CATECHOLS FROM THE CARBONIZATION OF NORTH DAKOTA LIGNITE

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INTRODUCTION

Catechol and its methyl homologs occur in a great variety of materials. These include tea, wine, grapes and other fruit, wood products, and coal tar. Of these materials only the last two have been considered as commercial sources for catechol. For example, extensive investigation has been carried out on the destructive distillation of lignin, wood, and bark as possible sources of catechols (1).

Low-temperature carbonization of coal, especially low-rank coals, is a particularly attractive source of catechols if the process can be justified by the improved fuel characteristics of the resulting char, the tar then being treated as a by-product. Also, since catechols are water-soluble, they are found not only in the tar but in the aqueous liquor as well, from which they are easily recovered.

Recovery of catechol from tar and process water has been considered feasible even when relatively low concentrations of the chemical are found. For example, Shono (2) proposes recovery of catechol from aqueous liquor, 50 liters of which contain only 220 grams catechol or 0.5 percent. Williams (3) obtained only 13 grams refined catechol from almost 2 kilograms raw tar (0.6 percent), although he obtained an equal amount of catechol from the associated liquor.

It is the purpose of this paper to show that the low-temperature carbonization products of North Dakota lignite are a rich source of catechol and its homologs.

ANALYTICAL METHODS

Catechols were found in North Dakota lignite tar early in our assay program. In the acid portion of this tar, catechol and the 3- and 4-methyl homologs are exceeded in concentration only by phenol. The relative abundance of these chemicals resulted in their crystallization from distilled fractions of the tar acids and prompted more intensive investigation. Several methods for quantitative estimation of the catechols have been used, depending on the type of mixture involved and the accuracy required.

The most accurate and universally applicable method is column partition chromatography as described by Barker and Hollingworth (4). This consists of a stationary phase of 0.1 N HCl on a support of Celite 535. The mobile phase is cyclohexane to which n-butanol is added in 1-percent increments up to 8 percent. The effluent is examined by UV spectrophotometry in a very sensitive range so that analysis is possible with quite small samples. This method was developed for analysis of ammoniacal liquors, but with slight variations can be used to determine catechols in whole tar.

A more rapid though less accurate method is gas-liquid chromatography of tar fractions or of extracts from the process water. Quantitative results are difficult with complex mixtures, but narrow-boiling fractions of tar acids and extracts of aqueous solutions can be estimated satisfactorily.

A good qualitative method for detecting catechols involves precipitation of their lead salts. The addition of lead acetate to slightly basic aqueous solutions containing catechol or the methyl catechols will result in precipitation of the insoluble lead catecholates. Under favorable conditions the precipitation is sufficiently complete for quantitative results; however, many of the more highly substituted catechols do not form lead salts, especially those substituted in the 3-position, adjacent to an OH (5).

Analysis of Low-Temperature Tar. As previously mentioned, Williams (3) extracted catechol in the amount of 0.6 percent of the raw tar. Gluud and Breuer (6) report the same percentage of catechol in low-temperature tar obtained from a Saar coal. For comparison, low-temperature tar from North Dakota lignite contains 1.0 percent catechol and, in addition, 2.8 percent 4-methyl catechol and 1.5 percent 3-methyl catechol.

Subsequent analysis of tar distillates indicated that the catechols were subject to degradation under conditions of atmospheric distillation. Distilling under vacuum greatly reduced this effect and resulted in considerable enrichment of catechols in the distillate. Tar, vacuum-distilled at 3 mm Hg to the equivalent of 240° at atmospheric pressure, gave an overhead representing 11 percent of the tar: this distillate contained 8 percent catechol, 9 percent 4-methyl catechol, and 0.6 percent 3-methyl catechol. Based on the figures given previously for gross tar, it would appear that there is too much 4-methyl catechol in this distillate and not enough 3-methyl catechol; however, it should be kept in mind that 3-substituted catechols are notoriously unstable and rearrangement or degradation of this material is the rule rather than the exception.

Analysis of Carbonizer Process Water. Catechol and 4-methol catechol are very soluble in water; 3-methyl catechol, although less soluble than these, can still be classed as soluble. For this reason, virtually every aqueous solution that comes in contact with the tar will extract catechols. This is a recognized fact, as evident from the number of investigations concerning recovery of chemicals from aqueous liquor. Subbarao, et al, (7) extracted carbonizer process water with butyl acetate and found, in addition to catechols, a number of other phenolics. Morgan and Pettet (8) extracted up to 1.7 grams catechol per liter of low-temperature carbonization liquid. Similar results have been obtained by others (9, 10, 11).

Butyl acetate extraction was carried out on aqueous liquor from a carbonizer operated at Dickinson, N. Dak. This is a Lurgi-type carbonizer used for production of char briquets from North Dakota lignite (12, 13). Exhaustive extraction of this liquid yielded 37 grams of extract per liter of process water. This extract, analyzed by gas-liquid chromatography, consisted principally of catechol, 3- and 4-methyl catechols with some phenol, cresols, and xylenols also present. Quantitative estimation from the chromatogram indicated 41 percent catechol, 19 percent 4-methyl catechol, and 9 percent 3-methyl catechol in the mixture. Thus a liter of process water contains about 15 grams catechol, 7 grams 4-methyl catechol, and 3 grams 3-methyl catechol. This aqueous liquor is somewhat richer in catechols than those mentioned in the literature, the extraction of which is regarded as commercially feasible.

YIELDS OF CATECHOLS

Carbonization of a ton of lignite at the Dickinson plant yields 5 gallons (42 lb) of tar (70 percent of assay) (12), and 20 gallons of process water (14). Thus from the previous figures we can expect one ton of lignite to yield 0.42 pounds catechol from the tar and 2.5 pounds catechol from the process water for a total of 2.9 pounds catechol per ton of lignite carbonized. Similarly, a ton of lignite should yield 2.2 pounds of 4-methyl catechol and 1.1 pounds of 3-methyl catechol. The amount of catechols actually recovered depends, of course, on the efficiency of the extraction process. While these figures represent the amount of catechols available, it may not be economically feasible to extract the entire amount.

RECOVERY METHODS

The phenosolvan process (7, 15, 16, 20) is the most popular method currently used to extract waste waters. It consists of countercurrent extraction with an ester mixture composed primarily of butyl acetate. Entrained ester is recovered by steam distillation, making the process highly efficient.

This method of recovery can also be used on solutions of buffers used to extract catechols from the tar (3, 17).

Others have extracted aqueous liquors with ether (2, 6), "ketone oil" (9), and cresilic acid (8).

Another interesting method of recovery involves adsorption of phenolics from liquor by activated charcoal (18) or coke dust (10). The phenolics were then desorbed by steam. Catechols were also recovered by precipitation of their lead salts before adsorption of the monohydroxy phenols on charcoal (18).

Separation of Recovered Catechols. Although catechol and 3-methyl catechol boil at about the same temperature (240° and 241° C respectively) at atmospheric pressure, they are separable by distillation under reduced pressure. Thus at 20 mm Hg, 3-methyl catechol has a boiling point of 129° C, whereas that of catechol is 134° and that of 4-methyl catechol is 147° (19).

Separation of catechol and 3-methyl catechol can also be achieved under certain conditions by precipitation of lead salts (5). Similarly 3-methyl and 4-methyl catechols can be separated by precipitation of the 4-methyl catechol with ammoniacal calcium chloride (19).

CONCLUSION

It has been shown that the low-temperature carbonization products of North Dakota lignite are a rich source of catechol, 3-methyl catechol, and 4-methyl catechol. Proven methods are available for recovery and separation of these valuable chemicals. Their potential abundance could result in development of many new uses and in expansion of present applications such as medicinals, antioxidants, plastics, glues, ore flotation, photo developers, and herbicides.

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