



Semicontinuous supercritical extraction
by Stanley Stephen Smith

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

Peat has been viewed as a possible alternate source of energy, and extractions with supercritical gases have been done to utilize such sources. The objective of this investigation is a screening study of the extraction of peat in a semicontinuous extractor with an alkaline methanol solvent in a supercritical state. The extraction column was a 12-inch long, stainless steel, one-inch diameter pipe. The solvent was pumped at the rate of 2.1 to 2.2 milliliters per minute. The solvent in the extract product was removed by a distillation under vacuum, and a moisture and, ash analysis was conducted on the residue. A Soxhlet extraction with tetrahydrofuran (THF) was also conducted on some of the residue products; thus, two yields were determined, a total moisture- and ash-free yield and a THF-soluble yield. The screening study entailed the four pressure and temperature combinations possible from 1760 and 2930 psia and 250° and 280° C. Two aqueous experiments were conducted to confirm a possible link between extract yields and pH of the solvent via the water gas-shift reaction. The ash analysis was not appropriate in the determination of yield for residue with large sodium hydroxide:organic content ratios. The sodium-hydroxide was also soluble in THF, which rendered problems with that yield determination. Changes in yield due to temperature and changes in yield due to basicity were pressure dependent. Carbon-13 nuclear magnetic resonance spectroscopy was used for characterization of some products. Future studies might include utilization of the extraction apparatus for residence time distribution studies and selective fractionation studies. Carbon monoxide /alkaline systems might also be studied.

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August 1983

APPROVAL

of a thesis submitted by

Stanley Stephen Smith

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Peat has been viewed as a possible alternate source of energy, and extractions with supercritical gases have been done to utilize such sources. The objective of this investigation is a screening study of the extraction of peat in a semicontinuous extractor with an alkaline methanol solvent in a supercritical state. The extraction column was a 12-inch long, stainless steel, one-inch diameter pipe. The solvent was pumped at the rate of 2.1 to 2.2 milliliters per minute. The solvent in the extract product was removed by a distillation under vacuum, and a moisture and ash analysis was conducted on the residue. A Soxhlet extraction with tetrahydrofuran (THF) was also conducted on some of the residue products; thus, two yields were determined, a total moisture- and ash-free yield and a THF-soluble yield. The screening study entailed the four pressure and temperature combinations possible from 1760 and 2930 psia and 250° and 280° C. Two aqueous experiments were conducted to confirm a possible link between extract yields and pH of the solvent via the water gas-shift reaction. The ash analysis was not appropriate in the determination of yield for residue with large sodium hydroxide:organic content ratios. The sodium hydroxide was also soluble in THF, which rendered problems with that yield determination. Changes in yield due to temperature and changes in yield due to basicity were pressure dependent. Carbon-13 nuclear magnetic resonance spectroscopy was used for characterization of some products. Future studies might include utilization of the extraction apparatus for residence time distribution studies and selective fractionation studies. Carbon monoxide/alkaline systems might also be studied.

INTRODUCTION

Because of a dwindling supply of petroleum resources, the search for alternate sources of energy and chemical feedstocks has been the center of many investigations in the last few decades. Coal has been given a large amount of attention as an alternative, but peat has also been getting some notice.

Many possibilities exist for the utilization of alternative fossil fuel resources. Presently, coal is used primarily as a fuel for power generating facilities. However, liquid hydrocarbons have been produced from coal for nearly two centuries. Various gasification and liquefaction processes exist for coal. Extraction by fluids under supercritical conditions may be a very promising method for recovery of hydrocarbons and related compounds. In the past decade, the National Coal Board in Great Britain has pioneered much of this type of work. Polar and caustic solvents have also been successful solvents for extraction of hydrocarbons.

Characterization of the extractive products is an important step toward utilization of the process under investigation. Techniques are continually improving, and characterization has been greatly simplified. Nuclear magnetic resonance spectroscopy is one method which has proven very useful.

A caustic polar solvent in a supercritical state may be successful in a hydrocarbon extraction. Because of peat's potential as an alternative energy and feedstock source, peat may serve as a suitable substrate.

RESEARCH OBJECTIVE

The main objective of this study was to investigate a supercritical extraction of peat with a basic methanol solvent. The extraction was to be done in a semicontinuous fashion, that is, the solvent would be the mobile phase in the extraction apparatus. Emphasis was to be put on an overall yield of organic material which was extracted from the peat, but some characterization of the products was also of interest.

Specific objectives might best be represented by two major divisions. The first was a screening study which would entail the supercritical extraction of peat with caustic methanol. The investigation was to be centered around two temperatures, two pressures, and three methanol solvents which varied in degree of alkalinity. This would require a method by which inorganic and organic fractions of the product might be distinguished to provide a basis for yield determination.

The second objective was to do fundamental characterization of various product outputs with carbon-13 NMR spectroscopy. The idea was to determine if the technique might be used to distinguish fundamental group differences which were caused by the various parameter and solvent changes.

BACKGROUND AND RELATED RESEARCH

Peat: An Alternative

Utilization of peat for energy is not a novel idea; peat has been used in Europe for centuries. Soper and Osbon {40:1} indicated that during World War I, an extensive survey of peat quantity and quality in the United States was done and possible uses of peat were suggested. Bodle, Punwani and Mensinger {7:559} stated that in the United States alone, some 1400 quadrillion British thermal units of easily recoverable fuel exist as peat. Peat also shows significant potential as a chemical feedstock.

Peat, the partially decayed debris of vegetable matter, is known as a young coal. The coal sequence begins with vegetative matter which is sequentially converted to peat, lignite, bituminous coal, anthracite and graphite (Soper and Osbon {40:7}). Peat is formed when the vegetable matter decays slowly via the regulation of available oxygen. This pertains to vegetation which is submerged in water. The fuel value of peat stems from the large portion of fixed carbon which is retained from the cellulosic structure during the slow decay process (Soper and Osbon {40:6-7}).

Like other fossil fuels, a large diversity exists in peat due to the plant varieties from which the peat had been formed, differences in climate, ages of deposits, water levels, and sediment deposits (Soper and Osbon {40:13}).

Peat is characteristically porous and very wet in its natural environment; however, peat can be air-dried very easily (Bodle, Punwani and Mensinger {7:561}). Peat also is acidic because of the presence of humic acids, the result of bacterial action (Higachi {17:1}). A typical ultimate analysis of peat on a moisture- and ash-free basis would be (Soper and Osbon {40:16}):

59.5	%	Carbon
5.5	%	Hydrogen
33.0	%	Oxygen
2.0	%	Nitrogen
0.2-0.6	%	Sulfur

Peat generally has a low content of sulfur, but the nitrogen content is generally high.

Soper and Osbon {40:17} indicated that ash can range from three to 30 percent of the dry weight of the peat and is traceable either to the plant cells or to mineral matter. Myklebust {23:8-9} indicated that the straight combustion of peat as a fuel has the same problems as the burning of coal; such problems are sulfur and nitrogen emissions and fly ash. But peat does have prospects of becoming a significant alternative to petroleum.

Extraction via Supercritical Fluids

Supercritical fluids. According to Smith and Van Ness {37:57-58}, homogeneous fluids are normally divided into two classes, liquids and gases, but the two phases become

indistinguishable at what is called the critical point. The vaporization curve of a pure material on a pressure versus temperature diagram terminates at the critical point, which has the coordinates of the critical pressure and critical temperature. These represent the highest temperature and pressure at which a pure material can exist in vapor-liquid equilibrium. Gangoli and Thodos {11:209} defined a supercritical gas as one which cannot be condensed to a liquid by an increase in pressure, that is, the temperature is above the critical temperature.

People in chromatographic sciences realized the benefits that a supercritical gas provided. Ample literature was available in this field about the characteristics of supercritical gases. Peaden et al. {27:1070} and Gere, Board and McMangill {12:736} stated some supercritical gas properties and characteristics, and they presented some advantages of the idea as it pertained to chromatography. Gere, Board and McMangill also investigated what effects a packed column had on supercritical gas properties. Such observations included: (1) as the mobile phase approaches the critical point, the density of the gas approaches that of a liquid; (2) solute diffusion coefficients are approximately two orders of magnitude more than those found in liquids; and (3) the fluid has a viscosity approximately that of gas and two orders of magnitude less than that of the corresponding liquid.

The characteristics that make a supercritical fluid an attractive solvent for chromatography are also attractive from an extraction standpoint. Williams {44:1769} summarized some advantages: (1) supercritical fluid extraction is particularly effective for the isolation of substances of medium molecular weight and relatively low polarity; (2) the separation can be accomplished at moderate temperatures and consequently be applied to the recovery of heat-labile substances of low volatility; (3) a supercritical fluid has high diffusivity and low viscosity, thus allowing rapid extraction and phase separation; (4) the solvent power can be varied over a wide range by varying pressure and temperature; and (5) the fluid is easily recovered from the extract and from extraction residue as a result of its high volatility.

An extraction with a supercritical fluid involves both an increase in vapor pressure and a phase separation, thus Williams {44:1769} pointed out the technique is related to distillation and extraction with liquid solvents. Work of Paul and Wise {26} offered a comprehensive review of the principles of extraction with compressed gases, and the relation to distillation and liquid-liquid extraction was discussed on a physical basis.

Paul and Wise {26:21-25} suggested that the solvent should have a critical temperature near the desired extraction temperature. This temperature should be such that the

solute is relatively volatile at the desired extraction pressure, which should be as high as possible.

Williams {44:1770-1772} also presented some theory of supercritical gas extraction with thermodynamic arguments, but with limited success. The availability of high-speed computers and the continuing effort which is being applied to thermodynamic analysis might lead to a better understanding of the dense fluid state and thus to the improvement of state equations and identification of new applications for supercritical gas extraction. He utilized experimental data to illustrate general principles and he classified phase behavior of some binary and ternary systems; a table was used to summarize the systems. Applications of supercritical extractions in various industries were also included.

Worthy {45} presented a general overview of the prospects of supercritical fluids. Gangoli and Thodos {11} indicated some properties and advantages of a supercritical gas along with some history about supercritical gas. They presented applications and compared liquid-liquid extraction to that of a supercritical gas extraction. Thermodynamic theory of supercritical extractions was also discussed.

Gangoli and Thodos {11:214-215} suggested a sequence of events which may occur during an extraction with a supercritical gas. The process sequence may be broken down into five steps: (1) the supercritical gas penetrates the micro-pore structure of the substrate; (2) the large molecular

aggregates are depolymerized and the resulting products dissolve in the solvent; (3) molecular bonds between the molecular species which are to be extracted and the substrate are broken; (4) the extract and the solvent gas diffuse from the micropore structure; and (5) the extract is recovered from the solvent gas as a precipitate or condensate by a reduction in pressure. They also proposed that the mechanism of gas flow through the substrate is a combination of Knudsen diffusion through the small pores and bulk diffusion through large pores, or permeation through the fracture system of the substrate.

Maddocks, Gibson and Williams {19} brought forth key points of a supercritical extraction process which included a view of process parameters such as solvent gas and coal type. They presented process economics and a flow model of a simplified, commercial scale supercritical extraction process. Results were listed which pertained to extraction of coal with toluene and paracresol.

Bott {8:232} also presented some of the economics of supercritical extraction processes. He pointed out that supercritical extraction techniques are high pressure processes which require special equipment. Unless the process includes energy recovery steps or maintains a low energy demand in some way, the technique might only be economical for high value products. Patents of various processes from a number of countries were listed. Some data on the

supercritical fluid extraction of tar sands and peat with n-pentane and benzene were given, as was information on supercritical carbon dioxide.

Scarrah {29} and Myklebust {23} both worked with supercritical extractions on peat in a batch extraction apparatus. The research was geared toward solvent behavior, and some solvents which were used were water, methanol and acetone. Scarrah ({30}, {31} and {32}) utilized a semicontinuous extraction apparatus and investigated the possibility of supercritical gas extractions on lignite and peat with various solvent systems and pressure fractionation.

Semicontinuous extraction. Most of the previous supercritical extraction work has been done in batch reactors. However, Scarrah {30:11} has done some work with the semicontinuous extraction of lignite with supercritical fluids, and he has discussed some of the advantages and disadvantages with the semicontinuous extraction apparatus. The pressure is easy to control, especially when compared to a closed batch system. The saturation of the solvent with solute is not a problem because pure solvent is always supplied in a continuous extraction. The last major advantage is the ease of product collection.

Some disadvantages of the semicontinuous method include the need for continual attention during an experiment, long experimental run times, and the increase in components which increase the chances for malfunctions (Scarrah {30:11}).

Another disadvantage is a plugging problem with some substrates and solvents.

Polar and alkaline solvents. For the success of an extraction process, the choice of solvent is significant. Various factors which make one solvent different from another include the ability to accept protons or contribute protons and dipolar characteristics.

Gangoli and Thodos {11:215} noted that polar solvents exert a stronger dissociating or depolymerizing action on coal than non-polar solvents in a supercritical state. Both water and methanol are polar in nature and both are relatively inexpensive. The major difference is that methanol is a strong proton-acceptor and a weak proton-donor but water is a strong proton-donor and weak proton-acceptor (Snyder {39:229}).

Methanol-water systems have been noted to extract up to 90 percent of the organics in oil shale at supercritical conditions {24:54}. The methanol was thought to be the major organic selective reagent. Scarrah {29} also suggested that methanol might be a good potential solvent for supercritical extractions.

Alkaline aqueous solvents have been successfully used to increase yields in hydrocarbon type extractions. Ross et al. {28} indicated that an increase in yield of benzene-soluble products from coal extractions is possible if the basicity of the aqueous solvent is increased. Basic

solvents have also been used to separate humic acids from coal (Higachi {17:1}).

The latter results indicate that a caustic polar solvent in a supercritical state may be successful in a hydrocarbon extraction. Because of its acidic nature, peat may serve well as a substrate in such investigations.

Characterization and Identification

Separations. A conglomerate of chemical species evolve from any type of effort which is geared toward the removal of hydrocarbons from fossil type resources. Uden et al. {43:38} suggested that the chemical species in such products may form the basis of major petrochemical feedstocks if characterization and separation can be achieved. They discussed the importance of characterization of hydrocarbon products, and they suggested a method for the separation of tar acid and tar base fractions of shale oil.

Farcasiu, Mitchell and Whitehurst {10} discussed a method for fractionation and characterization of Solvent Refined Coal through solvent extraction. Three major divisions exist. The oils are the hexane solubles, the asphaltene are the hexane insoluble-benzene soluble compounds, and the less soluble materials are benzene insoluble but soluble in pyridine. Sternberg, Raymond and Schweighardt {41:49} reported that the asphaltene fractions have generally an acid-base structure which can also be divided into the

two respective components. The hydrogen-bonded structure of the asphaltenes is compatible with their solubility characteristics. Thus, the characteristics of a solute are very dependent upon the solvent. Thin-layer chromatography, with the aid of visualization sprays, has been used to confirm the presence of aromatic phenols in the acidic component of petroleum asphaltenes. Mass spectrometry has been a very useful method for characterization studies (Ozubko, Clugston and Furimsky {25}). Nuclear magnetic resonance (NMR) spectroscopy, especially carbon-13 NMR, has also become very important in characterization studies.

Bartle, Martin and Williams {4} recognized the need for characterization of extraction products and reported on their work on a supercritical extraction of coal. The solvent was toluene. The characterization began with physical separations which utilized various solvents in a gel-permeation column. Work with NMR spectroscopy was also presented. The work of Bartle et al. {3} exemplified structural analysis of supercritical gas extracts of coal with emphasis on NMR spectroscopy.

NMR spectroscopy. Proton NMR spectroscopy can be used to distinguish the various environments which are present in the test sample, and thus provide an idea of aromatic versus aliphatic portions of the sample. When coupled with an ultimate analysis, the various components are often revealed. Carbon-13 NMR spectroscopy has become useful in that it

reveals direct structural information about the carbon groups which are present. This is especially useful for detection of those groups which do not contain hydrogen such as internal aromatic carbon, carbonyl, and aromatic ether. The advent of pulsed Fourier transform NMR and proton decoupling has made possible the distinction of well-resolved bands in both aromatic and aliphatic regions of the spectra of various coal derivatives (Snape, Ladner and Bartle {38:2189}).

Because of the distinct separation of aliphatic and aromatic carbon signals on a carbon-13 spectrum, when special precautions are taken, direct integration provides a ratio of aromatic to aliphatic carbon (Abraham and Loftus {2:150-160}, Sklenar et al. {35}, and Maekawa, Yoshida and Yoshida {20}). This has advantages over chromatographic-gravimetric methods for characterization of various compounds like aryl compounds with alkyl side chains. The physical separation of the aliphatic and aromatic carbon is impossible, and all the carbon of the compound is put in the aromatic or saturate fraction (Shoolery and Budde {34:1461}). However, any prior physical separation of a complex hydrocarbon mixture aids in the identification of groups or compounds.

Abraham and Loftus {2} presented a good background for the basic theory and terminology of NMR spectroscopy. Pulsed Fourier transform spectroscopy was also discussed.

The basis of NMR spectroscopy for identification of specific groups in different environments (shielding effects) is the chemical shift. A chemical shift is the response of various groups to radio frequencies in a magnetic field (Morrison and Boyd {22:419-420}). The spectrum is composed of signals which represent chemical shifts of various nuclei interactions. The reference point from which chemical shifts are measured is generally from an actual compound. Tetramethylsilane is a common reference compound and has been assigned the value of 0.0 part per million (ppm) on the delta scale (Abraham and Loftus {2:13-14}). This is on the right of the spectrum and most chemical shift signals occur downfield or to the left of 0.0 ppm.

Deuteriochloroform is often used as a solvent and reference because its signal at 77 ppm does not interfere with either the aliphatic or aromatic regions of the spectra field. The deuteriochloroform also provides the lock signal which is required for pulsed Fourier transform NMR spectroscopy. The lock signal merely keeps the radio frequency in synchronization with the inevitable small variations of the applied magnetic field (Abraham and Loftus {2:8}).

The most obvious division in a carbon-13 spectrum was that between aliphatic and aromatic carbon. Aliphatic carbon were represented in the 10 to 50 ppm range, and aromatic carbon were generally located downfield of 120 ppm. Snape

Ladner and Bartle {38:2189} suggested that solvent, concentration, and paramagnetic effects should not be forgotten because variations of up to 0.5 ppm had been observed in various situations.

Maekawa, Yoshida and Yoshida {20:864} stated that specific isolation of each individual compound was clearly impossible; however, some individual compound assignments might be done. Recent work with NMR spectroscopy was done by Coleman and Boyd {9} whereby the silicon-29 nucleus was used to determine hydroxyl-containing compounds in shale oil crude. Shelley and Munk {33} pointed out the availability of library searches for computer prediction of substructures from carbon-13 spectra. Carbon-13 enrichment procedures were used by Mikita, Steelink and Wershaw {21} for the determination of hydroxyl functionality in humic substances. Various chemical shifts which were common in humic substances were assigned.

The energy crisis has encouraged much research to be done with supercritical extraction and has focused some attention on peat as an alternative. The theory, characteristics, and applications of supercritical gas extractions are being developed. Characterization methods, especially those associated with NMR spectroscopy, are proving to be powerful tools in the search for alternatives.

RESEARCH DESIGN AND PROCEDURE

Experimental Design

The following approach towards the objective of this investigation was taken. Two water runs were planned to be conducted to confirm previous work by Ross et al. {28}, that is, an increase in alkalinity will increase the yield in an aqueous system. These experiments were to be done at 400°C and at a pressure of 3030 psia. One experiment would utilize pure water; the other experiment would employ a 0.5 molar sodium hydroxide solution.

The first objective, the screening study, was to be achieved with four pressure-temperature (P-T) combinations which are indicated in Table 1. A screening was to be done which involved three different methanol solvents of various degrees of basicity. Yield was to be based on the moisture- and ash-free (MAF) content of the peat. To

Table 1. Experimental Pressures and Temperatures.

Combination	1	2	3	4
Pressure (psia)	1760	1760	2930	2930
Temperature (° C)	250	280	250	280

psia - pounds per square inch absolute

° C - degrees centigrade

minimize organic degradation, the determination of the organic portion of the product output was to be initiated by removal of most of the solvent via a distillation under vacuum. A second method for determination of yield utilized a characterizing solvent, tetrahydrofuran (THF); the residue which remained after the bulk solvent removal step was subjected to a Soxhlet extraction with THF. The weight of the extracted organic material was then determined, and a yield was calculated. The two yields would agree only if all the organics were soluble in THF.

The first set of four experiments (one experiment for each of the four P-T combinations) was to be done with a methanol solvent which was one percent sodium hydroxide by weight. The second set of four experiments was to utilize a nine percent sodium hydroxide solution. The third set of four runs was to depend upon the outcome of the first eight runs. If no difference in yield was detected between the one and nine percent experiments, a solvent with less than one percent sodium hydroxide was to be used. If a difference was noticed, a five percent solution would be used for the four P-T combinations. Reliability of the experiments was to be checked via the duplication of various runs.

One experiment was to be performed with pure methanol at the P-T combination at which the screening experiment with the maximum yield was performed. In addition at this P-T combination, five optimization runs were to be conducted.

The five experiments were to investigate the effect of basicity of the methanol solvent. The runs were to consist of solvents with various degrees of sodium hydroxide concentrations with conditions centered about that of the maximum yielding screening experiment.

Carbon-13 NMR spectroscopy was to be used for the analysis of various product outputs. NMR experiments of two different fractions of the same methanol run were to be conducted to observe any changes during the course of an extraction. Differences between extracts which were caused by changes in pressure, temperature and basicity were also to be observed with appropriate NMR experiments.

Extraction products of different solvents were also of interest; thus characterization experiments which entailed the pure water run, the pure methanol run (material supplied by Granlund {14}), and a batch extraction of peat with acetone (material supplied by Myklebust {23}) were to be conducted.

Materials and Equipment

Materials. The peat was harvested in Michigan and was packed in plastic containers. The moisture content was 79 percent, and the combustible organic content was 20 percent by weight.

The methanol and tetrahydrofuran were technical grade, and the water was deionized and boiled. Primary grade sodium hydroxide pellets and concentrated hydrochloric acid were used for basic solutions and standard acid solutions,

respectively. The NMR work required primary grade deuterio-chloroform.

The extraction apparatus. Figure 1 depicts a schematic representation of the semicontinuous supercritical fluid extraction equipment. The manufacturer and model of the specific equipment is listed in Appendix A. A high pressure pump was used to feed the solvent and pressurize the system. Two back-pressure regulators were utilized. In lieu of a rupture disc, one was placed on the pump side of the column for a safety relief. The other was used to regulate the pressure in the system and was the location of the output stream of the system. The pressure of the system was measured by an electronic pressure sensor that was located in front of the column. Flow rate was measured by a calibrated glass column which was located beside the gravity-fed solvent feed container.

A check valve was located between the pump and the first back-pressure regulator. A high-pressure valve was placed between the pressure sensor and the column. Lines which preceded this valve were 1/4 inch lines, but a reduction to 1/16 inch lines followed the valve; the smaller lines were used throughout the rest of the system. Immediately following the column was a condenser which was cooled by water. A length of 1/16 inch tubing with appropriate fittings was available for a column bypass.

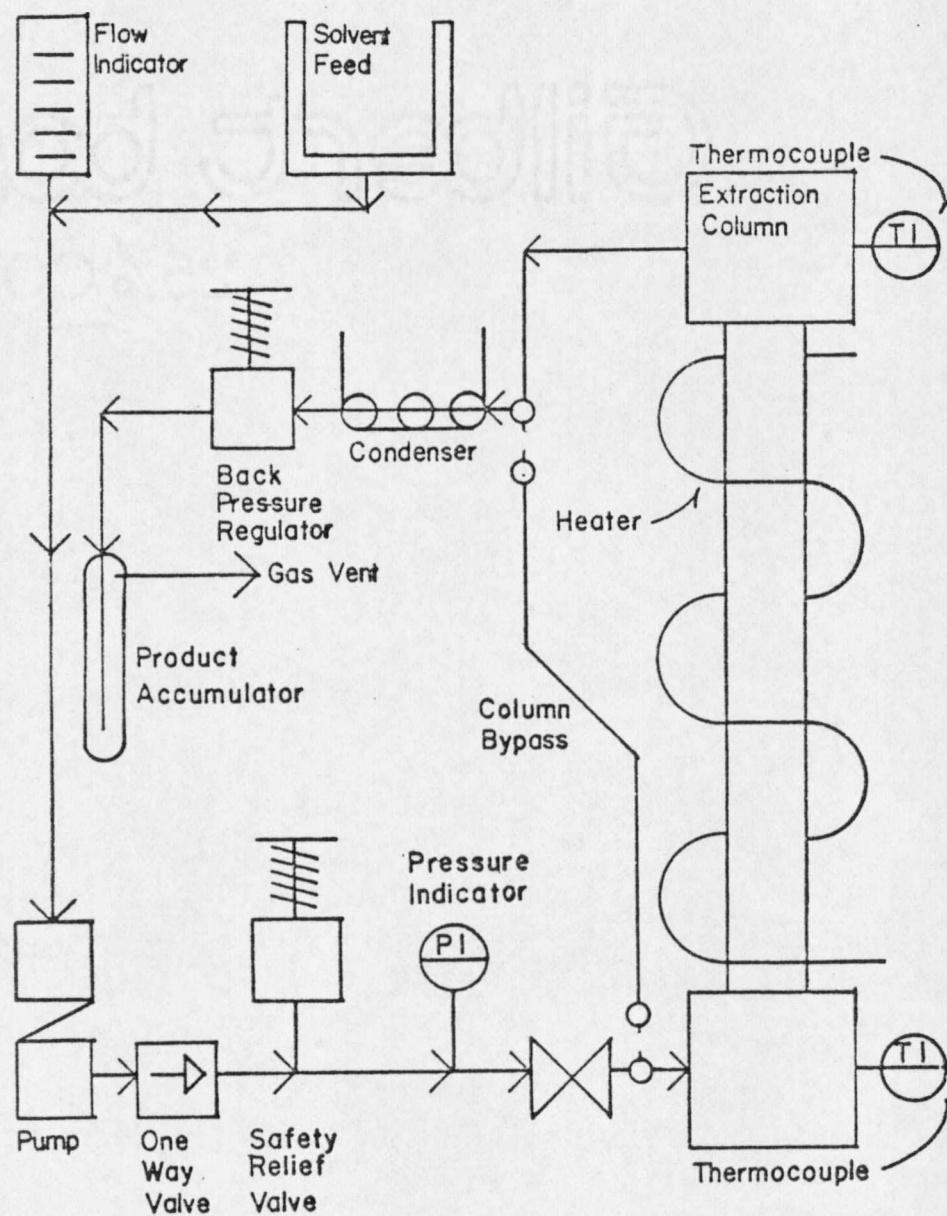


Figure 1. Flowsheet for Semicontinuous Supercritical Fluid Extraction.

The stainless steel column was 12 inches long and had an inside diameter of 0.62 inches (59.4 milliliter volume). The column was placed in an aluminum block and an electrical coil heater was used to bring the system to temperature. Temperature was monitored via two thermocouples, one placed on each end of the block, and a temperature recorder. Insulation was wrapped around the block to maintain temperature. The temperature was controlled by regulation of power input via a Powerstat variable transformer..

The product accumulator was such that any gaseous products from the system at the output could be drawn away by a gas vent. Detailed descriptions of the column and product accumulator are offered in Figure 2 and Figure 3 respectively.

Process and characterization. Major equipment which was used for processing included: a Buchi (Model R110) Rotavapor rotary evaporator for distillations under vacuum; a Soxhlet extraction apparatus; and two Mettler balances, one of which was capable of a weight determination to 0.0001 grams. A drying oven which was maintained between 100 and 110°C and a muffle furnace capable of temperatures of 700°C were necessary for moisture and ash analysis. A Varian gas chromatograph (Model 142010-00) and a Varian (Model 9176) recorder were used for both gas and liquid product analysis. Porapak Q was the packing of the gas analyses column. A Bruker Instruments WM-250 NMR spectrometer was used for characterization of final products. The operating parameters

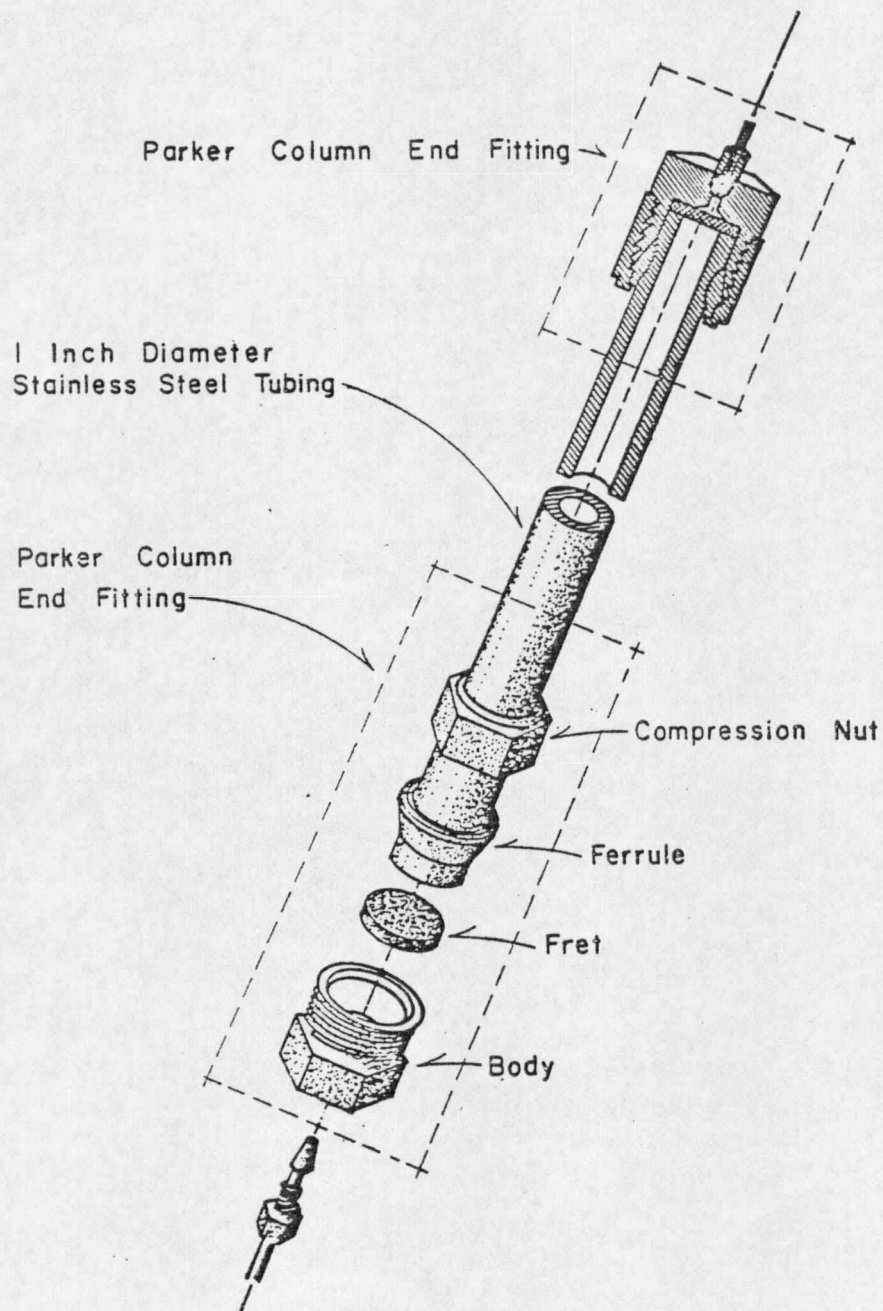


Figure 2. Extraction Column.

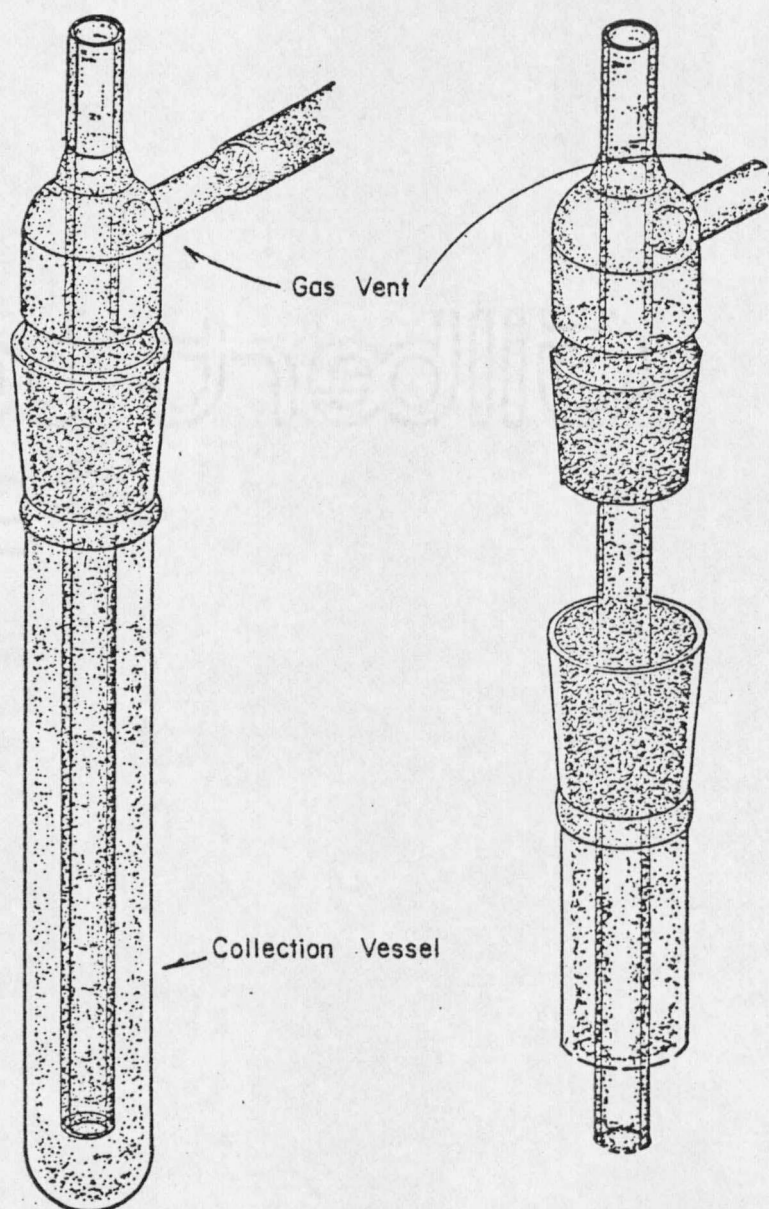


Figure 3. Product Accumulator.

that Abbott {1} had suggested for the NMR work are provided in Appendix B. Becker, Ferretti and Gambhir {5} discussed selection of optimum parameters for pulse Fourier transform NMR experiments.

Experimental Procedures

Moisture and ash analysis. The moisture and ash analysis was always done in duplicate whenever possible. The sample was placed in a clean, dry, tared crucible and the weight of the aliquot was determined. The crucible was then placed in an oven which was maintained between 100 and 110° C for 12 hours to ensure that all moisture and substances which were less volatile than water would be drawn off. The crucible was placed in a desiccator to cool before the weight was recorded. The crucible was then placed in a cool oven, and the temperature was brought up to 700° C. The oven was turned off after 12 hours and allowed to cool to approximately 100° C before placement of the crucible and lid into the desiccator. Again the weight was recorded. The amount of organics was assumed to be the loss in weight after combustion.

Experimental preparation. The solvent was prepared by dilution of a methanol solution, which was saturated with sodium hydroxide, to the desired concentration. Exact sodium hydroxide concentration of the solvent was determined via titrations with standard hydrochloric acid solutions at

ambient conditions. The indicator which was used in the titrations was phenolphthalein (Huber {18:91}).

A separate container with a small, sealable plastic bag was used for the storage of sufficient peat for approximately five experiments. Three times, which were random during the course of the investigation, a moisture and ash analysis was done on the peat. The extraction column was packed with approximately forty grams of peat and approximately one inch of space was left at the bottom of the column. To eliminate some potential for the column to plug up, a small hole was axially bored through the center of packed peat. The column was placed into the aluminum block. The heater was placed around the block, which was then placed on the extraction apparatus. The two thermocouples were put in place before the insulation was wrapped around the block.

The solvent was put in the feed tank and the pump was started. All lines which bypassed the column were filled. The safety relief-back pressure regulator was set at a pressure which was approximately 200 psi higher than the prospective run pressure.

Procedure of run. The column bypass was removed, and the bottom of the column was connected to the solvent line. The pump was started and heating was initiated. As soon as solvent reached the top of the column, the column was connected to the condenser line and the pressure was slowly increased to 500 psi by manipulation of the output back

pressure regulator. The pump was then shut off, but the pressure would continue to rise as the temperature of the column increased and the pressure was regulated with the back pressure regulator at the output port. When the run pressure was obtained, a collector vessel was placed at the outlet and the extract collection was started. Temperature was monitored and controlled until a steady temperature profile was maintained about the desired run temperature. The pump was then started and the solvent was fed at a rate of 2.1 to 2.2 milliliters per minute. A collection vessel was replaced after approximately 110 milliliters were collected. On occasional runs, a gas sample was obtained from the gas vent of the product accumulator for analysis.

A run was considered complete when the solvent output was clear. The pressure was released at the output regulator to collect any product which might have collected in the lines. The pump and heating coils were then shut off.

Post-run procedure. The bulk of the liquid product was distilled off at temperatures which did not exceed 65° C and at pressures such that water would vaporize. The distillation utilized a tared, 1000 milliliter boiling flask. After the distillation, all that remained was a "wet" residue of moderately heavy hydrocarbons, sodium hydroxide and any other ash that might have been collected. A portion of the residue was saved for possible future analysis and a moisture and ash analysis was conducted on another portion. For the

latter runs, a 24-hour Soxhlet extraction with tetrahydrofuran (THF) was done on the residue. The THF was removed via evaporation and the amount of the remaining product was determined by the weight of the previously tared 500 milliliter boiling flask. Control runs were necessary to determine the solubility of sodium hydroxide in THF.

Analysis of data. For each run, the total amount of organic material in the charged peat was determined on a moisture- and ash-free basis. This total weight of organic material was used as the basis of an overall yield.

Two different methods were used to determine this yield. The first (1) utilized the results of the moisture and ash analysis of the "wet" product, the other (2) utilized the results of the THF-soluble product after correction for the solubility of sodium hydroxide in THF. The two methods were:

$$(1) \text{ Total MAF Yield} = \frac{(\text{MAF of residue})^*}{\text{MAF peat}}$$

$$(2) \text{ THF-Soluble Yield} = \frac{(\{\text{THF-soluble}\} - \{\text{SSC}\})^*}{\text{MAF peat}}$$

* aliquot corrected to total weight

SSC- Sodium hydroxide solubility correction.

(note: multiply by 100 to obtain yield in percent)

The signal assignment method which was used for the analysis of the carbon-13 NMR spectra was suggested by Snape, Ladner and Bartle {38}. Since a large number of carbon-13

chemical shifts had been identified for many groups and associated compounds of coal-derived materials, pure analysis of the spectra was not necessary. Instead, an assignment scheme was used to derive structural information.

RESULTS

All percentages which appear in the following sections were based on weight. The organic basis for yield was the moisture- and ash-free content of the peat (MAF peat). The MAF peat was found to be 20.1 percent of the originally charged peat. The moisture content of the peat was 78.9 percent, and the ash content was one percent.

A general observation for the extraction runs was that the bulk of the extracted material precipitated out in the collecting vessels because of the drop in temperature and pressure. A filtration was conducted on the effluent from a preliminary run, but the particles were very small and many penetrated through the filter. A centrifugation was also conducted, and most of the particulate product formed a cake at the bottom. The solvent, however, was still colored. A THF-soluble portion of the precipitate was the subject of an NMR experiment, the results of which will be presented in a subsequent section.

Another observation was the drastic change in the extraction times for the screening experiments. For the three caustic methanol (one, five and nine percent sodium hydroxide) solvents, the effluent from the low pressure (1760 psia) runs at 280° C would clear after 400 to 500 milliliters of effluent were collected. Those low pressure (1760 psia) runs at 250° C required collection of 500 to 700 milliliters

of effluent. For the high pressure (2930 psia) runs with basic methanol solvents, 1200 to 1400 milliliters of effluent were collected before the effluent cleared. An exception was the nine percent sodium hydroxide run at 280° C, which required the collection of only 350 milliliters of effluent. The pure methanol run at 2930 psia and 280° C required the collection of 400 milliliters of effluent. Actual quantities of effluents which were collected for each of the runs may be found in Table 2.

Twenty successful extractions were conducted during the study. A description of each run's analysis is summarized in Table 3. The yields of eight methanol runs and the two water runs were calculated by the moisture and ash method, that is, the total MAF yields were determined. The yields of the remaining experiments were calculated by both the ashing method (total MAF) and the tetrahydrofuran-soluble method.

The total MAF yield of the pure water run was eight percent, whereas the total MAF of the 0.5 M sodium hydroxide aqueous run was 12 percent. The yield for the alkaline run was low because the run was not completed. However, an increase in yield was observed with the increase in basicity. The run was not completed because the column end cracked and pressure was lost in the middle of the run.

All the yields which were determined from this investigation are tabulated in Table 3. Table 3 indicates the various duplication runs that were both supportive and

Table 2. Run Descriptions.

Run #	Charged Peat (grams)	Solvent*	Pressure (psia)	Temper- ature (°C)	Amount Effluent (milliliter)
6	41.2	1.1	2930	280	1200
7	41.1	1.1	1760	280	500
8	40.0	1.0	2930	250	1200
9	47.0	1.0	1760	250	700
10	44.3	8.9	1760	250	700
11	40.6	8.9	2930	250	1400
13	41.4	9.0	1760	280	500
14	39.6	5.0	2930	250	1400
15	41.4	5.1	2930	280	1400
16	42.8	5.1	1760	250	500
17	41.8	9.0	1760	250	700
20	40.1	5.1	1760	280	400
21	43.3	9.1	2930	280	350
21'	39.3	9.1	2930	280	350
22	41.4	3.2	2930	280	1400
23	40.8	1.0	2930	280	1400
24	43.7	5.2	2930	280	1200
25	41.6	1.0	2930	280	1400
26	41.0	0.0	2930	280	400
27	43.1	water	3030	400	300
28	42.2	0.5M NaOH in water	3030	400	Stopped at 260

* percent sodium hydroxide (NaOH) in methanol unless stated.

Table 3. Yield Summary

Pressure (psia) → Temperature (°C) →		1760 250	2930 250	1760 280	2930 280	2930 280	3030 400
Solvent ↓	Yield ↓						
methanol	THF	----	----	----	----	30*(26)	----
1 % [∇]	MAF- THF	28 ^{±1} (9) ----	26 ^{±1} (8) ----	21 * (7) ----	38 ^{±3} (6) ----	40 ^{±2} (25) 25	----
3 % [∇]	MAF THF	----- ----	----- ----	----- ----	----- ----	150 ^{±50} (22) 24	----- ----
5 % [∇]	MAF THF	38 ^{±2} (16) ----	236 ^{±40} (14) 15	27 * (20) 14	216 ^{±50} [§] (15) 74	92 ^{±20} (24) 21	----- ----
9 % [∇]	MAF THF	41 ----- (10)	180 ^{±40} (11) -----	47 ^{±2} (13) -----	** (21)	** (21)	----- ----
H ₂ O	MAF	----	----	----	----	----	8*(27)
.5 M NaOH	MAF	----	----	----	----	----	12*(28)

(#) - Run number

* - No duplicate, not enough 'wet' product

** - Identical runs, liquid product after distillation under vacuum.

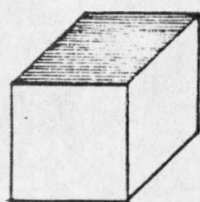
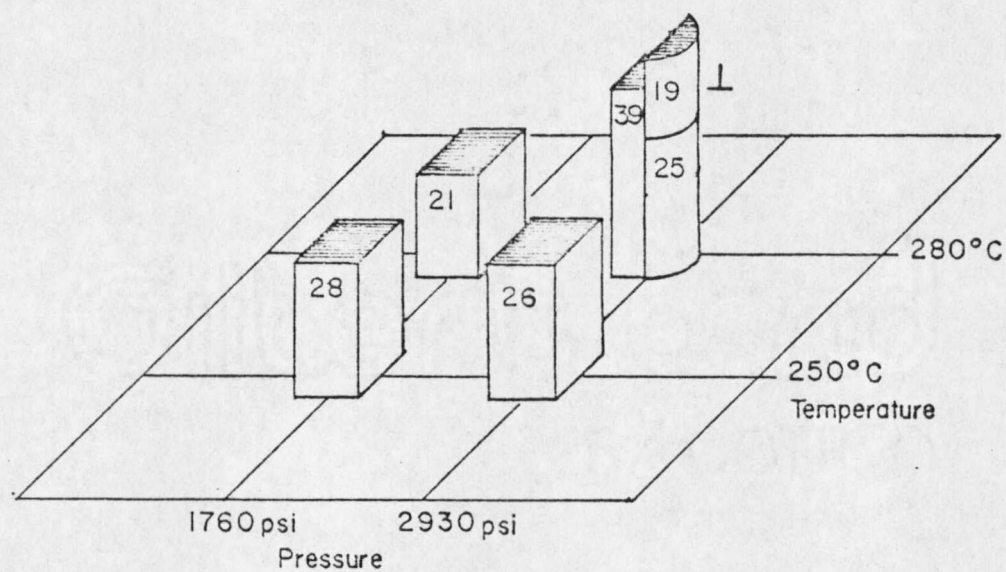
§ - Suspect weighing error

%[∇] - Weight percent sodium hydroxide in methanol.

non-supportive for the experimental procedures. The second duplication run (Run #25) of the 2930 psia and 280° C P-T combination of the one percent caustic methanol indicated a total MAF yield of 40 percent; this compared to a yield of 38 percent for the first run (Run #6) at those conditions. The first duplication run (Run #23) indicated a very high total MAF yield (87 percent) and the discrepancy was attributed to a weighing error. A second comparison concerned the first run (Run #15) of the five percent caustic solvent at 2930 psia and 280° C which had an extremely large THF-soluble yield of 74 percent. A duplication (Run #24) yielded a reasonable result of 21 percent.

The various yields of the methanol experiments are summarized in the following figures. Figure 4 depicts the total MAF yields of the one percent sodium hydroxide solvent for the four P-T combinations. The THF-soluble yield of 25 percent for the 2930 psia and 280° C run is shown beside the total MAF yield of 39 percent. The ashing result of the THF extract residue is also represented (19 percent); thus a direct comparison of the two yields was possible. The THF-soluble yields of the five percent sodium hydroxide experimental series are illustrated in Figure 5.

The changes in total MAF yield due to the change in alkalinity of the solvent at the low pressure runs are depicted in Figure 6. Figure 7 signifies the changes in THF-soluble yield because of solvent changes at 2930 psia.



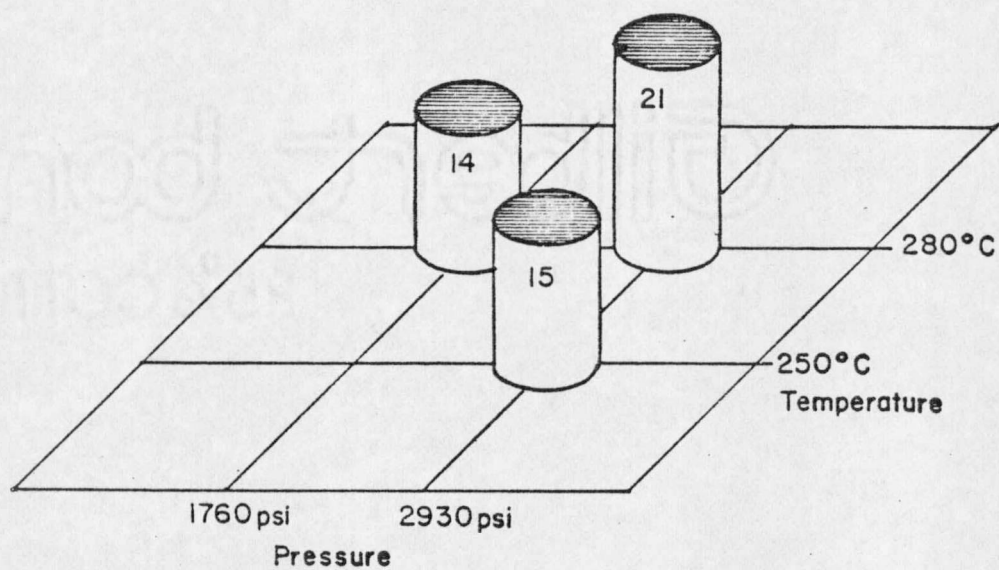
= Percent Total MAF Yield



= Percent THF-Soluble Yield

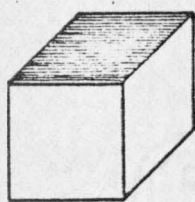
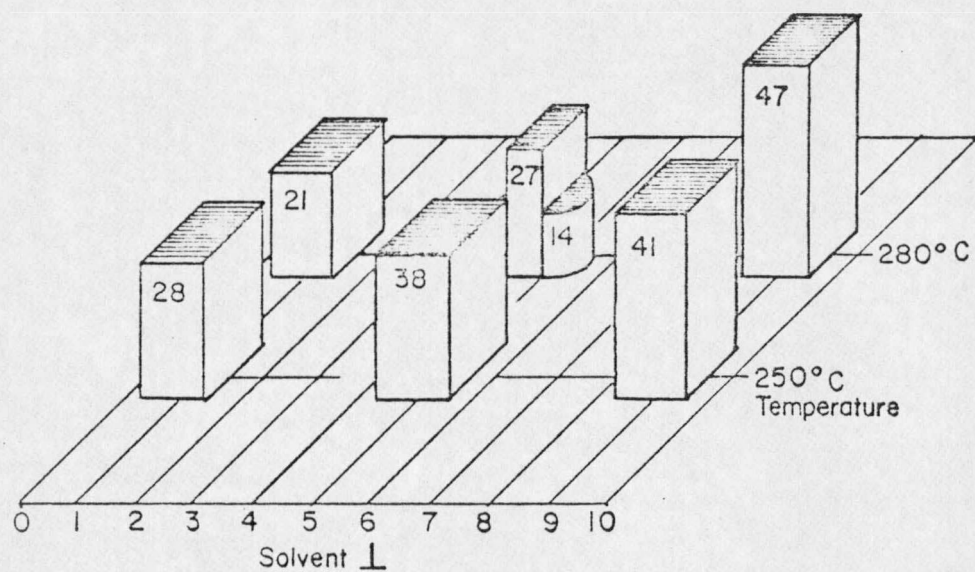
⊥ = Total MAF contribution of THF-insoluble residue

Figure 4. Percent Yield with One Percent Sodium Hydroxide in Methanol.



= Percent THF-Soluble Yield

Figure 5. Percent Yield with Five Percent Sodium Hydroxide in Methanol.



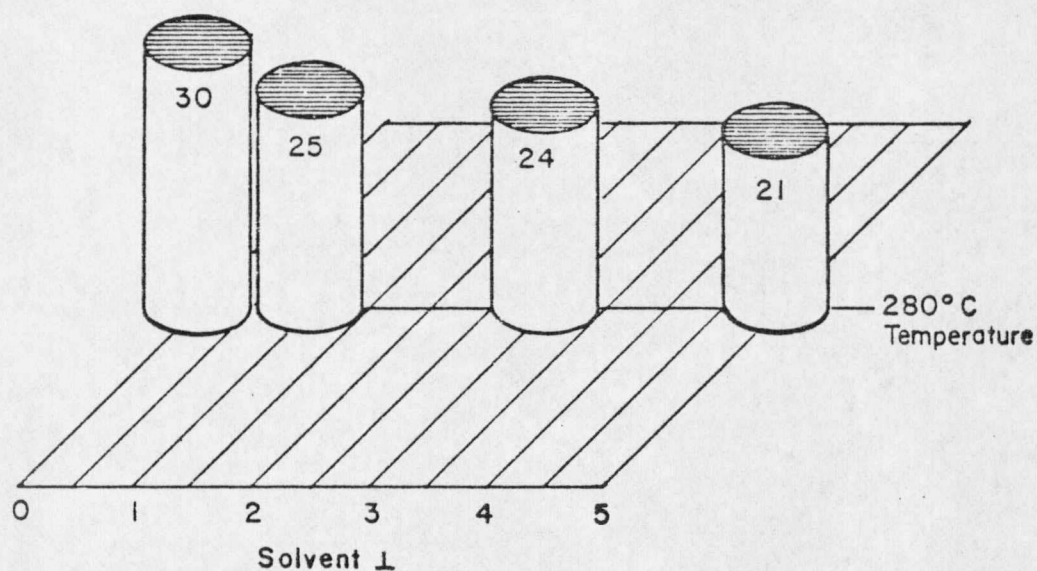
= Percent Total MAF Yield



= Percent THF-Soluble Yield

⊥ = Weight percent Sodium Hydroxide in Methanol

Figure 6. Percent Yield with a Constant Pressure of 1760 psia.



= Percent THF-Soluble Yield

L = Weight percent Sodium Hydroxide in Methanol

Figure 7. Percent Yield with a Constant Pressure of 2930 psia.

Figures 4 and 5 indicate that the best P-T combination was 2930 psia and 280° C for both the one and five percent sodium hydroxide in methanol series of runs. A total MAF yield of 39 percent for the one percent sodium hydroxide run and a 21 percent THF-soluble yield for the five percent sodium hydroxide run were obtained at the best P-T combination.

The total MAF yield dropped from 28 percent to 21 percent when the temperature increased from 250° C to 280° C at 1760 psia and 1 percent sodium hydroxide; however, the same increase in temperature at 2930 psia increased the total MAF yield from 26 percent to 39 percent. Yields from the 2930 psia and 280° C runs with the nine percent sodium hydroxide solvent were not calculated because the distillation of the extract under vacuum did not yield a solid due to extract-solvent reactions.

Figure 7 indicates that the THF-soluble yields at the 2930 psia and 280° C series of tests decreased from 30 percent for pure methanol to 21 percent for the five percent caustic solvent. However, as Figure 6 depicts, an increase in basicity did increase the total MAF yields of the two low pressure (1760 psia) series (28 to 41 percent at 250° C and 21 to 47 percent at 280° C).

The extractions of two runs (Run #21 and Run #21') with the nine percent caustic and at the high pressure and temperature condition were identical for all visual observations. Each required the collection of only 300 milliliters

of effluent, both were very prone to plugging, and the solvent of both extracts could not be removed via the distillation under vacuum.

The gaseous outputs of three runs were analyzed with the gas chromatograph. The major observation was the large quantity of carbon dioxide and evidence of hydrogen in the gas analysis of two of the runs, Run #13 and Run #28. Run #28 was the caustic aqueous run (3030 psia, 400° C and 0.5 M sodium hydroxide). The other run, Run #13, was the nine percent sodium hydroxide in methanol run at 1760 psia and 280° C. An analysis of Run #24, which was a run with five percent sodium hydroxide at 2930 psia and 280° C, indicated a small constituent of the gas sample was carbon dioxide. The presence of a small amount of methane was also verified. Carbon monoxide was presumed to be present, although air was located in the same position on the chromatogram and thus carbon monoxide could not be identified. The existence of some heavy compounds in the caustic water run (Run #28) was noted.

The gas chromatograms of the distillate from the solvent removal step of a caustic methanol run indicated that methanol was the major constituent. Water comprised approximately five percent of the distillate and an unknown trace compound comprised less than one percent of the distillate.

Three control experiments were conducted to determine the solubility of sodium hydroxide in THF during a Soxhlet extraction. One control consisted of 60 grams of sodium

hydroxide pellets. The other two controls were done with "wet" sodium hydroxide of 10 grams and 20 grams respectively. A simulated caustic methanol product solution was made by the addition of sodium hydroxide pellets to the distillate from a number of distillations under vacuum from previous runs. The solution was five percent sodium hydroxide. The "wet" substrate was the residue which remained after the latter solution was subjected to the solvent removal step of the post-run procedure, a distillation under vacuum. The "moisture" content of the residue was approximately 50 percent. The Soxhlet extractions were all done for a 24 hour period and the amount of sodium hydroxide was determined after the THF was removed. For all three cases, the sodium hydroxide "yield" was 0.15 grams.

Eight experiments were conducted on the NMR spectrometer. The spectra with a signal location summary are located in Appendix B. The eight NMR experiments and the various supercritical extraction process variables which could be examined are summarized in Table 4.

Table 4. NMR Experiments and Process Variables

NMR exp.#	Fig. #	Solvent	Run Data pressure (psia)	temperature (°C)	Comment*
E-1 [†]	9	methanol	2000	270	1 st fraction
E-2 [†]	10	methanol	2000	270	3 rd fraction
E-3	11	caustic**	2930	280	
E-4	12	caustic**	1760	280	
E-5	13	caustic**	2930	250	
E-6	14	caustic**	1760	250	precipitate
E-7	15	water	3030	400	
E-8 [§]	16	acetone	3915	430	batch extract

* all THF-soluble.

† same run; from Granlund {14}

** caustic implies five percent sodium hydroxide in methanol.

§ from Myklebust {23}

NMR Experiments

Process Variable

E-1, E-2

extraction time

E-2, E-4

pressure

E-3, E-5

temperature

E-1, E-7, E-8

solvent

DISCUSSION

The ensuing discussion encompasses six major divisions. (1) Problems with the extraction equipment and the general observations are discussed. (2) Work done by Ross et al. {28} is summarized to possibly explain some results, especially the water results. (3) A critique on the ashing method is offered to explain the problems of the method as it pertained to this study. (4) Problems also existed with the THF-soluble method of organic yield determination, and these are discussed in a similar fashion. (5) Results of the methanol runs prompted interesting questions which are discussed. (6) The differences in the various runs were obvious from NMR experiments, and a few observations are drawn from this evidence.

Equipment Problems and
General Observations

The advantages of the semicontinuous apparatus were confirmed. Pressure was in general easily controlled to within 20 psi of the desired pressure. The first few fractions of a particular run might have had a saturated solvent, but the extraction discharge always cleared with subsequent fractions. The extract was easy to collect for processing. The accessibility to the various components of the apparatus was also confirmed. Small equipment modifications were easily done.

Some disadvantages caused more problems than others. Plugs were quite common, especially from the moment when the solvent was introduced into the column and through the heat-up period. Not many plugs developed after the desired pressure and temperature were obtained. Granlund {14} developed a method whereby most of the initial plugs were avoided. During the loading of a column, prior to a run, a small hole was axially bored through the center of the packed peat. This allowed solvent to flow freely initially. No evidence of the holes were found when the columns were disassembled as the peat would migrate toward the column outlet during the extraction. Occasionally a plug would develop during a run at the column output or along the condenser.

The threat of a plug required continual attention during a run; as soon as a plug developed, the pressure would rapidly increase. After several rupture discs were destroyed, a back-pressure regulator was used for a safety relief, and it replaced the rupture discs. This provided the operator with a new pressure control option and the high pressures which were associated with plugs were avoided.

A major equipment problem which hindered this investigation involved the column end fittings. The Parker fittings, which were detailed in Figure 2, were not able to withstand constant usage at the torques which were required by high pressures. After five runs, the body would generally expand around the ferrule and the compression nut would

stretch, thus a high pressure seal was difficult or impossible to achieve. Because the column was disassembled after each run, the threads of the body and compression nut wore quickly. Twice during the course of a run the body cracked and the pressure of the system was lost.

The need of refinement of post-run procedure was evident. Because of the singularity of most runs, the need for further verification of reproducibility must be emphasized.

Results of the duplication runs indicated that some problems existed, however some support was also rendered. The two pair of identical runs with the one percent (Run #6 and Run #25) and nine percent (Run #21 and Run #21') caustic methanol both lent credibility to the experimental procedures. (Run #6 and Run #25 had total MAF yields of 38 and 40 percent respectively; and Run #21 and Run #21' were alike as to the visual clearing and plugging after 350 milliliters of effluent were collected.) The duplicate runs which yielded very different results indicated the need of further experimentation and procedural refinement. (The first duplication, Run #23, of Run #6 had a total MAF yield of 87 percent; Run #15 also had a very large THF-soluble yield of 74 percent, and the duplication run, Run #24, had a THF-soluble yield of 21 percent.) General observations of the extraction itself were good; however, the caustic solvents perplexed the yield determination.

The most obvious observation of the study was the sensitivity of the solvent power to pressure and temperature changes, which was evident from Figures 4, 5, 6 and 7. This supported what Williams {44:1769} had described as an advantage of supercritical gas extractions, that the solvent power could be varied with changes in pressure and temperature. Discussion of this observation will be curtailed to that section which discusses the caustic methanol experiments.

The reason for the large quantity of effluent which was associated with the high pressure might be explained by the first step of a supercritical extraction which Gangoli and Thodos {11:214} had suggested (page 8). This was the penetration of the solvent into the micropore structure. As pressure was increased, the degree of penetration into the micropore might be expected to increase.

The increase in pressure did not necessarily imply an increase in yield, as Figure 4 indicates with the runs at 250° C; thus the large extract quantity which was associated with the high pressure might suggest that the rate of pore diffusion decreases with an increase in pressure, at least at pressures above the critical point. Gangoli and Thodos {11:215} had proposed that both bulk diffusion and Knudsen diffusion were involved with gas transport through the large and small pores, respectively. Not much is known about diffusion rates at these pressures (Bird, Stewart and Lightfoot

{6:506}) and no attempt was made to predict the type of diffusion which was controlling. Since the increase in extract was also linked to the basicity of the solvent, other effects must be significant for micropore penetration. Such an effect might be the affinity of the acidic groups of peat for the basic solvent.

Existence of a precipitate in the collection vessel supported the supercritical extraction process mechanism which was proposed by Gangoli and Thodos {11:214}. Contradictorily however, the dark color of the solvent indicated that some material was dissolved in the solvent.

Since an overall yield was desired, the approach of solvent removal via distillation under vacuum was adopted. The vacuum enabled removal of solvent at temperatures which did not exceed 65° C, thus decomposition of organics was minimal. The gas chromatograms of the distillate confirmed that loss of organics was very minor (page 40). The organic content of the residue of this distillation ("wet" product) was then determined.

The total MAF yield method for organic determination was found to be insufficient for those experiments where the ratio of MAF carbon to sodium hydroxide content was very small in the "wet" product. Thus, the amount of THF solubles were determined for the remaining experiments. This problem is discussed in a subsequent section.

A conversion, which is usually based upon the organics which have not been removed from the substrate, was not determined for numerous reasons. The most common way for organic content determination was an ash analysis that was based on a constant ash content. However, in this investigation the caustic solvent was partially inorganic and the assumption that the ash content would remain constant could not be made because sodium hydroxide would accumulate in the extraction column with the substrate. The only way by which the conversion could be determined would be the removal of all the substrate from the column after an extraction run. This would have been a very difficult task as peat residue had to be washed off the column walls during cleaning; an indication that not all the substrate could be easily removed without some loss of substrate. An ash analysis of a portion of the material which remained in the extraction column after the three percent sodium hydroxide extraction at 280° C and 2930 psia (Run #22) indicated an ash content of 65 percent and a 35 percent organic content on a moisture-free basis. This corresponded to a conversion of 90 percent based on constant ash and indicated that problems were indeed present; the yield was much lower (24 percent THF-soluble yield).

Results of the gas chromatographic analysis (page 40) of the gaseous output were expected. Some decomposition of organics and some organic reactions were inevitable as the

existence of carbon dioxide and methane respectively verified. Hydrogen was also indicated to be present. The latter results all confirm the findings of Ross et al. {28}.

Aqueous Extractions

Work by Ross et al. Ross et al. {28} worked on the batch extraction of coal with a carbon monoxide and water system. The following is a summary of their work and fundamental observations that they made. The process conditions were 600 psi and 400° C, and 20 minutes constituted a run. The findings of Ross which were pertinent to this investigation are summarized in Figure 8.

Figure 8 indicates that the percent of benzene-soluble coal products increased dramatically as pH of the system increased above 12.6. A jump in carbon dioxide and hydrogen in the output gas was also noted at the pH of 12.6. An explanation was offered whereby the water gas shift reaction was assumed to be a dominant factor. Equal quantities of carbon dioxide and hydrogen are products of the water gas shift reaction, which has carbon monoxide and water as reactants. The carbon monoxide was thought to be a necessary constituent for the increase in conversion.

Water runs. Since Ross et al. used a nonorganic solvent (water), they were able to provide a closed mass balance of their whole system, which was a batch extraction. Such a balance was not possible in this investigation for two

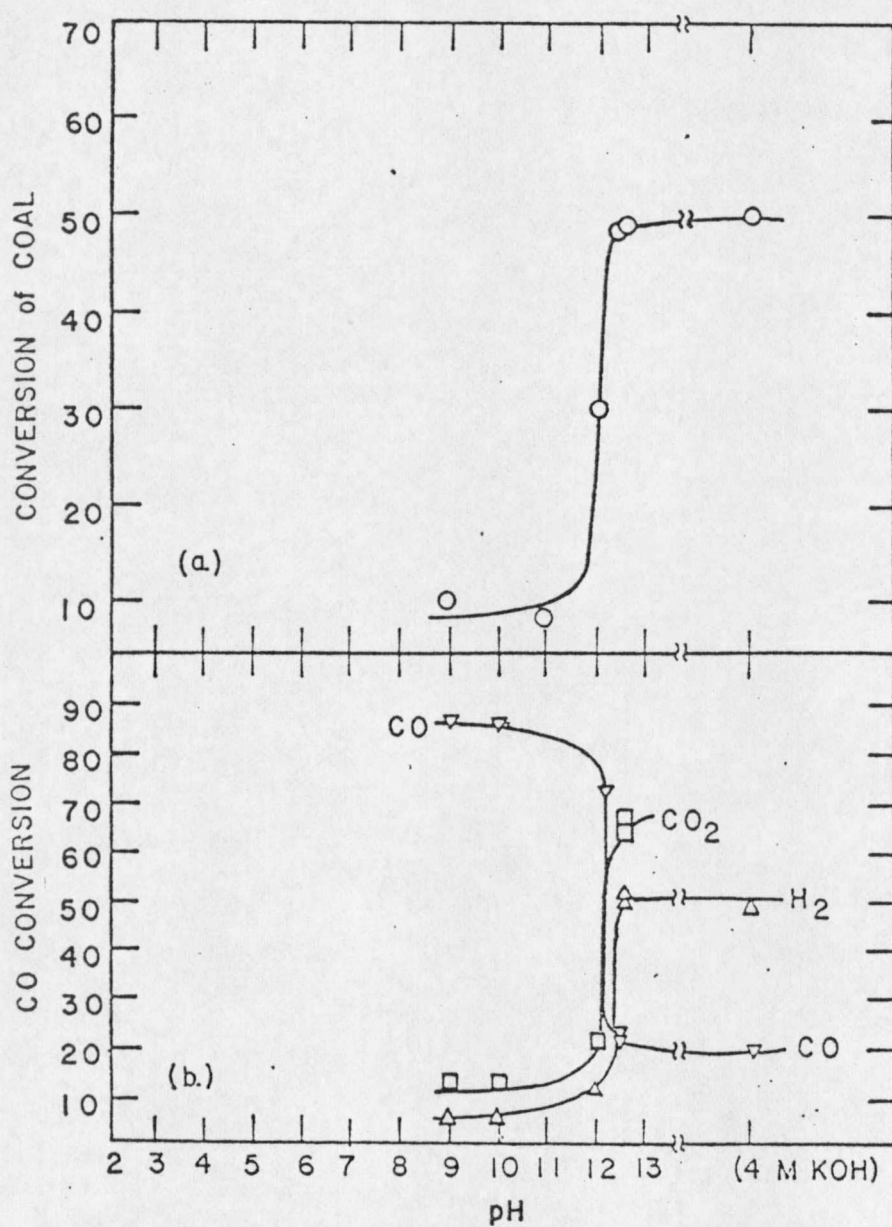


Figure 8. (a.) Conversion of Coal to Benzene-Soluble Fractions versus pH of Initial Medium (O=CO₂). (b.) CO Conversion (▽=CO; Δ=H₂; □=CO₂). (Ross et al.{28:B-3})

reasons. Because the solvent was methanol for the majority of the runs, the organic solvent could not be assumed to be chemically non-reactive. Indeed, the nine percent runs (Run #21 and Run #21') which were conducted at the high pressure and temperature indicated that a reaction involved the solvent; the resulting extracts boiled well above 100° C. The second problem would have been associated with the semicontinuous nature of the extraction; thus, output gas would continually change in composition as the extraction proceeded. This was also the reason that few gas analyses were done; because the gas compositions would vary, only relative amounts of the gases could be feasibly determined.

Evidence of a possible link between results of this investigation and observations of the former study existed. Since carbon dioxide was a significant gaseous product of the caustic run and the yield of the caustic run was larger than that of the pure water run, it is possible the water gas shift reaction might have taken place. Hydrogen was also detected in the output gas of the caustic run; this provided additional evidence for a probable connection. The latter hypothesis raised questions about possible sources for the carbon monoxide and water.

The pyrolysis of the peat during an extraction might be a possible source of the carbon monoxide. Timpe {42} did a pyrolysis study of various coals at temperatures greater than 500° C and carbon monoxide was noted to be a significant

product in the pyrolysis, second only to carbon dioxide. The original moisture in the peat could serve as the water source. No attempt was made to decipher the possible chemistry involved with the various extractions of this investigation.

Although the alkaline water run was not completed, the basicity did effect the yield. Results of the water experiments did confirm that an increase in basicity increased the yield (8 to 12 percent MAF yield) of an aqueous system.

Results of this investigation and those from Ross et al. suggested a few avenues of further study. Scarrah {29:3} had reported that the addition of four mole percent carbon dioxide had minimal effects on the conversion of coal in a water system. Because carbon dioxide production was proportional to an increase in conversion with basicity, the addition of carbon dioxide to an alkaline aqueous system might suppress the conversion.

Critique of Ash Analysis

The use of dry ashing for determination of organics had been studied in considerable detail. Skoog and West {36:618} expressed that a great deal of uncertainty always exists with respect to recovery of supposedly nonvolatile elements.

Many factors might change the analytical results: temperature of the oven, the length of time in the oven, number of samples in the oven and their position in the oven, the container's material construction, and the inert material

itself (Gorsuch {13}). Other factors existed as well; for instance, Hamilton, Minski and Cleary {16:258} indicated a variation of 50° C at a temperature of 450° C might exist in a muffle furnace. Myklebust {23:21-22} used 700° C for 12 hours to determine the ash content of peat and he achieved good reproducibility. Thus, 700° C for 12 hours was picked as the criteria for the dry ashing in this investigation. The main consideration was to get a uniform technique to apply to all the experiments such that a comparison might be made. The ashing was done in duplicate whenever it was possible for an indication of reliability.

The dry ashing technique was sufficient for the determination of the moisture and ash free content of the peat (MAF peat). The variations between the results were less than one percent. The MAF peat was 20.0 percent of the originally charged peat.

Unfortunately, as the caustic methanol results of Table 3 indicated, a deviation between the duplicate ashings of a sample developed for samples with small amounts of organics and a large mass of sodium hydroxide. This occurred when large quantities of extract were collected and the sodium hydroxide concentration was high in the solvents. The duplicates were always close in the moisture determination, but deviations of up to 100 percent were found in some ash determinations. Grove, Jones and Mathews {15:222} had indicated that alkali oxides might be lost at temperatures

between 500° and 900° C; however, similar results were obtained when the ashing was conducted at a temperature of 450° C.

Results of the ashing experiments where duplicates were within four percent of each other were deemed reasonable and these were used for the construction of Figures 4 and 6. Although some conclusions were drawn from these results, the source of these results should not be forgotten. At this point of the investigation, a new method for determination of organic yield was in order, the THF-soluble yield.

Critique of THF-Soluble Yield

The main problem with a yield which is based on solubility is that it becomes very selective. Not all of the organic material in the "wet" product was soluble in the THF, thus some of the organic material was not considered as part of the yield. Ross et al. {28:33} mentioned that the solubilities of coal conversion products in various solvents (pyridine, benzene, THF, etc.) were not simply parallel conversion criteria. The pyridine solubilities of two products might be similar while the THF and benzene solubilities might be quite different.

Another problem which was corrected by control experiments, was that sodium hydroxide was slightly soluble in THF. Results of the three control experiments were somewhat puzzling because they seemed independent of quantity, moisture content, or surface area of the sodium hydroxide substrate.

Since only time was a factor, the THF before each Soxhlet siphon was either saturated and/or the sodium hydroxide solubility was so small that the THF would have a very small concentration of sodium hydroxide regardless of the amount of substrate. This phenomenon made simple the correction of the THF-soluble runs, that is, 0.15 grams were merely subtracted from the weight of the THF-soluble portion before the yield was determined.

A measurement of accuracy for this correction and a tie between the two different yields came from the results of an ash test which were indicated in Figure 4. The organic material of the residue of the Soxhlet extraction resulted in the difference between the THF-soluble and total MAF yields. The THF-soluble yield was 25 percent and the organic content of the residue represented 19 percent of the MAF peat. The sum of the two account for 44 percent of the MAF peat, which was compared to 39 percent as determined by total MAF yield. The latter result indicated that the sodium hydroxide correction of 0.15 grams was probably low and part of the 25 percent THF-soluble yield was due to more sodium hydroxide being removed from the residue.

Caustic Methanol Runs

Figure 4 and Figure 5 indicated that a change in temperature and pressure parameters created many questions about the internal chemistry. Differences between the high and low pressures were drastic. The most obvious difference was

the decrease in yield (28 to 21 percent total MAF yield) with an increase in temperature (250° C to 280° C) at 1760 psia for the one percent series, but an increase in yield (26 to 39 percent total MAF yield) at 2930 for the same temperature increase and solvent. An increase in the THF-soluble yield for the five percent series (15 to 21 percent) was also noted at 2930 psia with the increase in temperature (250° C to 280° C).

Figure 4 indicated that an increase in pressure (1760 to 2930 psia) for the one percent sodium hydroxide solvent at 280° C almost doubled the yield from 21 percent to 39 percent on the MAF basis; Figure 5 indicated similar results with an increase of THF-soluble yield from 14 percent to 21 percent for the five percent sodium hydroxide series. This supported the suggestion of Paul and Wise {26:21-25} that a pressure as high as possible be used for supercritical extractions.

The effect of solvent basicity was different for the two pressures as well. For both the temperature series at 1760 psia, an increase in basicity from one percent to nine percent sodium hydroxide essentially doubled the yield. This was best illustrated by Figure 6. A jump from 28 percent to 41 percent was observed for the total MAF yields in the 250° C series, and a jump from 21 percent to 47 percent was the result of the 280° C runs. Such a result might link the chemistry of the low pressure extractions with that

reported by Ross et al. The existence of substantial carbon dioxide in the gaseous output of the nine percent sodium hydroxide run at 250° C also supported the possibility of a link.

Figure 7 indicated a decrease in THF-soluble yield from 30 percent to 21 percent with an increase in basicity from 0 to 5 percent sodium hydroxide for the 2930 psia and 280° C series of experiments. This observation suggested that the pressure increase changed some of the chemical equilibria which might be associated with the extraction. The decrease in yield with the increase in basicity might be associated with the fact that carbon dioxide was not a dominant component in the output gas of the five percent sodium hydroxide run. The addition of carbon monoxide to the extraction process might increase the organic yield for the alkaline solvents at this temperature and pressure as the addition of carbon monoxide increased the conversion for Ross et al. {28}.

Since the yield dropped with an increase in solvent basicity at the "best" P-T combination (2930 psia and 280° C), additional experimentation at this temperature and pressure was not feasible. The optimization study which was to be conducted at the "best" P-T combination was not completed for the latter reason.

NMR Spectra Analysis

The THF-soluble products were the most convenient to use for the NMR analysis. The THF-soluble products were not all soluble in deuteriochloroform. Thus THF was used for a

solvent, and a small amount of deuteriochloroform was added to provide the lock signal and reference point. Unfortunately, one of the major signals of THF falls at 24 ppm and some aliphatic results were not visible; however, the aromatic region was left intact and much detail of the aliphatic region was still visible.

All the experiments with the NMR included solutes which were soluble in THF, which provided a basis for which the various comparisons were made. The THF-soluble portion of the precipitate which resulted from the centrifugation of a preliminary caustic methanol run (five percent sodium hydroxide at 1760 psia and 250° C), was also subjected to an NMR experiment. Thus, the contribution of the precipitate in the effluent of the other NMR experiments could be determined. The only prominent signal was located at 28 ppm. A specific assignment of the peak was not possible without the aid of other methods of analysis.

Because all the NMR experiments consisted of peat extracts, some of the signals were evident in all the spectra. The prominent sharp signal at 29.6 ppm was assigned to methylene epsilon or further from the end of alkyl chains, or gamma or further from an aromatic ring in alkyl chains at least eight carbons long. A signal at 28 ppm was that signal which corresponded to the precipitate. Two unidentified signals which were common to most of the spectra were approximately located at 33.5 and -1.0 ppm. The negative signal seemed to stem

from the experiments where THF was used as a solvent and the solute was the result of a caustic run or a polar run (water). With the exception of the water experiment (Figure 15, Appendix B), the aliphatic carbon comprised more of the samples than did the aromatic carbon.

The fraction comparison of the methanol extract lent support to the experimental processing procedure whereby all the fractions were processed together. Although the spectrum of the first fraction was cluttered with many more signals than the third fraction's spectrum, every signal of the latter was evident in the first fraction. On the other hand, separation of fractions which are rich in selective compounds might be done for which extraction time would be the separation parameter. The aromatic activity in general was not prominent in the third fraction, and no carbonyl groups were located. The aryl alkyl ether signals were prominent in both fractions. The same environments for the methyl and methylene groups existed in both fractions.

The major effect of pressure was that much more aromatic signals were seen in the low pressure extract than the high pressure extract. This was evident in both the aromatic region and the aliphatic region. The very large signal at 28 ppm suggested that more product precipitated during the course of the extraction at the low pressure than the high pressure. This was indeed the case because the relative amount of precipitate as seen through the collecting

vessel walls of the first fraction was greater at 1760 psia than at 2930 psia. Most of the precipitate was found in the first fraction.

The change in temperature seemed to affect compounds which had a nitrogen structure. A nitrogen compound, possibly pyridine, was represented in the 250° C spectrum, and no sign of such signals were visible in the spectrum of the 280° C extract. The aryl alkyl ethers and naphthenic structures which were thought to preside in the extract of the high temperature, were not located in the low temperature extract.

Several curious observations were noted in the solvent study. Even at a very high pressure, 3900 psig, the acetone extract of the peat was well represented by aromatic compounds (Figure 16, Appendix B). Thus a high pressure did not mean the aromatic compounds would be suppressed in an extraction; the solvent played a significant role in compound selectivity. However, since the acetone run was the result of a batch extraction, this might indicate selective extraction of aliphatic compounds or cracking of aromatic structures with the semicontinuous method. Myklebust {23:55} had concluded acetone was the best solvent that he investigated.

Water proved to be an interesting solvent as well; the spectrum of the water extract (Figure 15, Appendix B) was well represented from all regions of the carbon-13 spectra.

field. This run was the only one in which the quantity of aromatic and aliphatic carbons were essentially the same. Carbonyl groups were evident, as were aromatic ether and phenolic hydroxyl groups. Quinoline and o-xylene might have been some of the individual constituents of the extract, as prominent signals for both compounds existed. The vast differences in the various solvent extracts indicated that solvent selectivity was very active, even at supercritical states.

If only one type of analysis was available for characterization study, carbon-13 NMR spectroscopy would be a good one. The former discussion indicated how carbon-13 NMR spectroscopy might be used to successfully differentiate various compounds and fundamental groups of the peat derivatives. However, much more characterization and identification than that which was done could be achieved if the carbon analysis was coupled with other methods of analysis. A proton NMR analysis would provide confirmation of aliphatic to aromatic ratios, and, then coupled with an ultimate analysis, many compounds might be identified or a general molecular weight might be assigned which would be based on the presence of fundamental groups. Mass spectrometry has also proven itself useful in characterization studies (Ozubko, Clugston and Furimsky {25}), as has infrared spectroscopy (Morrison and Boyd {22:410-412}). Any future characterization schemes should include additional analysis methods.

The carbon-13 experiments might also be designed such that accurate quantitative results are obtained.

CONCLUSIONS AND RECOMMENDATIONS

Specific conclusions and recommendations which were drawn from the latter results and discussion are indicated in the following sections. The concluding chapter was divided into three sections: (1) conclusions and recommendations of the semicontinuous extraction apparatus and method; (2) conclusions and recommendations of the post-extraction results and discussion; and (3) a proposal of future studies which might follow this study.

Semicontinuous Extraction:
Apparatus and Method

In general, the semicontinuous extraction apparatus performed well. Several advantages of the semicontinuous method versus batch extractions were confirmed. The following indicated some conclusions and recommendations which pertained to the extraction equipment and method:

(1) The extraction procedure was very adequate and reliable. Procedural refinement should not be necessary for subsequent extraction studies.

(2) Pressure and temperature were easy to control. Modifications of either subsystem is not recommended.

(3) The safety-relief system was very adequate and the utilization of a back pressure regulator in lieu of or with a rupture disc safety head is highly recommended.

(4) Wet peat had a tendency to plug the column or lines

during an extraction. Prior to an extraction run, the placement of a hole through any similar substrate which is packed in the column is suggested.

(5) The Parker column end fittings were not adequate. A column modification whereby an alternate type of fitting is used is recommended.

(6) The semicontinuous method indicated fractionating capabilities. Changes in extraction time, solvent, pressure and/or temperature might be used to selectively extract various compounds.

(7) Additional equipment, such as equipment which might be used for the determination of residence time distributions, would be easy to adapt to the extraction apparatus.

Post-Extraction

The following is a list of conclusions and subsequent recommendations which pertain to the post-extraction results and discussion of the supercritical extractions of peat:

(1) The formation of a precipitate in the product stream supported general principles of supercritical extractions. However, the dark color of the solvent and subsequent NMR work indicated a need to separate soluble organics from solvent. The distillation under vacuum was very adequate and is recommended for such separations.

(2) The mass diffusion rate in the caustic methanol extractions was very sensitive to changes in pressure above the critical point. In general the diffusion rate decreased

when the pressure increased.

(3) Evidence of solvent reactions during an extraction existed with the nine percent sodium hydroxide methanol solvent. Whenever an organic solvent is used, such reactions should not be overlooked.

(4) The organic total MAF yield increased with an increase in basicity of the aqueous solvent.

(5) The methanol experiments indicated that changes in yield due to temperature were pressure dependent; that is, as the temperature increased, the total MAF yield increased at 2930 psia but decreased at 1760 psia for the one percent sodium hydroxide in methanol solvent..

(6) Changes in yields due to changes in alkalinity of the methanol solvent were pressure dependent; that is, as alkalinity increased, THF-soluble yield decreased at 2930 psia and total MAF yield increased at 1760 psia.

(7) The use of THF as the solvent for the NMR experiments was convenient but some information in the aliphatic region was hidden by the solvent peak at 24 ppm. Different solvents might be incorporated into future studies to avoid this loss of information.

(8) The NMR studies were very useful for the determination of differences in product due to various changes in operating conditions and solvent changes. The methanol runs had no significant carbonyl groups present whereby the water run did. Aryl and alkyl ethers were represented in the

methanol runs; aromatic ethers and phenolic hydroxyl groups in the water run. Additional analyses with other analytical methods are recommended.

(9) The quantity of aliphatic carbon was greater than the quantity of aromatic carbon for all the extract products except the pure water run, where the quantities were essentially the same. NMR procedural refinement which can enhance the accuracy of quantitative carbon-13 analysis is recommended for future work.

(10) Nitrogen compounds which were represented in the 250° C extract spectrum were not found in the 280° C extract spectrum. Aryl alkyl ethers and naphthenic structures which existed in the 280° C extract were not represented on the spectrum of the 250° C extract.

(11) For the caustic methanol extracts, more aromatic signals were seen in the 1760 psia extract spectrum than that of the 2930 psia extract. However, the acetone NMR results indicated that high pressures would not necessarily crack the aromatics in a supercritical gas environment, as aromatics were well represented in the acetone extract spectrum. The acetone extraction was done at 3915 psig.

(12) Various links between this investigation and a similar investigation exist. Such a link suggested that the water gas shift reaction might be a factor in the yield of the extraction.

(13) The determination of yield needs refinement. The ash analysis was sufficient for MAF peat determinations but poor for organic analysis where the sodium hydroxide to organic ratio is large. The THF-soluble yields did not account for all the extracted organic compounds, and sodium hydroxide is slightly soluble in THF. A different solvent might be recommended.

Future Studies

The latter discussion pointed toward various avenues for subsequent investigations. The apparatus might be easily adapted for various studies which entail residence time distributions. Such studies might investigate gas properties in supercritical states, and pore size and diffusion studies of various substrates and solvents.

The possibilities for fractionation studies are many as extraction selectivity relies on the extraction time, pressure, temperature and solvent.

Specific studies which test the hypothesis that the water gas shift reaction might be used to increase yields would entail carbon monoxide. Two systems which might be promising are carbon monoxide/alkaline aqueous systems and carbon monoxide/alkaline methanol systems. Extractions with acetone might also be promising.

A separate study on an ash technique for the determination of organic portions of a sodium hydroxide-hydrocarbon residue might be in order before a caustic investigation is

done. Other studies which entail various solvents for selective organic removal from such caustic substrates might also be conducted.

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LITERATURE CITED

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APPENDICES

APPENDIX A

SEMICONTINUOUS
EXTRACTION
EQUIPMENT

SEMICONTINUOUS EXTRACTION EQUIPMENT

<u>Equipment</u>	<u>Manufacturer and Model</u>
pressure sensor	Autoclave Engineers DPS 0081
temperature recorder	Honeywell 452X21-FF-000-00-2274-G
variable autotransformer	Powerstat Type 3PN1168
safety relief back pressure regulator	Tescom 26-1722-64
back pressure regulator	Mity Mite S-91XW
pump	Milroyal HDB-1-30R

APPENDIX B

NMR SPECTRA

NMR SPECTRA

The carbon-13 NMR spectra were recorded on a Bruker Instruments WH-250 Fourier transform NMR spectrometer operating at a frequency of 63 MHz. All samples were THF soluble and deuterchloroform (CDCl_3) provided the internal lock. The spectra were obtained by using 8K data points over a 20,000 Hz spectral width. Broad-band decoupling was used and a line broadening with an exponential multiplication of three was used. Table 4 on page 42 summarizes the NMR experiments' process variables.

Parts per Million

130.0	30.8
128.9	29.6
127.1	29.1
118.3	27.9
113.2	27.1
68.2	25.9
60.8	25.6
52.8	24.8
19.1	23.8
43.7	22.9
37.4	22.6
34.0	13.9
32.7	

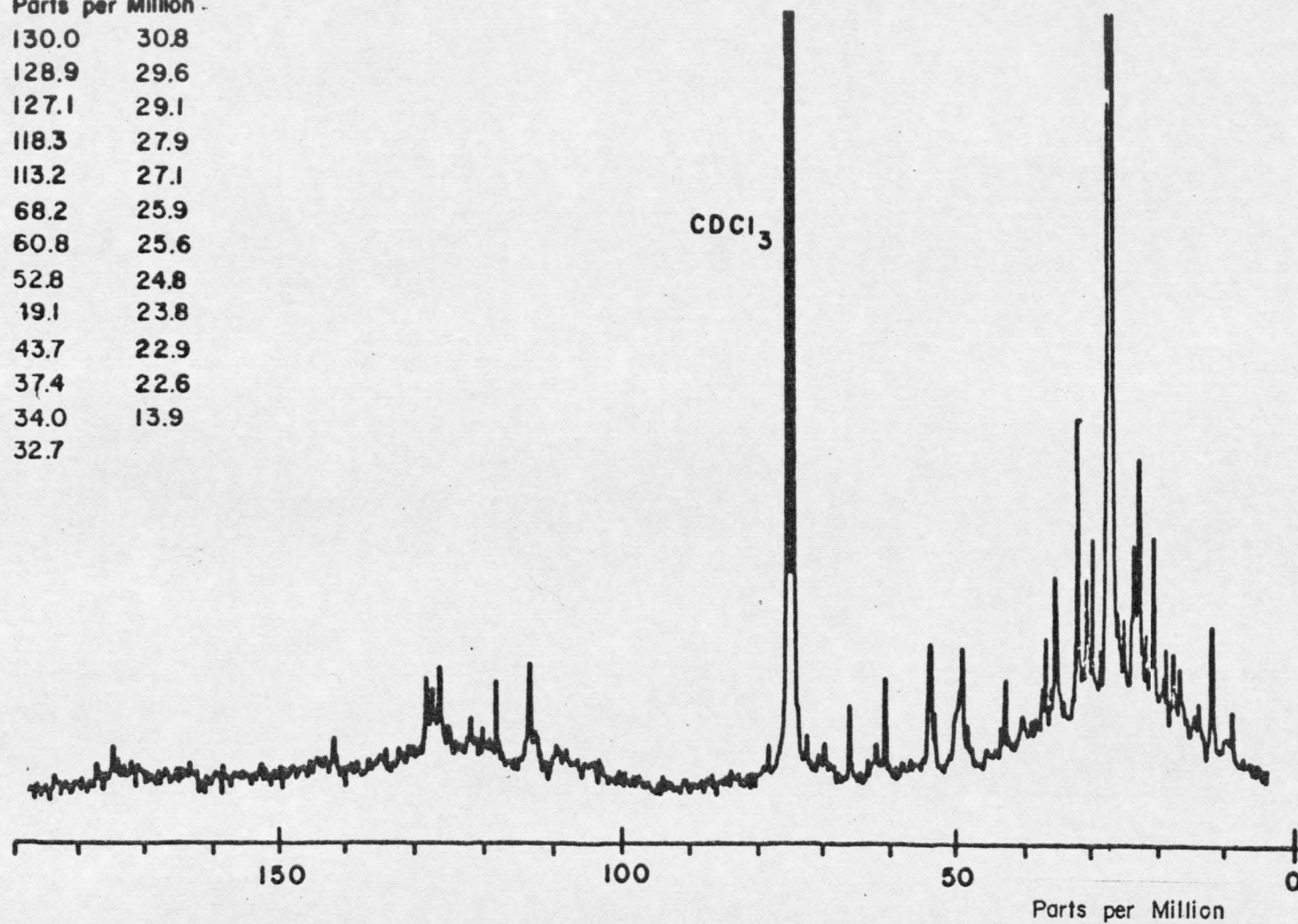


Figure 9. NMR Spectra E-1

Parts per Million

130.9

128.9

68.2

38.8

37.5

34.1

30.8

29.6

25.7

24.9

23.8

22.9

22.6

13.9

CDCl_3

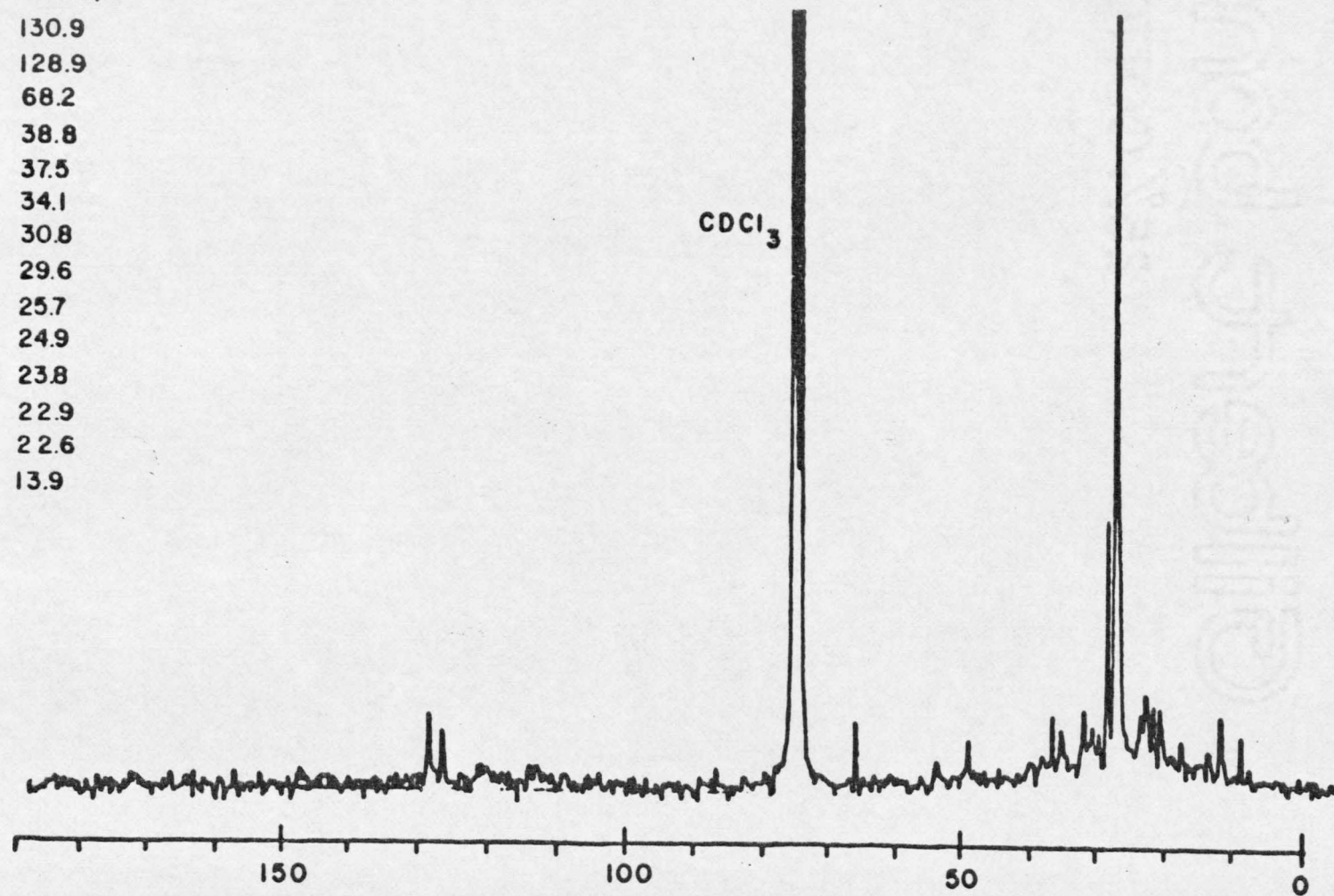


Figure 10. NMR Spectra E-2

Parts per Million

Parts per Million

143.7

33.0

28.7

28.4

27.9

26.7

25.8

23.1

-1.1

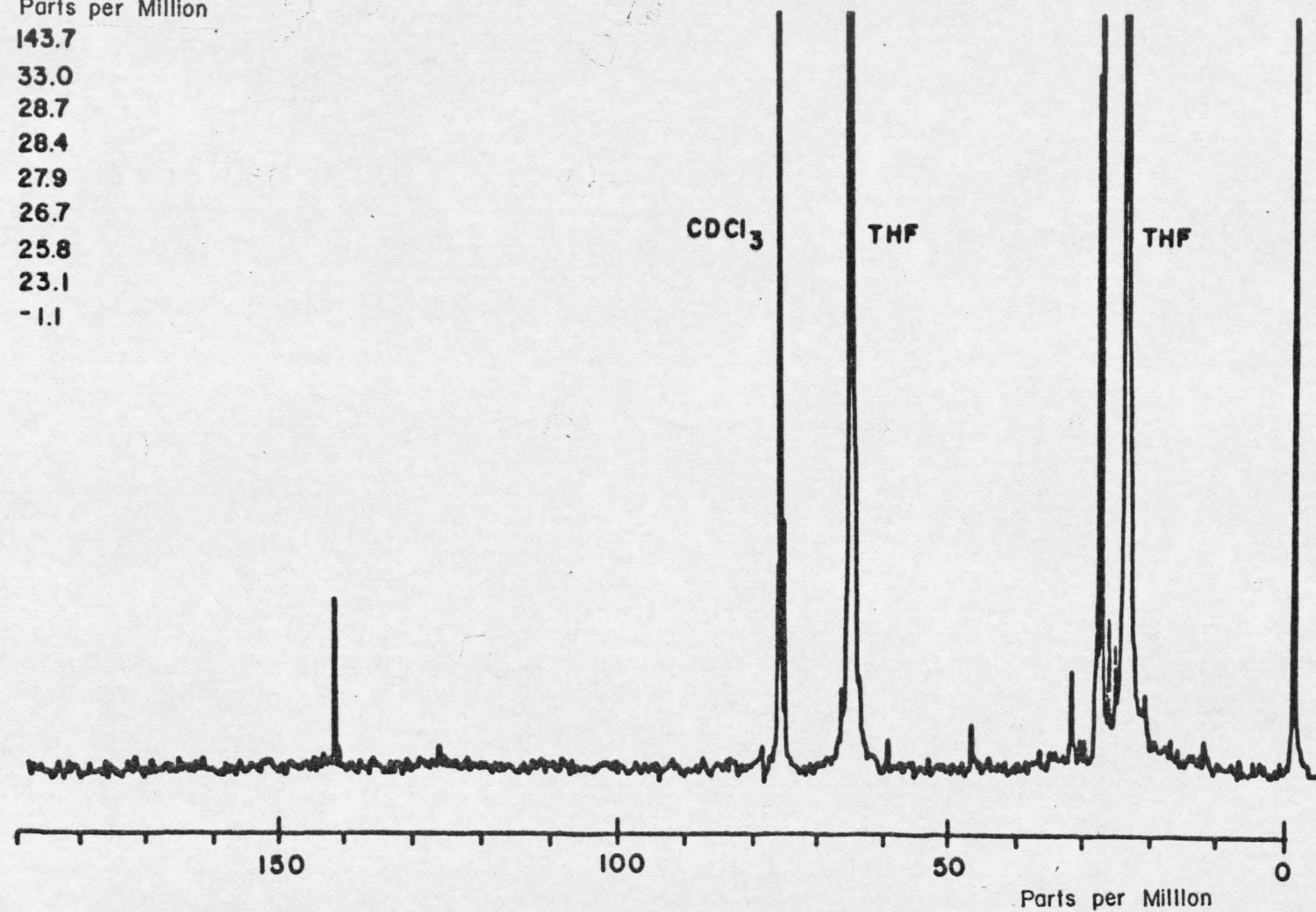


Figure 11. NMR Spectra E-3

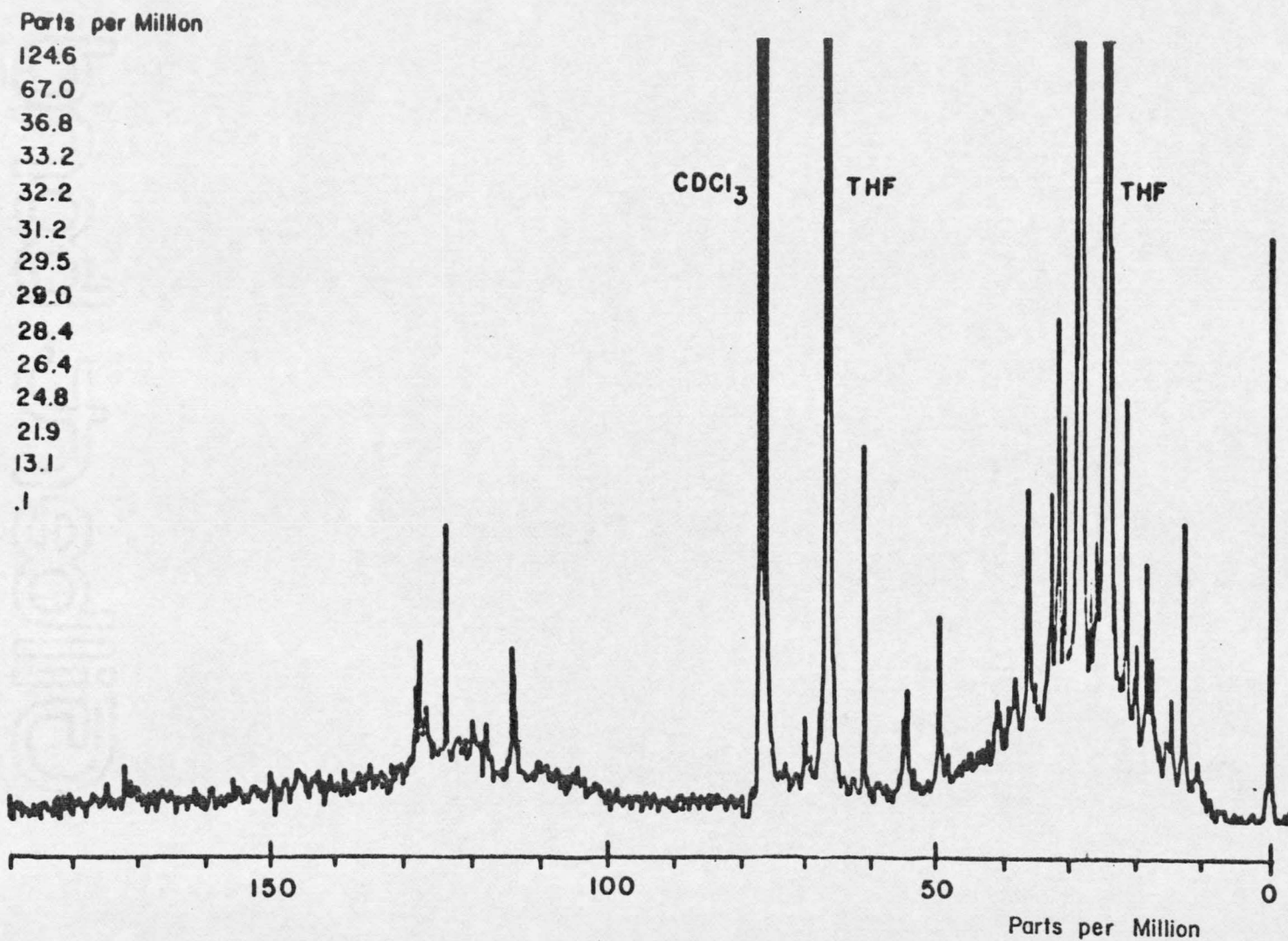


Figure 12. NMR Spectra E-4

Parts per Million

123.8

28.6

27.7

25.3

-.86

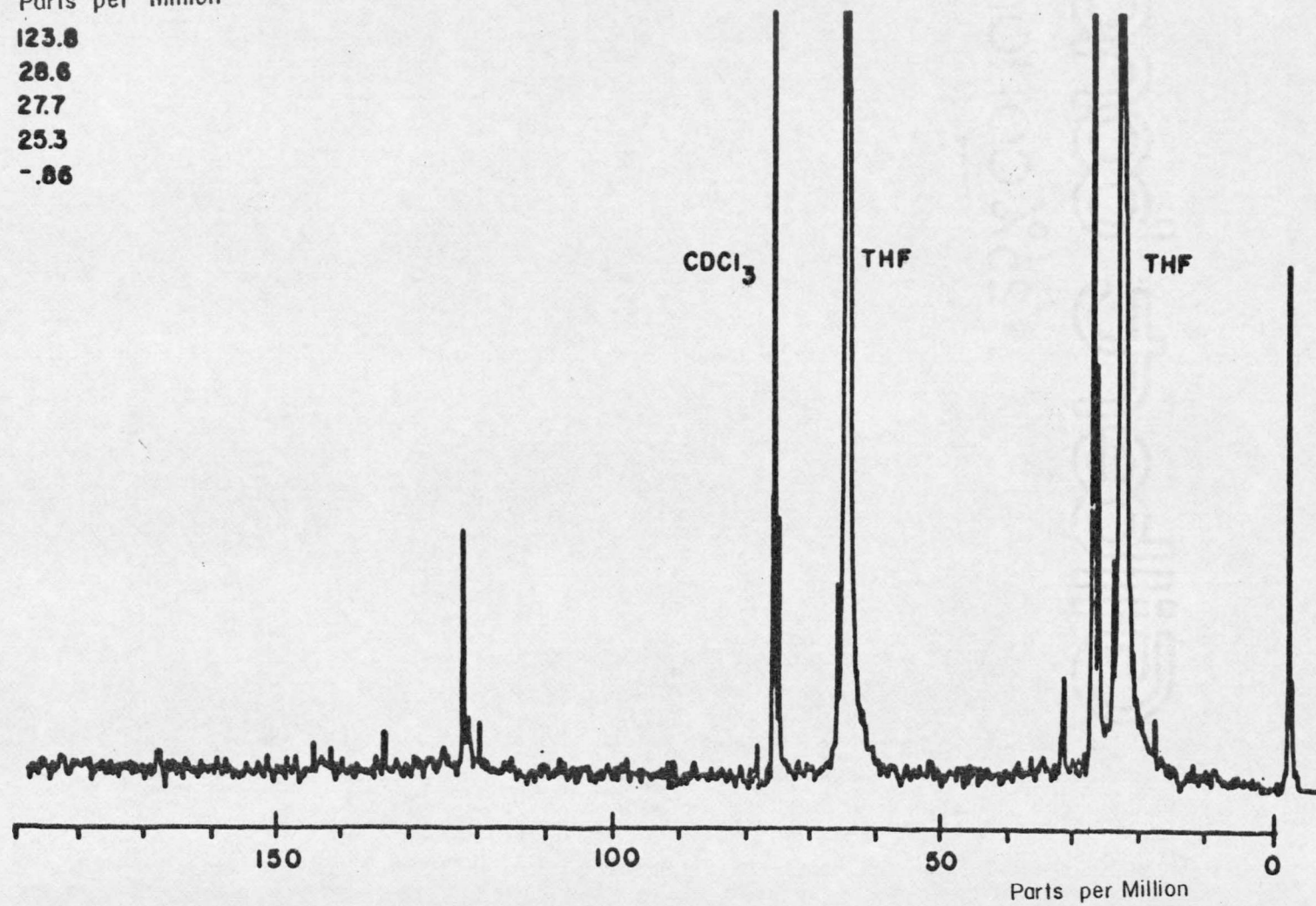


Figure 13. NMR Spectra E-5

Parts per Million

28.6

25.8

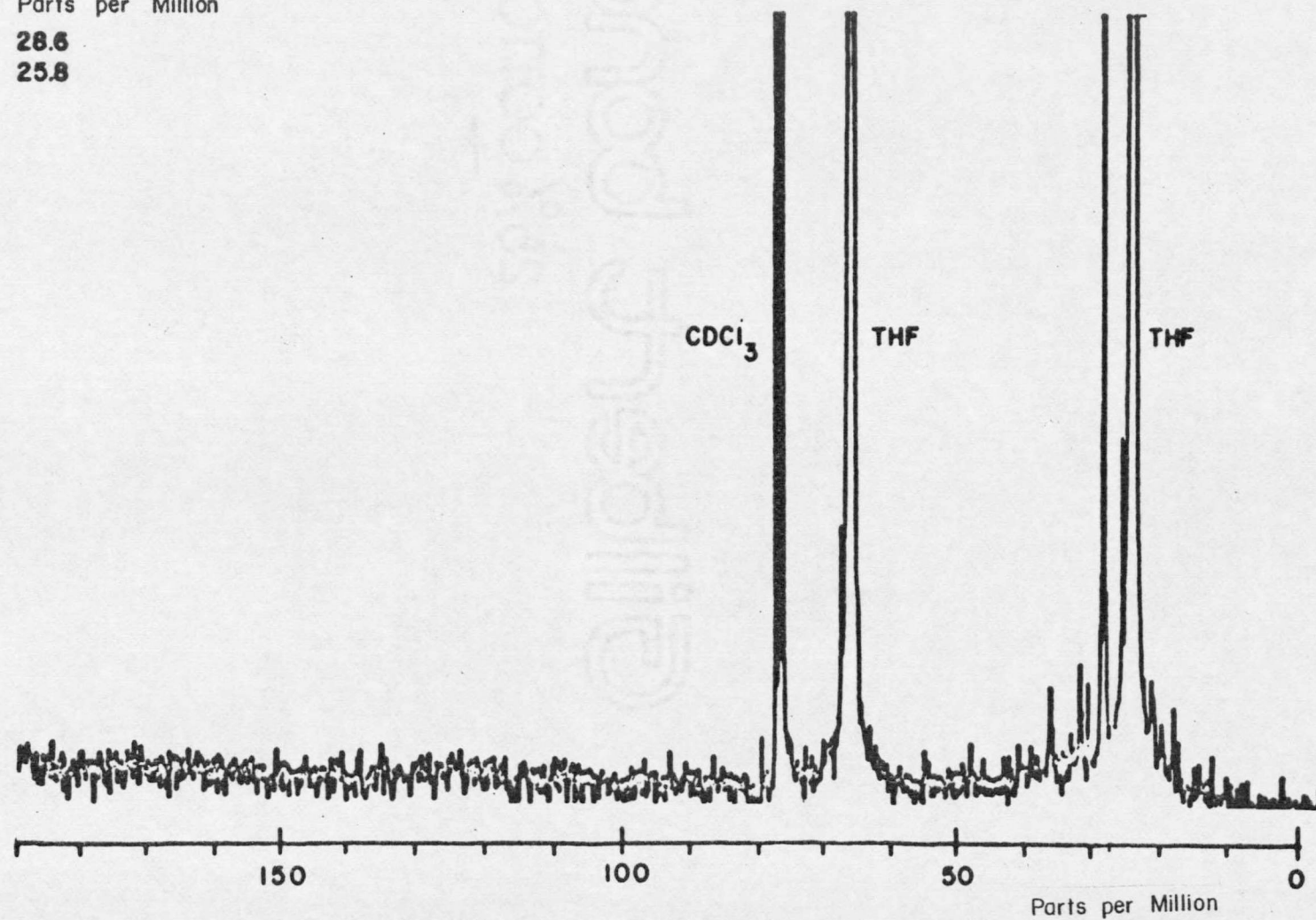


Figure 14. NMR Spectra E-6

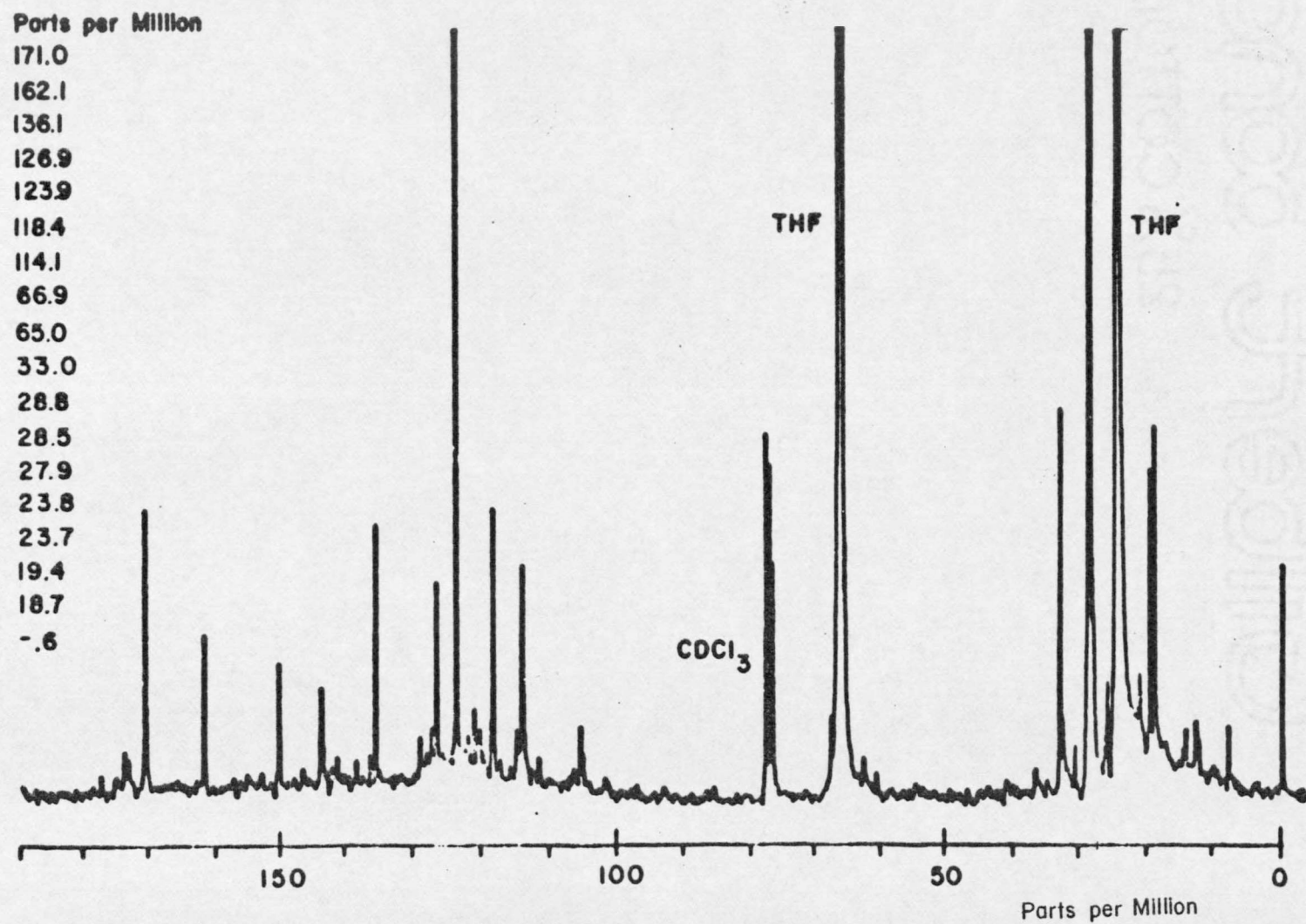


Figure 15. NMR Spectra E-7

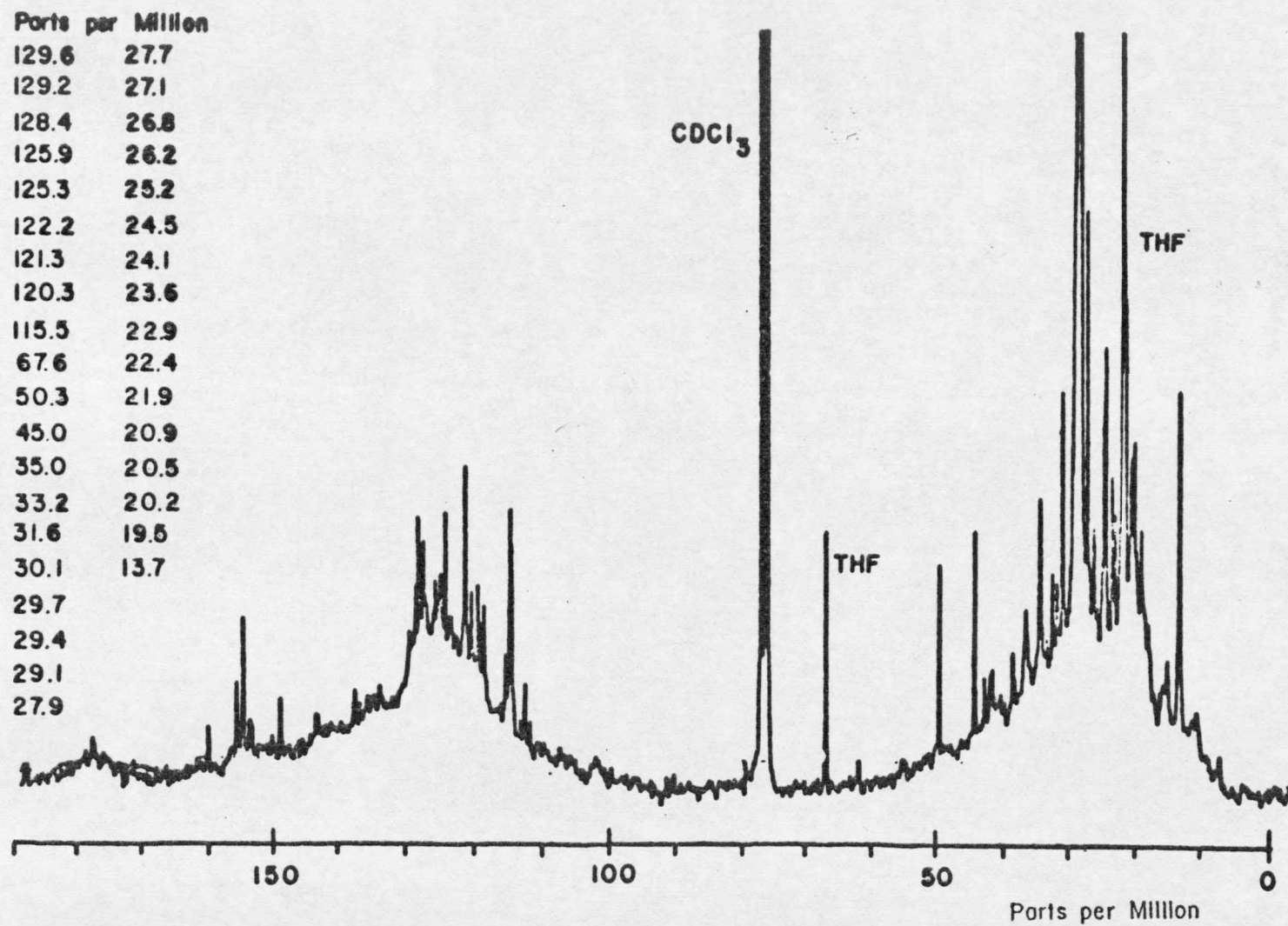


Figure 16. NMR Spectra E-8



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Smith, S. S.

Semicontinuous
supercritical extraction

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