
581	2.4	0.68	0.46	2.9	0.41	0.06	1.3	13.1	0.57
582	3.0	0.73	0.30	3.4	0.57	0.00	1.0	17.9	0.87
593	3.7	0.57	0.97	3.6	0.31	0.09	1.2	18.4	0.53
594	2.8	0.55	0.73	2.4	0.68	0.22	0.2	19.7	0.82
596	3.3	0.65	0.48	2.1	0.40	0.40	1.4	6.9	0.86
599	3.3	0.59	0.43	2.0	0.19	0.30	1.6	6.2	0.86
664	3.4	0.65	0.86	4.6	0.64	0.19	2.0	12.1	1.42
666	3.4	0.73	0.95	4.8	0.68	0.20	2.3	13.3	1.69
669	3.6	0.21	0.16	1.2	0.00	0.47	2.1	7.7	0.85
676	0.8	0.63	0.28	1.7	0.63	0.39	2.1	8.0	0.46
680	1.0	0.75	0.28	2.6	0.50	0.09	1.8	12.9	0.82
741	2.9	0.53	0.82	2.1	0.30	0.40	1.4	12.5	0.86
742	2.7	0.52	0.71	3.4	0.38	0.21	1.3	18.5	0.29
760	1.7	0.81	1.04	3.2	0.49	0.00	1.6	14.0	0.59
767	0.5	0.32	0.45	2.7	0.00	2.12	0.0	12.1	0.18
768	0.5	0.32	0.49	2.8	0.74	0.20	0.7	12.6	0.17
773	5.1	0.53	0.00	1.1	0.40	0.00	0.9	4.9	1.02
798	2.6	0.41	0.00	2.3	0.58	0.00	2.0	17.3	0.74
808	0.8	0.41	0.52	2.9	0.21	0.76	0.0	13.5	1.09
883	2.1	0.54	0.36	3.2	0.58	0.00	1.2	13.1	0.90
1018	3.3	0.00	0.00	1.8	0.00	0.00	2.5	11.5	0.00
1082	1.3	0.58	0.38	1.8	0.63	0.39	2.1	8.9	0.43
1083	1.1	0.63	0.29	1.8	0.89	0.44	3.0	8.9	0.46
1098	1.8	0.50	0.42	3.0	0.29	0.07	0.8	13.2	0.34

Coal, FSOC No.	(scan No. 283)	butane-trioic	phthalic	C_9-diacid	methyl-phthalic	(scan no. 332)	tere-phthalic	iso-phthalic	homo-phthalic	C_{10}-diacid
349	0.16	1.8	3.4	0.49	2.0	1.5	0.25	0.00	1.5	0.38
401	0.37	2.6	3.7	0.39	1.7	1.5	0.55	0.86	2.1	0.72
581	0.00	3.4	4.4	0.79	1.7	1.9	0.76	0.36	1.3	0.19
582	0.76	3.6	5.1	0.96	2.1	2.8	1.05	0.33	2.2	0.00
593	0.57	3.6	5.0	0.98	2.1	2.0	0.61	0.21	1.6	0.08
594	0.00	3.9	3.0	0.45	1.9	2.4	0.56	0.59	2.2	0.18
596	0.00	3.4	6.5	0.66	1.3	1.2	0.84	0.85	2.4	0.00
599	0.00	3.9	6.1	0.54	0.4	1.1	0.95	0.94	2.2	0.00
664	0.11	3.1	3.3	0.32	1.3	1.9	0.87	0.31	1.5	0.00
666	0.00	3.1	3.0	0.32	1.7	1.9	0.82	0.35	1.5	0.00
669	1.00	6.2	6.5	0.96	2.3	1.0	0.83	0.61	1.5	0.09
676	0.41	5.5	12.5	0.20	1.6	1.7	0.64	1.15	2.4	0.04
680	0.00	3.5	3.7	0.66	0.5	1.5	0.89	0.22	1.4	0.00
741	0.68	8.2	2.0	1.27	2.2	2.8	0.78	0.47	2.7	0.14
742	0.67	8.4	2.1	1.13	2.2	2.6	0.78	0.42	2.4	0.24
760	0.37	3.3	4.7	0.69	1.4	1.5	0.39	1.75	7.0	0.64
767	0.00	4.4	9.4	0.69	2.9	3.9	0.85	1.24	2.1	0.32
768	0.00	3.3	9.9	0.68	2.6	3.9	0.87	1.38	2.1	0.40
773	0.21	3.6	6.1	0.43	2.3	1.0	0.43	1.28	1.7	0.00
798	1.21	5.1	15.0	0.37	1.9	4.3	0.24	0.17	5.1	0.50
808	0.00	5.2	9.1	0.95	0.9	2.0	0.76	2.24	3.6	0.47
883	0.51	3.2	7.0	0.26	2.2	2.5	0.11	0.06	1.2	0.21
1018	0.00	2.7	8.4	0.68	1.5	1.6	0.00	0.96	1.6	0.00
1082	0.00	6.4	11.7	0.20	1.5	1.9	0.65	1.74	2.4	0.38
1083	0.00	6.9	10.1	0.40	1.3	2.0	0.87	1.78	1.0	0.47
1098	0.17	2.7	5.2	0.79	1.6	1.9	0.56	0.17	1.9	0.00

Coal, PSOC No.	(scan no. 332)	(scan no. 330)	oxirane-tetra-carbox.	methyl phthalic	hydroxy-phthalic	benzene 1,3,5-tri-carbox.	benzene 1,2,4-tri-carbox.
349	0.23	0.17	0.95	0.23	0.67	0.61	0.57
401	0.31	1.19	0.89	1.02	0.84	0.73	1.09
581	1.11	0.89	3.93	0.84	0.64	4.76	1.75
582	1.04	0.73	4.94	1.34	0.56	4.18	1.93
593	0.32	0.80	2.65	0.20	0.44	2.32	0.60
594	0.70	0.38	4.63	0.13	0.46	3.51	1.18
596	0.79	0.94	4.98	1.04	0.64	3.79	1.32
599	0.69	0.83	2.45	1.54	0.44	3.62	1.41
664	0.74	0.61	2.33	1.53	0.67	2.35	1.20
666	0.30	0.58	2.04	1.78	0.76	2.34	1.01
669	1.78	1.45	4.30	0.52	0.95	5.47	2.00
676	1.55	0.65	3.53	0.25	0.32	2.60	0.44
680	1.08	0.40	3.53	0.94	0.41	4.50	1.64
741	1.02	0.51	2.75	1.75	0.37	3.58	0.57
742	1.02	0.45	2.75	0.27	0.33	3.55	0.58
760	1.02	0.01	4.64	0.00	0.38	3.02	0.96
767	1.24	0.49	6.61	0.41	0.53	6.39	2.30
768	1.37	0.50	6.40	0.50	0.71	6.79	2.25
773	1.02	0.32	3.57	0.00	0.49	3.21	1.60
798	0.97	0.37	4.41	0.49	1.08	6.62	0.84
808	0.94	0.57	5.37	0.21	0.35	6.78	0.70
883	0.65	0.35	1.78	0.21	0.58	1.86	0.46
1018	0.74	0.00	2.69	0.00	0.47	3.86	0.65
1082	0.98	0.58	0.80	0.31	0.47	6.32	2.35
1083	0.98	0.87	6.08	0.00	0.46	5.99	2.81
1098	0.76	0.36	3.12	0.64	0.61	2.73	1.00

APPENDIX B

Correlation Matrix for Full Set of Forty Variables

Note: The variables are numbered, and the numbers are used
for identification. In order to save space, several correlation
coefficients are collected in each vertical column. Thus the
first entry under 18 at the bottom of page 214 indicates that
the correlation coefficient between 0 and item 1, f_a, is -0.10,
between 0 and item 8 (saturate fraction, HPLC) is 0.13, and between
0 and item 15 (oxygen-containing gases) is 0.50.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
1 FA	1.00																	
2 C	0.17	1.00																
3 H	-0.01	0.12	1.00															
4 N	-0.16	0.15	0.05	1.00														
5 Organic Sulfur	-0.07	-0.77	0.14	0.13	1.00													
6 Total Conversion	-0.42	-0.39	-0.09	-0.25	0.56	1.00												
7 Conversion to Asphaltenes	-0.44	-0.45	0.19	-0.18	0.20	0.85	1.00											
8 Saturate Fraction HPLC	-0.44	-0.14	-0.32	-0.03	0.38	0.29	0.27	1.00										
9 Aromatic Fraction HPLC	-0.26	-0.18	-0.54	-0.19	0.24	0.24	0.17	0.34	1.00									
10 Polar Fraction HPLC	-0.35	-0.56	-0.17	-0.24	0.51	0.65	0.52	0.45	0.46	1.00								
11 Hydrogen Gas	0.01	-0.15	-0.21	-0.38	0.12	0.16	0.08	0.55	0.17	0.15	1.00							
12 Hydrogen Sulfide	0.18	-0.30	-0.33	0.00	0.55	0.18	-0.07	0.19	0.32	0.25	0.34	1.00						
13 Methane	0.35	0.25	0.08	0.04	-0.624	-0.29	-0.23	-0.28	-0.24	-0.36	-0.16	0.05	1.00					
14 C2 Gases	0.09	-0.52	-0.27	-0.29	0.59	0.56	0.29	0.20	0.01	0.41	-0.20	0.25	-0.06	1.00				
15 Oxygen Containing Gases	0.13	-0.67	-0.04	-0.15	0.48	0.40	0.29	-0.16	0.13	0.29	-0.06	0.26	0.31	0.37	1.00			
16 Hydrocarbon Gases	0.37	0.18	0.02	-0.02	-0.23	-0.19	-0.16	-0.23	-0.25	-0.31	-0.10	-0.01	0.98	0.13	0.34	1.00		
17 C3 Gases	0.22	0.17	-0.34	-0.16	-0.12	0.15	0.11	0.1	-0.08	-0.22	0.27	0.10	0.16	0.44	-0.09	0.31	1.00	
18 O	-0.10	-0.82	-0.14	-0.15	0.49	0.51	0.38	0.13	0.15	0.47	0.15	0.06	0.23	0.39	0.50	-0.19	-0.22	1.00

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19 Aliphatic Aromatic Ratio (FTIR)

(1) -0.55 (2) -0.08 (3) 0.46 (4) 0.20 (5) 0.24 (6) 0.24 (7) 0.19
(8) 0.42 (9) 0.38 (10) 0.53 (11) 0.27 (12) 0.03 (13) 0.49 (14) 0.03
(15) -0.21 (16) -0.49 (17) -0.20 (18) 0.16 (19) 1.00

20 Acetylated Aromatic OH (FTIR)

(1) 0.04 (2) -0.57 (3) -0.37 (4) -0.09 (5) 0.43 (6) 0.28 (7) 0.04
(8) -0.02 (9) 0.49 (10) 0.42 (11) 0.11 (12) 0.32 (13) -0.25 (14) 0.08
(15) 0.36 (16) -0.25 (17) -0.18 (18) 0.64 (19) 0.04 (20) 1.00

21 Acetylated Alphatic OH (FTIR)

(1) 0.06 (2) -0.48 (3) -0.16 (4) -0.34 (5) 0.49 (6) 0.32 (7) 0.08
(8) -0.13 (9) 0.44 (10) 0.37 (11) 0.31 (12) 0.25 (13) -0.04 (14) 0.39
(15) 0.43 (16) -0.02 (17) -0.32 (18) 0.49 (19) 0.43 (20) 0.34 (21) 1.00

22 Acetylated Amino (FTIR)

(1) 0.37 (2) -0.32 (3) -0.09 (4) -0.08 (5) 0.28 (6) 0.25 (7) 0.14
(8) -0.14 (9) 0.22 (10) 0.17 (11) 0.14 (12) 0.28 (13) -0.37 (14) 0.01
(15) 0.16 (16) -0.38 (17) -0.30 (18) 0.36 (19) 0.39 (20) 0.27 (21) 0.44
(22) 1.00

23 Mineral Matter

(1) 0.04 (2) -0.23 (3) -0.22 (4) -0.19 (5) 0.45 (6) 0.24 (7) 0.11
(8) 0.02 (9) 0.18 (10) 0.18 (11) 0.07 (12) 0.59 (13) -0.33 (14) 0.17
(15) 0.20 (16) -0.30 (17) 0.04 (18) 0.17 (19) -0.09 (20) 0.22 (21) -0.05
(22) -0.43 (23) 1.00

24 Conversion to Gases

(1) 0.44 (2) -0.04 (3) 0.01 (4) -0.07 (5) 0.00 (6) -0.05 (7) -0.07
(8) -0.34 (9) -0.12 (10) -0.48 (11) -0.10 (12) 0.16 (13) 0.87 (14) 0.20
(15) 0.60 (16) 0.90 (17) 0.21 (18) -0.03 (19) -0.49 (20) -0.06 (21) -0.16
(22) -0.29 (23) -0.13 (24) 1.00

25 Conversion to Oils

(1) -0.43 (2) -0.42 (3) -0.20 (4) -0.26 (5) 0.39 (6) 0.63 (7) 0.53
(8) 0.56 (9) 0.54 (10) 0.97 (11) 0.21 (12) 0.25 (13) -0.40 (14) 0.36
(15) 0.15 (16) -0.35 (17) 0.15 (18) 0.34 (19) 0.24 (20) 0.33 (21) 0.34
(22) 0.17 (23) 0.18 (24) -0.19 (25) 1.00

26 Conversion to Lost Volatiles

(1) -0.18 (2) -0.60 (3) -0.26 (4) -0.02 (5) 0.65 (6) 0.57 (7) 0.23
(8) 0.01 (9) -0.04 (10) 0.10 (11) 0.09 (12) 0.26 (13) -0.42 (14) 0.45
(15) 0.17 (16) -0.33 (17) 0.07 (18) 0.48 (19) 0.28 (20) 0.31 (21) 0.27
(22) 0.46 (23) 0.40 (24) -0.26 (25) 0.04 (26) 1.00

27 Tetraline Naphthalene Ratio

(1) 0.31 (2) 0.64 (3) 0.10 (4) 0.06 (5) -0.42 (6) -0.74 (7) -0.61
(8) -0.14 (9) -0.08 (10) -0.48 (11) 0.10 (12) 0.06 (13) 0.08 (14) -0.43
(15) -0.53 (16) 0.03 (17) 0.15 (18) -0.60 (19) -0.15 (20) -0.19 (21) -0.42
(22) -0.30 (23) 0.02 (24) 0.31 (25) -0.39 (26) -0.48 (27) 1.00

28 Total Reactive Macerals

(1) -0.07 (2) 0.09 (3) 0.11 (4) 0.06 (5) -0.34 (6) -0.08 (7) -0.03
(8) 0.09 (9) -0.13 (10) -0.10 (11) -0.08 (12) -0.57 (13) 0.32 (14) 0.03
(15) -0.12 (16) 0.32 (17) 0.067 (18) -0.09 (19) 0.09 (20) -0.13 (21) 0.00
(22) -0.37 (23) -0.90 (24) 0.08 (25) -0.11 (26) -0.23 (27) -0.10 (28) 1.00

29 Vitrinite Content

(1) 0.07 (2) -0.53 (3) -0.40 (4) -0.23 (5) 0.40 (6) 0.42 (7) 0.28
(8) 0.16 (9) 0.29 (10) 0.23 (11) 0.04 (12) -0.04 (13) 0.07 (14) 0.43
(15) 0.39 (16) 0.14 (17) 0.16 (18) 0.50 (19) 0.12 (20) 0.41 (21) 0.31
(22) 0.01 (23) 0.06 (24) 0.14 (25) 0.14 (26) 0.32 (27) -0.40 (28) 0.23
(29) 1.00

30 Pyritic Sulfur
(1) 0.01 (2) -0.07 (3) 0.30 (4) -0.10 (5) 0.19 (6) -0.04 (7) -0.15
(8) 0.03 (9) 0.48 (10) 0.07 (11) 0.11 (12) 0.72 (13) -0.10 (14) -0.17
(15) 0.05 (16) -0.14 (17) -0.05 (18) 0.02 (19) 0.01 (20) 0.33 (21) 0.14
(22) 0.47 (23) 0.61 (24) 0.01 (25) 0.11 (26) 0.14 (27) 0.23 (28) -0.61
(29) -0.14 (30) 1.00

31 H/C Ratio
(1) -0.21 (2) -0.33 (3) 0.31 (4) -0.15 (5) -0.17 (6) -0.12 (7) -0.10
(8) -0.07 (9) -0.33 (10) -0.16 (11) -0.10 (12) 0.01 (13) -0.26 (14) -0.23
(15) 0.05 (16) -0.25 (17) -0.24 (18) -0.21 (19) -0.03 (20) 0.10 (21) 0.02
(22) -0.09 (23) 0.27 (24) -0.16 (25) -0.20 (26) 0.21 (27) -0.04 (28) -0.25
(29) -0.19 (30) 0.02 (31) 1.00

32 Total Sulfur
(1) 0.06 (2) -0.39 (3) -0.19 (4) -0.17 (5) 0.64 (6) 0.28 (7) -0.03
(8) -0.17 (9) 0.10 (10) 0.23 (11) 0.13 (12) 0.76 (13) -0.20 (14) 0.28
(15) 0.24 (16) -0.16 (17) -0.04 (18) 0.22 (19) -0.05 (20) 0.31 (21) 0.25
(22) 0.43 (23) 0.76 (24) 0.04 (25) 0.18 (26) 0.56 (27) -0.03 (28) -0.72
(29) -0.10 (30) 0.67 (31) 0.32 (32) 1.00

33 O/C Ratio
(1) -0.20 (2) -0.98 (3) -0.17 (4) -0.12 (5) 0.68 (6) 0.68 (7) 0.51
(8) 0.19 (9) 0.25 (10) 0.56 (11) 0.14 (12) 0.22 (13) -0.23 (14) 0.48
(15) 0.67 (16) -0.17 (17) -0.13 (18) 0.83 (19) 0.22 (20) 0.57 (21) 0.46
(22) 0.29 (23) 0.15 (24) 0.05 (25) 0.42 (26) 0.53 (27) -0.68 (28) -0.02
(29) 0.59 (30) 0.03 (31) -0.18 (32) 0.25 (33) 1.00

34 TPFA Products Aliphatic
(1) -0.04 (2) -0.02 (3) -0.27 (4) 0.23 (5) 0.08 (6) 0.25 (7) 0.19
(8) 0.38 (9) -0.08 (10) 0.18 (11) 0.22 (12) 0.22 (13) 0.02 (14) 0.26
(15) 0.02 (16) 0.10 (17) 0.46 (18) -0.04 (19) 0.01 (20) -0.02 (21) -0.27
(22) 0.15 (23) -0.10 (24) 0.04 (25) 0.21 (26) 0.02 (27) -0.19 (28) 0.13
(29) 0.02 (30) -0.17 (31) -0.34 (32) -0.06 (33) 0.05 (34) 1.00

35 TPFA Products Aromatic
(1) 0.27 (2) -0.07 (3) -0.20 (4) -0.13 (5) 0.20 (6) -0.19 (7) -0.23
(8) -0.29 (9) 0.29 (10) -0.12 (11) 0.16 (12) 0.37 (13) 0.03 (14) -0.11
(15) 0.31 (16) 0.02 (17) 0.12 (18) 0.07 (19) -0.19 (20) 0.46 (21) -0.02
(22) 0.17 (23) 0.41 (24) 0.21 (25) -0.15 (26) -0.05 (27) 0.37 (28) -0.46
(29) 0.07 (30) 0.48 (31) -0.21 (32) 0.36 (33) 0.04 (34) -0.08 (35) 1.00

36 TPFA Products Oxyranes
(1) 0.46 (2) 0.35 (3) -0.46 (4) 0.22 (5) -0.09 (6) -0.15 (7) -0.24
(8) -0.15 (9) -0.31 (10) -0.29 (11) -0.19 (12) 0.07 (13) 0.04 (14) 0.19
(15) -0.39 (16) 0.09 (17) 0.28 (18) -0.32 (19) 0.03 (20) -0.36 (21) 0.16
(22) 0.13 (23) 0.09 (24) -0.06 (25) -0.22 (26) 0.13 (27) 0.14 (28) -0.14
(29) -0.27 (30) -0.14 (31) 0.02 (32) 0.14 (33) -0.41 (34) 0.09 (35) -0.33
(36) 1.00

37 TPFA Products Containing Ethyl Groups
(1) 0.37 (2) 0.33 (3) 0.14 (4) -0.02 (5) -0.23 (6) -0.20 (7) -0.02
(8) -0.43 (9) -0.28 (10) -0.30 (11) -0.08 (12) -0.07 (13) -0.35 (14) -0.09
(15) -0.16 (16) -0.04 (17) 0.21 (18) -0.11 (19) -0.46 (20) -0.05 (21) -0.38
(22) 0.13 (23) 0.29 (24) -0.05 (25) -0.29 (26) -0.08 (27) 0.23 (28) -0.41
(29) -0.32 (30) -0.06 (31) 0.03 (32) 0.06 (33) -0.35 (34) -0.07 (35) 0.23
(36) 0.36 (37) 1.00

38 TPFA Products Containing Methyl Groups	(1) 0.04	(2) -0.07	(3) -0.28	(4) 0.20	(5) 0.19	(6) 0.30	(7) 0.16
	(8) 0.33	(9) -0.03	(10) 0.24	(11) 0.25	(12) 0.25	(13) 0.01	(14) 0.35
	(15) 0.08	(16) 0.11	(17) 0.46	(18) -0.06	(19) 0.03	(20) 0.02	(21) 0.15
	(22) 0.19	(23) -0.13	(24) 0.13	(25) 0.26	(26) 0.03	(27) -0.17	(28) 0.15
	(29) 0.06	(30) -0.18	(31) -0.27	(32) -0.04	(33) 0.08	(34) 0.92	(35) -0.05
	(36) 0.03	(37) -0.18	(38) 1.00				
39 TPFA Products Containing Propyl Groups	(1) 0.46	(2) 0.35	(3) -0.07	(4) 0.22	(5) -0.09	(6) -0.15	(7) -0.24
	(8) -0.15	(9) -0.31	(10) -0.29	(11) -0.19	(12) 0.07	(13) 0.04	(14) 0.19
	(15) -0.39	(16) 0.09	(17) 0.28	(18) -0.33	(19) 0.03	(20) -0.36	(21) -0.16
	(22) -0.13	(23) 0.09	(24) -0.06	(25) -0.22	(26) 0.13	(27) 0.14	(28) -0.14
	(29) -0.27	(30) -0.14	(31) 0.02	(32) 0.14	(33) -0.40	(34) 0.09	(35) -0.33
	(36) 0.86	(37) 0.36	(38) 0.03	(39) 1.00			