

CONTINUOUS FUSION PROCESS

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Based upon the determination of optimum conditions, a fusion trough has been developed which allows the continuous fusion of caustic soda and sawdust. Direct fusion with calcium hydroxide or with mixtures of sodium hydroxide and calcium hydroxide is not feasible. Continuous fusion gives higher yields and shorter fusion times than batch operation, due to the better control which is possible and the relatively small amount of material handled at any one time. These yields, on pilot-plant equipment, are as high as 79 per cent oxalic, 18.9 per cent acetic, and 3.86 per cent formic acid, all based on the dry weight of sawdust used.

A method of precise control for plant operations has been developed based on the color changes of the mass during the reaction. A particular shade indicates optimum conditions; and as the color variation on either side is wide, exact control is possible. A new system has been developed, tested, and standardized for complete analysis of the complicated systems of materials encountered.

A method for the recovery of the salts of oxalic, acetic, and formic acids is given, and a flow sheet of projected operation is presented.

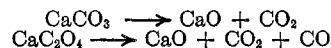
THE first paper indicated that the production of oxalic acid and other products from sawdust by fusion with caustic soda might be feasible. In determining the optimum conditions, it was found that satisfactory yields of oxalic, acetic, and formic acids and methanol could be obtained. However, efficient recovery and recycle of the caustic soda is necessary. It was felt that the development of a continuous fusion process would result in a more efficient use of the caustic soda as well as better control, a decrease in labor and heat costs, and similar advantages usually resulting from continuous processing.

An important additional need is an analytical method which will allow the determination of the several constituents individually and more readily and accurately than by conducting the sequence of operations as before. The analytical methods following gave more accurate results than the method of the first paper; the earlier analysis was made by securing final products, whereas in this case it was made on aliquot portions. Furthermore, the higher yields reported here over those shown in the previous paper may be due to the losses in processing when the preceding method of evaluation was used and to the return of salts of acids in the mother liquor. Repeated cycling of these liquors would probably have shown yields comparable to those reported here. The previous results were consistent among themselves, and while low in absolute values, may be regarded as adequately supporting the general conclusions.

METHODS OF ANALYSIS

The more convenient method of analysis was devised to facilitate control during continuous operation, and to make possible accurate material balances and determination of yields. The solution formed by taking up the fusion mass in water contains sodium carbonate, sodium hydroxide, sodium oxalate, sodium acetate, and sodium formate, as well as suspended organic matter. To determine these materials the following steps are carried out:

1. The humus is largely removed by filtering the solution through activated carbon, which is then washed well with hot water. The solution and washings are made up to a standard volume.
2. An aliquot portion is diluted with considerable water to reduce the subsequent precipitation of calcium hydroxide. Calcium chloride or calcium acetate solution is added until there is no more precipitation. If the precipitate is voluminous, it should be allowed to settle in the beaker, the liquid decanted, and the residue shaken with 200 cc. of warm distilled water. This precipitate is filtered on a weighed Gooch crucible and washed thoroughly with warm distilled water, until the filtrate is no longer alkaline to phenolphthalein. It is then dried, and contains only calcium carbonate and calcium oxalate if all the calcium hydroxide has been washed out. It is brought to dull red heat with a Meeker burner; the following reactions take place:



The blasted Gooch crucible may then be weighed to determine the amount of lime; and the total calcium ion is calculated as an equivalent of the sum of carbonate and oxalate.

3. Another aliquot portion is taken; and the same procedure is followed, except that it is not necessary to be so careful about washing out the calcium hydroxide precipitate. The Gooch crucible is placed in a large excess of 2:1 sulfuric acid (300 to 400 cc.) and heated to 90° C. This sample is titrated with potassium permanganate to determine oxalic acid. When this is calculated to calcium oxide and subtracted from total calcium oxide, the total carbonate equivalent may be obtained.

An alternate method, which avoids contamination of the precipitate with the large amounts of calcium carbonate in this step, consists in acidifying the aliquot portion with hydrochloric acid and boiling to eliminate carbonates before the precipitation of the oxalate. Any excess hydrochloric acid can be neutralized with ammonium hydroxide.

4. An aliquot sample of the fusion mass solution is taken again and titrated to the phenolphthalein end point with standard hydrochloric acid. This is equivalent to all of the sodium hydroxide plus half of the sodium carbonate. Half of the carbonate equivalent, as obtained in the last step, is subtracted, and the value for sodium hydroxide is obtained.

5. The method for determining acetic and formic acids depends upon their volatility. An aliquot sample is taken in a distilling flask, 2:1 sulfuric acid is added through a separatory funnel, and the acetic and formic acids are distilled over with some water. Additional water is added in small amounts until the distillate shows no acid. The distillate is made up to 500 cc. in a volumetric flask. An aliquot is taken and titrated with standard sodium hydroxide to determine the total acidity. Another aliquot is taken and treated with mercuric chloride, and the precipitate of mercurous chloride is weighed by the method mentioned in the first paper, page 262. This depends on the reducing property of formic acid and is shown by the following equation:



The value for formic acid is thus obtained and, when subtracted from the titration value, gives the amount of acetic acid.