

A METHOD
for the
PREPARATION OF OXALIC ACID FROM SAWDUST

Thesis

by

Joseph R. Alcock

In partial fulfillment of the requirements
for the degree of Bachelor of Science
in Chemical Engineering.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California.

1923.

INTRODUCTION.

This investigation was undertaken to find the best method of preparing oxalic acid from sawdust, either by one of the methods described in the literature or a modification of it. The first work consisted in following the procedure recommended by a previous experimenter in order to become acquainted with the methods which are now used and to discover their weak points. The procedures used commercially, and the experimental work of Thorn, described in "Utilization of Wood Waste" by E. Hubbard form the basis of the work. No recent literature could be found on the subject, the work of Thorn having been done nearly forty years before. Various commercial processes use slightly different methods; one uses KOH alone in the fusion and precipitates MgC_2O_4 by adding $MgCl_2$ to the $K_2C_2O_4$ solution; in another a preliminary fusion is carried on in a vacuum at 180° , followed by the regular fusion yielding a nearly colorless product. A process similar to that outlined by Thorn is also used.

The heating of sawdust with KOH results in the production of oxalic acid. Since NaOH is much cheaper, it is desirable to substitute it for KOH as far as possible. Thorn found that a mixture containing 40% KOH and 60% NaOH by weight gave almost as good a yield, when heated in thin layers, as pure KOH. The yield dropped off rapidly with a decreasing KOH percentage below 40%. He also found that the most satisfactory melt was made by using one part of sawdust to two parts of lye, striking a balance between large percentage yield from lye with more sawdust, and more organic im-

purities which are hard to remove if more sawdust is used. Soft wood gives a better yield than hardwood, and pure sawdust gives a better one than the lignose left after treating cellulose with HCl.

APPARATUS

The fusion of sawdust and lye was made in a five inch iron pan about $\frac{3}{4}$ inch deep. At first it was heated directly with a flame. Later a screen was placed about an inch below it. At the last a second pan was used, the pan containing was the mix being set on a screen in the other pan and a more even distribution of heat obtained. The melt was stirred with a thermometer so that the temperature was watched while the necessary stirring was done. Suction filters with asbestos were used at first, but later filter papers were used without suction.

PROCEDURE

In the first four experiments, 25 grams of sawdust was used and the pan was heated with a direct flame. In the next seven, 15 gram samples of sawdust were used and in the last six, 10 grams. One part of sawdust was placed in the pan, two parts of lye were dissolved in three parts of water and stirred into the sawdust. The mix was then heated, the temperature going to about 110°C while the water was evaporating, and then rising to 170° , when the reaction seemed to start. The temperature was kept at 180 -- 240° for 20 -- 40 minutes. The melt was dissolved in boiling water; the solution boiled down to 38°Bé and allowed to cool. The $\text{Na}_2\text{C}_2\text{O}_4$ separated and was filtered out, dissolved in hot water and an equivalent amount of milk of lime added to the hot solution. It was then boiled for an hour, the

CaC_2O_4 allowed to settle, and the liquid decanted off. Wash water was added and the suspension filtered with suction. Twice the equivalent amount of $2 \text{N} \text{H}_2\text{SO}_4$ was added slowly to a slurry made from the precipitate, and the mixture heated gently for one or two hours. The CaSO_4 was allowed to settle, the liquid decanted off through a filter, wash water added and the suspension filtered with suction. The filtrate was evaporated down to 1.116 specific gravity and cooled. The CaSO_4 which separated in asbestiform crystals was filtered out and the filtrate evaporated further to obtain oxalic acid, which could be purified by recrystallization. The yields in this method were low and a change in method was thought to be justified. The change which was tried came in the treatment after fusion. The melt was washed with a small amount of cold water as is done in some commercial methods. Then instead of dissolving and adding milk of lime, the theoretical quantity of H_2SO_4 to react with the $\text{Na}_2\text{C}_2\text{O}_4$ and the necessary water to dissolve at 70° the $\text{H}_2\text{C}_2\text{O}_4$ formed was added. The solution was then heated to boiling, dissolving the oxalate with formation of slightly ionized $\text{H}_2\text{C}_2\text{O}_4$. The solution was filtered while hot and some of the organic impurity or humus was retained on the filter. When the solution cooled, oxalic acid crystallized out, and the liquor was evaporated to obtain more. The oxalic acid was then purified by several recrystallizations as in the other process.

METHODS OF ANALYSIS.

The product of fusion was analyzed to determine the yield of oxalic acid by the following system. The melt was dissolved in hot water and the volume measured. A 10 cc ^{was} portion taken out for analy-

sis, 10cc of acetic acid added and the solution boiled to expel CO_2 . Then 8cc of CaCl_2 solution (1N) was added, the precipitate filtered out and transferred to a beaker. After the addition of 40cc of 3 N H_2SO_4 the solution was boiled down. After cooling, the CaSO_4 was filtered out and scraped into a crucible, with the filter paper placed on top of it. The crucible was ignited and weighed and the per cent yield of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ calculated from the weight of CaSO_4 .

The crystallized oxalic acid was analyzed for sulphate by the following system. A sample of about half a gram of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ crystals was weighed out and dissolved in about 100 cc of water, 3 cc of dilute HCl added and the solution heated to boiling. Hot BaCl_2 solution (10 cc of $\frac{1}{2}\text{N}$) was added to precipitate BaSO_4 . This was filtered out and transferred to a crucible, with filter paper placed on top. It was ignited, weighed and the per cent of sulphate in the oxalic acid calculated. A similar precipitate of BaSO_4 obtained by the same method was titrated with KMnO_4 and the oxalate found assumed to be BaC_2O_4 . This would decompose to BaO on heating, so the equivalent weight of BaO was subtracted from the sulphate determination and amounted to less than 5% of the total weight.

EXPERIMENTAL RESULTS

The first two heatings were made with a mix of 20% KOH and 80% NaOH and were heated to 240° and 230° respectively with the flame in direct contact with the bottom of the pan. The melts burned up in a similar manner to the 10% KOH and 90% NaOH mixture which

Thorn tried. After the flame was removed at 240° and 230° , the temperature kept rising rapidly and the mix turned black. The temperature went up above 360° C and an inflammable gas was evolved. If the temperature had been raised only to 180° , it would probably have been possible to heat the mixture successfully.

A 40 -- 60 mixture was next tried and was heated only to 200° . A lumpy yellow-brown product resulted and was treated as described under Procedure. Very little oxalic acid crystallized out of the mother liquor of H_2SO_4 .

The next batch was a 30 -- 70 mixture of caustic and was heated to 225° where the temperature rapidly rose to over 360° and the melt burned. A similar lot was heated separately to only 160 -- 180° without trouble. The product was treated as described in the Procedure, until some $H_2C_2O_4$ crystals were formed. They were mixed with asbestiform crystals of $CaSO_4$. An attempt was made to separate the $H_2C_2O_4$ by dissolving it in Na_2SO_4 solution, but it did not seem to dissolve much. The residue was then dissolved in a little hot water and on cooling some $H_2C_2O_4$ crystallized.

The fifth panful was heated with a screen about an inch below the pan to spread the heat more evenly. It was a 30 -- 70 mix and was heated to 210 -- 220° , cooled to 125° , then heated to 235° with no apparent change taking place. The melt was partly dissolved in water, and lime added to the solution without crystallizing $Na_2C_2O_4$ and redissolving. Sulphuric acid was added and the oxalic acid crystallized out as before. There was some difficulty from the large amount of organic impurity, called humus by Thorn, which colored the product brown. The total oxalic acid from this melt was not over four or five grams.

Thorn also found that the early addition of lime was unsatisfactory.

The NaOH solution obtained by adding milk of lime in the second solution is quite pure and can be used for the next fusion, while that obtained in this case is, like the original solution after crystallizing out $\text{Na}_2\text{C}_2\text{O}_4$, contaminated with humus. It must be calcined with sawdust and causticized with lime to make it suitable for use again.

The original solution left some residue which was dissolved in H_2SO_4 and some oxalic acid was obtained by evaporation and cooling.

In all the rest of the runs 40 -- 60 mixes of KOH and NaOH were used. In the sixth one the sawdust was dried in an oven at 120° for three quarters of an hour, then the warm alkali solution added and mixed thoroughly. It was then heated with a gradual rise in temperature to 250° when the mass solidified and the reaction seemed to be over. The mix melted where it was in contact with the hottest part of the pan at 170 -- 180° . When the temperature reached 220° the whole mass melted to a pasty yellow plastic. The mass now occupied about half the original volume, but if not stirred for a short time it was expanded by bubbles of gas forming in it. The color gradually got darker and after a short time the temperature went up to 230° and very gradually to 245° where the flame was removed. The temperature went up to 250° , the mass got darker and finally solidified. The product was 39.3 grams from 15 grams of sawdust and 30 of lye. It was dissolved in water, the volume measured, and two 10 cc samples taken to determine the yield as described in Methods of Analysis. The yield was 72% which is lower than the 80% obtained by Thorn. The main solution was treated to obtain oxalic acid crystals, but did not give a very large

amount.

The seventh batch was heated to 230° on the fusion and the yield was 66.4%. The $\text{Na}_2\text{C}_2\text{O}_4$ obtained by boiling down the solution was treated in a different manner than before. It was weighed, the equivalent amount of H_2SO_4 to react with it, and the amount of water necessary to dissolve at 70° the $\text{H}_2\text{C}_2\text{O}_4$ formed were calculated. A 15% excess of acid was mixed with the water, added to the $\text{Na}_2\text{C}_2\text{O}_4$ and heated to boiling. Another 15% excess of acid was added as dilute H_2SO_4 and the $\text{Na}_2\text{C}_2\text{O}_4$ all dissolved. When the solution cooled, some large crystals separated out of the rather dark solution. The solids were filtered out and some dark colored, slimy substance was left on the paper with the crystals. The solution was evaporated down and when it cooled, some purer looking crystals separated. The solution was cooled in a freezing mixture to -10°C and some more crystals formed.

The next mix was divided into two parts and heated a shorter time, the first half taking a total time of about three quarters of an hour and the second part only half an hour. The first part gave 57% yield and the second 40%, which indicates that the yield is increased by longer heating. Some of the solution of $\text{Na}_2\text{C}_2\text{O}_4$ was shaken with fuller's earth to see how much color was removed, but the decrease in color was not appreciable. Aluminum hydroxide was also found to be unsatisfactory as an absorbent of the colored impurities.

The ninth mixture was heated one hour at $220 - 240^{\circ}$, the product was twice washed with 30 cc of water and filtered. The

residue was dried in an oven and weighed 19 grams. Twice the calculated amount of acid and the calculated amount of water (15 cc conc. H_2SO_4 , 30 cc H_2O) were used and the solution filtered while hot to remove some of the black organic matter. A larger quantity of crystals was obtained than in any previous experiment.

Batch ten was heated with too large a flame to 245° and burned up. Number eleven was only heated to 230° before the flame was removed but it also burned up. In both these cases the sawdust and lye solution were mixed several days before the heating. Eleven was not stirred enough before starting heating so that a liquid film remained on the bottom and a crust of solid lye formed when it was heated.

Lot number twelve was mixed with only 10 grams sawdust and heated to 220° . The product was broken up into small pieces in a mortar and washed with 29 cc of water. Then 15 cc of alcohol was added to try its effect as a solvent of the organic impurities, but it was only colored a light brown, while wash water became almost black. This showed that alcohol is not a satisfactory solvent for washing out impurities. The $\text{Na}_2\text{C}_2\text{O}_4$ was then treated with acid to obtain oxalic acid, and the mother liquor, after being boiled down several times, was titrated with 1 N NaOH and found to be 13 N in acid, in which solution oxalic acid was negligible. From this it was calculated that there was 2.4 cc or about 15% excess of H_2SO_4 added.

The thirteenth mixture was prepared several days before heating and was heated to 230° before the flame was removed. The temperature

slowly rose to 245° when black spots began to appear and the pan was set in cold water to cool it, but the melt continued to burn and was spoiled.

Batch fourteen was heated to 205 -- 215° for about ten minutes, then to 235° until it was thought that the reaction was almost over. The mix was then heated to 250° to see if that would cause it to burn up when the reaction was nearly over. The flame was removed at 250° , but the temperature went up to 260° at which point cold water was poured in to stop the burning. The product was treated to obtain oxalic acid and some was obtained which was darker colored than usual.

Number fifteen was mixed at the same time as number fourteen and was let stand two days before heating. It was heated to 220° , the flame removed, then replaced and it was heated to 230° and the flame again removed. The temperature slowly rose to 245° where water was added to stop the burning.

The next panful was heated with the pan set on a screen placed in another pan. The temperature was raised to 190 -- 205° and stayed in that range for about 20 minutes. The 27 grams of product was washed and treated with acid as before.

The seventeenth batch was heated to 220° for a longer time than the preceding one and the product looked darker. Thorn states that at 240 -- 250° the humus seems to undergo decomposition as shown by a paler colored solution, and the yield of oxalic acid increases.

Apparently a longer heating at 220° does not increase the yield and seems to increase the dark color of the product. The melt was

washed, dissolved in hot water (165 cc for 27 grams product) and the solution boiled down to about 40 cc and filtered, but no more was done.

The purification of the oxalic acid was started, but only one recrystallization was tested for sulphate. It was found to contain 30% sulphate and was again recrystallized. The qualitative test of the oxalic acid obtained by the use of lime looked about the same as that of the oxalic acid obtained by treating $\text{Na}_2\text{C}_2\text{O}_4$ with H_2SO_4 and probably contains nearly as much sulphates.

CONCLUSIONS

Since the oxalic acid must be purified from sulphate by several recrystallizations, there does not seem to be much advantage in obtaining a colorless product of $\text{Na}_2\text{C}_2\text{O}_4$ because the organic impurities will be removed in the recrystallizations.

As a result of these experiments, it is recommended that a modification of the procedure outlined by Thorn which was tried only on a small laboratory scale be investigated on a larger scale. A mixture of 40% KOH and 60% NaOH is dissolved in one and a half times its weight of sawdust. The mix is heated slowly in thin layers (0.4 to 0.5 inch) to 220 -- 240° with continuous stirring and even heating for about an hour. It is twice extracted with a volume of water equal to that used to dissolve the lye. The residue is ground in the second liquor, filtered out and weighed. Assuming all the residue to be $\text{Na}_2\text{C}_2\text{O}_4$, although there are hydroxides and carbonates present, the equivalent amount of H_2SO_4 is calculated and 1.7 times this amount is used. The 96% acid is mixed with twice its volume of water, added to the residue and heat-

ed to boiling. The hot solution is filtered and some coagulated organic impurities are thereby removed. When the solution cools, oxalic acid separates out and the solution can be decanted off and evaporated down to obtain more crystals. The second crop may contain more Na_2SO_4 and H_2SO_4 than the first one. The crystals may be washed with a small amount of cold water to remove mother liquor and then dissolved in hot water and recrystallized. The wash water of the recrystallization may be used to wash the first crop and then the second crop of crystals from the original solution, and then if it does not contain too much Na_2SO_4 it may be used as the water to mix with the H_2SO_4 for treating the $\text{Na}_2\text{C}_2\text{O}_4$. After several recrystallizations, the number depending on the purity desired in the product, the oxalic acid is filtered out and dried by suction and then in a drier at not much over 60°C .

The solution obtained in washing the product contains lye, carbonates and humus, and the second wash water also contains a little oxalate. The lye may be recovered by calcining with sawdust to convert to Na_2CO_3 , leaching and treating with milk of lime.

SUMMARY

The methods of making oxalic acid from sawdust were investigated.

A new method of recovery of oxalic acid from the fusion was proposed and studied.

A process for larger scale use was outlined.