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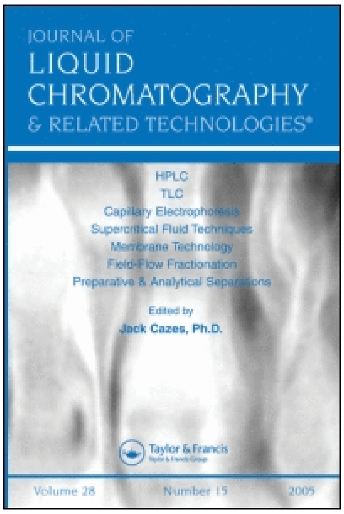

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Pyrolysis Coupled with Capillary Supercritical Fluid Chromatography

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PYROLYSIS COUPLED WITH CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY

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ABSTRACT

Pyrolysis coupled with gas chromatography and carbon dioxide supercritical fluid extraction/supercritical fluid chromatography was used to study the affect of pyrolysis temperature (500 or 999°C) and pyrolysis atmosphere (helium or carbon dioxide) on the resulting chromatographic profiles of asphaltenes. The use of the lower pyrolysis temperature yielded fewer and less volatile components than did the high pyrolysis temperature. This was supported by both gas chromatographic profiles and the profiles obtained after supercritical fluid extraction and chromatography. Fast atom bombardment/Mass spectrometry (FAB/MS) and Fourier Transform Infrared Spectrophotometric (FTIR) studies revealed, for these experiments, that although the pyrolysis process greatly altered the structure of the asphaltenes, the effect of the atmosphere present during pyrolysis appeared to have little affect on the fragments formed when these reactions were carried out at ambient pressure.

INTRODUCTION

Pyrolysis is a process in which an organic material is heated, usually in an inert atmosphere, to a relatively high temperature to cause the thermal disruption of the chemical bonds of the component(s) of the material. When incorporated into an analytical scheme, the resulting pyrolysis products are subsequently analyzed by a variety of techniques including mass spectrometry (MS), gas chromatography (GC), or gas chromatography/mass spectrometry (GC/MS) to obtain both qualitative and quantitative information (1-4). Pyrolysis in combination with GC/MS (Py-GC/MS) has been used to study a wide range of materials including modern and fossil plant cuticles (5), melanoidins (6), pheomelanins (7), plant polymers in peats (8), beech milled wood lignin (9) and other complex biomaterials (10), petroleum asphaltenes (11, 12), and the coal asphaltenes derived from a supercritical toluene extraction (13). These studies demonstrated that "fingerprints" of the materials could be obtained under controlled pyrolysis conditions and that some of this information was useful in the structural characterization of these substances.

Although Py/GC can provide a great deal of information, a major limitation, especially with regard to structural analysis, is the requirement that the pyrolysis products be volatile. If the pyrolysis temperature is sufficiently high, extensive fragmentation occurs and the volatility requirements are easily achieved. However, this extensive fragmentation is usually accompanied by substantial rearrangements of the original structures such that the formed products often bear little resemblance to their structure in the unpyrolyzed material. This fact greatly complicates structural elucidation based on pyrolysis products. In addition, as the size of the fragments decrease, a great deal of specificity is lost as the structures of the products become more and more fundamental. Larger fragments would be much more specific to the original material and the ability to analyze these would provide an additional degree of selectivity over the analysis of the smaller products. Studies have shown that the products formed from asphaltenes are quite dependent on the temperature at which the pyrolysis occurs (11,12). The study of the large fragments remaining in an asphaltene after pyrolysis at different temperatures would provide insight into the possible analytical utility of these higher molecular weight products. These large fragments might well posses insufficient volatility to be effectively separated by GC, however. Supercritical fluid chromatography (SFC), with its ability to analyze compounds with limited volatilities, should be able to handle such fragments. This aspect is the main focus of the current work. SFC has been applied to the separation and analysis of relatively high molecular weight coal and petroleum products including middle distillate fuel (14), a catalytically cracked petroleum vacuum residue (15), and asphaltenes (16).

This paper describes experiments we have performed on asphaltenes to investigate the feasibility and utility of SFC in the analysis of pyrolysis products. First, Py/GC of asphaltenes was studied at 500 and 999°C pyrolysis temperatures under a helium atmosphere. Next, the residue remaining after pyrolysis was extracted with supercritical carbon dioxide and the extracted components were focused onto a cooled retention gap prior to capillary SFC separation. We also investigated the effect of a CO_2 pyrolysis atmosphere in the same manner and compared the resulting chromatograms. Fourier transform infrared spectroscopic (FTIR) analysis and fast atom bombardment (FAB) MS analysis were used to see if the CO_2 atmosphere resulted in the formation of products chemically distinct from those formed in a He atmosphere. This study of the effect of a CO_2 atmosphere was important as we ultimately desired to study this process under high pressure, supercritical fluid conditions.

MATERIALS AND INSTRUMENTATION

AC-20 grade asphalt, compliments of Dr. Paul Khosla (North Carolina State University, Raleigh, NC) was fractionated, following the procedure (D4124) described in the American Society for Testing and Materials (17), to yield the asphaltenes.

Pyrolysis/Gas Chromatography.

A Pyroprobe 122 pyrolysis unit (Chemical Data Systems, Inc., Oxford, PA) with a 1/4 in. standard coil probe was interfaced with a Varian 3700 GC (Varian Associates, Walnut Creek, CA). The probe held a quartz pyrolysis tube packed with quartz wool which accepted the liquid sample. The separation was achieved using a 30 m x 250 μm i.d. DB-5 column with a film thickness of 0.25 μm (J&W Scientific, Inc., Rancho Cordova, CA). The detector was flame ionization (FID) and the resulting pyrogram was recorded on an HP3390A integrator (Hewlett-Packard, Avondale, PA). Electrometer settings were the same for each chromatogram shown in this work.

The pyrolysis tubes were cleaned by submerging them in concentrated sulfuric acid at 50°C for two hours, rinsed with deionized water and dried in an oven at 110°C. The tubes were then packed with quartz wool that had been rinsed in methanol and dichloromethane, heated in a tube furnace at 600°C and continously purged with air for a minimum of two hours. Finally, they were placed in an extraction cell (described below) and extracted on a modified Lee Scientific Model 501 SFC (Lee Scientific, Salt Lake City, UT) with supercritical carbon dioxide (SFC grade, Scott Speciality Gases, Plumsteadville, PA) at 100°C and 400 atmospheres until the FID signal resulting from supercritical fluid extraction/supercritical fluid chromatography (SFE/SFC) of the tubes returned to baseline.

Supercritical Fluid Extraction/Supercritical Fluid Chromatography

The extraction and chromatography were performed on a modified Lee Scientific Model 501 SFC. A diagram of the system as modified for this work is shown in Figure 1. In the extraction mode (3-way valve opened, 2-way valve closed and the retention gap disconnected from the column), the effluent from the extraction cell was expanded through a 20 cm x 15 μm i.d. deactivated fused silica restrictor (SGE, Inc., Austin, TX). The restrictor was inserted through a 1/16 in. Swagelok tee and 2 cm into a 3 cm x 0.01 in. i.d. stainless steel tube. A 0.5 m x 220 μm i.d. deactivated fused silica, aluminum clad retention gap (SGE) was connected to the 3 cm stainless steel tube with a 1/16 in. to 1/32 in. reducing union (Valco Instruments Co. Inc., Houston, TX). It was found that placement of the retention gap into a solid/liquid acetonitrile bath (dry ice/acetonitrile, -45°C) and insertion of a 2 μm screen in the 1/16 in. side of the reducing union improved focusing of the extracted components. In the chromatographic mode (3-way valve closed, 2-way valve opened and retention gap connected to column), the CO_2 mobile phase was delivered to the 1/16 in. tee where it flows around the restrictor, through the

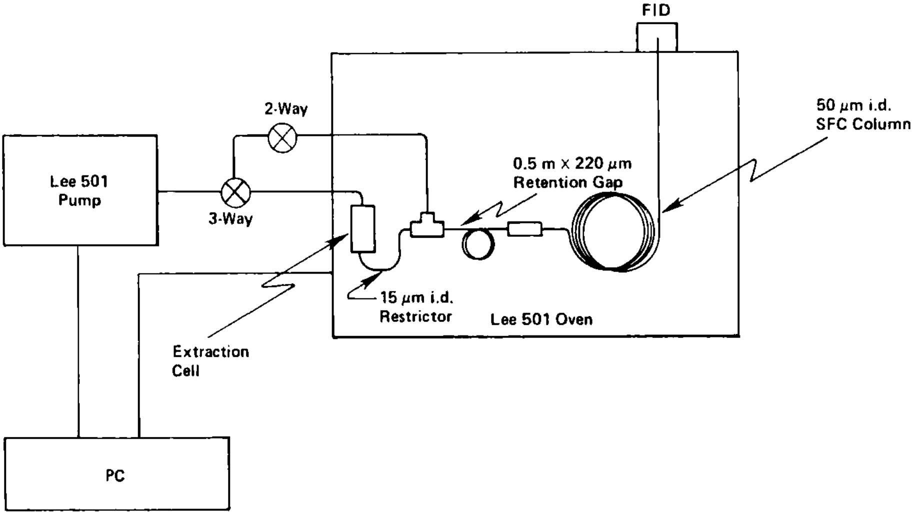


Figure 1. SFE/SFC instrumentation used in this study.

stainless steel tube into the retention gap and on through the column to an FID. The column was 7 m x 50 µm i.d. coated with Phenyl-5 with a film thickness of 0.25 µm (Lee Scientific).

The extraction cell was constructed from a 3.3 cm length of 1/4 in. o.d. x 5.3 mm i.d. stainless steel tubing and Parker 1/4 in. fritted column end fittings. These dimensions resulted in a cell volume of 0.7 mL. The cell was cleaned by sonication in methanol and dichloromethane followed by extraction with supercritical carbon dioxide at 100°C and 400 atmospheres until the FID signal returned to baseline.

Large-scale Extraction for Structural Studies

In order to obtain structural information regarding the compounds extracted from the pyrolysis residue, it was necessary to increase the mass extracted to ensure adequate amounts of material for FAB/MS and FTIR analysis. An extraction cell was constructed from a 17.9 cm length of 1/4 in. o.d. x 4.0 mm i.d. stainless steel tubing with Parker fritted column end fittings yielding a cell volume of 2.2 mL. This cell held seven pyrolysis tubes containing residue generated under the same conditions as for the SFE/SFC analysis. The extraction system was the same as above except that the 15 μm restrictor carried the extract out of the oven into a scintillation vial containing 10 mL of methanol which served to trap components as the effluent expanded to a gas. The solvent was removed and the residue dissolved in a minimal amount of solvent. Half of the sample was analyzed by FAB/MS (ZAB-E, VG Instruments, Danvers, MA) and the other half analyzed by FTIR (Sirius 100, Mattson Instruments, Madison, WI).

PROCEDURES

Pyrolysis/Gas Chromatography

A clean quartz tube packed with quartz wool was placed in the 1/4 in. standard coil probe. Five 1.0 μL aliquots of a 4.0 mg/mL solution of asphaltenes in dichloromethane were applied to the quartz wool. The solvent was allowed to evaporate for ten minutes. The probe was inserted into the interface box of the Pyroprobe 122 which was maintained at its maximum temperature of 210°C. A 0.5 m section at the head of the column was immersed in a solid/liquid acetonitrile bath to cryogenically focus the volatile pyrolyzed compounds. The interface box was purged with helium for five minutes to remove any air and to allow time for thermal equilibration of the probe. The final pyrolysis temperature was set at either 500°C or 999°C and the pyrolysis unit activated for an interval of two seconds. The ramp rate was approx. 75°C/ms. The interface box was purged with helium for ten minutes to sweep the volatile components onto the cooled section of column. The GC oven was then brought to 45°C, the acetonitrile bath removed and the oven temperature programmed to 300°C at 5°C/min. After GC analysis, the probe was withdrawn, the quartz tube containing the pyrolysis residue was removed and placed into a 1 dram vial. The vial was kept refrigerated until extraction. The situation in which pyrolysis was carried out under carbon dioxide atmosphere employed the same procedure except that after insertion of the probe, the interface box was purged with CO_2 for five minutes prior to pyrolysis to thoroughly exchange the atmospheres. Two minutes after the pyrolysis, the inlet gas was switched to helium for the ten minute focusing period.

Supercritical Fluid Extraction/Supercritical Fluid Chromatography

With both valves closed, i.e. no CO_2 flow, a quartz tube was placed in the small extraction cell. The system was switched to the extraction mode and the pressure was raised to 400 atmospheres with the oven at 40°C to provide a fluid density of 0.96 g/mL. When the pressure reached 400 atmospheres, the pump volume was read and a timer started. After 29 minutes the flow was stopped and the final volume recorded. The measured extraction volume was at least 3 mL of liquid CO_2. After the extraction was completed, the pressure was lowered and the system switched to the chromatographic mode. The retention gap was removed from the acetonitrile bath and the oven temperature was raised to 100°C. A multilinear density program was used to separate the compounds. All electrometer settings were the same for all of the chromatograms shown in this work.

Supercritical Fluid Extraction for Structural Studies

Seven quartz pyrolysis tubes containing material generated using the same pyrolysis conditions as for Py/GC were loaded into the large extraction cell. The extraction conditions here were the same as for the single tubes except that the extraction time was extended to 150 minutes to compensate for the increased cell volume. After extraction the receiving solvent volume was reduced with the aid of a water bath at 50°C and a gentle stream of cryotrapped nitrogen. When the volume reached about 0.75 mL the solution was transfered to a 1-mL conical vial. The scintillation vial was rinsed with 3 1-mL aliquots of methanol which were added to the conical vial. The sample was taken to dryness, capped and stored in the refrigerator for further analysis.

Immediately prior to analysis, the sample was dissolved in 100 μL of dichloromethane. One half of the solution was dissolved in a diethanolamine matrix. FAB/MS spectra were obtained over a mass range of 150 to 1200 atomic mass units. The remaining solution was deposited onto a KBr disk and a transmission IR spectrum obtained (400 to 4000 cm^{-1}) at a resolution of 4 wavenumbers.

RESULTS AND DISCUSSION

Pyrolysis/GC

The results of changes in the gas chromatograms of the pyrolysis products as a result of changes in both pyrolysis

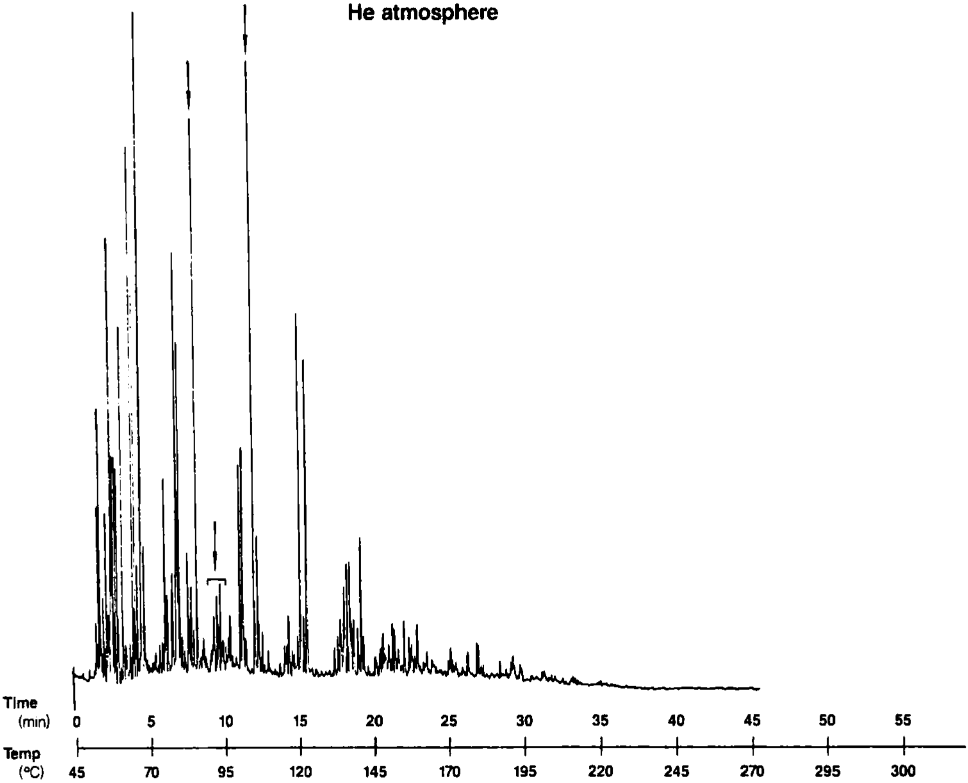


Figure 2. GC profile resulting from the pyrolysis of asphaltenes in a helium atmosphere at 999°C.

temperature and atmosphere are shown in Figures 2-4. It is apparent from the chromatograms of Figures 2 and 3 that the pyrolysis of asphaltenes at 999°C results in the formation of predominantly volatile fragments; the majority of components eluted before 140°C. Replicate Py/GC analysis of these samples revealed consistent chromatographic profiles of the fragments. Figure 4 shows the profiles obtained after pyrolysis of asphaltenes at 500°C which differ markedly from those of Figures 2 and 3 (999°). The lower temperature pyrolyses

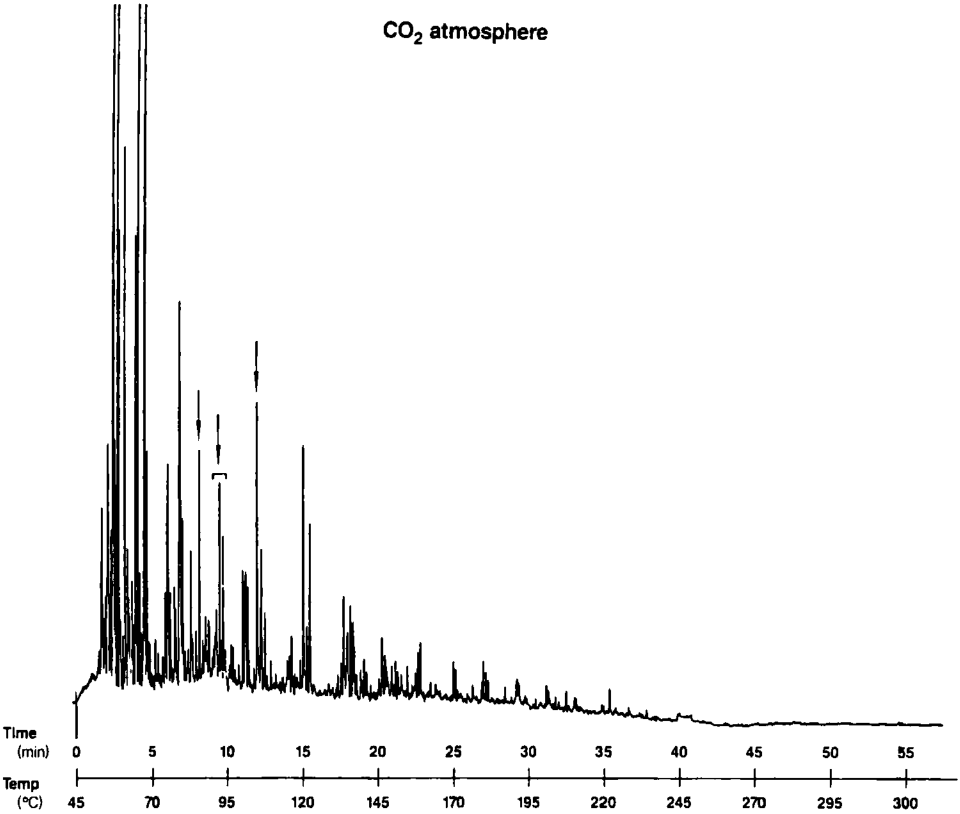
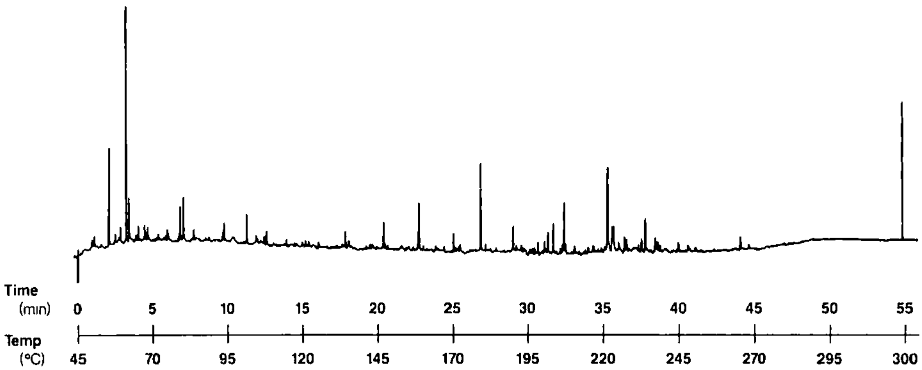
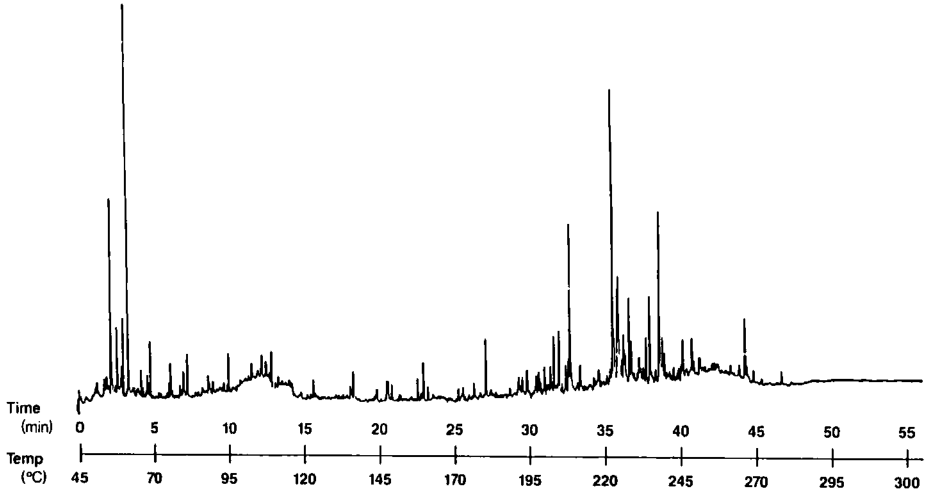


Figure 3. GC profile resulting from the pyrolysis of asphaltenes in a carbon dioxide atmosphere at 999°C.

resulted in a shift to less volatile fragments, as much of the material does not begin to elute until approximately 170°. In addition, the total detected peak areas were much lower than for the high temperature situation indicating that the asphaltene structure was less disrupted at 500°. Given that the total mass of asphaltenes subjected to pyrolysis in each case was constant, it would be expected that a greater proportion of that mass remained in the pyrolysis tube.



A. He atmosphere



B. CO_2 atmosphere

Figure 4. Comparison of Py/GC profiles obtained at a pyrolysis temperature of 500°C in helium (A) and CO_2 (B) atmosphere.

The atmosphere surrounding the samples during pyrolysis appeared to have an influence on the chromatograms; the resulting differences also seem to be more quantitative than qualitative in nature, i.e., peak intensities appear to change rather than a particular peak appearing upon pyrolysis in a given atmosphere. In both cases the general patterns of fragmentation were preserved. A comparison of Figures 2 and 3 (999°) reveals that the relative peak heights within the overall profile were altered in some cases. This is especially evident in the three regions indicated in Figures 2 and 3 where the first and third regions were elevated, relative to other regions and components, when pyrolysis took place in a helium atmosphere. The second region was elevated, relative to the others, when carbon dioxide surrounded the sample. Some other, more subtle differences were also apparent for components which eluted after 120°C. Similarly, there were also differences observed from the Py/GC separations of the products formed at a pyrolysis temperature of 500°C. The components eluted between 195 and 270°C were much more abundant following pyrolysis in CO_2 than was the case where the sample was pyrolyzed in a helium atmosphere. These results were consistent when the experiments were repeated. A possible explaination for these atmosphere-dependent differences might be found in the different heat transport properties of the two gases, but much more work would be needed to see if this is an issue. The results of the FAB/MS and FTIR work on the residue extracts, presented later, might indicate structural differences in the extracts from different conditions and support structural differences in the volatile fractions as well.

Supercritical Fluid Extraction/Supercritical Fluid Chromatography

As indicated in the experimental section, the quartz pyrolysis tubes were extracted with supercritical CO_2 after the Py/GC experiment and this extract was analyzed using SFC. The presence of less volatile, CO_2 soluble fragments remaining in the residue should be revealed here. A quartz tube onto which the dichloromethane solvent was deposited and evaporated, was carried through the pryolysis/SFE/SFC experiment and resulted in the "blank" chromatogram of Figure 5-A. The components which eluted before 0.6 g/mL were very consistent, yet the unresolved portion at 0.76 g/mL was somewhat variable; the significance of variations in this region must therefore be interpreted with caution. For reference, 20 μg of asphaltenes were applied to the quartz tube and subjected to SFE/SFC in the absence of a pyrolysis step so that any components detected which might arise from any residual, unpyrolyzed material would be detected. This profile is shown in Figure 5-B and indicates that very little of the unpyrolyzed asphaltene sample was soluble in supercritical CO_2. The baseline rise between 0.3 and 0.4 g/mL suggests the presence of some soluble material but, given the mass loaded and the known sensitivity of the SFC/FID system, represents only a small proportion of the sample. This is consistent with other work (unpublished) in our laboratory where CO_2 was shown to be a poor mobile phase for the SFC analysis of asphaltenes.

Figure 6 shows the profiles for the asphaltene residues from the 999°C pyrolysis. Both chromatograms indicate much more material was eluted in the low density (0.1 to 0.3 g/mL) region as compared to the blank, and the observed differences as a result of the atmosphere change appear to be more quantitative than qualitative in nature. The differences observed in the 0.7 g/mL region must be viewed with caution, as indicated above.

The chromatograms of Figure 7 show that a great deal more mass was extracted from the 500°C pyrolysis residue than from the residue obtained from the higher temperature pyrolysis. Most of the components, many of which remain unresolved in this

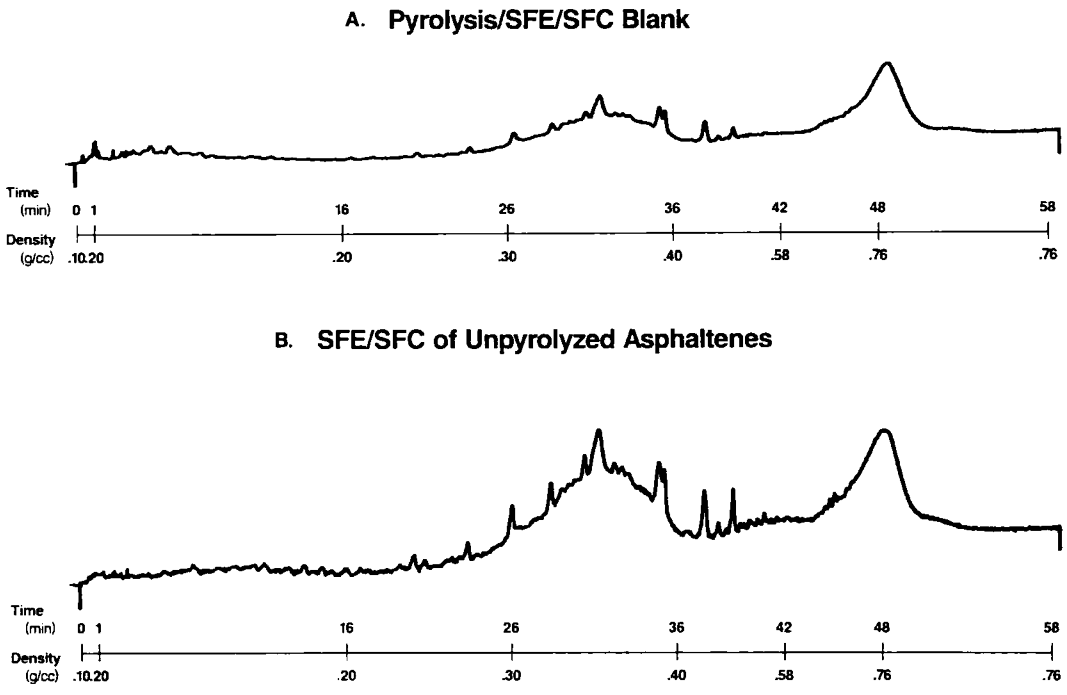


Figure 5. SFE/SFC profiles obtained from pyrolysis of solvent blank (A) and unpyrolyzed asphaltenes (B) in helium atmosphere.

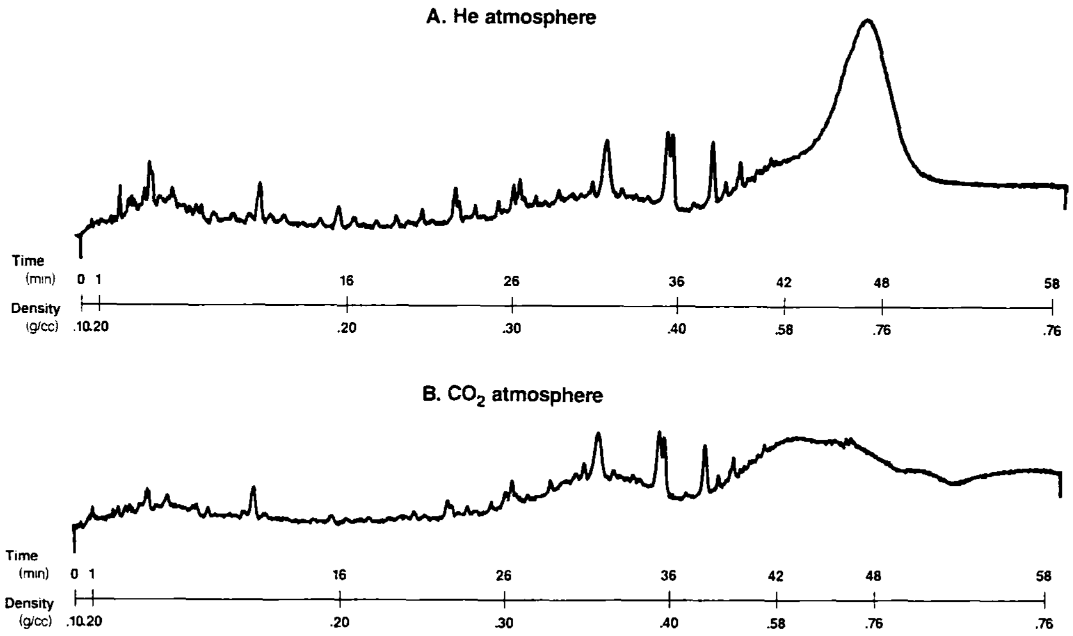


Figure 6. Py/SFE/SFC profiles from 999°C pyrolysis in helium (A) and carbon dioxide (B) atmosphere.

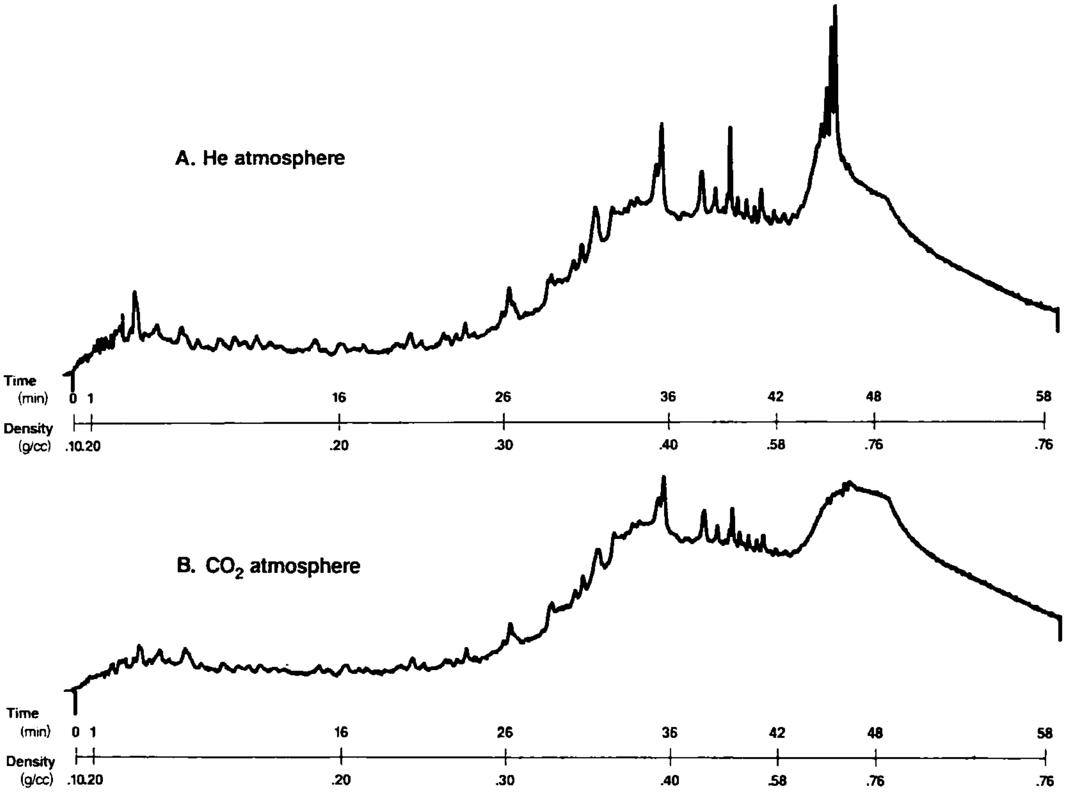


Figure 7. Py/SFE/SFC profiles from 500°C pyrolysis in helium (A) and carbon dioxide (B) atmosphere.

chromatographic configuration, elute above 0.3 g/mL supporting our hypothesis that the lower temperature would result in the formation of larger, extractable fragments. The dependence of the SFC profile on the pyrolysis atmosphere is again subtle, if it exists at all. With the exception of the components eluted at high density when helium was the pyrolysis atmosphere, the differences were more quantitative in nature.

Strutural Studies

In order to determine if the pyrolysis atmosphere caused the production of chemically distinct species that could be extracted by supercritical CO_2, several tubes of asphaltene were pyrolyzed and extracted in bulk, as described above, in order to obtain greater masses of the extracts. We chose to use FAB/MS analysis because this technique is known to provide information on high molecular weight components, such as might be expected in this situation. We also chose to examine only the 500° pyrolysis because of the observed extractable mass. The measurement of ions clearly associated with either pyrolysis atmosphere would, presumably, reflect pyrolysis processes affected by the chemical nature of the atmosphere. The ions not observed in the extraction blank analysis yet found in the samples are listed in Table 1 along with the ions from unpyrolyzed asphalt.

The results of Table 1 indicate that the chemical nature of the asphaltene sample has been greatly altered as a result of pyrolysis. However, the conclusions which can be reached regarding differences resulting from the pyrolysis atmosphere are not as clear. Although the ions observed in each case were different, the lack of many ions from the CO_2-pyrolyzed sample makes a definitive statment impossible. The reason for the poor response from the CO_2-derived sample is unclear.

TABLE 1.
FAB/MS Ion Comparison for Asphaltenes

Unpyrolyzed m/z	Helium Atmosphere m/z	Carbon dioxide atmosphere m/z
247, 249	238	316
352, 354	281	
457	343	
501	384	
562	448	
590	550	
670	553	
	594	
	847	

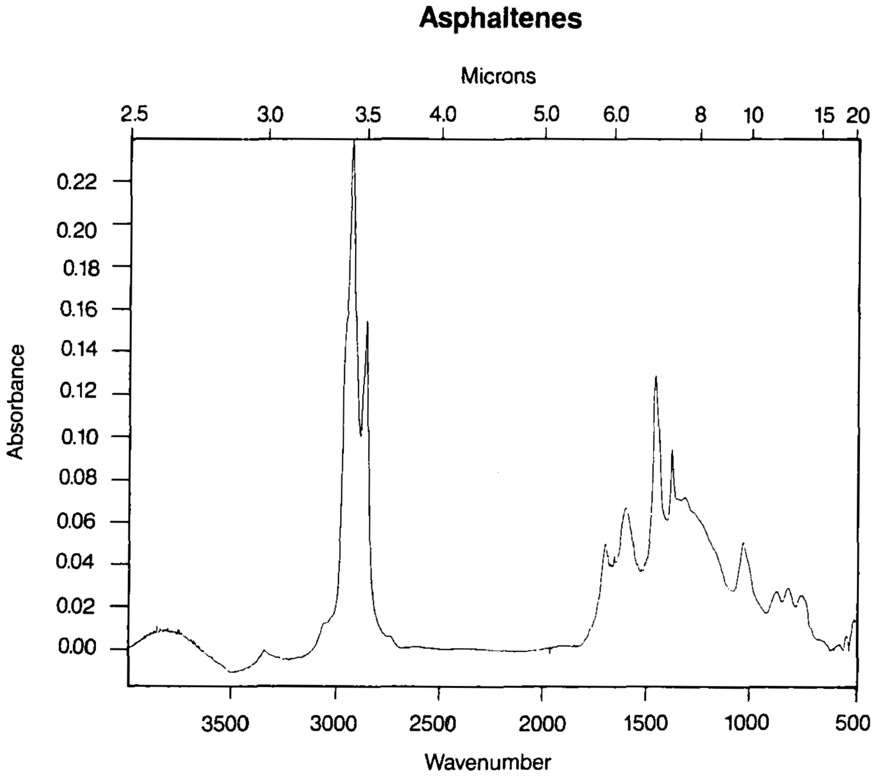


Figure 8. FTIR absorbance spectrum of unpyrolyzed asphaltenes.

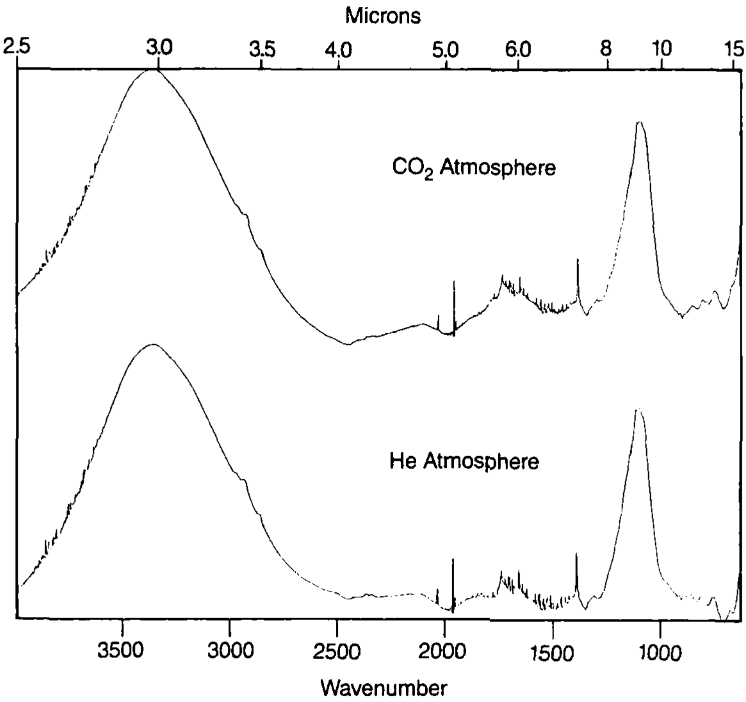


Figure 9. FTIR spectra of the supercritical CO_2 extracts from asphaltenes pyrolyzed at 500°C in CO_2 and He atmosphere.

Similar results were obtained from the FTIR studies of the unpyrolyzed asphaltenes, SFE blank, and the extracts from the asphaltenes pyrolyzed at 500°C in the two different atmospheres. The FTIR spectrum of the extraction blank indicated very little material except for residual methanol. Maximum absorbance was 0.01 absorbance units. The spectrum of the unpyrolyzed asphaltenes is shown in Figure 8 for comparison to the spectra of Figure 9 in which the extractable fragments after pyrolysis in helium and carbon dioxide are compared. The maximum absorbance for these spectra was approximately 0.22

absorbance units. Again it is clear that pyrolysis greatly altered the structure of the asphaltenes and that the differences between the two atmospheres are small. There is a subtle difference in the 1800-1900 cm-1 region where the CO_2-pyrolyzed sample shows a larger absorbance.

CONCLUSIONS

This work has shown that the analysis of pyrolysis products by SFE/SFC is feasible. SFE/SFC of the pyrolysis residues revealed that more material was recovered from the 500°C pyrolysis than from the 999°C pyrolysis. This supports the fact that the products produced as a result of pyrolysis are dependent upon the pyrolysis temperature both as previously reported (11,12) and shown in our Py/GC studies of asphaltenes. These larger fragments, produced by a reduced pyrolysis temperature, and their analysis by SFE/SFC can add another dimension to Py/GC because of the complementary natures of the data obtained. The ability to produce and analyze large fragments from high molecular weight species might have many implications for structural characterization when detectors which provide qualitative information (MS, FTIR) are used in conjunction with SFC. There appeared to be some alterations of the Py/GC and Py/SFE/SFE profiles resulting from changes in the pyrolysis atmosphere when the pyrolyses were carried out at ambient pressure. More work is needed to determine if these small differences are derived from reactions dependent on the chemical nature of the pyrolysis atmosphere or from physical properties of the atmosphere which could result in alterations of the kinetics of the pyrolysis process. More work is also needed to clarify the importance of CO_2 pressure, i.e., density, as work progresses towards an integrated, on-line pyrolysis/SFC method.

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