

Proceedings of the Iowa Academy of Science

Volume 39 | Annual Issue

Article 26

1932

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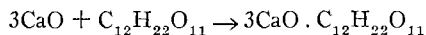
Bartow, Edward and Little, E. C. (1932) "Action of Solvents on Steffen's Waste Water From the Manufacture of Beet Sugar," *Proceedings of the Iowa Academy of Science*, 39(1), 139-148.
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ACTION OF SOLVENTS ON STEFFEN'S WASTE WATER FROM THE MANUFACTURE OF BEET SUGAR

EDWARD BARTOW AND E. C. LITTLE

The Steffen's process for the recovery of sugar from beet molasses consists of a cold and a hot precipitation. The molasses has a specific gravity of about 1.3 and a sucrose content of approximately 50 per cent. It is diluted with water until it has a specific gravity of about 1.05, and contains 5 to 6 per cent of sucrose. To this solution cooled to 15°C, powdered lime is added, with agitation, in the proportion of one part calcium oxide to one part sucrose. In the cold precipitation process, insoluble tri-calcium saccharate is precipitated.



Some fairly soluble di-calcium saccharate is also formed so that the filtrate contains about 0.5 per cent sucrose. Almost all of this remaining sugar is recovered by the hot precipitation process. The filtrate is heated to 80°C at which temperature the di-calcium saccharate decomposes and gives a precipitate which has been given the formula of $4\text{CaO} \cdot \text{C}_{12}\text{H}_{22}\text{O}_{11}$. The insoluble material is removed by filtration and the filtrate, called Steffen's waste, constitutes the starting material for the work presented in this paper.

The waste contains some sugars, lime, nearly all of the potassium extracted from the beets and organic compounds such as leucine, asparagine, malic acid, succinic acid, betaine, and glutamic acid. Potassium, betaine and glutamic acid are present in the largest amounts and our chief interest has been in their recovery.

A number of methods have been developed for obtaining betaine and glutamic acid from Steffen's waste. The separation of the two is difficult.

Ehrlich (4) obtained betaine hydrochloride from beet molasses by extracting with 95 per cent ethyl alcohol. Betaine and some potassium compounds dissolved in the alcohol. Potassium chloride was obtained as a precipitate by the addition of concentrated hydrochloric acid. After removal of the potassium chloride by filtration and concentrating the filtrate, betaine hydrochloride crystallized out.

Stoltzenburg saturated beet molasses, specific gravity 1.42, with hydrogen chloride gas. After several days the resulting precipitate was filtered off and the filtrate concentrated to a thick syrup. The betaine hydrochloride was then extracted with alcohol and filtered off after concentration.

Andrlik (2) tried other acids upon concentrated molasses using the Stoltzenburg method. He worked with sulfuric and phosphoric acids precipitating glutamic acid along with the inorganic salts, and then trying to separate them by fractional crystallization. This was found to be very difficult. He next precipitated potassium acid tartrate by the addition of tartaric acid. The insoluble acid tartrate was filtered off and the filtrate seeded with glutamic acid crystals. After standing twelve hours, glutamic acid separated out. The betaine remained in the filtrate.

Barta (3) applied the procedure used by Ehrlich on beet molasses to Steffen's waste concentrated to a specific gravity of 1.40. He extracted the betaine with ethyl alcohol, precipitated the potassium by addition of concentrated hydrochloric acid, filtered off the KCl and concentrated the filtrate to obtain betaine hydrochloride. He used Andrlik's method for the preparation of glutamic acid from the insoluble residue.

Tressler (6a) obtained a patent on a process very similar to Ehrlich's to separate the betaine and glutamic acid in the concentrated waste. By passing hydrogen chloride gas into the cold solution, potassium chloride and betaine hydrochloride were precipitated, glutamic acid hydrochloride remaining in solution. The precipitate was filtered off and the betaine hydrochloride separated from the potassium chloride by extraction with hot alcohol. When the alcohol cooled, betaine hydrochloride crystallized out. In his second patent (6b) metallic chlorides were used with sulfuric acid to produce an insoluble sulfate and hydrogen chloride in solution. To cold concentrated Steffen's waste, he added a solution of calcium chloride and then sulfuric acid. Betaine hydrochloride and inorganic chlorides were precipitated and separated as in the first patent. The filtrate was heated in order to hydrolyze its compounds to obtain glutamic acid. In Tressler's third patent (6c) calcium chloride was added to salt out the inorganic salts as chlorides and betaine as the hydrochloride after acid had been added to the concentrated waste. Glutamic acid was not precipitated if the solution was kept cool. The chloride and hydrochloride were filtered off and the filtrate heated to 80-90° for an hour. After neutralizing the solution with sodium carbonate, glutamic acid precipitated.

The following method was developed by Ikeda of Japan (5). Sulfuric acid was added to the concentrated Steffen's waste precipitating potassium sulfate. This was filtered off and more sulfuric acid added to the filtrate. This solution was then heated for several hours at 80-180° in order to hydrolyze its compounds to glutamic acid. The sulfates were removed by addition of powdered limestone or slaked lime. After filtering the solution was allowed to stand several days and glutamic acid separated out. After this was filtered off, oxalic acid was added to precipitate betaine oxalate. Free betaine was obtained by treating the solution with lime.

Albrook's (1) work consisted of an attempt to (1) devise a better method for the separation of betaine and glutamic acid, (2) to determine the best method of separating potassium from the alcoholic solution and from the residue containing glutamic acid, (3) to explain in what form betaine and glutamic acid existed in Steffen's waste, and (4) to find a good method for obtaining glutamic acid.

His conclusions were that:

(1) Addition of the waste concentrated to a sp. g. of 1.4 to alcohol agitated by an electrically driven mechanical stirrer was a better means of extraction than the ball mill,

(2) The best way to remove potassium was through precipitation with concentrated hydrochloric acid from the alcoholic solution,

(3) Betaine probably existed as a salt of potassium,

(4) The best method for obtaining glutamic acid was to concentrate the residue from the betaine extraction, precipitating the potassium with concentrated hydrochloric acid, filtering and refluxing the solution for four to six hours, and obtaining on cooling the glutamic acid hydrochloride.

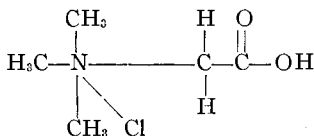
A procedure was used which was worked out in part by Barta (3) and improved by Albrook (1), for the preparation of glutamic acid hydrochloride and betaine hydrochloride.

Steffen's waste water with a specific gravity of 1.02, as it was received from the factory of the American Beet Sugar Co. at Mason City, Iowa, was concentrated to a specific gravity of 1.4. Before concentration the calcium hydroxide was removed, as far as possible, by passing carbon dioxide into the solution. Denatured alcohol containing 10 per cent methyl alcohol dissolved betaine and potassium compounds from the concentrated solution. The concentrated solution was poured into the alcohol, which was being stirred by an electric motor attached to a glass stirrer.

Concentrated hydrochloric acid was added to the alcoholic ex-

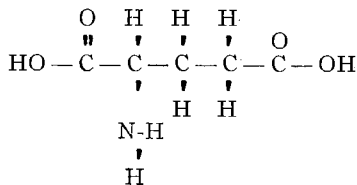
tract until potassium chloride ceased precipitating. This potassium chloride was removed by filtration and the filtrate concentrated on a water bath under reduced pressure. A small amount of potassium chloride crystallized out during the concentration. This was removed and the concentration continued until the material was a thick syrup. On cooling, crude betaine hydrochloride crystals separated out. The crude crystals were brown in color. After decolorizing with wood charcoal and recrystallization from water, the betaine hydrochloride crystals melted at 227°. Upon recrystallization from hot alcohol, their melting point was 240°.

The accepted structure for betaine hydrochloride is



Glutamic acid was prepared by adding concentrated hydrochloric acid to the alcohol insoluble residue, removing the precipitated potassium chloride and refluxing the filtrate for twelve hours. Carbon was formed in the process. It was removed and the solution decolorized with wood charcoal and concentrated. More potassium chloride was separated from the solution and glutamic acid hydrochloride was obtained in the concentrated solution.

The structure of glutamic acid is



PURPOSE

It was the purpose of our work after checking that of Barta (3) and Albrook (1) to:

(1) Determine the best concentration of alcohol to use in the extraction of potassium and of betaine compounds from Steffen's waste.

(2) To find out the most satisfactory proportion of concentrated hydrochloric acid to use in the preparation of glutamic acid.

(3) To discover, if possible, a better method of separating potassium.

EXPERIMENTAL

Four different concentrations of alcohol were used in the ex-

traction of betaine and the potassium compounds from concentrated Steffen's waste. The moisture content of the waste was first determined; this was found to be 30 percent. From this percent and the known amount of water in the alcohol, the concentration was calculated, and enough water added to produce the desired percent. The alcohol percentages were 60 percent, 70 percent, 80 percent, and 90 percent.

Two hundred and fifty grams of waste were used for each test. The alcohols of the different concentrations were placed in beakers and the waste slowly added while the mixture was being agitated with the mechanical stirrer. After twenty to thirty minutes agitation, the insoluble portion of each was allowed to settle and the alcoholic extract decanted.

Upon addition of concentrated hydrochloric acid to the alcoholic extract, a heavy precipitation of potassium chloride occurred in the 80 percent and 90 percent alcoholic solutions. There was no precipitation in the 60 percent and very little in the 70 percent. After removing the potassium chloride by filtration, the filtrates were concentrated. During their concentration, more crystallization of potassium chloride occurred, in the 60 percent and 70 percent alcohol extracts, and only a little in each of the more concentrated solutions. After the potassium chloride had been removed and the filtrate evaporated to a thick syrup and cooled, betaine hydrochloride crystals were obtained.

Concentrated hydrochloric acid was added to the insoluble residue. An immediate precipitation of potassium chloride occurred. After filtration the filtrate was refluxed for twelve hours. At the end of this time the carbon, formed through the charring of organic compounds, was removed, by filtration and the filtrate decolorized with wood charcoal, and concentrated under reduced pressure. Glutamic acid hydrochloride and some potassium chloride crystallized out. These were later separated by recrystallization from water; the glutamic acid hydrochloride separating out first, leaving the potassium chloride in the mother liquor.

From the results obtained by the experiment, (see Figure 1) the 60 percent alcoholic solution dissolves all the waste, and therefore it is not practical to prepare glutamic acid, using the 60 percent alcoholic solution as a solvent.

The waste is much less soluble in the 70 percent, 80 percent, and 90 percent solutions. As the concentration of alcohol increases, the solubility of the waste in the solution decreases. A separation occurs and the insoluble material which contains the compound or

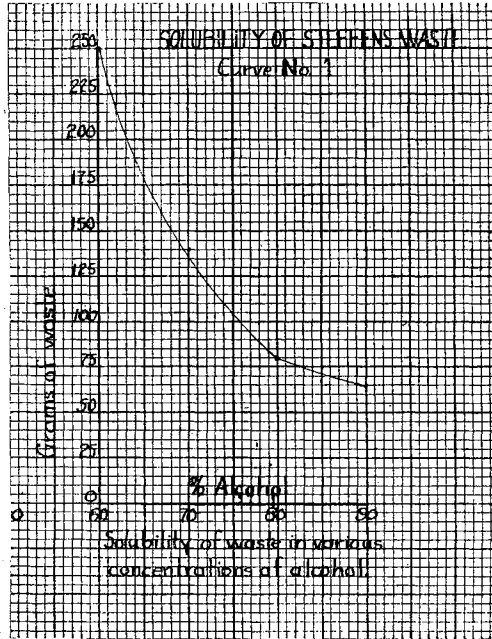
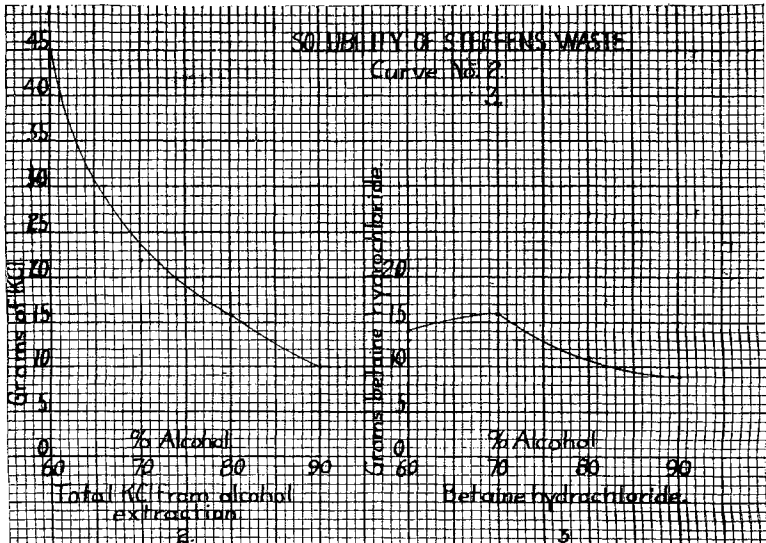


Figure 1



Figures 2 and 3

compounds hydrolyzable to glutamic acid settles to the bottom.

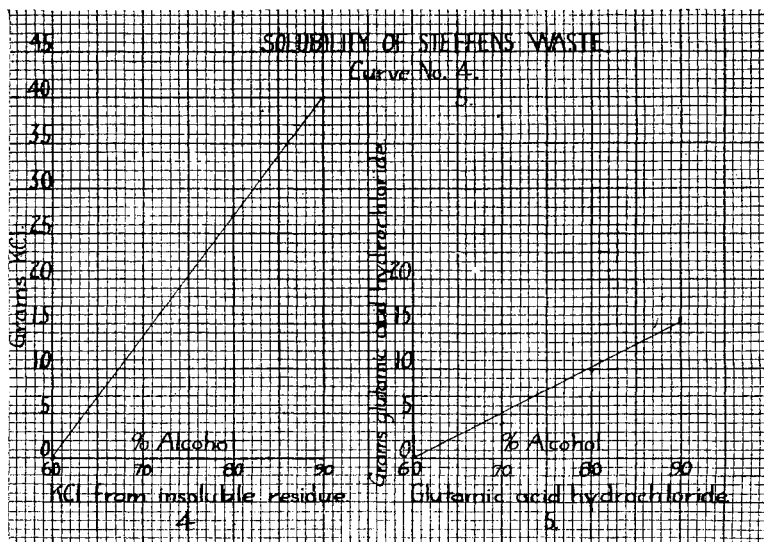
Since all of the waste is dissolved in the 60 percent alcoholic solution, all of the potassium should be precipitated as potassium chloride upon addition of hydrochloric acid and concentrating. The amounts of potassium chloride obtained from the 70 percent, 80 percent, and 90 percent extracts vary with the amount of waste dissolved by the alcohol.

The similarity is shown by a comparison of Figures 1 and 2.

The largest yield of betaine hydrochloride was obtained from the 70 percent alcoholic solution (see figure 3). This was probably due to the large amount of syrupy material in the 60 percent solution which prevented precipitation of the betaine hydrochloride. These results show that the more dilute alcohol removes more of the betainate compound.

When concentrated hydrochloric acid was added to the insoluble residue, it dissolved leaving potassium chloride as a precipitate in all of the samples except the 60 percent from which no insoluble residue had been obtained. The amount of potassium chloride produced varies with the alcoholic concentration (see Figure 4). The residue from the alcohol with the greater concentrations had the largest precipitation.

Glutamic acid hydrochloride was obtained from the residues of the 70 percent, 80 percent, and 90 percent alcoholic extraction. The



Figures 4 and 5

yield varies directly with the alcoholic concentration (see Figure 5).

From this series of tests, it was found that the more concentrated alcohol was the better solvent for the separation of betaine and potassium compounds and the compounds from which glutamic acid is hydrolyzed. The 90 percent alcohol gave the highest yield of glutamic acid hydrochloride. If the chief interest was betaine, 70 percent alcohol is the most satisfactory solvent because it gives a higher yield of betaine hydrochloride. There is very little variation in the total amount of potassium chloride obtained. It was all precipitated and recovered either from the alcoholic extract or from the insoluble residue.

A successful attempt was made to prepare glutamic acid from the alcohol insoluble residues by substituting heat and pressure generated in an autoclave rather than refluxing the material for twelve hours.

Two hundred and fifty grams of the insoluble material were used, the potassium chloride being precipitated with 150 cc. of concentrated hydrochloric acid, the crystals removed by filtration, and the filtrate heated in an autoclave (1) for three hours under a pressure of 50 to 60 pounds. After the autoclave had cooled the mixture was filtered to remove the carbon formed during hydrolysis, the filtrate decolorized with wood charcoal and concentrated. Potassium chloride and glutamic acid hydrochloride crystallized. These were separated by fractional crystallization from water.

It having been shown that glutamic acid could be prepared by heating the insoluble residue with concentrated hydrochloric acid under pressure, a series of ten portions of the insoluble residue were mixed with varying amounts of concentrated hydrochloric acid to determine the optimum amount of acid to be used for the hydrolysis of the glutamic acid compounds and produce a maximum yield of glutamic acid (see Table 2).

For 250 grams of waste in each test, the quantity of acid was varied by increments of 25 cc. from 125 cc. to 350 cc. There was not much variation in weight of the precipitated chlorides of potassium, calcium, etc., caused by adding the acid. Potassium chloride was leached out and recrystallized. The variations were not important.

The weight of each was taken before and after heating in an autoclave. The samples with the larger amount of acid lost more weight.

The variation of the weight of the carbon formed was unimportant.

Table No. II

| | NUMBER | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|----------------------------------|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Grams of insoluble residue..... | 250 | 250 | 250 | 250 | 250 | 250 | 250 | 250 | 250 | 250 | 250 |
| Acid used, c.c..... | 125 | 150 | 175 | 200 | 225 | 250 | 275 | 300 | 325 | 350 | 350 |
| Weight of ppt..... | 62 | 63 | 50 | 58 | 59 | 62 | 64 | 52 | 60 | 62 | 62 |
| Weight KCl..... | 27 | 33 | 26 | 28 | 30 | 31 | 32 | 29 | 28 | 31 | 31 |
| Weight insoluble..... | 35 | 30 | 24 | 30 | 29 | 31 | 32 | 23 | 32 | 31 | 31 |
| Weight before heating..... | 407 | 413 | 456 | 505 | 518 | 566 | 567 | 643 | 620 | 677 | 677 |
| Weight after heating..... | 400 | 402 | 435 | 477 | 486 | 523 | 525 | 600 | 555 | 620 | 620 |
| Loss in weight..... | 7 | 11 | 21 | 28 | 32 | 43 | 42 | 43 | 45 | 57 | 57 |
| Weight of carbon..... | 13 | 12 | 11 | 10 | 10 | 11 | 10 | 10 | 8 | 7 | 7 |
| Weight KCl..... | 13 | 12 | 13 | 14 | 11 | 13 | 14 | 11 | 13 | 12 | 12 |
| Total KCl..... | 40 | 45 | 39 | 43 | 41 | 44 | 46 | 40 | 41 | 43 | 43 |
| Glutamic acid hydrochloride..... | 0 | 9 | 17 | 19 | 24 | 23 | 19 | 17 | 15 | 14 | 14 |

The weight of potassium chloride from the crystallization and recrystallization of glutamic acid added to that obtained by the first precipitation gave the total potassium chloride which did not vary materially. The yield of glutamic acid hydrochloride was quite variable. No. 1 sample with 125 cc. of acid did not give glutamic acid. Samples number 5 and 6 which contained 225 and 250 cc. of acid respectively, produced the highest yield of the series.

The proportion of acid to insoluble material for the greatest amount of hydrolysis should be 1 to 1 or 1 gm. of insoluble matter to 1 cc. of concentrated hydrochloric acid.

SUMMARY

When Steffen's waste having a specific gravity of 1.012 was concentrated in a vacuum pan to 1.4 and the concentrate added to 60, 70, 80 and 90 percent alcohol, the amount of concentrate dissolved varied inversely with the percent of alcohol.

The amount of KCl obtained by precipitation from the alcoholic extract with HCl and the amount of betaine hydrochloride obtained by concentration of the filtrate from the KCl varied inversely with the percent of alcohol used.

The amount of glutamic acid obtained from the insoluble portion varied directly with the percent of alcohol used.

Glutamic acid was prepared by treating the insoluble portion with concentrated HCl, filtering, decolorizing, concentrating, and crystallization. The test in which 90 percent alcohol was used as a solvent gave the highest yield of glutamic acid; therefore it is considered the most satisfactory concentration for extraction.

Glutamic acid was prepared from the insoluble material by heating under pressure in an autoclave for three hours, and then treating the resulting mixture as in the previous method in order to produce glutamic acid.

A test made with a series of 10 portions of insoluble material and varying amounts of acid showed that the optimum amount of acid to use was in the proportion of 1 gram insoluble to 1 cc. of concentrated hydrochloric acid.

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