RECOVERY OF PRODUCTS RESULTING FROM TREATMENT OF WOOD WITH CAUSTIC

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The separation and recovery of products from the treatment of wood with caustic is the step following the study of optimum conditions and the development of a method and equipment for large-scale production. This paper reports work on one of the methods applicable to industrial use.

Caustic fusion produces a cake containing humus materials, sodium oxalate, sodium acetate, sodium formate, sodium carbonate, and excess sodium hydroxide. A separation process for the five sodium compounds from aqueous solution which would be applicable to manufacturing operations was the first consideration; this complex system was first studied using a synthetic cake containing these materials, added in the known ratio of salts present in the fused material. Of the several methods which might be used to obtain salable products, successive steps of fractional crystallization and precipitation, following evaporation to the desired concentration, were used to give preliminary separation of the oxalate, of the acetate and formate together, and of the carbonate and caustic. Double decomposition with lime produced calcium salts of the oxalic acid, which are more economical for treatment with sulfuric acid for recovery of the acid; this treatment also recausticized the carbonate for re-use.

The separation of the constituents of the actual cake was hampered by the presence of humus materials. The use of activated carbon as a preliminary treatment in obtaining the crystallizable salts was found helpful.

Flow sheets and material balances of the separation and recovery steps are presented.

IN THE two previous papers the variables affecting causticization during the fusion of sawdust with alkali were described. The minimum ratio of caustic soda to sawdust and the maximum yield of oxalic acid per pound of caustic soda used and not recoverable, and per pound of dry sawdust, were major factors (page 262) as well as the development of a continuous, workable, fusion process (page 268). The methods of separation and recovery of the products resulting from the treatment of wood with caustic were not satisfactory, however, and further study was desirable. The products formed as a result of the above treatment are sodium oxalate, formate, acetate, carbonate, volatile constituents such as methanol, noncondensables such as carbon dioxide, carbon monoxide, nitrogen, and oxygen, complex organic impurities identified here as humus, and excess alkali.

Until about the time of the first World War, there was a commercial process based on the fusion of sawdust with caustic soda; oxalic acid was the product of chief interest. After fusion the mass was dissolved in the smallest possible quantity of water. The hot solution was then adjusted to 38° Bé. and allowed to cool. The sodium oxalate crystallized out and was freed by a centrifugal extractor. The crystallized sodium oxalate was then redissolved in hot water and a calculated amount of milk of lime added. Calcium oxalate and sodium hydroxide were thus formed. The precipitate of calcium oxalate was allowed to settle, and the supernatant caustic solution drawn off and used for another cycle, along with that from the first centrifuging. The calcium oxalate was washed with water, and the first washings were also added to the sodium hydroxide for recycle. The calcium salt was next decomposed with sulfuric acid to form oxalic acid and calcium sulfate. The calcium sulfate was filtered from the solution of oxalic acid. The oxalic acid was then crystallized from solution by evaporation.

The above process described by Hubbard (*3*), must have presented difficulty in operation with regard to the recycling of the caustic soda, aside from complications due to the salts of acetic and formic acids which, besides being wasted, must have interfered with the separation of the oxalate salts. The humus would have accumulated with each recycle until the caustic soda was unduly contaminated, which would necessitate the discard of caustic periodically, to decrease the humus content of the recycle caustic soda.

Koller (*5*) suggested that the mother liquor from the 38° Bé. solution at the beginning of the process be evaporated to dryness, burned to get rid of organic material, and fused to sodium carbonate. This was then to be recausticized with lime to caustic soda for recycling. Several plants did employ this treatment of the mother liquor, other plants did not. Evidently, then, it was merely a question of economics, based on the size of the plant, whether to purge the recycled caustic periodically or to install fusion pots, a recausticizing plant, and evaporators to concentrate the weak caustic liquors to the proper concentration for re-use in fusing the sawdust.

Sodium formate and sodium acetate were not considered in the early production of oxalic acid, since efforts were directed only to the yield of oxalic acid and the recovery of excess caustic soda for recycle. The additional revenue obtainable from the recovery of these sodium salts of the volatile acids would help to defray the expense of the production of the major product and might make the process commercially feasible in competition with the methods now used.

Little or no work has been done on the problem of separating the constituents existing in the mother liquor after crystallized sodium oxalate has been removed from the 38° Bé. solution discussed above (*2*).

Five salts are present in the fusion cake—sodium oxalate, acetate, formate, carbonate, and hydroxide. Few descriptions of separation methods for such complex systems of pure salts have been given. In this case the separation is further complicated by the presence of organic material in the fused cake, which interferes with crystallization.

The tools available for such a separation may be considered:

1. The salts may be dissolved in water and a precipitating agent added which reacts with one or more components of the system. The new solid phase may be filtered.
2. The salts may be dissolved in a solvent and an agent added which precipitates a component or components, but does not react chemically.

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