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CHEMICAL PRODUCTS FROM MINNESOTA PEAT *

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The peat deposits of Minnesota have today only limited value to the people of the state. The amount of good quality peat in Minnesota has been estimated at more than six billion tons¹, but to date only minor amounts have been used, mainly for soil improvement and to some extent for fuel. There is much need of research which can lead to development of the uses of this potentially important raw material.

It is well known that peat is the first intermediate product in the process of the formation of coal from vegetable matter. During the decomposition process the original plant substances, including lignins, cellulose, waxes and others, undergo slow decay in which oxygen and hydrogen are eliminated and the remaining carbon structures become more and more highly condensed. As compared with succeeding members of the coal formation series, namely, brown coal, lignite, bituminous coal and anthracite, the relatively undecayed peat contains a greater variety of carbon compounds including aliphatic, heterocyclic and carbocyclic structures. In contrast with peat we find that graphite, the extreme end product in coal formation, has a completely condensed carbocyclic structure.

In common with all members of the coal series peat undergoes a number of chemical reactions, including hydrolysis, hydrogenation, oxidation, chlorination and sulfonation. In general it shows greater reactivity and gives rise to a greater variety of reaction products than the later members of the coal series. Thus peat may be regarded as a potential source of useful chemical products.

A number of publications have reported that mild oxidation of coal substances, including peat, results in significant yields of aromatic organic acids. This has been shown especially by W. A. Bone,² et al., using alkaline permanganate solution on cellulose, peat, lignite, bituminous coal and coke. The oxidation products of the first substances are characterized by larger proportions of carbonic acid, the simpler aliphatic acids, and the lower members of the benzene-carboxylic acid series; the later materials give rise to larger proportions of acids of the benzene polycarboxylic series.

More recently H. C. Howard³ and associates at Carnegie Institute of Technology have applied high pressure oxidation in alkaline solution to bituminous coal. This group announced in 1946⁴ a com-

* An investigation sponsored by the Graduate School, University of Minnesota.

¹ Soper, E. K., The peat deposits of Minnesota, Minn. Geol. Survey Bull. 16 (1919).

² Bone, W. A., et al., Proc. Roy. Soc. (London) A148: 492-522 (1935).

³ Howard, H. C., et al., J. Am. Chem. Soc. 61: 2398 (1939).

⁴ Franke, N. W. and Kiebler, M. W., Chem. Ind. 58:580 (1946).

mercial process for producing mixed benzene polycarboxylic acids from coal. These mixed acids are predicted to have a potentially large market, especially in the alkyd resin field. In the form of esters of higher alcohols the polycarboxylic acids might well find useful application as solvents or plasticizers for synthetic plastics and resin formulas. The metal salts of the acids may be found useful as paint pigments. Other uses based on their intermediate molecular weight and polyfunctionality would probably arise.

Based on the favorable possibilities indicated in the above cited and other literature sources, an investigation of processes for obtaining useful chemical products from peat has been started in the Department of Chemical Engineering of the University of Minnesota. In this research project peat is envisaged as a source of relatively valuable chemicals, selling for, say, 15 to 20 cents per pound, in sharp contrast to previous uses as fuel or fertilizer, which are valued at not more than a fraction of a cent per pound.

The initial phase of the project has been devoted to study of the oxidation of peat to obtain mixed benzene polycarboxylic acids, since such a process would appear to lead most directly to a product of commercial value.

In order to ensure an adequate supply of peat of uniform composition, a master batch was prepared from 250 pounds of air dried peat by drying it to 10% moisture, mixing and grinding it to pass a ten mesh screen. The peat was taken originally by the Nutria Peat Sales Company from a bog of sedge peat on the area of the Northwestern Terminal in Minneapolis. This peat deposit varies from five to eight feet in depth and is underlaid with marl. An analysis for carbon, hydrogen, ash and moisture showed the master sample to be typical of the peat found in the Twin Cities region. The slightly low value of carbon content indicated it to be perhaps slightly younger or less decayed than the average.

Experiments to date have consisted of small scale oxidations in alkaline permanganate solution following a method similar to that used by the English worker, W. A. Bone and his associates. The purpose of the initial experiments was to compare the types and relative yields of product substances obtained from Minnesota peat with those found by Bone in work with Turraun Irish peat, Canadian lignite and coals. Larger scale oxidations are now being made to furnish sufficient product for experimentation in developing uses for the products obtained from the local peat.

In the small batch experiments 5 gram samples of peat were suspended in 500 ml. of CO₂-free distilled water containing 8 grams of potassium hydroxide. With the mixture refluxing continuously, a 3.5% aqueous potassium permanganate solution was added in small increments, time being allowed after each addition for fading of the purple color. At the end of the reaction period the mixture was cooled and filtered to remove the precipitated manganese

oxide. The filtrate was then analyzed for four types of carbon compounds: (1) carbonate carbon, (2) volatile acids (as acetic acid), (3) oxalic acid, and (4) higher acids, the latter being determined by difference between the first three and a total carbon determination. These higher acids were subsequently found to contain a small fraction of aliphatic acids, the remainder being aromatic.

Data for a typical oxidation of Minnesota peat, expressed as percentage of the carbon charged which appeared in the products, were as follows: carbonate carbon 52%, oxalate carbon 30%, volatile acids 4.5%, and the remaining acids, mainly aromatic, by difference, 13.5%. This composition resulted after an amount of permanganate had been added equal to 87% of the total amount which could react. In later experiments when the reaction was carried to completion by addition of permanganate to a permanent purple color, the proportions of the volatile acids and of the benzenoid acids by difference remained the same while the carbonate increased and the oxalate approached zero, indicating selective oxidation of the oxalate. At permanganate ratios somewhat less than 87% of the end point value the oxalate passed through a maximum. At permanganate ratios below about 80% of the end point value there appeared more complex acids which were soluble only in alkaline solution and which interfered with the later recovery of the simple benzenoid acids. As stated previously a small part of the "difference" acids was found to be aliphatic, probably of molecular weight just above the volatile fraction collected by steam distillation of the acidified solution.

These results for Minnesota peat are in substantial agreement with Bone's data for Irish peat and also correspond in general to the stepwise mechanism of the oxidation as outlined by Bone and other workers. According to this theory the first oxidation products of coal substances are complex alkali-soluble acids (humic acids) plus carbon dioxide; then by further oxidation the complex acids are broken down into simple, acid-soluble, aromatic (and aliphatic) acids plus more or less of oxalic and acetic acid and additional carbon dioxide. The proportions of these products vary with the type of coal substance as well as with the degree of oxidation.

It was necessary to determine experimentally the best conditions for separation of the free benzenoid acids from the alkaline reaction mixture. Recovery of the free acids was effected by treatment of the final reaction mixture in the following steps: (1) filtration to remove the precipitated hydrous manganese oxide; (2) neutralization and acidification with concentrated sulfuric acid to a 3 normal acidity; (3) addition of manganese dioxide to oxidize the oxalic acid followed by boiling to eliminate the volatile aliphatic acids; (4) solvent extraction at room temperature first with benzene to remove the aliphatic acids, then with methyl ethyl ketone to separate the benzenoid acids, and finally (5) evaporation and vacuum

drying of the ketone solution to obtain the free acids in crystalline form. The preliminary solvent extraction with benzene was found necessary in order to eliminate the aliphatic acids which had prevented satisfactory crystallizing of the benzene acids in the vacuum drying step. The pH of the aqueous solution during solvent extraction with methyl ethyl ketone affected critically the transfer of benzene acids to the ketone phase. The optimum pH was found to be less than 1.0.

The product from the vacuum drier, which consisted of mixed benzene polycarboxylic acids, was a light yellow-brown, very hygroscopic powder. Results of analysis for carbon and hydrogen were 44.79%, and 4.01%, respectively. This is equivalent to an average molecular structure corresponding to a benzene tricarboxylic acid, assuming only the simple benzene polycarboxylic acids to be present, and assuming also that the sample contained 13.1% moisture. The equivalent weight determined by titration with standard alkali was 73.3 as compared with 70.0 for the pure tricarboxylic acid.

The yield of benzenoid acids indicated by the analytical data was about 13% (based on carbon charged and recovered), including the aliphatic fraction. Deducting about one-fifth for the latter leaves an indicated yield of approximately 10% for the aromatic acids. The actual yield from a larger scale oxidation starting with 3.33 pounds of peat was 0.2 pounds, a 7.4% yield. Incomplete recovery of the aromatic acids during the single batch operation was indicated. Aside from an improved recovery procedure, two possibilities exist for improving the yield of benzenoid acids: (1) use of peat which is older or more decayed than that used to date since Bone's results indicated increased yields from older peat, and (2) use of a stepwise oxidation procedure for better control.

The economic feasibility of this process will depend on the success to be obtained in improving yields and reducing operating cost. Obviously the relatively expensive potassium permanganate must be replaced as oxidizing agent by either compressed oxygen or air. Materials costs will then depend mainly on the alkali used. A flow sheet must be developed for the process which will lead to more efficient overall operation and recovery.

While these experiments have demonstrated the possibility of obtaining benzene polycarboxylic acids from Minnesota peat, they have also demonstrated that it will not be easy to develop a successful economic process for their production. Nevertheless it is felt that such research is essential to the continued development of the industrial potentialities of the state.