Production of By-Products of the Sugar Beet Industry

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Technical men outside of the sugar industry are apt to view the manufacture of sucrose from sugar beets as a most interesting and somewhat complex process. Those of us who are not sugar technologists are frequently astonished at the amount of knowledge that has been developed in that industry, at the smoothness of its operation, at the degree of operational standardizing which has taken place between competitors, and, finally, at the uniformity and purity of the product.

Presumably it is because those in the sugar industry have spcialized in producing the highest grade product at the lowest possible cost that such a degree of perfection has been attained. At any rate, the development of an extensive enterprise based on the treatment of the wastes of the sugar industry has in part been carried out by others. These waste products are the raw materials for a number of different manufacturing operations.

As an example, beet molasses is the raw material needed for the production of yeast and much of the citric acid produced in the United States. Sugar beet pulp has become a very useful part of the animal feed industry and even the beet tops now seem to be useful in the manufacture of a certain specialized animal food.

In the case of molasses the technical progress of the sugar technologists caught up with yeast and citric acid manufacturers through the steffenizing of molasses so that now there is competition for molasses by the producers of yeast and citric acid on the one hand and the Steffens plants on the other. We are advised that beet molasses is actually now being imported from Holland by the fermentation industries.

It remained, however, for one of the sugar producers, James E. Larrowe, to initiate the commercial production of by-products from Steffens waste. During the first World War, a number of the beet sugar plants, including a factory owned by Mr. Larrowe, produced a crude potash salt by concentrating Steffens waste and burning the concentrate. After the war, when potash production from this source was no longer profitable, it was noticed that even at temperatures of 30° below Fahrenheit zero the Steffens concentrate was still quite fluid. Detroit, even then, was the center of the motor car industry and Mr. Larrowe, as a fellow resident, knew many of the leaders in this field.

Drivers of automobiles were using their cars during the winter and a good, low freezing coolant competitive to alcohol and glycerine was greatly desired. At the request of an interested party, Mr. Larrowe had some of the

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concentrate packed in cans. This was sold for antifreeze. It turned out to be an excellent product from the standpoint of protection of the cooling system from freezing. However, it had a most questionable value in the field of repeat orders because within a short time the user found it necessary to order a new radiator and soon thereafter a new engine block. While it prevented freezing, it also corroded metal parts when it was diluted and heated. The story of this phase of development as told by Mr. Larrowe gave us many a pleasant moment.

Threatened with abatement proceedings against his sugar factories because the Steffens waste polluted the rivers, and still thinking that future use for this material might lie in the antifreeze field, Mr. Larrowe arranged for work to be carried out at the Mellon Institute on this problem. The material's glutamic acid content indicated that it might be a source of raw material for the production of monosodium glutamate and preliminary designs were made for a plant. Publication of this in a technical journal resulted eventually in a combination of the Larrowe interests with those of the Japanese firm of S. Suzuki and Company for the purpose of manufacturing monosodium glutamate, then being sold under the trade name of Ajino-moto.

Glutamic acid is a very interesting and peculiar chemical substance. It exists in three different chemical forms. These are the L and D isomers and the racemic mixture. The monosodium salt of the L or naturally occurring form has the property of bringing out flavors of substances to which it is added. Not all of these flavors are pleasant—it can and does intensify some of the poor ones as well as the good.

Originally it was made commercially from sea weed and then from wheat gluten. In the case of gluten it is liberated from the protein by hydrolysis effected by a mineral acid. Made from this raw material, it is quite difficult to purify. The non-amino acid products of the action of a mineral acid on a gluten containing some starch are extremely flavorsome and were not all removed by the methods then used for production of monosodium glutamate. Consequently, monosodium glutamate was credited with having a meat-like flavor, which when pure it does not possess.

Troubles beset the Larrowe-Susuki enterprise, mainly because of the corrosive nature of the reagents used in the process and the lack of knowledge as to the chemistry of the constituents of the Steffens waste water. As to the latter, we now know that the technical department of at least one large beet sugar company had developed through years of research a considerable amount of fundamental chemical knowledge on the constitutents of Steffens waste.

Commercial production of high purity monosodium glutamate from any raw material, although it may appear simple, is successfully carried out only by means of a complex and exacting process. Originally the precursor of glutamic acid in the sugar beet was thought to be a protein. Now it is pretty definitely known that it is glutamine and that this constitutes a means of storing nitrogen for later use by the beet in its metabolic process. Had research developed that fact at an earlier date, a large amount of money might have been saved.

Most of the glutamine in the sugar beet passes as such into the diffusion juice, and there it begins to decompose, forming ammonia and the internal anhydride of glutamic acid, pyrrolidone carboxylic acid. This reaction may go nearly to completion during lime defecation. Since pyrrolidone carboxylic acid is hydrolyzed to glutamic acid quite easily, and since this change is reversible, an equilibrium between the two can be established in any aqueous system, depending upon the conditions of temperature, pH and possibly the concentration of certain other constituents. Consequently, both glutamic acid and pyrrolidone carboxylic acid are usually present in Steffens wastes. However, because of the equilibrium conditions, there is a much higher proportion of the anhydride than glutamic acid.

In much of the earlier work described in the literature on Steffens waste, it apparently was not recognized that the waste as discharged from the filters was very unstable and subject to bacterial decomposition. Certainly it was not generally known at that time that most bacteria can and do use glutamic acid in their growth. Consequently, the results of some of the earlier work must be viewed with doubt because of the possibility of bacterial decomposition.

Since the precursor of glutamic acid in the Steffens solution is in reality its anhydride, pyrrolidone carboxylic acid, the change to glutamic acid is an hydrolysis in the true sense of the word. One molecule of water is added by the reaction. This accounts for the fact that the hydrolysis can be saitsfactorily carried out by either acid or alkali as the hydrolyzing agent. On the other hand, in the hydrolysis of proteins such as the cereal glutens, the use of an alkali as the hydrolytic agent invariably results in the production of the racemic form of the amino acids.

As pointed out above, glutamic acid exists in three chemical forms. The same is true of the monosodium salt. Only the L form, or natural isomer, is active as far as the property of flavor enhancement is concerned. There is no simple low cost method known by which the racemic mixture can be resolved and the L form separated from the D.

As previously stated, however, the hydrolytic change of pyrrolidone carboxylic acid to glutamic acid may be effected without racemization through the use of an alkali as well as an acid. The process originally developed by the Mellon Institute and used by Mr. Larrowe made use of hydrochloric acid as the hydrolyzing agent. Knowing with what great difficulty we handle this acid even today, we can well sympathize with the management of the plant who watched the equipment literally dissolve in the solution within a relatively few months. Professor Ikeda of the Suzuki technical staff developed a process using sulfuric acid instead of hydrochloric, but this presented difficulties which even today have not yet been entirely solved.

Throughout all of this early development period, there is no record of anyone having courage enough to doubt the then accepted idea that glutamic acid was present in the Steffens waste as a part of a protein. About the time the plant dissolved in the solutions being processed, Dr. Albert E. Marshall was employed as a consultant by Mr. Larrowe, and it was he who decided to attempt the hydrolysis with caustic soda. This is the basis of the

process now used by International Minerals and Chemical corporation in its plants at Rossford, Ohio, and San Jose, California.

The use of alkali, although much more satisfactory than acid from the standpoints of equipment and process, is not altogether free from difficulties because racemization of the L glutamic acid can be caused by treatment with alkali under certain conditions. However, this can be prevented and a nearly perfect hydrolysis attained through exact control of temperature, time, pH, and ratio of total alkali to the concentrated Steffens filtrate used.

Amino acids are complex and peculiar chemicals. Much too little is known of their chemical properties and particularly of their solubility relationships in aqueous solutions as influenced by the presence of other substances, both organic and inorganic. The sugar beet itself is a storehouse of miscellaneous organic compounds. After these have passed through the treatment given the diffusion juice in the production of sugar, including the Steffenizing and recycling operations, this raw material for the production of glutamic acid becomes a fearful and wonderful collection of variables. Many of the substances in the Steffens waste change and decompose into other interfering products during processing with alkalis, acids and heat.

In any chemical process the first care of the management is to do as much as possible to see that the raw materials are uniform. This has been the endeavor of beet sugar technologists working with the beet growers. Reduction of so-called "harmful nitrogen" and increase in purity of the beet have been and are a constant means towards this end.

Some problems which we encounter in the manufacture of monosodium glutamate are related directly to the methods used by the manufacturer of beet sugar to overcome his difficulties. Others are due to the unique characteristics of the glutamic acid itself.

First, an attempt to reduce the "harmful nitrogen" in the sugar beets may result in a reduction of the already small percentage of glutamine in the beet and consequently the glutamic acid in the Steffens liquor resulting from the processing of these beets. Dr. Hac and her co-workers at our Woodland, California, laboratory have shown that increasing the application of plant food nitrogen to the soil results in a large increase in the glutamine content of the beet, while the reduction in purity may be compensated for by a considerable increase in tons of sugar per acre.

Increased use of nitrogen fertilizers to build up a higher glutamic acid content in the beet itself does increase what is termed "harmful nitrogen." This has long been objectionable to sugar technologists. The sugar producer wants his sugar factory liquors as free from "harmful nitrogen" as possible. Conversely, the glutamic acid producer wants his starting material as high in glutamic acid as possible. Although these ideas have usually been considered incompatible, we now find different schools of thought on this subject, and there is some hope for the belief that the problem can eventually be solved to the mutual benefit of both parties.

Very laudably there is a free interchange of technical information among sugar technologists. This gave some reason for our perhaps rather naive

assumption that, within reasonable limits, the sugar content of the concentrated Steffens wastes produced by most factories would be as low as possible and fairly uniform. We installed large multiple effect evaporators in a number of Steffens plants and contracted to purchase the concentrated waste for a long period of years. Great was our surprise when analysis of the Steffens concentrate showed the sugar content to vary from about 5 per cent to as high as 18 per cent, based on 65 per cent solids in the concentrate. One producer sold us Steffens concentrate containing several thousand tons of sugar in one season. The sugar is a distinct detriment to us since it greatly lowers the extraction of glutamic acid by decreasing the concentration of glutamic acid in the concentrate and increasing the end liquor losses. It has sometimes seemed to us that the Steffens house is an orphan child at many sugar factories, for certainly many hundreds of thousands of tons of sugar have been wasted because this part of the sugar process is not always as well operated as the rest of the plant. There is some evidence that sugars in Steffens concentrate many result in the formation of substances which interfere with the extraction of the glutamic acid values. Research is in progress on this at the present time. Those of us who are concerned with returning values to you for the Steffen waste produced in sugar operations do respectfully invite your attention to the possibility of recovering more sugar from molasses by better operation in the Steffens house.

It is evident from the foregoing that the production of glutamic acid from Steffens waste water really begins with the molasses as it enters the desugaring process. In the future it may begin with the beet grower, but the research upon which this idea is based is not yet entirely complete.

In the production of monosodium glutamate, the thin Steffens liquor is carbonated as soon as produced and the calcium carbonate thereby precipitated is removed by thickening and filtration. It is then concentrated to about 65 percent solids in evaporators usually having five to six effects with one high concentrator. This concentration ratio is between twenty and twenty-five to one. The concentrate is run into storage tanks and shipped at intervals to our San Jose factory where it is blended with concentrate from other points and stored in seven large tanks, each of 1,500,000 gallons capacity. During storage some salts crystallize out. The term "waste," when applied to anything connected with beet sugar operations, is frequently associated with the foul smell which emanates from the cattle feeding lots using undried beet pulp. We have therefore chosen to call our raw material "Concentrated Steffens Filtrate" or "C.S.F."

Passing now into the process, the C.S.F. is first weighed and then filtered by an Oliver precoated filter to remove suspended solids. If concentration has not been carried far enough at the sugar plant, it is reconcentrated at this point but this is a step not usually needed. The filtered C.S.F. is then run into steel hydrolyzers where it is carefully mixed with a 50 percent solution of caustic soda. Careful control of the total alkali, temperature and time are required at this point to make sure the conversion of the pyrrolidone carboxylic acid is as complete as possible and that there is no racemization of the L glutamic acid.

Following hydrolysis, the liquid is cooled by a heat exchanger and partially acidified with hydrochloric acid. Automatic pH control insures proper processing in this step. The solution is then concentrated in a single effect flash-type evaporator. In this evaporator all parts in contact with the liquid and vapor up to the jet condenser are rubber lined with the exception of the heater and forced circulation pump. The outside heater and pump are made of type 316 stainless steel. The concentration results in the crystallization of mixed sodium and potassium chlorides containing about 30 percent K_2O. This is removed by means of Bird centrifugals.

After removal of the inorganic salts, the filtrate is further acidified, the pH being adjusted to 3.2, the isoelectric point of glutamic acid. The acidified solution is then cooled and run into large rubber-lined crystallizers. The crystallizing of the glutamic acid is a slow process requiring from five to eight days. When this step is finished, the crystals are separated by centrifugals operating at a speed somewhat higher than that usually used in the centrifuging of sugar. The filtrate is the end liquor from the process and is either processed for production of betaine or is discarded.

The crude glutamic acid is then purified, dissolved in a solution of caustic soda, decolorized, concentrated and finally crystallized in La Feuille crystallizers. The monosodium glutamate crystals are separated by centrifuging, dried, screened, and packed. The mother liquor is reboiled several times for additional crystals, the final mother liquor being returned to the process.

The purity of the product exceeds 99 per cent. Impurities consist mostly of exceedingly small quantities of sodium chloride and aspartic acid.

Corrosion is an exceptionally difficult problem throughout the process after the hydrolysis step. A mixture of mineral acid, especially hydrochloric, with glutamic acid will act on all but a few metals.

Any possibility of noxious fumes from the plant is avoided by venting all tanks and reaction vessels into a fume collecting and treating system. The fumes are passed through an alkaline scrubbing system and then vented to the boiler stack.

Although glutamic acid is currently the most valuable substance recoverable from Steffens filtrate, there are also other constituents which deserve consideration. The most conspicuous among these is betaine, a methylated derivative of glycine. Betaine has long been known to occur in beet juices in greater abundance, on the average, than any individual component of the so-called "harmful nitrogen" group, although in exceptional cases it ranks second to glutamic acid. Betaine is highly soluble, relatively inactive chemically, and practically none of it is removed *in* the normal sugar purification processes but is carried through the sugar factory into the molasses and into the Steffens filtrate.

Among beets from different sources, the betaine content appears to be much more uniform and constant than is the case with glutamic acid. Molasses usually contains approximately 4 to 5%, while 8 to 10% is normally found in concentrated Steffens filtrate.

The isolation and recovery of betaine from crude raw materials is based upon the fact that its hydrochloride has a low solubility in strong hydrochloric acid. When aqueous solutions containing betaine in appropriate concentration are strongly acidified with hydrochloric acid, betaine hydrochloride is deposited in crystalline form. The yield and purity depend upon the original concentration of betaine and upon the nature and quantity of associated substances present in the starting solution. Concentrated Steffens filtrate can be used satisfactorily as a raw material for the isolation and recovery of betaine hydrochloride by this method. Other source materials from which betaine is similarly recoverable are the concentrated residues from the alcoholic fermentation of beet molasses and the waste liquor resulting from the processing of concentrated Steffens filtrate for the recovery of glutamic acid.

Several expired patents, including those of Tressler (1), Ikeda (2), and Takayama (3) have disclosed various modifications of procedure based upon recovery of betaine, as the hydrochloride, from these types of raw materials. A relatively recent patent of Bennett (4) teaches the processing of thin Steffens waste water by means of ion exchange resins to recover the nitrogenous constituents in concentrated form, thereby providing an appropriate starting material for betaine production. It also discloses an alcohol extraction process applied to concentrated Steffens filtrate, followed by an ion exchange purification of the extracted betaine.

When betaine hydrochloride is precipitated from beet waste liquors with strong hydrochloric acid, it is usually contaminated with sodium and potassium chlorides. The precipitate may also contain glutamic acid hydrochloride if a substantial amount of this amino acid was present in the starting material. One method of purifying the betaine hydrochloride is to extract it with hot. alcohol, from which it may be crystallized on cooling. Another consists of dissolving the crude product in hot water, decolorizing with carbon, concentrating and recrystallizing the hot solution.

Betaine, itself, as the monohydrate, can be prepared from the hydrochloride by any of several different methods. One consists of extraction with hot alcohol, after neutralization of the hydrochloride. Another involves heating with sulfuric acid to drive off the chloride, followed by precipitation of the sulfate with calcium or barium. Also, the hydrochloric acid may be removed by passing a solution of betaine hydrochloride through an anion exchange resin. In view of the extraordinary hydroscopicity of the betaine monohydrate, it is preferably stored and dispensed in the form of its hydrochloride, rather than as the monohydrate.

Potentially the quantity of betaine recoverable from waste beet liquors is obviously very great. So far, however, the market demand is relatively small. Betaine can be used successfully as a starting material for the preparation of dimethylamine and trimethylamine, and for methyl-chloride, but apparently it does not compete successfully with other and more economical materials available for such purposes.

Several patents have been issued covering the use of betaine acid chloride as a starting point for derivatives, of which some are claimed to have useful properties as surface active agents, fungicides, insecticides, corrosion in-

hibitors, textile improvers, and as solubilizers for various dyes and pharmacologically active compounds. There is no evidence known to us that these derivatives are actually used commercially to an extent involving large tonnages. It is possible, of course, that they are utilized industrially to a much greater degree than is generally realized, but that the betaine is made synthetically instead of being recovered from natural sources.

Medicinal preparations of betaine hydrochloride under the name of "Acidol" have for many years been used for administration to persons troubled with insufficient gastric acidity, and various other minor pharmaceutical uses have been noted.

Betaine is apparently non-toxic, and although formerly regarded as physiologically "inert" more recent findings indicate that it functions usefully as a methylating agent in metabolic processes. The presence of labile methyl groups for transmethylation purposes is now regarded as of nutritional importance equal to that of vitamins and other essential dietary constituents which cannot ordinarily be synthesized in the body but must be supplied in food. Reactions involving transmethylation are particularly essential to the proper functioning of the liver and kidney. Although methionine and choline were at first considered to be the exclusive transmethylating agents it has since been reliably established that betaine can also serve effectively as a methyl donor, and that it can act as a capable substitute for either methionine or choline insofar as the function of transmethylation is concerned.

Several investigators have reported that betaine is especially effective as a supplement in poultry feeding, and that for certain types of rations (those of plant origin) it has a higher supplementary value than either choline or methionine. A possible explanation for this is offered by Dubnoff (5) who presented experimental evidence to the effect that choline must be oxidized to betaine before its methyl groups can become labile and thereby available for transmethylation purposes. This oxidation is accomplished by a choline oxidase enzyme, and Dubnoff's studies indicate that choline is effective only in those animals which have choline oxidase. Since the chick is one of several species said to be lacking in the enzyme which transfers choline to betaine a plausible explanation for the superior supplementary value of betaine in poultry rations is afforded. If there is adequate verification of the concept that choline can function as a methyl donor in metabolic process only after conversion to betaine, it is certain that betaine will assume a status of greatly increased importance as a nutritional factor.

The value of betaine as a methylating agent may well have implications extending far beyond its use as a supplement in poultry feeding. These include alleviation of pathological conditions such as fatty degeneration of the liver and arteriosclerosis. For these and related conditions, administration of choline has shown promising results, according to recent clinical reports, and there is basis for supposing that betaine may also fit into this picture.

Realization of the possible importance of betaine in nutrition and in

medicine is of such comparatively recent origin that much further investigation is required before its full status can be fully understood. It seems possible that the use of betaine as a dietary supplement in poultry feeding may eventually become a leading factor in creating a substantially enlarged market for this by-product of the sugar beet industry.

In addition to glutamic acid, several other amino acids are known to occur in lesser and in varying quantities in beet juice as members of the class of substances which the beet technologists designate as "harmful nitrogen" compounds. The more conspicuous members of this group are aspartic acid, tyrosine, leucine and isoleucine. These amino acids can be recovered from concentrated Steffens nitrate but the method for their isolation in reasonably pure form is extremely laborious, time consuming and costly. There is currently no evidence of any market demand for them at a price commensurate with the cost of their recovery. The "leucine fraction," as isolated from concentrated Steffens filtrate, is unique in that *isoleucine* constitues 50% or more of the total. This is probably the highest ratio of isoleucine to leucine which is encountered in any known biological substance.

Concentrated Steffens filtrate ordinarily contains approximately 14% of non-nitrogenous organic acids based on the weight of its total solids, with varying ratios of volatile and non-volatile acids. Acetic acid constitutes the greater portion of the volatile fraction. These acids are largely of short chain length, being those which escaped precipitation during lime defaction treatment. No commercial value which would justify the recovering of these organic acids has yet become apparent.

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