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INDUSTRIAL CHEMICALS FROM INDIGENOUS CARBOHYDRATE RAW MATERIALS (SUCRO-BASED CHEMICALS)

ST/PHI/81/001

PHILIPPINES

Technical Report*

01 October - 30 November 1985

Prepared for the Government of the Philippines
by the United Nations Industrial Development Organization,
acting as the executing agency for United Nations Development Programme

Based on the work of Jiri Kominek,
Consultant in Citric Acid Production by Submerged
Fermentation based on Sucrose

United Nations Industrial Development Organization
Vienna

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1. INTRODUCTION

The aim of the "Sucro-based Chemicals Project" is the application of the by-products and/or wastes of the sugar-cane industry as raw materials for fermentation industry.

The consultant was required to advise on sub-project B: "Integrated Citric Acid Project" whose aim is to develop an up-to-date and economic technology for citric acid production. Other particulars of the project are given below:

Location:	National Institute of Science and Technology, Pedro Gil-Street, Ermita, Metro Manila, The Philippines
Project Director:	Dr. Filemon A. Uriarte, JR., NIST
Project Co-ordinator:	Dr. Lydia M. Joson, NIST
Project Leader:	Dr. Natividad D. Palo, NIST
Assistant Project Leader Sub-project A:	Mr. Romeo Cabacang, NIST
Duration of consultancy:	2 months 1 October to 30 November 1985

The citric acid is the most versatile and widely used food acidulant. It is used as a flavour enhancer, a perservative, an antioxidant and as salt and salt/acid mixture for the purpose of regulating the pH.

In 1984 the demand for citric acid in the Philippines was 1800 metric tons, which is expected to rise by about 140 tons/year. The entire amount of citric acid has to be imported.

The Philippines sugar industry produces approx. 2.8 million tons of sugar and approx. 0.8 million tons of molasses per year.

These products as well as the "sweet water" (which is the liquid by-product from sugar production containing 18-20% sugar) are interesting raw materials for fermentation.

The sweet water is not transportable, because it is easily contaminated, but if the citric acid plant is integrated in a sugar mill, there should be no problem to bring the hot sweet water into the citric acid plant.

In its letter of intent of 16 January 1985 to the National Institute of Science and Technology (NIST), the Victorias Milling Company Inc. of Negros Occidental accepted the NIST citric acid technology on condition that a pilot plant would be installed in the sugar mill and that the development of this plant would be carried out by NIST.

The consultancy was divided into four parts:

- Evaluation of the Citric Acid Plant Process;

- Assistance in the design, construction and operation of the Citric Acid Pilot Plant;

- Recommendation of process changes, and

- Lectures on Fermentation Engineering, Process Plant Design and Operation.

2. EVALUATION OF THE CITRIC ACID PILOT PLANT PROCESS

The great problem in the projection of the citric acid plant from pilot plant to the large scale Plant is:

1. scale up
2. The fact that not all technology steps can or must be simulated in the small plant.

Citric Acid Process

a) Fermentation:

NIST has developed a submerged citric acid fermentation method according to SHU and Johnson. Duration of fermentation was 7 - 10 days. The yields approx. 80 % (0,8 conversion sugar to citric acid), refined cane sugar has been used and copper as inhibitor, batch process. This process took place in 2 l and 14 l stirred glass fermenters. The steel quality of the baffles, agitator, sparger and cooler is unknown (in the documentation of Brunswick the specification of the steel quality is missed).

The submerged citric acid fermentation can be carried out in rather simple tower fermenters. s.c. bubble column reactor.

The tower fermenter shows simple construction and easy handling. The tower fermenter has no movable parts, and, therefore, low maintenance costs will arise accompanied by comparatively low investment cost. The only disadvantage is the higher quality of air that will be needed for aeration, as the effectiveness of oxygen utilization is normally not very high in a tower ferm. The fermenter is normally equipped with a simple sprinkling cooling, usually divided into two or three sections and can be regulated individually according to the fermentation heat evolved and the temperature of the cooling water.

In tropical countries with high relative humidity difficulties with cooling water do arise (high wert bulb temperature. In this case it is necessary to use chilled water.
Advantageouser as batch process is a fed batch fermentation. The principle of this process is that a part of the sugar solution is diluted with water in the fermenter to give about 50 - 60 % of the total working volume. The procedure has the advantage that the fungus is not confronted with the high sugar concentration and osmotic pressure at the beginning of the fermentation, and, therefore will grow much faster; this results in a shorter overall fermentation time.
The tower fermenters are suitable for the laboratory and pilot plant as well as production plant.

The production and pilot plant fermenters have not to be sterilized under pressure, but merely by steam at 130° C at 2,5 bar, before the expansion. The highest temperature in the fermenter is approx. 98° C. Absolute sterility is not necessary, because the citric acid fermentation is to some extent autosterile due to the low pH-value. Only during the first stages of the fermentation, when the spores are germinating and the pH is in the range of 4 to 6, there is some danger of infection. The steaming under atmospheric pressure allows that the thickness of the fermenter wall not exceeds 5 - 6 mm in case of 150 m^3 fermenter volume.
The material of the fermenter suitable for the citric acid production must be at least AISI 316 or better (316L, 316Ti).

For the Philippines I can recommend the submerged fed batch fermentation, tower fermenters, chilled water as cooling water, if cane sugar molasses or sweet water will be used. In case of decationised refined cane sugar it is of advantage to use the tower fermenters but batch fermentation.

Strain Choice, Strain Preservation, and Improvement

Not each strain of aspergillus niger is suitable for the citric acid production, not each strain is improvable.
NIST works with more strains. Partly they are proper isolates, partly they are the foreign strains.

The foreign strain a. niger 72 - 4 has given good results in 2 l and 14 l stirred fermenters. The conversion after 7 - 10 days was up to 0,8 at the refined cane sugar concentration of 16 % W./V.
UV mutant of a. niger 72 - 4 has produced 20 % more citric acid than parent strain. The result could not be reproduced. I presume in this case the connection with the steel quality in the fermenters. The working range between iron and inhibitor is too small and the success borders on the accident. Indeed it is the reality, but for the industrial use it is not sufficient reliable.

NIST isolation and screening methods of a. niger are all right, the preservation and the industrial increase (production of spores), were discussed with Messrs. Dr. Jonson and Staff.

The Recovery of Citric Acid

After the removing of mycelium the citric acid is precipited as unsoluble calcium salt by lime. NIST explored the conditions of the precipitation according to the quantity. By this step also the quality of the citrate was important.
The conditions in the precipitation as temperature, low pH, and the time are presuppositions for a high quality (measured as "The Concentrated Sulfuric Acid Easy Carbonizable Substances".) The pH over 5,0 to 5,2 is not only senseless, but brings the bad quality of citrate. The losses of 3,0 to 3,5 in the precipitation are unavoidable (Solubility of citrate in the slops). The 97,11 % yields reported by NIST in the precipitation are real.

The Purification of Citric Acid

An up-to-date technology works in the decomposition of calcium citrate with higher concentration of citrate and sulfuric acid. It does not work by diluted (50 % V/V, like NIST), but by concentrated sulfuric acid. The reaction is exothermic and cooling is necessary to avoid the formation of calcium sulfate semihydrate.
The citric acid concentration after the decomposition is 220 % W/V and more. With sulfuric/acid excess of 0,2 - 0,5 W/V will be calculated. The citric acid after the removing of gypsum must be decolorized and purified. Now it will be done by activated carbon or absorption resins and by cation and anion exchange.
Preferred is the granulated a-carbon and the chemical regeneration by 5 % W/V caustic soda. After a certain time of thermic regeneration the anorganic impurities will be removed by cation and anion exchange. The old method with Potassiumferrocyanide (iron removing) and Bariumcarbonate (sulfate removing) has historical signification.

Evaporation and Crystallization

2.000 mt/year is a small plant and it is possible to crystallize citric acid either by the atmospheric pressure or in vacuum. In both cases it is necessary to evaporate up the thin citric acid solution to the concentration of 40 - 45° Bé (approx. 800 gm citric acid/litre). Continuous crystallization in vacuum is not interesting.

NIST is not in the position to estimate all parameters for a crystallization, and also it is not necessary. The know-how for the evaporation and crystallization will be delivered by firms, which construct the vacuum evaporators and crystallizers (SVENSON, LURGI, ESCHER WYSS a.s.o.).

Messrs. Dr. JONSON and staff and Messrs. PALO are in the position to achieve a good deal of chemical and microbiological work.

3. ASSISTANCE IN THE DESIGN, CONSTRUCTION AND OPERATION OF THE CITRIC PILOT PLANT

The existing Pilot Plant on paper
with 200 litres stirred fermenters with antifoam centrifuge and illumination insiae of the fermenter.

1. More and more tower fermenters are used nowadays for the Citric Acid-Fermentation (Miles, USA, 80.000 mt/year, Gadot, Israel, 20.000 mt/y, Jungbunzlauer Austria, 35.000 mt/year).
   The costs and maintenance of agitator and antifoam centrifuge are high, the danger of infection from sealing medium is given, the baffles are necessary.

2. The foam formation period is very short (only some hours), an antifoamoil is sufficient.

3. The optical supervision in dark and aerated solutions in Situ is not possible and not necessary. The lighting is normally on the top and outside of the fermenter. The looking glass can be cleaned by steam or mechanically by wiper. First of all iron can be brought into the fermenter or other impurities, in the second case there is danger of infection by the straight-way-valve.
   In co-operation with Mr. Romeo Cabacang I have discussed all technological steps of citric acid production, and I recommended to construct and investigate only 3 steps:

   1. The Fermentation
   2. The Precipitation of citric acid
   3. The Decomposition of Calcium Citrate

4. RECOMMENDATION OF PROCESS CHANGES

1. Instead of batch, a fed batch fermentation is to investigate.

2. Do not use stirred, but tower fermenters without foam centrifuge, with trickle film cooling.

3. Regulate precipitation of citric acid to obtain a very pure citrate

4. Decomposition of calcium citrate by concentrated sulfuric acid

5. To use granulated active carbon or better decolorized resins.

6. If necessary to produce the Pharmacopoe quality, use ion exchange or a second crystallization.

7. Do not crystallize the mother liquor but bring back the same into the purification.

8. Don't investigate the steps which cannot be simulated on a small scale.

5. LECTURES ON FERMENTATION ENGINEERING, PROCESS PLANT DESIGN, AND OPERATION

Following was realized during discussions and experiments in the laboratory:

Particularly:
- Analytical methods - for example determination of demand of Potassium Hexacyanofferrate of molasses
- determination of surplus of Potassium-Hexacyanoferrate in the molasses
- Determination of iron in range from 0,002 to 0,1 ppm
- Microbiological methods e.g. strain preservation,
- selection of a niger by means of surface cultures,
- culture mediums suitable for the surface cultures or deep fermentation
- production of spores on the large scale,
- the morphology of a niger during the deep fermentation a.s.o.

6. RECOMMENDATIONS

Resulting from my experience I like to recommend as follows:

- to execute in future fermentation trial in the fermenters with sufficient steel quality (AISI 316, 316 L or 316 Ti).

- Use of the high performance a. niger-strains is absulutely necessary.

- Concerning the instrumentation of the Pilot Plant it is not necessary to send a consultant.
  I shall send the specifications of the instrumentation and the Philippines specialists shall decide, whether the information is sufficient.

- For the NIST-members should be of interest the operation in the fermentation Pilot Plant (tower fermenter 70 l) at the Technical University in Vienna).
  I like to call your attention to
  Mr. RÖHR,
  Ordinarius of Institute of Biological Technology and Microbiology
  as specialist of the theory and modeling of fermentation especially originate and regulation of Citric Acid by a.niger.