DE-AC22-91PC91042-TPR-2

Effects of Low-Temperature Catalytic Pretreatments on Coal Structure and Reactivity in Liquefaction

DOE/PC/91042--T1

DE92 018479

Technical Progress Report
January 1992 - March 1992

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

Fuel Science Program
Department of Materials Science and Engineering,
The Pennsylvania State University
209 Academic Projects Building, University Park, PA 16802

May 1992

Prepared for the U.S. Department of Energy
under Contract No.
DE-AC22-91PC91042

MASTER

TABLE OF CONTENTS

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 second quarterly period. Significant progress has been made in the spectroscopic characterization of fresh and THF-extracted samples of Wyodak subbituminous coals, catalytic and thermal low-temperature pretreatments in the absence and presence of hydrogen-donor and non-donor solvents, and the spectroscopic characterization of thermally and catalytically pretreated coals using cross-polarization magic angle spinning (CPMAS) solid-state ^{13}C NMR, pyrolysis-GC-MS and FT-IR techniques. Characterization of the raw coal revealed that Wyodak coal is rich in oxygen-containing compounds such as phenol and catechol-type compounds. The results of low-temperature pretreatments showed that both dispersed catalyst and solvent affect the coal conversion and product quality at 350°C. The reactions at 300°C caused little increase in coal conversion, but pyrolysis-GC-MS indicated that pretreatments at 300°C induce some structural changes which are not easily detectable by CPMAS ^{13}C NMR and FT-IR.

INTRODUCTION

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 catalysts 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 has been discussed in relation to the catalytic pretreatments in the previous report (Song et al., 1992c). 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. Recently, we have demonstrated that the combined use of solid-state NMR and pyrolysis-GC-MS has the potential to reveal the major and minor structural changes in the macromolecular network of coal induced by low-temperature liquefaction (Song et al., 1991b, 1992b). 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.

TECHNICAL PROGRESS

Characterization of Structure and Low-Temperature Liquefaction Reactions of Wyodak Subbituminous Coal

During this quarter, we focused our experimental work on Wyodak subbituminous coal and have performed 1) structural characterization of raw and THF-extracted raw coal; 2) low-temperature catalytic and thermal pretreatments at 300 and 350°C in the absence of any solvent and in the presence of hydrogen-donor tetralin or non-donor 1-methylnaphthalene; and 3) structural characterization of the THF-insoluble part (residue) of the pretreated coal samples.

Experimental

The coal used was a Wyodak subbituminous coal provided by the Penn State Sample Bank (DECS-8). The characteristics of this coal are as follows: 32.4% volatile matter, 29.3 % fixed carbon, 9.9% ash and 28.4% moisture, on a as-received basis; 75.8% C, 5.2% H, 1.0% N, 0.5% S and 17.5% O, on a dmmf basis. The coal was dried in a vacuum oven at 100°C for 2 h before use.

The pretreatments (or low-temperature liquefaction) of coal were carried out at 300 and 350°C with and without catalyst (ammonium tetrathiomolybdate, 1 wt% of molybdenum of the dmmf coal) and solvents. The solvents used were tetralin, a known H-donor, and 1-methylnaphthalene (1-MN), a non-donor. Liquefaction was carried out in 25 ml microautoclaves using 4 g of coal and 4g of solvent, under 1000 psi H_2 (cold) pressure. The reaction time was 30 minutes plus 3 minutes for the heat-up time for autoclave to attain the reaction temperature. After the reaction, the liquid and solid products were separated by sequential extraction with hexane, toluene and THF. After the extraction the THF-insoluble residues were washed first with acetone and then with pentane in order to remove all the THF, followed by drying at 110°C for 6 h under vacuum.

The residues were analyzed by pyrolysis-GC-MS (Py-GC-MS), cross-polarization and magic angle spinning (CPMAS) solid state ^{13}C NMR and FTIR techniques. The advantages of CPMAS and Py-GC-MS and the experimental details have been described in recent papers (Hatcher et al., 1989; Song et al., 1992b).

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 μm, 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 close-to-inlet part of the capillary column by cooling with liquid nitrogen. The column temperature was programmed from 30°C (or 40°C) 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 FTIR analysis of the samples was performed on a Digilab FTS 60 FTIR spectrometer. The samples were analyzed as KBr pellets. A accurately weighed amount (approximately 3 mg) of the vacuum dried samples were ground with a pre-weighed amount of KBr (approximately 300 mg). The pellets were pressed under a pressure of 10 tons. The pellets were dried at 100°C under vacuum for 24 h before recording their infrared spectra.

RESULTS AND DISCUSSION

Characterization of DECS-8 Wyodak subbituminous coal

The CPMAS ^{13}C NMR spectrum of THF-extracted DECS-8 raw coal, shown in Figure 1, did not show any noticeable difference as compared to that of the unextracted raw coal in terms of aromaticity and functionality. The loss of 8% of organic materials of coal did not produce any apparent changes in its chemical structure. This may not be true for some coals; the THF-extracted sample may display a substantially different spectrum. The NMR spectrum shows two major very broad bands between 0-60 ppm and 90-165 ppm. The first band (0-60 ppm) is due to aliphatic carbons and may also include aliphatic ether carbons. The second region (90-165) is identified as an aromatic region. This band consists of three types of aromatic carbons: an intense peak around 130 ppm (aromatic C), first shoulder at 142 ppm (catechol-like C) and another at 152 ppm (phenolic or aromatic ether C). The other weak and broad bands at 181 and 212 ppm are attributed to carboxylic and ketonic carbons, respectively. The FTIR spectrum of the THF-extracted raw coal was also recorded and compared with that of the unextracted raw coal and there was no significant difference between the two samples.

Figure 2 shows the total ion chromatogram (TIC) from Py-GC-MS of the THF-extracted raw coal up to the retention time 30 minutes, which is a part of the total pyrogram. All the major structural units produced by the flash pyrolysis of the coal other than the alkanes and alkenes are listed in Table 2. The low-rank coals are known to have higher oxygen functionalities: therefore, phenol, alkylphenols, catechol and alkylcatechol are the most intense peaks in the pyrogram of the raw coal. The other minor oxygen-containing compounds identified are indanol, alkyl-indanol and hydroxyindene. Among the most abundant hydrocarbons other than alkanes and alkenes are toluene, xylenes and C_3-benzenes. Indene, alkyl indene, dihydroindene, alkyldihydroindene and alkyl naphthalenes are also identified in minor amounts. There are several intense peaks between 0-2 min (RT) of the pyrogram (Figure 2). These peaks are C_5-C_8 alkanes plus alkenes which coelute. There is another quite intense peak around 25 minutes (RT); it is a branched alkene with m/z 266. There are many more peaks over the whole pyrogram, and selective ion monitoring at m/z 71 indicates that they are long chain alkanes and alkenes. Overall, Py-GC-MS of the THF-extracted raw coal indicates that Wyodak subbituminous coal contains significant amount of oxygen containing structures including phenol, alkylphenols, catechol and other benzenediols as well as indanols. These observations are consistent with our earlier findings (Song et al., 1992a, 1992b).

Low-Temperature Thermal and Catalytic Reactions

The liquefaction at 300°C (with H_2, solvent and no catalyst) shows a very small conversion (11-15%). This conversion is not very significant as compared to the total THF-soluble materials (8%) extracted from the raw coal. The presence of solvents (tetralin or 1-methylnaphthalene) seems to have no appreciable effect on the conversions. The presence of catalyst also did not cause any appreciable increase in the conversion at 300°C, because at low temperature ATTM is less likely to decompose into catalytically active phase.

The results from the liquefaction at 350°C, given in Table 1, show an appreciable effect of catalyst and solvent on the total conversion and quality of the products. In the non-catalytic liquefaction the variation in the total conversion with the solvent is quite significant, with a maximum conversion in presence of tetralin. The total conversions in a solvent-free run and the run with 1-MN are not much different from that at 300°C but with tetralin as a solvent the difference is significant. The presence of catalyst (ATTM) in the liquefaction at 350 °C shows a drastic increase in the total conversion with or without solvent. The larger increase in conversion is in the solvent-free liquefaction, though the total conversion is maximum in the presence of tetralin.

Characterization of the residues from the liquefactions.

CPMAS ^{13}C NMR

Figure 1 compares the CPMAS ^{13}C NMR spectra for the THF-extracted raw coal and the coal after liquefaction at 300 and 350°C without any solvent or catalyst. The residue from the reaction at 300°C displays a spectrum very much similar to that of the residue from the raw coal. Integration of the spectrum gives only a slight increase in the aromaticity. The residues produced after the liquefaction at 300°C in presence of solvents with and without catalyst were also analyzed by NMR, and there was no significant difference observed, except a slight increase in the relative intensity of the aromatic region. This increase was relatively less in the case when catalyst was used in the liquefaction reaction.

The residues from runs at 350°C show different spectra as compared to the raw coal. The catecholic (142 ppm) and carboxylic (181 ppm) bands almost disappeared after the run at 350°C and there is a slight decrease in the intensity of the phenolic (152 ppm) band (Figure 1). The residues obtained from the liquefaction at 350 °C in presence of a solvent (tetralin or 1-MN) were also characterized by NMR. As compared to that of the solvent-free run, the residue from the run with tetralin shows slightly more of catechol-like carbons, but less intense than that of the THF-extracted raw coal. Also a decrease in the aliphatic band is observed. With 1-MN as a solvent the decrease in the aliphatic band is very prominent but the aromatic region shows similar functionality to that of the residue from solvent-free run.

We have seen that the presence of catalyst improves the total conversion at 350°C. However, CPMAS NMR spectra of the samples from catalytic runs appear to be similar to those from thermal runs.

FTIR Spectroscopy

The analysis of the residues produced from liquefaction at 300°C showed no marked changes in the FTIR spectrum as compared to that of the THF-extracted raw coal, except a slight decrease in the aliphatic band in the 2950 cm^{-1} region. Using a solvent during the liquefaction also did not cause any appreciable difference in the FTIR spectra of the residues. The residue produced after the liquefaction in presence of catalyst showed a slight decrease in the ether region (1110-1300 cm^{-1}).

Figure 3 shows the FTIR spectra of the residues from liquefaction at 350°C (solvent-free) with and without catalyst, along with that of the residue from the raw coal. There are substantial changes apparent in the structure of coal after liquefaction at 350°C. There is a significant decrease in the carbonyl band at 1700 cm^{-1} and hydroxyl region at 3400 cm^{-1} (presumably carbonyl loss). In the presence of catalyst, which improves the total conversion at 350°C, the effect on the ether region is significant. It appears that catalyst has enhanced the cleavage of the ether bonds in the coal network.

PYROLYSIS-GC-MS

Figure 2 shows the selected retention time region of the Py-GC-MS chromatogram of the THF-extracted raw coal and the residues from the liquefaction at 300 and 350°C (solvent- and catalyst-free). The major peaks which are identified are listed in Table 2. Compared to the pyrogram of the THF-extracted raw coal, all the major species such as phenol, alkylphenols, alkylbenzenes, as well as alkanes and alkenes, are formed from the pyrolysis of the residues from the liquefied coal, but there are apparent differences. A substantial decrease in the intensity of the catechol and alkylcatechol peaks in the pyrogram of the residue from the run at 300°C, and the disappearance of these peaks from the pyrogram of the residue from 350°C run, are the most significant. This change in the residue from the 300°C run is not apparent from NMR, but after liquefaction at 350°C the shoulder at 142 ppm in the CPMAS ^{13}C NMR spectrum disappears completely. From this it is clear that reaction at 300°C did cause some structural changes in the coal network.

The residues from the liquefaction experiments at 300 and 350°C in presence of solvents and with and without catalyst were also characterized by Py-GC-MS. The pyrogram of the residues from liquefaction at 300 and 350 °C in presence of tetralin as solvent (with and without catalyst) are shown in Figure 4. The peaks identified are given in Table 2. The peaks marked with a letter in the pyrograms are the new peaks observed after liquefaction in presence of a solvent. An intense methylnaphthalene peak observed here was also seen in the case of a solvent-free run, but with a very low intensity. These new peaks appear to have come from the adduction of solvent because they were not observed in the Py-GC-MS profiles of the residues from the solvent-free runs. When 1-methylnaphthalene was used as solvent, the tetralin and dihydronaphthalene peaks were not observed and the 1-methylnaphthalene peak was very intense, showing that it is due to the solvent . The naphthalene peak was relatively weak in presence of 1-methylnaphthalene, as compared to that in the presence of tetralin. Since the residue was extracted with THF for 24 h and dried, the solvent remaining in the residue must be either chemically bound or physically entraped in the solvent-inaccessible micropores, or both, as also noted in an earlier work (Song et al., 1992b). In the residue from the liquefaction in the presence of catalyst and solvent, the adduction of solvent was decreased, as shown by the decreased intensity of the solvent peak in the pyrogram. The reason for the decreased adduction of solvent molecules could be due in part to the formation of reduced number of free radicals from the solvent molecules in presence of catalyst. This is also supported by the decreased amount of hydrogen transfer from tetralin and increased amount of hydrogen gas consumption during liquefaction in presence of catalyst compared to that of the catalyst-free experiment.

Table 3 shows the relative ratios of the oxygen-containing units to the alkylbenzenes before and after liquefaction. For oxygen-containing species the areas of the phenol, alkylphenols and catechol peaks were added and for alkylbenzenes, toluene, xylenes and C_3-benzenes were used. As compared to that for raw coal, the ratio decreased for the sample from solvent-free run at 300°C, and the sample from the run at 350 °C with 1-MN or without solvent. There ratios show that the presence of solvent does make a difference in the loss of specific type of species from the coal network and it is independent of the catalyst. In solvent-free reaction and with non-donor solvent (1-MN), more oxygen-containing species are lost during liquefaction. In presence of tetralin during the liquefaction, this ratio did not decrease much from that of the raw coal and is highest as compared to the others.

The above results, though preliminary, have shown that there are significant changes in the coal structure as a consequence of the low-temperature catalytic pretreatments. Further work on the identification of specific changes in the coal structure is now in progress.

REFERENCES

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.

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.

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

Hatcher, P. G.; Wilson, M.A.; Vassallo, A. M.; Lerch, III, H.E., Int. J. Coal Geol., 1989, 13, 99.

Huang, L.; Song, C.; Schobert, H.H., Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992, 37 (1), 223-227.

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.

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.

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

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, 1987a, 66, 1225.

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 (2), 524-532.

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 (2), 976-983.

Song, C.; Hatcher, P.G.; "Compositional Differences between Coal-derived and Petroleum-derived jet Fuels", Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1992, 37 (2), 529-539.

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 ^{13}C NMR and Pyrolysis-GC-MS Studies of Coal Structure and Liquefaction Reactions", Am. Chem. Soc. Div. Fuel Chem. Prepr., 1992b, 37, in press.

Song, C.; Saini, A.K.; Huang, L.; Wenzel, K.; Hatcher, P.G.; Schobert, H.H. "Effects of Low-Temperature Catalytic Pretreatments on Coal Structure and Reactivity in Liquefaction", Quarterly Technical Progress Report TPR-1 for the Period October 1991 - December 1991, prepared for the U.S. Department of Energy under Contract No. DE-AC22-91PC91042, January 1992c, 90 pp.

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.

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.

TABLE 1. Products distribution (dmmf wt %) for the liquefaction at 350°C with and without catalyst.

Solvent	Gas	Oils	Asphaltenes	Preasphaltenes	Total Conversion
Thermal					
none	3.3	2.1	2.6	4.5	12.5
Tetralin	4.2	4.1	7.6	10.0	25.9
1-MN	4.0	1.1	5.8	7.4	18.3
Catalytic					
none	3.0	10.0	5.4	11.4	29.8
Tetralin	3.0	10.2	12.9	10.6	36.4
1-MN	2.6	6.1	10.1	12.3	31.1

TABLE 2. Major identified peaks in pyrograms.

No.	MW	Identified Compounds
1	92	Toluene
2	106	p-Xylene
3	106	o-Xylene
4	120	C_3-benzene
5	120	C_3-benzene
6	120	C_3-benzene
7	94	Phenol
8	118	Indane
9	116	Indene
10	108	o-Cresol
11	108	m-+p-Cresol
12	132	Methylindane
13	130	Methylindene
A*	132	Tetralin
14	122	Ethylphenol
B*	130	Dihydronaphthalene
15	122	Ethylphenol
16	122	Dimethylphenol
C*	128	Naphthalene
17	146	Dimethylindene
18	122	Dimethylphenol
19	136	C_3-Phenol
20	110	Catechol
21	136	C_3-Phenol
22	144	Dimethylindene
23	136	C_3-Phenol
24	124	Methylcatechol
25	124	Methylcatechol
D*	142	2-Methylnaphthalene
E*	142	1-Methylnaphthalene
26	110	1,3-Benzenediol
27	134	Indanol
28	134	Indanol
39	132	Hydroxyindene
30	138	C_2-Catechol
31	156	C_2-Naphthalene
32	170	C_3-Naphthalene

* The compounds identified in Py-GC-MS profiles of the residues from the liquefactions in presence of tetralin or 1-methylnaphthalene solvent.

TABLE 3. Ratios of the amount of the oxygen-containing units to the alkylbenzene units.

		Ratio Phenolic/Alkylbenzenes	
Temperature (°C)	Solvent	Thermal	Catalytic
Raw Coal		3.6	
300	none	2.4	2.5
300	Tetralin	3.5	3.1
300	1-MN	3.6	3.2
350	none	2.3	2.4
350	Tetralin	3.2	3.1
350	1-MN	1.9	2.3

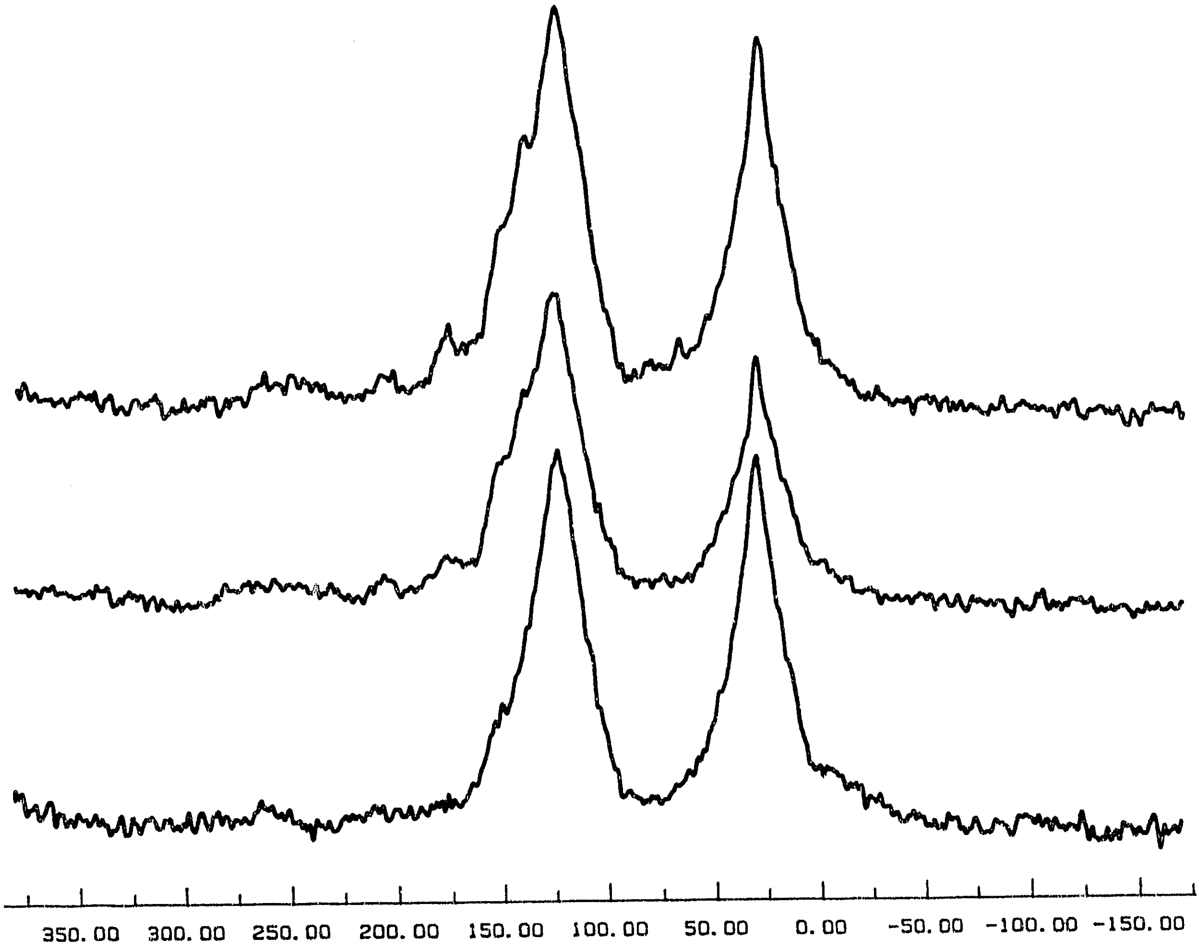

FIGURE 1 CPMAS ^{13}C NMR spectra of (a) THF-extracted raw coal and the residues from the solvent free thermal liquefactions at (b) 300°C, and (c) 350°C.

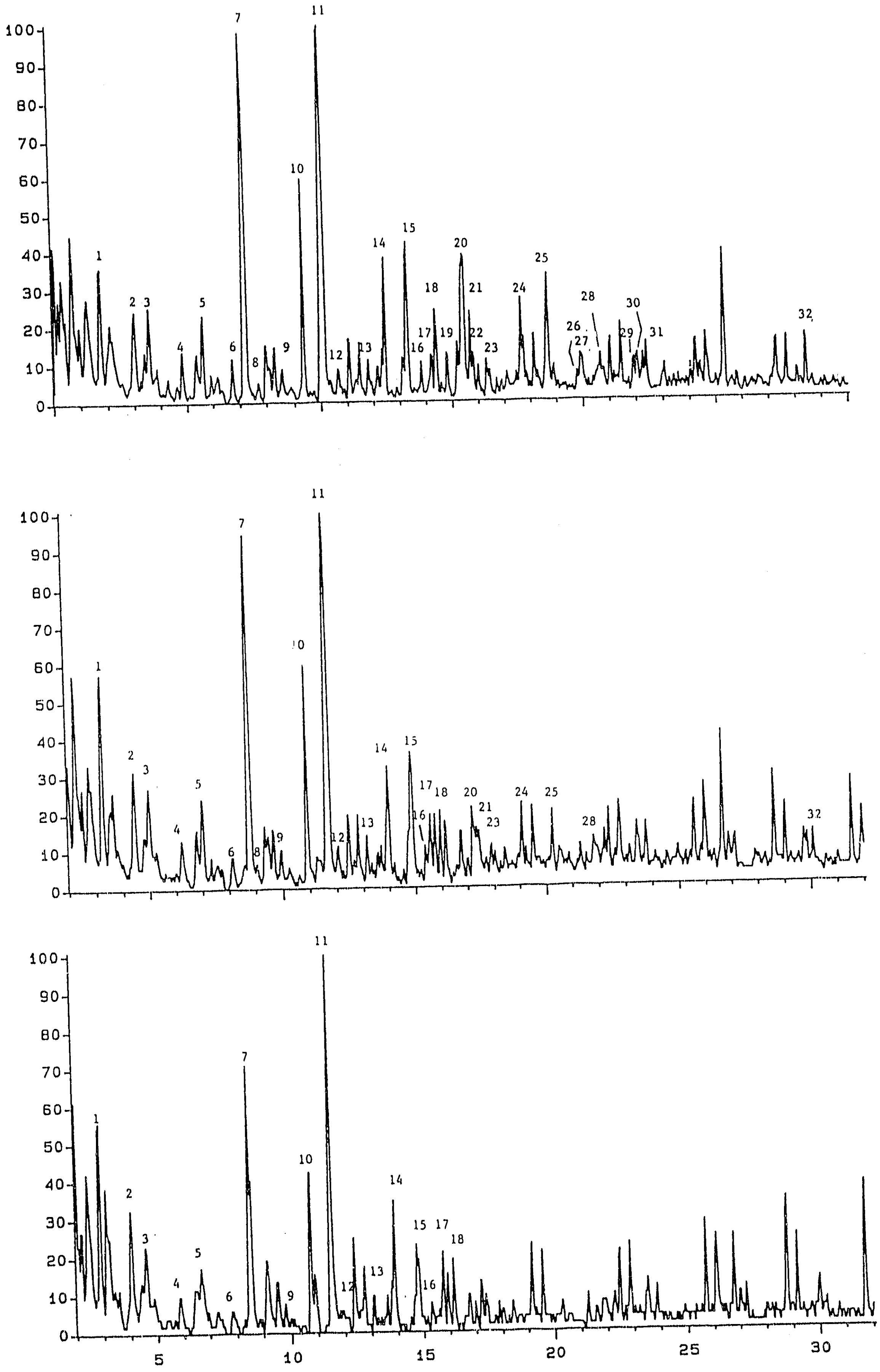

FIGURE 2. Py-GC-MS profiles of (a) THF-extracted raw coal and the residues from the thermal liquefactions at (b) 300°C, and (c) 350 °C.

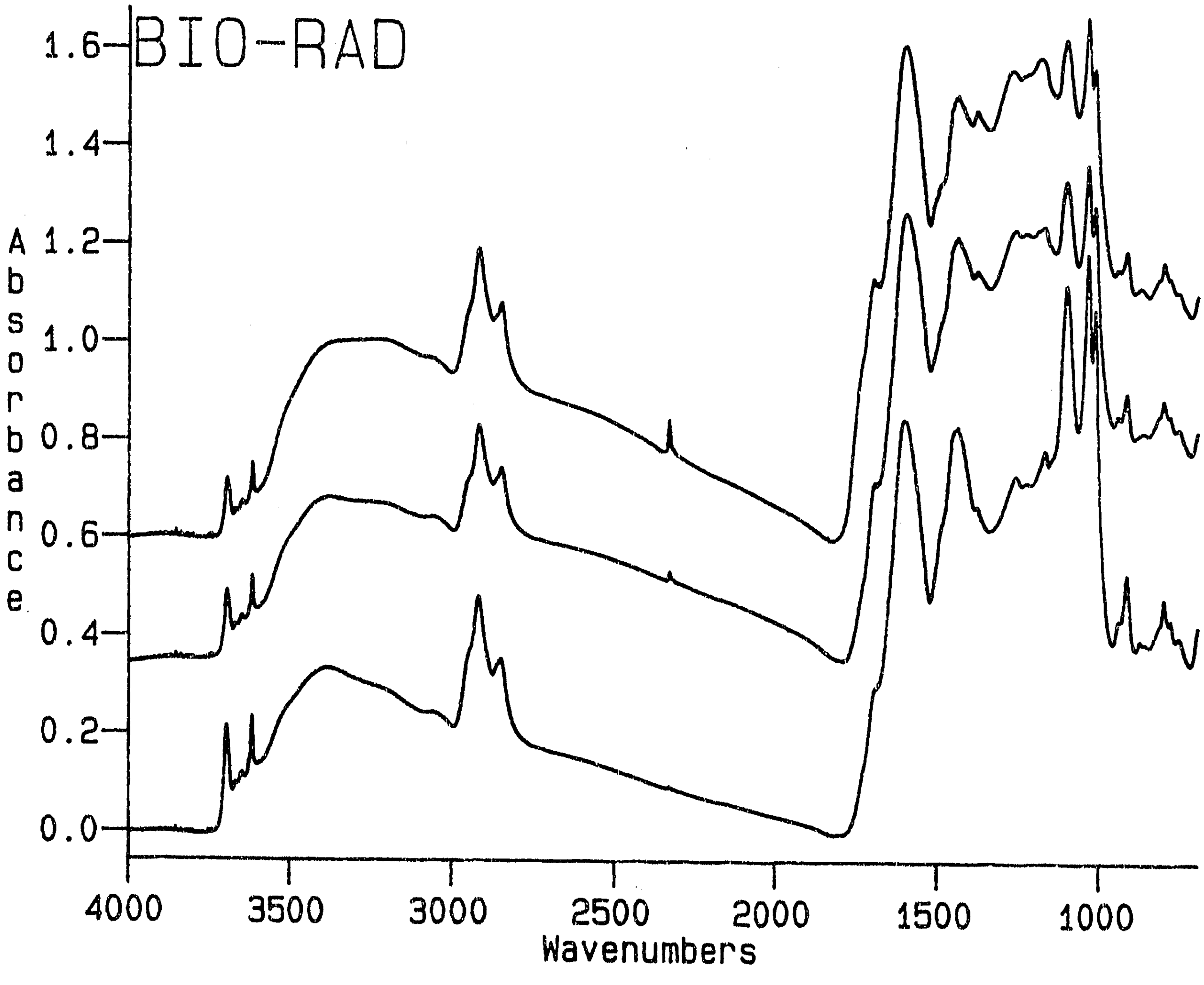

FIGURE 3. FTIR spectra of (a) THF-extracted raw coal and the residues from the solvent-free, (b) thermal, and (c) catalytic liquefactions at 350°C

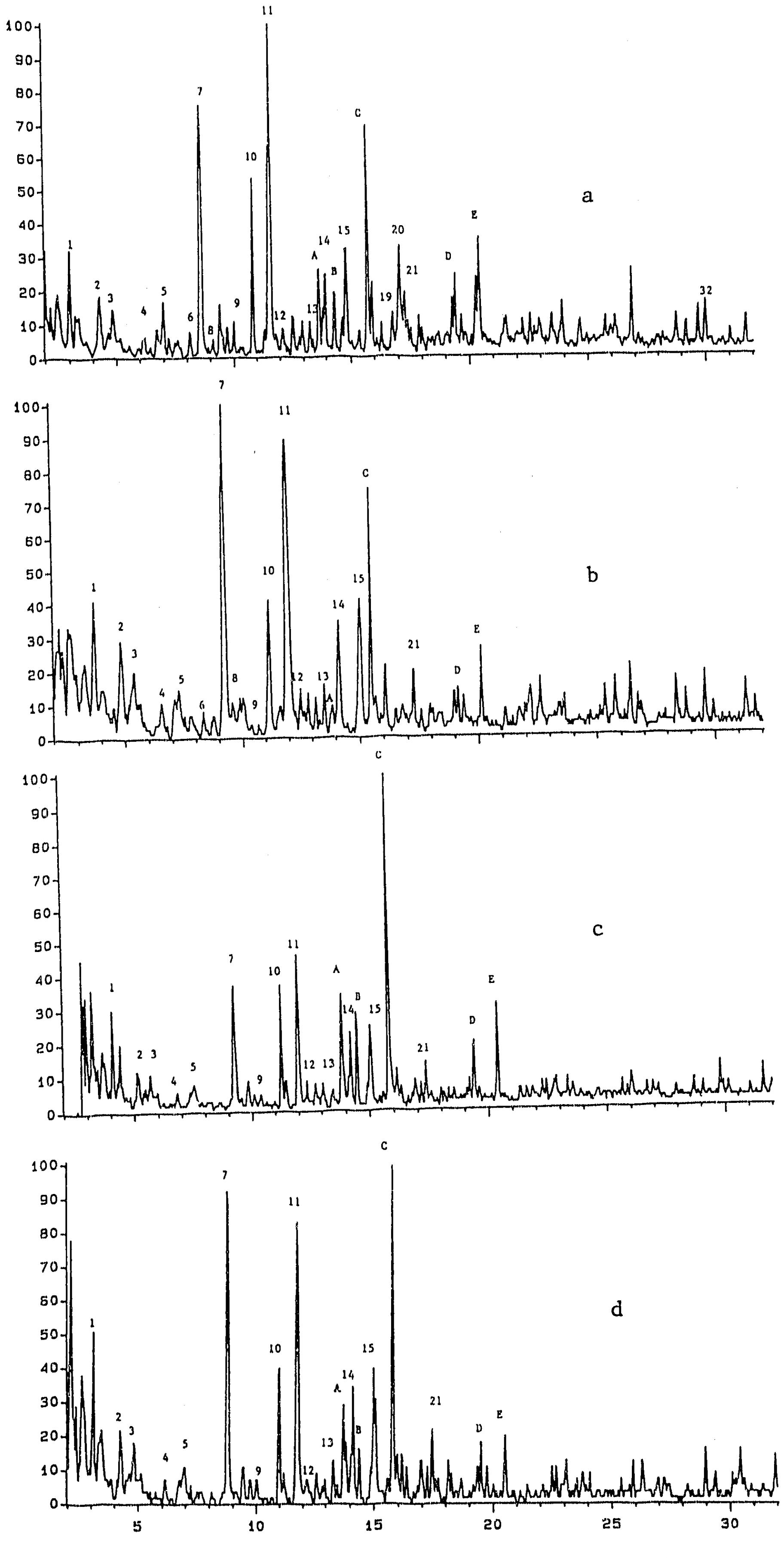

FIGURE 4. Py-GC-MS profiles of the residues from the liquefactions in presence of tetralin, (a) thermal, (b) catalytic at 300°C, and (c) thermal, (d) catalytic at 350°C.

Conf papers cycled separately, ds

END

DATE
FILMED

9/17/92