



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
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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.

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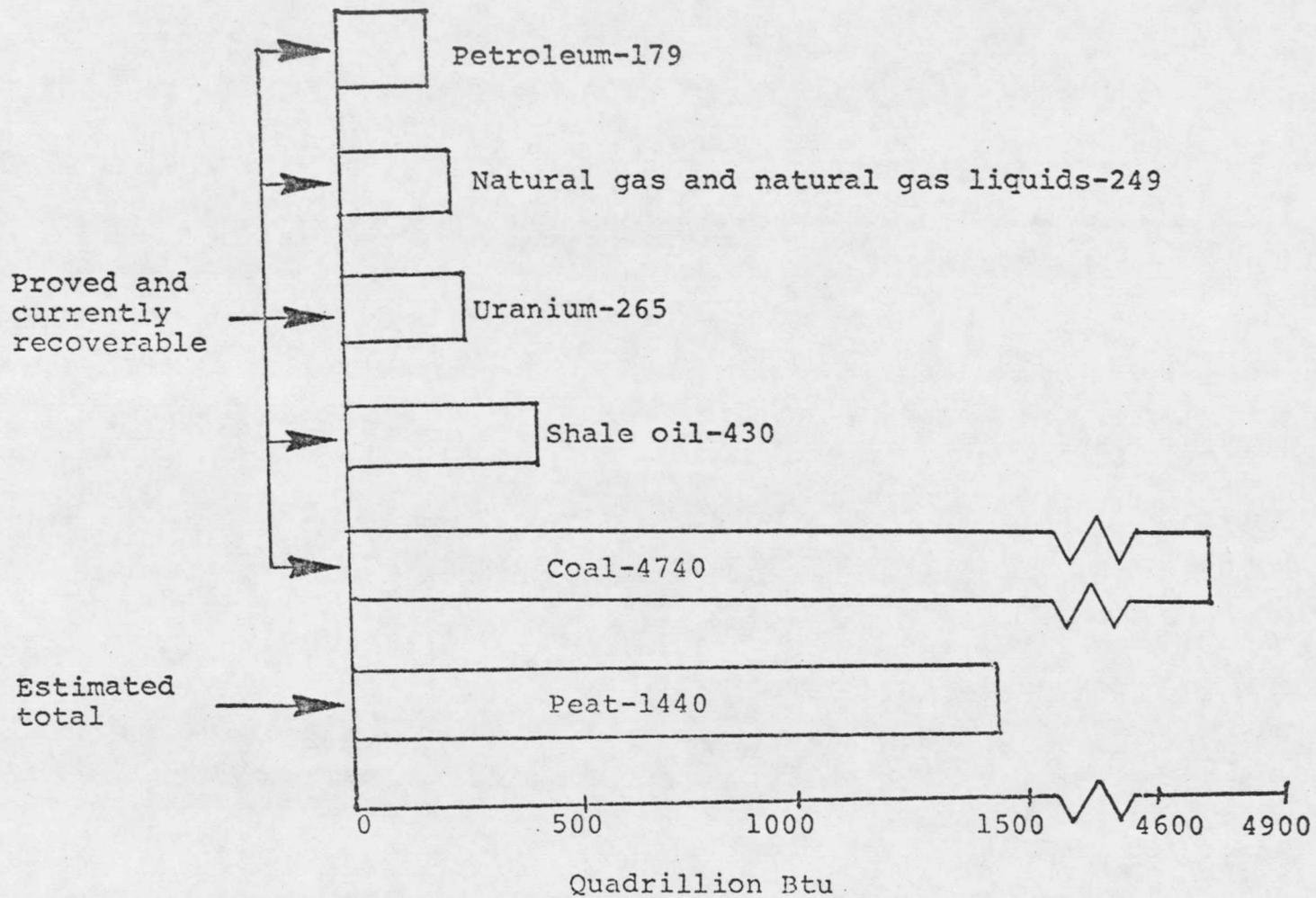
INTRODUCTION AND PREVIOUS RESEARCH

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



2

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 classifies 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 super-critical 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

