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## Technical Progress Report
October 1991 - December 1991

C. Song, A. Saini, L. Huang, K. Wenzel, P.G. Hatcher and H.H. Schobert

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# ABSTRACT

Low-temperature catalytic pretreatment is a promising approach to the development of an improved liquefaction process. This work is a fundamental study on effects of pretreatments on coal structure and reactivity in liquefaction. The main objectives of this project are to study the coal structural changes induced by low-temperature catalytic and thermal pretreatments by using spectroscopic techniques; and to clarify the pretreatment-induced changes in reactivity or convertibility of coals in the subsequent liquefaction. This report describes the progress of our work during the first quarterly period. Substantial progress has been made in the spectroscopic characterization of fresh and THF-extracted samples of two subbituminous coals and fresh samples of three bituminous coals using cross-polarization magic angle spinning (CPMAS) solid-state $^{13}C$ NMR and pyrolysis-GC-MS techniques. CPMAS $^{13}C$ NMR and pyrolysis-GC-MS provided important information on carbon distribution/functionality and molecular components/structural units, respectively, for these coal samples. Pyrolysis-GC-MS revealed that there are remarkable structural differences in structural units between the subbituminous coals and the bituminous coals.

Furthermore, significant progress has been made in the pretreatments and spectroscopic characterization of catalytically and thermally pretreated as well as physically treated Wyodak subbituminous coal, and temperature-staged and temperature-programmed thermal and catalytic liquefaction of a Montana subbituminous coal. The analytical results show that both catalytic and thermal pretreatments result in some changes in coal structure. In many cases such structural changes are subtle and not easily detectable by conventional analytical methods such as FT-IR. We have detected the changes in coal macromolecular structure by using a combination of pyrolysis-GC-MS and CPMAS $^{13}C$ NMR as well as FT-IR. Liquefaction data indicates that low-temperature catalytic pretreatments enhance coal conversion and oil production. Among the two different liquefaction procedures incorporating pretreatments, temperature-programmed liquefaction of a Montana subbituminous coal using dispersed Mo catalyst has been shown to be superior to the temperature-staged liquefaction.

# INTRODUCTION

The importance of coal liquefaction to produce liquid transportation fuels is well documented (Lumpkin, 1988; DOE COLIRN, 1989). Liquefaction is also one of the important routes for producing useful aromatic chemicals and advanced materials from coals (Song and Schobert, 1992a). However, the coal conversion into liquids is an extremely complex process and involves both chemical and physical transformations. Despite enormous strides in coal liquefaction research and process development, coal-derived liquids are still not competitive with petroleum crudes. Further improvements are required and the most promising approach would be the development of improved catalytic process. It is known that direct liquefaction of coals proceeds through two loosely defined stages, coal dissolution into solvent-soluble materials, followed by upgrading of the solubilized products. The distribution and quality of primary liquefaction (coal dissolution ) products depend on the coal, catalyst, solvent and process conditions used in the first stage. The upgrading of primary liquefaction products into transportation fuels requires an overall upgrading of heavy materials to distillable materials, followed by the upgrading of different distillate fractions to liquid products with the necessary properties for use as transportation fuels including gasoline, jet fuels, and diesel fuels.

The conventional concept for high-severity conversion of coal is that coal must be heated to high temperatures (400-450°C) causing thermal cleavage of bonds in organic matrix of coal to yield free radicals, which are capped by hydrogen to form low-molecular-weight products. However, recent fundamental research in coal liquefaction and pyrolysis has revealed that coal is more reactive than had been thought previously. The thermally initiated reactions of coal can take place very rapidly (Whitehurst et al., 1980a, 1980b) and, especially for low-rank coals, can occur at lower temperatures (Neavel, 1982; Suuberg et al., 1985, 1987). Temperature-programmed pyrolysis (TPP) of different coals ranging from brown to bituminous coals clearly showed that more bonds in low-rank coals are thermally broken at lower temperatures as compared to bituminous coals, and a concept of bond energy distribution has been developed from TPP (Song et al., 1991a; Song and Schobert, 1992b). Considerable work at Penn State (Davis et al., 1986, 1989; Derbyshire et al., 1986a, 1986b, 1989; Stansberry et al., 1987; Burgess and Schobert, 1990; Burgess et al., 1991) has demonstrated that the combination of low-temperature catalytic reaction followed by the high temperature catalytic reaction using dispersed molybdenum significantly enhanced coal conversion and oil production. More recent work in this laboratory has shown that temperature-programmed liquefaction using programmed heat-up is more effective for converting low-rank coals (Song et al., 1991b; Song and Schobert, 1992b; Huang et al., 1992].

All these results point to the beneficial effects of reactions at lower temperatures as compared to conventional high-severity processes.

The above results strongly suggest that low-temperature catalytic pretreatment or preconversion is a promising approach and deserves further detailed study. An important fact noted from previous work is that the low temperature pretreatments using dispersed catalyst do not appreciably alter the solubility of coal in THF, and the main effects become apparent only upon subsequent reaction at higher temperature (Derbyshire, 1988; DOE COLIRN, 1989). Probably the catalytic pretreatment affects the early reaction stage most significantly. The importance of, and potential problems, associated with early steps in direct liquefaction will be discussed in relation to the catalytic pretreatments in the section on Survey of Relevant Literature. Briefly, the most important issue in the early stage of coal dissolution is to suppress the retrograde reactions to produce higher yields of less refractory liquids for the down-stream catalytic upgrading. The appropriate low-temperature catalytic pretreatments followed by high-temperature catalytic reactions could improve yield and quality of distillate products and increase coal conversion and the efficiency of hydrogen utilization, provided that the pretreatment can induce desirable structural modification in coal that will improve its reactivity and reduce retrograde reactions upon liquefaction. The study of coal structure and reactivity associated with catalytic pretreatment and subsequent liquefaction could lead to the development of most effective preconversion and liquefaction procedures. These advantages are of great importance to the potential commercial applications, not only in coal hydroliquefaction, but also in coal co-processing as well as coal hydropyrolysis. An apparent disadvantage of introducing catalytic pretreatment is that it increases the process units, equipment costs and complexity of operation. This disadvantage can be offset by the prospective gains in yields and quality of distillate products and suppression of unnecessary $H_2$ consumption. It is undisputable that the development of a low-severity catalytic liquefaction process has great potential to improve overall process efficiency and to reduce operating costs for producing transportation fuels from coal.

## PROJECT OBJECTIVES

This work is a fundamental study of catalytic pretreatments as a potential preconversion step to low-severity liquefaction. The ultimate goal of this work is to provide the basis for the design of an improved liquefaction process and to facilitate our understanding of those processes that occur when coals are initially dissolved. The main objectives of this project are to study the effects of low-temperature pretreatments on coal structure and their impacts on the subsequent liquefaction. The effects of pretreatment temperatures, catalyst type, coal rank and influence of solvent will be examined.

The specific objectives are to identify the basic changes in coal structure induced by catalytic and thermal pretreatments by using spectroscopic, thermochemical and chemical techniques; and to determine the reactivity of the catalytically and thermally treated coals for coal liquefaction. Combining the two lines of information will allow us to identify the pretreatment-induced desirable/undesirable basic changes in coal structure; to clarify the impacts of pretreatments on coal liquefaction; to identify the structures responsible for retrograde reactions; to evaluate the structural differences resulting from different catalytic actions in relation to the overall catalytic effects in liquefaction; and ultimately, to develop a structure-reactivity relationship for liquefaction associated with catalyst type, coal rank and solvent. Furthermore, this research will contribute greatly to the development of effective pretreatment procedures which will allow coals to be liquefied more efficiently than the current practice. Finally, much of the knowledge to be generated from this research is not only critical for developing advanced hydroliquefaction processes, but also very useful to development of coal/petroleum resid co-processing, pyrolysis and hydropyrolysis processes.

## SURVEY OF RELEVANT LITERATURE

The present research project involves the tests using dispersed catalysts. An extensive review of catalysts and pretreatments relevant to the proposed work are discussed below. The following literature review and discussion on **chemistry of coal pretreatment and preconversion** covers catalytic pretreatments, thermal pretreatments, special chemical pretreatments, and physical pretreatments.

**Catalytic Pretreatment.** Sulfided molybdenum is a typical hydrogenation catalyst. Extensive research at Pittsburgh Energy Technology Center (Bockrath et al., 1984, 1986, 1991; Utz et al., 1989) and at Penn State (Davis et al., 1986, 1989; Derbyshire et al., 1986a, 1986b, 1989; Stansberry et al., 1987; Burgess and Schobert, 1990; Burgess et al., 1991) has demonstrated the potential of dispersed molybdenum catalyst. In most cases, the catalyst was impregnated on coal as a precursor salt such as sulfided ammonium molybdate or ammonium tetrathiomolybdate, which decomposes upon heating to higher temperatures to form $MoS_2$ (Naumann et al., 1982) and thus disperses $MoS_2$ on coal (Stansberry et al., 1987; Utz et al., 1989). These previous investigations have demonstrated that low-temperature catalytic reaction using dispersed molybdenum catalyst can improve coal reactivity. In the temperature-staged liquefaction, conducting the reaction using sulfided molybdenum at low-temperature leads to higher oil yield upon reaction at high temperature, without remarkable increase of hydrocarbon gas. The low-temperature stage is apparently more than a simple slow-down of thermal fragmentation of coal. Recent work in this laboratory has revealed that the reactions using dispersed molybdenum catalysts remarkably enhanced hydrodesulfurization of high-sulfur lignites at the temperatures as low as about 300°C (Garcia and Schobert, 1988, 1989a, 1989b, 1990, 1991).

On the other hand, even in the presence of finely dispersed molybdenum catalyst, the low-rank coals were found to be more sensitive to the temperature of catalytic pretreatment and higher pretreatment temperature (350°C) resulted in higher extent of retrograde reactions such as crosslinking in the residue part of a subbituminous coal (but not for a bituminous coal) as suggested by microscopic examination (Derbyshire, 1988). Consequently, lowering the temperature of catalytic treatment reduced crosslinking (Derbyshire and Luckie, 1986). The pretreatments (up to 300°C), in general, do not remarkably increase liquid yield. However, catalytic pretreatment of a subbituminous coal at 300°C for 1 h increased the swelling ratio of chloroform-insoluble residues and this was attributed to the removal of crosslinks (Derbyshire et al., 1986b) from comparison to thermal treatment which decrease swelling ration (Suuberg et al., 1985). From the above results, it was inferred that low-temperature reaction using sulfided molybdenum catalyst appears to cause subtle changes in coal structure, and the main effects of which become apparent <u>only</u> upon subsequent liquefaction at high temperature (Derbyshire, 1988). **Two key questions that arise are:** if such pretreatments result in the modification to coal structure that rendered it more reactive to the subsequent liquefaction, what are the basic changes in coal structure ? and how can we enhance such desirable change ? These questions need to be answered with respect to the effects of the pretreatments on coal structure and reactivity.

Another type of dispersed catalyst is Lewis acidic metal halide. $ZnCl_2$ is a typical Lewis acidic molten salt catalyst. Since the work of Zielke et al. (1966a, 1966b), this catalyst has been widely studied both in liquefaction of coal and in the reaction of model compounds, as reviewed by Derbyshire (1988). While the insufficient recovery and corrosive nature of this acid catalyst hindered its practical application, the catalyst chemistry is sufficiently attractive to warrant a continuing research effort (Derbyshire, 1988). Although $ZnCl_2$ has been demonstrated to be an active liquefaction catalyst, the low-temperature pretreatment using $ZnCl_2$ has been little studied. Recently, Shabati et al. (1985a, 1985b, 1986) reported a procedure of multi-stage liquefaction, in which the first stage reaction of bituminous and subbituminous coals using Lewis acid ($ZnCl_2$,

$FeCl_3$) catalysts at 250-275°C results in higher conversions in the subsequent stages. While the pretreatment has impact on the subsequent stages, it did not appreciably alter the yields of THF solubles. Again, the question as to what structural changes occurred during the pretreatment remains to be answered. It has been found that $NiCl_2$-LiCl-KCl ternary salt is an excellent dispersed catalyst for coal hydroliquefaction (Song et al., 1986a). This catalyst becomes molten at >360°C, and can substantially enhance coal conversion in low temperature pyrolysis (300-400°C) even under $N_2$ atmosphere, and significantly promotes oil production in liquefaction at 400°C, especially for subbituminous coals (Song and Nomura, 1986a, 1986b, 1987a; Song et al., 1988a, 1988b, 1991a).

The pioneering investigations on liquefaction using dispersed catalysts were reported by Weller and Pelipetz (1950, 1951) and summarized by Hawk and Hiteshu (1965). Besides the water-soluble catalysts like those mentioned above, Hawk and Hiteshu (1965) and more recent reports (Watanabe et al., 1984; Suzuki et al., 1985) also showed that other types of dispersed catalysts, oil-soluble organometallic compounds such as Mo naphthenate, $Fe(CO)_5$, and $Mo(CO)_6$ are effective catalysts or precursors for (high-severity) liquefactions. The use of oil-soluble catalyst (or precursor) in coal/resid co-processing has also been reported to be successful (Curtis et al., 1987). However, the low-temperature catalytic activity or organometallic compounds has not been studied and deserves further study in catalytic pretreatment.

The influence of solvent in catalytic pretreatment will also be examined in this project. The use of solvent is important in catalytic reactions from both physical (dilution, heat and mass transfer) and chemical (H-donor, synergistic effects) viewpoints, although in general catalysts plays a more important role. The use of ammonium molybdate (Bockrath et al., 1986) and $NiCl_2$-LiCl-KCl catalyst (Song et al., 1987, 1988) in liquefaction of bituminous coals has been found to reduce the demands placed on the solvent. However, an important effect of decreasing the total hydrogen consumption (sum of hydrogen consumed from $H_2$ and tetralin) was observed with the co-presence of tetralin solvent and $NiCl_2$-LiCl-KCl catalyst, as compared to the solvent-free catalytic liquefaction (Song et al., 1987a, 1988b). The use of LiCl-KCl (without $NiCl_2$), at various loading levels (from 0.1:1 to 1:1 weight ratios) on a subbituminous coal (which showed little catalytic effect on oil production and conversion) in the presence of tetralin, dramatically eliminated the consumption of gas phase $H_2$ - below the detectable level (Song et al., 1988b). Garg et al. (1985) also observed a synergistic effect between dispersed Mo catalyst and high-boiling solvents in improving liquefaction of a bituminous coal at 440°C.

These prospective results strongly suggest that some catalyst and solvent can act in concert to enhance oil production with reduced $H_2$ consumption. It has yet to be established what is the synergistic mechanism behind such a desirable effect. N-containing solvents may also be beneficial to catalytic pretreatments, although they are widely considered to be poisons and deactivators for supported Ni-Mo catalysts in hydrotreating. Recent work in this laboratory has revealed that the addition of a small amount of THQ to coal/naphthalene system using sulfided ammonium molybdate or incorporating THQ into precursor salt improved conversion and oil yield in temperature-staged liquefaction of a subbituminous coal, although adding THQ had little apparent effect for the low temperature (350°C) stage (Burgess and Schobert, 1990). Based on the foregoing, the influence of solvent in catalytic pretreatments will be studied in this work using H-donor (such as tetralin), non-donor (such as methylnaphthalene), a process recycle solvent, and a petroleum resid.

**Thermal Treatment.** Thermal treatments will also be conducted in this project as baseline to assess the effects of catalytic pretreatments. Purely thermal reactions are, in general, not easily controllable and in most cases are undesirable. For low-rank coals, the thermally initiated retrograde reactions may be of most significance during the heat-up period (to high temperatures) where the radical-capping ability of the system is relatively low. Low-rank coals generally have higher oxygen functionality and lower aromaticity (Schobert, 1990). The high thermal reactivity of low-rank coals has been demonstrated by Suuberg et al. (1985, 1987), who studied coal pyrolysis and evaluated crosslinking by using the solvent-swelling method (Green et al. 1982, 1984). For the lignite studied, the swelling ratios decreased very early and continued to decline with increasing temperature, indicating that the onset of cross-linking occurs much earlier in lignites than in bituminous coals. They further observed that the low-temperature crosslinking associated with low-rank coals appeared to correlate with the evolution of $CO_2$. This correlation was also confirmed in recent work reported by Solomon et al. (1988) and Deshpande et al. (1988), who further found that the loss of carboxyl groups correlated well with the evolution of $CO_2$. On the other hand, McMillen et al. (1985b) suggested the possibility of retrograde reactions involving polyhydroxy aromatic structures.

The apparently mildest thermal treating, pre-drying coals to improve the economics of handling the raw coals, has been a standard practice (Deurbrouck, 1981). However, some recent work on the influence of pre-drying in pyrolysis and liquefaction (Suuberg et al., 1985; Serio et al. 1990) raises the question of whether this is "economic". It has been found that drying the coal had a negative impact on the liquefaction yields of low-rank coals such as lignite and subbituminous coal, especially for lignite, but it had little effect on bituminous coal (Serio et al., 1990). This work provided striking evidence of the extremely sensitive nature of low-rank coals to thermal treating. It is not clear whether the results associated with drying were caused by physical (e.g. water removal) or chemical effects. Many researchers have reported that low-rank coals are less easily liquefied than bituminous coals, although there is evidence to the contrary (Whitehurst et al., 1980, 1980b; Derbyshire and Stansberry, 1987). In general, low-rank coals show high propensity to undergo crosslinking upon heating, which renders them less amenable to liquefaction.

It should be noted that, however, thermal treatments in the presence of some solvent may have positive effect depending on the coal and solvent used. Snape et al. (1990) found pre-soaking of bituminous coal/solvent slurries at 250°C increased coal conversions (SCT: 400°C for 10 minutes) for 9,10-dihydrophenanthrene but not tetralin. Narain et al. (1983) found similar improvements in SCT liquefaction with 1-methylnaphthalene. Recent work in this laboratory demonstrated that in temperature-programmed liquefaction of low-rank coals, the programmed heat-up in H-donor tetralin solvent is superior and affords considerably higher coal conversion than the rapid heat-up (Song and Schobert, 1992b; Song et al., 1992a). Miller et al. (1990) showed that the use of tetrahydroquinoline (THQ) in both low (350°C) and high (440°C) severity process improves conversions of subbituminous and bituminous coals in liquefaction and co-processing. It has been reported that the addition of a small amount of THQ to the naphthalene solvent for temperature-staged non-catalytic liquefaction of a subbituminous coal remarkably increased conversion but the effect at the first stage (350°C) was very small (Burgess and Schobert, 1990). Hydrothermal treatment of coal with water has also been shown to have some modest effect on coal liquefaction in terms of enhanced conversion (Bienkowski et al., 1987) or improved product quality.

**The above review raises a series of important questions.** What kinds of chemical and physical structures make coals, especially low-rank coals, so thermally sensitive ? Which bonds break first ? What are the structures responsible for retrograde reactions ? How can these reactions be controlled ? Is there any effect of catalyst and solvent on bond cleavage and bond-forming or stabilization at low temperatures ? These questions are critical to the initial stage in all of the liquefaction, co-processing, and pyrolysis as well as hydropyrolysis processes, and need to be answered by clarifying the "reactive" structures and developing a structure-reactivity relationship. Clarification of these important issues is one of the main objectives of this work.

**Special Chemical Pretreatment.** It is not the purpose of this work to study the effects of special chemical and physical treatment on coal liquefaction, but recent progress will be briefly mentioned here. While chemical treatment using special chemical reagents or organic reactions may be too expensive or too slow as a commercial pretreatment step, such studies contribute to our knowledge of liquefaction mechanism. Recently, pretreatment of coal using an O-alkylation method, which was first developed by Liotta et al. (1981) and later modified by Ettinger et al. (1986), has been found to be beneficial to coal liquefaction (Miller et al., 1989; Baldwin et al., 1990; Serio et al., 1990). Schlosberg et al. (1980) first reported that Friedel-Crafts alkylation was a beneficial pretreatment step for liquefaction under high-severity conditions. Baldwin et al. (1990, 1991) alkylated a subbituminous coal and observed a remarkable increase in THF-solubles with increasing O-methylation degree of the coal in its liquefaction and co-processing. They attributed this effect to the suppression of retrogressive reactions by introducing methyl groups to oxygen sites. From these results, they inferred that oxygen sites may be initiators for retrograde reactions during the initial stages of coal liquefaction. Serio et al. (1990) further compared the effects of O-methylation, demineralization by HCl/HF and ion-exchange (to remove Ca, Na, and K cations) on liquefaction of lignite, subbituminous and bituminous coals and concluded that the extent of retrograde reactions for low-rank coals (lignite and subbituminous') is significantly reduced by methylation and demineralization but these treatments do not have much impact on bituminous coal.

**Physical Pretreatment.** Some physical treatments have also been reported in the literature. The typical physical treatment is solvent swelling, as reported by Rincon and Cruz (1988), who found that pre-swelling coals in THF increases conversions in both anthracene oil and tetralin. Joseph (1991) also reported on the beneficial effects of pre-swelling coals in polar solvents for coal liquefaction. Recent work in this laboratory showed that pre-swelling coals in some polar solvents could improve coal conversion at low temperatures, depending on the solvent, coal and catalyst (Artok et al., 1991). Another type of physical pretreatment is solvent extraction. Snape et al. (1990) reported some surprising results that pre-extraction with THF significantly increased conversions of a bituminous coal in polyaromatics such as pyrene. The suggested explanation is that pyrene is an effective H-shuttler for available hydrogen in the coal but solvent-extractable materials limit access for larger polyaromatics such as pyrene. This finding is, however, in distinct contrast to those of other liquefaction (Larsen t al., 1980; Chamberlin and Schobert, 1991) and pyrolysis (O'Brien et al., 1987) studies where prior removal of chloroform-extractable materials significantly reduced conversions. These treatments are apparently associated with modification in either physical structure (by solvent swelling or extraction) or some change in chemical composition which is caused by the removal (via extraction) of the so-called mobile phase (Given et al., 1986). The information from above-mentioned chemical and physical pretreatments, though indirectly, could also be useful in examining the effects of catalytic and thermal pretreatments.

## Statement of Work

The major technical approaches to be adopted are 1) spectroscopic, thermochemical and chemical characterization to assess the structural changes induced by pretreatments using different catalysts in the absence and presence of solvent, with thermal treatments as baseline; 2) liquefaction of pretreated samples to examine the effects of catalytic and thermal pretreatments on coal reactivity and product selectivity, with the runs for original coals and untreated catalyst-loaded coals as baseline. The pretreatments, structural characterization and liquefaction will be directed to examining the above issues associated with the effects of catalyst type, coal rank and solvent. The experimental efforts can be divided into seven Tasks.

### **Task 1.** Selection of Samples

The objective of this task is to select coals and solvents. Two lignites, two subbituminous and two bituminous coals shall be selected from the Penn State Coal Sample Bank. For direct comparison of results, one lignite, one subbituminous and one bituminous coals that are being used in on-going DOE projects are to be used. A hydroaromatic compound (such as tetralin), and a aromatic compound (such as 1-methylnaphthalene) shall be selected as representative H-donor and non-donor solvents, respectively. A process vehicle solvent and a petroleum resid will also be selected. The process solvent will be one of the liquefaction recycle solvents or middle distillates, preferably one of those from Advanced Two-Stage Coal Liquefaction Plant at Wilsonville. The resid shall be one of those used in the current co-processing project.

### **Task 2.** Characterization of Coals

The objectives of this task are to study the structure and thermal reactivity of coals using a combination of modern spectroscopic and thermochemical analytical techniques including cross-polarization (CP), and dipolar-dephasing (DD) magic angle spinning (CPMAS and DDMAS) solid state $^{13}$C NMR, flash pyrolysis-gas chromatograph-mass spectrometer (Py-GC-MS), FT-IR, and TGA-DTA. CPMAS and DDMAS NMR will be used to determine distributions of aliphatic and aromatic carbons and their degree of protonation. FT-IR will be used to determine chemical functionality in addition to CPMAS $^{13}$C NMR. Flash pyrolysis-GC-MS will be conducted at different temperatures to clarify the type and distribution of structural units of the coals. To examine thermal reactivity of coals, TGA-DTA measurements shall be performed for both isothermal and non-isothermal analyses at different temperatures and heating rates. To evaluate and quantify the "reactive" structures in coals, a number of specific chemical reaction methods (Task 5) shall be used in combination with the spectroscopic and thermochemical techniques.

Most of the characterization methods to be used in Tasks 2, 4, and 6 are state-of-the-art analytical techniques including CPMAS and DDMAS $^{13}C$ NMR, FT-IR, Py-GC-MS, and TGA-DTA. Many papers have described the use of CPMAS $^{13}C$ NMR (Maciel et al., 1979; Earl et al., 1980; Wilson et al., 1984; Hatcher et al., 1989a; Song et al., 1992); DDMAS $^{13}C$ NMR (Alemany et al., 1983; Hatcher et al., 1987, 1988a); FT-IR (Painter et al., 1983; Senftler et al., 1984; Fraser and Griffiths, 1990); Py-GC-MS (Saiz and Leeuw, 1984; Hatcher et al., 1988b, 1989b; Song et al., 1992b) which is a combination of pyrolysis-GC and MS (Gallegos, 1979; Meuzelaar et al., 1983); GC-MS (Mudamburi and Given, 1985; Song and Hatcher, 1992); TGA-DTA (Song et al., 1986a, 1987a, 1989); and solvent-swelling (Liotta et al., 1983; Green et al., 1982, 1984; Artok, et al., 1991).

**Task 3**. Coal Pretreatment

This task involves low-temperature pretreatments using two dispersed catalysts, which will be impregnated onto the coals (1 wt% active metal based on coal, daf basis).

1) sulfided molybdenum catalyst by using ammonium tetrathiomolybdate (ATTM) as precursor salt. The precursor salt will be loaded onto coal by using incipient wetness impregnation method with the solution of ATTM in organic or aqueous-organic solvent system.

2) molybdenum catalyst by using molybdenum naphthenate or hexacarbonyl as precursor. The precursor will be impregnated on to coals in light hydrocarbon solvent followed by gentle evaporation.

The impregnated coals will be stored in $N_2$ atmosphere before use. The pretreatments shall be conducted in 25 ml microautoclave reactor with 7 MPa $H_2$ (cold) for 30 min. Since low-rank coals are more sensitive to temperature, the influence of pretreatment temperature will be studied in the range of 250-350°C at 50°C intervals for the two catalysts in the presence and absence of H-donor (such as tetralin) and non-donor (such as 1-methylnaphthalene) solvents. Two representative temperatures will then be selected and used in the catalytic pretreatments of all coals with and without solvent. Thermal pretreatments shall also be performed as baseline, both in the absence and presence of solvent. Each of the pretreatments shall be conducted at least two times to provide samples for characterization and liquefaction, respectively.

It should be noted that previous work showed that low-temperature pretreatments have little impact on the increase in solvent-extractable materials relative to thermal treatment. Therefore, to derive useful information, the characterization in Task 4 shall be focused on the (insoluble) organic network of pretreated and original coals. The liquid products in pretreated coals or physically entrapped materials in original coals shall be removed prior to characterization by exhaustive THF (tetrahydrofuran) extraction. The yields of solvent-extractable materials as well as gaseous products (if any) shall also be determined for assessing the apparent effects of pretreatments. Our previous analysis showed that even after vacuum drying at 110°C for over 6 h, trace amount of THF remains in the residue, which affects the solid state NMR and Py-GC-MS analysis. Therefore, the THF-insoluble residue will be washed sequentially by acetone and pentane to remove THF completely, followed by vacuum drying at 110°C for 6 h. The samples (for characterization) shall be stored under $N_2$ atmosphere.

### **Task 4**. Effect of Pretreatment on Coal Structure

This task aims at clarifying the basic changes in coal structure that are caused by catalytic and thermal pretreatments. Spectroscopic and thermochemical techniques such as solid state CPMAS and DDMAS $^{13}C$ NMR, FT-IR, flash pyrolysis-GC-MS (Py-GC-MS), and TGA shall be used to characterize the structure and thermal reactivity (in the ways described in Task 2), and the results will be compared with those for original coals. The advantages of applying CPMAS $^{13}C$ and Py-GC-MS techniques to characterizing coal structure and liquefaction processes have been demonstrated by our recent work (Song et al., 1991b, 1992b). To identify "reactive" structures and to clarify their change during the pretreatment processes, modern spectroscopic techniques shall be combined with specifically designed chemical reaction methods. CPMAS $^{13}C$ NMR and FT-IR combined with chemical methods shall be used for identifying and quantifying the change of reactive oxygen functional groups (such as COOH and OH, which are rich in low-rank coals) between pretreated and original coals.

The chemical methods to be considered include ion-exchange (Hengel and Walker, 1984), acetylation (Painter, 1982) and O-methylation (Liotta et al., 1981). These methods (to remove or to add metal cations to carboxylic groups; to add a specific substituents to hydroxyl groups) will allow detailed analyses of COOH and OH groups and associated aromatics and eliminate the influence of water (OH signal overlapping in FT-IR) present in coals especially low-rank coals. Chemical hydrogen-donation tests of the pretreated and the raw coals will also be performed for several coal samples (two subbituminous, one lignite, and one bituminous coal). Such tests involve hydrogen transfer from mobile hydrogens present in coal or pretreated coal to a polyaromatic compound such as anthracene at 400°C for 5-10 minutes. This technique is very useful for quantifying the transferrable hydrogens present in coal macromolecular network before and after pretreatment. A number of catalytically and thermally pretreated as well as raw coals and THF-extracted raw coals shall also be comparatively examined for their swelling behavior in a solvent such as pyridine.

Task 4 and Task 5 represent the most important parts of our experimental efforts. The most novel approach of this research is the way in which we seek to develop fundamental understanding on coal structure and reactivity relationship with the emphasis on the catalytic preconversion and liquefaction. This approach will provide the most needed information on the basic structural features of coals at the molecular level; dependence of characteristic structures on coal rank; the nature of coal reactivity; "reactive" structures in coals; the structures responsible for retrograde reactions; effects of catalyst on coal structure at low temperatures; the structural differences resulting from using different catalysts; influence of solvents and their additive/synergistic effects with catalyst at low temperatures. The knowledge on the identity of "reactive" structures and the structures responsible for retrograde reactions to be generated from this research will enable the competitive reaction between stabilization of coal-derived reactive fragments and their retrogression to be more clearly understood. This knowledge could be used to develop a key technique to efficiently enhance coal reactivity and suppress the retrograde reactions. This approach, if successful, will advance the state-of-the-art of our knowledge and will contribute significantly to improve the efficiency of liquefaction processes.

**Task 5**. Effect of Pretreatment on Liquefaction

The specific objective of this task is to examine the effects of catalytic pretreatments on coal reactivity in coal liquefaction. The liquefaction of pretreated coals shall be performed at two or three temperatures in the range of 375-425°C (at 25°C intervals) for 30 minutes. After the reaction, the gaseous products shall be analyzed by GC. The liquid and solid products shall be separated by Soxhlet extraction into oil (hexane-solubles), asphaltene (hexane-insoluble toluene-soluble), preasphaltene (toluene-insoluble THF-soluble), and THF-insoluble residue. In most cases, the molybdenum catalysts will remain in the residue. The liquefaction reactivity of pretreated coals shall be evaluated from conversion and and product selectivity. For evaluating the net effects of the low temperature stage, liquefaction of impregnated coals, without any pretreatment, shall also be performed. Liquefaction of all the raw coals shall be performed as baseline runs. Both the liquid and solid products shall be stored under $N_2$ atmosphere.

For selected coals, especially low-rank coals, temperature-programmed liquefaction (TPL) will also be carried out, which incorporates the pretreatment in the programmed heat-up from a low temperature (200-300°C) to a final temperature (350-425°C) followed by holding at that temperature for a certain time period (30 minutes). We have shown that TPL is a promising approach for converting low-rank coals such as a Montana subbituminous coal and a Texas lignite (Song et al., 1991b; Song and Schobert, 1992a, 1992b; Huang et al., 1992).

**Task 6.** Effect of Pretreatments on Product Quality

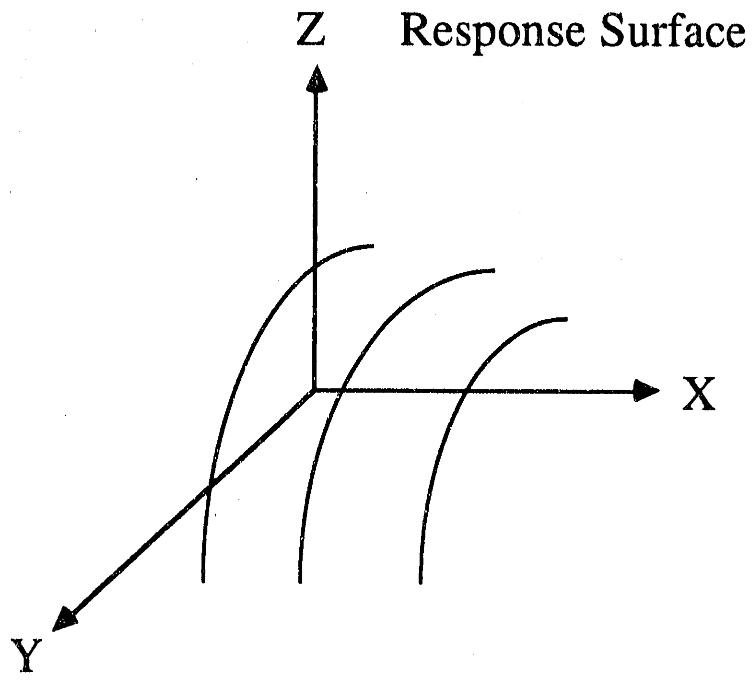
The objective of this task is to evaluate the effects of catalytic pretreatments on the quality and composition of liquefaction products. A set of liquefaction products from a number of representative experiments (in Task 5) shall be analyzed. Emphasis on product quality shall be placed on oil products. The analysis of asphaltene, preasphaltene and residue shall be directed to the structural correlation with pretreated coals and original coals. All the products from selected experiments will be subjected to elemental analysis. The oil products shall be analyzed by capillary GC-MS and capillary GC for product identification, liquid chromatography for product distribution in terms of functionality (LC or HPLC) and molecular weight (GPC), and liquid $^1$H and $^{13}$C NMR. The asphaltene, preasphaltene, and the residue from a number of typical experiments will be characterized by solid state CPMAS & DDMAS $^{13}$C NMR, and Py-GC-MS.

**Task 7.** Evaluation of Catalytic Pretreatments

The main objective of this task is to make an overall evaluation of the effects of catalytic pretreatments on coal structure and reactivity. The specific objectives are to evaluate the effects of pretreatment temperature, effects of catalysts and their type, coal rank dependence and influence of solvents. This task involves an extensive, comparative examination, and is a process of scientific integration and reduction of data generated from Tasks 1 through 7.

The subtasks include I) comparative examination of the structural differences between the catalytically and thermally pretreated coals and the original coals, and identifying the basic changes that are caused by catalytic and thermal treatments, respectively; II) comparative examination of liquefaction results (conversion, product distribution, and $H_2$ consumption) of catalytically and thermally treated coals, original coals and untreated catalyst-loaded coals to clarify the effects of low-temperature pretreatments, high-temperature reactions and overall catalytic effectiveness for coal conversion and product selectivity; and to identify the pretreatment-induced reactivity change of coal in liquefaction; 3) correlation of I and II; IV) elucidation of "reactive" structures in pretreated and raw coals; V) elucidation of structures responsible for retrograde reactions in coal liquefaction; VI) comparison of composition of liquefaction products from catalytically and thermally pretreated coals, untreated catalyst-loaded coals, and original coals to assess the effects of pretreatments on product quality; VII) development of a structure - reactivity relation ship for coal preconversion and liquefaction associated with effects of temperature, effects of catalysts and their type, coal rank dependence, and influence of solvent composition. As applicable, we shall use computer-based chemometrics in the work relating to the development of structure - reactivity relationships.

Finally, comprehensive examination of all the relevant results to be derived from this project may allow us to generate some kind of "response surface" which represents three process response (Z). The concept of the "response surface" is illustrated in Scheme 1.



**X: Structural Characteristics**
**Y: Process Severity**
**Z: Process Response (such as conversion, oil yield, etc.)**

**Scheme 1**. Conceptual "response surface" that might be generated from this project.

The process response (Z) could be total coal conversion, oil yield, asphaltene yield, etc. The structural characteristics need to be represented by a "reactive structural parameter" that varies in some regular fashion with coal rank or other coal properties, and which can be determined by the standard analytical techniques and/or their combinations. While we still do not know what the most appropriate structural characteristic is, we seek to define such a parameter through combinations of spectroscopic, chemical, thermochemical and reaction techniques. The process severity usually refers the temperature, time and pressure, etc. However, we need to define a single variable that combines the effects of temperatures and times. Since the severity parameter does not involve catalysis, different sets of graphs will be generated for thermal runs and for catalytic runs.

## TECHNICAL PROGRESS

### Task 1. Selection of Samples

The coals selected are the Department of Energy Coal Samples (DECS-series) stored in Penn State Coal Sample Bank, as listed in Table 1.1. These samples were recently collected by Energy and Fuels Research Center and stored in multilaminate foil bags under argon atmosphere. As described by Davis et al. (1991), all the fresh coal samples were collected from channel seams in active underground coal mines. The samples were immediately placed in barrels filled with argon for transport and storage. Working cuts of 100-300 g are taken from storage, ground to < 60 mesh and stored in nitrogen. The detailed properties of these coals are given in Appendix 1.

**Table 1.1.** DOE/Penn State Coal Samples To Be Used in This Project

| State | Number | Name/Rank | C%, daf |
|---|---|---|---|
| ND | DECS-11 | North Dakota (Beulah) Lignite | (74.2%C) |
| TX | DECS-1 | Texas (Bottom) Lignite/Subbituminous | (74.3%C) |
| WY | DECS-8 | Wyodak (Smith-Roland) Subbituminous | (75.8%C) |
| MT | DECS-9 | Montana (Diez) Subbituminous | (76.1%C) |
| WY | DECS-7 | Wyoming (Adaville) Subbituminous/Bituminous | (77.1%C) |
| UT | DECS-5 | Hiawatha Bituminous | (79.5%C) |
| UT | DECS-6 | Blind Canyon Bituminous | (81.3%C) |
| PA | DECS-12 | Pittsburgh #8 Bituminous | (84.8%C) |

Table 1.2 shows the solvents selected. We are planning to use four solvents: 1) tetralin (1,2,3,4-tetrahydronaphthalene); 2) 1-methylnaphthalene; 3) middle distillates (204-343°C) produced from two-stage liquefaction of Pittsburgh #8 bituminous coal using Shell 324 Ni-Mo catalyst in Run 259E at Advanced Two-Stage Coal Liquefaction Plant, Wilsonville, Alabama; and 4) Hondo petroleum resid which contains about 16% asphaltene, and 84% maltene. The major part of experimental work in Tasks 2-6 in this project will be carried out using the six coals (two lignites, two subbituminous and two bituminous coals) among the eight coals shown in Table 1.1, and four solvents mentioned above. For some comparison experiments, two other coals (one lignite or subbituminous coal and one bituminous coal among those shown in Table 1.1) and two other solvents may be selected and used as deemed necessary. Examples of such solvents are decalin, which is a poor H-donor as compared to tetralin, and pyrene, which can act as a hydrogen-shuttler (Table 1.2). Such solvents may be used in some experiments for comparative examination of solvent effects.

**Table 1.2.** Solvents To Be Used in This Project

| Solvent | Compound Class | Chemical Functions |
|---|---|---|
| Main Selection | | |
| 1-Methylnaphthalene | Aromatics | Non-donor |
| Tetrahydronaphthalene | Hydroaromatics | Hydrogen-donor |
| Wilsonville Middle Distillates | Aromatic Mixture | Process Recycle |
| Hondo Resid | Aliphatic Mixture | Co-Processing |
| Additional Candidates | | |
| Decalin | Cycloalkane | Weak H-donor |
| Pyrene | Polyaromatics | Hydrogen Shuttler |

## Task 2. Characterization of Coals

The coals used in the first quarterly period were two subbituminous coals including Wyodak coal (DECS-8 ), a Montana coal (DECS-9), and DECS-1 coal which is on the boundary between lignite and subbituminous, and three bituminous coals including Adaville #1 (DECS-7) Blind Canyon (DECS-6) and Pittsburgh #8 (DECS-12) coals. The coals were classified using conventional coal parameters, ultimate and proximate analysis, and vitrinite reflectance data. Table 2.1 shows the proximate analysis data and Table 2.2 shows the ultimate analysis data for the three bituminous coals. Coals are listed according to increasing rank. These data were provided by the DOE/Penn State Coal Sample Bank maintained by the Energy and Fuels Research Center at Penn State.

**Table 2.1** Proximate analysis of selected coals

| Coal (as rec'd) | DECS-1 Texas Lig | DECS-8 Wyodak | DECS-9 Montana | DECS-7 Adaville #1 | DECS-6 Blind Canyon | DECS-12 Pittsburgh #8 |
|---|---|---|---|---|---|---|
| % moisture | 30.00 | 28.42 | 24.68 | 17.34 | 4.73 | 2.40 |
| % ash | 11.07 | 9.90 | 4.80 | 3.45 | 5.56 | 10.00 |
| % volatile | 33.18 | 32.38 | 33.46 | 38.11 | 42.40 | 35.16 |
| % fixed carbon | 25.75 | 29.30 | 37.06 | 41.11 | 47.31 | 52.44 |

**Table 2.2** Ultimate analyses of selected coals

| Coal | Name | Rank | % C [a] | % H [a] | % N [a] | %S [c] | %O [b] | % Vit.. | % Res. |
|---|---|---|---|---|---|---|---|---|---|
| DECS-1 | Texas | Lig/Sub C | 76.13 | 5.54 | 1.50 | 1.05 | 15.78 | nd [d] | nd [d] |
| DECS-8 | Wyodak | Sub C | 75.84 | 5.15 | 1.02 | 0.51 | 17.48 | nd [d] | nd [d] |
| DECS-9 | Montana | Sub B | 76.11 | 5.14 | 0.91 | 0.33 | 17.50 | nd [d] | nd [d] |
| DECS-7 | Adaville #1 | HVCb | 77.45 | 5.51 | 1.04 | .91 | 15.09 | nd [d] | nd [d] |
| DECS-6 | Blind Canyon | HVB/Ab | 81.72 | 6.22 | 1.56 | .40 | 10.10 | 69.1 | 5.0 |
| DECS-12 | Pittsburgh #8 | HVAb | 84.75 | 5.66 | 1.40 | .83 | 7.37 | 83.0 | 2.6 |

a dmmf
b dmmf, determined by difference
c organic
d not determined

Characteristic chemical changes occur with increasing rank. Notice, as rank increases the percent carbon increases from 75.8 % to 84.8 % and the oxygen content decreases from 17.5 % to 7.4 %. Both the percent volatiles and moisture content decreases with increasing coalification. Based on this data Adaville #1 is a HVC bituminous coal, and Pittsburgh #8 is a

HVA bituminous coal. For the Blind Canyon coal the proximate analysis data classifies this coal as a HVA bituminous where as the reflectance data classifies it as a HVB bituminous. Thus it is probably on the boundary between high volatile B/A bituminous.

## Activity 1. Characterization of Subbituminous Coals

Wyodak subbituminous coal (DECS-8) and a Montana subbituminous coal (DECS-9) were characterized by using solid-state CPMAS $^{13}$C NMR and Py-GC-MS. The NMR spectra were acquired on a Chemagnetics M-100 NMR spectrometer by using the combined high power proton decoupling, cross-polarization and magic-angle-spinning (CPMAS) techniques. The measurements were carried out at a carbon frequency of 25.1 MHz. About 0.4-0.6 g of a sample was packed in a bullet-type Kel-F rotor (0.4 ml capacity); the spinning speed of the rotor was about 3.5 kHz. The experimental conditions for all the samples are as follows: a cross-polarization contact time of 1 ms and a pulse delay time of 1 s. An instrumental calibration test was performed with the rotor containing hexamethylbenzene, which was adjusted to the magic angle (54.7°) to give the correct chemical shifts. To assure good spectra with high signal-to-noise ratios, the number of pulses accumulated for obtaining a spectrum was at least 10,000, and most of the spectra were obtained with numbers of scans between 20,000 to 35,000.

Py-GC-MS analysis was performed on a Du Pont 490B GC-MS system fitted with a 30 m x 0.25 mm i.d. capillary column DB-17 coated with 50% phenylmethylsilicone stationary phase with a film thickness of 0.25 um, and interfaced to a Chemical Data Systems Pyroprobe-1000 pyrolyzer. Helium was used as a carrier gas. The data acquisition and data processing were controlled through a computer-aided system. Prior to the start of data acquisition, the samples were flash-pyrolyzed at 610°C for 10 seconds, during which the pyrolysates (pyrolysis products) were retained in the clsoe-to-inlet part of the capillary column by colling with liquid nitrogen. The column was held at 40°C for 5 minutes and subsequently programmed to 280°C at a rate of 4°C/min. The mass spectrometer was operated in the electron impact mode at 70 eV. In order to derive information related to the macromolecular network, the low molecular weight species in the coal and coal liquefaction products were removed by THF extraction prior to Py-GC-MS analysis. The other experimental details about the NMR and Py-GC-MS are similar to those described by Hatcher et al. (1988).

## CPMAS $^{13}$C NMR

The NMR data and Py-GC-MS data for DECS-8 coal are reported in Task 4, together with those of the pretreated samples from DECS-8. Figure 2.1 shows the CPMAS $^{13}$C NMR spectra of the fresh DECS-9 coal and the unreacted but THF-extracted DECS-9 coal. It is interesting to note that the THF-extracted coal, which lost about 8 % THF-soluble materials, gave a spectrum similar to that of the raw coal in terms of the aromaticity and functionality (see below). Integration of the spectra gives only a slightly higher aromaticity (fa) value for the THF-extracted coal than for the raw coal. It should be noted that for some coals, the THF-extracted samples may display substantially different spectra. In addition, a general observation is that these NMR spectra are relatively poorly resolved, as compared to the spectra of pure materials, primarily because of the presence of a large number of different molecular species that have only slightly different chemical shifts.

## Pyrolysis-GC-MS

Py-GC-MS analysis can provide information on the molecular components or structural units of coal macromolecular network when using the THF-extracted raw coal samples. With the aid of computer-based data processing, it is now possible to perform a compound type analysis of coal pyrolysis products by using the selective ion monitoring technique in Py-GC-MS, as has been used for hydrocarbon type analysis of liquid fuels by GC-MS (Song and Hatcher, 1992). Low rank coals are known to have higher oxygen functionalities (Schobert, 1990), and therefore we have examined the oxygen compounds as well as hydrocarbons in the pyrolysis products by using the characteristic ion masses for phenol (m/z 94), cresol (m/z 107, 108), xylenols and ethylphenol (m/z 122), and catechol (m/z 110). The hydrocarbon compounds usually show characteristic ions at different m/z: long-chain paraffins (m/z 71), alkylbenzenes (m/z 91, 105), naphthalene or nonane (m/z 128) and alkylnaphthalenes (m/z 141). Figures 2.2-2.5 show the total ion chromatogram (TIC) and selected ion chromatograms (SIC) for the above-mentioned characteristic ions. Within the retention time (RT) range of 2-22 minutes, the four most predominant peaks in the TIC are all phenolic compounds. Also found in this sample are catechol and methylcatechol. The two relatively large peaks around RT of 3 min are p- and o-xylene, in that order. It should be noted that there are a number of major hydrocarbon peaks which appeared between 0 to 2 min and whose intensities are higher than the largest peak phenol in Figure 2.2. Those peaks are $C_5$-$C_8$ alkanes plus alkenes, which are not well separated, and toluene, the second largest peak. There are many other small peaks appeared over the whole RT region, and selective ion monitoring at m/z 71 indicates that they are long-chain alkanes and alkenes (Figure 2.4). Overall, these results show that the DECS-9 coal contains significant amounts of oxygen-containing structural units such as phenol and alkylphenols as well as alkylbenzenes and catechols. It is also interesting to note that the long-chain aliphatics still exist after long time Soxhlet extraction with toluene and THF.

## Activity 2. Characterization of Bituminous Coals

The maceral content of the three bituminous coals has been determined in white and fluorescent light for the whole coal samples, as shown in Table 2.3.

**Table 2.3** Maceral analyses of selected coals

| DMMF % (vol.) | DECS-6<br>Blind Canyon coal | DECS-12<br>Pittsburgh #8 coal |
|---|---|---|
| vitrinite | 69.1 | 83.0 |
| fusinite | 1.8 | 2.7 |
| semifusinite | 5.6 | 4.0 |
| macrinite | 5.3 | 1.4 |
| micrinite | 0.9 | 0.8 |
| sporinite | 10.8 | 5.5 |
| resinite | 5.0 | 2.6 |
| alginite | 0.4 | 0.0 |
| cutinite | 0.8 | 0.0 |

These results show that the dominant maceral is vitrinite, particularly in the HVA bituminous coal. In comparing the liptinitic macerals, sporinite and resinite, the Blind Canyon coal has twice the amount of each of these as compared to the Pittsburgh #8 coal. As for alginite and cutinite the Blind Canyon has these present where as the higher rank Pittsburgh #8 has none. As it will be shown these macerals are important in which pyrolysis products are formed.

### Pyrolysis-GC-MS

Using a heated filament pyrolysis method, work has been initiated to determine the relationship between coal structure, its chemistry and the types of compounds and their relative abundances released during flash pyrolysis. Depending on a coal's volatility, between 0.5 mg to 1.5 mg of a coal is placed in the probe of a CDS pyroprobe. For the Pittsburgh #8 coal a larger amount of sample is required compared to the Adaville #1 to get comparable yields. The probe is then placed into the injection port of a GC at which time the pyroprobe is started. The sample is heated at a rate of $5^{o}$C/ms to $610^{o}$C for 10s. The pyrolyzate is cryotrapped then separated by the GC and analyzed by a Dupont GC/MS according to the method described Hatcher et al (1988). Figures 2.6-2.8 show the pyrograms for each of the coals.

Comparing the total ion chromatograms (TIC) of each of the coals distinct compositional differences are readily apparent. These differences are directly related to the differences in rank as well as maceral content of the coals The Adaville #1 pyrogram, Figure 2.6, is dominated by a homologous series of alkanes and alkenes with the most dominant peak being C-19, prist-1-ene. Carbon numbers range from C-4 to C-31. The Blind Canyon coal, Figure 2.7, also shows this trend as well as having a strong bicyclic sesquiterpenoid component. Pittsburgh #8, Figure 2.8, shows an entirely different pyrogram. It is composed mainly of a complex mixture of aromatic compounds, benzene and alkyl-benzenes, ions 78, 92, 120, Figure 2.9, alkylnaphthalens, ions 128,142,156, Figure 2.11, phenol and alkylphenols, ions 94, 108,122, Figure 2.10. There are only a minor amount of alkanes-alkenes. See Table 2.4 for the list of components and nomenclature.

**Table 2.4** Nomenclature for Figures

| Components | Nomenclature |
|---|---|
| Alkanes-Alkenes | C4-C31 |
| Phenol, methyl phenol, etc. | P, C1-P, C2-P |
| Indene, methyl-indene | I, C1-I |
| Naphthalene, methyl-naphthalene, etc | N, C1-N |

The nature and origin of the various chemical components of the pyrolyzate is determined by the coals rank and maceral content. The homologous series of alkanes are derived form the liptinitic macerals. A high concentration of sporinite and resinite with minor amounts of cutinite and alginite in the Blind Canyon produce a high yield of these compounds. However the Pittsburgh #8 lacked some of these or had a low concentration of other in this group of macerals resulting in a low yield of the alkanes-alkenes. On the other hand this high rank coal had a high concentration of vitrinite which produced a high yield of phenol, alkylphenols, benzene, alkyl-benzenes and alkyl naphthalenes. The lower rank coals produced a much lower amount of these aromatic compounds.

In the Blind Canyon another major series of compounds is produced, Figure 2.7, because of the high concentration of resinite. Resins are composed of bicyclic sequiterpenoids and diterpenoids (Crelling et al., 1991). When thermally degraded they produce a series of two ring compounds from fully saturated bicyclic sequiterpane,m/z 208, through partially saturated compounds, m/z, 206,204,202,to a fully unsaturated C-5 naphthalene, m/z, 198 (Crelling et al., 1991).

A thermal desorption experiment was conducted on this resin-rich coal. Instead of immediately pyrolyzing the coal once the probe has been inserted into the GC's injection port the sample is first thermally desorbed at 280°C for 30 minutes. The coal is then pyrolyzed and the pyrolyzate analyzed, Figure 2.13. This procedure removes any volatiles that are not bond to the coals macromolecular structure. By comparing the Blind Canyon's pyrograms, Figures 2.7 and 2.13 in the region in which the sesquiterpanoids are eluted, between C-15 and C-20, it is seen that these resins have been completely volatilized at 280°Cand are not present in the thermally desorbed pyrogram.

In conclusion it is apparent that there are definite compositional differences of the pyrolysis products from each of the coals which are due to the differences in maceral concentrations,and differences in rank. Further steps will be taken to determine the relationship of these differences and how they relate to the products that are generated during pyrolysis. Thermal desorption experiments will be run on the Pittsburgh #8 and the Adaville coals. Also flash pyrolysis GC/MS will be conducted at different temperatures to further help quantify the relationship between the structure of the coals and the products generated.

## Task 3. Coal Pretreatment

Various pretreatments were performed using Wyodak subbituminous coal. The pretreatments include catalytic and thermal reactions in the absence of any solvent and in the presence of a H-donor tetralin and a non-donor 1-methylnaphthalene vehicle. We also examined the effects of drying by analyzing the fresh samples with the samples dried in vacuum and in air at 95 °C for 2 h.

### Catalyst Loading

The coal used was a Wyodak subbituminous coal (DECS-8) and a Montana subbituminous coal (DECS-9). The catalyst precursor, ammonium tetrathiomolybdate (ATTM) (purchased from Aldrich, 99.97%), was dispersed on coal by incipient wetness impregnation method. The loading was 1% of molybdenum on the basis of dmmf coal. In an effort to achieve a better dispersion, a mixture of $H_2O$/THF (44 : 56) was employed as impregnation solvent. In some experiments, aqueous solution of ATTM was used for comparison. After loading of the catalyst precursor, the coal sample was dried in vacuum for 2 h at 105°C, then removed and stored under a nitrogen atmosphere.

**Pretreatments**

The pretreatment/preliquefaction experiments were carried out in tubing bomb microautoclaves at 300 and 350 °C, and $H_2$ pressure of 1000 psi (7 MPa) cold. The solvents used were tetralin and 1-methylnaphthalene. Both the thermal and catalytic experiments were performed with and without solvents. The amounts of predried coal (vacuum dried at 95 °C for 2 hours) and solvents used for various experiments are about 4 g. The reactor bombs containing samples were heated by immersion in fluidized sand bath for 30 minutes plus 3 minutes for reactor heat-up. After the reaction, the bombs were cooled by immersing quickly in water for a very short contact time, enough to bring the temperature of the reactor to below 200 °C, followed by cooling to room temperature in air. The bombs were then vented to determine the volume of the gases by volumetric measurement. The gases were analyzed by gas chromatography (Perkin-Elmer AutoSystem). The liquid and solid products were separated by sequential extraction (Song and Schobert, 1992b) into oils (hexane-soluble), asphaltenes (hexane-insoluble, toluene-soluble) and preasphaltenes (toluene-insoluble, THF-soluble). The final residues (THF-insoluble) were first washed with acetone and then with pentane followed by drying under vacuum at 110 °C for six hours. The residues were then analyzed by solid State $^{13}C$ NMR, Py-GC-MS and FT-IR techniques.

Table 3.1 shows the results of Soxhlet extraction of the fresh (as received) Wyodak coal and the vacuum dried coal. The yields of total toluene- and THF-solubles are almost the same. In fact, we also conducted the same experiments for fresh and vacuum dried Montana coal. The total yield of THF-extractable materials was 7.2 % for the fresh (as received) coal, and about 7 % for the vacuum dried coal. Therefore, the vacuum drying does not seem to have any significant effect on the yields of toluene and THF extracts of the raw coal.

**Table 3.1** Extraction of the Fresh and Vacuum-Dried DECS-8 Wyodak Subbituminous Coal

| Expt. No. | 3 | 3a |
|---|---|---|
| Sample | Undried, fresh | Vacuum dried |
| dmmf coal | 3.162 g | 3.869 g |
| | Product Distribution, dmmf wt% | |
| Hexane solubles (Oil) | 0.92 | 1.60 |
| Toluene soluble (Asph) | 1.99 | 2.20 |
| THF-Soluble (Preasph) | 3.86 | 3.69 |
| | | |
| Total conversion | 8.76 | 8.50 |

## Thermal Pretreatment at 300 and 350 °C

As shown in Table 3.2, thermal pretreatment at 300 °C appears to have a little effect on the product yields as compared to that of the raw coal. There is a very little increase in the product yields of the experiment without any solvent or catalyst (Table 3.2). The presence of solvent increases the total conversion, but only by 2-4%. Preliquefaction at 350 °C without any solvent have only a slight increase in the total conversion as compared to that at 300 °C. This is mainly due to the gain in the THF-solubles. But with the presence of solvents the increase in the yields are appreciable. There is an increase from 13.38 to 19.92% in presence of tetralin and from 15.83 to 21.99 % in presence of 1-methylnaphthalene. This increase is essentially due to the increase in the yield of all type of products except with 1-methylnaphthalene the hexane solubles have decreased slightly. The gases produced as a result of the pretreatment of the coal at 350 °C are given in Table 3.2. The GC data for runs at 300 °C are not available yet.

## Pretreatment at 300 and 350 °C with Mo Catalyst

Table 3.3 shows the product distributions for the pretreatment experiments at 300 and 350 °C in presence of catalyst. The total conversion at 300 °C is expected to be same as without catalyst because at this temperature the catalyst is less likely to decompose into a catalytically active specie. At 350 °C the total conversion has increased markedly as compared to the catalyst free pretreatment. In the solvent free run the total conversion has increased from 12.5 to 28.8 %. This increase is essentially due to the increase in the yields of all the products. In presence of tetralin as solvent the increase is from 24.1 to 36.0 % and with 1-methylnaphthalene the increase is from 18.0 to 31.1 %. With tetralin the increase is mainly due to the increase in the yields of hexane and Toluene solubles, THF-solubles remaining the same. With 1-methylnaphthalene the increase is due to the increase in the yields of all the products.

The quantitative analysis of the gases collected after the reaction is also given in Table 3.3. The gases produced as a result of the pretreatment of the coal and identified are CO, $CO_2$, methane, ethane, ethylene, propane, propylene (propene), n-butane, isobutane, and butene.

Table 3.2. Products distribution for the preliquefaction of DECS-8 coal without catalyst.

| Temp. | 300° C | | | | | | 350° C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Expt. # | 4 | | 5 | | 6 | | 7 | | 8 | | 9 | |
| Coal | 4.095 g | | 4.021 g | | 4.140 g | | 4.063 g | | 4.057 g | | 4.125 g | |
| dmmf | 3.448 g | | 3.386 g | | 3.486 g | | 3.422 g | | 3.416 g | | 3.474 g | |
| Solvent | none | | Tetralin | | MN | | none | | Tetralin | | 1-MN | |
| wt.Sol. | ----- | | 4.100 g | | 4.335 g | | ------ | | 4.586 g | | 4.411 g | |
| | wt. in g. | wt. % | wt. in g. | wt. % | wt. in g. | wt. % | wt. in g. | wt. % | wt. in g. | wt. % | wt. in g. | wt. % |
| Gases | 0.078 | 2.26 | 0.061 | 1.80 | 0.088 | 2.52 | 0.090 | 2.63 | 0.138 | 4.04 | 0.130 | 3.74 |
| Hexane solubles | 0.071 | 2.06 | 0.097<br>(diff.) | 2.86 | 0.169<br>(diff.) | 4.85 | 0.081 | 2.37 | 0.295<br>(diff.) | 8.63 | 0.101<br>(diff.) | 2.91 |
| Toluene Solubles | 0.089 | 2.58 | 0.142 | 4.19 | 0.133 | 3.81 | 0.089 | 2.60 | 0.402 | 11.77 | 0.279 | 8.03 |
| THF Solubles | 0.098 | 2.84 | 0.152 | 4.49 | 0.162 | 4.65 | 0.154 | 4.50 | 0.187 | 5.47 | 0.254 | 7.31 |
| Residue | 3.706 | | 3.568 | | 3.588 | | 3.634 | | 3.035 | | 3.361 | |
| Total Conversion | 0.389 | 11.28 | 0.453 | 13.38 | 0.552 | 15.83 | 0.429 | 12.54 | 1.022 | 29.92 | 0.764 | 21.99 |
| | GAS ANALYSIS | | | | | | | | | | | |
| Gases | | | | | | | wt. g. | | wt. g. | | wt. g. | |
| CO | | | | | | | 8.600E-3 | | 6.90E-3 | | 7.100E-3 | |
| $CO_2$ | | | | | | | 159.0E-3 | | 128.0E-3 | | 149.0E-3 | |
| $C_1$ ($CH_4$) | | | | | | | 4.000E-3 | | 3.396E-3 | | 4.408E-3 | |
| $C_2$ ($C_2H_6$,$C_2H_4$) | | | | | | | 1.137E-3 | | 1.328E-3 | | 1.241E-3 | |
| $C_3$ ($C_3H_8$,$C_3H_6$) | | | | | | | 1.293E-3 | | 1.127E-3 | | 1.212E-3 | |
| $C_4$ ($C_4H_{10}$,Iso-But) | | | | | | | 0.591E-3 | | 0.412E-3 | | 0.455E-3 | |
| $C_5$ | | | | | | | | | | | | |

Table 3.3. Products distribution for the preliquefaction of DECS-8 coal in presence of ATTM as catalyst.

| Temp. | 300° C | | | | | | 350° C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Expt. # | 13 | | 14 | | 15 | | 19 | | 22 | | 12 | |
| Coal | 4.106 g | | 4.026 g | | 4.117 g | | 4.042 g | | 4.126 g | | 4.186 g | |
| dmmf | 3.458 g | | 3.391 g | | 3.467 g | | 3.404 g | | 3.475 g | | 3.525 g | |
| Solvent | none | | Tetralin | | MN | | none | | Tetralin | | MN | |
| wt.Sol. | ----- | | 4.303 g | | 4.249 g | | ------ | | 4.239 g | | 4.459 g | |
| | wt. in g. | wt. % | wt. in g. | wt. % | wt. in g. | wt. % | wt. in g. | wt. % | wt. in g. | wt. % | wt. in g. | wt. % |
| Gases | 0.031 | 0.89 | 0.032 | 0.94 | 0.035 | 1.00 | 0.094 | 2.76 | 0.108 | 3.16 | 0.113 | 3.27 |
| Hexane solubles | 0.084 | 2.42 | 4.004 w/sol. | | 4.431 w/sol. | | 0.264 | 7.75 | 5.115 w/sol. | 13.9 | 4.985 w/sol. | 5.43 |
| Toluene Solubles | 0.041 | 1.18 | 0.091 | 2.68 | 0.071 | 2.04 | 0.138 | 4.05 | 0.345 | 10.09 | 0.348 | 10.06 |
| THF Solubles | 0.211 | 6.10 | 0.135 | 3.98 | 0.176 | 5.07 | 0.349 | 10.25 | 0.301 | 8.81 | 0.426 | 12.32 |
| Residue | 4.007 | | 3.907 | | 3.874 | | 3.060 | | 2.826 | | 3.030 | |
| Total Conversion | 0.367 | 10.60 | | | | | 0.982 | 28.84 | 1.230 | 36.00 | 1.075 | 31.09 |
| | GAS ANALYSIS | | | | | | | | | | | |
| Gases | wt. g. | | wt. g. | | wt. g. | | wt. g. | | wt. g. | | wt. g. | |
| CO | 5.057E-3 | | 2.072E-3 | | 2.098E-3 | | 7.240E-3 | | 5.068E-3 | | 3.926E-3 | |
| $CO_2$ | 43.94E-3 | | 34.92E-3 | | 36.91E-3 | | 81.72E-3 | | 104.1E-3 | | 116.6E-3 | |
| $C_1$ ($CH_4$) | 0.736E-3 | | 0.836E-3 | | 0.809E-3 | | 5.680E-3 | | 5.450E-3 | | 4.940E-3 | |
| $C_2$ ($C_2H_4$,$C_2H_6$) | 0.348E-3 | | 0.458E-3 | | 0.611E-3 | | 3.569E-3 | | 2.338E-3 | | 1.982E-3 | |
| $C_3$ ($C_3H_6$,$C_3H_8$) | 0.137E-3 | | 0.259E-3 | | 0.371E-3 | | 3.129E-3 | | 1.479E-3 | | 1.351E-3 | |
| $C_4$ ($C_4H_{10}$,iso-But) | .077E-3 | | 0.070E-3 | | 0.193E-3 | | 1.383E-3 | | 0.322E-3 | | 0.326E-3 | |
| $C_5$ | | | | | | | | | | | | |

## Task 4. Effects of Pretreatment on Coal Structure

The main objectives of this Task are to identify the basic changes in coal structure that are caused by pretreatments and to correlate them with coal reactivity changes in liquefaction. In this quarter, the effects of thermal and catalytic pretreatments using dispersed Mo catalyst at different temperatures and with different solvents have been examined. Spectroscopic studies on the effects of drying coal in vacuum and in air and THF-extraction on coal structure are also reported in this quarter.

### Analysis of Residue

The CPMAS $^{13}C$ NMR spectra and Py-GC-MS profiles were obtained by using the same equipments and operational parameters described in Activity 1 of Task 2. The infrared spectra were recorded on Digilab FTS60 FT-IR system. The transmission spectra of the samples were recorded using finally ground samples pressed in KBr pellets. A small amount of predried samples (2.0 mg to 3.0 mg) were weighed (to ±0.01 mg) in dry aluminum weighing dishes and added to a weighed amount (about 300 mg determined to +0.1 mg) of KBr. The KBr and samples were mixed by grinding in stainless steel grinding capsules for 30 seconds and pressed into a 13 mm diameter pellet in an evacuated die. The pellets were then weighed and the sample weight per $cm^2$ of pellet area was determined.

### FT-IR Analysis

<u>Untreated raw coal</u>

Quantitative FT-IR functional group analysis was performed on the starting coal before and after drying and on the residue of the THF-extracted raw coal. The drying of coal does not seem to have any effect on its functionality other then the broad band center at 3400 cm-1 decreases in intensity which also includes the hydroxyl bands (Figure 4.1). The infrared spectra of the THF-extracted coal also does not show any apparent differences.

<u>Preliquefaction at 300 °C</u>

Figures 4.2 and 4.3 show the FT-IR spectra of the THF-insolubles after pretreatment at 300 °C. Preliquefactions without catalyst (Figure 2) produced spectra quite similar to each other except a slight reduction in the aliphatic region and hydroxyl region as compared to that of the raw

coal. The presence of solvents like tetralin or 1-methylnaphthalene also seem to produce no effect on the spectra. In presence of catalyst (ATTM) the infrared spectra show some noticeable differences (Figure 4.3). Compared to the raw coal and to the non-catalytic runs all the spectra showed a reduction in the aliphatic and the ether region. The hydroxyl region also seems to be reduced appreciably. The catalyst seems to have more effect on the ether region. Again the presence of solvent did not produce any noticeable difference in infrared spectrum as compared to the solvent free run.

### Preliquefaction at 350 °C

FT-IR analysis of the residua produced at 350 °C showed appreciable differences from that of the raw coal. The infrared spectra of the pretreatment experiments at 350 °C are shown in Figures 4.4 and 4.5. In the catalyst free runs (Figure 4.4) the spectra showed noticeable reduction in the relative intensities of almost all the bands. The presence of solvents seem to produce slightly more reduction in the spectra compared to that of solvent free run. The ether region seems to be more affected by the solvents. The FT-IR spectra of the pretreatment runs in presence of catalyst are shown in Figure 4.5. The presence of catalyst has further reduced the intensities of the aliphatic, hydroxyl and the ether bands. The ether region seems to be more reduced than the other region as compared to the catalyst free runs.

## CPMAS $^{13}$C NMR

Figure 4.6 shows the CPMAS $^{13}$C NMR of the raw coal and after THF-extraction of the unreacted raw coal. The NMR spectrum of the raw coal shows two major broad bands between 0-60 ppm (aliphatic region) and 80-200 ppm (aromatic region). The aromatic region has three peaks: an intense peak around 130 ppm (aromatic C), and two shoulders, one at about 142 ppm (possibly catechol like C), and another at 152 ppm (phenolic or aromatic ether C). A peak near 180 ppm (carbonyl C) and a broad band near 210 ppm (ketone ar aldehyde C) define rest of the spectrum. The NMR spectra of dried and undried raw coal do not show any changes in their functionalities. The two spectra perfectly match with the NMR spectrum of the raw coal. For the pretreated coal at different conditions there are some noticeable changes in the structure of the coal discussed below.

## Preliquefaction at 300 °C

Figure 4.7 shows the comparison of the CPMAS $^{13}C$ NMR spectra of the THF-extracted coal after the reaction at 300 °C without catalyst and in presence and absence of solvents. As compared to the spectrum of the raw coal there are very little but noticeable changes in the aliphatic (0-60 ppm) as well as in aromatic (80-200 ppm) regions. In general, the intensity of the aliphatic region decreases, and the aromaticity increases. This change is more in the presence of solvents. The shoulders on the low energy side of the aromatic peak are apparent but slightly weak as compared to that of the raw coal. The peaks at 182 and 212 are much weaker after pretreatment in presence of solvents.

The pretreatment performed at 300 °C in presence of catalyst (ATTM) did not show any drastic effect on the coal structure. There is only a slight reduction in the aliphatic region. The CPMAS $^{13}C$ NMR spectra shown in Figure 8 are for the THF-insolubles from the pretreatment experiments in the presence of catalyst at 300 °C with and without solvents and compared with that of the raw coal.

## Preliquefaction at 350 °C

The CPMAS $^{13}C$ NMR spectra from the pretreatment experiments at 350 °C without catalyst are shown in Figure 4.9. There are several structural differences which are apparent as a result of pretreatment of coal at 350 °C. The relative intensity of the aromatic and the aliphatic bands in the solvent free run seems to be similar to that in the NMR spectrum of the raw coal. But there are reduction in the shoulders of the aromatic band on the low energy side. The shoulder at 142 ppm seems to have disappeared, or it is very weak. The other bands at 182 and 212 ppm are also very weak compared to those of the raw coal and the pretreatment experiments at 300 °C. The presence of solvents have also shown a drastic effect on the coal structure (Figure 10). The aliphatic region seems to be reduced relatively increasing the aromaticity. The peaks at 142 and 212 ppm are weaker compared to the raw coal but relatively stronger than in the solvent free run. The type solvent used also seems to have effect on the structure of the coal. The presence of 1-methylnaphthalene as a solvent seems to have reduced more aliphatic carbons as compared to the experiment with tetralin as solvent. The shoulder at 152 ppm is stronger but the at 142 ppm is weaker in the experiment with 1-methylnaphthalene is stronger than with tetralin.

The pretreatment at 350 °C in presence of the catalyst (ATTM) has shown more severe effect on the coal structure. The FT-IR spectra of the THF-isolubles are shown in Figure 4.10. The aromatic region seems to be more effected then the aliphatic region. The aliphatic region seems to be affected in a similar fashion as in the catalyst free runs. The reduction of the aliphatic band is observed in the experiment with 1-methylnaphthalene as solvent. The aliphatic band in solvent free run and with tetralin seems to have very little effect.

The effect of catalyst on the aromatic band is much more clearer. The shoulder on the aromatic band at 142 ppm has disappeared along with the band at 212 ppm. The shoulder at 152 ppm is weaker in the experiment with tetralin but in the solvent free and with 1-methylnaphthalene runs this shoulder is quite comparable to the shoulder in the NMR of the raw coal.

## Pyrolysis-GC-MS Results

### Pyrolysis of the raw coal and effect of drying

Figure 4.11 shows the Py-GC-MS chromatograms of the raw coal and the coal dried under vacuum and in air. The pyrolysis of the unreacted raw coal has produced several aromatic compounds along with the alkanes and alkenes. The major aromatic peaks identified are given in Table 4.1. The drying of coal does not seem to have any effect on the pyrolysis products as all the major bands are common in all the spectra having similar relative band intensities. Figure 4.12 shows the Py-GC-MS chromatograms of the undried (as received, fresh), vacuum-dried, and air-dried (THF-extracted) raw coal. Relative to the unextracted raw coal, there are apparent differences in Py-GC-MS profile of the extracted raw coal. The major difference is the presence of intense methylnaphthalene band in the chromatogram of the THF-extracted undried raw coal and vacuum dried raw coal. This peak is also present in the THF-extracted air-dried raw coal but is relatively weak. The methylnaphthalene peak is missing in the Py-GC-MS of the unextracted raw coal. All the other peaks corresponding to the compounds listed in Table 4.1 (compounds 1 to 11) can be identified in the Py-GC-MS chromatogram of the THF-extracted raw coal but their relative intensities are low. The drying of coal has also effected the alkane and alkene peaks. Their intensities have also been reduced. There are apparent differences among the Py-GC-MS chromatograms of the THF-extracted raw coal. The major difference is the relative intensities of the bands other then methylnaphthalene band. All the bands are more intense in the air-dried THF-extracted coal. The C2-phenol peaks are either missing or they are too weak to be detected in the undried THF-extracted raw coal. The alkane and alkene peaks are more intense in the air-dried coal.

### Pyrolysis of THF-extracted coal pretreated at 300 °C

Py-GC-MS chromatograms of the THF-extracted coal, and the samples from thermal runs at 300 °C with and without solvent are shown in Figure 4.13. The major compounds which are identified are given in Table 4.2. As these chromatograms are compared with that of the THF-extracted dried raw coal (Figure 4.12) the differences occurred in the structure of the coal after pretreatment are obvious. There are several new compounds have appeared after the pretreatment of the coal, such as tetralin, dihydronaphthalene and naphthalene. The intensities of the other compounds have reduced drastically. The intensities of the peaks due to tetralin, dihydronaphthalene, naphthalene and methylnaphthalene also vary with the solvent.

The presence of catalyst in the pretreatment experiments at 300 °C also affects the structure of the coal. The structural changes produced, compared to the thermal pretreatment, are apparent by the Py-GC-MS chromatograms shown in Figure 4.14. The major compounds produced by the flash pyrolysis of the THF-extracted residues and identified are listed in Table 4.3. Compared to the pyrolysis products produced in the catalyst free experiments the major difference is the relative intensities of the peaks due to various compounds. Particularly, the phenol peak is very intense in experiments with the catalyst. The C3-benzene peaks are also observed which were not detected or were too weak to be detected in the thermal runs.

Table 4.1. Major identified peaks in Py-GC-MS chromatograms of the raw coal.

| No. | Identified Compounds |
|---|---|
| 1 | Toluene |
| 2 | p-Xylene |
| 3 | o-Xylene |
| 4 | $C_3$-Benzene |
| 5 | $C_3$-Benzene |
| 6 | Phenol |
| 7 | o-Cresol |
| 8 | m- + p-Cresol |
| 9 | $C_2$-Phenol |
| 10 | $C_2$-Phenol |
| 11 | $C_2$-Phenol |
| 12 | Naphthalene |
| 13 | Methylnaphthalene |

Table 4.2. Major identified peaks in Py-GC-MS chromatograms of the THF-extracted coal preliquefied at 300 °C without catalyst.

| No. | Identified Compounds |
|---|---|
| 1 | Toluene |
| 2 | p-Xylene |
| 3 | o-Xylene |
| 4 | Phenol |
| 5 | o-Cresol |
| 6 | m- + p-Cresol |
| 7 | Tetralin |
| 8 | Dihydronaphthalene |
| 9 | $C_2$-Phenol |
| 10 | Naphthalene |
| 11 | Methylnaphthalene |

### Pyrolysis results of THF-extracted coal preliquefied at 350 °C

Figure 4.15 shows the Py-GC-MS chromatograms of the THF-extracted coal reacted at 350 °C without catalyst. The compounds identified are given in Table 4.4. Compared to the pyrolysis results for the pretreatment at 300 °C there are apparent changes in the pyrolysis profile of the residues from pretreatment at 300 °C. The major compounds are the same but there is a severe effect on the relative intensities of the peaks. Particularly, the tetralin peak which is present in the all the pretreatment experiments at 300 °C is either very weak or disappears at 350 °C. The naphthalene peak also shows the similar changes at higher temperature pretreatment runs. From these results, the structural changes seem to be severe at higher temperature particularly in presence of a solvent.

The presence of the catalyst considerably affects the relative intensities of various peaks. The Py-GC-MS chromatograms for the THF-extracted coal reacted at 350 °C in presence of the catalyst are shown in Figure 4.16 and the pyrolysis products are listed in Table 4.5.

Table 4.3. Major identified peaks in Py-GC-MS chromatograms of the THF-extracted coal preliquefied at 300 °C in presence of ATTM.

| No. | Identified Compounds |
|---|---|
| 1 | Toluene |
| 2 | p-Xylene |
| 3 | o-Xylene |
| 4 | $C_3$-Benzene |
| 5 | $C_3$-Benzene |
| 6 | Phenol |
| 7 | o-Cresol |
| 8 | m- + p-Cresol |
| 9 | Tetralin |
| 10 | Dihydronaphthalene |
| 11 | $C_2$-Phenol |
| 12 | $C_2$-Phenol |
| 13 | Naphthalene |
| 14 | Methylnaphthalene |

Table 4.4. Major identified peaks in Py-GC-MS chromatograms of the THF-extracted coal preliquefied at 350 °C without catalyst.

| No. | Identified Compounds |
|---|---|
| 1 | Toluene |
| 2 | p-Xylene |
| 3 | o-Xylene |
| 4 | Phenol |
| 5 | o-Cresol |
| 6 | m- + p-Cresol |
| 7 | Tetralin |
| 8 | Dihydronaphthalene |
| 9 | $C_2$-Phenol |
| 10 | $C_2$-Phenol |
| 11 | Naphthalene |
| 12 | Methylnaphthalene |

Table 4.5. Major identified peaks in Py-GC-MS chromatograms of the THF-extracted coal preliquefied at 350 °C in presence of ATTM.

| No. | Identified Compounds |
|---|---|
| 1 | Toluene |
| 2 | p-Xylene |
| 3 | o-Xylene |
| 4 | $C_3$-Benzene |
| 5 | $C_3$-Benzene |
| 6 | Phenol |
| 7 | o-Cresol |
| 8 | m- + p-Cresol |
| 9 | Tetralin |
| 10 | Dihydronaphthalene |
| 11 | $C_2$-Phenol |
| 12 | $C_2$-Phenol |
| 13 | Naphthalene |
| 14 | Methylnaphthalene |

### Py-GC-MS of Thermally Treated Montana Coal

Figures 4.17-4.20 show the specific and total ion chromatograms from Py-GC-MS (pyrolysis at 610°C) of the THF-insoluble residue from a non-catalytic, temperature-programmed liquefaction (TPL) of Montana coal at final temperature of 300 °C in tetralin. Details of TPL may be found elsewhere (Song and Schobert, 1992b). Figures 4.17-4.20 are comparable to the corresponding Py-GC-MS data for the THF-extracted but unreacted DECS-9 Montana coal (Figures 2.2-2.5). Phenol, alkyl phenols, alkylbenzenes, catechols as well as alkanes and alkenes are formed from flash pyrolysis of the THF-extracted raw coal. Relative to this sample, there is apparent change in Py-GC-MS profile of the residue from TPL at 300°C. The appearance of a major peak for naphthalene and disappearance of catechol differentiate the latter from the former. This is especially interesting, since the NMR spectra of these two samples (Song et al., 1992a, 1992b) and the corresponding yields of THF-solubles (7-9%) are similar to each other. From these results, it is clear that the reaction at 300°C did cause some structural change. The naphthalene peak in Figure 3 is due mainly to the use of tetralin solvent, because this peak was found to be very small with other solvent or without solvent. Since the residue has been extracted by THF for over 24 h, washed by acetone and pentane (to remove THF completely) and dried in vacuum at 90-100°C for 6 h, the naphthalene/tetralin remained in the residue must be either chemically bound to other species or physically entrapped in solvent-inaccessible micropores or closed pores which can not be removed by solvent extraction.

From comparative examination of the data from different analytical techniques, it appeared that Py-GC-MS can detect some subtle differences in coal structure which are not easily detectable by CPMAS NMR and FT-IR.

## Task 5. Effects of Pretreatment on Liquefaction

Effects of pretreatments of coals on their liquefaction reactivity were examined by conducting the thermal and catalytic liquefaction of Montana coal under conventional rapid heat-up, single stage (SSL), temperature-staged (TSL), and temperature-programmed (TPL) conditions.

### Pretreatment

The coal was dried at 95°C in vacuum for 2 h before use. For comparison, the dried coal was extracted by solvents in the order of hexane, toluene and THF. The results showed that the hexane soluble (oil) was 3.1 %, toluene soluble but hexane insoluble (asphaltene) was 0.2 % and THF soluble but toluene insoluble (preasphaltene) 3.5 %. For the catalytic runs, ammonium tetrathiomolybdate (ATTM) was dispersed on predried coal (1 wt% Mo on dmmf coal) by incipient wetness impregnation method. After loading of the catalyst precursor, the coal sample was dried in vacuum for two hours at 105°C, then removed and stored under a nitrogen atmosphere.

## Coal Liquefaction

Liquefaction experiments were conducted in microautoclave reactors (tubing bombs) in a preheated fluidized sandbath. For each reaction, 4 g of coal and 4 g of Wilsonville Middle Distillate (WI-MD) as reaction solvent were added to the reactor, following which hydrogen was purged three times, with a final pressure of 7 MPa at room temperature. The reactor was then plunged into the sandbath and agitated at 200 cycles per minute. The tubing bomb reached the reaction temperature in about three minutes. For a single-staged liquefaction (SSL), the tubing bomb was rapidly heated-up to 400°C and held for 30 minutes followed by rapid quench. For a temperature-programmed liquefaction (TPL), the tubing bomb was rapidly heated-up to a relatively low temperature (200-300 °C) and soaked in sandbath at that temperature for 15 minutes. The temperature was then gradually increased to a higher temperature level (400-450 °C) and held for 30 minutes, followed by rapid quench. The rate of temperature increase was 3 °C/min to 8.3°C/min, depending on the difference between the lower temperature and the higher temperature. The heat-up period was about 30 minutes, and the total reaction time was about 75 minutes. Temperature-staged liquefaction (TSL) was a different procedure from TPL. A tubing bomb was rapidly heated-up to a low temperature (200-300 °C), soaked at that temperature for 15 minutes, then it was immediately (without a heating period) transferred to another sandbath of a higher temperature (400 °C) and held for 30 minutes followed by rapid quench. Since there was no heating period between two temperature stages, the total reaction time was about 45 minutes, which is different from TPL.

After the reaction, the gaseous product was vented into a gas sample bag and later analyzed by gas chromatography. The liquid and solid products and residue were washed into a tared ceramic thimble using hexane. Then the products were separated under a nitrogen atmosphere by Soxhlet-extraction using hexane, toluene and THF as solvents. After extractions, solvents were removed by rotary evaporation and the products were dried in vacuum at 110 °C for about 12 hours, except for the hexane solubles. The solid residue was washed first by acetone and then by pentane several times and dried in the same procedure as the reaction products. The asphaltene, preasphaltene and residue were then weighed, and conversion and product distributions were calculated based on dmmf coal.

Table 5.1 compares the coal conversion and distribution of products from TPL and SSL. In the absence of a catalyst, TPL total conversion is 6.4 % higher than SSL. This is mainly due to the gains in asphaltene and preasphaltene yields, while the oil yield remains almost identical in both cases, about 30.2%. In the presence of ATTM as catalyst precursor, total conversion increases again in TPL by 6.6 %, similar to those experiments without catalyst. It is noticed that, different from non-catalytic liquefaction, the oil yield increases drastically by 8.8 % in TPL, while asphaltene decreases by 4.9 %. This may suggest that TPL, with presence of the catalyst, promotes the further cracking or hydrogenation of asphaltene to oil, though the detailed mechanism is not yet clear.

Another comparison has been made for the liquefaction with and without catalyst. In SSL runs, total conversion increases 32.2 % by employing ATTM as catalyst. This is mainly due to an oil yield increase (by 12.5 %) and an asphaltene yield increase (by 16.4 %), and to a lesser extent, to a preasphaltene yield increase (by 3.3 %). In TPL runs, catalytic liquefaction affords 32.4 % higher total conversion (than non-catalytic run). Increases in the yields of oil plus gas are the predominant (by 21.2%) contribution to the increase in total conversion. Asphaltene and preasphaltene increase by lesser amounts, 6.7 and 4.4 % respectively. This comparison indicates that the addition of ATTM as catalyst significantly improves both the total conversion of liquefaction and the selectivity of products to the more desirable oils.

As mentioned in previous section, in the procedure of sample preparation, both $H_2O$ and $H_2O$/THF (44 : 56) were employed as impregnation solvents. The volume of the $H_2O$/THF mixture required to achieve incipient wetness is about three times of that of pure water. It is considered that the mixture has higher affinity toward the coal surface than water. This difference in affinity may lead to a different dispersion of the catalyst precursor on coal, which will subsequently result in a difference of catalyst performance. Table 5.1 provides the conversion data to compare the solvent effect on liquefaction. For SSL runs, samples prepared using $H_2O$/THF appear a bit more active than samples prepared using $H_2O$. For TPL runs, the difference is more pronounced. By using $H_2O$/THF as impregnation solvent, total conversion increases by 10.4 %, which is due to the increase of gas and oil yield (by 10.3 %). The asphaltene and preasphaltene yields are identical within experimental error. This set of data supports the assumption that by employing $H_2O$/THF, better catalyst dispersion will be achieved, thus leading to a better catalyst performance.

Temperature-programmed liquefaction may be advantageous over temperature-staged liquefaction because TPL provides a heating period which could slowly generate radicals and allows hydrogenation to take place. Table 5.2 compares TPL with TSL. For 200/400 runs (the first number indicates the first stage temperature and the second number indicates the second stage temperature), the total conversion increases slightly (1.5 %) in TPL with a remarkable increase in gas and oil yield (7.5 %). In contrast, the asphaltene and preasphaltene yields decrease slightly. For 300/400 (the temperatures for lower and higher temperature stages, respectively, in °C) runs, the same phenomenon is observed, though in 300/400 runs, both TPL and TSL achieve higher total conversion and gas oil yield. It is apparent that TPL is more favorable to achieve high conversion and better product selectivity. Consistent with the previous observations, the asphaltene yield decreases in TPL experiments. This again reflects the fact TPL promotes the conversion of asphaltene to oils.

Figure 5.1 shows the conversion as a function of the temperature in the first stage in TPL runs. The curve starts at room temperature, which is in fact the SSL run. The total conversion reaches a maximum at 200 $^{\circ}$C (91%) and starts to decrease as temperature increases, 86.6% at 250 $^{\circ}$C and 89.7% at 300 $^{\circ}$C. The oil yield changes in a very similar way as total conversion, 51.5% at 200 $^{\circ}$C, 46.8% at 250 $^{\circ}$C and 50.6% at 300 $^{\circ}$C. The low temperature stage is used to allow time for the reaction solvent to penetrate into the interior of coal particles (Song et al., 1991b; Song and Schobert, 1992b). If the temperature of this stage is too high, the reaction solvent may evaporate before penetration. In this case, less solvent will be in the interior of coal and this could result in reduced H-transfer to the coal radicals, which will consequently cause poor liquefaction results. The temperature of the first stage may also affect the activation of catalyst precursor, but how this will subsequently affect the liquefaction is still unknown.

The effect of changing temperature of the second stage in TPL is shown in Figure 5.2. Although the total conversion, as well as the yields of asphaltenes and preasphaltenes, show a trend of decreasing, the gas and oil yields show a remarkable increase as the temperature increase from 400$^{o}$C to 450$^{o}$C (51.5% to 62.4%). This indicates that an increase of second stage temperature may not favor high total conversion of liquefaction, but it has some benefit in achieving high yield of oil and gas. The decrease of total conversion might be caused by retrogressive reactions. At temperatures as high as 450$^{o}$C, radicals formed in thermal cracking immediately crosslink and recombine with one another to form some very stable compounds that are difficult to liquefy.

In summary, addition of ATTM as catalyst precursor will increase the total conversion substantially. In the impregnation procedure, using organic compounds in the impregnation solvent may lead to a better dispersion of catalyst precursor thus giving a higher conversion. Temperature-programmed liquefaction is advantageous over temperature-staged and single-staged liquefaction regardless of whether a catalyst is used. The change of first and second stage temperature in TPL will influence the conversion, though determining the reasons for these influences relies on future research.

**Table 5.1.** Comparison of TPL and SSL of DECS-9 Montana coal

| Temperature | Condition. | Tot. Conv dmmf wt %. | Oil + Gas dmmf wt %. | Asph. dmmf wt %. | Preasph. dmmf wt %. |
|---|---|---|---|---|---|
| Non-cat | SSL | 52.22 | 30.21 | 12.46 | 9.55 |
| | TPL | 58.57 | 30.27 | 17.24 | 11.06 |
| ATTM THF/$H_2O$ | SSL | 84.4 | 42.73 | 28.86 | 12.82 |
| | TPL | 91 | 51.49 | 23.93 | 15.5 |
| ATTM $H_2O$ | SSL | 83.24 | 38.98 | 19.46 | 24.8 |
| | TPL | 80.57 | 41.18 | 23.4 | 15.42 |

Oil: hexane soluble.
Asphaltene: toluene soluble but hexane insoluble.
Preasphaltene: THF soluble but toluene insoluble

**Table 5.2.** Comparison of TPL with TSL of DECS-9 Montana Coal

| Temperature | Condition. | Tot. Conv dmmf wt %. | Oil + Gas dmmf wt %. | Asph. dmmf wt %. | Preasph. dmmf wt %. |
|---|---|---|---|---|---|
| 200/400 | TPL | 91 | 51.49 | 23.93 | 15.5 |
| | TSL | 89.46 | 43.98 | 27.62 | 17.87 |
| 300/400 | TPL | 89.67 | 50.61 | 22.67 | 16.4 |
| | TSL | 87.91 | 42.66 | 28.37 | 16.89 |

# LITERATURE CITED

Alemany, L.B., Grant, D.M., Alger, T.D. and Pugmire, R.J., J. Am. Chem. Soc., 1983, 105, 6697.

Artok, L.; Davis, A.; Mitchell, G.D.; Schobert, H.H., "Catalyst Dispersion and Activity under Conditions of Temperature-Staged Liquefaction", Proceedings of DOE Liquefaction Contractors' Review meeting, Sept.3-5, 1991, Pittsburgh, pp.422-444.

Baldwin, R.M., Nguanpraesert, O, Kennar, D.R. and Miller, R.L., ACS Fuel Chem. Prepr., 1990, 35, 70.

Baldwin, R.M.; Kennar, D.R.; Nguanpraesert, O; Miller, R.L., Proceedings of DOE Liquefaction Contractors' Review meeting, Sept.3-5, 1991, Pittsburgh, pp.616-624.

Beinkowski, P.R., Narayan, R., Greenkorn, R.A. and Chao, K-C., Ind. Eng. Chem. Res., 1987, 26, 202.

Bockrath, B.C., in"Coal Science", Vol. 2, Academic Press, New York, 1982, 65.

Bockrath, B.C., Finseth, D.H. and Illig, E.G., Fuel Proc. Technol., 1986, 12, 175.

Bockrath, B.C.; Illig, E.G.; Hough, M., "Physical Organic Chemistry of Coal Liquefaction", ACS Fuel Chem. Prepr., 1990, 35 (1), 232-240.

Bockrath, B.C., Illig, E.G., Keller, M.J., III, Solar, J.G., Bittner, E.W., and Finseth, D.H., "Low Temperature Liquefaction Catalysis", Proceedings of DOE Liquefaction Contractors Review Meeting, September 3-5, 1991, Pittsburgh, pp.387-397.

Burgess, C. and Schobert H.H., ACS Fuel Chem. Prepr., 1990, 35, 31.

Burgess, C.; Artok, L.; Schobert H.H., ACS Fuel Chem. Prepr., 1991, 36 (2), 462-469.

Chamberlin, P.L. and Schobert, H.H., Fuel Proc. Technol., 1991, 28, 67-76.

Comolli, A.G., Ganguli, P., Harris E., MacArthur, J.B., NcLean, J.B. and Smith, T.P., "New Technology Concept for Two-Staged Liquefaction", DOE-PC-60017-Ta, New Jersey, Hydrocarbon Research Inc., 1985, 413 pp.

Crelling, J.; Pugmire R, R.; Meuzelaar, H; McClenen, W.; Huai, H.; and Karas, J., Energy and Fuels, 1991, 5, 688-694

Curtis, C.W., Tsai, K-J. and Guin, J.A., Ind. Eng. Chem. Res., 1987, 26, 12.

Davidson, R.M., "Molecular Structure of Coal", ICTIS-TR-08, London, UK., IEA Coal Research, 1980, 86p.

Davis, A., Derbyshire, F.J., Finseth, D.H., Lin, R., Stansberry, P.G. and Terrer, M-T., Fuel, 1986, 65, 500.

Davis, A., Derbyshire, F.J., Mitchell, G.D. and Schobert, H.H., "Enhanced Coal Liquefaction by Low-Severity Catalytic Reactions", U.S. Department of Energy, Final Report DOE-PC-90910-F1, July, 1989, 175 p.

Davis, A., Schobert, H.H., Mitchell, G.D. and Artok, L., "Catalyst Dispersion and Activity under Conditions of Temperature-Staged Liquefaction", Progress Report DOE-AC-22-89PC89877, January, 1990.

Davis, A.; Glick, D.C.; Mitchell, G.D., Proceedings of DOE Liquefaction Contractors' Review Meeting, Sept. 3-5, 1991, Pittsburgh, p.398-410.

Derbyshire, F.J. and Whitehurst, D.D., Fuel, 1981, 60, 655.

Derbyshire, F.J., Davis, A., Epstein, M. and Stansberry, P., Fuel, 1986a, 65, 1233.

Derbyshire, F.J., Davis, A., Lin, R., Stansberry, P. and Terrer M-T., Fuel Proc. Technol., 1986b, 12, 127.

Derbyshire, F.J. and Stansberry, P., Fuel, 1987, 66a, 1741.

Derbyshire, F.J., Catalysis in Coal Liquefaction: New Directions for Research, IEA Report, IEACR/08, June, 1988, 69p.

Derbyshire, F.J., Energy & Fuels, 1989, 3, 273.

Derbyshire, F.J., Davis, A. and Lin, R., Energy & Fuels, 1989, 3, 431.

Derbyshire, F.J.; Davis, A.; Schobert, H.; Stansberry, P.G. Am. Chem. Soc. Div. Fuel Chem. Prepr. 1990, 35, 51.

Deshpande, G.V., Solomon, P.R. and Serio, M.A., ACS Fuel Chem. Prepr., 1988, 33, 310.

Deurbrouck, A.W. and Hucho, R.E., "Coal Preparation in "Chemistry of Coal Utilization, Supp. Vol. 2", M. Elliot Ed., Wiley and Sons, New York, 1982, 571-607.

DOE COLIRN Panel, "COAL LIQUEFACTION - A Research and Development Needs Assessments", DOE DE-AC01,87ER30110, Final Report, Vol. 1 and Vol. 2, 1989.

Earl, W.L. and VanderHart, D.L., J. Am. Chem. Soc., 1980, 102, 3251.

Ettinger, M., Nardin, R., Mahasay, S.R. and Stock, L.M. J. Org. Chem., 1986, 51, 2840.

Fraser, D.J. and Griffiths, P.R., Appl. Spectrosc., 1990, 193, 44.

Gallegos, E.J., in "Chromatography in Petroleum Analysis", K.H. Altgelt and T.H. Gouw Eds., Marcel Dekker, New York, 1979, pp. 162-184.

Garcia, A.B. and Schobert, H.H., ACS Fuel Chem. Prepr., 1988.

Garcia, A.B. and Schobert, H.H., Coal Preparation, 1989, 7, 47.

Garcia, A.B. and Schobert, H.H., Fuel, 1989, 68, 1613.

Garcia, A.B. and Schobert, H.H., Fuel Processing Technol., 1990, 24, 179.

Garcia, A.B. and Schobert, H.H., "Liquefaction Behavior of High-Sulfur Lignites", in "Coal Science II", H.H. Schobert, K.D. Bartle, and L. Lynch Eds., ACS Sym Ser. 461, 1991, 213-224.

Garg, D., Miller, R.M., Hoover, D.S., Givens, E.N., Schweighardt, F.K., Tarrer, A.R., Guin, J.A., Curtis, C.W. and Luckie, P., "Evaluation of the Effect of Solvent Modification and Coal Pretreatment and Beneficiation on Liquefaction", DOE/TIC-50003-28, Air Products and Chemicals, Inc., PA.

Given, P.H., Marzec, A., Barton, W.A., Lynch, L.J. and Gerstein, B.C., Fuel, 1986, 65, 155.

Gould, K.A., Gorbaty, M.L. and Miller, J.D., Fuel, 1978, 57, 510.

Green, T.K. Kovac, J. and Larsen, J.W., in "Coal Structure", R.A. Meyers Ed., Academic Press, New York, 1982, p. 199.

Green, T.K., Kovac, J. and Larsen, J.W., Fuel, 1984, 63, 935.

Hatcher, P.G., Org. Geochem., 1987, 11, 31.

Hatcher, P.G., Energy & Fuels, 1988a, 2, 48.

Hatcher, P.G., Lerch, H.E., Kotra, R.K. and Verheyen, T.V., Fuel, 1988b, 67, 1069.

Hatcher, P.; Lerch, H.; Kotra, R.; and Verheyen, T., Fuel, 1988c, 67, 1069-1075

Hatcher, P.G., Lerch, H.E., Bates, A.L. and Verheyen, T.V., Org. Geochem., 1989a, 14, 145.

Hatcher, P.G., Lerch, H.E. and Verheyen, T.V., Int. J. Coal Geol., 1989b, 13, 65.

Hawk, C.O. and Hiteshue, R.A., Bulletin 622, Bureau of Mines, US Department of Interior, 1965, 42 pp.

Hengel, T.D. and Walker, P.L., Fuel, 1984, 63, 1214.

Huang, L.; Song, C.; Schobert, H.H., Am. Chem. Soc. Div. Fuel Chem. Prepr. 1992, 37, in press.

Janikowski, S.K. and Stenberg, V.I., Fuel, 1989, 68, 95.

Joseph, J.T., Fuel, 1991, 70, 139.

Larsen, J.W., Sams, T.L. and Rogers, B.R., Fuel, 1980, 59, 666.

Larsen, J.W., Green, T.K. and Kovac, J., J. Org. Chem., 1985, 50, 4729.

Liotta, R., Rose, K. and Hippo, E.J., J. Org. Chem., 1981, 46, 277.

Liotta, R., Brons, G. and Issacs, J., Fuel, 1983, 63, 781.

Lumpkin, R.E., Science, 1988, 239, 873.

Lynch, L.J.; Sakurovs Proc. 1991 Int. Cof. Coal Sci., Newcastle upon Tyne, 1991, 592.

Maciel, G.E., Bartuska, V.J. and Mikinis, F.P., Fuel, 1979, 58, 391.

Mahajan, O.P.; "Porosity of Coals and Coal Products", in Analytical Methods for Coal and Coal Products, Vol.1, C. Karr, Ed., Academic Press, New York, 1978, p.125-162.

Malhotra, R. and McMillen, D.F., "A Mechanistic Numerical Model for Coal Liquefaction Involving Hydrogenolysis of Strong Bonds. Rationalization of Interactive Effects of Solvent Aromaticity and Hydrogen Pressure", Energy & Fuels, 1990, 4, 184-193.

Masunaga, T and Kageyama Y. Proc. 1989 Int. Cof. Coal Sci., Tokyo, 1989, 819.

McLean, J.B., Comolli, A.G. and Smith, T.O., ACS Fuel Chem. Prepr., 1986, 31, 268.

McMillen, D.F., Malhotra, R., Hum, G.P., Chang, S-J. and Nigenda, S.E., Proc. Inter. Conf. Coal Sci., Sydney, Australia, 1985a, p. 91.

McMillen, D.F., Chang, S-J., Nigenda, S.E. and Malhotra, R., ACS Fuel Chem. Prepr., 1985b, 30, 414.

McMillen, D.F.; Chang, S.; Nigenda, S.E.; Malhotra, R. Proc. 1985 Int. Cof. Coal Sci., Sydney, 1985, 153.

McMillen, D.F., Malhotra, R., Hum, G.P. and Chang, S-J., Energy & Fuels, 1987, 1, 193.

McMillen, D.F., Malhotra, R., Tse, D.S., "Interactive Effects between Solvent Components: Possible Chemical Origin of Synergy in Liquefaction and Coprocessing", Energy & Fuels, 1991, 5, 179-187.

Meuzelaar, H.L.C., Haverkamp, J. and Hileman, F.D., "Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials", Elsevier, Amsterdam, 1982, 286 pp.

Miller, R.L., Armstrong, M.E. and Baldwin, R.M., ACS Fuel Chem. Prepr., 1989, 34, 873.

Moroni, E.C., ACS Fuel Chem. Prepr., 1986, 31, 340.

Mudamburi, Z. and Given, P.H., Org. Geochem., 1985, 8, 441.

Naumann, A.W., Behan, A.S. and Thorsteinson, E.M., Proc. 4th Int. Conf. Chem. & Uses of Molybdenum (H.E. Barry and C.N. Mitchell Eds.), 1982, p. 313.

Neavel, R.C., in "Coal Sciencae" Vol. 1, Academic Press, New York, 1982, pp. 1-19.

Narain, N.K., Appell, H.R. and Utz, B.R., ACS Fuel Chem. Prepr., 1983, 28, 161.

Neuworth, M.B. and Moroni, E.C., Fuel Proc. Technol., 1984, 8, 231.

O'Brian, R.J., Gibbins, J.R. and Kandiyoti, R., Fuel Proc. Technol., 1987, 15, 71.

Painter, P.C., in "Coal and Coal Products: Analytical Characterization", E.L. Fuller Ed., Am. Chem. Soc. Sym. Ser., 1982, 205, 47.

Painter, P.C., Starsinic, M., Squires, E. and Davis, A., Fuel, 1983, 62, 742.

Raaen, V.F. and Roark, W.H, Fuel, 1978, 57, 650.

Rincon, K.M. and Cruz, S., Fuel, 1988, 67, 1162.

Ross, D.S. and Hirschon, A., ACS Fuel Chem. Prepr, 1990, 35, 37.

Saiz-Jimenez, C. and De Leeuw, J.W., Org. Geochem., 1984, 6, 417.

Schlosberg, R.H.; Neavel, R.C.; Maa, P.S.; Gorbaty, M.L., Fuel, 1980, 59, 45.

Schobert, H.H., Tomic, J., Moyer, D. and McConnie, J., "Inhibition of Retrograde Reactions in Coal/Petroleum Co-Processing", Technical Progress Report, DOE DE-FG22-88PC888935, June, 1990.

Schobert, H.H., Resources, Conservation and Recycling 1990, 3, 111.

Senftle, J.T.; Kuehn, D.; Davis, A.; Brozoski, B.; Rhoads, C.; Painter, P.C., Fuel, 1984, 63, 245-250.

Serio, M.A., Solomon, P.R., Kroo, E., Bassilakis, R., Malhotra, R. and McMillen, D., ACS Fuel Chem. Prepr., 1990, 35, 61.

Shabtai, J., Oblad, H.B., Katayama, Y. and Saito, Y., ACS Fuel Chem. Prepr., 1985a, 30, 495.

Shabtai, J.,Skulthai, T. and Saito, Y., ACS Fuel Chem. Prepr.,, 1986, 31, 15.

Snape, C.E., Derbyshire, F.J., Stephens, H.P., Kottenstette, R.J. and Smith, N.W., Fuel Proc. Technol., 1990, 24, 119.

Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A. and Deshpande, G.V., Energy & Fuels, 1988, 2, 405.

Solomon, P.R.; Serio, M.A.; Despande, G.V.; Kroo, E. Energy & Fuels 1990, 4, 42.

Sondreal, E.A., "A Review of U.S. Low-Rank Coal: Policy, Resource and technology",Paper presented at the Information Transfer Session, Cooperative Program in Coal Research, The Pennsylvania State University, Nov. 18-19, 1991.

Song, C. and Nomura, M., Fuel, 1986a, 65, 922.

Song, C. and Nomura, M., Bull. Chem. Soc. Japan, 1986b, 59, 3643.

Song, C. and Nomura, M., Fuel, 1987a, 66, 1225.

Song, C., Nomura, M. and Hanaoka, K., Coal Sci. Technol., 1987b, 11, 239.

Song, C., Ono, T. and Nomura, M., Bull. Chem. Soc. Japan, 1988a.

Song, C., Hanaoka, K. and Nomura, M., Energy & Fuels, 1988b, 2, 639.

Song, C., Hanaoka, K. and Nomura, M., Fuel, 1989, 68, 287.

Song, C.; Nomura, M.; Ono, T., Am. Chem. Soc. Div. Fuel Chem. Prepr., 1991a, 36 (2), 586-596.

Song, C.; Schobert, H., H.H.; Hatcher, P.G., Proc. 1991 Int. Conf. Coal Sci., University of Newcastle upon Tyne, UK, 1991b, pp. 664-667.

Song, C.; Schobert, H.H., "Specialty Chemicals and Advanced Materials from Coals: Research Needs and Opportunities", Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992a, 37, in press.

Song, C.; Schobert, H.H., "Temperature-Programmed Liquefaction of Low-Rank Coals in H-donor and Non-donor Solvents", Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992b, 37, in press.

Song, C.; Hatcher, P.G.; "Compositional Differences between Coal-derived and Petroleum-derived jet Fuels", Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1992, 37, in press.

Song, C.; Schobert, H., H.H.; Hatcher, P.G., "Temperature-Programmed Liquefaction of a Low Rank Coal", Energy & Fuels, 1992a, 6, in press.

Song, C.; Schobert, H.H.; Hatcher, P.G., "Solid State 13C NMR and Pyrolysis-GC-MS Studies of Coal Structure and Liquefaction Reactions", Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992b, 37, in press.

Spears, D.R.; Sady, W.; Kispert, L.D., Am. Chem. Soc. Div. Fuel Chem. Prepr. 1991, 36 (2), 1277.

Stansberry, P.G., Lin, R., Terrer, M-T., Lee, C.W., Davis, A. and Derbyshire, F., Energy & Fuels, 1987, 1, 89.

Stenberg, V.I., Gutenkunst, V. and Sweeny, P.G., Fuel, 1989, 68, 95.

Stenberg, V.I., Gutenkurt, V., Nowok, J. and Sweeny P.G. Fuel 1989, 68, 133.

Stock, L.M., in "Chemistry of Coal Conversion", H. Schlosberg Ed., Plenum, New York, 1985, pp. 253-316.

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

Suuberg, E.M.; Unger, P.E.; Larsen, J.W. Energy & Fuels 1987, 1, 305.

Suzuki, T., Yamada, O., Then, J.H., Ando, T. and Watanabe, Y, Proc. 1985 Inter. Conf. Coal Sci., Sydney, Australia, 1985, p. 205.

Utz, B.R., Cugini, A.V. and Frommell, E.A., ACS Fuel Chem. Prepr., 1989, 34, 1423.

Watanabe, Y., Yamada, O., Fujita, K., Takegami, Y. and Suzuki, T., Fuel, 1984, 63, 752.

Weber, W. and Steward, N., EPRI Journal, 1987, 12, 40.

Weller, S., Pelipetz, M.G., Friedman, S. and Storch, H.H., Ind. Eng. Chem. Chem, 1950, 42, 330.

Weller, S. and Pelipetz, M.G, Ind. Eng. Chem. Chem., 1951, 43, 1243.

Whitehurst, D.D., "Coal Liquefaction Fundamentals", Am. Chem. Soc. Sym. Ser. 1980, 139, 132.

Whitehurst, D.D., Mitchell, T.O. and Farcasiu, M., "Coal Liquefaction", Academic Press, New York, 1980.

Wilson, M.A., Aleman;y, L.B., Woolfenden, W.R., Pugmire, R.J., Given, P.H., Grant, JD.M. and Karas, J., Anal. Chem., 1984, 56, 933.

Zielke, C.W., Struck, R.T., Evans, J.M., Costanza, C.P. and Gorin, E., Ind. Eng. Chem. Process Des. Dev., 1966a, 5, 151.

Zielke, C.W., Struck, R.T.,Evans, J.M., Costanza, C.P. and Gorin, E., Ind. Eng. Chem. Process Des. Dev., 1966b, 5, 158.

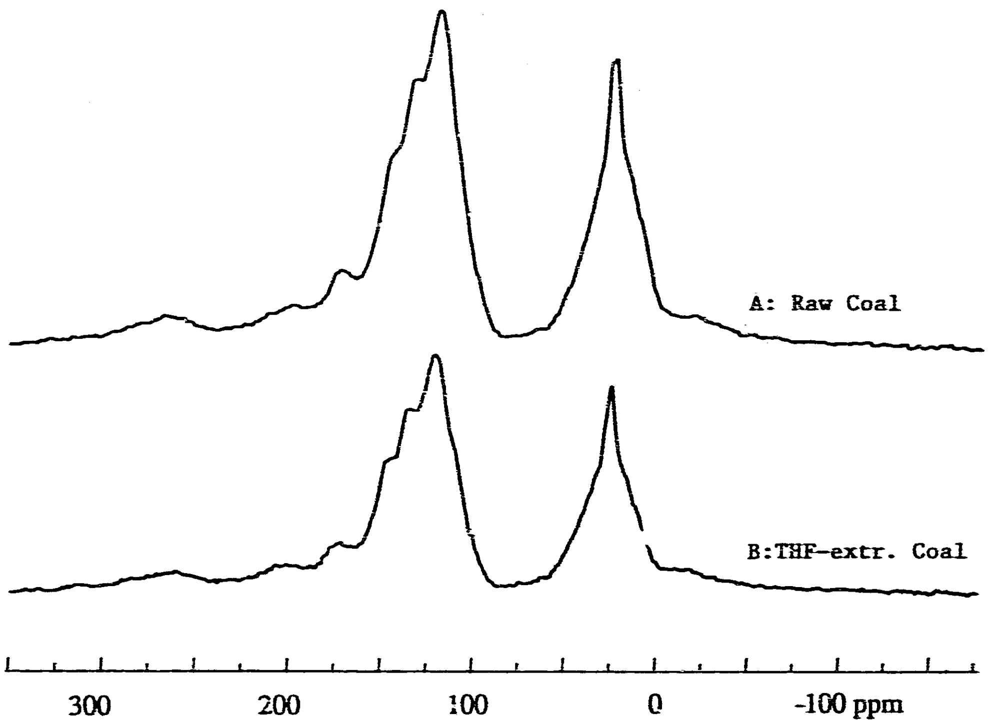


**Figure 2.1** Solid state CPMAS $^{13}C$ NMR spectra of dried raw DECS-9 Montana subbituminous coal (A) and the THF-extracted coal (B, THF-insoluble part).

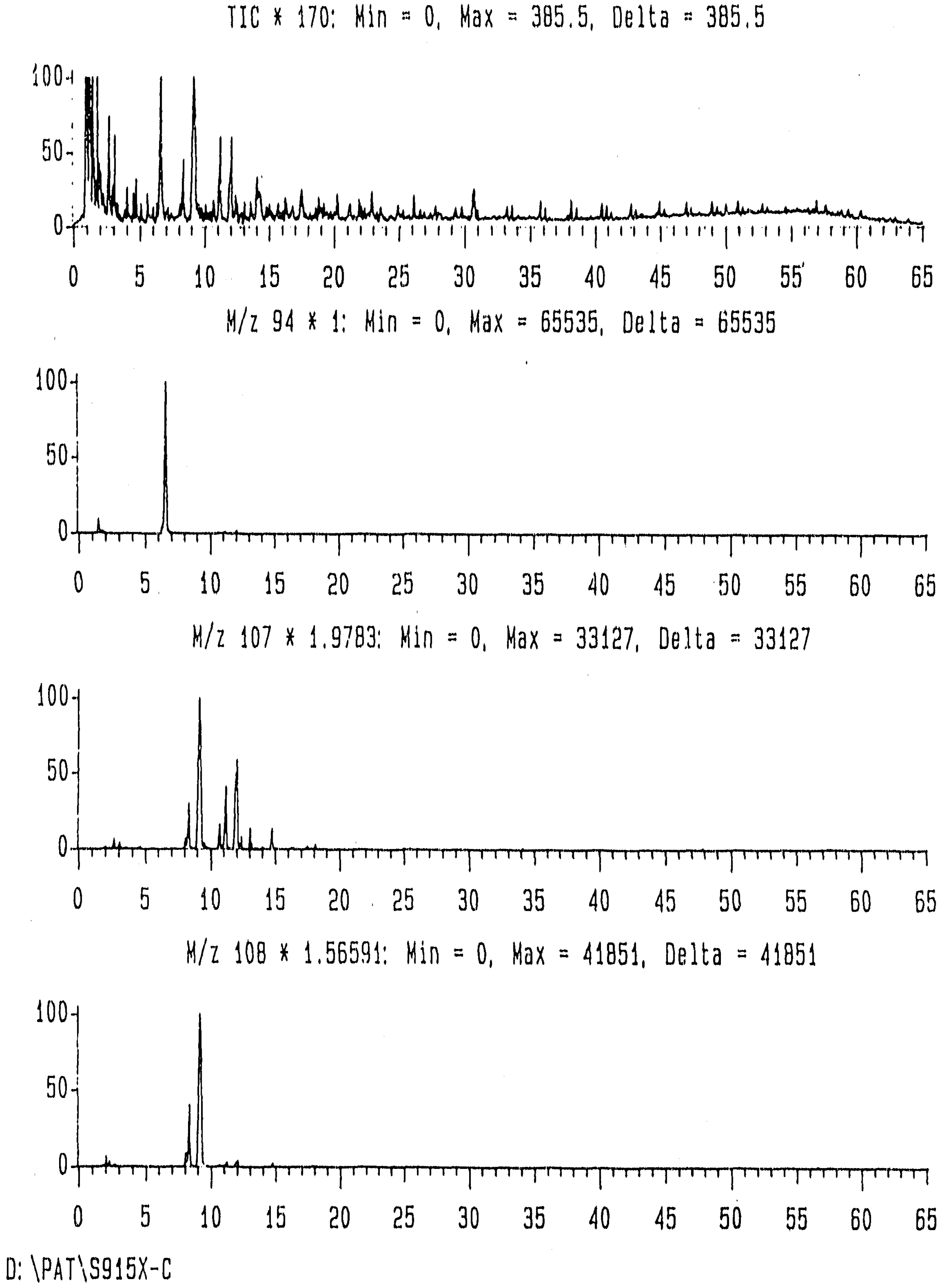


**Figure 2.2** Specific ion chromatograms (SIC) at m/z 94, 107 and 108 and total ion chromatogram (TIC) from Py-GC-MS of the THF-extracted DECS-9 Montana subbituminous coal (pyrolysis: 610°C for 10s; heating rate: 5 °C/ms).

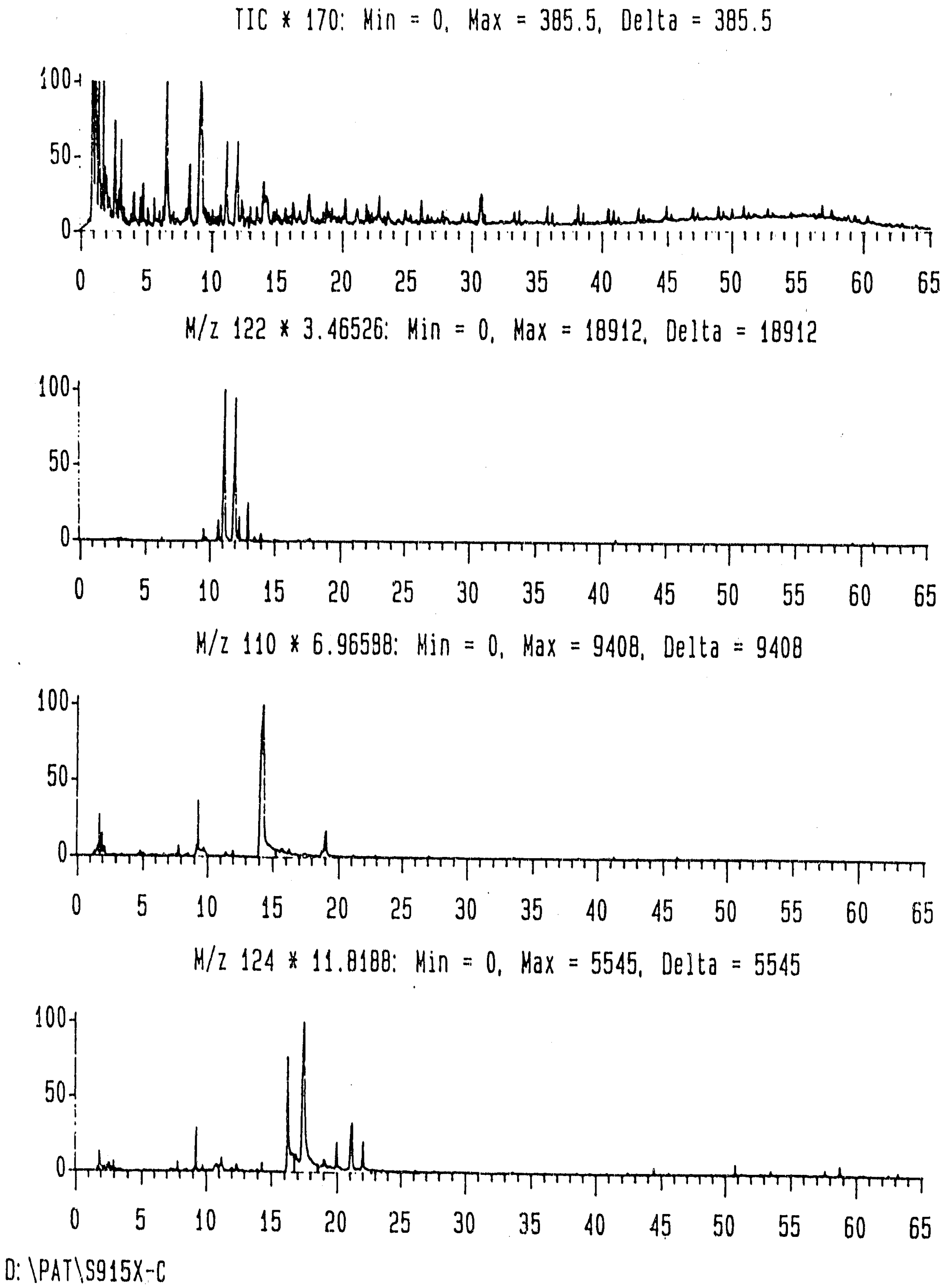


**Figure 2.3** Specific ion chromatograms (SIC) at m/z 122, 110 and 124 and total ion chromatogram (TIC) from Py-GC-MS of the THF-extracted DECS-9 Montana subbituminous coal (pyrolysis: 610°C for 10s; heating rate: 5 °C/ms).

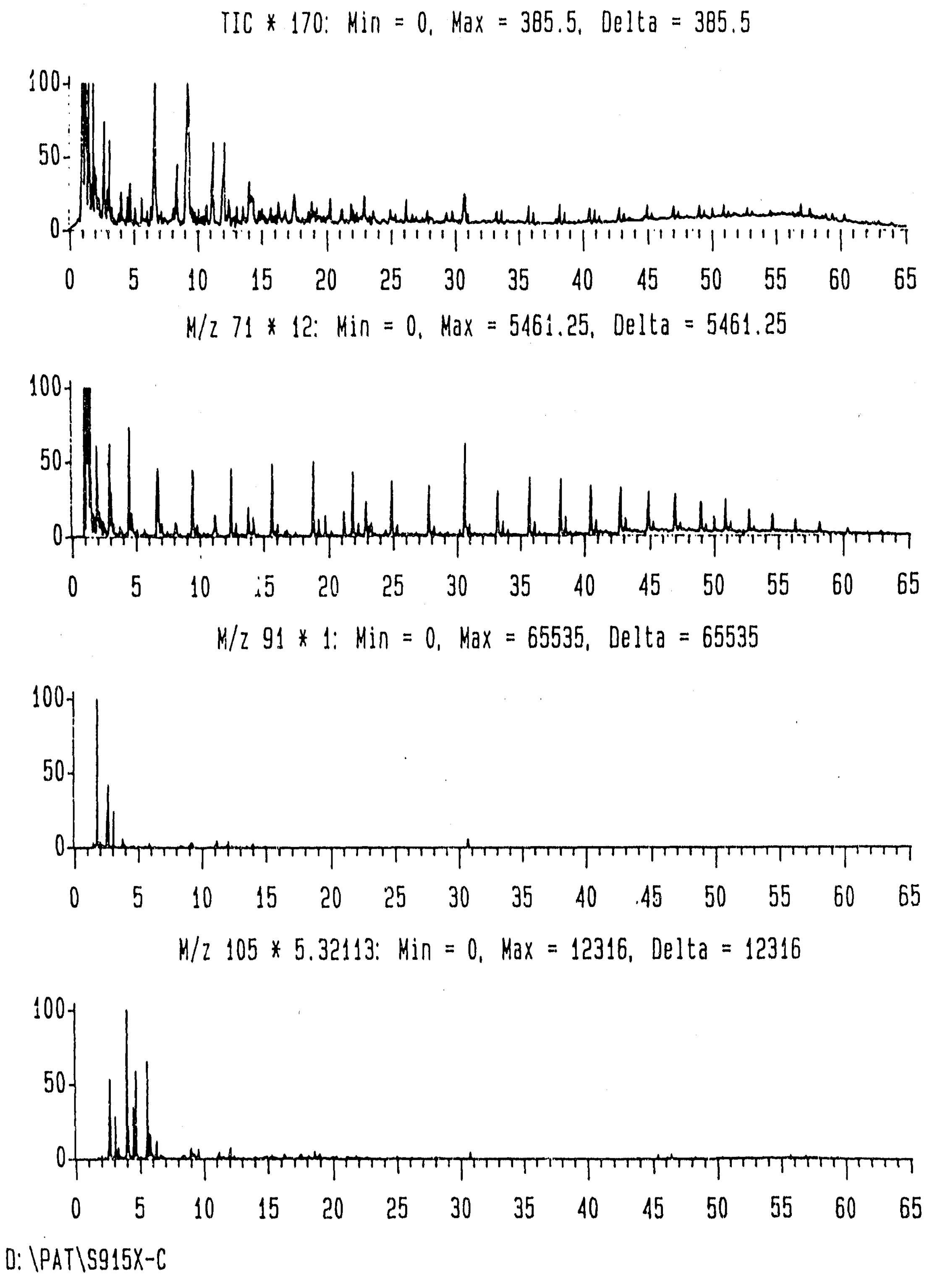


**Figure 2.4** Specific ion chromatograms (SIC) at m/z 71, 91 and 105 and total ion chromatogram (TIC) from Py-GC-MS of the THF-extracted DECS-9 Montana subbituminous coal (pyrolysis: 610°C for 10s; heating rate: 5 °C/ms).

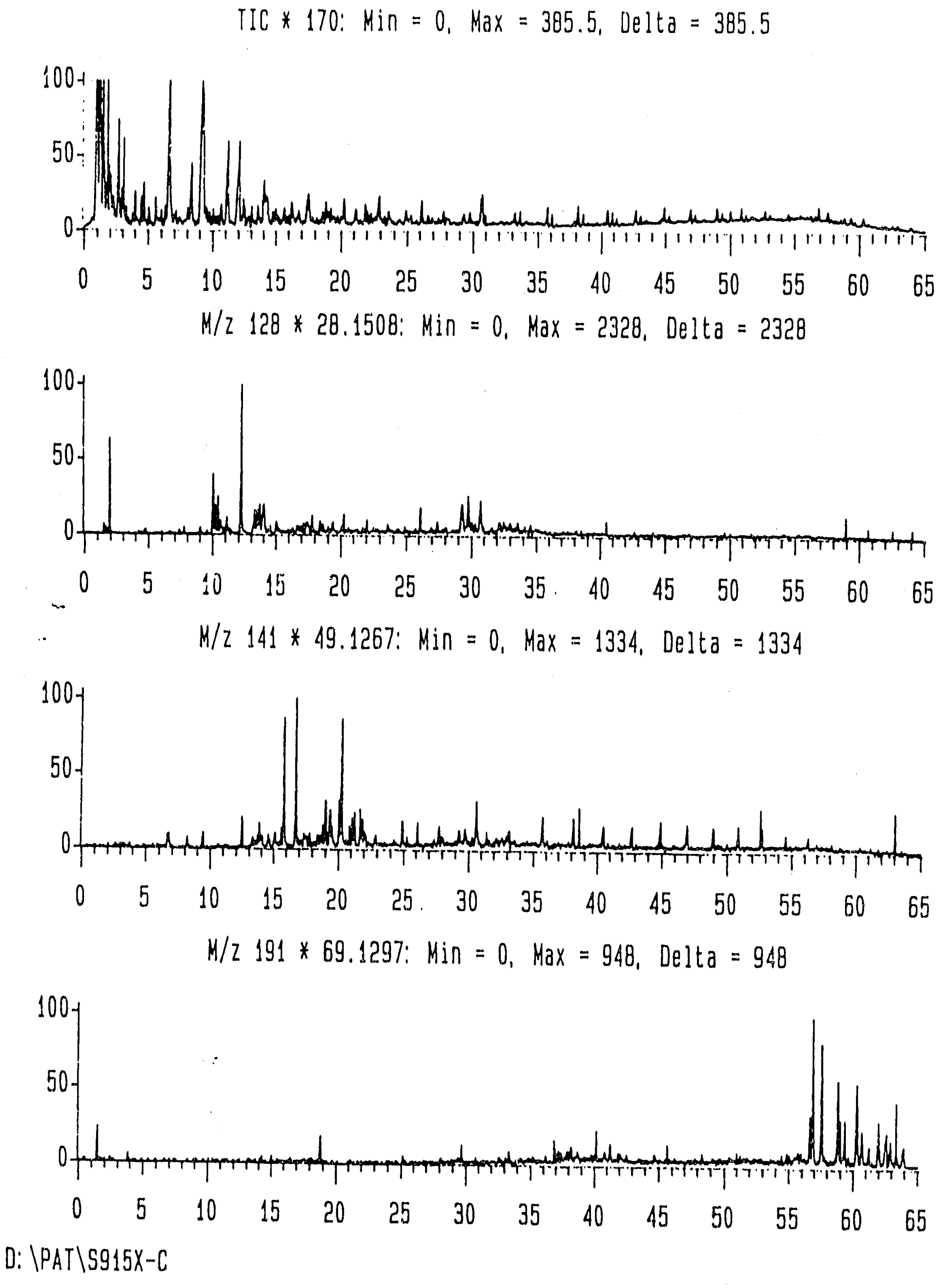


**Figure 2.5** Specific ion chromatograms (SIC) at m/z 128, 141 and 191 and total ion chromatogram (TIC) from Py-GC-MS of the THF-extracted DECS-9 Montana subbituminous coal (pyrolysis: 610°C for 10s; heating rate: 5 °C/ms).

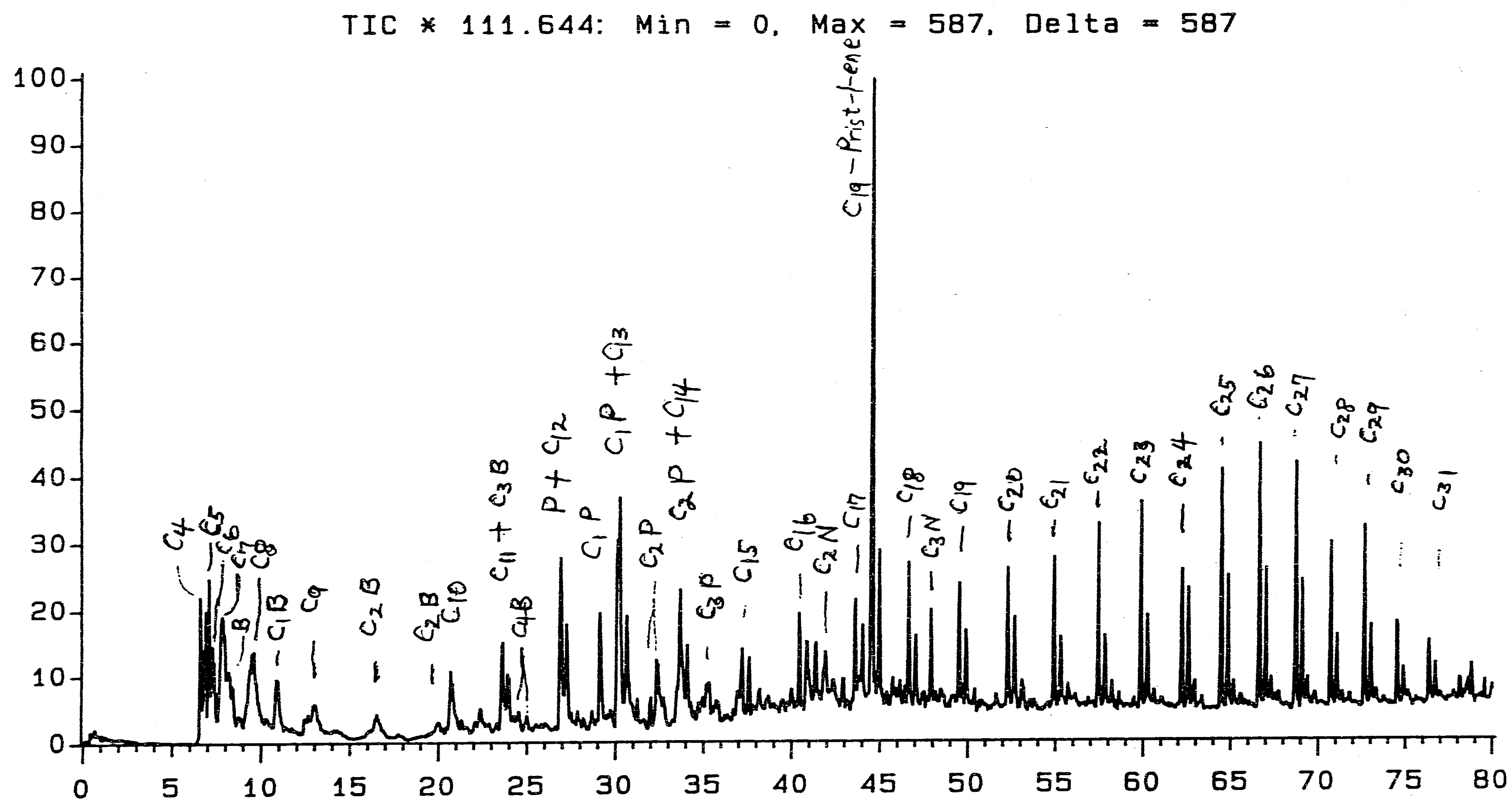


**Figure 2.6** Pyrolysis/GC/MS chromatogram of the Adaville #1 coal (DECS-7).

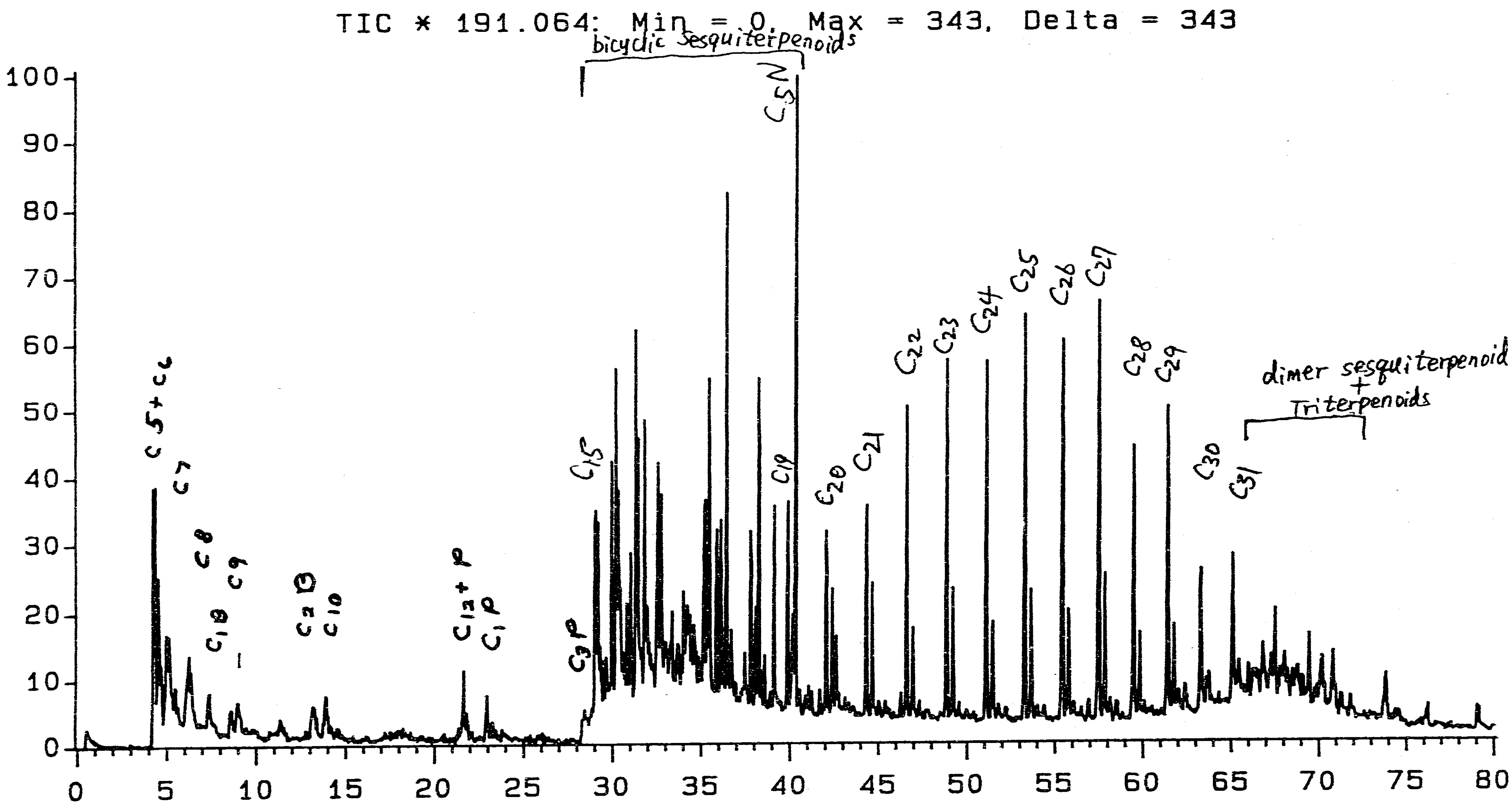


**Figure 2.7** Pyrolysis/GC/MS chromatogram of the Blind Canyon coal (DECS-6).

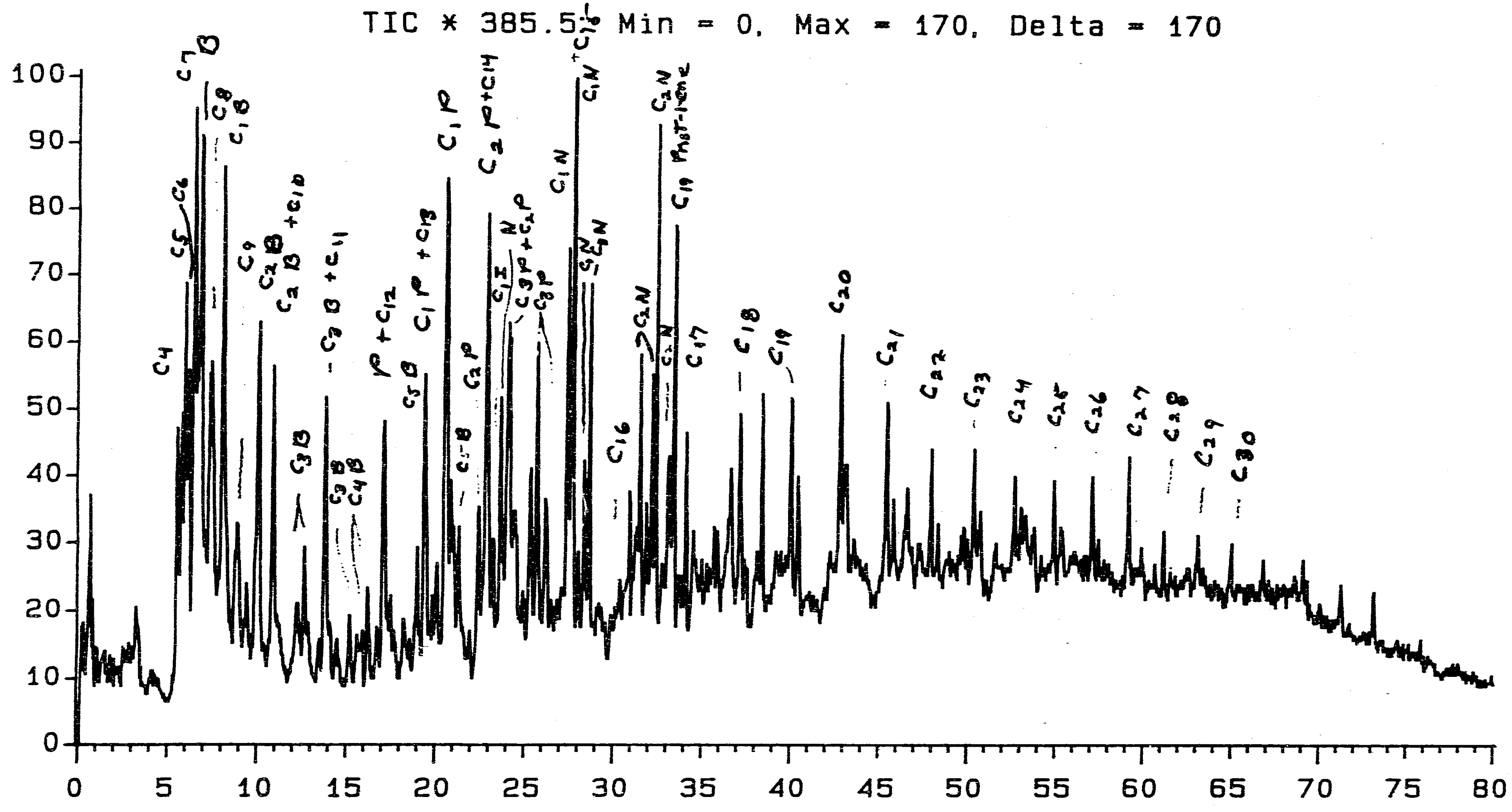


**Figure 2.8** Pyrolysis/GC/MS chromatogram of the Pittsburg #8 coal (DECS-7).

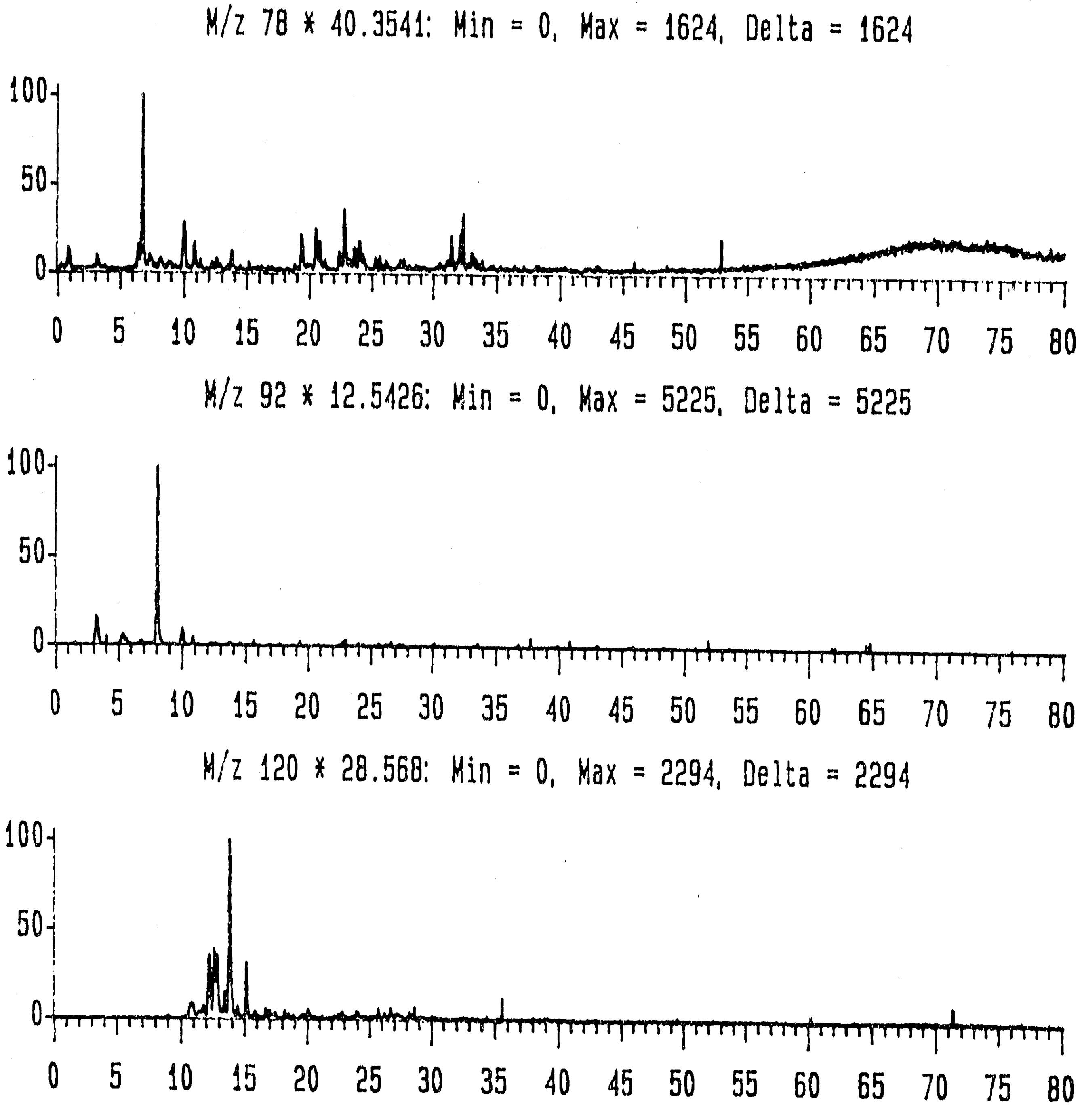


**Figure 2.9** Pyrolysis/GC/MS single ion chromatagrams representing the benzene/alkyl-benzene fraction from the Pittsburg #8 coal.

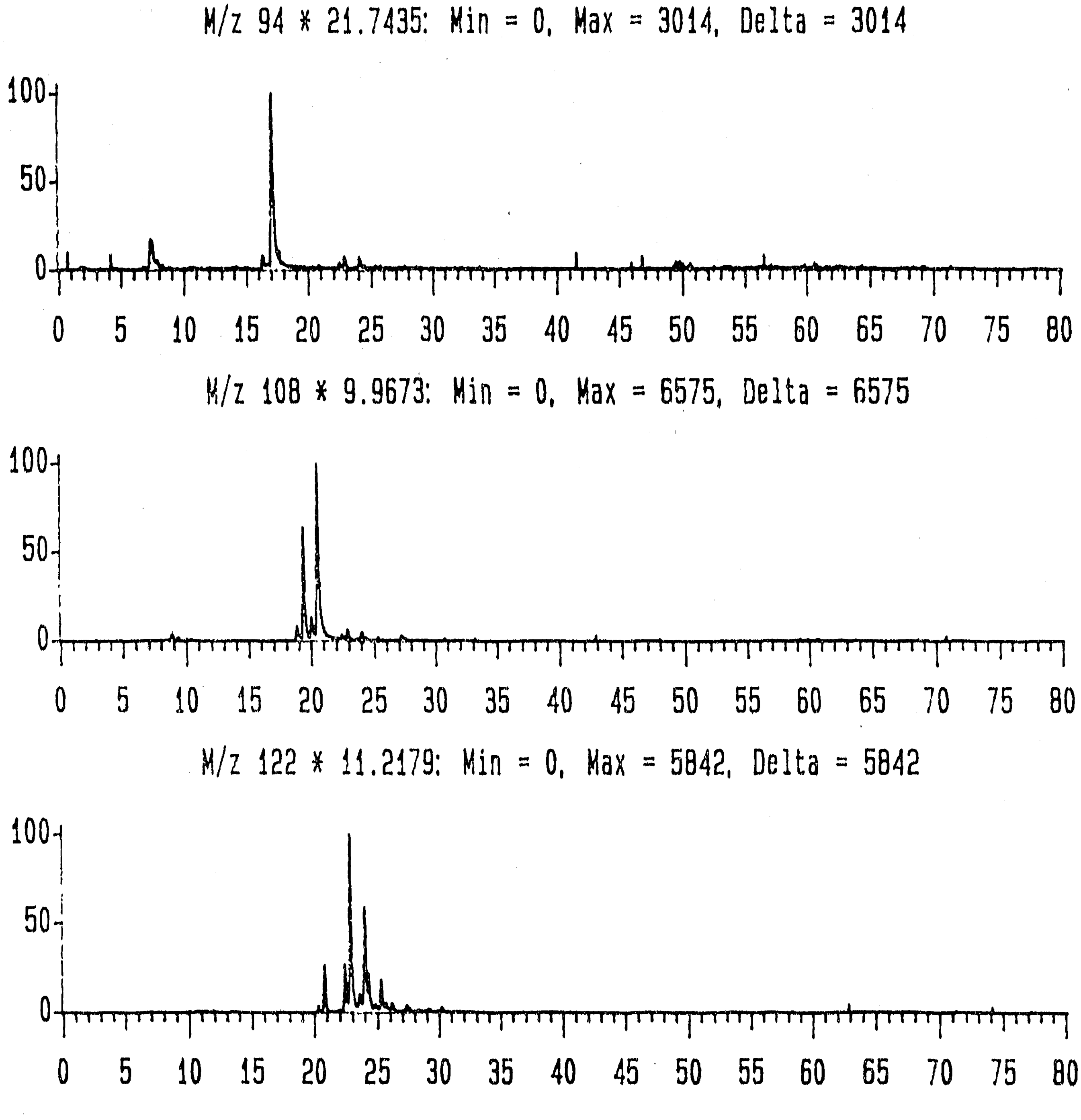


**Figure 2.10** Pyrolysis/GC/MS single ion chromatograms representing the phenol/alkyl-phenol fraction from the Pittsburg #8 coal.

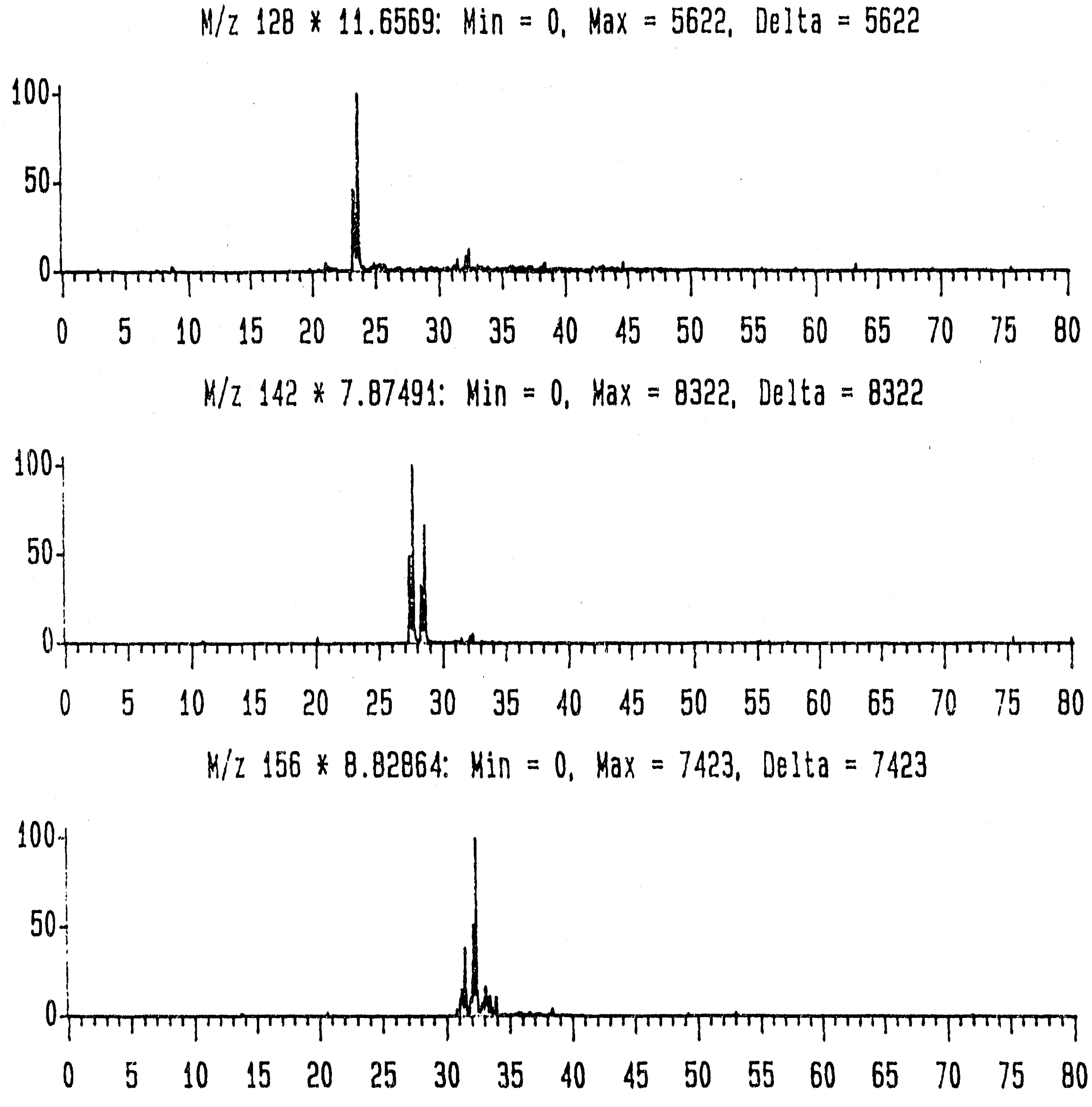


**Figure 2.11** Pyrolysis/GC/MS single ion chromatograms representing the naphthalene/alkyl-naphthalene fraction from the Pittsburg #8 coal.

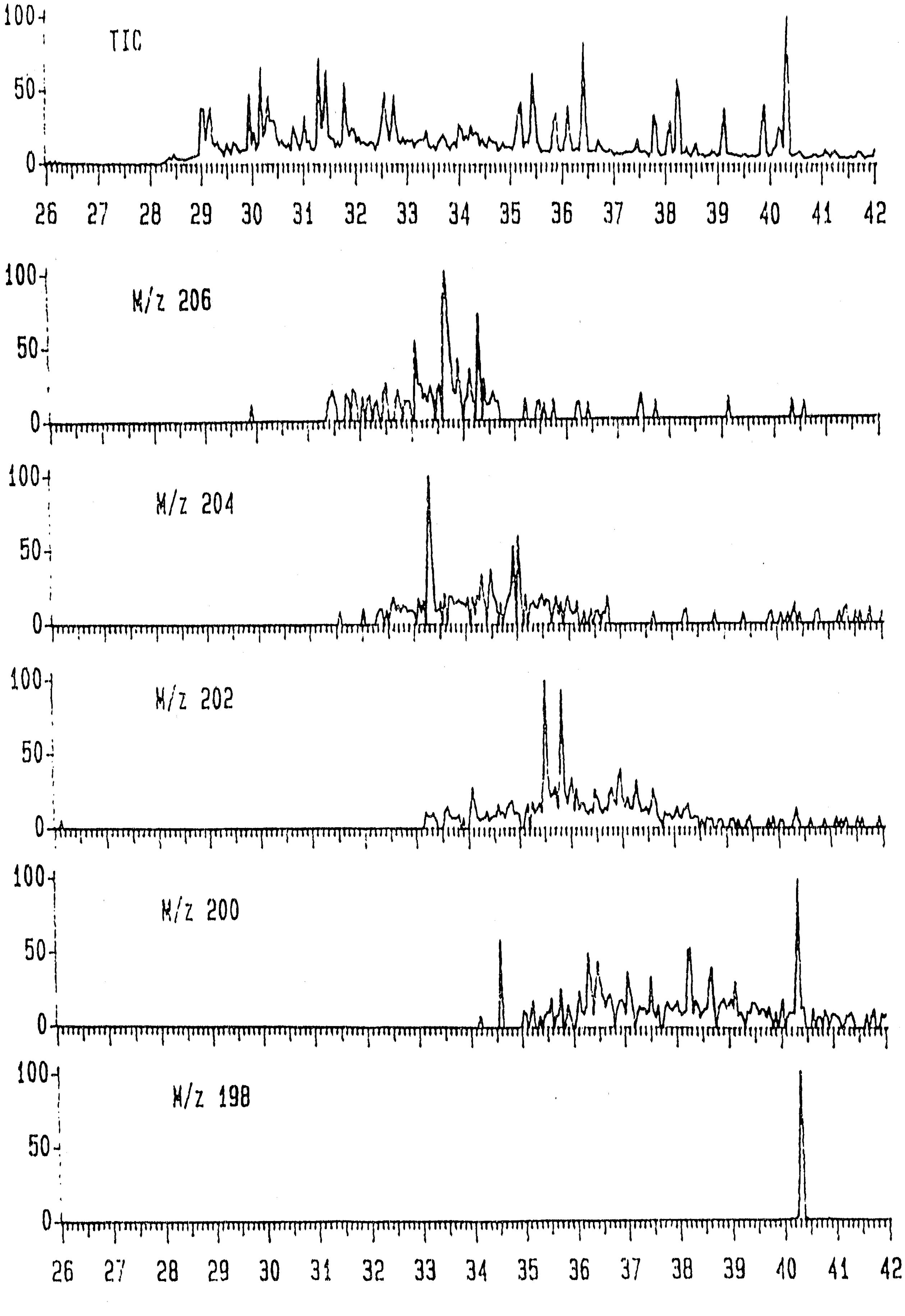


**Figure 2.12** Pyrolysis/GC/MS Tic and single ion chromatograms from the sequiterpanoid region of the Blind Canyon coal.

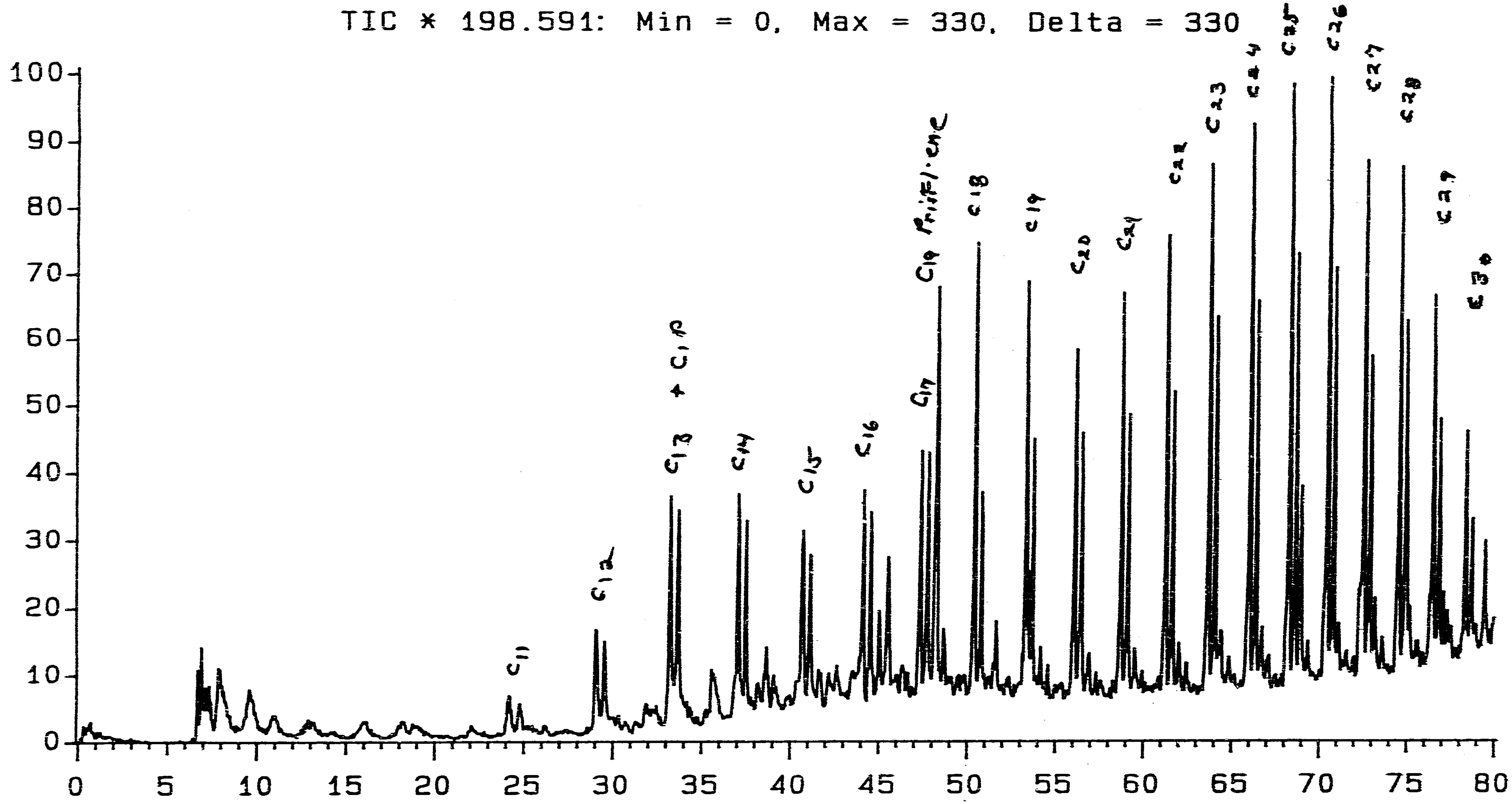


**Figure 2.13** Pyrolysis/GC/MS chromatogram of the thermally desorbed Blind Canyon coal.

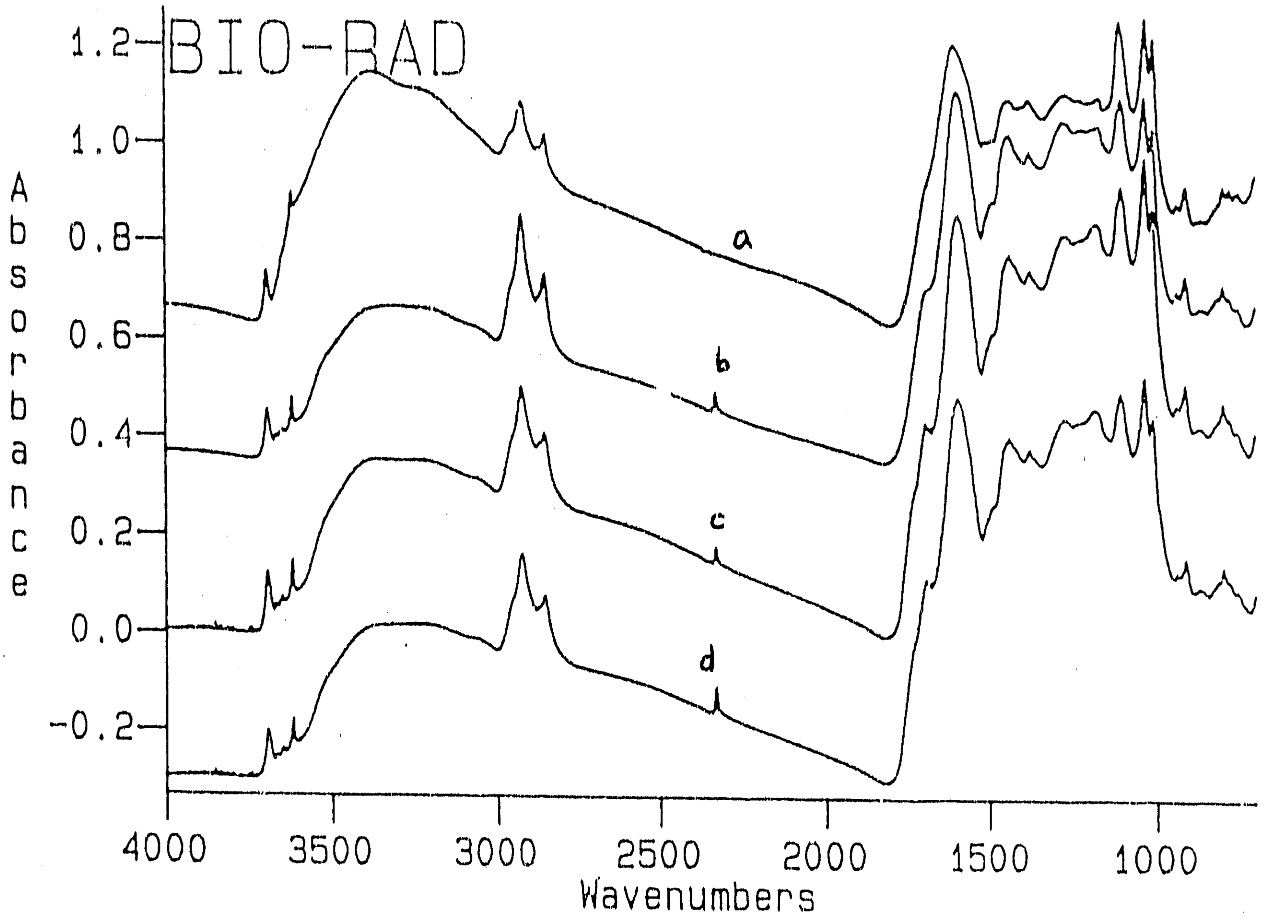


**Figure 4.1** FTIR spectra of
a) Undried and unextracted raw coal;
b) Dried and Unextracted raw coal;
c) Undried and THF-extracted raw coal;
d) Dried and THF-extracted raw coal.

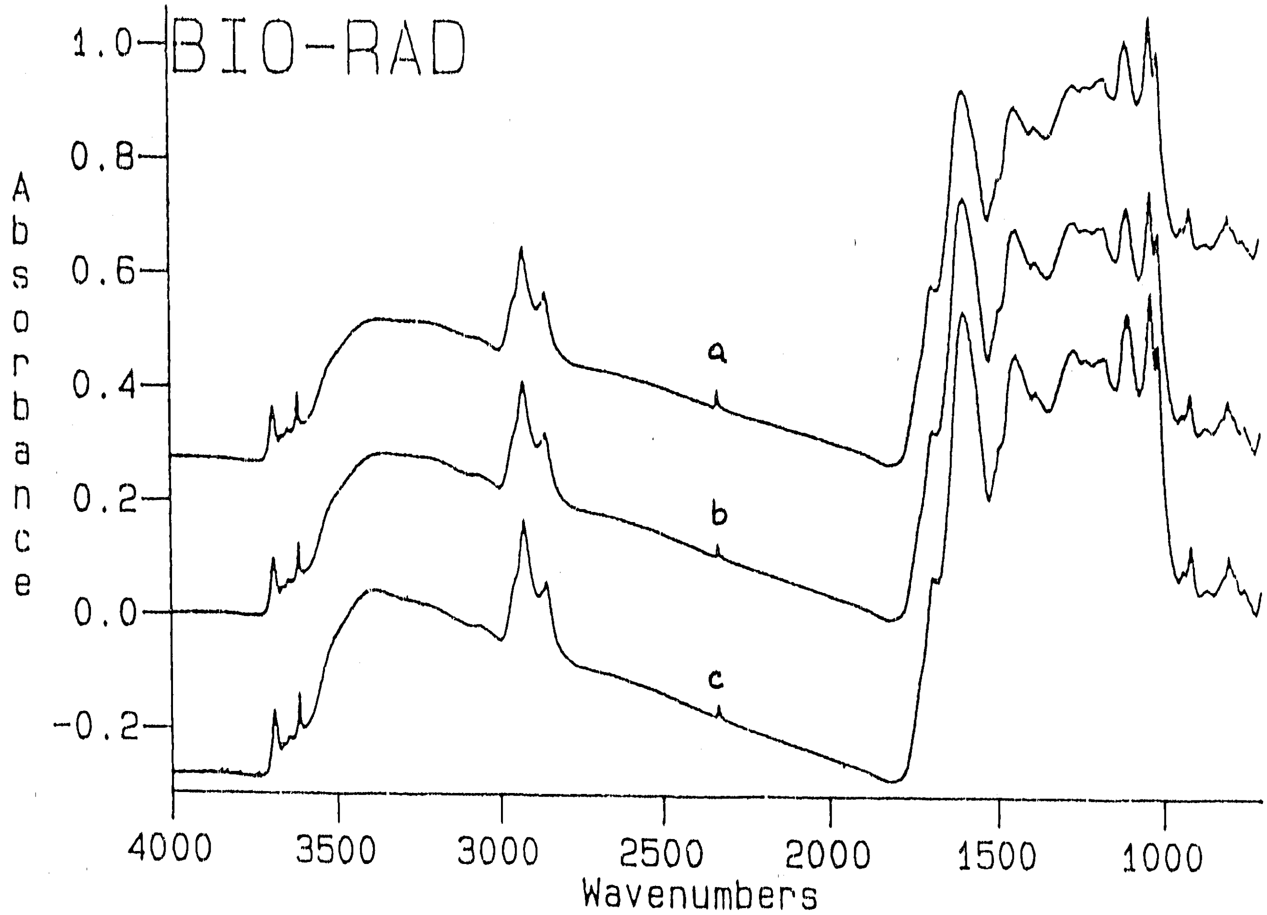


**Figure 4.2** FTIR spectra of the THF-extracted coal preliquefied coal at 300 °C without catalyst;
a) solvent free;
b) with tetralin as solvent;
c) with 1-methylnaphthalene as solvent.

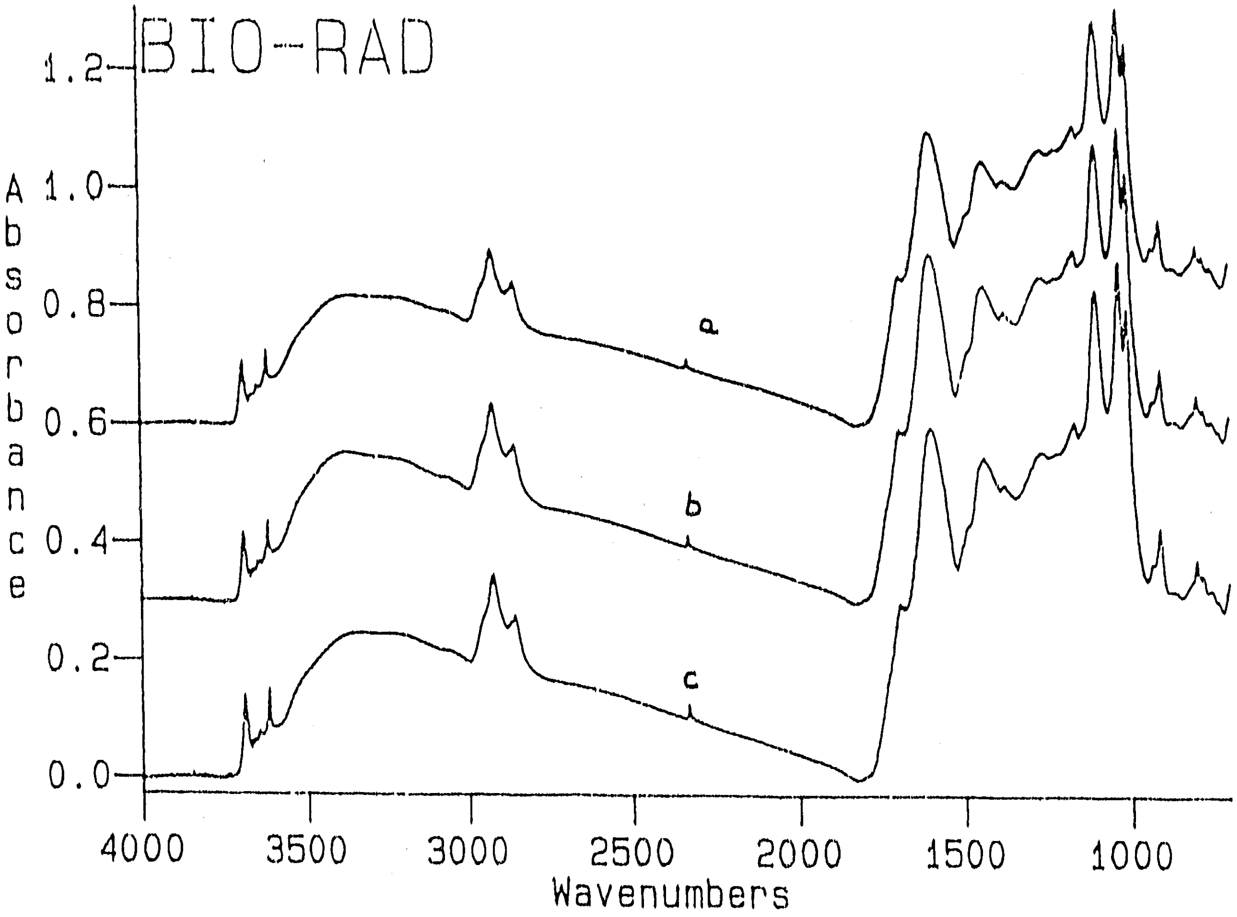


**Figure 4.3** FTIR spectra of the THF-extracted coal preliquefied at 300 °C in presence of ATTM;
a) solvent free;
b) with tetralin as solvent;
c) with 1-methylnaphthalene as solvent.

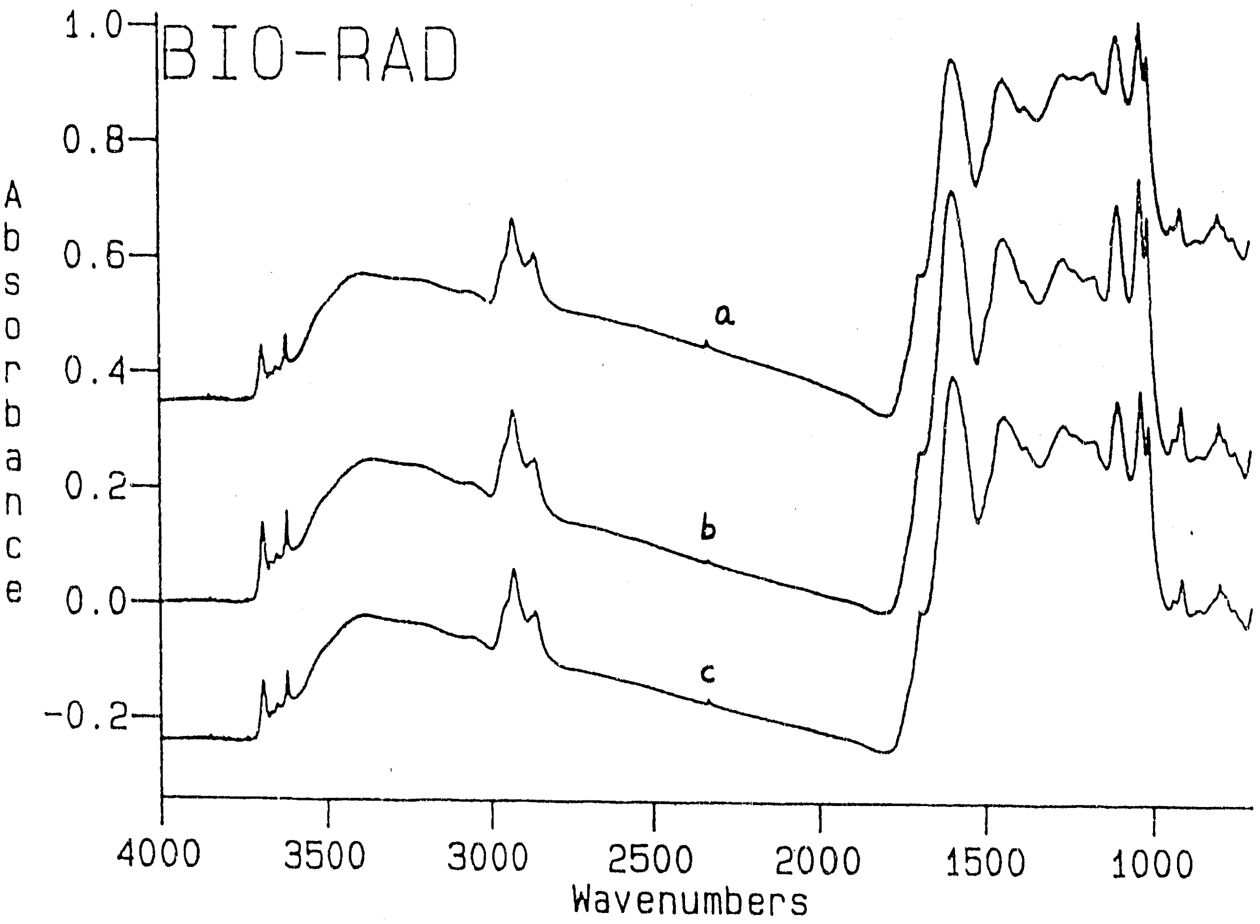


**Figure 4.4** FTIR spectra of the THF-extracted coal preliquefied at 350 °C without catalyst;
a) solvent free;
b) with tetralin as solvent;
c) with 1-methylnaphthalene as solvent.

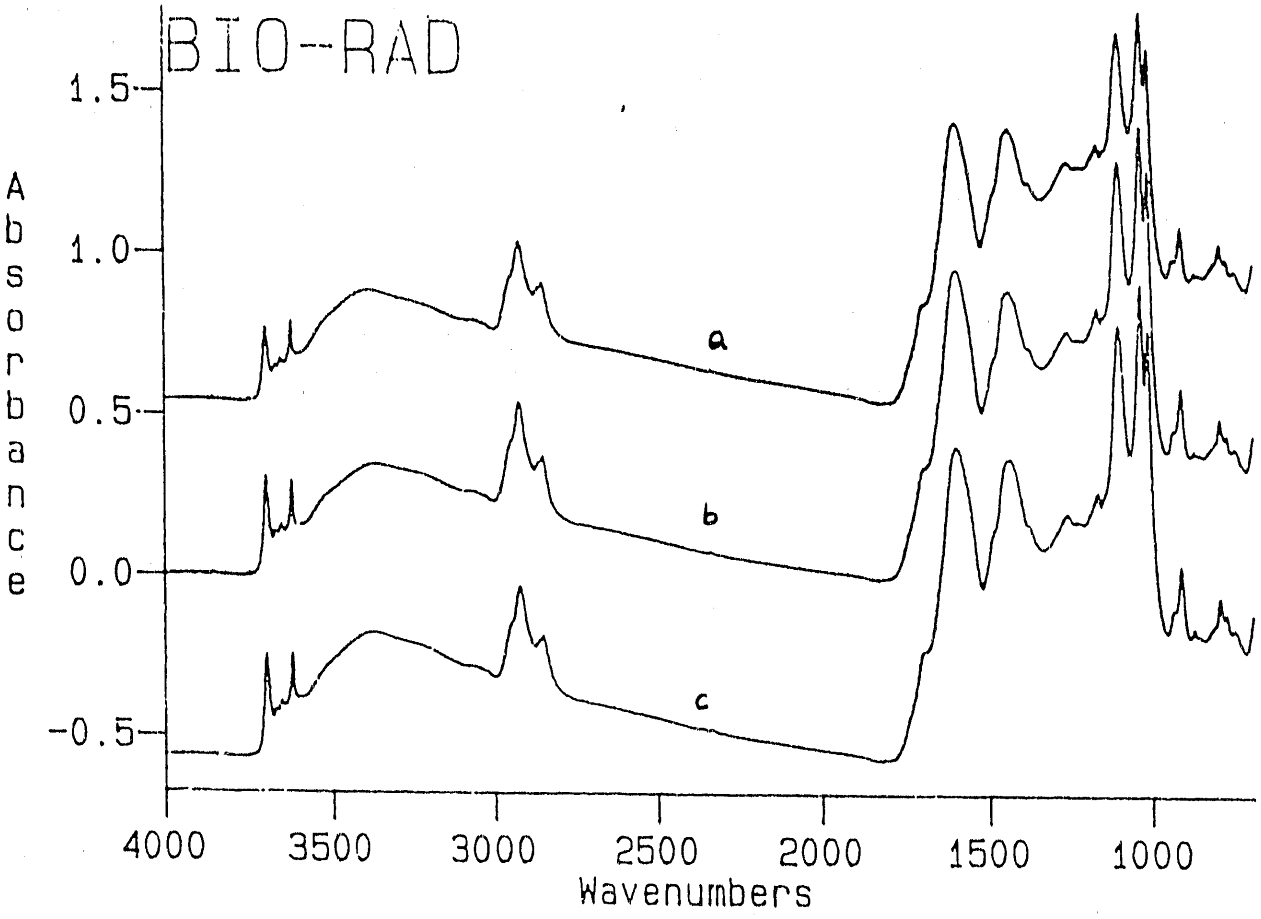


**Figure 4.5** FTIR spectra of the THF-extracted coal preliquefied at 350 °C in presence of ATTM;
a) solvent free;
b) with tetralin as solvent;
c) with 1-methylnaphthalene as solvent.

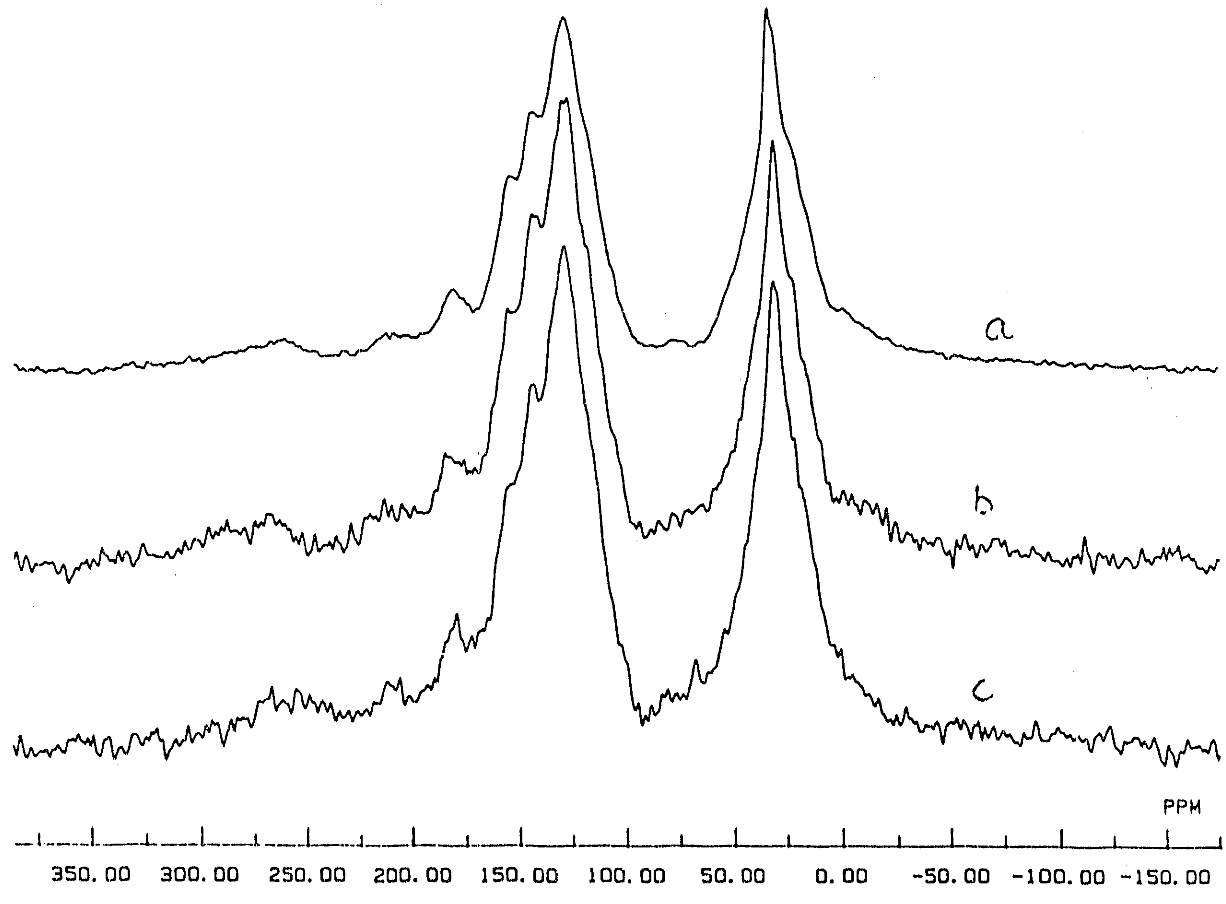


**Figure 4.6** CPMAS $^{13}C$ NMR spectra of the;
a) raw coal;
b) undried and THF-extracted raw coal;
c) dried and THF-extracted raw coal.

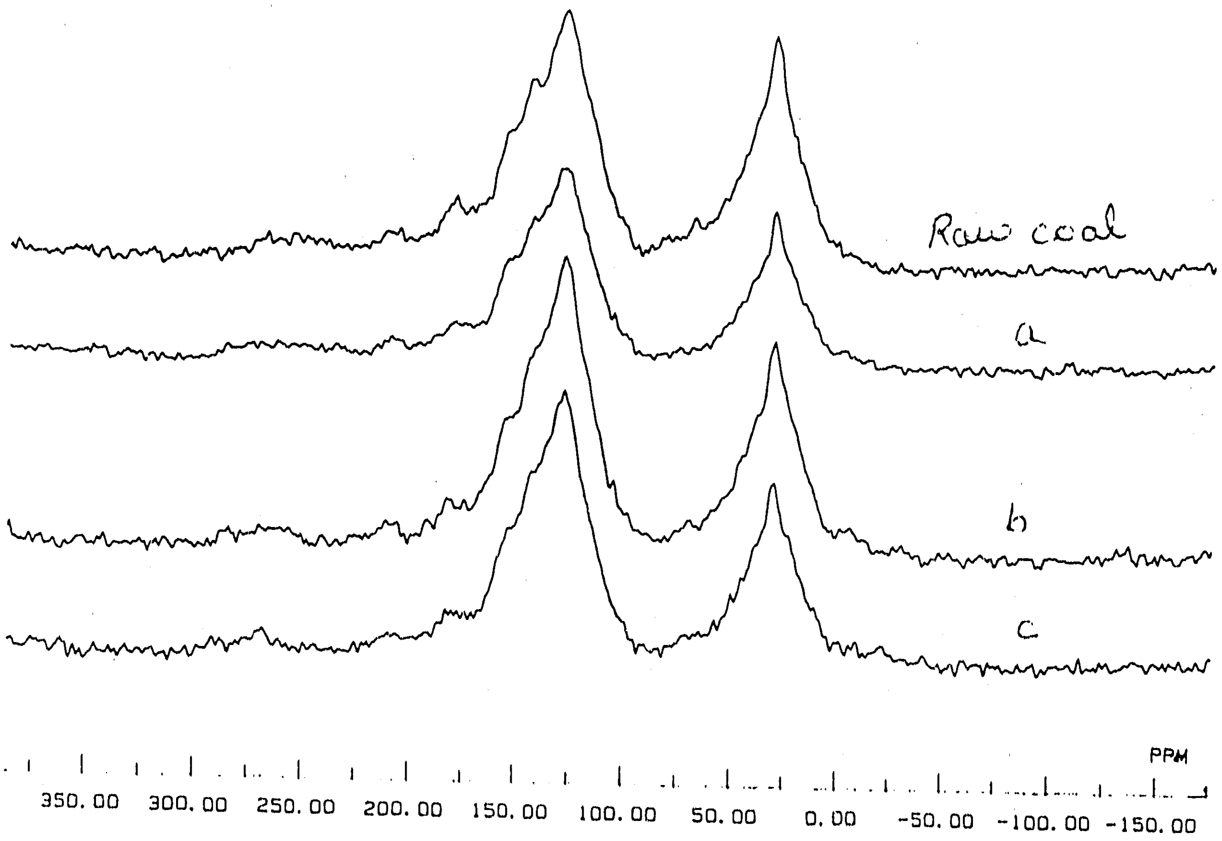


Figure 4.7 CPMAS $^{13}C$ NMR spectra of THF-insoluble residues from preliquefaction of coal at 300 °C without catalyst
a) solvent free;
b) with tetralin as solvent;
c) with 1-methylnaphthalene as solvent.

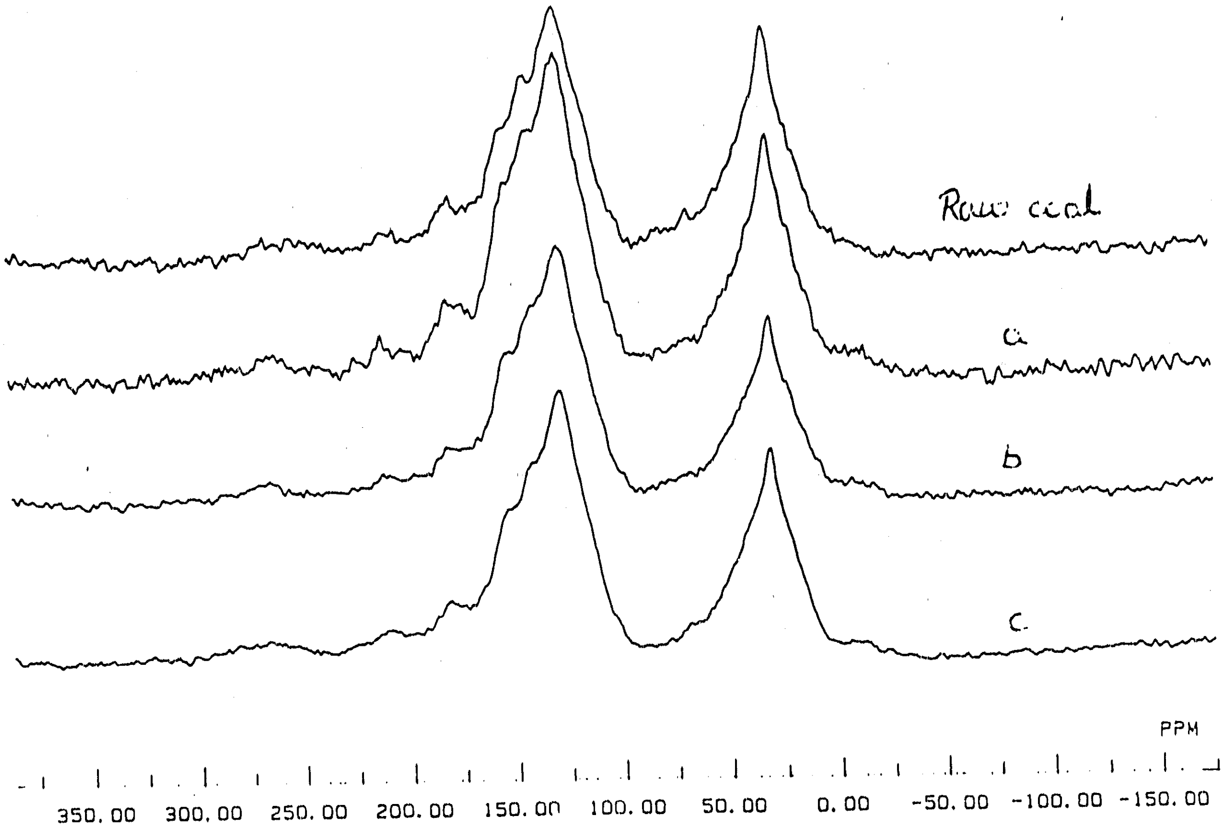


**Figure 4.8** CPMAS $^{13}C$ NMR spectra of THF-insoluble residues from preliquefaction of coal at 300 °C in presence of ATTM;

a) solvent free;
b) with tetralin as solvent;
c) with 1-methylnaphthalene as solvent.

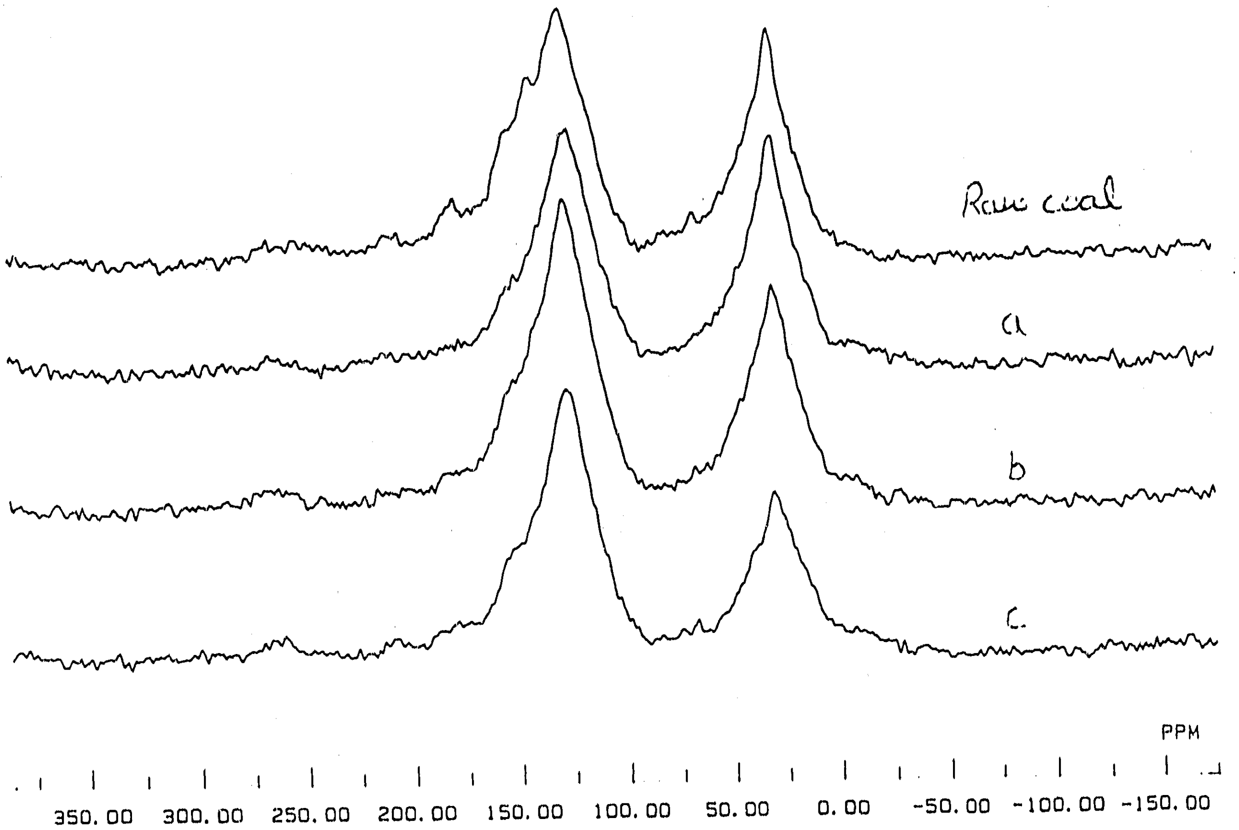


**Figure 4.9** CPMAS $^{13}$C NMR spectra of THF-insoluble residues from preliquefaction of coal at 350 °C without catalyst
a) solvent free;
b) with tetralin as solvent;
c) with 1-methylnaphthalene as solvent.

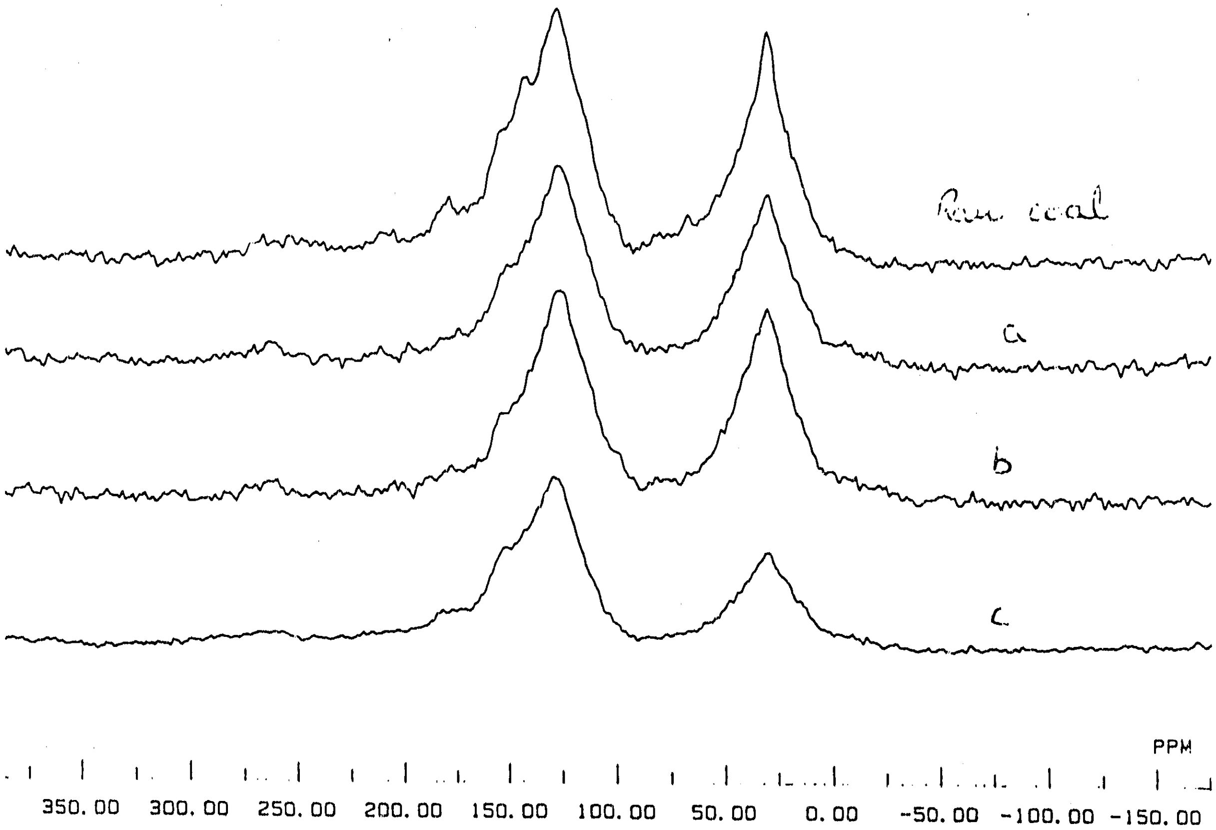


**Figure 4.10** CPMAS $^{13}C$ NMR spectra of THF-insoluble residues from preliquefaction of coal at 350 °C in presence of ATTM;
a) solvent free;
b) with tetralin as solvent;
c) with 1-methylnaphthalene as solvent.

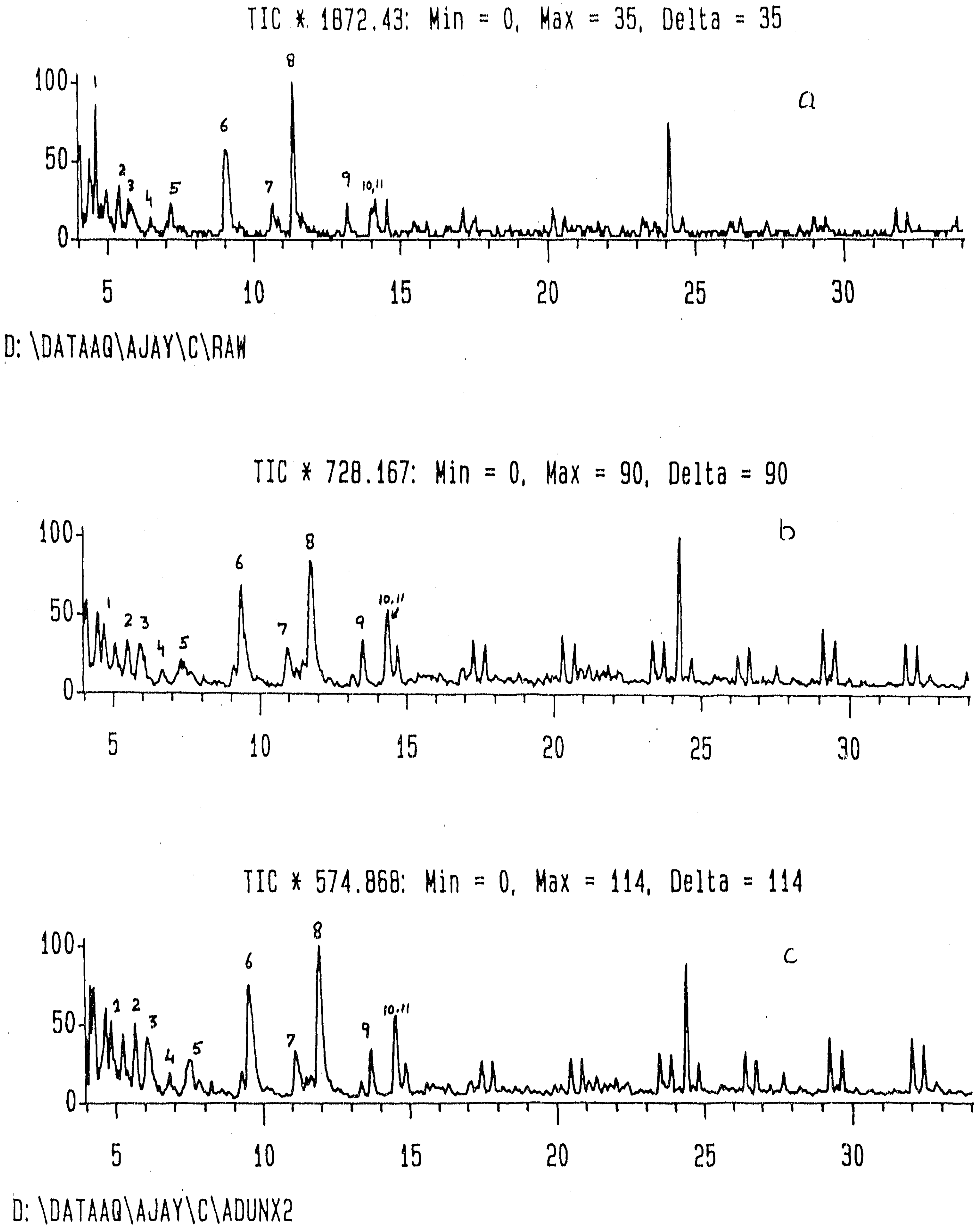


**Figure 4.11** Py-GC-MS profiles of a) raw coal; b) vacuum-dried and unextracted raw coal; c) air-dried and unextracted raw coal.

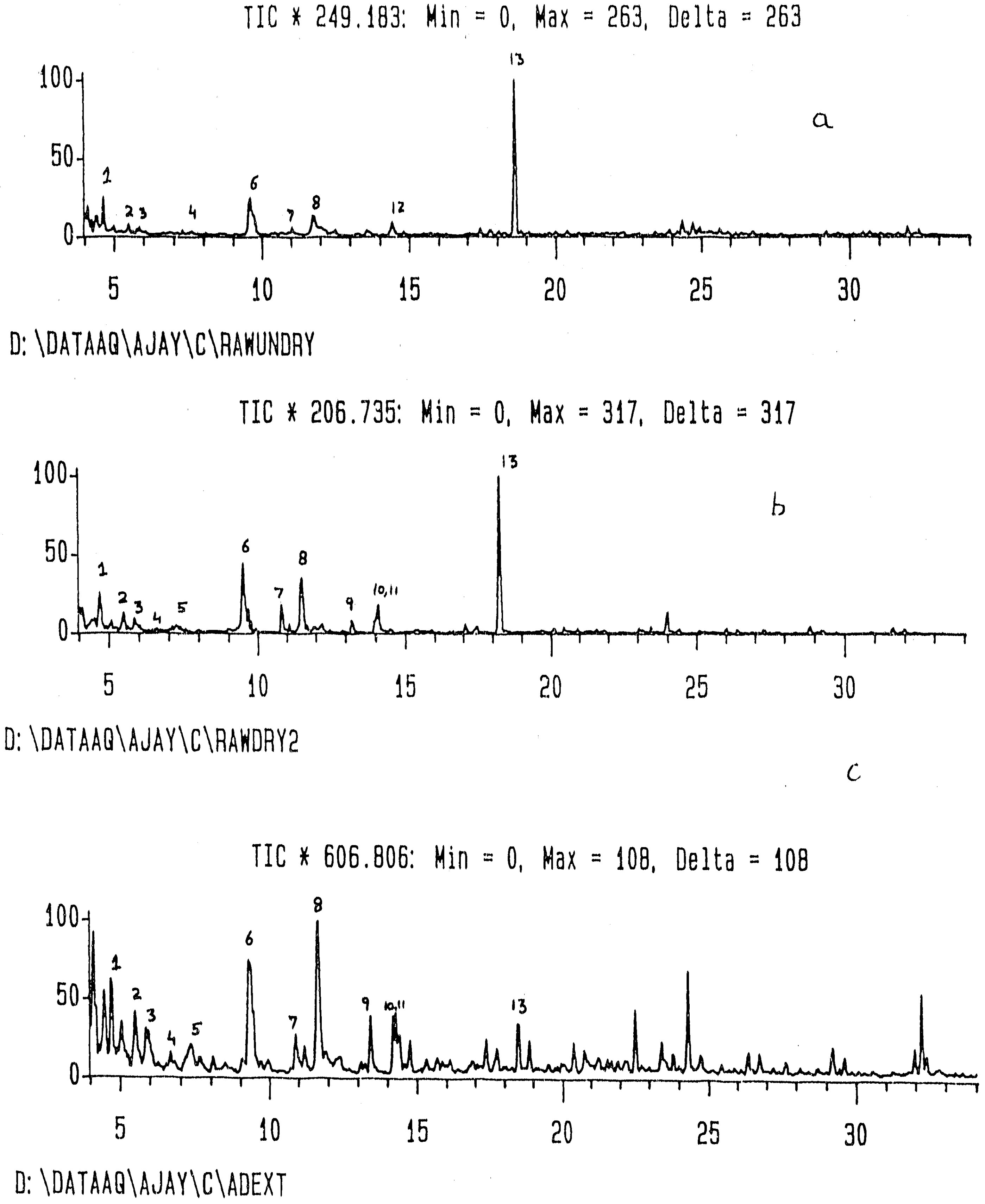


**Figure 4.12** Py-GC-MS profiles of the THF-extracted a) undried unreacted coal; b) vacuum dried unreacted coal; c) air-dried unreacted coal.

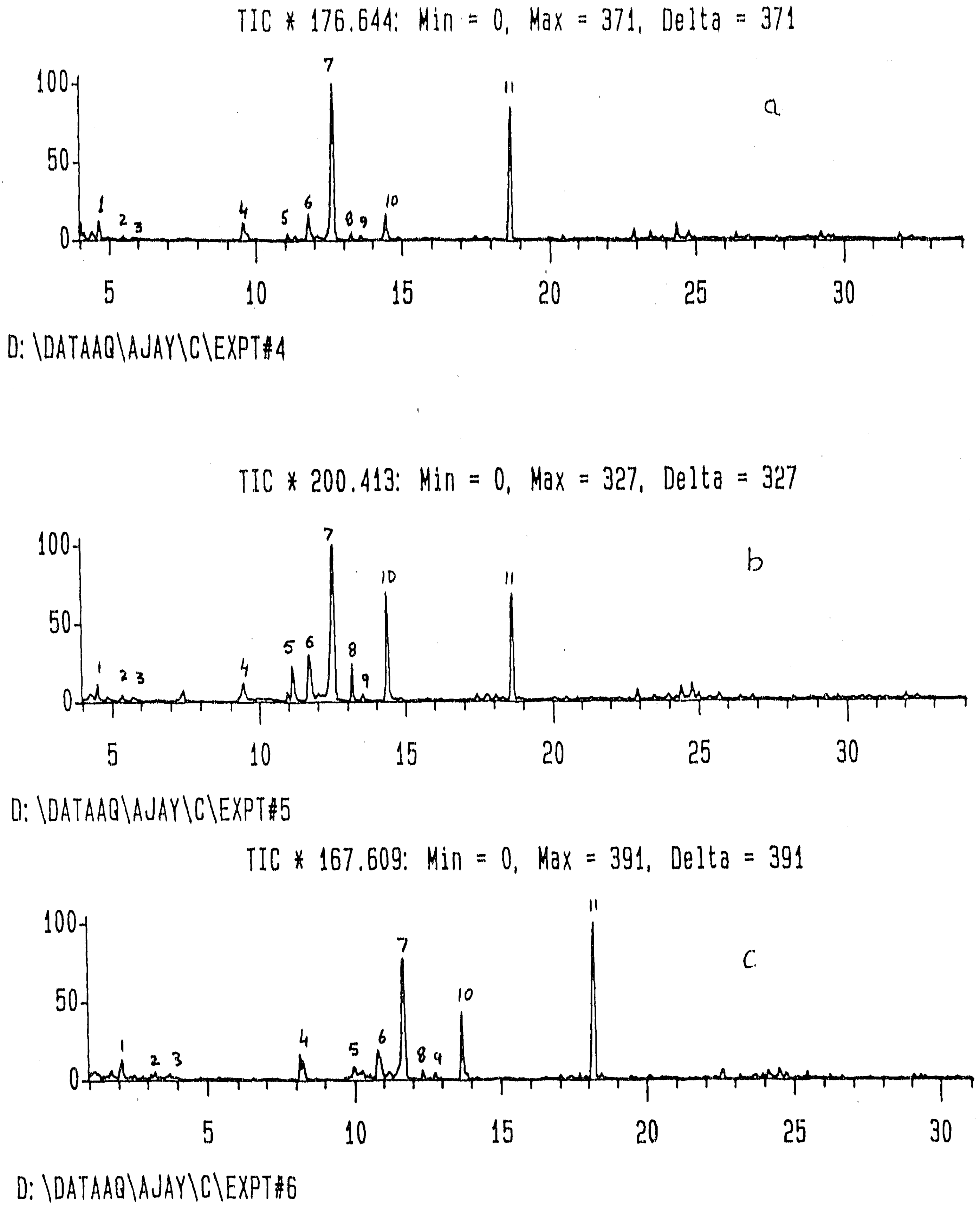


**Figure 4.13** Py-GC-MS profile of the THF-extracted coal reacted at 300 °C without catalyst a) solvent free; b) with tetralin; c) with 1-methylnaphthalene.

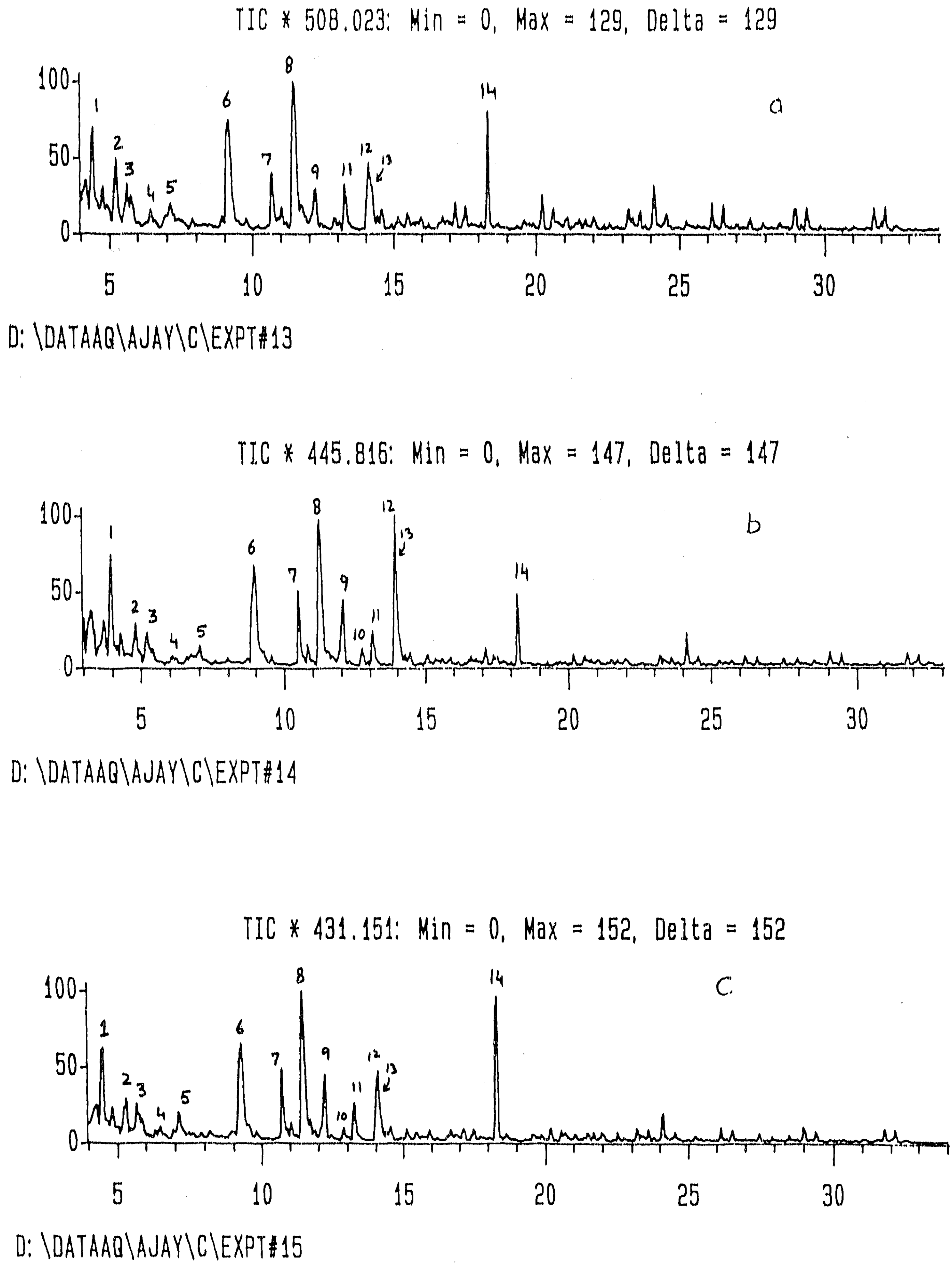


**Figure 4.14 .** Py-GC-MS profile of the THF-extracted coal reacted at 300 °C in presence of ATTM a) solvent free; b) with tetralin; c) with 1-methylnaphthalene.

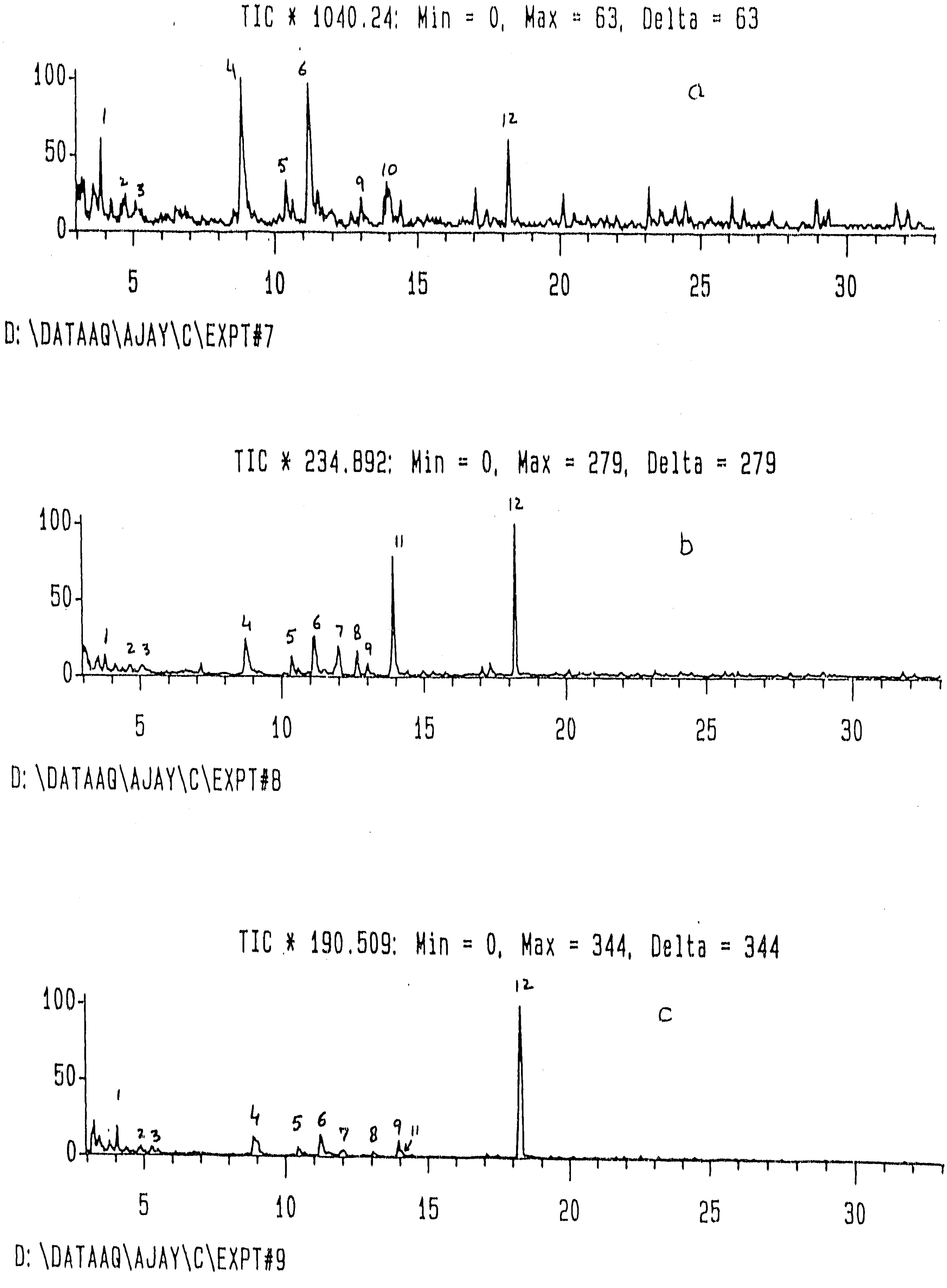


**Figure 4.15** Py-GC-MS profile of the THF-extracted coal reacted at 350 °C without catalyst a) solvent free; b) with tetralin; c) with 1-methylnaphthalene.

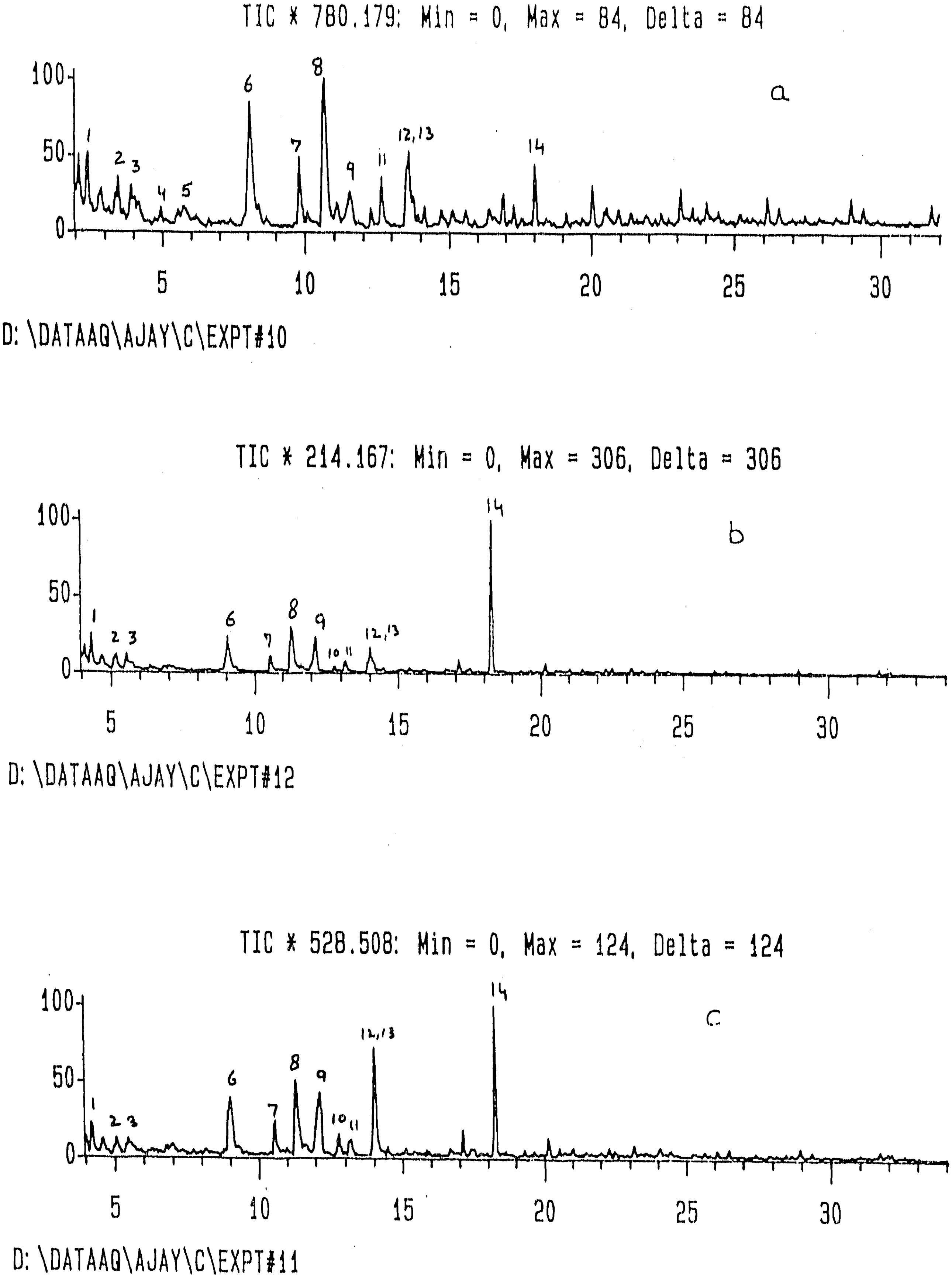


**Figure 4.16** Py-GC-MS profile of the THF-extracted coal reacted at 350 °C in presence of ATTM a) solvent free; b) with tetralin; c) with 1-methylnaphthalene.

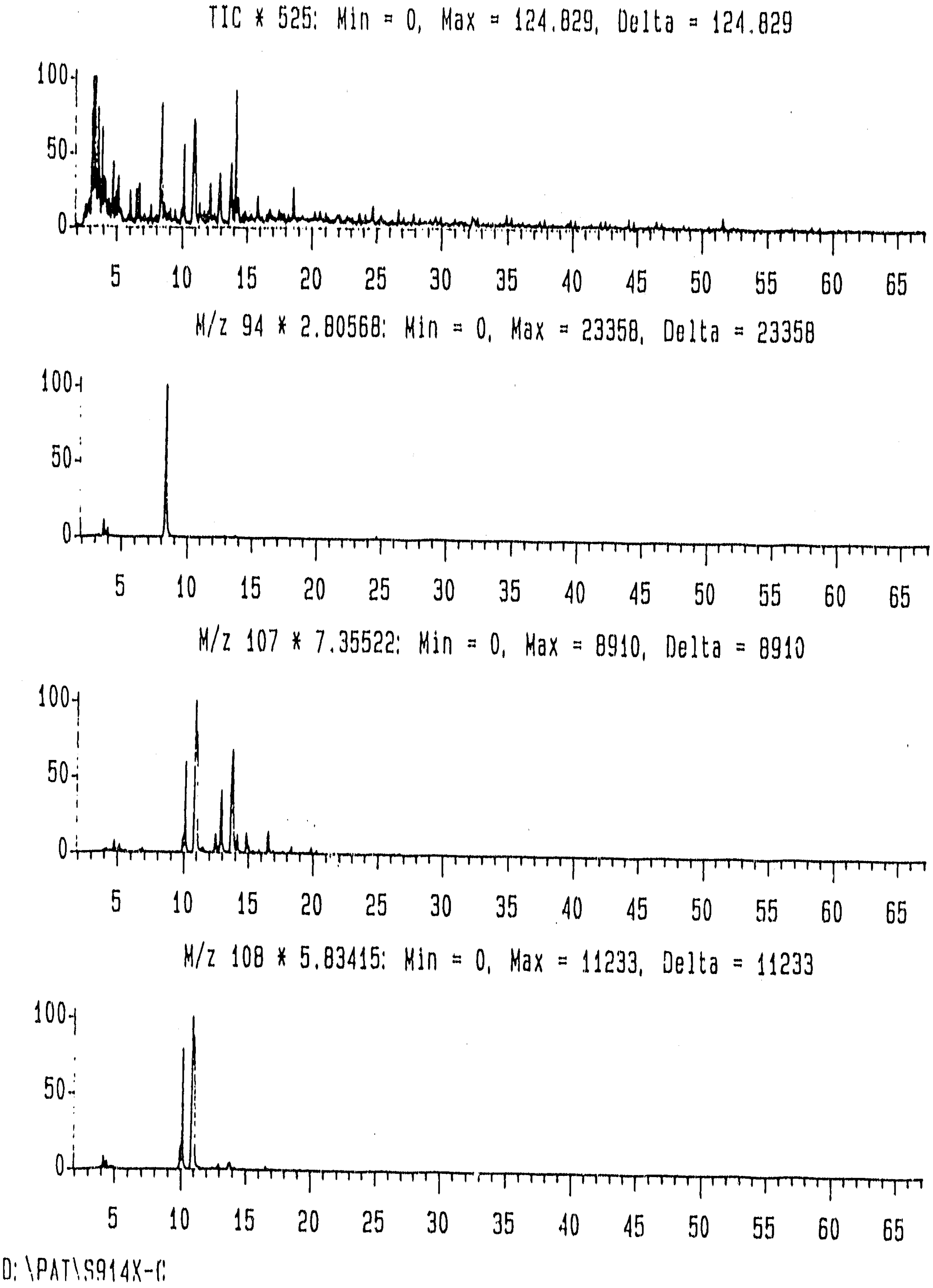


**Figure 4.17** Specific ion chromatograms (SIC) at m/z 94, 107 and 108 and total ion chromatogram (TIC) from Py-GC-MS of the THF-insoluble residue of DECS-9 Montana coal reacted in TPL at 300°C (pyrolysis: 610°C for 10s; heating rate: 5 °C/ms).

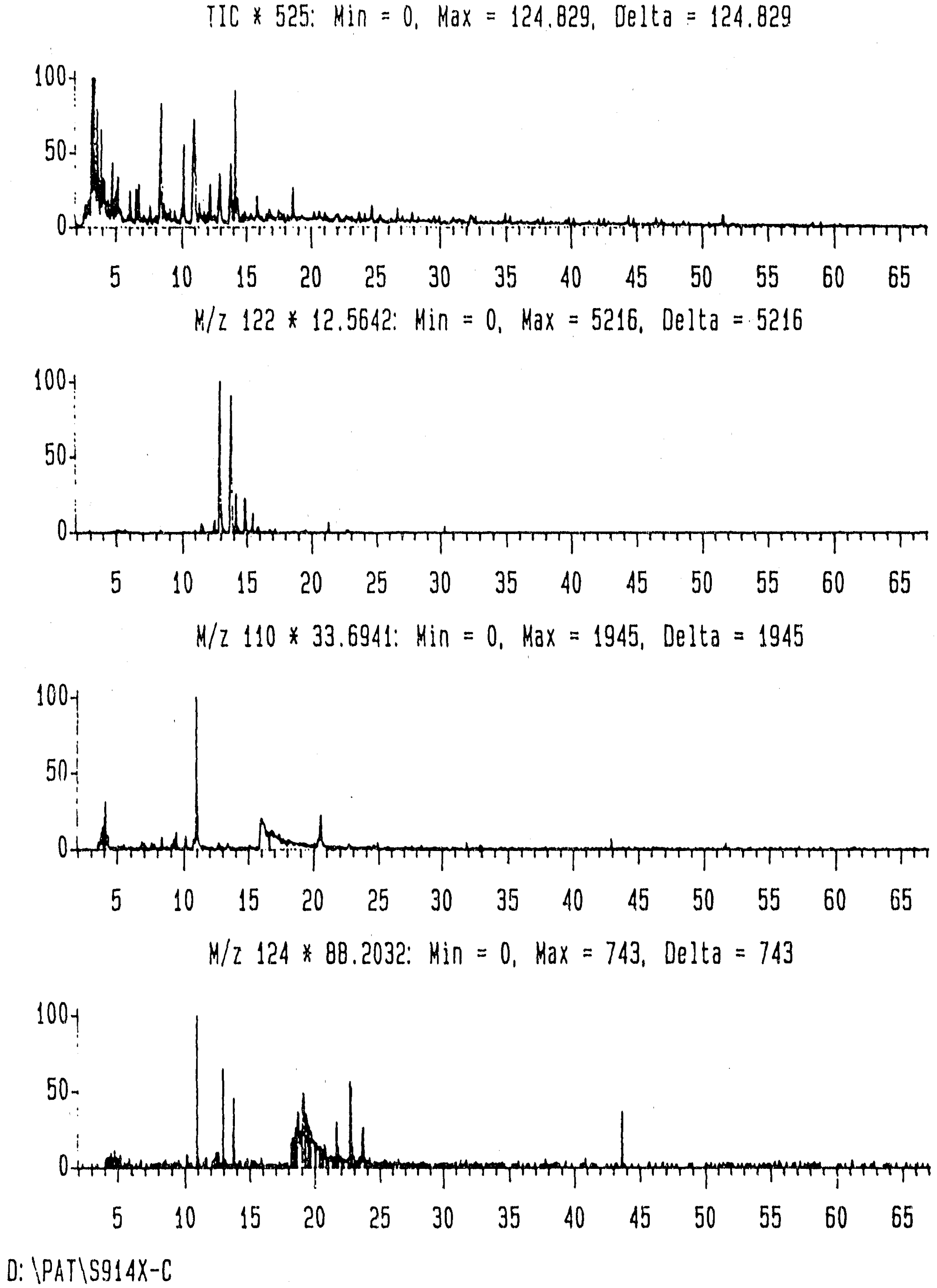
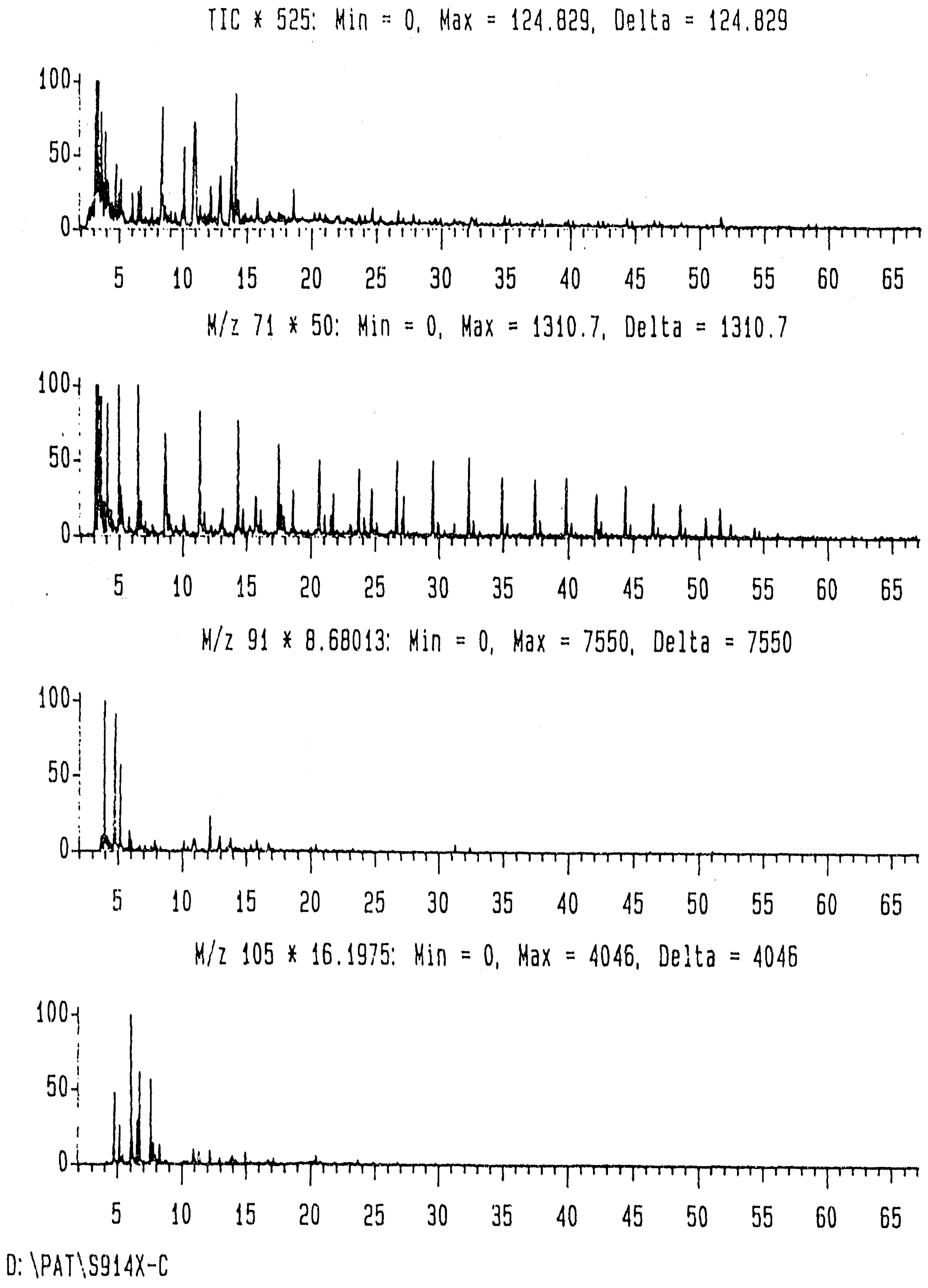


**Figure 4.18** Specific ion chromatograms (SIC) at m/z 122, 110 and 124 and total ion chromatogram (TIC) from Py-GC-MS of the THF-insoluble residue of DECS-9 Montana coal reacted in TPL at 300°C (pyrolysis: 610°C for 10s; heating rate: 5 °C/ms).


TIC * 525: Min = 0, Max = 124.829, Delta = 124.829

M/z 71 * 50: Min = 0, Max = 1310.7, Delta = 1310.7

M/z 91 * 8.68013: Min = 0, Max = 7550, Delta = 7550

M/z 105 * 16.1975: Min = 0, Max = 4046, Delta = 4046

**Figure 4.19** Specific ion chromatograms (SIC) at m/z 71, 91 and 105 and total ion chromatogram (TIC) from Py-GC-MS of the THF-insoluble residue of DECS-9 Montana coal reacted in TPL at 300°C (pyrolysis: 610°C for 10s; heating rate: 5 °C/ms).

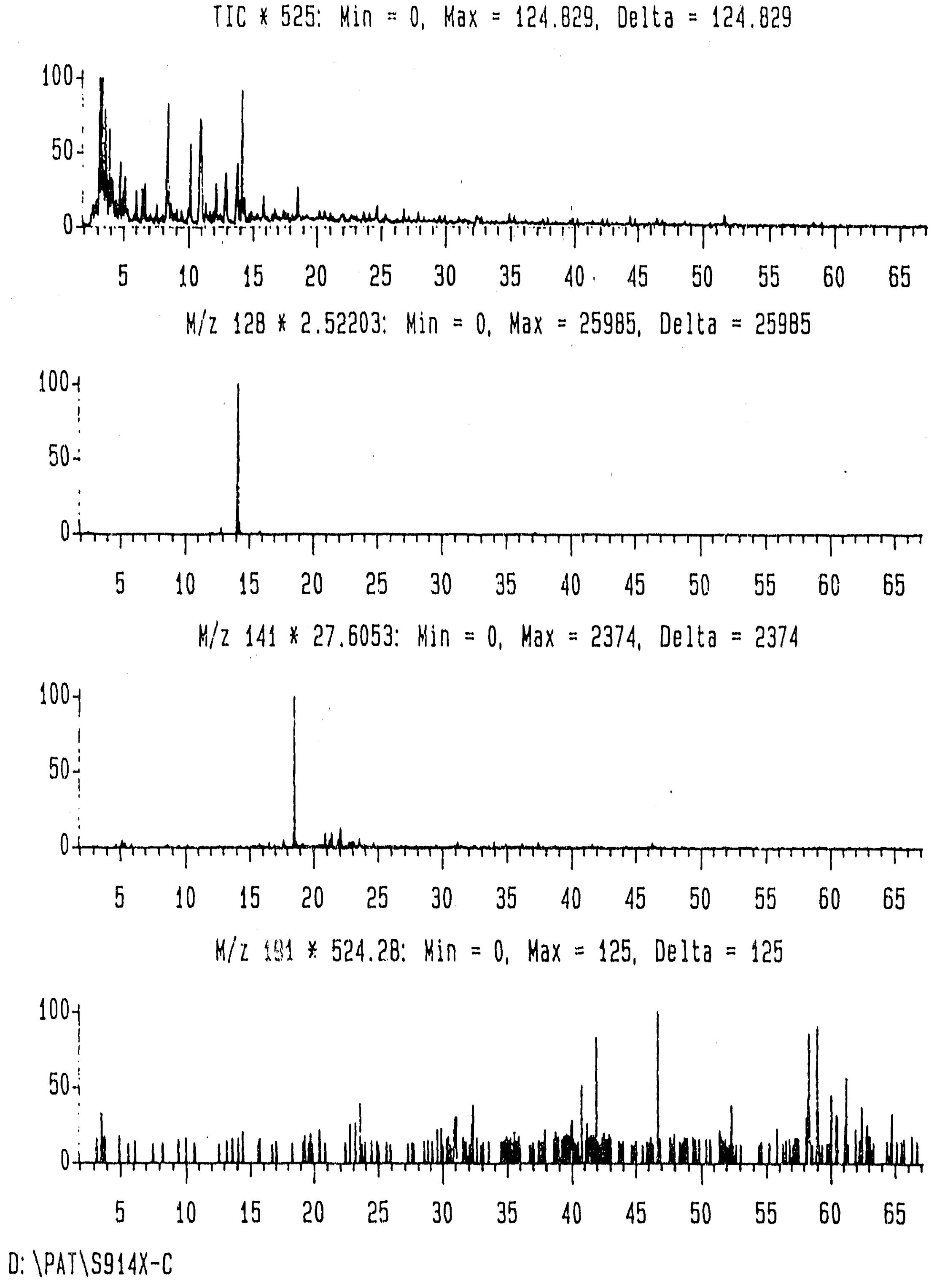


**Figure 4.20** Specific ion chromatograms (SIC) at m/z 128, 141 and 191 and total ion chromatogram (TIC) from Py-GC-MS of the THF-insoluble residue of DECS-9 Montana coal reacted in TPL at 300°C (pyrolysis: 610°C for 10s; heating rate: 5 °C/ms).

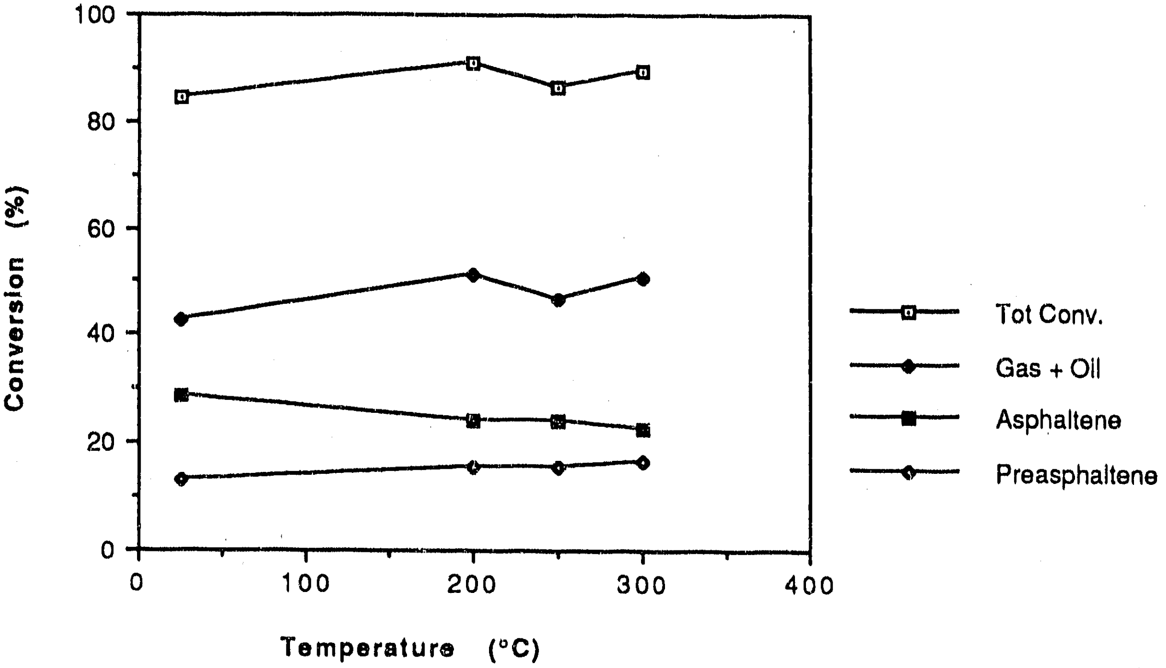


**Figure 5.1.** Conversion as a function of first stage temperature in temperature-programmed liquefaction (TPL) of DECS-9 coal.

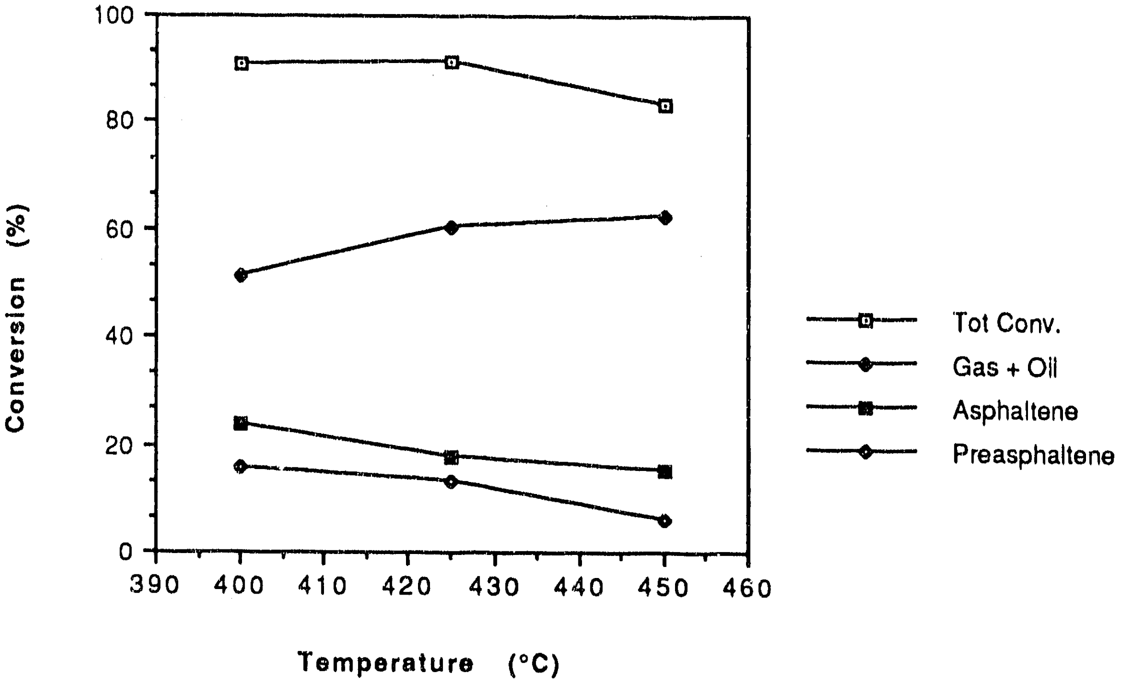


**Figure 5.2.** Conversion as a function of second stage temperature in temperature-programmed liquefaction (TPL) of DECS-9 coal.

# Appendix 1

## Complete Data Sheets for Eight Coals Selected

| | | |
|---|---|---|
| DECS-1 | Texas (Bottom) Lignite/Subbituminous | (74.3%C) |
| DECS-5 | Hiawatha Bituminous | (79.5%C) |
| DECS-6 | Blind Canyon Bituminous | (81.3%C) |
| DECS-7 | Wyoming (Adaville) Subbituminous/Bituminous | (77.1%C) |
| DECS-8 | Wyodak (Smith-Roland) Subbituminous | (75.8%C) |
| DECS-9 | Montana (Diez) Subbituminous | (76.1%C) |
| DECS-11 | North Dakota (Beulah) Lignite | (74.2%C) |
| DECS-12 | Pittsburgh #8 Bituminous | (84.8%C) |

```
SAMPLE IDENTIFICATION:                                         SAMPLE LOCATION:                  ** PENN STATE COAL DATA BASE **
------ ---------------                                         ------ ---------                                **                   **
   PSU NUMBER              -> DECS-1                                COUNTRY        -> USA                   **   DECS-1          **
   SEAM NAME               -> BOTTOM                                                                        **                   **
   ALTERNATE SEAM NAME     ->                                       STATE          -> TEXAS                 **   12/02/91        **
   APPARENT RANK           -> SUBBIT C                                                                      **   PAGE  2         **

                                        * * * * *  C H E M I C A L   D A T A  * * * * *

PROXIMATE ANALYSIS     AS REC'D      DRY        DAF       DMMF(PARR)

  % MOISTURE            30.00                                           % EQUILIBRIUM MOISTURE = 31.47

  % ASH                 11.07       15.81                                                MM-FREE = 35.89

  % VOLATILE            33.18       47.40      56.30       55.52

  % FIXED CARBON        25.75       36.79      43.70       44.48


ULTIMATE ANALYSIS      AS REC'D      DRY        DAF       DMMF(PARR)    ELEMENTAL ANALYSIS     DRY     DMMF(MOD.P)  DMMF(DIR.)

  % ASH                 11.07       15.81                 (17.62%MM)                                  (17.97%MM)   (      %MM)

  % CARBON              43.77       62.53      74.27       75.90         % CARBON             62.45      76.13

  % HYDROGEN             3.32 (*)    4.75       5.64        5.77         % HYDROGEN            4.55       5.54

  % NITROGEN             0.86        1.23       1.46        1.49         % NITROGEN            1.23       1.50

  % TOTAL SULFUR         0.69        0.99       1.18                     % ORGANIC SULFUR      0.86       1.05

  % OXYGEN(DIFF)        10.28 (*)   14.69      17.45       16.84         % OXYGEN(DIFF)       12.94      15.78

                   (*)-EXCLUDES MOISTURE                                 % MINERAL MATTER     17.97
                                                                          (INCL.  0.21% FES2)

SULFUR FORMS          % PYRITIC   % SULFATIC   % ORGANIC   % TOTAL      DRY % CHLORINE =  0.11    DRY % CO2 =  0.29

    DRY                 0.11        0.02        0.86        0.99        MOTT-SPOONER DIFFERENCE =  -115.

    DAF                 0.13        0.02        1.02        1.18

                                   AS REC'D     EQUIL.
CALORIFIC VALUE         DRY         MOIST.      MOIST.                 ATOM RATIOS (DMMF)       PARR     MOD.PARR     DIRECT
(GROSS. BTU/LB)

  MM-CONTAINING        10956.       7669.       7508.                   ATOMIC H/C            0.9124     0.8744

  MM-FREE (PARR)       13239.       8709.       8501.                   ATOMIC O/C            0.1665     0.1556

  MM-FREE (MOD. P)     13349.       8768.       8558.

  NET CV, DMMF BTU/LB  12812.
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SAMPLE IDENTIFICATION:                                        SAMPLE LOCATION:                ** PENN STATE COAL DATA BASE **
------ ---------------                                        ------ ---------                **                          **
   PSU NUMBER             -> DECS-5                              COUNTRY      -> USA           **   DECS-5                 **
   SEAM NAME              -> HIAWATHA                                                          **                          **
   ALTERNATE SEAM NAME    ->                                     STATE        -> UTAH          **   12/02/91               **
   APPARENT RANK          ->   HVC                                                             **   PAGE  2                **

                                   * * * * *  C H E M I C A L   D A T A  * * * * *

PROXIMATE ANALYSIS    AS REC'D     DRY        DAF     DMMF(PARR)

  % MOISTURE            7.54                                        % EQUILIBRIUM MOISTURE =  7.88

  % ASH                 7.90       8.54                                            MM-FREE =  8.66

  % VOLATILE           37.29      40.33      44.10      43.58

  % FIXED CARBON       47.27      51.13      55.90      56.42


ULTIMATE ANALYSIS     AS REC'D     DRY        DAF     DMMF(PARR)    ELEMENTAL ANALYSIS      DRY     DMMF(MOD.P)  DMMF(DIR.)

  % ASH                 7.90       8.54               ( 9.53%MM)                                    ( 9.80%MM)   (     %MM)

  % CARBON             67.22      72.70      79.49      80.36        % CARBON              72.40      80.27

  % HYDROGEN            4.58 (*)   4.95       5.41       5.47        % HYDROGEN             4.84       5.37

  % NITROGEN            1.05       1.14       1.25       1.26        % NITROGEN             1.14       1.26

  % TOTAL SULFUR        0.52       0.56       0.61                   % ORGANIC SULFUR       0.28       0.31

  % OXYGEN(DIFF)       11.20 (*)  12.11      13.24      12.91        % OXYGEN(DIFF)        11.53      12.78

                  (*)-EXCLUDES MOISTURE                              % MINERAL MATTER       9.80
                                                                      (INCL.  0.51% FES2)

SULFUR FORMS         % PYRITIC  % SULFATIC  % ORGANIC  % TOTAL       DRY % CHLORINE =  0.05    DRY % CO2 =  1.09

     DRY               0.27       0.01       0.28       0.56        MOTT-SPOONER DIFFERENCE =    40.

     DAF               0.30       0.01       0.31       0.61

                                 AS REC'D    EQUIL.
CALORIFIC VALUE         DRY       MOIST.     MOIST.                 ATOM RATIOS (DMMF)      PARR     MOD.PARR     DIRECT
(GROSS, BTU/LB)

  MM-CONTAINING        12760.     11798.     11755.                  ATOMIC H/C            0.8178     0.8036

  MM-FREE (PARR)       14073.     12910.     12858.                  ATOMIC O/C            0.1206     0.1196

  MM-FREE (MOD. P)     14131.     12959.     12906.

  NET CV, DMMF BTU/LB  13622.
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SAMPLE IDENTIFICATION:                                      SAMPLE LOCATION:             ** PENN STATE COAL DATA BASE **
------ ---------------                                     ------ ---------                  **                      **
   PSU NUMBER              -> DECS-6                           COUNTRY      -> USA           **  DECS-6              **
   SEAM NAME               -> Blind Canyon                                                   **                      **
   ALTERNATE SEAM NAME     ->                                  STATE        -> UTAH          **  12/02/91            **
   APPARENT RANK           ->   HVA                                                          **  PAGE  2             **

                                        * * * * *  C H E M I C A L   D A T A  * * * * *

PROXIMATE ANALYSIS    AS REC'D      DRY       DAF      DMMF(PARR)

 % MOISTURE             4.73                                          % EQUILIBRIUM MOISTURE =  4.85

 % ASH                  5.56        5.84                                                MM-FREE =  5.18

 % VOLATILE            42.40       44.50     47.26      46.94

 % FIXED CARBON        47.31       49.66     52.74      53.06


ULTIMATE ANALYSIS     AS REC'D      DRY       DAF      DMMF(PARR)     ELEMENTAL ANALYSIS     DRY      DMMF(MOD.P)  DMMF(DIR.)

 % ASH                  5.56        5.84               ( 6.53%MM)                                    ( 6.67%MM)   (      %MM)

 % CARBON              72.91       76.53     81.28      81.87          % CARBON            76.27      81.72

 % HYDROGEN             5.60 (*)    5.88      6.24       6.29          % HYDROGEN           5.80       6.22

 % NITROGEN             1.39        1.46      1.55       1.56          % NITROGEN           1.46       1.56

 % TOTAL SULFUR         0.38        0.40      0.42                     % ORGANIC SULFUR     0.37       0.40

 % OXYGEN(DIFF)         9.42 (*)    9.89     10.50      10.27          % OXYGEN(DIFF)       9.43      10.10

                    (*)-EXCLUDES MOISTURE                              % MINERAL MATTER     6.67
                                                                        (INCL.  0.04% FES2)

SULFUR FORMS       % PYRITIC  % SULFATIC  % ORGANIC   % TOTAL          DRY % CHLORINE =  0.12    DRY % CO2 =  0.96

    DRY               0.02       0.01       0.37        0.40           MOTT-SPOONER DIFFERENCE =   -72.

    DAF               0.02       0.01       0.39        0.42

                                 AS REC'D    EQUIL.
CALORIFIC VALUE        DRY        MOIST.     MOIST.                    ATOM RATIOS (DMMF)     PARR     MOD.PARR     DIRECT
(GROSS, BTU/LB)

  MM-CONTAINING       13923.     13264.     13248.                     ATOMIC H/C           0.9228     0.9141

  MM-FREE (PARR)      14874.     14124.     14105.                     ATOMIC O/C           0.0942     0.0928

  MM-FREE (MOD. P)    14917.     14163.     14144.

  NET CV, DMMF BTU/LB 14333.
```

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SAMPLE IDENTIFICATION:                                      SAMPLE LOCATION:                 ** PENN STATE COAL DATA BASE **
------ ---------------                                      ------ ---------                     **                      **
   PSU NUMBER               -> DECS-7                           COUNTRY       -> USA             **   DECS-7             **
   SEAM NAME                -> ADAVILLE #1                                                       **                      **
   ALTERNATE SEAM NAME      ->                                  STATE         -> WYOMING         **   12/02/91           **
   APPARENT RANK            ->   HVC                                                             **   PAGE  2            **

                                   * * * * *  C H E M I C A L   D A T A  * * * * *

PROXIMATE ANALYSIS      AS REC'D      DRY        DAF      DMMF(PARR)

  % MOISTURE              17.34                                              % EQUILIBRIUM MOISTURE = 18.40

  % ASH                    3.45       4.17                                                  MM-FREE = 19.15

  % VOLATILE              38.11      46.10      48.11      47.78

  % FIXED CARBON          41.11      49.73      51.89      52.22


ULTIMATE ANALYSIS       AS REC'D      DRY        DAF      DMMF(PARR)      ELEMENTAL ANALYSIS       DRY      DMMF(MOD.P)  DMMF(DIR.)

  % ASH                    3.45       4.17               ( 5.04%MM)                                         ( 4.79%MM)   (      %MM)

  % CARBON                61.09      73.90      77.12      77.82           % CARBON              73.74       77.45

  % HYDROGEN               4.38 (*)   5.30       5.53       5.58           % HYDROGEN             5.25        5.51

  % NITROGEN               0.82       0.99       1.03       1.04           % NITROGEN             0.99        1.04

  % TOTAL SULFUR           0.81       0.98       1.02                      % ORGANIC SULFUR       0.87        0.91

  % OXYGEN(DIFF)          12.12 (*)  14.66      15.30      15.55           % OXYGEN(DIFF)        14.37       15.09

                    (*)-EXCLUDES MOISTURE                                  % MINERAL MATTER       4.19
                                                                            (INCL.  0.19% FES2)

SULFUR FORMS          % PYRITIC  % SULFATIC  % ORGANIC   % TOTAL           DRY % CHLORINE =  0.06    DRY % CO2 =  0.60

   DRY                   0.10       0.01       0.87       0.98             MOTT-SPOONER DIFFERENCE =    52.

   DAF                   0.10       0.01       0.91       1.02

                                  AS REC'D    EQUIL.
CALORIFIC VALUE            DRY      MOIST.     MOIST.                      ATOM RATIOS (DMMF)      PARR      MOD.PARR      DIRECT
(GROSS, BTU/LB)

  MM-CONTAINING          13068.     10802.     10663.                      ATOMIC H/C            0.8614      0.8548

  MM-FREE (PARR)         13710.     11230.     11079.                      ATOMIC O/C            0.1500      0.1463

  MM-FREE (MOD. P)       13720.     11243.     11093.

  NET CV, DMMF BTU/LB    13204.
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SAMPLE IDENTIFICATION:                                        SAMPLE LOCATION:              ** PENN STATE COAL DATA BASE **
------ ---------------                                        ------ ---------                 **                        **
   PSU NUMBER              -> DECS-8                              COUNTRY      -> USA            **   DECS-8               **
   SEAM NAME               -> SMITH-ROLAND                                                       **                        **
   ALTERNATE SEAM NAME     -> WYODAK                              STATE        -> WYOMING        **   12/02/91             **
   APPARENT RANK           -> SUBBIT C                                                           **   PAGE  2              **

                                  * * * * *  C H E M I C A L   D A T A  * * * * *

PROXIMATE ANALYSIS     AS REC'D     DRY        DAF      DMMF(PARR)

 % MOISTURE             28.42                                           % EQUILIBRIUM MOISTURE = 28.41

 % ASH                   9.90      13.83                                               MM-FREE = 32.03

 % VOLATILE             32.38      45.23      52.49      51.77

 % FIXED CARBON         29.30      40.94      47.51      48.23


ULTIMATE ANALYSIS      AS REC'D     DRY        DAF      DMMF(PARR)     ELEMENTAL ANALYSIS     DRY     DMMF(MOD.P)  DMMF(DIR.)

 % ASH                   9.90      13.83               (15.34%MM)                                    (15.78%MM)  (      %MM)

 % CARBON               45.91      64.14      74.43      75.76          % CARBON             63.87      75.84

 % HYDROGEN              3.23 (*)   4.51       5.23       5.33          % HYDROGEN            4.34       5.15

 % NITROGEN              0.62       0.86       1.00       1.02          % NITROGEN            0.86       1.02

 % TOTAL SULFUR          0.52       0.73       0.85                     % ORGANIC SULFUR      0.43       0.51

 % OXYGEN(DIFF)         11.40 (*)  15.93      18.49      17.90          % OXYGEN(DIFF)       14.72      17.48

                    (*)-EXCLUDES MOISTURE                               % MINERAL MATTER     15.78
                                                                         (INCL.  0.52% FES2)

SULFUR FORMS        % PYRITIC  % SULFATIC  % ORGANIC   % TOTAL          DRY % CHLORINE =  0.05    DRY % CO2 =  0.98

    DRY                0.28       0.02       0.43       0.73            MOTT-SPOONER DIFFERENCE =   178.

    DAF                0.32       0.02       0.50       0.85

                                AS REC'D    EQUIL.
CALORIFIC VALUE        DRY       MOIST.     MOIST.                     ATOM RATIOS (DMMF)     PARR     MOD.PARR     DIRECT
(GROSS, BTU/LB)

 MM-CONTAINING        11168.     7994.      7995.                       ATOMIC H/C          0.8446     0.8153

 MM-FREE (PARR)       13148.     8951.      8952.                       ATOMIC O/C          0.1773     0.1730

 MM-FREE (MOD. P)     13243.     9000.      9002.

 NET CV, DMMF BTU/LB  12747.
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SAMPLE IDENTIFICATION:                                    SAMPLE LOCATION:                 ** PENN STATE COAL DATA BASE **
------ ---------------                                    ------ ---------                     **                      **
   PSU NUMBER              -> DECS-9                         COUNTRY      -> USA                 **   DECS-9             **
   SEAM NAME               -> DIETZ                                                              **                      **
   ALTERNATE SEAM NAME     ->                                STATE        -> MONTANA             **   12/02/91           **
   APPARENT RANK           -> SUBBIT B                                                           **   PAGE  2            **
                                      * * * * *  C H E M I C A L   D A T A  * * * * *

PROXIMATE ANALYSIS    AS REC'D      DRY        DAF      DMMF(PARR)

  % MOISTURE           24.68                                          % EQUILIBRIUM MOISTURE = 24.57

  % ASH                 4.80        6.37                                         MM-FREE = 26.00

  % VOLATILE           33.46       44.43      47.45      47.10

  % FIXED CARBON       37.06       49.20      52.55      52.90


ULTIMATE ANALYSIS     AS REC'D      DRY        DAF      DMMF(PARR)   ELEMENTAL ANALYSIS     DRY    DMMF(MOD.P)  DMMF(DIR.)

  % ASH                 4.80        6.37                ( 7.11%MM)                              ( 7.28%MM)   (      %MM)

  % CARBON             53.27       70.73      75.54      76.14        % CARBON              70.57     76.11

  % HYDROGEN            3.65 (*)    4.85       5.18       5.22        % HYDROGEN             4.77      5.14

  % NITROGEN            0.63        0.84       0.90       0.90        % NITROGEN             0.84      0.91

  % TOTAL SULFUR        0.31        0.41       0.44                   % ORGANIC SULFUR       0.31      0.33

  % OXYGEN(DIFF)       12.65 (*)   16.80      17.94      17.74        % OXYGEN(DIFF)        16.23     17.50

                  (*)-EXCLUDES MOISTURE                                % MINERAL MATTER       7.28
                                                                        (INCL.  0.15% FES2)

SULFUR FORMS        % PYRITIC  % SULFATIC  % ORGANIC   % TOTAL       DRY % CHLORINE =  0.09    DRY % CO2 =  0.58

    DRY               0.08       0.02       0.31       0.41          MOTT-SPOONER DIFFERENCE =   201.

    DAF               0.09       0.02       0.33       0.44

                                AS REC'D    EQUIL.
CALORIFIC VALUE       DRY        MOIST.     MOIST.                  ATOM RATIOS (DMMF)     PARR     MOD.PARR     DIRECT
(GROSS, BTU/LB)

  MM-CONTAINING      12330.      9287.      9301.                    ATOMIC H/C           0.6236    0.8116

  MM-FREE (PARR)     13251.      9796.      9811.                    ATOMIC O/C           0.1749    0.1726

  MM-FREE (MOD. P)   13294.      9822.      9838.

  NET CV, DMMF BTU/LB 12809.
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SAMPLE IDENTIFICATION:                                       SAMPLE LOCATION:                  ** PENN STATE COAL DATA BASE **
------ ---------------                                       ------ ---------                     **                        **
   PSU NUMBER                 -> DECS-11                        COUNTRY      -> USA                **   DECS-11              **
   SEAM NAME                  -> BEULAH                                                            **                        **
   ALTERNATE SEAM NAME        ->                                STATE        -> NORTH DAKOTA       **   12/02/91             **
   APPARENT RANK              -> LIGNITE                                                           **   PAGE  2              **
                                      * * * * *  C H E M I C A L   D A T A  * * * * *

PROXIMATE ANALYSIS    AS REC'D      DRY        DAF      DMMF(PARR)

 % MOISTURE            33.38                                       % EQUILIBRIUM MOISTURE = 35.22

 % ASH                  6.37       9.56                                          MM-FREE = 37.92

 % VOLATILE            37.36      56.08      62.01      61.63

 % FIXED CARBON        22.89      34.36      37.99      38.37


ULTIMATE ANALYSIS     AS REC'D      DRY        DAF      DMMF(PARR)    ELEMENTAL ANALYSIS      DRY      DMMF(MOD.P)  DMMF(DIR.)

 % ASH                  6.37       9.56                (10.73%MM)                                     (10.99%MM)   (      %MM)

 % CARBON              44.07      66.15      73.14      74.10        % CARBON              66.05     74.20

 % HYDROGEN             2.68 (*)   4.03       4.46       4.51        % HYDROGEN             3.91      4.39

 % NITROGEN             0.60       0.90       1.00       1.01        % NITROGEN             0.90      1.01

 % TOTAL SULFUR         0.49       0.74       0.82                   % ORGANIC SULFUR       0.39      0.44

 % OXYGEN(DIFF)        12.40 (*)  18.62      20.59      20.37        % OXYGEN(DIFF)        17.76     19.96

                  (*)-EXCLUDES MOISTURE                              % MINERAL MATTER      10.99
                                                                      (INCL.  0.58% FES2)

SULFUR FORMS         % PYRITIC  % SULFATIC  % ORGANIC   % TOTAL       DRY % CHLORINE =  0.08     DRY % CO2 =  0.38

    DRY                 0.31       0.03       0.39       0.74         MOTT-SPOONER DIFFERENCE =    179.

    DAF                 0.34       0.03       0.43       0.82


                                 AS REC'D    EQUIL.
CALORIFIC VALUE         DRY       MOIST.     MOIST.                 ATOM RATIOS (DMMF)     PARR     MOD.PARR     DIRECT
(GROSS, BTU/LB)

  MM-CONTAINING        11062.     7370.      7166.                   ATOMIC H/C           0.7317    0.7114

  MM-FREE (PARR)       12350.     7910.      7676.                   ATOMIC O/C           0.2064    0.2019

  MM-FREE (MOD. P)     12409.     7940.      7703.

  NET CV, DMMF BTU/LB  11989.
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SAMPLE IDENTIFICATION:                                  SAMPLE LOCATION:                  ** PENN STATE COAL DATA BASE **
------ ---------------                                  ------ ---------                  **                          **
   PSU NUMBER              -> DECS-12                      COUNTRY      -> USA            **   DECS-12                **
   SEAM NAME               -> PITTSBURGH                                                  **                          **
   ALTERNATE SEAM NAME     -> #8                           STATE        -> PENNSYLVANIA   **   12/02/91               **
   APPARENT RANK           ->   HVA                                                       **   PAGE  2                **

                                    * * * * *  C H E M I C A L   D A T A  * * * * *

PROXIMATE ANALYSIS    AS REC'D      DRY        DAF       DMMF(PARR)

 % MOISTURE             2.40                                          % EQUILIBRIUM MOISTURE =  2.88

 % ASH                 10.00       10.25                                               MM-FREE =  3.26

 % VOLATILE            35.16       36.02      40.13       39.35

 % FIXED CARBON        52.44       53.73      59.87       60.65


ULTIMATE ANALYSIS     AS REC'D      DRY        DAF       DMMF(PARR)   ELEMENTAL ANALYSIS      DRY      DMMF(MOD.P)  DMMF(DIR.)

 % ASH                 10.00       10.25                (11.69%MM)                                     (11.88%MM)   (      %MM)

 % CARBON              72.99       74.78      83.32       84.68        % CARBON              74.69      84.75

 % HYDROGEN             4.99 (*)    5.11       5.69        5.79        % HYDROGEN             4.98       5.66

 % NITROGEN             1.20        1.23       1.37        1.39        % NITROGEN             1.23       1.40

 % TOTAL SULFUR         1.09        1.12       1.25                    % ORGANIC SULFUR       0.73       0.83

 % OXYGEN(DIFF)         7.33 (*)    7.51       8.37        8.15        % OXYGEN(DIFF)         6.49       7.37

                   (*)-EXCLUDES MOISTURE                               % MINERAL MATTER      11.88
                                                                        (INCL.  0.71% FES2)

SULFUR FORMS       % PYRITIC  % SULFATIC  % ORGANIC   % TOTAL          DRY % CHLORINE =  0.23    DRY % CO2 =  0.34

    DRY              0.38       0.01        0.73        1.12           MOTT-SPOONER DIFFERENCE =    61.

    DAF              0.42       0.01        0.81        1.25

                                AS REC'D    EQUIL.
CALORIFIC VALUE      DRY        MOIST.      MOIST.                    ATOM RATIOS (DMMF)      PARR     MOD.PARR     DIRECT
(GROSS, BTU/LB)

  MM-CONTAINING     13532.      13207.      13142.                     ATOMIC H/C           0.8208     0.8016

  MM-FREE (PARR)    15259.      14846.      14763.                     ATOMIC O/C           0.0722     0.0653

  MM-FREE (MOD. P)  15332.      14916.      14833.

  NET CV, DMMF BTU/LB 14795.
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# END

DATE
FILMED

5/1/92