Oxalic Acid from Sawdust

OPTIMUM CONDITIONS FOR MANUFACTURE

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The fusion of sawdust with caustic soda to produce salts of oxalic and acetic acids was the commercial source of oxalic acid for many years. Because of current prices and demand for these acids, the fusion operation has been studied from the standpoint of more efficient recovery of by-products, as well as an increase of yield by accurate control of the process variables.

The optimum values of the variables investigated were: ratio of NaOH to sawdust, 3:1; concentration of NaOH used, 50 per cent; time and temperature of fusion, 3 hours and 200–220° C.; depth of fusion mass, as shallow as possible; type of wood, dependent on cellulose content. Carrying out the fusion in thin layers or blowing air over the mass increased the yields of oxalic acid.

Runs made on seven types of wood showed that oxalic acid yield was dependent upon the cellulose content, although the yields were always higher by a constant percentage than the theoretical yield based on the results of fusion with pure cellulose.

Since the sodium hydroxide is the most expensive raw material used, its efficient recovery is a requisite of the successful operation of the process. Runs showed the necessity for a considerable make-up of sodium hydroxide. However, a careful material balance indicated that it should be possible to reduce this to 3 per cent make-up.

Methanol and formic acid are produced in quantities large enough to warrant their separation and recovery. Enough data were collected to provide a basis for the study of continuous manufacture, which, with its attendant advantages, seems the desirable way to operate the process.

ESTIMATES indicate that more than 8,000,000 tons of sawdust are either burned as fuel or wasted annually in this country. The utilization of sawdust and wood waste in the production of oxalic acid, of which there is a shortage, by the fusion of sawdust with alkali is therefore a study of potential commercial importance. The production of oxalic acid from sawdust is not a new process. It was manufactured in 1829 by Gay-Lussac and applied by Dale in 1856 (*4*). The technique remained unchanged until comparatively recently, when all plants utilizing this method had stopped production.

Oxalic acid is an important organic acid; in the United States some 10 million pounds are used annually (*2*). Laundries consume a large amount as an acid rinse. It is used in the production of celluloid and rayon, manufacture of explosives, purification of glycerol and stearin, leather manufacture and dressing, tanning, calico printing, bleaching straw and wax, preparation of certain dyes, extraction of rare earths from monazite, manufacture of indigo blue for laundry work, etc.

Oxalic acid is now made commercially by the action of nitric acid on cellulose, or other carbohydrate material, by passing hot carbon monoxide over a mixture of sodium hydroxide and hot coke to form sodium formate, which is later converted into the oxalate, and as a by-product in the fermentation of citric acid (both acids occurring as the calcium salts).

The object of this investigation was to determine whether the commercial production of oxalic acid and acetic acid (a valuable by-product) from waste sawdust by fusion with alkali would again be profitable by modern chemical methods, and to determine the optimum procedure if such methods are used.

Although the literature gives yields of oxalic acid per pound of sawdust when treated with alkali, this is not the vital factor. The value of dry sawdust, on the basis of its heat content, ranges between 50 and 60 cents per ton. Caustic soda for the fusion, lime for recausticization, and sulfuric acid for conversion are the raw materials needed; all three are cheap chemicals but are expensive compared to sawdust. Lime and sulfuric acid are required in almost stoichiometric amounts; any excesses are almost wholly due to caustic losses and may be proportional to such losses. The feasibility of the process depends more, therefore, upon the efficiency of caustic recovery than upon any other single factor. Since none is represented in the products formed, the make-up requirements are due only to losses, which should be minimized. A further requirement for commercial success is an economical process for separating the materials resulting from the fusion.

Methanol and acetic acid as by-products of this reaction have been mentioned in the literature without extensive data as to amounts, effect on production, or cost of production. No mention is made of the evolution of combustible gases during the reaction.

METHODS OF OPERATION AND ANALYSIS

Thorne (*5*) found that 2 parts of caustic alkali (80 per cent potash, 20 per cent soda) heated with 1 part of sawdust to 200° C. yielded a quantity of oxalic acid equal to 36 per cent of the dry wood substance (d. w. s.) in the sawdust. By increasing the caustic:sawdust ratio to 4:1, he obtained a yield of 42 per cent oxalic acid; and when he reacted the latter quantities in a thin layer, the yield was 52.15 per cent. He leached the fusion cake with water to produce a solution of sodium oxalate which was evaporated until crystals formed. They were separated from the mother liquor and redissolved, and the solution was boiled with milk of lime. The calcium oxalate formed was separated and treated with sulfuric acid to produce oxalic acid, which was subsequently crystallized and purified by recrystallization.

The fusion step was operated according to the methods later described. Early work showed that the caustic potash gave higher yields; but the greater cost did not warrant its