Semicontinuous supercritical fluid extraction of peat
by Craig Roger Granlund

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

Abstract:
Experiments were run to investigate semi continuous subcritical and supercritical fluid extraction as a means of separating the organic portion of peat from the undesirable mineral portion. Emphasis was put on the overall yield of extracted organic material, but a brief characterization of the products was of interest. Temperature and pressure were held constant at 270 C and 2920 psig respectively, so that variations in yield would arise from differences in the solvents themselves. Three types of solvents were utilized; a proton donor (acetic acid), a proton acceptor (methyl alcohol) , and a strong dipole (methyl ethyl ketone). The flow of solvent through the column of approximately 40 grams of peat was two milliliters a minute until 400 milliliters of solvent had been used.

Best results were obtained with acetic acid as the subcritical solvent, which extracted from 39 wt% to 74 wt% of the organics contained in the peat. Supercritical methyl ethyl ketone yields (25 wt% to 66 wt%) were slightly higher than those from supercritical methanol (28 wt% to 41 wt%) . The average yield for acetic acid, methyl ethyl ketone, and methanol was 55 wt%, 41 wt%, and 33 wt%, respectively. Methylene chloride and formamide were also utilized as solvents, but were not stable, and either reacted or degraded in the column. Since acetic acid is a proton donor solvent, proton donor solvents may be expected to be the most effective in the supercritical extraction of peat.

For all three solvents it was noted that as the polarity index (P') rose above 3.0, the yield remained relatively constant. Some products stayed in solution after changing from supercritical to ambient conditions.

The C-13 NMR studies on the tetrahydrofuran-soluble products showed that a larger variety of products was extracted during the earlier periods of extraction, and that each solvent extracted a different group of unidentified organic compounds from the peat. Also noticed was that predominately aliphatic compounds, rather than aromatic compounds, were extracted.

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APPROVAL

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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.

December 6, 1982
Date

Warren P. Scarrah
Chairperson, Graduate Committee

Approved for the Major Department

December 6, 1982
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

12-8-82
Date

Michael P. Malone
Graduate Dean

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ABSTRACT

Experiments were run to investigate semicontinuous subcritical and supercritical fluid extraction as a means of separating the organic portion of peat from the undesirable mineral portion. Emphasis was put on the overall yield of extracted organic material, but a brief characterization of the products was of interest. Temperature and pressure were held constant at 270 C and 2920 psig respectively, so that variations in yield would arise from differences in the solvents themselves. Three types of solvents were utilized; a proton donor (acetic acid), a proton acceptor (methyl alcohol), and a strong dipole (methyl ethyl ketone). The flow of solvent through the column of approximately 40 grams of peat was two milliliters a minute until 400 milliliters of solvent had been used.

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INTRODUCTION AND PREVIOUS RESEARCH

Introduction

Due to the decreasing availability of petroleum resources and increasing political instability in the Middle East, there has been pressure on the United States to search for alternative sources of energy. Coal, shale oil and solar energy have been getting the majority of publicity and attention. There is, however, another energy source that is getting an increasing share of attention, peat.

Peat in the United States has been estimated to contain 1440 quadrillion BTU's of energy. This is more than the proven reserves of petroleum, natural gas, uranium, and shale oil combined. Only coal surpasses the energy potential of peat (see Figure 1). Alaska, Minnesota and Michigan together possess almost 75% of the U.S. peat reserves. Table 1 gives a state-by-state breakdown of these reserves. Table 2 gives the distribution of the world's peat reserves (1).

Evidence suggests that peat is formed in a layer by a relatively short biochemical process carried out by aerobic micro-organisms. This layer is on the surface

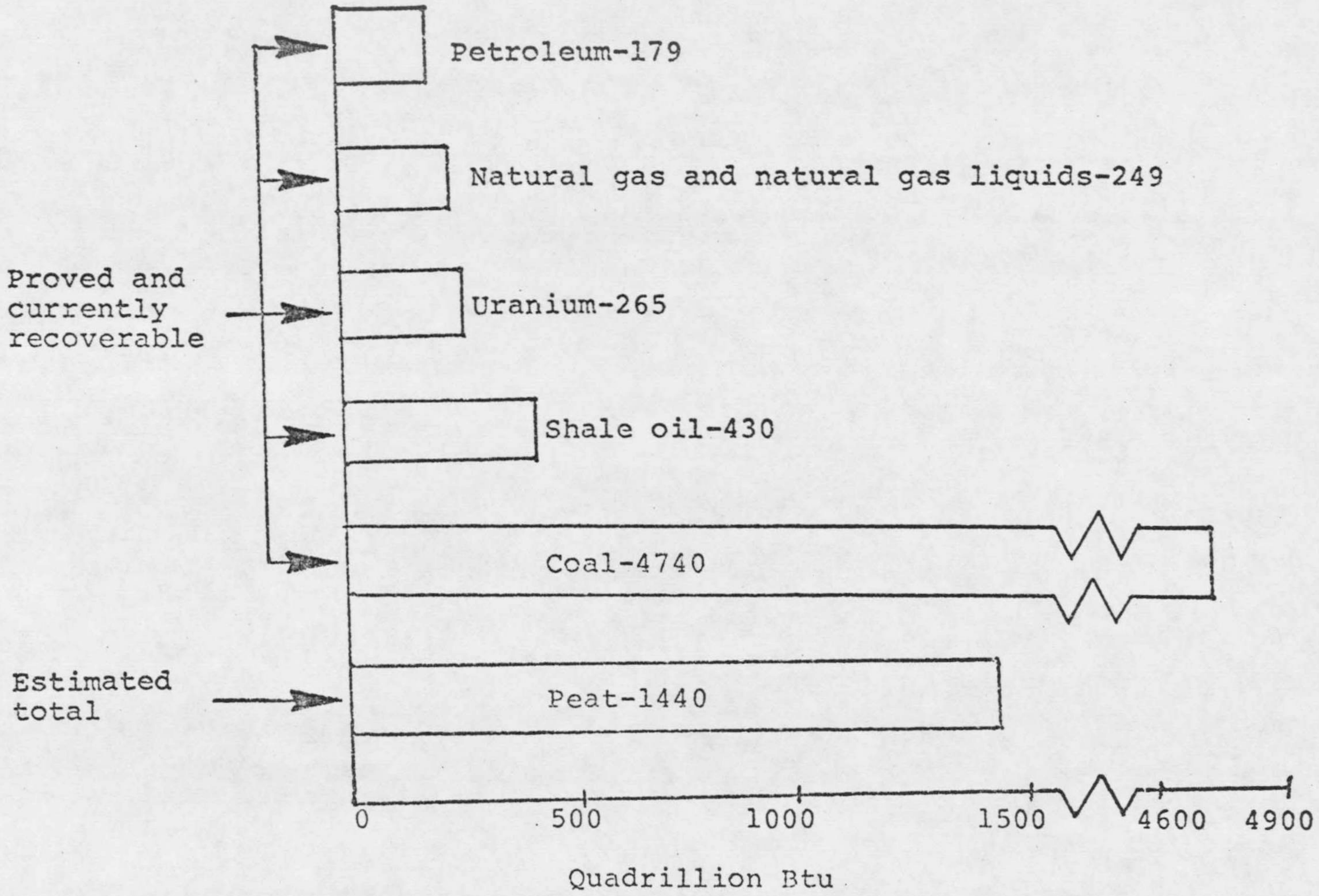

Figure 1. United States Energy Resources (1)

State	Acres (millions)	Potential energy (10^{15} BTU)
Alaska	27.0	741
Minnesota	7.2	198
Michigan	4.5	123
Florida	3.0	82
Wisconsin	2.8	77
Louisiana	1.8	49
North Carolina	1.2	33
Maine	.77	21
New York	.65	18
All Others	3.66	101
Total	52.58	1,443

TABLE 1: State-by-State Distribution of Peat (1)

Country	Acres (millions)
Soviet Union	228.0
U.S.	52.6
Finland	35.6
Canada	34.0
East and West Germany	13.1
Sweden	12.7
Poland	8.6
Ireland	7.3
Great Britain	5.8
Indonesia	3.3
Norway	2.6
All Others	5.2
Total	408.8

TABLE 2: Worldwide Distribution of Peat (1)

and grows during periods of low sub-soil water. As the peat formed in this manner is buried by its continued formation, it is exposed to anaerobic conditions. This leads to a mummifying condition, where the production of peat slows down and ceases. This is evident in the fact that peat formed during inter-glacial periods differs very slightly from "young peat" (2).

Experiments were done with a pure culture of the fungus Merulius lacrimans and peat-forming matter (optimum conditions of aeration and humidity) (2). This resulted in the fungus destroying the carbohydrate structure of the peat-forming matter and acidifying the lignin into a dark-colored matter soluble in alkalis. This dark-colored matter could not micro-morphologically or chemically be distinguished from peat. Kurbatov concluded that peat is not formed slowly and gradually, but rather spasmodically, which is deduced from how peat is often found to be in distinct layers. His data correlated with Stan Smith's results (3). Smith found that the extracted organic material he recovered from peat was very soluble in an alkali water solution after the alkali methanol solvent was distilled off.

Because peat is formed from different plant varieties, its composition varies in as many ways. R.S. Farnham says there are various classification systems for peat in the U.S., most of which are patterned after those developed in Europe (4). Identification of peat has depended on the type of plant remains or on the stage of decomposition. Sweden and the U.S.S.R. classify peat into ten classes, while the USDA classifys it into only three (5). Soper and Osbon (6), give the typical composition of moisture and ash-free peat as:

59.5 wt%	carbon
33.0 wt%	oxygen
5.5 wt%	hydrogen
2.0 wt%	nitrogen
0.2-0.6 wt%	sulfur

The fuel value of peat, though not as high as coal, comes from the high percentage of fixed carbon present. Peat air-dried to 50 wt% water contains 4,000-5,000 BTU/lb compared to 11,000 BTU/lb or higher for coal. Peat, however, has a higher content of volatile matter, 70 wt% vs only 30 wt% for coal (1). Soper and Osbon (6) indicated that ash can range from 3 to 30 wt% of the dry weight of peat, while the ash content in coal ranges from 3 to 12 wt%.

Peat, though plentiful, has its drawbacks. In nature, peat contains approximately 90 wt% water which is difficult to remove because of the peat's colloidal nature. Unless dried, combustion is impossible, and peat can only be air dried to 50 wt% water. Filtration, for example, can only remove 30 wt%. So much water also precludes, for economic reasons, the transportation of peat over great distances. This means that synfuel plants would have to be built near bogs or swamps.

Once dried, the direct combustion of peat would have its environmental drawbacks. Since peat is high in nitrogen, nitrogen emissions would be significant. Also, the same problems would be present as in the combustion of coal such as sulfur emissions and fly ash (1). Despite these problems, Russia has seventy-six electric generating plants using peat as fuel, more than one-third of the thermally generated electric power in Ireland comes from peat, and Finland is in the process of building peat-fueled power plants (5).

Because of the environmental problems associated with the direct combustion of peat an economical way to extract the hydrocarbons (for use as potential chemical feedstocks) from peat without combustion is desired. Recent attention has been drawn to the use of supercritical fluids to do this extraction.

Supercritical Fluids

All substances possess a critical temperature, above which the liquid phase of a pure substrate cannot exist. The pressure which must be applied to bring about condensation at that temperature is called the critical pressure. Alternatively, the critical pressure can be regarded as the vapor pressure of the liquid at its critical temperature (7).

When a liquid sample is heated in a sealed tube, the properties of the liquid and vapor approach one another near the critical temperature. Below the critical temperature there are two distinct phases. As one heats the sample through the critical temperature, the meniscus separating the two phases disappears and one phase results. This phase is referred to as a "supercritical fluid". The word "fluid" is used to distinguish the fact that it is in reality neither a gas nor a liquid.

Supercritical fluids are of interest in applying them to extractions. Volatility has been noted to increase 10,000-fold under some circumstances (8). Gangoli and Thodos have theorized that both Knudsen diffusion within the pores and bulk diffusion through the fracture system of the substrate are important in the extraction mechanism. They propose that five basic steps are involved in extractions with supercritical fluids (9):

1. The solvent fluid penetrates the micropore structure of the substrate.
2. Large molecular aggregates are depolymerized and the resulting products are dissolved in the solvent fluid.
3. Molecular bonds between the molecular species to be extracted and the substrate are broken.
4. The solvent fluid and the extract diffuse out of the micropores.
5. The extract is recovered from the solvent fluid by reducing the pressure.

Gangoli and Thodos also report that supercritical fluid extraction (SCFE), in its application to coal, has many advantages over conventional extraction techniques. These are listed below:

1. Grinding of the substrate is not required due to the unique properties of supercritical fluids which allow penetration of the substrate structure. This also permits the extraction of components which are not normally recoverable without thermal degradation.
2. The solvent power of a supercritical fluid may be varied simply by altering the pressure or temperature. To change the solvent power of a liquid it is necessary to either vary the temperature or mix it with a different solvent. Physical properties of the fluid extractants are more important than their chemical nature. Fluid mixtures may prove to be more useful as solvents than pure fluids.
3. There is very little, if any, chemical degradation of extracts when a supercritical

fluid extraction process is used. The chemical structure of the extract is virtually unchanged from the original structure prior to the extraction.

4. SCFE is utilized at relatively low temperatures which minimizes thermal degradation of compounds which are unstable at higher temperatures.

5. Better separation of the solvent from the extract and the residue results in lower contamination of the product. Separation of the undissolved material from the solution is easier than in conventional solvent extraction because gas densities and viscosities under normal conditions are considerably lower than those of liquid solvents.

6. The extract can be fractionated to a certain extent by lowering the pressure in stages, thereby precipitating the heavier fractions first.

7. By varying the extraction temperature, the degree of breakdown of the extract can be controlled to yield desired chemicals.

8. The presence of moisture in the substrate could be advantageous because water is a polar substance and could be a good supercritical solvent.

9. A certain amount of hydrogenation is obtainable in the extraction stage.

10. Hydrogen can be produced by gasifying the undissolved char residue with steam. This hydrogen can then be used to further process the extract.

11. It has been shown that high sulfur bearing extracts, such as coal or peat, can be processed by supercritical fluid extraction techniques to yield a low sulfur extract.

12. By simply reducing the molecular weight of the extract many chemical feedstocks, especially benzene and alkyl hydrocarbons, may be produced.

13. Experiments have shown that extracts obtained from SCFE are richer in hydrogen (6.9 wt% compared to 4.9 wt%) and have lower molecular weights (500 compared to 2000) than those obtained using anthracene oil type solvents in the absence of hydrogen gas. Therefore, supercritical fluid extracts may be readily converted to hydrocarbon oils and chemicals.

Solvent Behavior

There have been several solvent classification schemes developed over the past 30 years. Some of these include the Hildebrand solubility parameter treatment, extensions of this that recognize specific intermolecular interactions, and the Rohrschneider scheme for gas chromatographic phases. L.R. Snyder has developed a scheme that transforms 82 solvents into a corresponding set of solvent characterization parameters (10). These parameters (P', X_e, X_d, X_n) are approximately corrected for solute-solvent interactions and molecular weight effects, which Hildebrand's parameter does not correct for.

Snyder defines a polarity index (P'), which is a measure of the ability of the solvent to interact with various polar test solutes. The quantities X_e, X_d, and X_n represent the fraction of P' contributed by interactions associated with ethanol, dioxane and nitromethane, respectively (see below). The parameter P' increases with solvent polarity and can roughly be compared with the Hildebrand solubility parameter (δ). The difference between P' and δ, however, is that δ is measured for the pure solvent, while P' is measured against a variety of solutes that encompass all possible types of interactions. Since δ is measured only for the pure solvent, it can only reflect interactions that exist in the pure solvent and does not account for molecular weight effects.

It is useful (but not precise) to consider the selectivity parameters X_e, X_d, and X_n as reflecting the relative ability of the solvent to function, respectively, as a proton acceptor, a proton donor, or a strong dipole interactor. Thus, for example, solvents with large X_e values will interact more strongly with ethanol than with dioxane or nitromethane, presumably via hydrogen bonding between ethanol and proton-acceptor solvents. When these fractional contributions are plotted on the triangular diagram shown in Figure 2, it can be seen that the solvents fall into eight selectivity groups. Table 3 gives some of the compounds and groups of compounds that fall in each of these groups.

When seeking the best solvent for a given application, Snyder states that it is useful to separate the effects of P' and selectivity on the operation in question. He says this can be done by first determining the effects of P' by studying the performance of a series of blends of a particular polar and non-polar

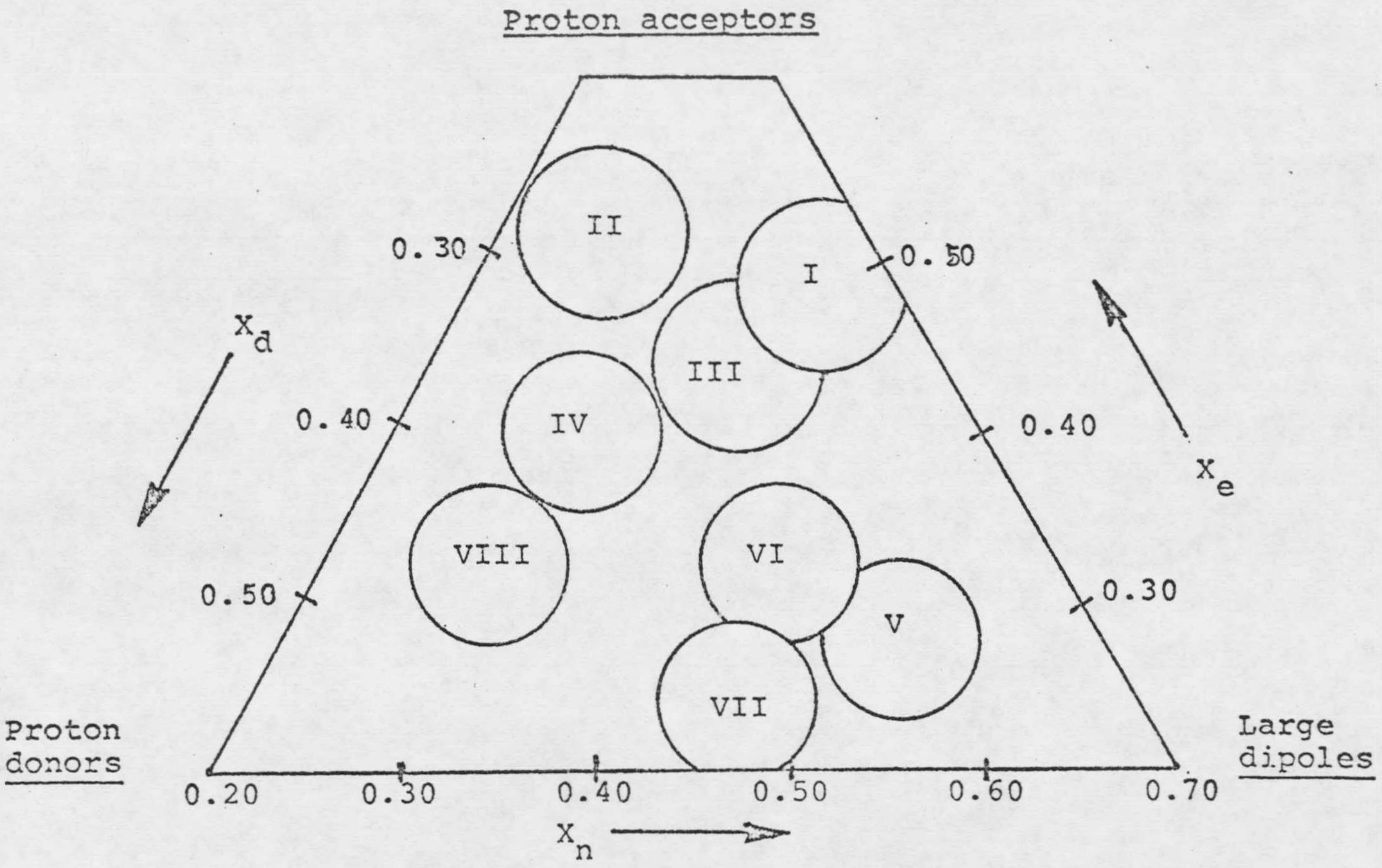

Figure 2. Grouping of pure solvents by selectivity(10)

Group	Solvents
I	Aliphatic ethers, tetramethylguanidine, hexamethyl phosphoric acid amide, trialkylamines
II	Aliphatic alcohols
III	Pyridine derivatives, tetrahydrofuran, amides (except formamide), glycol ethers, sulfoxides
IV	Glycols, benzyl alcohol, acetic acid, formamide
V	Methylene chloride, ethylene chloride
VI	Aliphatic ketones and esters, polyethers, dioxane, sulfones, nitriles
VII	Aromatic hydrocarbons, halo-substituted aromatic hydrocarbons, nitro compounds, aromatic ethers
VIII	Fluoroalkanols, m-cresol, water, chloroform

TABLE 3: Classification of Solvent Selectivity (10)

solvent pair. When the optimum value of P' has been found, the effect of solvent selectivity can be explored by using solvents of similar P' (the optimum) but different selectivity. These should be chosen from the other selectivity groups.

The polarity index (P') was varied for each solvent by diluting it with hexane. The resulting value for P' is given by

$$P' = \phi_a P_a + \phi_b P_b$$

where ϕ_a and ϕ_b are the volume fraction of the solvents and P_a and P_b are the P' values for the pure solvents. Using hexane as the dilutant allows for the maximum variation in P' since the P' value for hexane is 0.0 . At present, nothing has been published that has applied this solvent behavior approach to supercritical fluids.

Giddings et al. (11) found a correction for solubility parameters as a function of temperature and pressure for a number of supercritical fluids at liquid densities. They suggest that there are two factors that influence the "solvent power" of a gas. These are the "physical effect" (pressure and temperature) and the "chemical effect". The "chemical effect" is unique to each chemical species and is dependent on its polarity, acid-base properties, and hydrogen bonding tendencies.

Their expression defining the parameter is

$$\delta = 1.25 \, P_c^{\frac{1}{2}} \, \rho_r/\rho_L$$

where P_c is the critical pressure in atmospheres, ρ_r is the reduced density and ρ_L is the reduced density of liquids, assumed to be about 2.66. Here the "physical effect" may be identified with the ρ_r/ρ_L term. The other factor, $1.25 \, P_c^{\frac{1}{2}}$ may be associated with the "chemical effect" and has been used to correlate solubility phenomena in liquids.

A comprehensive review of the principles of extraction with compressed gases is given by Paul and Wise (12). They suggest that the critical temperature of the solvent should be as close to the extraction temperature as possible, and that the corresponding temperature should be such that the solute is relatively volatile. They also recommend that the pressure be as high as possible.

Previous Research

Myklebust has done supercritical extractions on peat using a batch apparatus (13). He reported recovering up to 30 wt% of the moisture-and-ash-free (MAF) peat with his solvents, which included methanol, acetone, and water. Myklebust also reported that other researchers have used supercritical fluids to extract organic material from shale oil, tar sands and coal. Methylcyclohexane (440 C and 1500 psig) was used to extract a yield of 16.4 wt% organic material from shale oil (14). These researchers (Williams and Martin) also report that tetrahydrofuran at 310 C and 1500 psig was used to extract a yield of 9.3 wt% organics from tar sands (14).

T.R. Bott listed some of the economic considerations associated with supercritical extractions (15). He says that because of the high pressures and temperatures involved, not only is special equipment needed, but also that unless special energy conservation measures are present, the technique may only be economical for high value products.

Scarrah has done work on the supercritical extraction of peat and lignite using a semicontinuous extraction apparatus (16). He says the advantages of a semicontinuous operation are: the pressure is easy to control when compared with a batch system, the products are easy to collect, and there is no problem with the solvent becoming saturated with solute since pure solvent is continuously being applied.

RESEARCH OBJECTIVE

The purpose of this study was to investigate semicontinuous subcritical and supercritical fluid extraction as a means of separating the organic portion of peat from the undesirable mineral portion. Emphasis was put on the overall yield of extracted organic material, but a brief characterization of the products was of interest. Temperature and pressure were held constant so that variations in yield would be due to differences in the solvents themselves.

Research was directed in the same manner as suggested by L.R. Snyder (10). Solvents from three selectivity groups were utilized. These solvents covered a wide range of properties from proton donating and proton accepting to being a strong dipole interactor.

MATERIALS, EQUIPMENT, AND PROCEDURE

Materials

The peat used in this project came from Michigan and was sent from the U.S. Department of Energy's Grand Forks Energy Technology Center in Grand Forks North Dakota. This peat was used "as is", being taken straight from the ground. It had a moisture content of 79 wt% and an ash content of 1 wt%.

Methanol, hexane, and methyl ethyl ketone were technical grade solvents, while formamide, acetic acid, and methylene chloride were reagent grade. All solvents came from the Baker Chemical Company. Table 4 gives the critical temperatures and pressures for each solvent (17). Snyder's parameters for each solvent are given in Table 5, while Figure 3 shows each solvent plotted on a graph similar to that shown in Figure 2. It must be noted, however, that no temperature or pressure corrections were made for the data in Table 5. There should be a correction, but at this time none is available.

Solvent	Formula	(MW)	Critical Temperature (K)	Critical Pressure (atm)
MEK	C_4H_8O	(72.107)	535.6	41.0
Methanol	CH_4O	(32.042)	512.6	79.9
Acetic Acid	$C_2H_4O_2$	(60.052)	594.4	57.1
Hexane	C_6H_{14}	(86.178)	507.4	29.3
Methylene Chloride	CH_2Cl_2	(84.933)	510.0	60.0
Formamide	CH_2NO	(45.040)	724.0	48.5*

* estimated

TABLE 4: Critical Data for Solvents

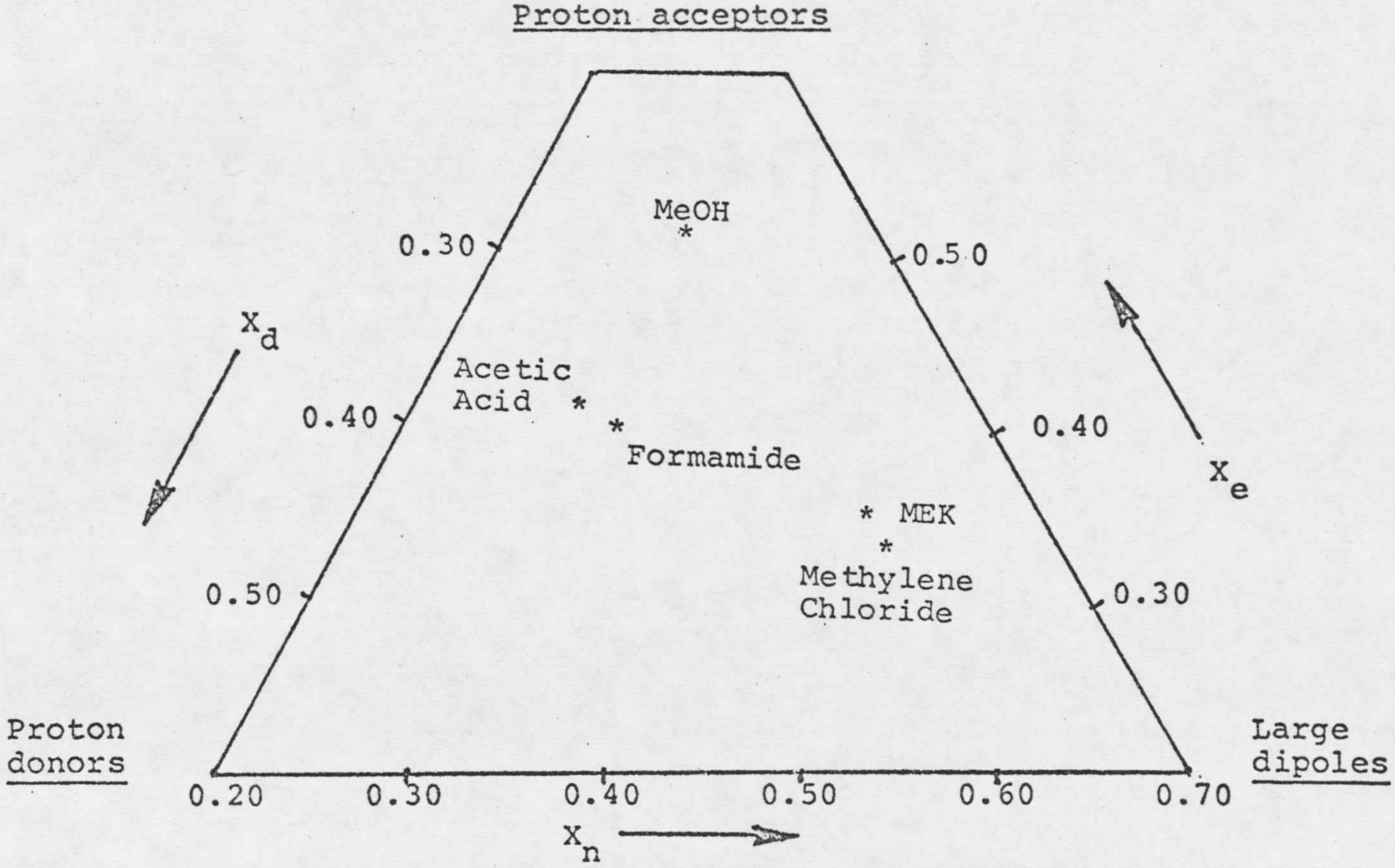

Figure 3. Snyder's Parameters for Solvents (10)

Solvent	P'	X_e	X_d	X_n
Hexane	0.0			
Methylene Chloride	3.4	.34	.17	.49
Methyl Ethyl Ketone	4.5	.36	.17	.47
Acetic Acid	6.2	.41	.29	.30
Methanol	6.6	.51	.19	.30
Formamide	7.3	.40	.28	.32

TABLE 5: Snyder's Parameters for Solvents

Apparatus

The apparatus was set up to facilitate extracting hydrocarbons from peat on a semicontinuous basis. A schematic of the extraction apparatus is given in Figure 4.

The solvent was poured into a stainless steel Griffin beaker on which an impeller was mounted to keep the solution uniform (when immiscible solvents were used). A vortex breaker was placed in the bottom of the vessel to prevent a vortex from developing which would draw air bubbles down into the solvent line. This vortex breaker consisted of a flat stainless steel disc, one-half inch thick, and about two inches in diameter with three screws in the bottom to raise it slightly off

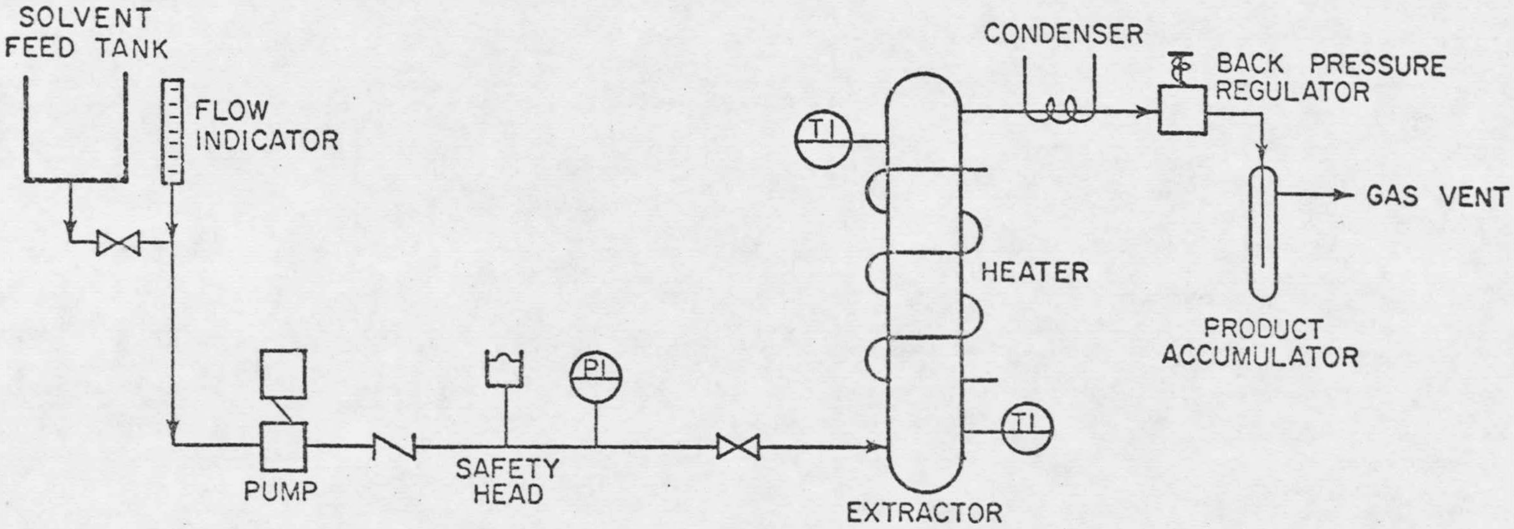

Figure 4. Schematic of Extraction Apparatus

the bottom of the beaker. The solvent would flow radially between the disc and the beaker and no vortex could form. The solvent was then gravity fed to a Milton Roy pump Model HDB-1-30R. This pump, used for the majority of the runs, had a maximum pumping capacity of 2 milliliters a minute at 2920 pounds pressure. The flow rate was measured by means of a burette and valve apparatus as shown in Figure 4. When problems developed with the pump, a Model A Milton Roy pump was installed for use in the last few runs. The solvent was then pumped through 1/4 inch stainless steel lines past the check valve, pressure indicator, and into the column. The pressure was measured by a Model DPS 0081 electronic pressure sensor made by Autoclave Engineers. Just before the column, a midway high-pressure valve was installed after which all solvent moved through 1/16 inch stainless steel lines.

The column itself was 12 inches long with an inside diameter of 0.62 inches and outside diameter of 1 inch. The ends were fitted with Parker fittings, which were equipped to take a 1/16 inch Parker fitting from the solvent lines. Two frits, one placed over each end of the column and inside the Parker end fittings, were used. These frits were porous (10μ) stainless steel discs about 1/16 inch in thickness. Heating was done by placing the column in a machined aluminum block over which an electrical coil heater was fitted. A Powerstat Type 3PN1168 variable autotransformer was used to regulate power input to the heater. Temperature was monitored by two thermocouples placed on each end of the column into holes in the aluminum block. A Honeywell temperature recorder gave a continuous record of the column temperature. The column and block were completely wrapped with insulation to minimize heat loss.

Immediately following the column was a water-cooled condenser to cool the product stream before it reached the back pressure regulator. Pressure was regulated by a Mity-Mite Model S-91XW back pressure regulator. Back pressure for this was supplied by a Parr Instrument Company Series 4000 high pressure bomb filled with up to 5000 psi of nitrogen. This 500 milliliter high pressure bomb was constructed of Inconel 757-S alloy.

The product, after passing through the back pressure regulator, was collected in 25 mm x 200 mm glass separable vacuum traps 100 milliliters at a time. The separable vacuum traps had a gas vent to allow any gaseous products escape.

It should be noted that two different safety relief systems were employed. For the first half of the runs, a rupture disc was installed just after the check valve and before the pressure indicator. The disc would rupture when the pressure reached 3300 psi. Because the cost of rupture discs was getting prohibitive, an available spring-loaded Tescom Model 26-1722-64 back pressure regulator was installed and set at 3300 psi. This provided the same protection as the rupture disc, and saved a lot of time and money.

In the event of a plugging problem, a 1/16 inch line was available to by-pass the column and reverse the solvent flow to provide pressure to release the plug. This line was also used for cleaning purposes. Before each run, excess solvent and organics from previous runs were flushed from the system.

Once the product was collected, the solvent was evaporated with a Buchi Model R110 Rotavapor rotary evaporator. This evaporator was able to distill off solvent under vacuum, which was supplied by a water aspirator. The product was then weighed on a Mettler balance. The moisture content of the product and peat were determined by drying samples in an oven kept at 100-110 C and weighing them in a Mettler Model 1-180 balance, which is accurate to within 0.0001 grams. Ash analysis was done in the same way except a muffle furnace was used that brought the temperature up to 700 C. A Varian gas chromatograph Model 142010-00 and a Varian Model 9176 recorder were used to analyze the liquid distillate off the Rotavapor. This distillate was analyzed for organic compounds extracted from the peat, but that have lower boiling points than water and the solvent used. The chromatograph column was 1/8 inch in diameter, sixteen feet long, and was packed with Porapak Q. Porapak Q is made by Waters Associates. It is used for identifying aliphatic and aromatic hydrocarbons and also organics containing heteroatoms (sulfur, nitrogen, oxygen, halides) when there is a water contaminant. Water is not absorbed by the lipophylic polymer beads, so the water peak does not tail and elutes well before any organic liquid peak.

As a means of qualitatively determining the presence of either aliphatics or aromatics, a Bruker Instruments WH-250 Fourier transform NMR Spectrometer was used to provide C-13 NMR spectra.

Carbon-13 NMR spectoscopy is useful in that it reveals direct structural information about the carbon groups that are present. There is a distinct separation at 77 ppm between the aromatic and aliphatic carbon signals on a carbon-13 spectrum. This is a distinct advantage over chromatographic characterization methods, since there is no physical means to separate the aliphatic and aromatic compounds.

The difference in the absorption position of a particular proton from the absorption position of a reference proton is called the chemical shift of the particular proton. The most generally used reference compound is tetramethylsilane (TMS). TMS is assigned a value of 0.00 on the delta scale (ppm). Chemical shifts can be expressed in dimensionless units (δ), independant of the applied frequency, by dividing v, the operating frequency, by the applied frequency and multiplying by 10^6. Thus a peak at 60 Hz (v=60) at an applied frequency of 60 MHz would be at 1.00 on the delta scale.

$$\delta \text{ or ppm} = \frac{60}{60\times10^6} \times 10^6 = 1.00$$

Since δ units are expressed in parts per million, the expression ppm is used.

Experimental Procedure

-Moisture and Ash Analysis

A sample of peat was placed in a clean, dry, tared crucible and its weight recorded. The crucible was then placed in an oven kept at 100-110 C for up to 144 hours to ensure that all moisture and solvent were driven off. Samples that were only dehydrated took considerably less time than those where solvents (MEK and formamide) had to be evaporated off. The crucible was then cooled in a desiccator before the dry weight was recorded. Ash analysis was done by placing the crucible in a cool oven and bringing the temperature up to 700 C for twelve hours. The crucible was then cooled to 100 C, placed in the desiccator, and weighed. It was assumed that all volatile matter underwent combustion, leaving only ash in the crucible.

-Run Preparation

The column was loaded with approximately 40 grams of as-received peat. In later runs, a small hole was bored through the center of the column to eliminate problems with plugs. This was done by pushing a 1/4 inch diameter rod through the peat in one end of the column, then pulling it out the other end to form a 1/4 inch hole down the middle. The porous stainless steel frits were placed over the ends of the column and the column was sealed up. To assure a constant moisture content of the peat, a small supply (up to 300 grams) of peat was kept in a sealable plastic bag. The peat used in loading each column was taken from this bag, as were peat samples from which the moisture and ash analyses were made. Moisture and ash analyses were done throughout the course of the experiments.

After the column was sealed, it was pressure tested at 800 psi to check for possible leaks. Once the leaks were closed off by tightening the Parker fittings, the column was placed in the aluminum block, the heater was placed around the block, the thermocouples were fitted into place, and the solvent lines were hooked to the column.

The final step in preparing to start the run was mixing up the desired solvent, filling the feed tank, and starting up the impeller (if needed). Since methanol/hexane and formamide/hexane solutions were immiscible when hexane was more than 30% of the total volume, this impeller mixing system was employed only for the methanol and formamide runs. This mixing system made sure that the solvent stayed at a uniform concentration.

-Run Procedure

Initially, solvent was flushed through the lines to clean them of old solvent and organics. The power to the heater was then turned on and the pump started. In the initial runs, the back pressure regulator was turned up to the desired pressure and when the pressure in the column reached 2920 psig the pump was shut off until the column reached 270 C. However, this procedure was prone to plugging and was abandoned after approximately twenty runs. The remaining runs were started by turning the heater and the pump on, but leaving the system at atmospheric pressure until the temperature reached 270 C. Once this temperature was reached, the back pressure regulator was turned up gradually so that the flow through the system was never halted for more than thirty seconds. The output from the extraction system was collected during this pressurization time. When the pressure reached 2920 psig, the run was considered to be started. Here a fresh collecting tube was placed at the output and 100 milliliters were collected into it. Usually, 400 milliliters were collected in this fashion (100 milliliters at a time) before the run was completed. The solvent flow through the column was maintained at a constant two milliliters per minute. When the extract leaving the system turned clear or very light brown color, the run was terminated. The heat was turned off and the pump was shut down.

Once all the extract was collected, the liquid product was distilled off in the Rotavapor at temperatures which never exceeded 85 C under aspirator-induced vacuum. After the solvent and water had been boiled off, the 1000 milliliter tared boiling flask used in the distillation was weighed and the weight of the collected product was recorded. During the MEK, formamide, and a few acetic acid runs, not all the solvent was able to be distilled in the Rotavapor. In these cases, the "wet" weight was recorded and a sample was dried in the oven in the same manner as outlined previously. Then the recorded weight of the product was actually a corrected value in which the wt% of solids in the sample was multiplied by the total product that was weighed "wet". A sample of the collected product was saved for possible future analysis.

The distillate from the Rotavapor was saved in three runs involving 100% acetic acid (Run 34), 100% MEK (Run 28), and 100% methanol (Run 18). This distillate was then distilled in an apparatus shown in Figure 5, and the temperature and milliliters collected at each temperature were recorded. The distillate from this distillation was then run through the gas chromatograph for the possible identification of organic compounds other than the solvent.

Samples of extracted product were dissolved in THF for use in the NMR analysis. A 10 milliliter sample of product saturated in THF was prepared into which was added two milliliters of deuterochloroform to provide an internal lock at 77 ppm on the delta scale. The samples were then analyzed by the Bruker Instruments NMR spectrometer operating at a frequency of 63 MHz. The

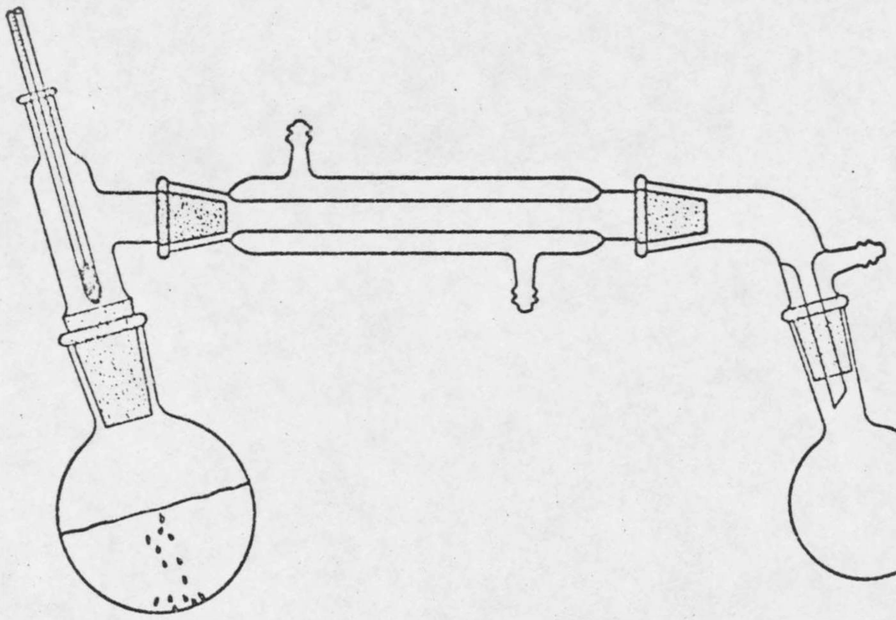

Figure 5. Distillation Apparatus

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.

RESULTS AND DISCUSSION

Introduction

Altogether, thirty-nine runs were successfully started and completed to provide some form of data. Thirty-six runs provide actual yield data, one fractioning run was performed at 2000 psig, and two runs were done only to provide data for experiments on the distillate from the Rotavapor. Table 6 gives a complete tabulation of all thirty-nine runs with the yield, temperature, pressure, and milliliters of solvent used in each case. It is worthy to note that for every successful run there was at least one additional run that had to be aborted for some reason. The reasons for aborting varied from pump and pipe failure to plugging in the lines. Despite these and a few other problems, the advantages of a semicontinuous apparatus were soon apparent. Pressure and temperature were both easily controlled. The extract was easy to collect, and small equipment changes were easily done. Saturation of the solvent was never a problem, since the extractions were performed until the extract stream was nearly clear.

Run No.	Vol % Solvent Diluted with Hexane	P'	Pressure (psig)	Fractional MAF Yield	Milliliters of Solvent Used	MAF Peat Accounted for After Mass Balance
1	30% MeOH	1.98	2920	.28	400	-
2	50% MeOH	3.30	2920	.31	400	-
3	50% MeOH	3.30	2920	.32	400	-
4	60% MeOH	3.96	2920	.32	400	-
5	60% MeOH	3.96	2920	.34	400	-
6	70% MeOH	4.62	2920	.41	400	-
7	70% MeOH	4.62	2920	.30	400	-
8	70% MeOH	4.62	2920	.30	400	-
9	80% MeOH	5.28	2920	.26	400	-
10	80% MeOH	5.28	2920	.38	400	-
11	80% MeOH	5.28	2920	.29	400	-
12	90% MeOH	5.94	2920	.29	400	-
13	90% MeOH	5.94	2920	.38	400	-
14	90% MeOH	5.94	2920	.34	400	-
15	100% MeOH	6.60	2920	.27	400	-
16	100% MeOH	6.60	2920	.34	400	-
17	100% MeOH	6.60	2920	.38	400	-
18	100% MeOH	6.60	2920	-	400	-
19	100% MeOH	6.60	2000	-	400	-

TABLE 6: Run Data Taken at 270 C

Run No.	Vol % Solvent Diluted with Hexane	P'	Pressure (psig)	Fractional MAF Yield	Milliliters of Solvent Used	MAF Peat Accounted for After Mass Balance
20	30% MEK	1.35	2920	.26	400	-
21	30% MEK	1.35	2920	.59	400	-
22	30% MEK	1.35	2920	.31	400	-
23	70% MEK	3.15	2920	.25	400	-
24	70% MEK	3.15	2920	.66	400	-
25	70% MEK	3.15	2920	.39	400	-
26	100% MEK	4.50	2920	.36	400	-
27	100% MEK	4.50	2920	.42	400	86%
28	100% MEK	4.50	2920	-	400	-
29	30% Acetic Acid	1.86	2920	.45	400	90%
30	30% Acetic Acid	1.86	2920	.39	400	-
31	70% Acetic Acid	4.34	2920	.61	400	-
32	70% Acetic Acid	4.34	2920	.55	400	-
33	100% Acetic Acid	6.20	2920	.56	400	-
34	100% Acetic Acid	6.20	2920	.74	400	-
35	100% Acetic Acid	6.20	2920	.57	400	-
36	100% Hexane	0.00	2920	.18	400	-
37	100% Methylene Chloride	3.40	2920	.13	200	-
38	30% Formamide	2.19	2920	.24	100	-
39	70% Formamide	7.30	2920	1.46	300	-

TABLE 6: Continued

Reliability of Data

The fractional yield, depending on the solvent used, varied from 0.13 to 0.74 of the original MAF peat. The formamide run with a yield of 1.46 was not a usable run. The yield was the fraction of MAF peat recovered in the Rotavapor after distilling off the solvent:

$$\text{Fractional yield} = \frac{\text{grams MAF organics extracted}}{\text{grams MAF peat charged to column}}$$

A minimum of two runs was made at each point to check on consistency. When a large variation was found, a third run was performed. For the solvents that provided useful data, statistical methods were employed in an attempt to fit a curve to the data points. This proved to be unsuccessful, since there was too much random scatter to the data. What can be noted, however, was the general trend that the data from each curve took. Of the thirty-nine runs completed, two of the MEK runs (Runs 21 and 24) showed large variations in results. They had yields of 0.59 and 0.66, respectively. Even though these were not discarded as data points, the large variations were noted.

This variation could have come from a number of sources. Because peat is a non-uniform mixture of partially-decayed vegetable matter, and since the peat used in each run is somewhat small (40 grams), variations in the peat samples themselves could have caused variations in yields. Variations could also arise during the Rotavapor step of the process. The Rotavapor had no problem evaporating the solvent off during the methanol and hexane runs. However, MEK and acetic acid proved difficult to evaporate completely off. The oily residue left in the Rotavapor varied considerably in solvent and moisture content. During these runs, a sample was removed from the Rotavapor flask and dried in an oven for up to a week to determine the actual weight of organics recovered. Because the material in the Rotavapor flask tended to be non-uniform, a sample that proved to be a fair representation was difficult to obtain.

Two overall mass balances were done on Runs 27 and 29 to determine how much product could actually be accounted for. On a moisture-free peat basis it was found that 86 wt% and 90 wt% respectively, of the original peat charged to the column could be accounted for after each of these runs were completed. The missing organic material could have disappeared as the result of three reasons. First of all, some material undoubtedly adhered to the equipment itself (inside pipe walls and collecting tubes) and was not measured. Secondly, very low boiling organics could be extracted, but lost through the vent above the collection tube. Because of the odor escaping during the runs, some loss, possibly significant, could be attributed to this. Stan Smith, in doing a gas chromatograph analysis of this vent gas, found large quantities of carbon dioxide and some hydrogen present (3). Thirdly, lighter boiling organics could conceivably be extracted with the solvent and actually evaporate off with the solvent in the Rotavapor. The procedure is somewhat limited in this respect, in that organics with boiling points lower than the solvent cannot be recovered. An attempt was made to check on the possibility of this occuring. On three runs involving 100% methanol (Run 18), MEK (Run 28), and acetic acid (Run 34), respectively, the distillate after the Rotavapor step was distilled batch-wise and the temperature and milliliters of each fraction were recorded (see Figures 6-8). The liquid collected after this distillation was then run through a gas chromatograph to check for additional peaks (see Figures 9-11). The MEK run shows no unknown peaks on the chromatograph although the boiling point graph shows quite a spread. Acetic acid shows two additional peaks on the chromatograph.

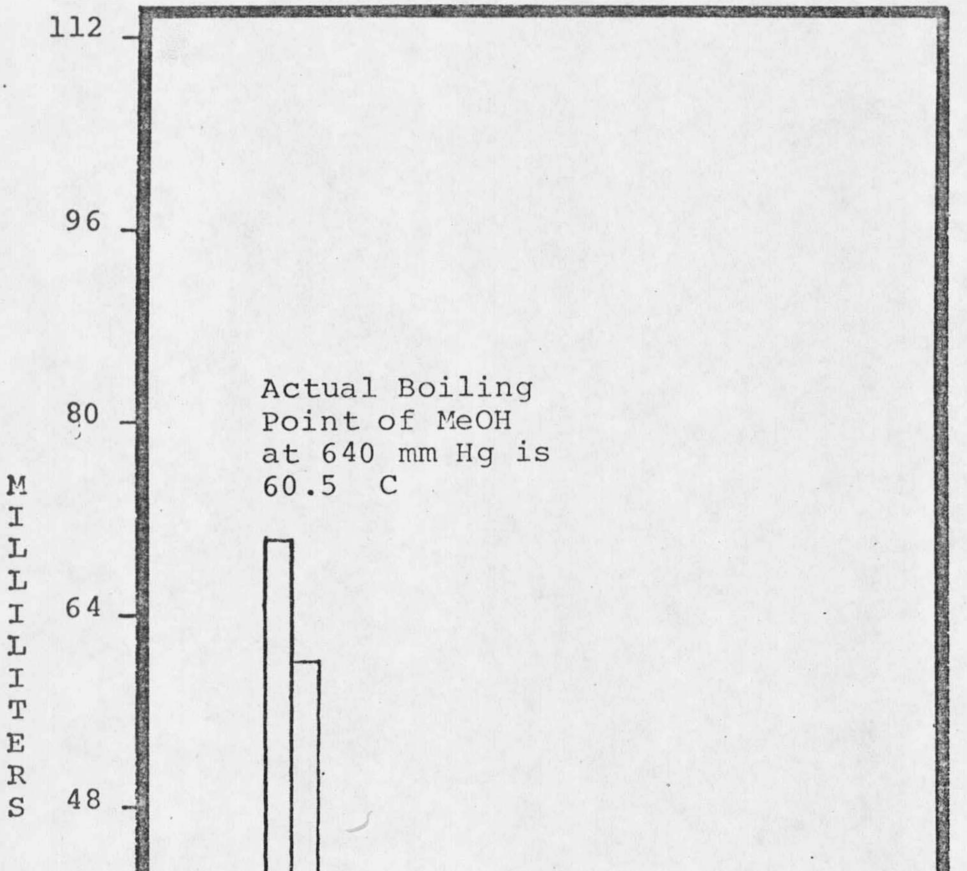

Figure 6. Boiling Point Distribution at 640 mm Hg for Methanol Distillate (Run 18)

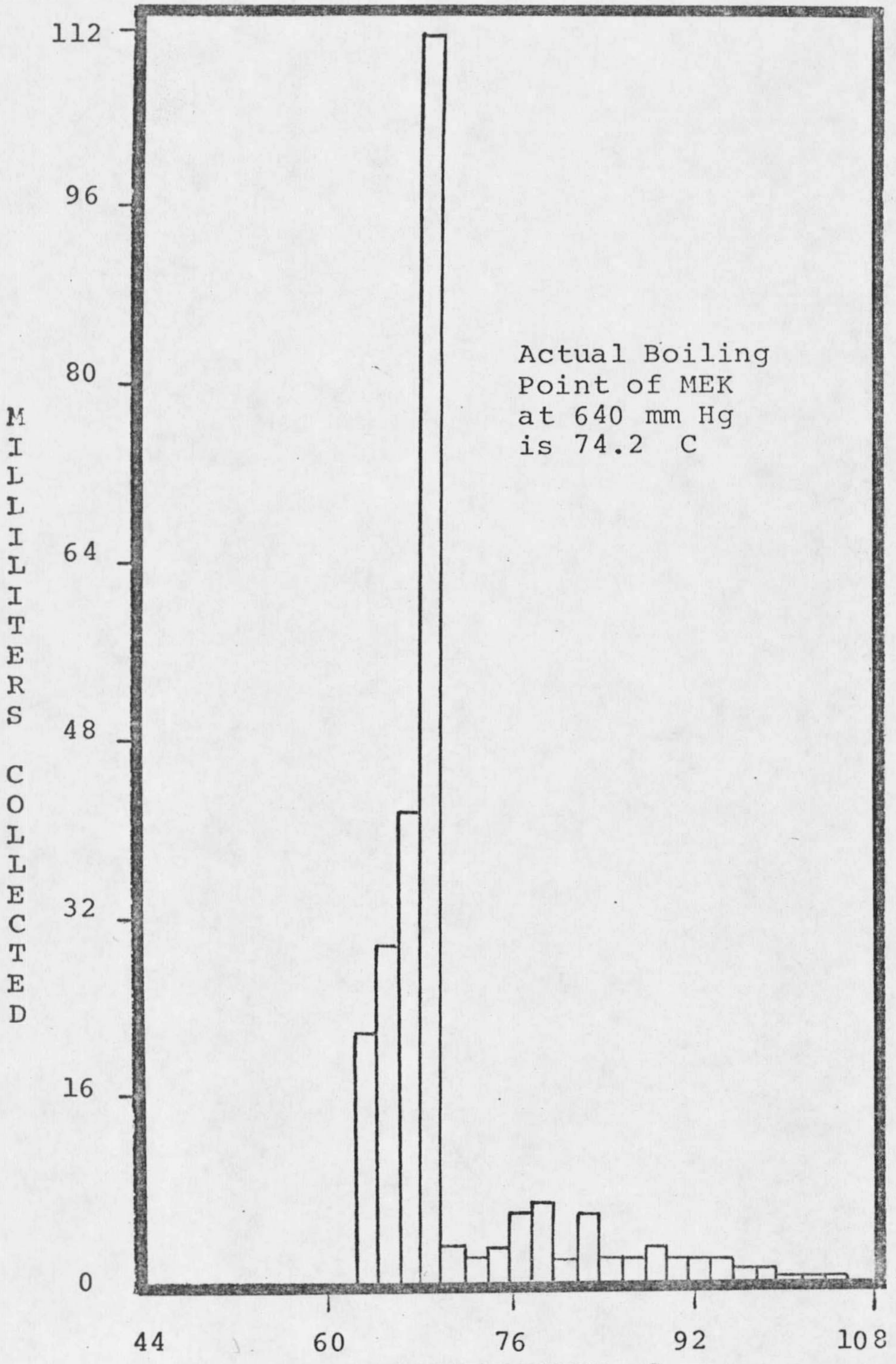

Figure 7. Boiling Point Distribution at 640 mm Hg for MEK Distillate (Run 28)

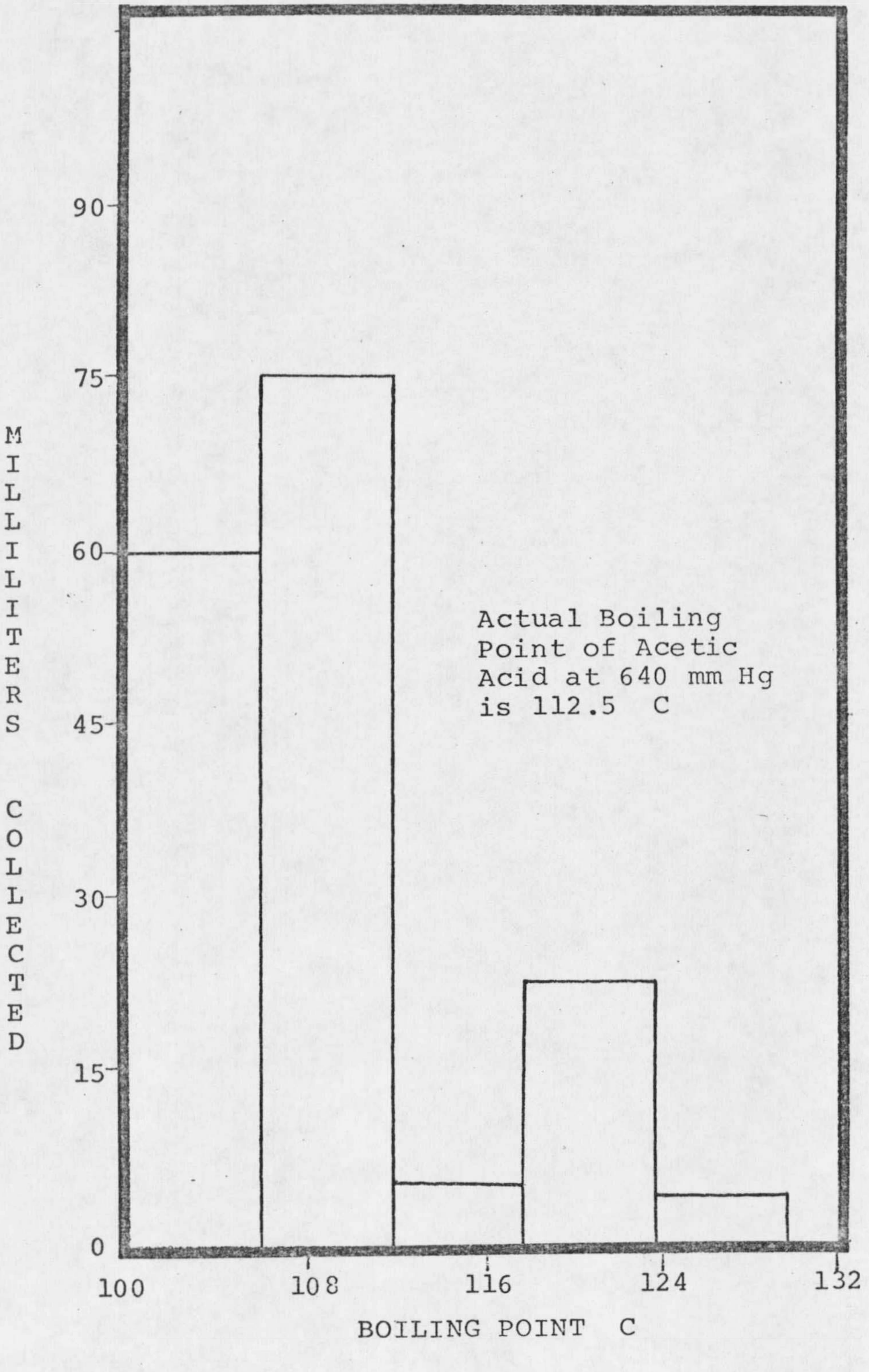

Figure 8. Boiling Point Distribution at 640 mm Hg for Acetic Acid Distillate (Run 34)

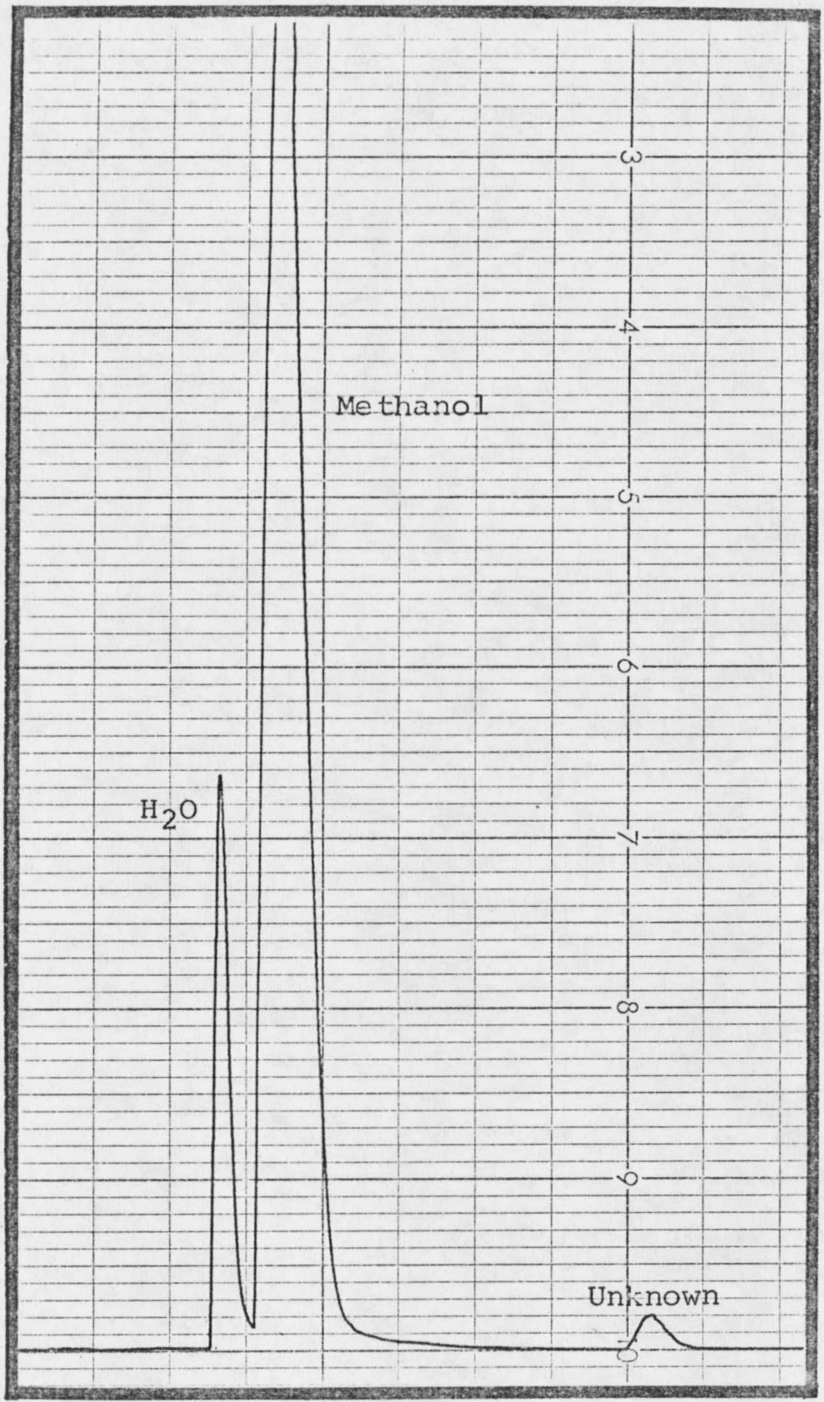

Figure 9. Gas Chromatograph of Methanol Distillate (Run 18)

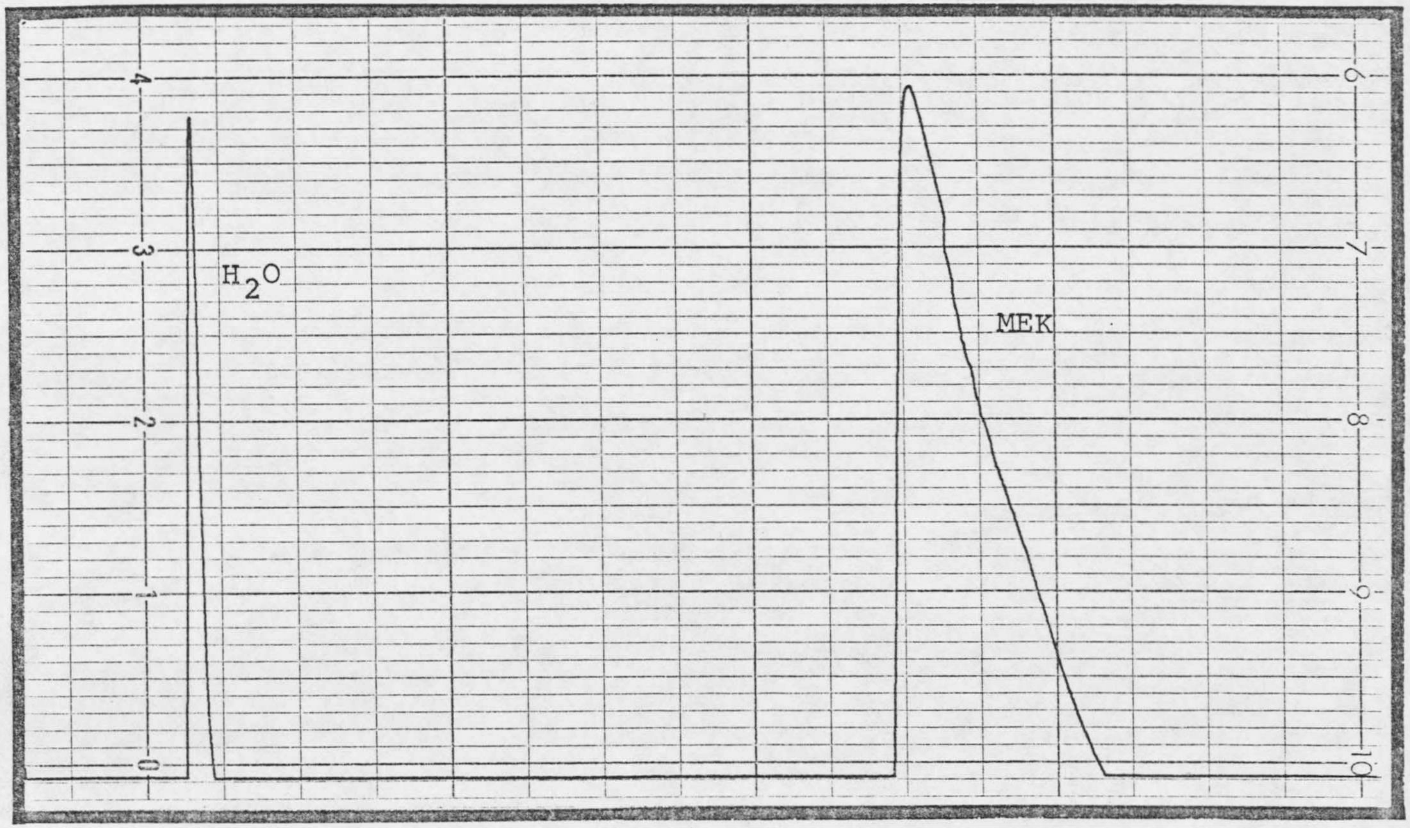

Figure 10. Gas Chromatograph of MEK Distillate (Run 28)

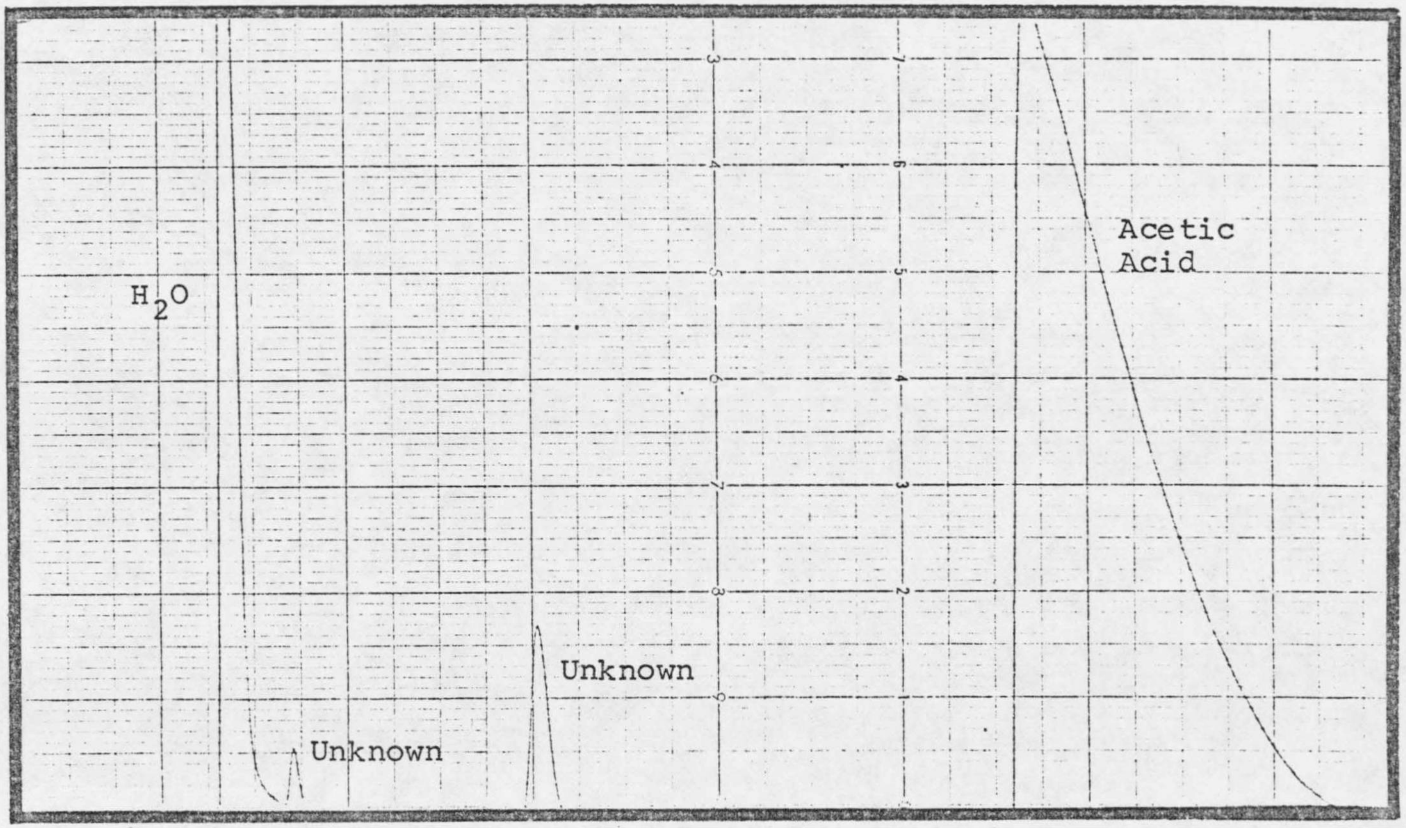

Figure 11. Gas Chromatograph of Acetic Acid Distillate (Run 34)

The methanol run gives one small additional peak. Individual samples of ethanol, methanol, methyl acetate, and ethyl acetate were made up and run through the gas chromatograph. This was done to see if these compounds would match up with the unknown peaks, which none of them did. Whether or not these peaks came from organics extracted from the peat, reactions taking place in the column, or the solvent itself decomposing was hard to ascertain. Without further analysis, no conclusions could be made.

To determine how much solvent should be used in the extraction, two fractioning runs were performed before any solvents were investigated. Both runs were made with methanol at 270 C, but one was at 2000 psig (Run 19) and the other at 2920 psig (Run 15). During these runs, the weight of extracted organics was recorded for each 100 milliliters of solvent used. This data is recorded in Table 7. As can be seen, the majority of the product is extracted with the first 200 milliliters of solvent. To be consistent throughout the experiment, 400 milliliters of solvent was used in each extraction. The exception to this was in two runs with formamide (Runs 38 and 39) and one run with methylene chloride (run 37) where the extract was so clear at the outlet that the runs were terminated early.

	Grams first 100 mls	(cumulative % of total)	Grams second 100 mls	(cumulative % of total)	Grams third 100 mls	(cumulative % of total)	Grams fourth 100 mls	(cumulative % of total)
Run 1*	2.00	(81.6%)	.36	(96.3%)	.05	(98.4%)	.04	(100%)
Run 2**	1.86	(75.0%)	.50	(95.2%)	.10	(99.2%)	.02	(100%)

TABLE 7: Fractionating Runs Using Methanol as the Solvent

*2000 psig, 270 C
**2920 psig, 270 C

Even though possibilities for error existed, the data showed some degree of consistency, which will now be discussed.

Method of Data Analysis

As mentioned before, data was recorded as grams of dry recovered product. This was then put on a yield basis, to facilitate comparing the effects of different solvents. It is stressed that this yield, as a function of solvent selectivity and strength, is what was to be maximized. Gas chromatographic analysis of the solvents and lighter organics and C-13 NMR analysis of the THF-soluble extract were run only to give a qualitative idea of any differences between the products extracted. A Soxhlet extraction was done on each of the products to determine their respective solubility in THF.

The solvents were selected on the basis that they all had a dominant special solvent force (Figure 3), yet maintained basically similar critical properties (Table 4). This aided the comparison in that it was assumed that the slight variation in critical properties had no effect on the yield. It is emphasized that acetic acid was not utilized as a supercritical solvent since a solvent with proton donating capabilities could not be found that had critical properties close to that of methanol. Acetic acid was the proton donating solvent (characterized by Snyder) with the lowest critical temperature. It was decided at the outset of the experiment to hold temperature and pressure constant rather than to hold the reduced temperature and pressure constant. Although this prevents the direct comparison of data in the supercritical state, it was decided that it was more practical to hold the actual temperature and pressure constant.

Experimental Results

Research was started using methanol as the solvent, a strong proton acceptor (methanol is in Group II). Figure 12 gives a plot of yield vs P' for the methanol runs. As outlined by Snyder, it was the goal to optimize the P' value, and from there to optimize the solvent selectivity group using the optimum P'. Even through the fractional yield ranged from 0.26 to 0.41, it can be seen that there was very little variation in yield over the entire range of methanol concentrations. This led to the abandonment of Snyder's approach, and to the attempt of optimizing P' for each individual solvent used.

It was noticed not only in the methanol runs but in all runs, that as the first 200 milliliters of solvent

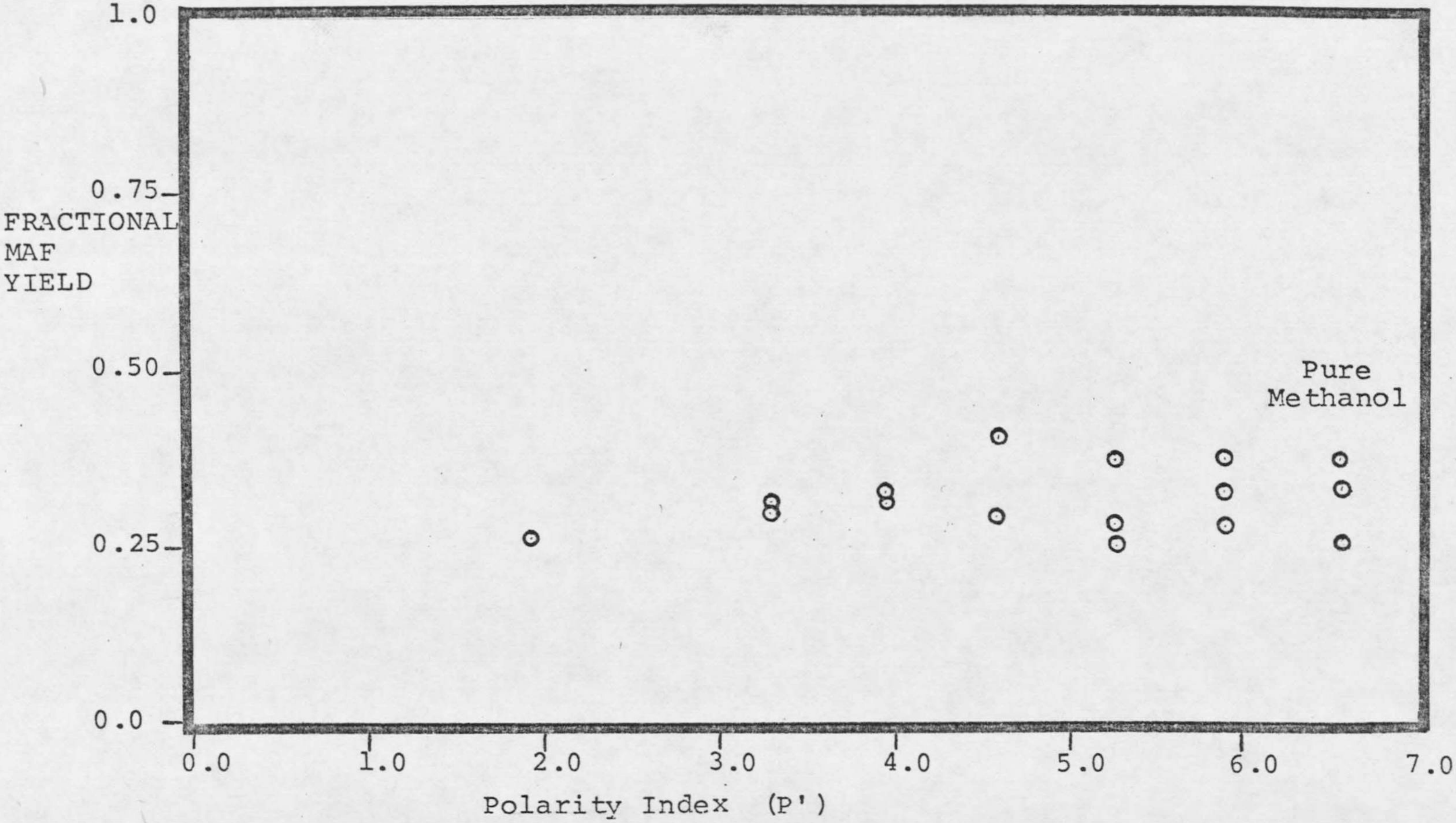

Figure 12. Fractional Yield vs P' for Methanol-Hexane Mixture

was collected a precipitate settled to the bottom of the separable vacuum traps. This was consistent with the general principles of supercritical solvents in that at the supercritical conditions in the column, much more product was soluble than at the ambient conditions at which the extract was collected. Also, it was noticed by the dark color of the solvent that some of the extracted product remained in solution even after the conditions changed from supercritical to ambient at the outlet of the extraction apparatus.

The second solvent to be tried was one lying in the lower right-hand corner of Snyder's solvent diagram (Figure 2), where solvents with large dipole characteristics are found. This was where several problems were encountered. The first solvent to be tried and abandoned here was methylene chloride (Group V). The first five runs of methylene chloride resulted in the rupture of the 1/16 inch tube coming from the column within five minutes of the start of the run. Finally a successful run was completed (Run 37), but the product was very acidic. Chlorine gas (identified by its odor) was found to be violently bubbling up from the collecting tube, leading to the conclusion that methylene chloride was degrading in the column to chlorine gas. Hydorchloric acid was probably produced when this chlorine encountered water from the moist peat. After 200 milliliters of product was collected from this successful run, essentially no more organics were extracted as the solvent coming out of the column was clear. The yield was very low, showing that methylene chloride has very poor solvent properties when used as a supercritical fluid for peat. Further research into this matter showed the same problem had occurred in previous research (18). What happened was that catastrophic stress and corrosion cracking was occurring at the critical places where aqueous hydorchloric acid was condensing (in the 1/16 inch tube coming from the column). To overcome this problem, it is suggested to use materials that are not subject to stress corrosion cracking (Inconel 600 or Inconel 625). Figure 13 gives a sketch of the actual corrosion areas.

The third solvent to be tried was methyl ethyl ketone, which also has large dipole characteristics. Methyl ethyl ketone is in Group V. A plot of these runs (Yield vs P') is given in Figure 14. A little more variation in yield can be noticed here, with values running between 0.25 and 0.66. These values were a little higher than the methanol runs. Again it is pointed out that these variations were probably caused by the difficulty encountered in evaporating off all the

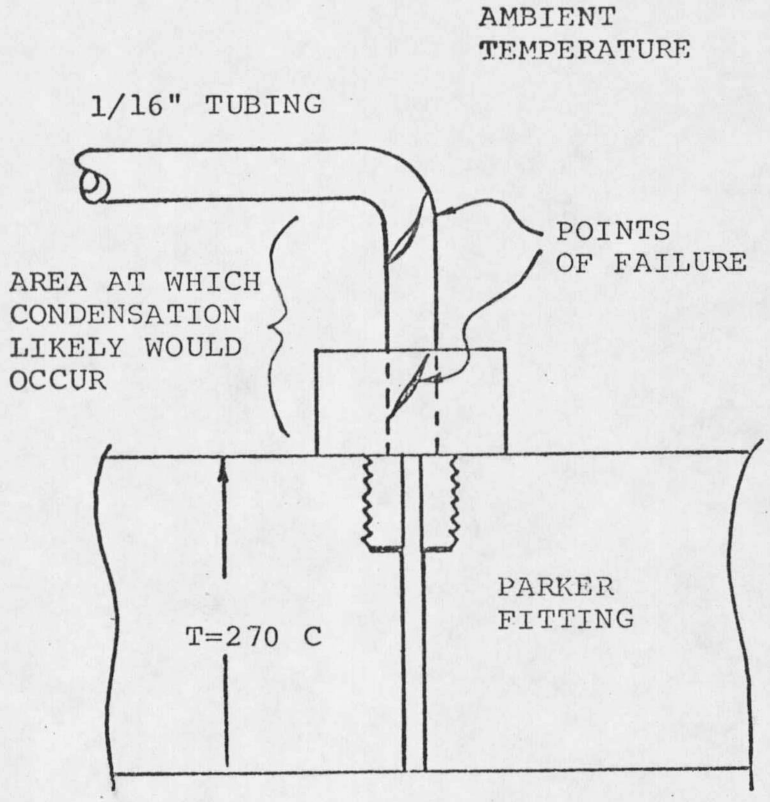

Figure 13. Corrosion Areas in Methylene Chloride Runs

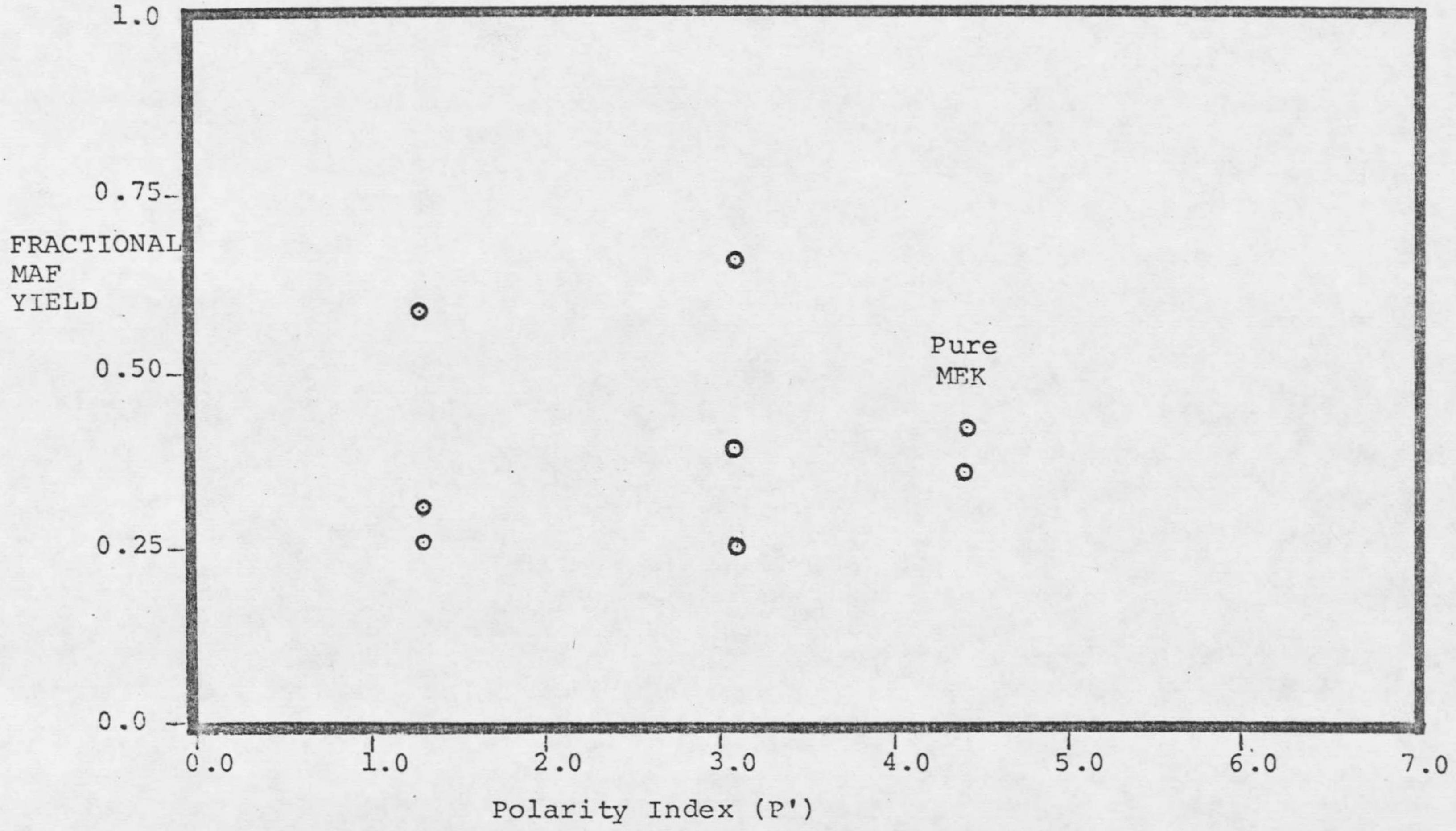

Figure 14. Fractional Yield vs P' for MEK-Hexane Mixture

solvent in the Rotavapor. The basic trend of the data, however, is the same as with methanol. The higher the P', the higher the yield, with the yield leveling off at the higher P' values. During the MEK runs, several problems occurred where the column would plug up causing the run to be aborted. This problem was finally solved by pushing a rod lengthwise into the peat once it was packed in the column and then removing it. This created a hole for the solvent to initially travel through, eliminating the plugging problem, while at the same time not influencing the yield.

The next solvent to be tried and abandoned was one in Group IV, formamide. Formamide has proton donor characteristics and had three problems. First, it caused plugs to develop that even with the rod treatment were impossible to prevent. Secondly, when formamide was diluted with hexane, being immiscible, it had to be mixed before entering the system. This ordinarily would not be a problem, but after thirty minutes, the formamide/hexane mixture formed into a viscous syrup-like solution that probably contributed to the plugging problem. Thirdly, the formamide/product mixture proved very difficult to evaporate in the Rotavapor. During Run 39, only 100 milliliters of the 300 milliliter solution could be evaporated, leaving approximately

2 grams of solid material in 200 milliliters of formamide. The last two problems could have been overcome, but the consistent plugging problem resulted in the abandonment of formamide as a possible solvent.

The solvent that proved to be most effective was acetic acid even though it was not in the supercritical state. It should also be noted that no critical properties could be found for the solvents when mixed with hexane. Therefore, it was not determined whether or not the solvent-hexane mixtures were in the supercritical state. Acetic acid is also in Group IV (Group IV compounds have strong proton donor characteristics). A plot of yield vs P' for this solvent is given in Figure 15. As can clearly be seen, acetic acid gave by far the best results; yields were consistently higher than the supercritical methanol and MEK runs, while the data followed the same general pattern as both of them.

Carbon-13 NMR spectra of the THF-soluble part of the products extracted with methanol, MEK, and acetic acid are shown in the Appendix. To determine how much of the product was soluble in THF, a Soxhlet extraction was done on the products extracted with methanol, methyl ethyl ketone, and acetic acid. This revealed that only 30.2 wt%, 38.6 wt%, and 23.1 wt%, of the product respectively, was soluble in THF. These spectra show

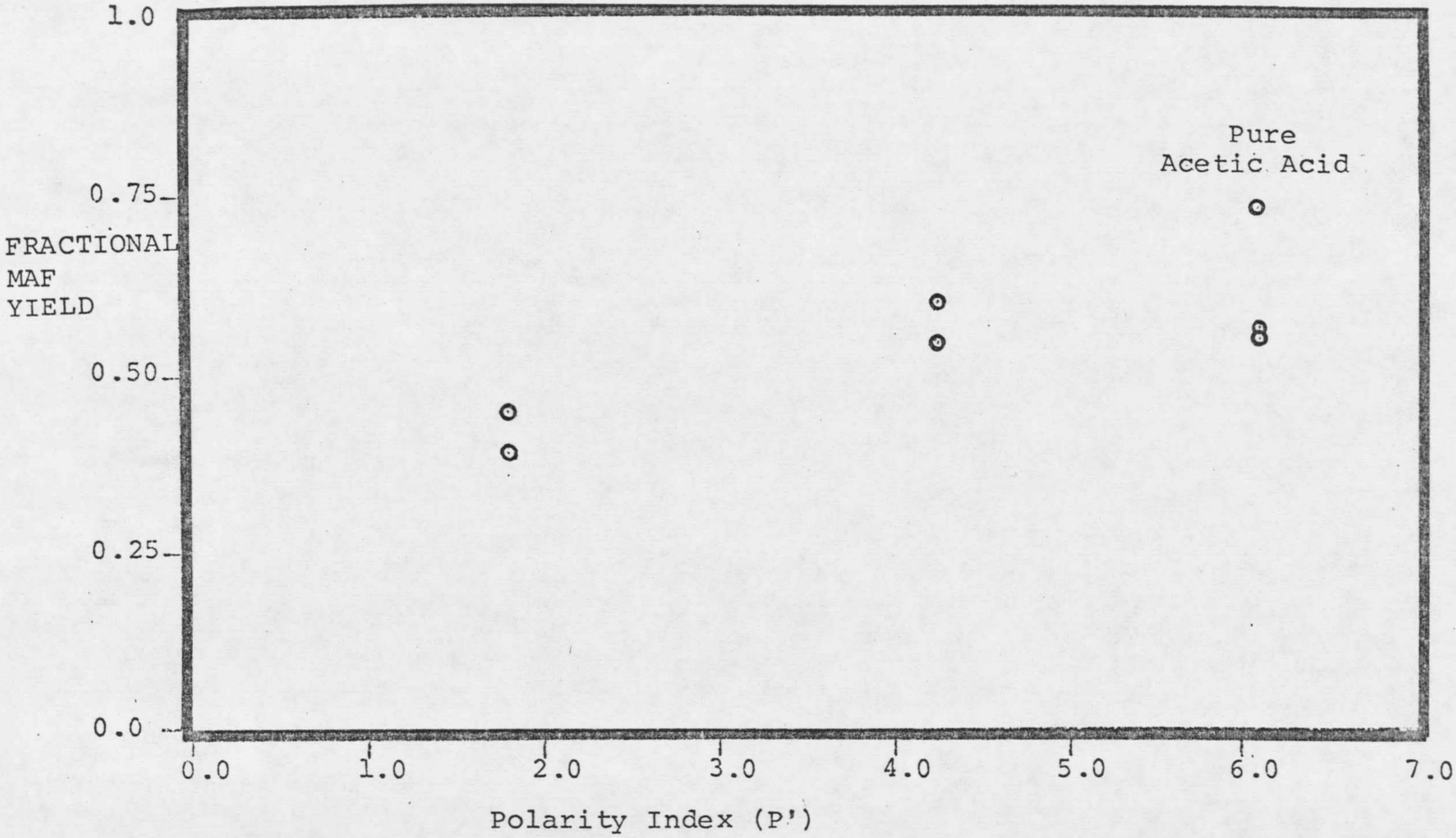

Figure 15. Fractional Yield vs P' for Acetic Acid-Hexane Mixture

that more aliphatic compounds were extracted than aromatics. Methanol extracted a few aromatic compounds (Figures 16 and 17) and acetic acid extracted something with a lone aromatic peak at 171 ppm (Figure 19). The spectra for the methanol run (Run 15) was divided into two spectra. The products from the first and second fractions from one of the fractionating runs was analyzed. As Figures 16 and 17 show by the peaks being in different locations, a wider variety of products was extracted during the initial period of the extraction.

Even though direct identification of the compounds extracted was impossible, the NMR spectra were useful in identifying that the majority of the THF-soluble compounds extracted with all solvents were aliphatic rather than aromatic (Figures 16-19). THF was convenient to use as a solvent, but some information in the aliphatic region was hidden by the solvent peak at 24 ppm.

Reliability of Equipment

Because of the severe environment (corrosive chemicals, high temperature, high pressure) several problems developed with regard to the experiment. The Parker fittings used in the column did not hold up very well to repeated opening and closing. Some fittings did not last more than a few runs before having to be discarded. Since operation was maintained at such high pressures, the slightest crack or scratch often meant that the part had to be discarded. Additional research should be done with equipment able to withstand repeated opening and closing and not Parker-type fittings. If a potentially corrosive solvent is used, care should be taken to use construction materials compatible with the solvent.

SUMMARY

This investigation into the semicontinuous extraction of peat using subcritical and supercritical solvents has produced the following summary:

1. The operation of a semicontinuous extraction apparatus using supercritical solvents to extract the organic material from peat is possible. Specific items involving operation and use of equipment are listed below:
   a) Temperature and pressure were both easy to control.
   b) A plugging problem was present when using wet peat. Driving a small rod lengthwise through the column of peat and removing it created a hole which allowed solvent and extract to freely flow and greatly alleviated the plugging problem.
   c) The Parker fittings on the column wore out much too fast. Future designs should be modified or changed.
   d) The use of a back pressure regulator is recommended over the use of a rupture disc for a safety relief system.

   e) Use of stainless steel parts will result in severe corrosion problems if methylene chloride is used as the supercritical solvent.

2. Product distillation using the Rotavapor was not adequate for the MEK and formamide runs.
3. Acetic acid, a proton donor solvent, was more effective at subcritical conditions than supercritical methanol (proton acceptor) or MEK (strong dipole) in extracting organics from peat.
4. For all the solvents, it was noticed that once the polarity index reached a value of around 3.0, the yield seemed to level off and any further increase in polarity index had little effect on yield.
5. All the solvents seemed to give slightly better yields when used in the pure form and not diluted with hexane.
6. Evidence of solvent reactions in the column existed during the acetic acid and methanol runs.
7. The formation of a precipitate in the product stream after going from supercritical to ambient condition is consistent with the general principles of supercritical extractions.
8. Some of the extracted product remained in solution even after the conditions changed from

supercritical to ambient at the outlet of the extraction apparatus.

9. C-13 NMR studies on the THF-soluble product (23.1 wt% to 38.6 wt% of total product) resulted in the following conclusions:
    a) All the solvents extracted more aliphatic compounds than aromatics. Methanol extracted a few aromatic compounds and acetic acid extracted a compound that shows a lone aromatic peak at 171 ppm.
    b) A wider variety of predominately aliphatic products were extracted during the initial period of the extraction.
    c) The use of THF as the solvent was convenient, but some information in the aliphatic region was hidden by the solvent peak at 24 ppm.

RECOMMENDATIONS FOR FUTURE STUDY

1. Because of the effectiveness of acetic acid as a subcritical solvent, additional research could possibly investigate solvents with similar properties (Group IV) to see if any improvement in yield could be found.
2. A thorough analytical study of the products extracted using various solvents could be done, which would greatly facilitate the process of choosing the best solvent.
3. A study should be done to investigate the influence of recycling the solvent.
4. Efforts should be made to find equipment that will be able to withstand the abuse associated with high pressure and high temperature operation.
5. An economic feasibility study should be done to determine if there is any future in commercial supercritical extraction of peat.
6. Because of the wide range of organic compounds in peat, research into the effect of mixing different solvents from different selectivity groups would be of interest.

7. A study could be done to investigate the effect of using acetic acid as a supercritical solvent.

APPENDIX

C-13 NMR Spectra

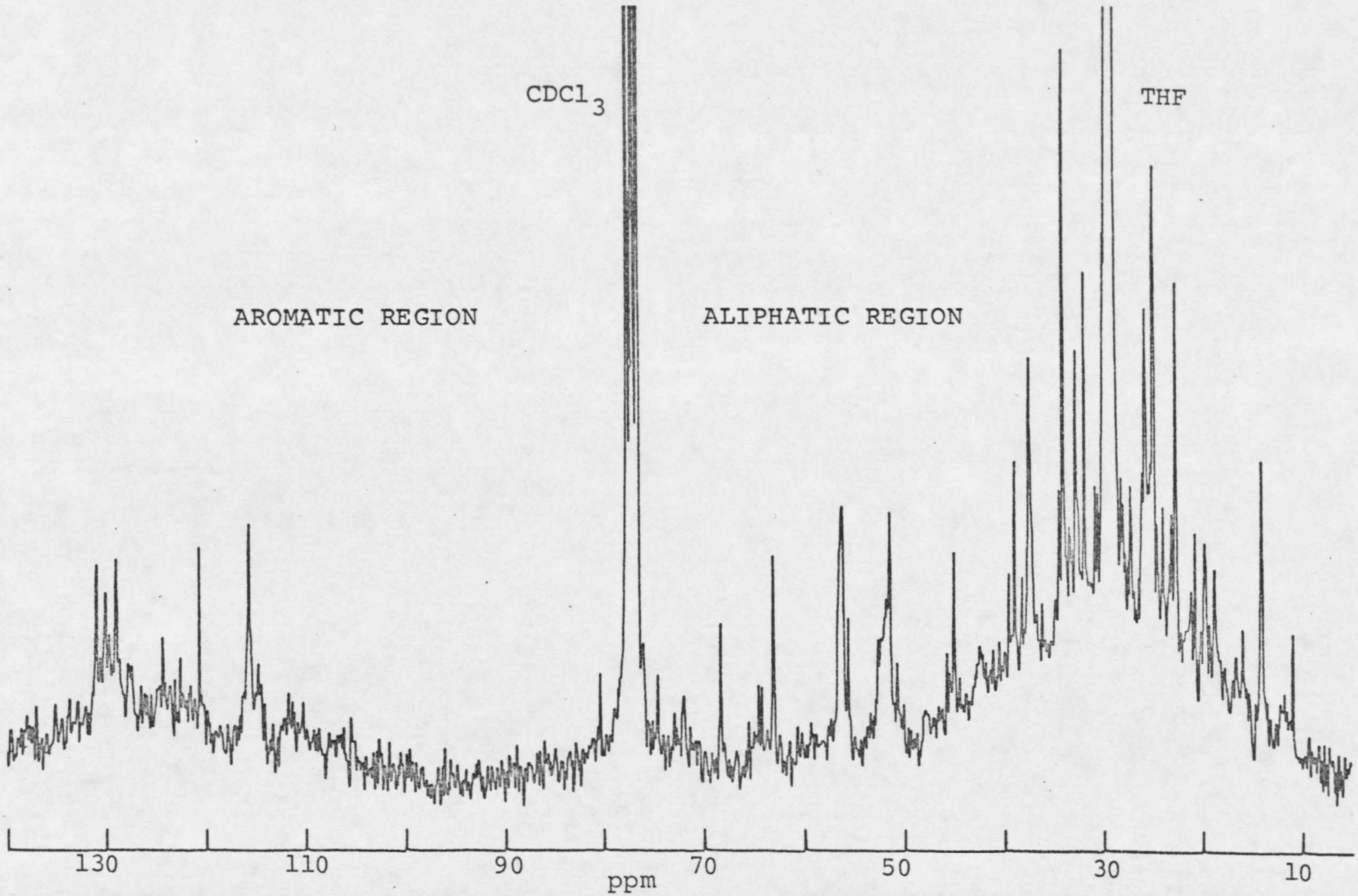

Figure 16. C-13 NMR Spectra for First Methanol Fraction

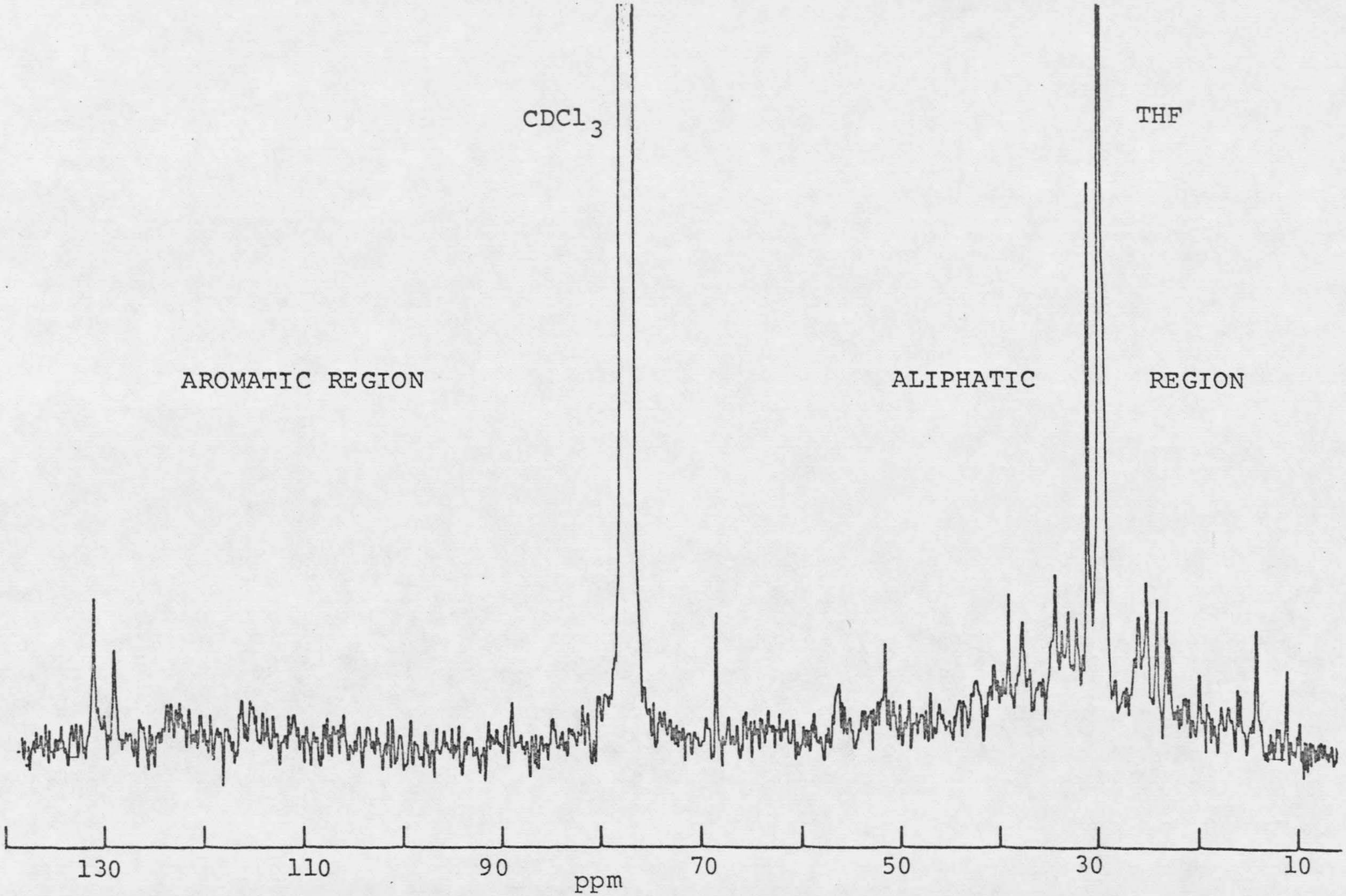

Figure 17. C-13 NMR Spectra for Second Methanol Fraction

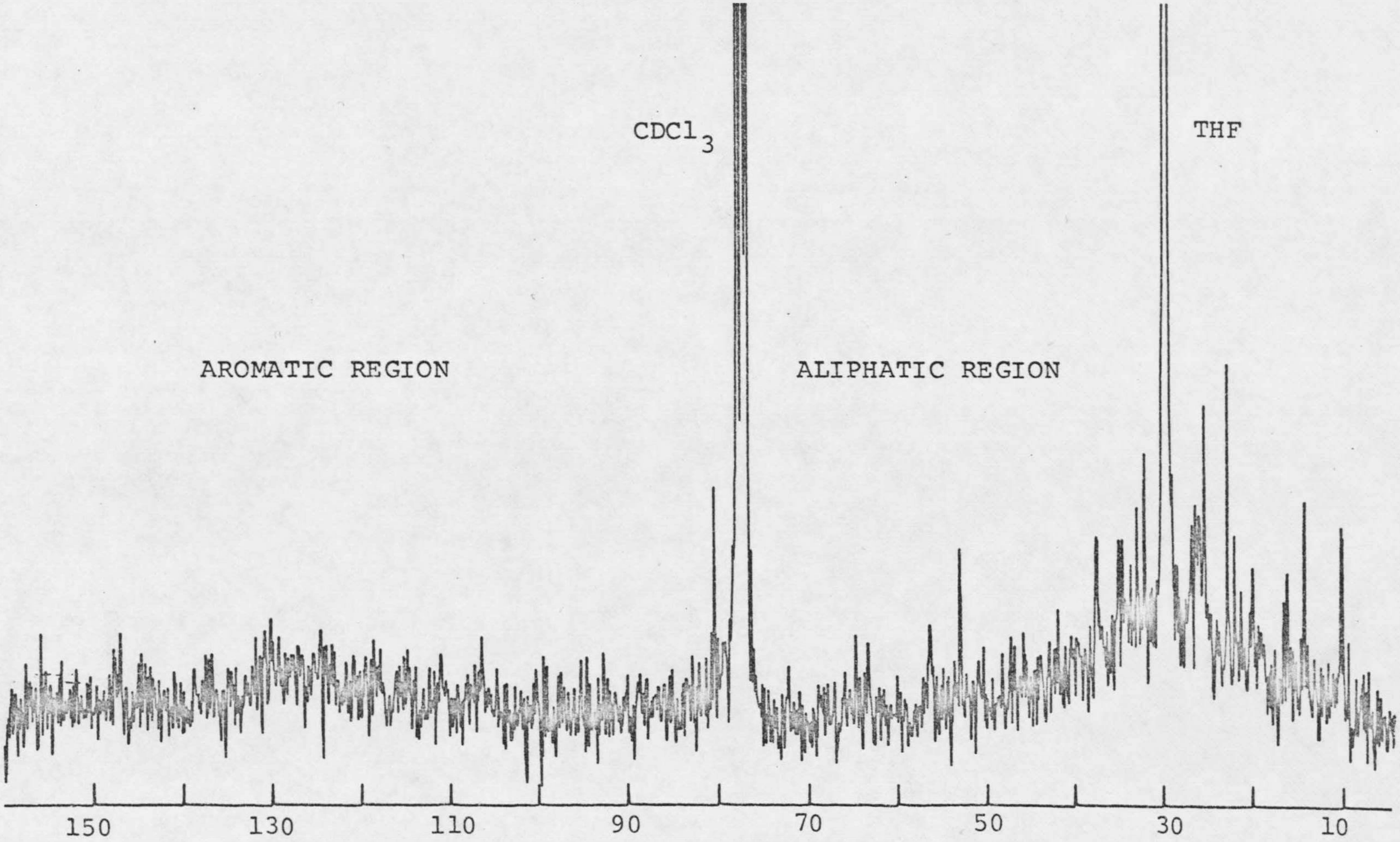

Figure 18. C-13 NMR Spectra for MEK Run

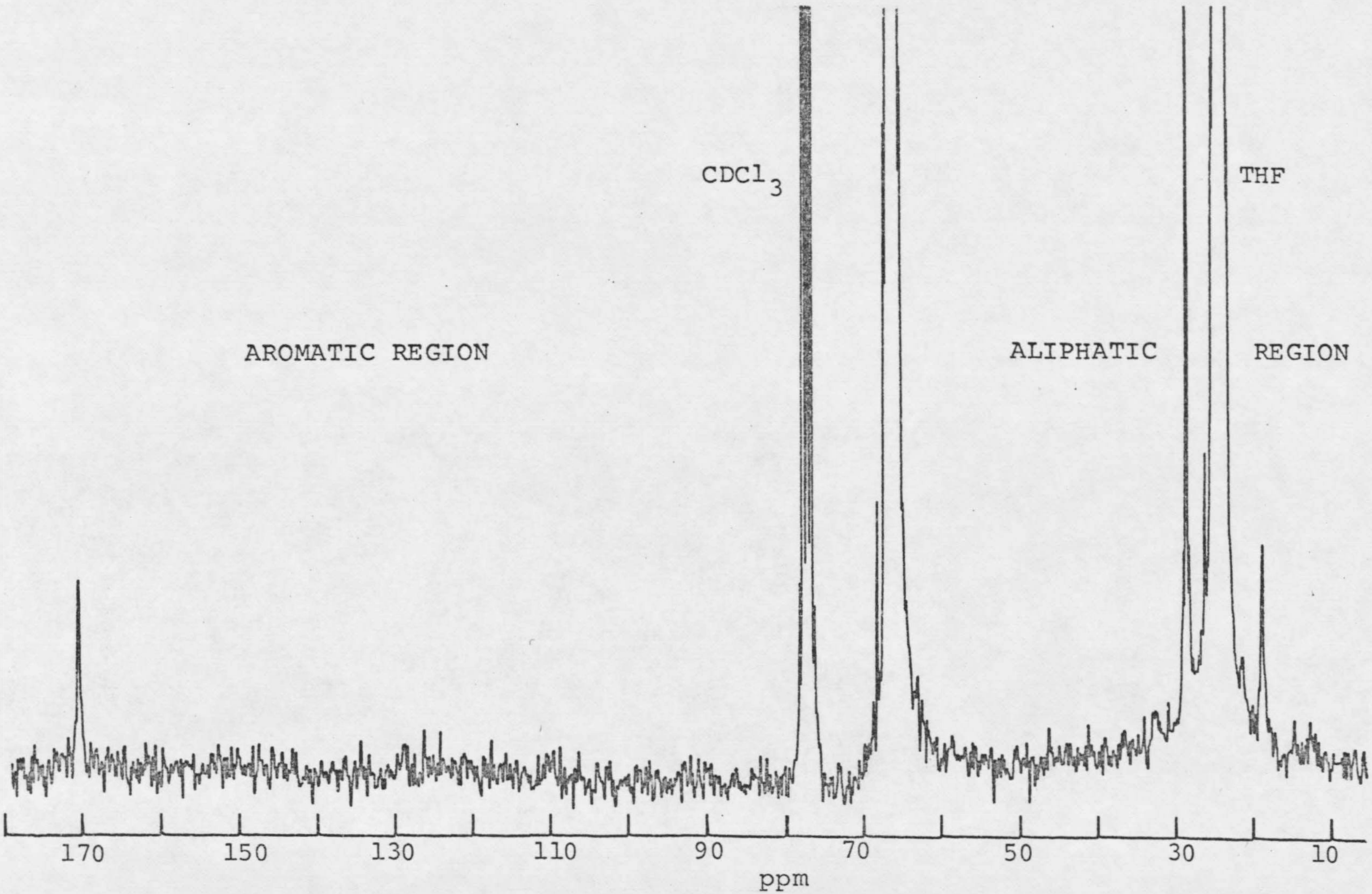

Figure 19. C-13 NMR Spectra for Acetic Acid Run

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