Supercritical fluid extraction of peat
by Kenneth Lewis Myklebust, Jr

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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The experimental runs were made in a 500 milliliter Inconel rocking autoclave apparatus. The operating time was one hour after attainment of the desired operating temperature.

A maximum amount of organic yield was obtained using acetone as the supercritical fluid at very high pressures (almost 50 weight-percent at 4800 psig). All water-based runs gave very poor yields (a maximum of 26 wt-% of the original moisture- and ash-free peat), and methyl alcohol gave intermediate results (a maximum of 36 wt-%).

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Date February 4, 1982

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Approved:

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ABSTRACT

Experiments were conducted to determine the feasibility of utilizing supercritical fluid extraction to remove the organic portion of agricultural peat from the mineral portion. The variables involved in this investigation were operating temperature, operating pressure, and type of solvent. The operating conditions covered the widest range of values which was practical with the lower limits being at or near the critical values of the solvent under consideration. Operating pressure covered a range of 800 to 4800 pounds per square inch (gauge), and operating temperature was varied from 240 to 430 degrees centigrade. The actual limits varied with different solvents. Three solvents were utilized; water, methyl alcohol, and acetone.

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I. INTRODUCTION AND PREVIOUS RESEARCH

A. Introduction

1. Peat

Due to the recent increases in the price of crude oil and decreasing availability of petroleum products, a new demand for alternative sources of energy has arisen. A potential major source is peat. It has been estimated that there are about 1440 quadrillion British thermal units of energy in the form of peat in the United States alone (1).

Peat is the first step in the geologic sequence involved in the formation of coal beds. The sequence is initiated by living vegetation and then goes to peat, lignite, subbituminous coal, bituminous coal, semi-anthracite, anthracite and finally to meta-anthracite or graphite. For this reason, peat has often been called "young coal". Peat is formed when a mass of dead vegetable matter is protected from the action of air and aerobic bacteria by being submerged in water. Peat contains a large portion of the carbon and hydrogen of the original organic mass.

Since peat is only formed while it is under water,

considerable amounts of water can be retained in its porous structure, even after the peat is removed from the ground. Peat has a much higher water content than higher coals, as is shown in Table I. If the peat is 90 wt-% water, the heat required to evaporate the water is more than the heat obtained by burning the peat, so no combustion can occur (see Table II). However, the peat can be dried to about 50 wt-% by simply exposing it to the sun and air for awhile.

World peat resources and production are shown in Table III. The U.S.S.R. produces about 96% of the world's peat and has almost 60% of the world total peat reserves. Table IV shows the U.S. peat reserves as determined by two different studies, one study done in 1922 (4) and the other done in 1977 (5). It should be noted that regions that have large peat reserves have very little in the way of other fuel resources. Alaskan peat deposits have been estimated to be in excess of 62 billion tons. The peat deposits of the entire U.S. are an energy source of over 1440 quadrillion Btus. This is equivalent to over 240 billion barrels of crude oil and, as shown in Figure 1, exceeds the combined 1123 quadrillion Btus in other

Table I. Properties of typical U.S. coals (1).

	Moisture (wt-%)	Volatile matter (wt-%)	Fixed carbon (wt-%)	Ash (wt-%)	Higher heating value (Btu/lb_m)
Reed sedge peat	90	65	27	8	8,500
North Dakota lignite	34	40	49	11	10,700
Montana subbitumi-nous	10	39	48	13	11,800
Illinois no. 6 bitumi-nous	13	42	48	10	13,900
Pennsyl-vania anthracite	3	10	78	12	13,600

Table II. Heat required to evaporate water from peat (1).

	Per lb_m of dry peat		
Wt-% water	Lb_m of water	Btus to evaporate water	Evaporation, % of Btus in peat
90	9.0	9000	106
70	2.3	2333	27
50	1.0	1000	12
30	0.4	429	5
10	0.1	111	1

Table III. Peat resources and production (Million short tons air-dried peat) (1).

	Resource (2)	Production	
		1973 (2)	1977 (3)
U.S.S.R.	138,000	211.200	211.000
Finland	36,000	0.436	0.400
Poland	24,000	0.050	NA
United States	14,000	0.635	0.974
Sweden	10,000	0.106	NA
Iceland	2,200	NA	NA
United Kingdom	1,800	NA	NA
West Germany	1,000	2.245	2.700
Denmark	600	0.006	NA
Japan	550	0.080	NA
Ireland	440	4.330	6.300
Canada	220	0.359	0.410

Table IV. Peat reserves (1).

	Soper (4) (1922)		Farnham (5) (1977)	
	Million acres	Million tons	Million acres	Million tons
Minnesota	5.2	6835	7.2	16,500
Michigan	---	1000	4.5	10,300
Florida	---	2000	3.0	6,900
Wisconsin	1.0	2500	2.8	6,400
Louisiana	---	2	1.8	4,100
North Carolina and Virginia	---	700	1.5	3,400
Maine	---	100	0.8	1,800
New York	0.8	480	0.7	1,500
All other states (not including Alaska and Hawaii)	---	210	2.8	6,600
TOTAL	---	13,827	25.1	57,500

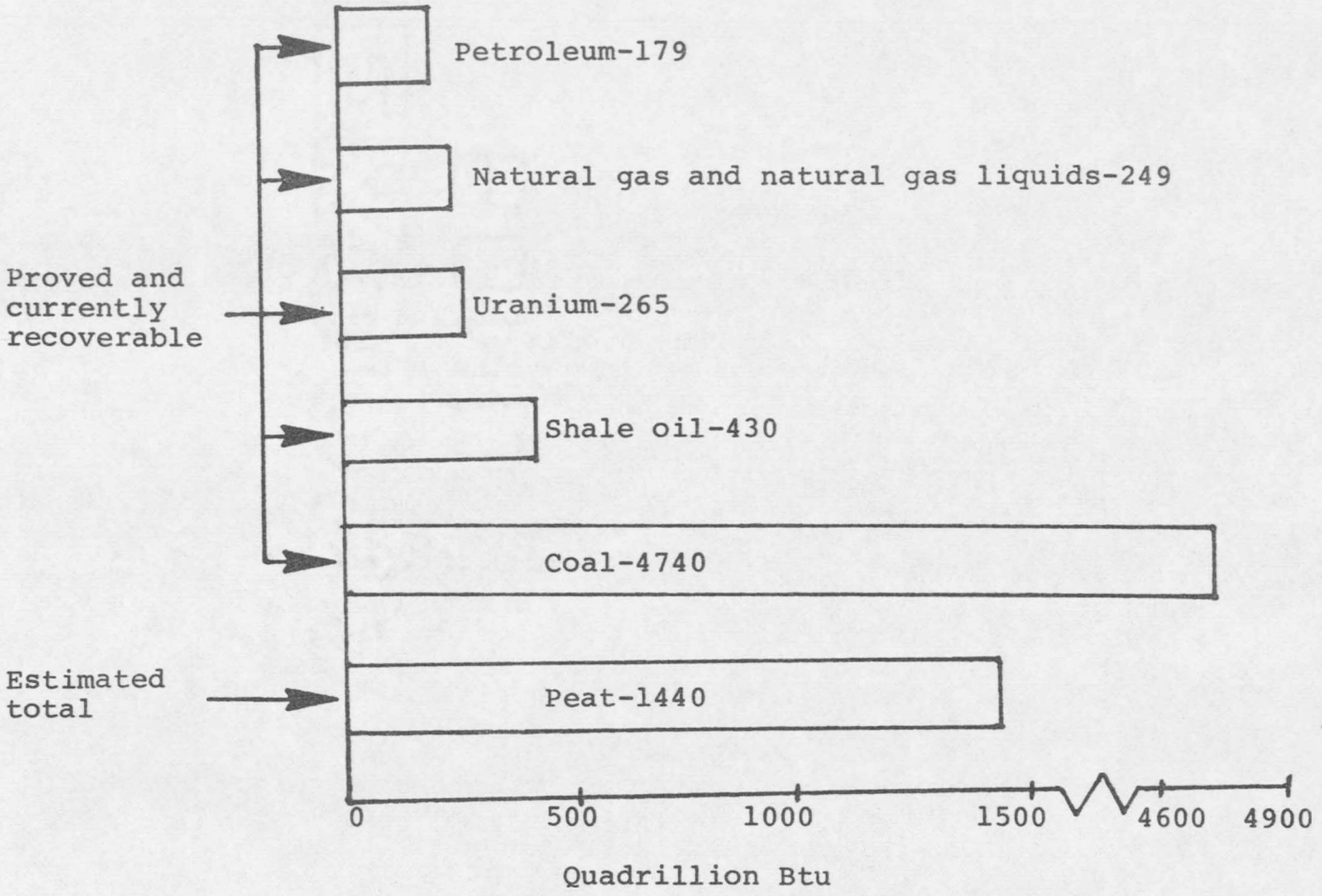

Figure 1. United States Energy Resources (1).

natural fuels (excluding coal).

The first step in peat production is the draining of the bog, usually through the use of drainage ditches. This usually reduces the water content of the peat from about 95 wt-% to about 85 wt-%. After draining, the bog surface can support machinery for leveling and removing trees and stumps. Due to the large amount of surface disturbance involved in harvesting peat, there is significant impact on local plant and wildlife habitats, both aquatic and terrestrial. The ecology of a peat bog is especially delicate, and in some places may be considered protected wetlands (6).

Acidic qualities of the water in a peat bog may be toxic to downstream wildlife unless sufficiently diluted. This contamination could happen during preliminary bog drainage, especially if the effluents from dewatering procedures were released untreated into other bodies of water. Other pollution could occur from the concentrations of heavy metals in peat, which are at levels comparable to those in coal.

Although peat can be burned in the same manner as coal, it also has many of the problems that are

associated with the burning of coal. Some of these problems are fly ash pollution, equipment abrasion, nitrogen and sulfur oxide emission, etc. Because of these problems, it is desirable to convert peat into a cleaner, more usable liquid or gaseous substance. A promising method of separating the organic portion of the peat from the mineral portion is supercritical fluid extraction. Most of the research in this area has been done on coal, but results seem to improve as the volatile matter content of the coal increases. Since peat has a higher volatile matter content than coal, this method may be feasible for use with peat also (7).

2. Supercritical Fluid Extraction

Supercritical fluid extraction (SCFE) is similar to both distillation and solvent extraction in principle, but takes place under conditions that make the two processes almost indistinguishable, at least from a physical standpoint. The dissolution of a substance by a stream of liquid is a form of solvent extraction, but the evaporation of a substance into a stream of gas is a kind of distillation. A fluid can exist as a liquid

below its critical temperature; however, above this temperature the fluid will be in the gaseous state regardless of the pressure. At temperatures below the critical point, a gas can be liquefied simply by increasing the pressure. However, at temperatures above the critical point, the fluid cannot be liquefied and is referred to as a "supercritical fluid". The pressure required to liquefy a gas at its critical temperature is called the critical pressure. At temperatures and pressures near the critical point, the division between the gaseous and liquid phases becomes indistinct, and the differentiation between distillation and liquid solvent extraction becomes very difficult.

The basic principle behind SCFE is the increase in the volatility of a substance that occurs in the presence of a compressed supercritical gas. Under some circumstances an increase in volatility of up to 10,000 times may occur (8). This effect disappears as the pressure is lowered which facilitates recovery and separation of the solvent and solute because the solute precipitates out of the solvent.

There are five basic steps involved in solvent extraction with a supercritical fluid (9). These are:

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.

Supercritical fluid extraction has many advantages over conventional extraction techniques (9). Some of these are:

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 (7).

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% compared to 4.9%) 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.

SCFE has many other possible applications than just extraction of solid fuels (10). Some of these are:

1. Extraction of food substances and flavors, for example, decaffeinating coffee or removing nicotine from tobacco could be accomplished using SCFE.

2. Waste materials can be treated using SCFE to recover valuable raw materials or to make liquid foods.

3. Waste water can be "extracted" to recover raw materials and reduce pollution. This is also applicable to the desalinization of sea water.

4. Supercritical fluids have much potential in the area of chromatography. They may provide higher yields and improved efficiency of separation than either liquids or gases at normal conditions.

5. SCFE may be used to remove spent products from catalyst pellets.

3. Solvent Behavior

Behavior of a solvent is determined by its ability to selectively interact with other compounds. These specific-interaction capabilities can be divided into three basic types: dipole, proton donor, and proton acceptor. The degree to which each of these capabilities affects a solvent's behavior can be expressed in terms of its fractional contribution, or solvent selectivity values. These are X_n (dipole contribution), X_e (proton acceptor contribution), and X_d (proton donor contribution). When these fractional contributions are plotted on a triangular diagram, it is seen that the solvents fall into eight selectivity groups, as shown in Figure 2. Also, solvents with the same functional groups tend to fall into the same selectivity groups, as shown in Table V. Because the degree of dipole or hydrogen bonding interactions which a solvent is capable of is determined by the functional groups in the solvent molecule, this verifies the classification scheme of Figure 2 (11).

B. Previous Research

Oil shale has been extracted using supercritical

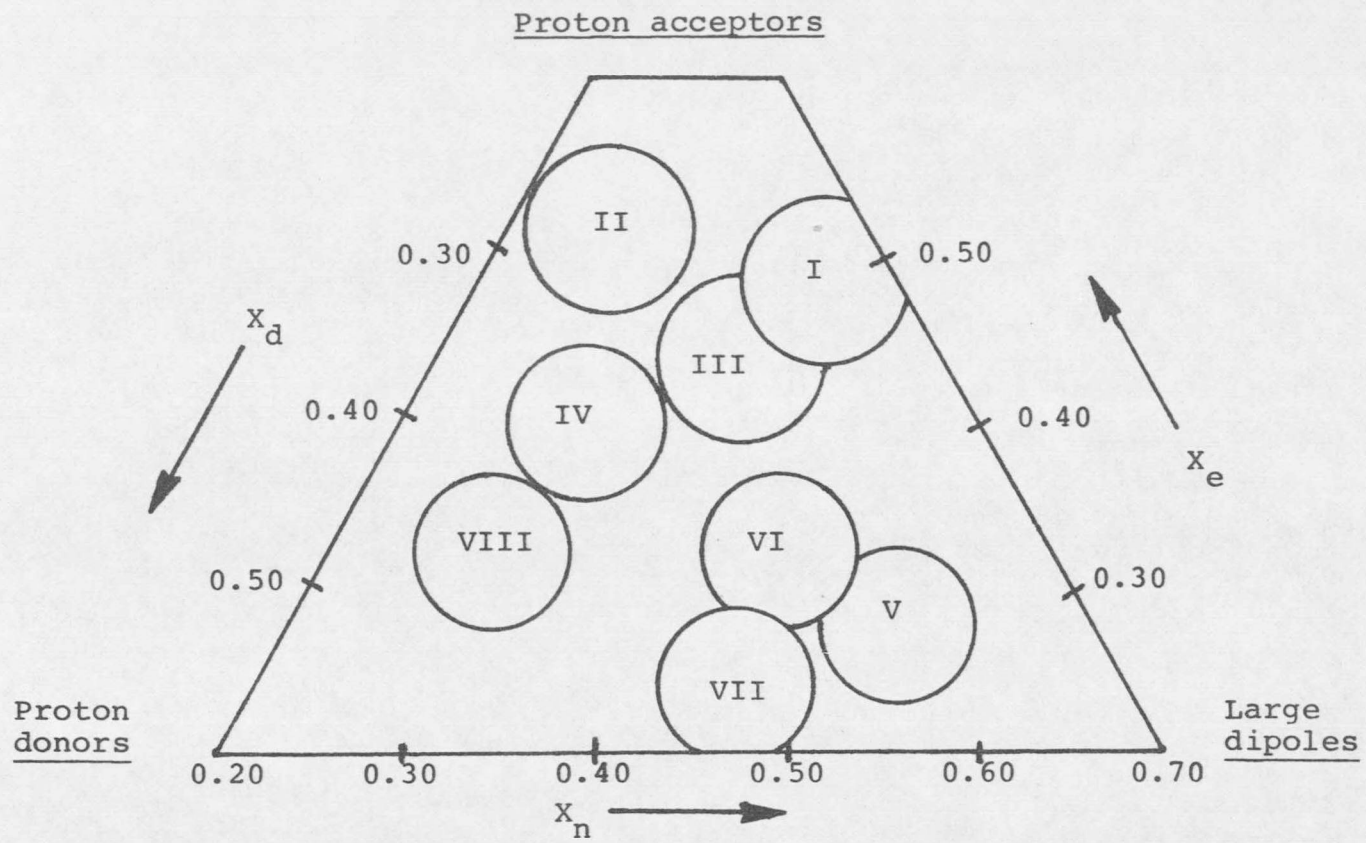

Figure 2. Grouping of pure solvents by selectivity (11).

Table V. Classification of solvent selectivity (11).

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

methylcyclohexane at 440 °C and 1500 psig (10,440 kPa) (12). The yield obtained was 16.4 wt-% of the dry shale, and only 8.0 wt-% of the original organic material remained after the extraction. Also, SCFE has been used to remove the organic components of tar sand from the mineral portion (12). The solvent was tetrahydrofuran at 310 °C and 1500 psig (10,440 kPa) and the yield was 9.3 wt-% of the sand.

Maddocks et. al. (13) performed extractions on the high-volatile, low sulfur coal found in the western U.S. (Wyodak coal), using toluene and para-cresol as solvents. Toluene has a critical temperature of 320.8 °C and a critical pressure of 611.5 psia (4,215 kPa); para-cresol has a critical temperature of 431.4 °C and a critical pressure of 746.8 psia (5,147 kPa). Temperatures were limited to a small range near the critical point of the solvent.

The results obtained with supercritical toluene were a yield of 21.2 wt-% of the dry coal, with 5.8 wt-% of the coal being converted to gas and 3.3 wt-% to water. Over 99% of the toluene solvent was recovered. Significant hydrogen sulfide was present in the gas, indicating

that SCFE may be useful with high sulfur coals. The extract had a lower sulfur content than the feed coal (0.15 wt-% as compared to 0.35 wt-%), a much higher hydrogen content, and contained very little mineral matter.

The para-cresol runs yielded much better results. The average extract yield was 34.2 wt-% and the average char yield was 69.7 wt-%. Because this is greater than 100% of the dry coal, it was suggested that the solvent reacted with the coal or decomposed to produce material collected as extract. This view is supported by the fact that heat was generated during the extraction.

Other runs using a mixture of 90% para-cresol and 10% water increased extract yields greatly, to about 64.8 wt-%. Of this, approximately 40% was actual extract and the remaining 25% was extract-like material produced from decomposition of the solvent and possible reaction with the coal. This material was difficult to distinguish and separate from the actual extract.

Coal moisture content had little effect on the extract yield. To facilitate handling and reduce the heat

load on the apparatus, air-drying seems to be indicated.

The chemical structure of two extractions prepared by supercritical extraction of low rank coals were studied by Bartle et. al. (14). One extraction, done in the absence of hydrogen, gave a yield of 27.0 wt-% of the coal and contained aromatic structures linked by ring-joining methylene or heterocyclic groups. The other extraction was done in the presence of hydrogen and a catalyst. A yield of 47.5 wt-% was obtained and the product was more condensed and contained smaller molecules, apparently from cleavage of heterocyclic groups in the coal.

II. RESEARCH OBJECTIVE

The purpose of this investigation was to determine the feasibility of supercritical fluid extraction as a means of separating the organic portion of peat from the undesirable mineral portion. Solvents utilized were water, methyl alcohol (CH_3OH), and acetone (CH_3COCH_3). This choice of solvents provided a fairly wide range of properties such as critical temperature and pressure, hydrogen bonding ability, and proton donating or accepting ability. The range of temperatures and pressures investigated for each solvent was as wide as possible, within the limits of the equipment and the limits imposed by the physical behavior of the solvent itself.

III. MATERIALS, EQUIPMENT, AND PROCEDURE

A. Materials

All peat used in this project was standard agricultural peat, as received. The moisture content of this peat was between 59.0 and 61.0 wt-%, and the ash content was between 5.9 and 8.9 wt-%. All solvents were technical grade, except water, which was distilled.

B. Pre-run Preparation and Reaction Apparatus

All results, yields, and conversions reported in this thesis are based on a moisture- and ash-free mass of peat, usually 25 grams. So, the moisture and ash contents of the peat were required before anything else could be done. To determine the composition of the peat, several 10 gram samples were placed in a drying oven at approximately 110 ^{o}C until completely dry. To be sure of complete dryness, the samples were removed from the oven at 30 minute intervals, weighed, stirred carefully, and replaced in the oven. When two successive weighings were the same (2-3 hours), the weight was recorded and the percent loss was taken as the moisture content of the peat. The dried samples were then placed in an ignition oven at about

700 ^{o}C for at least 12 hours to drive off everything except the ash. The amount of ash remaining was then compared to the initial sample amount to determine the ash content of the peat. All measurements were accurate to ± 0.005 grams, which represents an error of well under 0.1% in all cases. The moisture and ash analyses were repeated periodically to guard aginst radical changes in composition due to drying of the peat. Because the peat was stored in an airtight container, the moisture content did not vary by more than one percent between analyses.

Once the composition of the peat was known, the amount of actual peat required to obtain 25 grams of moisture- and ash-free (MAF) peat could be found. This was calculated by

$$\text{Actual peat} = (25\text{g MAF}) \times \frac{(\text{Actual peat})}{(\text{g MAF peat})}$$

where the fraction in the second term is found by

$$\frac{(\text{Actual peat})}{(\text{g MAF peat})} = \frac{100}{100 - (\%\ \text{moisture}) - (\%\ \text{ash})}$$

Once this calculation had been made, the amount of ash which should be present in this quantity of actual peat could be found. Because the ash should go through all

extractions unchanged, an indication of the reliability of the results can be obtained by comparing the amount of ash actually present after the run with the predicted amount. The percent difference was found by

$$\% \text{ Difference} = \frac{(\text{Actual ash}) - (\text{Predicted ash})}{(\text{Actual ash})} \times 100\%.$$

The basic reaction apparatus consisted of a Parr Instrument Company Series 4000 Pressure Reaction Apparatus, and is shown in Figure 3. The apparatus includes a 500 milliliter bomb constructed of Inconel 757-S alloy, which has a pressure rating of 7000 psia at 500 ^{o}C, and a rocking resistance heater which has a power rating of 2250 watts. The power input to the heater was controlled by a Powerstat variable transformer, and the voltage and amperage output of the Powerstat was monitored to prevent equipment damage. Initially, the temperature of the bomb was monitored by an iron-constantan (J-type) thermocouple and was recorded on a Honeywell temperature recorder. However, when difficulties developed with the recorder, use of a Cole-Parmer Digi-

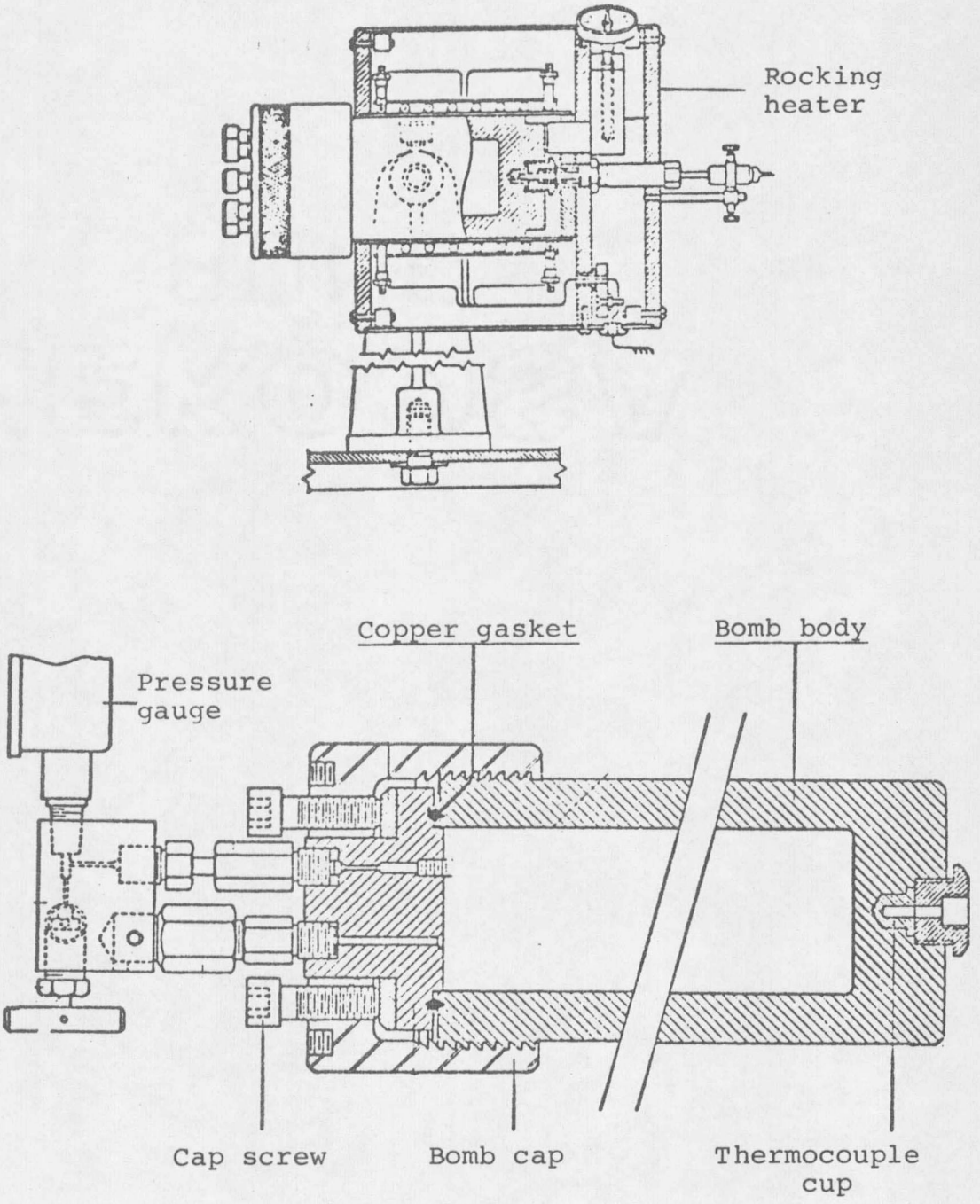

Figure 3. Bomb and rocking heater details.

Sense digital thermocouple thermometer was initiated, with a chromel-alumel (K-type) thermocouple. This occurred about Run #25, so in earlier runs the temperature was measured to within 2 ^{o}C, and in later runs to within 1 ^{o}C. This is a maximum error of 1%. The Powerstat was sensitive enough to prevent temperature fluctuations of more than 5 ^{o}C.

C. Run Procedure--Loading of the Bomb, Run Conditions, and Actual Run

After the amount of actual peat required to obtain 25 grams of MAF peat was determined, this quantity was placed in a dried, tared, alundum Soxhlet extraction thimble. This allowed the solvent to freely contact the peat while simultaneously containing the substrate. This reduced spillage losses, facilitated separation of the liquid product from the solid char, and greatly simplified cleaning of the bomb. The thimble was then placed in a stainless steel rack, shown in Figure 4, and placed in the bomb. Also placed in the bomb was a sufficient amount of solvent to give the desired pressure at the temperature under consideration. With water as the solvent, the amount required was calculated using van der

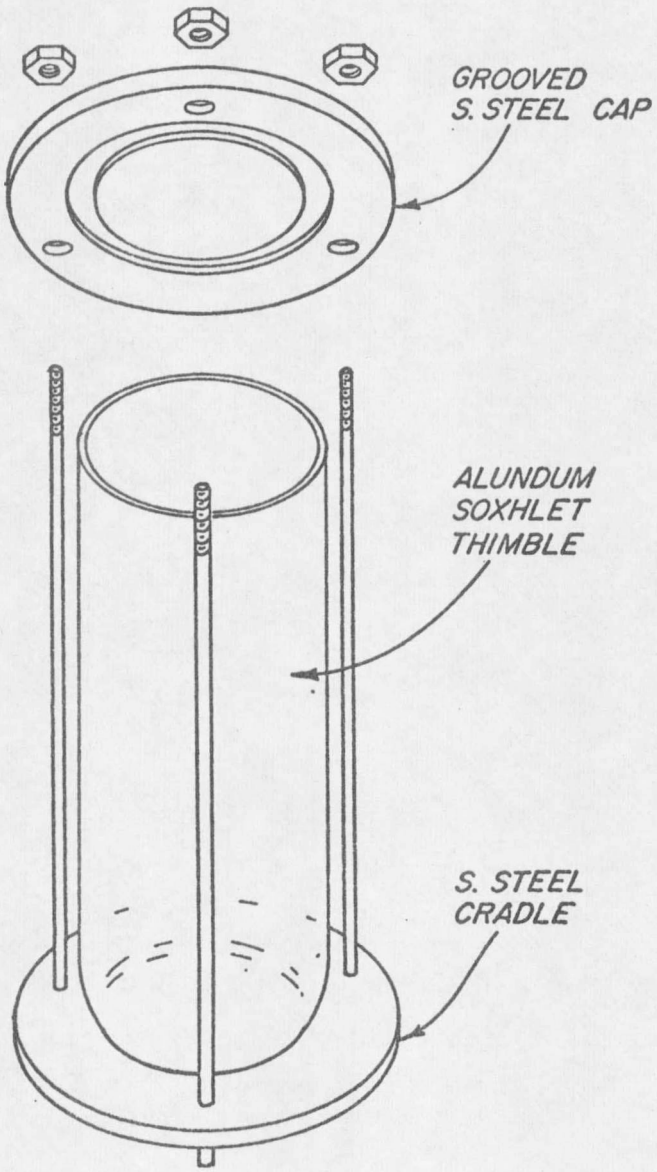

Figure 4. Soxhlet thimble and rack assembly details.

Waal's equation of state (15), and the pressure was predicted quite well. However, with either methanol or acetone as the solvent this equation gave very poor results, and the amount of solvent needed was determined by trial and error. See Appendix D for data on amount charged for given conditions. The bomb cap was then screwed on and the cap bolts were tightened with a torque wrench to assure an even pressure distribution on the copper gasket. With a new gasket, the torque applied to the cap bolts was about 50 ft-lb_f. The torque was increased by 2-3 ft-lb_f per run, until a maximum of 110 ft-lb_f was reached, and the gasket was then replaced. The bomb was then placed in the rocking heating jacket and the power to the resistance heater turned on. An upper limit was placed on the power input to the heater of about 1600 watts to prevent damage to the heater or to the wiring of the apparatus. This corresponds to a setting of about 75% on the Powerstat, or about 15 amperes and 110 volts AC. The rocker motor was then started and the temperature was brought up to the desired value. When the temperature reached this value, a short period of time was allowed to elapse (usually about 10 minutes) to enable the

pressure to stabilize before any readings were taken. The temperature and pressure were then recorded at 10-minute intervals for a period of one hour. The power and the rocker were then turned off and the bomb was allowed to cool overnight. The following day the bomb was opened, the liquid contents were placed in a tared beaker, and the solvent was allowed to evaporate from both the thimble and the beaker in a hood.

D. Recovery of Liquid Product

Product was considered to be any portion of the contents of the bomb after a run which was soluble in tetrahydrofuran (THF), which is an excellent organic solvent. The remaining bomb contents were either an insoluble organic char, ash, or solvent from the run. Separation of the product from the char was accomplished using the Soxhlet extraction apparatus shown in Figure 5, with THF as the working solvent. The alundum thimble was placed inside the apparatus, and a quantity of THF was placed in the still pot and heated to boiling. Enough THF must be in the still pot to insure that it will not boil to dryness and burn any product which is in the

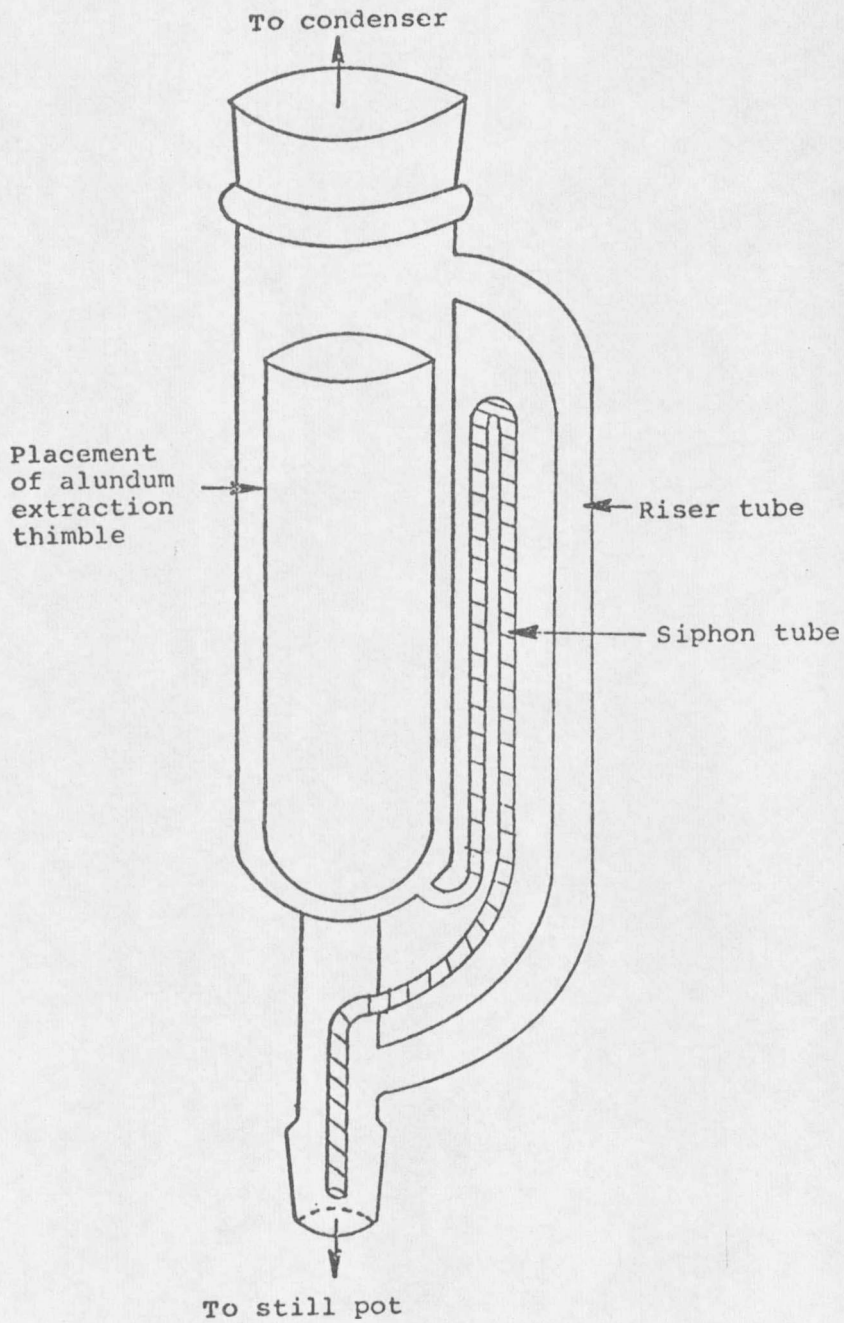

Figure 5. Soxhlet extraction apparatus.

still pot. As the THF boils, vapor proceeds up the riser tube to the condenser, where it reliquefies and drips into the thimble. The THF dissolves part of the product in the thimble and carries it out through the pores. When the level of the THF-product mixture rises above the top bend of the siphon tube, the thimble chamber empties its entire liquid contents back into the still pot, where the THF is heated back to boiling. This cycle is allowed to repeat until no more product is dissolved and the THF in the thimble chamber is clear when viewed through the siphon tube, usually 24 to 48 hours. The thimble is then removed from the apparatus and allowed to air-dry in a hood. The thimble is then placed in an oven at about 110 ^{o}C to dry completely. Conversion was taken as the amount of MAF peat which was not present in the thimble as char. After the thimble and contents were dry, they were weighed and the conversion was calculated by

$$\% \text{ Conversion} = \frac{(\text{Initial MAF Peat}) - (\text{Net Contents of Thimble}) - (\text{Predicted Ash})}{(\text{Initial MAF Peat})}$$

The liquid THF-product solution was placed in the same

beaker as the liquid contents of the bomb, and the THF was allowed to evaporate in a hood. The yield was taken to be the percentage of the initial MAF peat which was present as product, and was calculated by

$$\% \text{ Yield} = \frac{(\text{Net Product in Beaker})}{(\text{Initial MAF Peat})} \times 100\%.$$

The ash content was found by placing the contents of the thimble in tared crucibles and then into an oven at about 700 ^{o}C overnight. The ash balance was calculated as described previously.

E. Cleaning of Thimbles

The alundum extraction thimbles required cleaning after every run, or the pores became clogged very rapidly. When this happened, the THF would not seep through the pores and the thimble would fill up to the top. The THF would then spill over the top of the thimble, carrying char particles with it into the still pot. This gave erroneously high yields and poor results. Thimbles were cleaned by the following procedure:

1. The thimble was thoroughly scrubbed with a strong detergent to remove any superficial residue, and was allowed to dry.
2. The thimble was then placed in a bath of

concentrated hydrochloric acid and allowed to soak for 1-2 hours to dissolve or loosen any residue in the pores, and placed in a hood to dry.

3. The thimble was finally placed in an ignition oven at about 700 °C for 3-4 hours to burn off any remaining carbon.

This cleaning procedure was found in the Van Waters and Rogers Scientific Equipment catalog. Any concentrated acid will work, but hydrochloric acid was found to be the easiest to use.

F. Hot Removal of Solvent

At the outset of this investigation, the feasibility and usefulness of removing the solvent gas from the bomb while the gas was still hot and under pressure was examined. This was done with water as the SCFE solvent; two runs were made removing the gas while still hot and two runs were made opening the bomb after it was allowed to cool. When the gas was removed hot, the solvent gas was passed through two ice-water cold traps in succession to insure that all the solvent and product was condensed out and none was lost to the air. The only difference observed between the two methods was that when the solvent was removed while still hot a large proportion of the

product was taken off along with it, so less product remained in the thimble. This reduced the time required in the Soxhlet apparatus, but this was the only advantage. The hot gas removal procedure was abandoned as not being worth the effort.

IV. RESULTS AND DISCUSSION

In all, 72 runs were made for the purpose of collecting data. Of these, 59 were deemed successful and were included in the statistical analysis. Appendix C contains a complete tabulation of all successful runs, along with a list of the unsuccessful runs and the reasons for their rejection. Of the 59 successful runs, 9 used H_2O as the SCFE solvent, 19 used methyl alcohol, 25 used acetone, and 6 used H_2O under an atmosphere of 500 psig of hydrogen gas. The three solvents gave a wide range of physical characteristics such as critical temperature, pressure, and solvent selectivity values, as is shown in Table VI. The runs made under a hydrogen atmosphere were made to determine if the presence of a reducing atmosphere would have any effect on the yield.

A. Mass Balance.

In most cases, the conversion obtained was in the range of 65-80 wt-% of the initial MAF peat, while the yields obtained were usually 15-40 wt-%. This indicates that up to 60 wt-% of the original peat was removed from the char but is not present in the product. Run #11 was made for the purpose of an overall mass balance to try to

Table VI. Physical properties and range of variables for solvents.

Solvent*	Critical pressure (psig)	Critical temperature (°C)	Solvent selectivity values (16)**			Range of variables	
			X_n	X_d	X_e	Temp (°C)	Pressure (psig)
Water	3200	375	0.25	0.37	0.37	400 only	3000 to 4500
Methyl alcohol	1180	240	0.31	0.22	0.48	270 to 350	1000 to 3000
Acetone	690	235	0.42	0.23	0.35	250 to 430	750 to 4800

* Using the classification system given in Snyder (11) and discussed in the Introduction section of this thesis, water is a Group VIII solvent, methyl alcohol is a Group II solvent, and acetone is a Group VI solvent.

** X_n is a measure of the dipolarity of a solvent, X_d is a measure of a solvent's proton donating ability, and X_e is a measure of a solvent's proton accepting ability. Water, methyl alcohol, and acetone have dipole moments of about 1.85, 1.70, and 2.88 debyes.

determine if this amount was actually being lost, or if it was being converted to another substance which was not being collected as product. The bomb was charged with 50 grams of actual peat and 50 grams of water and the run was made as usual. The operating temperature was 400 ^{o}C and the operating pressure was 3300 psig. The gas released upon opening the bomb was measured with a wet-test meter and included in the balance under the assumption that it was pure carbon dioxide with a molecular weight of 44 grams per mole. Also included in the balance was a small amount of liquid which condensed in the tubing which led to the wet-test meter and was assumed to be pure water. The contents of the bomb were

93.3 grams of solid and liquid in the bomb,

3.4 grams (0.08 ft^3) of gas through wet-test meter,

and 1.5 grams of liquid in tubing (estimated).

This accounts for approximately 98.2% of the initial mass, so the discrepancy is probably due to the conversion of a large portion of the peat into either,

1. light, volatile hydrocarbons which were lost in the soxhlet extraction step,
2. gaseous products which were not collected,

3. products which were soluble in the SCFE solvent and were not separated from it, or

4. water.

Very little quantitative analysis was done to determine which of these, (if any), contained most of the "lost" organic material. However, a few qualitative observations can be made. A mass-spectrographic analysis of the gaseous contents of the bomb showed that the gas was almost entirely carbon dioxide (about 12 wt-% of the MAF peat), with traces of water and methane. While the liquid phase produced in a water-based run appeared clear when first removed from the bomb and filtered, dark solid particles appeared after about a week. An attempt was made to obtain an analysis of the total organic carbon content of this liquid, but circumstances precluded this. The loss of light hydrocarbons is indicated by a solvent balance performed on Run #65. The run was made with 130 grams of acetone as the SCFE solvent. The contents of the bomb were weighed immediately after they were removed from the bomb and were then allowed to dry in a hood. The weight loss from drying was 137 grams, which is greater than the 130 grams of solvent charged, so some of the product may have been lost in the drying

step of the analysis. More investigation is required to discover the source of this discrepancy and to find a way of reducing or eliminating it. It should be noted that for runs using acetone as the SCFE at an operating temperature of 250 ^{o}C the conversion is within 5.0 wt-% (of the initial mass) of the yield. This means that very little of the original MAF peat removed from the char was not collected as product. This seems to happen due to a combination of the relatively low temperature and the high polarity of the solvent. This is indicated by the fact that either raising the temperature or changing the solvent to methyl alcohol causes the difference between the conversion and the yield to increase greatly. Determining the nature of this interaction could be an important objective of future research.

B. Research Variables and Experimental Design.

The variables investigated in the course of this research were temperature, pressure, and physical properties of the solvent. The range of values investigated is given at the beginning of this section in Table VI. Initially, a factorial statistical experimental design was used in which various combinations of different values of the

variables are investigated. This would give data points at high temperature and high pressure, high temperature and low pressure, and so on, for each solvent. However, due to difficulties encountered in controlling the pressure, this approach was abandoned. Instead, runs were made at a given temperature and a wide variety of pressures. The pressures usually had a lower limit of the critical pressure of the solvent and an imposed upper limit of about 4500 psig. Then the temperature was changed and a range of pressures would be investigated again. The temperature levels varied from a lower limit of the critical temperature of the solvent to an upper limit of about 430 ^{o}C. The entire process was then repeated with a new solvent. The results were analyzed using standard linear regression techniques and yield-pressure isotherms were plotted.

C. Method of Analysis of Data.

The data was analyzed by using a multiple regression computer program (MREGRESS) from the program library of the Statistics Department of Montana State University (MSUSTAT). This program is very convenient and easy to use and is highly recommended. Due to the limited

number of different temperature levels investigated, a completely bivariate analysis was not employed, but indicator variables were utilized to distinguish between the different temperature levels. In order to find a linear equation that reasonably approximates the data, the method of least squares was used to test the following models:

1. For water-based runs

$$Y_{H_2O} = A_o + A_1 P \ ,$$

2. For water-hydrogen-based runs

$$Y_{H_2O\text{-}H_2} = B_o + B_1 P \ ,$$

3. Methyl alcohol-based runs

$$Y_{MeOH} = C_0 + C_1 P + C_2 D + C_3 PD \ ,$$

4. Acetone-based runs

$$Y_{acetone} = G_o + G_1 P + G_2 D_1 + G_3 D_2 + G_4 D_1 P + G_5 D_2 P \ ,$$

where P is the operating pressure,
D_i are temperature indicator variables,
A_i, B_i , C_i, and G_i are constants.

The water- and water-hydrogen-based runs had only one temperature level, so no temperature indicator variables appear in the model. Similarly, the methyl alcohol-based

runs had only two temperature levels, so only a single indicator variable is in the model. Acetone, however, had three different temperature levels so the model for acetone has two different indicator variables. The terms involving the product of the operating pressure and an indicator variable are included to account for possible interactions between operating temperature and pressure. The method of least squares selects the "best" equation to describe the data by minimizing the sum of the squares of the deviations of the actual observed values from the values projected by the model. This method is explained in more detail in Appendix A. The equations so obtained involve all possible combinations of the independent variables.

The next step in the analysis was to determine if the complete set of variables given above was the "best" set to describe the data, or if any of the variables could be eliminated from the model. This was accomplished through the use of a backward elimination variable selection procedure. In this procedure, a variable is eliminated from the complete, or full model, and this reduced model is then analyzed using the method of least

squares. The two models were then compared to determine if the statistical significance of the model had been appreciably diminished by the elimination of the variable. The method of comparison is fully explained in Appendix B, and a sample calculation is given there also. The "best" models will simply be presented here and discussed one at a time.

D. Experimental Results.

1. Water-based runs.

Runs using water as the SCFE solvent were done at a single operating temperature of 400 ^{o}C due to the high critical temperature of water (T_c = 375 ^{o}C). The pressure was also restricted to a narrow range from about 3200 psig (P_c=3200) to about 4500 psig. Consequently, the only independent variable involved in this model is operating pressure. The "best" model obtained was

$$Y_{H_2O} = 58.13 - (0.0104)P.$$

This model has an F-value of F* = 18.48 and a coefficient of determination of r^2 = 0.725. The meaning of these statistics is discussed fully in Appendix B, but they indicate that this model is statistically significant and

approximates the data reasonably well. The model and the actual data are given in Figure 6. The yield is seen to decrease rapidly as the operating pressure increases.

2. Water-Hydrogen-based runs.

As in the water-based runs, pressure is the only independent variable involved in this model. The operating temperature was again 400 ^{o}C, and the pressure ranged from 3300 to 4500 psig. The data obtained were very erratic and not reproducible, and thus gave little or no useful data. The initial H_2 pressure was 500 psig. The "best" model and its related statistics were

$$Y_{H_2O-H_2} = 5.81 + (0.00533)P,$$

$$F^* = 1.59, \text{ and}$$

$$r^2 = 0.2755.$$

Though the yield is seen to increase with increasing pressure, the model is not statistically significant. More investigation is required to determine the effect of a reducing atmosphere on the yield. The model and data are shown in Figure 7.

3. Methyl alcohol-based runs.

Due to methyl alcohol's lower critical temperature (T_c = 240 ^{o}C), two temperature levels were investigated.

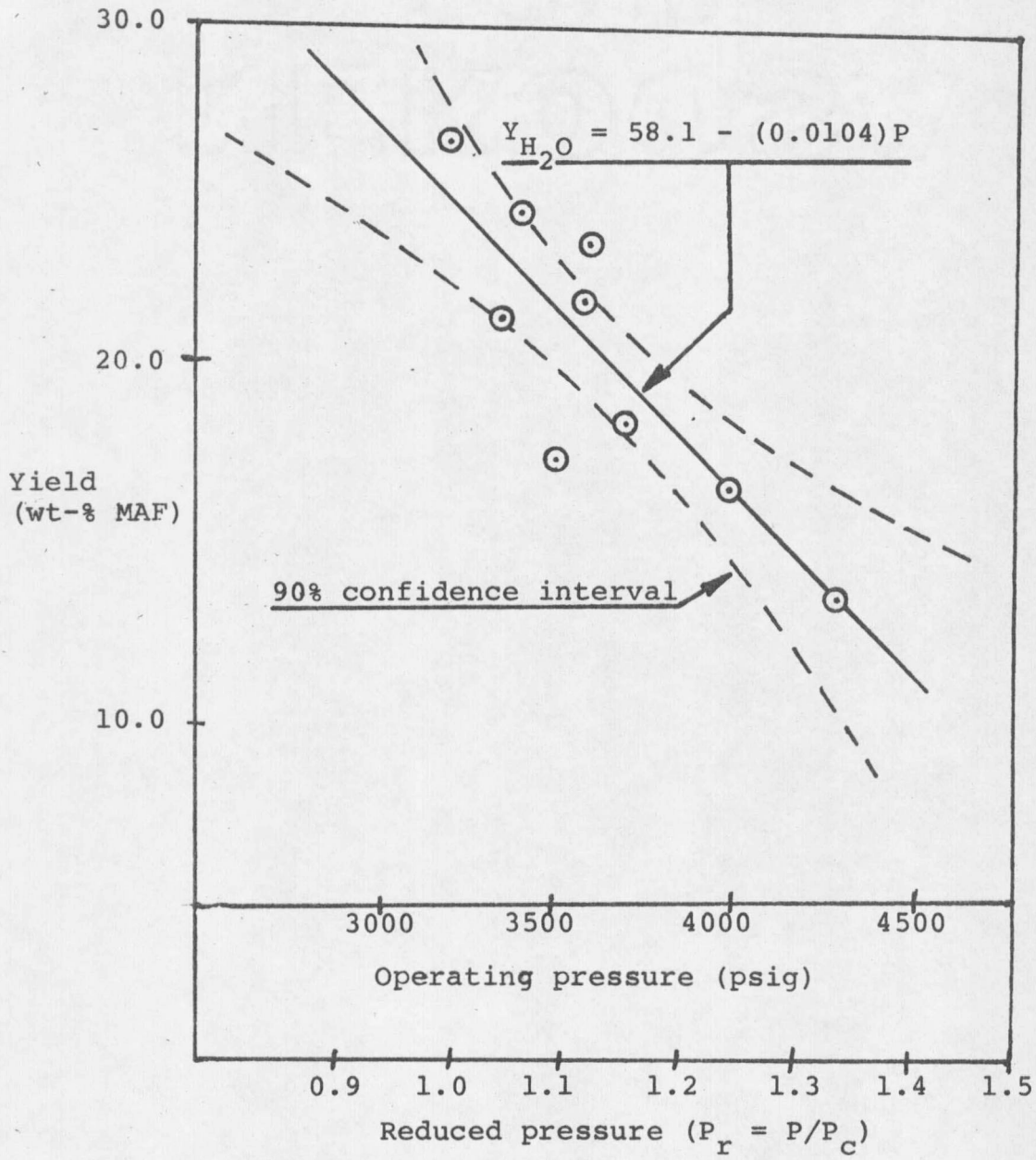

Figure 6. Yield as a function of operating pressure for runs using water as the SCFE solvent.

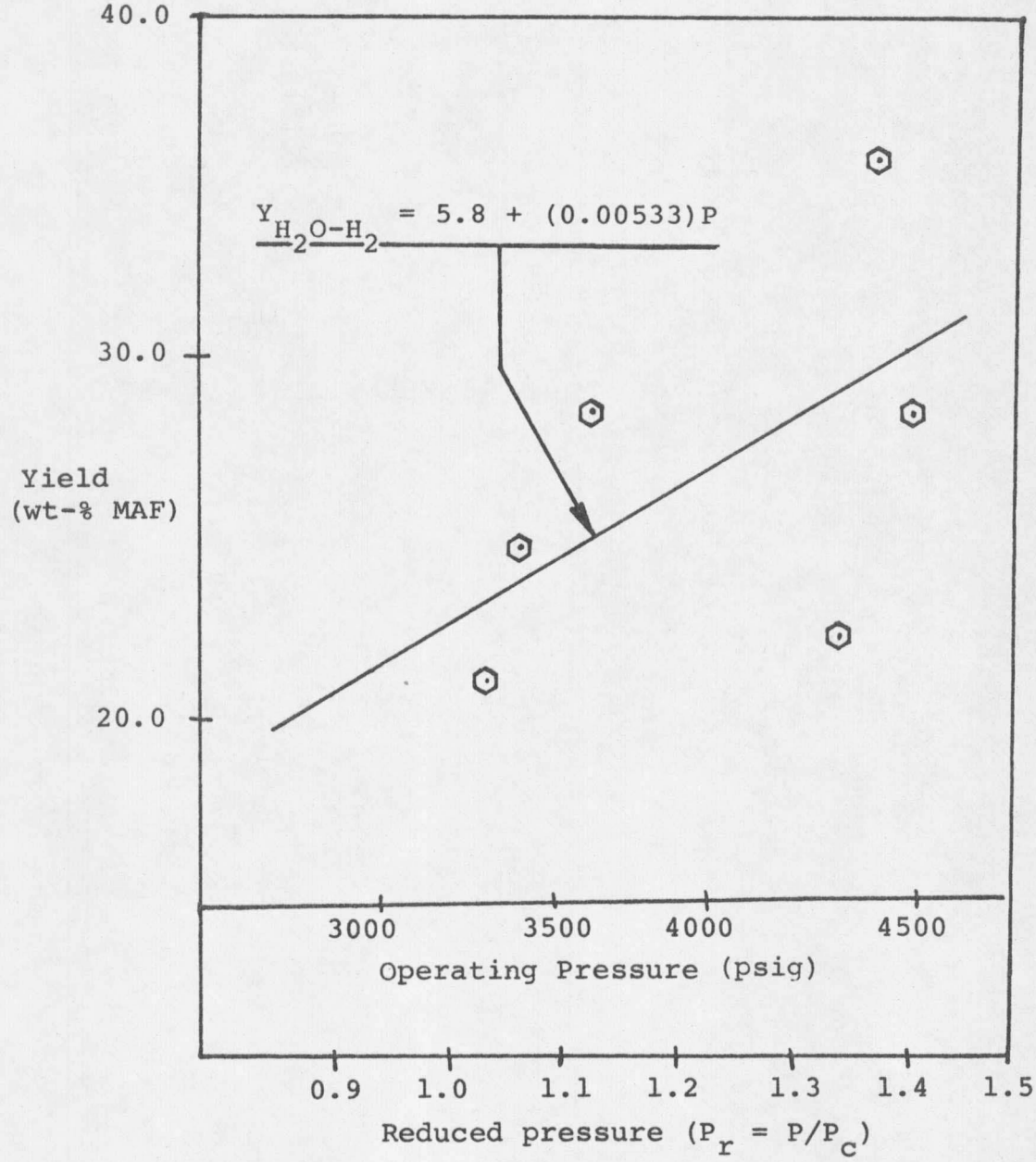

Figure 7. Yield as a function of operating pressure for runs using a water-hydrogen mixture as the SCFE solvent.

These temperatures were 270 and 350 ^{o}C. The critical pressure of methyl alcohol is also much lower than that of water (P_c = 1180 psig), so a wider range of pressures was investigated. The operating pressure varied from a value of 1000 psig up to a value of 3000 psig. Because of the two temperature levels utilized, an indicator variable was necessary. The indicator variable had a value of +1 for runs at an operating temperature of 270 ^{o}C and a value of -1 for runs at an operating temperature of 350 ^{o}C. The "best" model obtained and its pertinent statistics were

$$Y_{MeOH} = 33.59 - (0.00117)P + (0.000914)PD ,$$

$F^* = 6.11$, and

$r^2 = 0.441$.

This model and the data are shown in Figures 8 and 9. The data have a much higher degree of scatter than the H_2O data, as is shown by the lower value of r^2. However, the data still have some significance and yield some useful information. The yield decreases with increasing operating pressure for both temperature levels, although at the lower temperature of 270 ^{o}C the decrease was very slight.

4. Acetone-based runs

Acetone has a fairly low critical temperature and

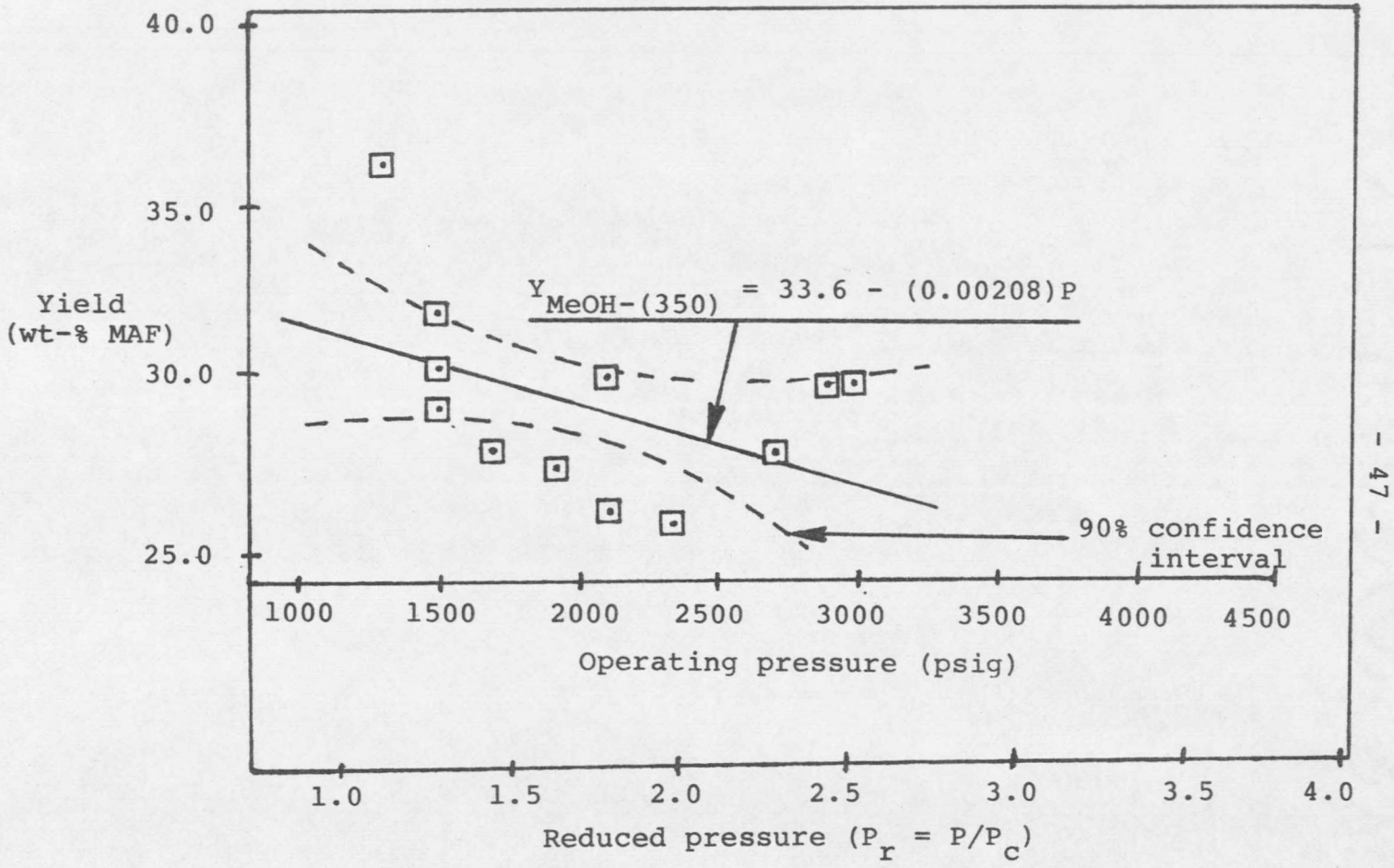

Figure 8. Yield as a function of operating pressure for runs using methyl alcohol as the SCFE solvent at an operating temperature of 350 °C.

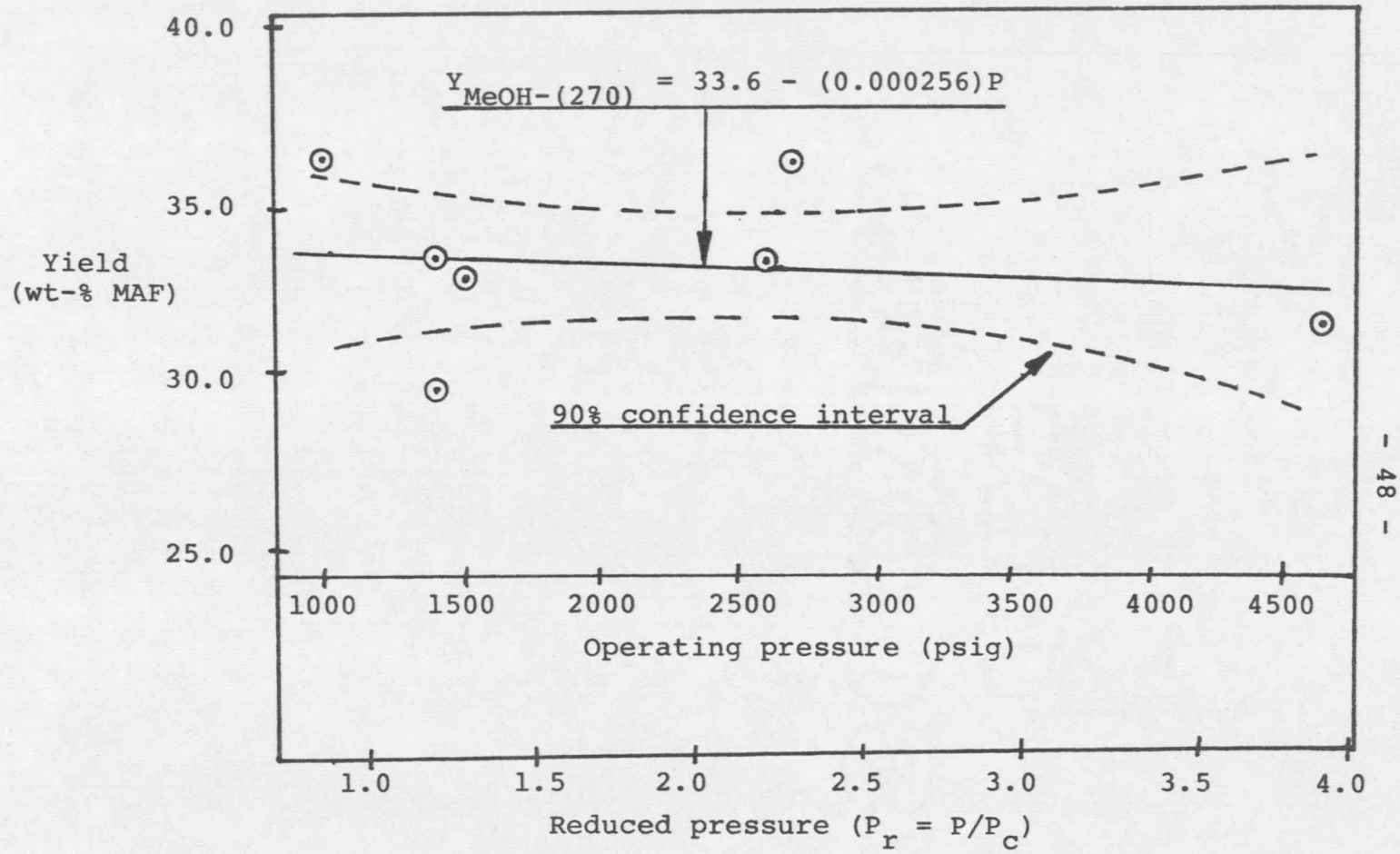

Figure 9. Yield as a function of operating pressure for runs using methyl alcohol as the SCFE solvent at an operating temperature of 270 ^{o}C.

critical pressure compared to water (T_c = 235 °C, P_c = 691 psig), so the range of variation of the independent variables was large. Three levels of temperature were utilized; 250, 340, and 430 °C, and the pressure varied over a range from 750 to 4800 psig. Due to the three levels of temperature, two indicator variables were required, and the values of these variables were set up as follows:

Temperature	D_1	D_2
250 °C	-1	-1
340 °C	+1	0
430 °C	0	+1

The "best" set of independent variables was found to be the complete set, because no terms could be eliminated from the model without impairing the statistical validity of the model. The "best" equation was found to be

$$Y_{acetone} = 17.28 + (0.00554)P + (3.165)D_1 - (33.85)D_2 + (0.000928)PD_1 + (0.00876)PD_2 ,$$

with $F^* = 39.31$ and $r^2 = 0.9119$. This model and the data are shown in Figures 10, 11, and 12. The high values of the F-statistic and the coefficient of determination show that the model is statistically significant and approxi-

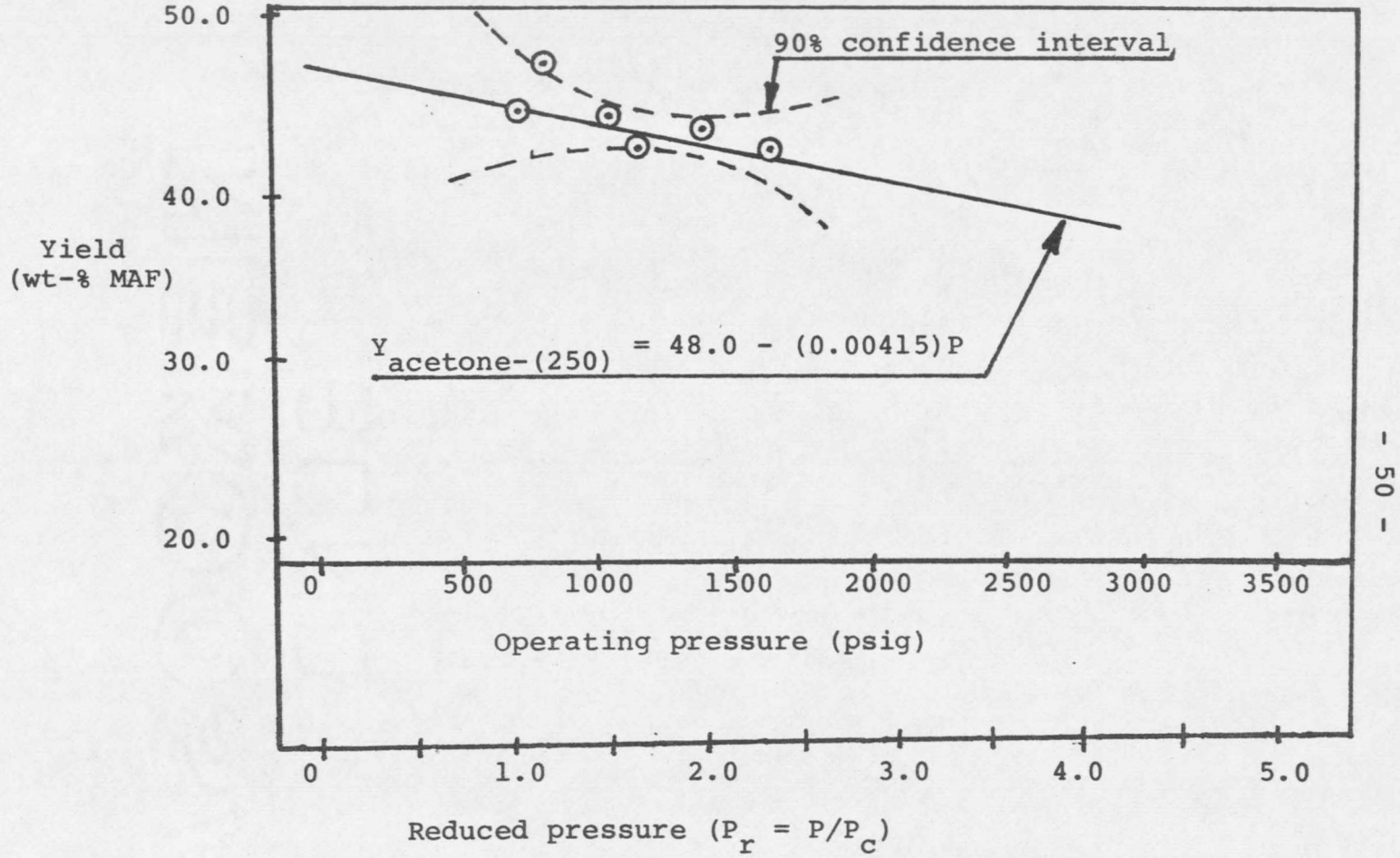

Figure 10. Yield as a function of operating pressure for runs using acetone as the SCFE solvent at an operating temperature of 250 °C.

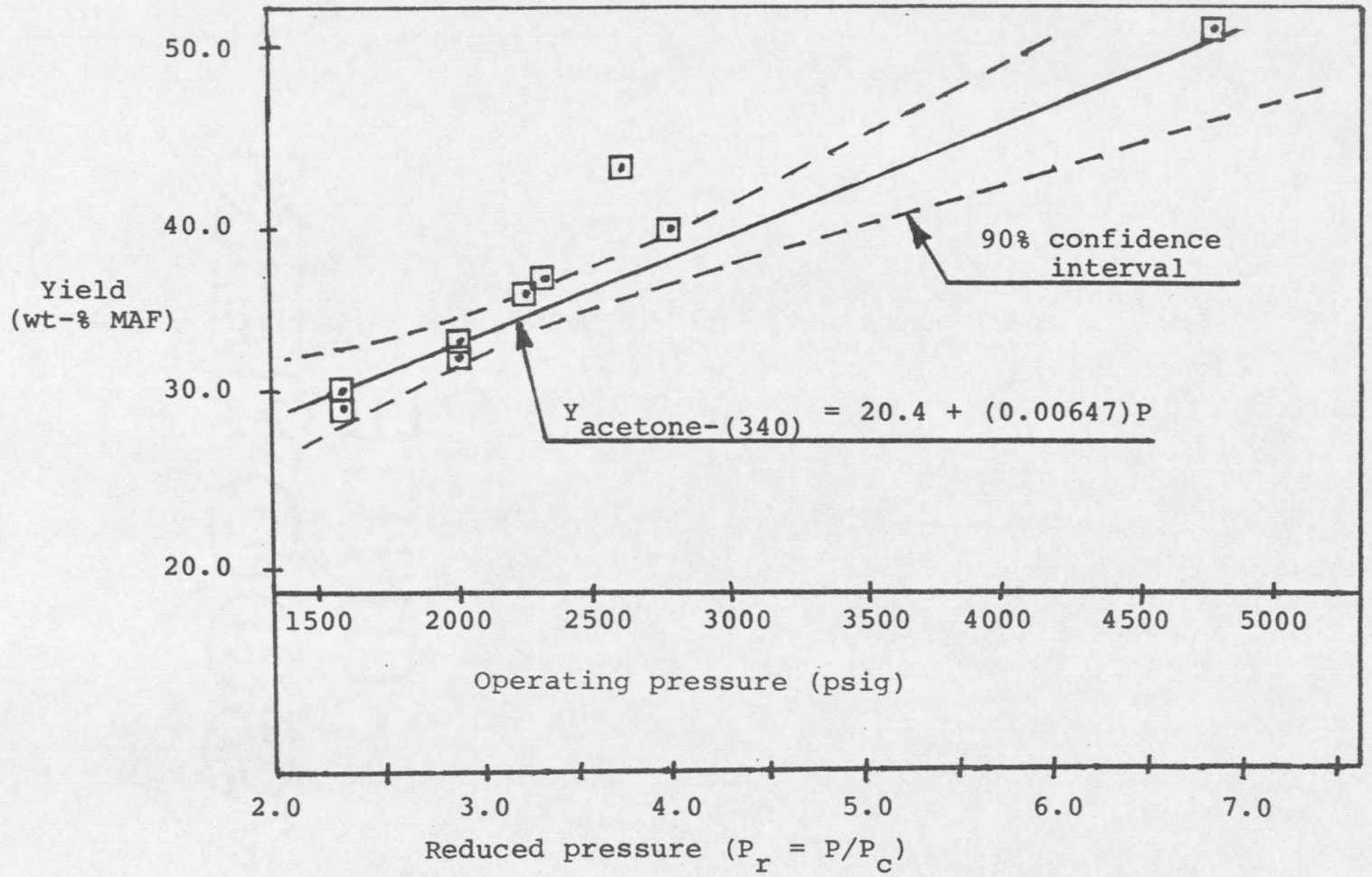

Figure 11. Yield as a function of operating pressure for runs using acetone as the SCFE solvent at an operating temperature of 340 °C.

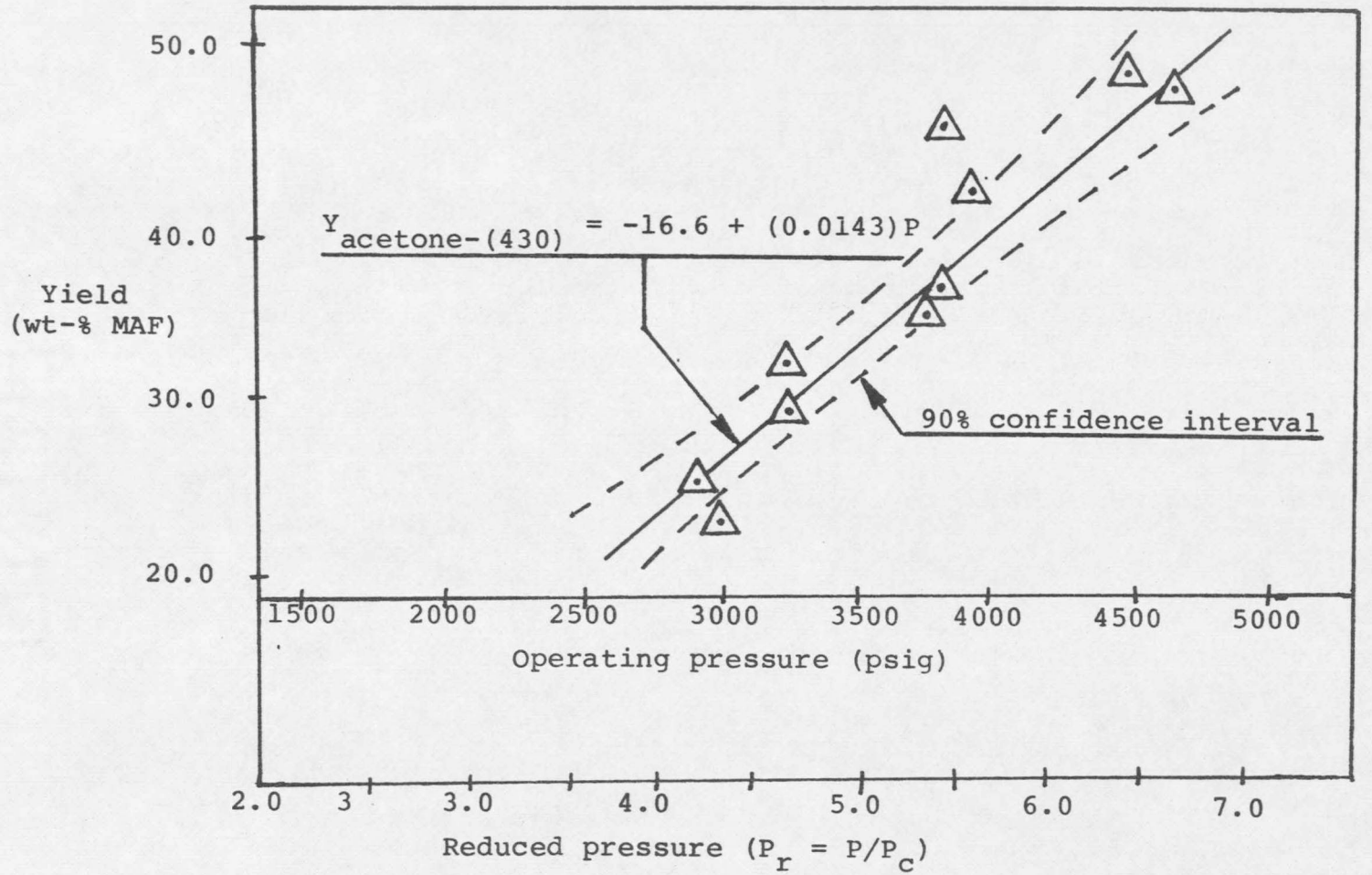

Figure 12. Yield as a function of operating pressure for runs using acetone as the SCFE solvent at an operating temperature of 430 °C.

mates the data very well. The slope of the model changes radically as the temperature increases. At the lower temperature of 250 ^{o}C, yield decreases gradually as the operating pressure is increased. However, at the intermediate temperature of 340 ^{o}C and the higher temperature of 430 ^{o}C the yield increases quite rapidly as the pressure is increased. This indicates a strong interaction between the operating temperature and the operating pressure with a strongly dipolar solvent. This could also indicate some type of a chemical reaction between the acetone and the peat, which does not occur at lower temperatures and pressures.

V. CONCLUSIONS

This investigation of the extraction of peat using supercritical fluids as solvents produced the following conclusions:

1. In most cases, best yields were obtained at conditions as close to the critical temperature and critical pressure of the solvent as possible.

2. Acetone produced the highest yields in this investigation, methyl alcohol gave intermediate yields, and water gave the lowest yields.

3. Introduction of a reducing hydrogen atmosphere into the bomb prior to a run increased the yield to a certain extent, but results were erratic and not reproducible.

4. Temperature and pressure interacted to change the slope of pressure-yield isotherms as the temperature was changed. All isotherms were well approximated by linear functions. This interaction caused the slope of the acetone isotherms to change radically from a small negative value at low temperature to a large positive value at higher temperatures. The effect on the methyl alcohol isotherms was minimal.

5. Yield decreased with increasing operating pressure in runs with either water or methyl alcohol as the solvent, and in runs with acetone as the solvent at the lowest temperature level. Yield increased with increasing operating pressure in runs using acetone as the solvent at the two higher temperature levels.

6. Highest yield was obtained with acetone as the solvent at very high pressures (about 4800 psig) and at the higher temperature levels.

7. A large amount of the initial moisture- and ash-free peat was removed from the char but not collected as product, except when using acetone at the lowest temperature level. This indicates that a significant portion of the MAF peat was "lost", or converted into a form which was not recovered.

8. Removal of the solvent while it was still at or near the operating temperature and pressure provided no appreciable benefits over cold removal.

VI. RECOMMENDATIONS FOR FUTURE STUDY

1. A semi-continuous operation of this process should be the next step in the investigation of SCFE of peat. This would facilitate the investigation of a wider range of variables and would approximate an industrial application more closely.

2. Because acetone yielded the best results during the course of this investigation, more experimentation with solvents of the strong dipole type would be useful for the purpose of identifying more effective or economical solvents.

3. Solvent recovery and recycle must be investigated in order to render this process economically feasible.

4. Partial fractionation of the product by stepwise depressurization should be studied. The ability to do this would greatly simplify utilization of the product.

APPENDICES

Appendix A. Method of Least Squares.

For simplicity, this method will be demonstrated for a linear function with only one independent variable. The function will be assumed to be of the form

$$Y_i = B_1 X_i + B_o \; ; \quad i = 1, 2, 3, \ldots , n,$$

where B_1 is the slope of the line and B_o is the y-intercept. The deviation of Y_i from its projected value at each point is given by

$$e_i = Y_i - B_1 X_i - B_0.$$

In the method of least squares, the sum of the squares of the n deviations is the function under consideration, which is denoted as Q, and is found by

$$Q = \sum e_i^2 = \sum (Y_i - B_1 X_i - B_o)^2.$$

The estimated values of B_1 and B_o which minimize the value of Q are denoted by b_1 and b_o, and are computed by

$$b_1 = \frac{\sum [(X_i - \bar{X})\ (Y_i - \bar{Y})]}{\sum (X_i - \bar{X})^2}$$

$$b_o = \bar{Y} - b_1 \bar{X} \quad ,$$

where $\bar{X}$ and $\bar{Y}$ are the mean values of X_i and Y_i (17). All summations are over the entire interval of i from i = 1 to i = n.

Appendix B. Backward elimination variable search procedure (17).

1. Definitions.

Before an explanation of this procedure can be undertaken, a number of definitions are required. These are given below.

a. The error sum of squares (SSE) is the sum of the squares of the differences between the actual value of the dependent variable and the value predicted by the model under consideration. In equation form, this is

$$SSE = \sum (Y_i - \hat{Y}_i)^2$$

where Y_i is the actual observed value of the ith occurrence,
$\hat{Y}_i$ is the predicted value of the ith occurrence, and
n is the number of actual data points.
If SSE = 0, all the data points lie exactly on the model line.

b. The error mean square (MSE) is the SSE divided by the number of degrees of freedom associated with the model. The number of degrees of freedom is found by subtracting the number of coefficients in the model from the number of observed data points, or

$$MSE = \frac{SSE}{n - c},$$

where c is the number of coefficients involved in the model under consideration.

c. The total sum of squares (SSTO) is the sum of the squares of the differences between the observed

value of the dependent variable and the average of all observed values, or

$$SSTO = \sum(Y_i - \bar{Y})^2$$

where $\bar{Y} = \frac{1}{n}\sum Y_i$.

This is the total variation of the dependent variable with no consideration of the independent variable. If the data are completely random, the line is horizontal through $\bar{Y}$, $\bar{Y} = \hat{Y}$, and SSTO = SSE.

d. The coefficient of determination (r^2) is the amount of reduction of total variation obtained through the use of the independent variable, and is found by

$$r^2 = 1 - \frac{SSE}{SSTO} .$$

If all the data lie exactly on the line, then SSE = 0 and $r^2 = 1$. However, if the data are randomly distributed then SSTO = SSE and $r^2 = 0$. Therefore, the closer r^2 is to unity, the more closely the data fits the model.

2. Test procedure.

The general test used to determine if a particular independent variable may be eliminated from the model without impairing the model's validity is essentially a test of two hypotheses:

C_1 is the hypothesis that the coefficient of the variable under consideration is equal to zero ($B_1=0$), and C_2 is the hypothesis that the coefficient of the variable is not equal to zero ($B_1 \neq 0$).

The full model is taken as the model with the independent variable under consideration included and will be denoted

by an F in parentheses (F). The reduced model will be taken as the model from which the independent variable under consideration has been eliminated and will be denoted by (R). Both models are fitted to the data using the method of least squares and the error sum of squares for each is determined, along with the error mean square for the full model. The actual test statistic utilized is an F-statistic and is found by

$$F^* = \frac{1}{MSE(F)} \frac{SSE(R) - SSE(F)}{df_R - df_F}$$

where df_R and df_F are the number of degrees of freedom associated with the reduced and full models, respectively.

The criterion for elimination of a variable was taken to be $F^* < 0.8$. If the F^* computed had a value less than 0.8, the variable being tested was dropped from the model, the reduced model became the full model for the next iteration, and the process was continued. The value of 0.8 for the criterion was chosen in a somewhat arbitrary manner after all variables had been tested. It was taken as a compromise value that was neither so lenient that any blatantly insignificant variables were included in the model, nor so rigorous that any variables of possible or

borderline significance were eliminated. This method will now be demonstrated, using the data given in the "Results and Discussion" section of this thesis for the runs using methyl alcohol as the SCFE solvent. The full model for the initial iteration was taken to be

$$Y(F)_{MeOH} = B_o + B_1P + B_2D + B_3PD ,$$

and the statistics obtained from the least squares analysis were

$$SSE(F) = 97.48$$

$$MSE(F) = 6.499$$

$$df_F = 15 .$$

The first variable to be tested was D, the temperature indicator variable. The hypotheses to be tested were

$$C_1: \ B_2 = 0$$

$$C_2: \ B_2 \neq 0 .$$

The reduced model and its pertinent statistics were

$$Y(R)_{MeOH} = B_o + B_1P + B_3PD$$

$$SSE(R) = 97.80$$

$$MSE(R) = 6.11 , \text{ and}$$

$$df_R = 16.$$

The F-statistic obtained from these data was found to be

$$F^* = \frac{97.80 - 97.48}{6.499} = 0.049 .$$

This value is much less than the criterion for elimination, 0.8, so hypothesis C_1 is assumed to be true ($B_2 = 0$). The term involving the temperature indicator variable in the initial model is eliminated and the reduced model above becomes the full model for the next iteration. The next term tested was the pressure-temperature interaction term, PD. The reduced model and its statistics were

$$Y(R) = B_o + B_1 P$$

$$SSE(R) = 170.4$$

$$df_R = 17$$

$$F^* = \frac{170.4 - 97.8}{6.11} = 11.9 .$$

Because this value is much greater than 0.8, elimination of this variable has a large effect on the validity of the model. Hypothesis C_2 ($B_3 \neq 0$) is assumed to be true, and the variable is retained in the model. This procedure is repeated until all terms of the model have been tested (see Table VII).

3. Significance of model.

In order to test the statistical significance of the "best" model, another F-statistic was employed. This

Table VII. Results of statistical test procedure.

Solvent used	Terms in full model	Term(s) tested*	F-value	Decision**
Methyl alcohol	P, D, PD	P	1.93	retain
	"	D	0.05	eliminate
	"	PD	0.90	retain
	P, PD	P	2.75	retain
	"	PD	11.91	retain
Acetone	P, D_1, D_2, PD_1, PD_2	D_1, D_2	50.13	retain
	"	PD_1, PD_2	18.53	retain
	"	P	19.12	retain

* The temperature indicator variables for the acetone runs were tested in pairs because both of them, taken together, constituted a single variable.

** The criterion for elimination of a term was chosen to be 0.8 due to the borderline values of two of the variables in the methyl alcohol runs. A value of 1.0 or 2.0 would have caused one or both of these terms to be eliminated from the model, but the model would only be improved slightly and some valuable information could have been lost. The lower value was therefore chosen in order to keep these two terms in the model without affecting any of the other terms. 1.0 is a value which is commonly employed in statistical analysis.

statistic is given by the equation

$$F^* = \frac{SSTO - SSE}{MSE} .$$

If the data is completely random, SSTO = SSE and $F^* = 0$. The greater the difference between SSTO and SSE the greater the amount of variation in the dependent variable that is accounted for by the model. Therefore, the larger the value of the F-statistic, the greater the statistical significance of the model.

4. Confidence interval.

The confidence intervals in Figures 6-12 were constructed in a point-by-point fashion. Predicted values for the dependent variable ($\hat{Y}_h$) are obtained from the appropriate model at several values of the independent variable(s). The confidence interval for each point is obtained through the use of the estimated standard deviation at each point $\left[S(\hat{Y}_h)\right]$ and a t-statistic. $S(\hat{Y}_h)$ is found by

$$S^2(\hat{Y}_h) = MSE \left[\frac{1}{n} + \frac{(X_h - \bar{X})^2}{(X_i - \bar{X})^2} \right]$$

where X_h is the chosen value of the independent variable, and
$\hat{Y}_h$ is the predicted value of the dependent variable at X_h.

Tables of t-statistics can be found in most introductory statistics texts. The t-statistic for a 90% confidence interval is evaluated at

$1 - \alpha = 0.95$, and

$\nu = n - c$

where ν is the number of degrees of freedom which are associated with the model,

n is the number of data points, and

c is the number of coefficients in the model.

The 90% confidence interval is then found by

$$\hat{Y}_h - t(0.95, n-c)S(\hat{Y}_h) \leq Y_h \leq \hat{Y}_h + t(0.95, n-c)S(\hat{Y}_h).$$

This means that there is 90% confidence that the actual value of the dependent variable is within a range around the predicted value defined by the product of the appropriate t-statistic and the estimated standard deviation of the predicted value.

Appendix C. Run data.

1. Data from runs utilized in statistical analysis, grouped by solvent.

Run number	Solvent used	Operating pressure (psig)	Operating temperature (°C)	Conversion (wt-%)	Yield (wt-%)	Ash balance (wt-%)
6	H_2O	3350	400	79.0	21.4	+0.2
7	"	4300	400	81.2	13.8	-6.5
9	"	3500	400	77.3	17.6	+1.2
12	"	3700	400	81.8	18.6	+5.0
15	"	4000	400	81.5	16.5	-1.2
38	"	3600	405	69.4	23.5	-3.2
43	"	3400	410	67.2	24.6	-2.6
44	"	3200	405	64.6	26.4	-3.9
45	"	3600	400	73.3	22.2	+1.8
14	MeOH	1500	265	70.0	32.7	+4.2
16	"	1400	265	74.4	33.1	-4.2

Appendix C. Run data (cont.).

1. Data from runs utilized in statistical analysis (cont.).

Run number	Solvent used	Operating pressure (psig)	Operating temperature (°C)	Conversion (wt-%)	Yield (wt-%)	Ash balance (wt-%)
18	MeOH	1400	270	68.8	29.2	+2.0
19	"	1000	265	48.1	36.4	+3.1
21	"	2650	270	70.9	32.9	+3.9
22	"	4600	270	72.5	31.4	+2.2
23	"	2700	275	69.4	36.0	+6.5
24	"	3000	350	72.7	29.3	+2.7
25	"	2900	355	72.5	29.3	+1.8
26	"	2700	350	72.6	27.9	-1.9
28	"	1900	350	71.7	27.5	+1.8
29	"	2300	350	69.3	26.6	-0.2
30	"	2100	350	68.8	26.9	+0.2
31	"	2100	350	70.6	29.8	-5.9

Appendix C. Run data (cont.).

1. Data from runs utilized in statistical analysis (cont.).

Run number	Solvent used	Operating pressure (psig)	Operating temperature (°C)	Conversion (wt-%)	Yield (wt-%)	Ash balance (wt-%)
32	MeOH	1700	345	67.5	27.8	+16.2
33	"	1500	350	60.6	28.8	-1.4
34	"	1500	345	63.8	29.8	-0.7
35	"	1400	350	59.8	36.1	-5.7
36	"	1500	350	62.3	31.7	-2.6
39	H_2O-H_2	3600	410	68.8	28.4	-3.8
40	"	3300	405	58.1	21.0	+2.4
41	"	4300	405	78.0	22.2	-1.8
42	"	4400	400	76.2	35.8	+0.6
46	"	3400	400	60.8	24.4	+1.6
47	"	4500	400	77.7	28.4	+3.3

Appendix C. Run data (cont.).

1. Data from runs utilized in statistical analysis (cont.).

Run number	Solvent used	Operating pressure (psig)	Operating temperature (°C)	Conversion (wt-%)	Yield (wt-%)	Ash balance (wt-%)
48	acetone	800	255	49.3	46.6	+2.7
49	"	1100	250	45.4	43.0	-2.4
50	"	1600	250	43.3	41.8	-3.5
51	"	750	255	48.7	44.0	+1.8
52	"	1150	250	46.1	41.6	-1.8
53	"	1400	255	46.7	42.6	+2.9
54	"	3700	430	67.4	37.9	-1.2
55	"	3300	430	64.5	30.6	-2.6
56	"	3650	430	65.9	36.6	+1.0
57	"	3300	430	66.0	28.4	+0.8
58	"	2900	430	64.1	24.8	+0.6

Appendix C. Run data (cont.).

1. Data from runs utilized in statistical analysis (cont.).

Run number	Solvent used	Operating pressure (psig)	Operating temperature (°C)	Conversion (wt-%)	Yield (wt-%)	Ash balance (wt-%)
59	acetone	3000	430	63.2	22.8	-1.4
60	"	4000	430	70.8	42.1	+0.4
61	"	3900	430	68.8	45.8	+2.4
62	"	4600	430	72.6	48.7	-2.1
63	"	2000	340	61.0	33.1	-1.2
64	"	2800	340	64.3	40.1	-1.4
65	"	4800	430	73.6	47.8	-1.2
66	"	2300	340	63.4	35.4	+1.0
67	"	4800	340	57.7	49.6	+2.5
68	"	2000	340	53.4	31.8	-1.5
69	"	1600	340	62.0	29.1	-0.6

Appendix C. Run data (cont.).

1. Data from runs utilized in statistical analysis (cont.).

Run number	Solvent used	Operating pressure (psig)	Operating temperature (°C)	Conversion (wt-%)	Yield (wt-%)	Ash balance (wt-%)
70	acetone	2400	340	54.9	36.2	-0.8
71	"	2700	340	72.9	42.2	+1.4
72	"	1600	340	59.0	30.1	+1.1

Appendix C. Run data (cont.).

2. Runs not utilized in statistical analysis.

Of the 72 runs made for the purpose of producing data, 13 were deemed unsuccessful and were not included in the statistical analysis of the data. Four runs were unsuccessful due to equipment failure, and these are summarized below:

Run number	Reason for rejection
8	The pores of the soxhlet extraction thimble were clogged, causing it to overflow during the product recovery step. This caused a large amount of solid char to be carried out of the thimble with the actual product, giving erroneously high results.
10	Gas leaked from the bomb during the run due to a worn copper gasket, rendering the run invalid.
20	The temperature recorder malfunctioned during the run, and the run was aborted.
37	Gas leaked from the bomb during the run.

Runs #13 and 27 were rejected because the pressure remained well below the desired operating value when the desired operating temperature had been reached. Run #17

produced very singular results. Due to inattention on the part of the experimenter, the temperature of the apparatus was allowed to reach a value in excess of 350 ^{o}C instead of the desired operating value of 250 ^{o}C. This caused the pressure in the bomb to rise well above 5000 psig. When the bomb was opened, a large amount of brown solid material was found outside the thimble, along with a quantity of green liquid. Also the stainless steel thimble rack was nearly destroyed, with the two disc-shaped parts being severely scarred and the legs being weakened to the point of uselessness. The green liquid was analyzed with a gas chromatograph, but the only two compounds detected were methyl alcohol and water. Because methyl alcohol was the SCFE solvent used in this run and the peat was over 60 wt-% water, the presence of these two compounds is completely normal. The presence of inorganic impurities is indicated by the green color and by the fact that the liquid was much heavier than methyl alcohol and even heavier than tetrahydrofuran (the specific gravities of MeOH and THF are 0.79 and 0.89, respectively). These impurities could be either from the stainless steel of the bomb and rack or from the copper gasket. Run #11

was made for the purpose of a mass balance only, and was not analyzed for yield. Runs #1-5 were not included in the statistical analysis for the following two reasons:

1. The soxhlet extraction solvent used in these runs was toluene, while the subsequent runs used tetrahydrofuran. Because THF is a much better organic solvent than toluene, the yields obtained in the first five runs were consistently lower than those obtained in the following runs. In order to find out how large an effect this change had on the results a control soxhlet extraction was performed on ordinary peat with toluene and then repeated with THF. The toluene extracted 4.1 wt-% of the moisture- and ash-free peat, while the THF extracted 9.8 wt-%. Since this is a significant improvement, it was concluded that although Runs#1-5 were technically successful, they yielded no meaningful results and should be rejected.

2. The peat used in Runs #1-5 was sun- and air-dried and had a moisture content of about 32 wt-%, while the subsequent runs used peat as received which had a moisture content of about 60 wt-%. The effect of moisture content on yield was not investigated.

Appendix D. Procedural Data.

1. Pressures obtained from a given amount of solvent at a given temperature.

Solvent used	Mass of solvent charged (g)	Operating temperature (^{o}C)	Operating pressure (psig)
H_2O	45	405	3350
	110	400	4300
	125	400	4700
MeOH	10	350	1500
	15	350	1700
	25	350	2100
	50	350	2700
	90	350	3000
	200	350	5000
	95	260	1500
	150	265	1800
	200	265	2650
H_2O-H_2	27	410	3400
	100	400	4300

Appendix D. Procedural Data (cont.).

1. Pressures obtained from a given amount of solvent at a given temperature (cont.).

Solvent used	Mass of solvent charged (g)	Operating temperature (^{o}C)	Operating pressure (psig)
Acetone	75	255	800
	150	250	1100
	200	250	1600
	75	340	1600
	100	340	2000
	125	340	2300
	150	340	2800
	200	340	4800
	25	430	3300
	75	430	3700
	100	430	4000
	130	430	4600

Appendix D. Procedural Data (cont.).

2. Typical power input during the course of a run.

The power input to the resistance heater during the initial heat-up period was approximately 1500 watts, or 14-15 amperes of current.

Temperature desired (^{o}C)	Heat-up period (min)	Current at steady state (amperes)
250	45	9.0
340	60	10.5
430	75	12.0

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