OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

RESTRICTED

1641

24 July 1987
ENGLISH

PILOT PLANT PRODUCTION OF CITRIC ACID

ST/PHI/85/010

Technical report: Consulting for the Design and Instrumentation of Citric Acid Pilot Plant

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

By: Di Jiri Kominek,
UNIDO Consultant

United Nations Industrial Development Organization
Vienna

This document has been reproduced without formal editing.

TABLE OF CONTENTS

	Page
General Information	1
Introduction	2
Stage of the Citric Acid Pilot Plant Project	2
Recommendations	3
Citric Acid Fermentations	7
Working Programme, 1987, Time Schedule	9
Commentary to the Working Programme	10

GENERAL INFORMATION

1.	Project Title	Pilot Plant Production of Citric Acid
2.	Project location	National Institute of Science and Technology (NIST), Ermita, Pedro Gil St., Manila, Philippines NIST, Bicutan, Tagung, Manila, Philippines
3.	Project coordinator	Dr. Lydia M. Joson
4.	Project leadeer	Mrs. Natividad D. Palo
5.	Assistant Project Leaders:	
	Recovery of citric acid	Mr. Erwin Casareno
	Design and Engineering	Mr. Romeo Cabacang

ORGANIC ACIDS FERMENTATION STAFF

Leader:	Mrs. Natividad D. Palo	Pharmacologist
	Mrs. Cynthia P. Madrid	Chemist
	Mrs. Rosemary M. Gutierrez	Biologist
	Mrs. Blauquita B. de Guzman	Biologist
	Mr. Viracion Martin	Chemist
	Mr. Romeo Cabacang	Chemist
	Mr. Erwin Casereno	Chemist
	Mr. Francis Perita	Chemist
	Mr. Vic. Custodio	Not grad.
	Mr. Melchor Valdecanas	Mach. Eng.

INTRODUCTION

This is a Report on a two months visit made to the National Institute of Science and TEchnology (NIST), Ermita, Pedro Gil St. and Bicutan, Tagung, Metro Manila, Philippines, between February 10 and April 7, 1987

The visit was undertaken to assist in the design and instrumentation of CITRIC ACID PILOT PLANT EQUIPMENT, in the selection of imported equipment and auxiliaries, in the instrumentation of the CITRIC ACID PILOT PLANT and in the practice of small scale citric acid and other fermentations (laboratory fermenters, net volume 9 litres).

Stage of development of the CITRIC ACID PILOT PLANT PROJECT:

In a building of 350 m^2 (20 x 17,5 m) in Bicutan the following utilities are at the project's disposal: steam, water (of drinking quality) and electricity. The maximum temperature of the water is lower than 24°C, hence is usable as cooling water also.

The electric mains are unreliable and an emergency generator is considered essential. The Citric Acid Pilot Plant is projected as a transportable assemblage, consisting of three frame constructions. One of them is ready, but the vessel and instruments are still missing. It appears that the earlier difficulties at the procuring of the deep dished heads for the fermenters and other vessels have been overcome.

The project instrumentation (Measuring and Control Equipment) is an assembly of laboratory instruments, which are not appropriate. Each unit contains the probe, transmitter, regulator, indicator and recorder. The plant is provided with 22 measuring and control circuits, and thereby 22 recorders.

Only four, six-channel compensating recorders are necessary. Local mounting of these instruments is not advised. The accurate and expensive instruments should be mounted in one or two boxes away from the Pilot Plant.

RECOMMENDATIONS

Fermentation Part:

- three fermenters each 200 litres net volume
- one fermenter with agitator, two fermenters type tower fermenter, bubble column (without agitator)
- instrumentation per fermenter
- temperature indication, control, registration

probe 2 x Pt 100	for ex. Siemens
transmitter	for ex. H&B
regulator	for ex. H&B
indicator	for ex. Siemens
two solenoid valves	
1. channel of the multi- channel printing recorder	for ex. JUMO

Temperature compensation by Pt 100
pH-indication, registration

pH electrode	Ingold
transmitter	for ex. H&B
indicator	for ex. Siemens
2 channel of the multi-channel printing recorder	for ex. Jumo

PO2-indication registration

PO2 electrode (polakogr.)	Ingold
transmitter	Ingold
indicator	integrated in transmitter
channel of the multi chan. printing recorder	for ex Jumo

indication, registration

CO_2 analyzer, indication, registration

analyzer	for ex. Unor GN by Maihak
indication	integrated in the analyzer

4. channel of the multi-chan. printing rec. f.e. Jumo

O_2 analyzer, indication, registration

analyzer	for ex. Oxygor GN by Maihak
indication	integrated in the analyzer

5. channel of the multi chan. printing reg. for ex. Jumo

moisture reducing

automatic condensate separator e.g. [illegible] 07 AB by Maihak

Changer for the CO_2 and O_2 analyzer for ex. Maihak

The both last instruments are useful for all fermenters.

The instrumentation can be mounted in an air-conditioned box.

In a second box the measuring and control instruments of the isolation and purification could be accommodated:

- Precipitation of Citric Acid and Decomposition of Calcium Citrate (the same vessel can be used for both processes).

- Temperature indication, control and registration

probe	e.g. Siemens
transmitter	e.g. H&B
regulator, 2 outputs	e.g. H&B
indicator	e.g. Siemens
two solenoid valves	e.g. Gemü

1. channel of the multi-channel printing reg. JUMO

- pH indication, control, registration

pH-electrode	e.g. Ingold
transmitter	e.g. H&B
regulator, 1 output	e.g. H&B
indicator	Siemens
one solenoid valve	Gemü

2. channel of the multi-printing recorder e.g. JUMO

Conductivity indication, control, registration:

probe e.g. Siemens, Foxboro
transmitter)
regulator) integrated e.g. Siemens Foxboro
indicator)
two solenoid valves e.g. Demü
3. channel of the multi-chan. printing registr. Jumo

2. Drying of Citric Acid:

2.1 Temperature indication, control (register)

probe PT 100 e.g. Siemens
transmitter e.g. H&B
regulator e.g. H&B
relay (electr. heating) e.g. Siemens

The vacuum and the pressure can be measured locally by means of vacuo- and manometer. Registration is not necessary.

The boxes and the air conditioning for the boxes
from e.g. Rittal

The best pH and pO2 electrode, in my opinion, is from Ingold. The transmitters and regulators from Hartmann and Braun or Siemens and Jumo instruments are the praiseworthest combination at a high quality. I only know the European products and the European assembling firms, but I am not so well informed about the American instruments such as Honeywell and Foxboro.
It is enough to define the measuring and control circuits, to give the ranges of valves to know the preferred products and to order it at the assembling firm.
Example: the temperature indication, control and recording in the fermenter.

Temperature range 0 - 60°C

Feeler 2 x Pt 100 (temp. control and temp. compensation of pH measuring)
straight for low pressure.
length 100 mm, material of the covering of AISI 316 Ti (W. No. 1.4571)
Special completion of fixing in the Ingold 15° special holder (order number 007641014).

Note: The range from 0°C to 60°C is suitable for the fermentation (40 - 45°C at the time of inoculation. 28 - 35°C is the working temperature). During the sterilization(approx. 100°C), the circuit is disconnected.

transmitter	the distance feeler/transm. abt. 0 m
regualtor	two outputs (two solenoid valves will be set in motion. max. current each mA)
indicator	scale 0 - 20 mA resp. 0 - 60°C profile form, 96 x 24, accuracy class 1.5, built-in instrument,

all instruments are plug-in units

Registration 1 channel of a 6 channel compensating register (writer)

Preferred firms:		
	feeler	Siemens
	transmitter	H&B
	regulator	H&B
	indicator	Siemens
	special holder	Ingold
	register	Jumo

according to decision.

Duties: The temperature controller regulates the temperature in the fermenter by means of steam/hotwater and coldwater. The temperature must be adjustable in the range from 28 to 45°C. An indication and registration is necessary. Panel mounting in 19" module is desired.

Citric Acid Fermentation

Two fermenters, each 14 litres total volume are at disposal. Both fermenters are products of New Brunswick, New Jersey, U.S.A. Type Microferm. The material certificate is missing.
At the beginning of fermentations we had difficulties with the growth of mycelium. but it could not be prevented. The following are possible causes:
- too low inhibition
- dissolving of fermenter
- metal parts in the broth
- the quality of molasses
- the effect of the precipitation of the molasses formed during the cleaning of the mould.

The antifoam oil is a problem for fermentation.
Molasses comes from the Sugar Mill in Don Pedro. The HCF requirement (it is the amount of potassium hexacyanoferrate which must be added to the formation of excess of free HCF before fermentation) is very high, 16 g/kg molasses (normally the requirement is approximately 1,5 - 6,0 g/kg and 200 ppm HCF excess).

A further sample of the molasses also comes from the Sugar Mill Don Pedro and is brought to the same requirement.
In Future it will be necessary to choose the molasses by test in the Pilot Plant before purchasing.
Trouble preventing with the precipitation can be done by settling, filtration or centrifugation of molasses after the cleaning.

For initial molasses solution the clean Supernatant is used at the producduction plant and the precipitation comes afterwards as feeding to the fermentation. The setting free of iron is a heavy disadvantage of the fermentation plant. The most important requirement is high-quality steel for the fermenter. Material No. 1.4571 (AISI 316 T, DIN x 10 CrNi Mo Ti 1810) is recommended.

Both the small New Brunswick fermenters (first fermenter has a designation Model 38170, M 1014-7260, the designation of the second fermenter could not be identified) were passivated by means of approximately 5% sulfuric and nitric acid and the iron was determined.

The determination of iron as Fe^{3+} was made by a photometric method by means of potassium sulfocyanide. A more sensitive method suitable for the concentrations from 0.01 to 4 ppm was the determination of iron as Fe^{2} + by 1,10 phenanthroline. The phenanthroline and the method do not exist in Manila, but will be sent for the next expert's mission.

The first fermenter (M 1014-7260) is apparently in order. The second fermenter was not in order and the trial must be repeated. Note: In the first fermenter the use of clean molasses (without presipitation) led to success, but this was not repeated in the second).

The suspect corn oil (antifoam agent) was successful substituted by 5% octadecanol in paraffin oil.

In future it will be necessary to use a mixture of corn oil, paraffin oil, and octadecanol. Should the last mentioned ingredient be cheap and available in the Philippines, the use of lard oil becomes conceivable and has to be tested as well as the other oils as coconut or palm oil.

Inportant Issues

1. Establish suitable quality of the fermenter material for citric acid fermentation.
2. Good molasses with low requirement on HCF is necessary.
3. The optimization, or better the reducing, of nutrients is to be planned.
4. The aspergillus niger strain has to be selected.
5. For the homogeneity of the spores the processing of a monospore-culture and constant conditions during the propagation period are important.
6. A practice of each single member of the staff at an institute for technical microbiology, fermentology and event. at an engineering company would be profitable.

WORKING PROGRAMME 1987

THE SCHEDULE

MONTHS:

1. Improvement of fermentation technology
   - a) strain improvement — 1 - 3 4 - 6 7 - 9 10 - 12
   - b) optimization of parameters for the production of citric acid
   - c) recovery and purification of citric acid

2. Pilot plant production
   - a) fabrication of local equipment
   - b) installation of equipment
   - c) preliminary run
   - d) operating

3. Training of engineers and technologists in design, construction and operating of Citric Acid — 1 - 3 4 - 6

4. **Consultant visits**
   - a) J. Kominek — 2 - 3
   - b) A. Celineo — 2 - 3
   - c) M. Röhr

5. Construction of the Pilot Plant building — 1 - 4

COMMENTARY TO THE TIME SCHEDULE

To point 1:

Letter a) the strain improvement is an uninterrupted work, and it is necessary to use only tested spores.
In this case Prof. RÖHR in Vienna with one and another of the citric acid team can also help, Mrs. Cynthia, Madrid is provided.

Letter b) Conditional correction; the parameters are mostly dependent on the plant (e.g. the aeration is dependent on the fermenter geometry). The optimization of the process must be done at the beginning after each change of the plant or with each scale-up or scale-down.

Letter c) Recovery of Citric acid as difficult soluble calcium citrate.
It is necessary to purify the raw Citric Acid solution before evaporation and crystallization.
There exist 2 kinds of purification: - the old clasical method (iron/potassium ferrocyanide, sulfate/barium salt)
and - the ion exchange;

the last method is easier and it is not necessary to use the extreme toxic barium compound.
The decolourizing of citric acid solution is done by means of granulated active carbon in the column or as powder, or by resin.
The granulated active carbon and the ion exchange resins are not available in the Philippines. For removing of active carbon powder of the solution one needs a vacuum filter (and a vacuum plant) and this filter is to be imported too.

To Point 2:

Letter a) When the plant is constructed, three fermenters are considered. If this plant is planned for citric acid fermentations, only the tower fermenters without agitator (bubble column) are used.

It appears that in a low viscose system, when using equal total power input per unit volume, a bubble column fermenter provides equal liquid mixing, mass and heat transfer, compared with a stirred fermenter. The advantage of a bubble column is a simple construction, easy handling no movable parts and therefore low maintenance-investment costs.

Very important is the stainless steel quality; preferably it is used material No. 1.4571 or 1.4586 (DINx10 CrNi Mo Ti 1810 and DINx5 Ni Cr Mo Cu Hb 2218). Only the stainless steel material No. 1.4571 has an American equivalent, which is AISI 316 Ti.

Letter b) The plant will be mounted in three frame constructions of steel. These frames are relatively narrow. In this cases will be put the measuring and control instruments and unfavourably too (hydrochloric acid vapours, steam sprinkling water, hot termperature a.s.o.).
A separated mounting of these instruments in an integrated unit is of no use.

Letter c) The following measures are very important before start-up:

- cleaning of the plant inside and outside
- water test, leak proof test, function test (piping, pumps)
- instruments test
- water running of the whole plant.

Letter d) Putting to work and training of technologists in the process.

To point 3: Training of engineers and technologist in design- and construction of citric acid plant should be practicable in Vienna at VOGELBUSCH GES.M.B.H. (in accordance with the management of VOGELBUSCH). The training of technologist is also possible at Prof. Max. RÖHR, Vienna.

To point 4:

Letter a) I am ready to come, but not before the Pilot-Plant is ready for operating (finished). I can put the plant into operation, conduct the training and technologists and help in the scale-up.
Letter b) and c) cannot be commented myself.
Training and practice of any members of the citric acid staff outside of Philippines.

Programme proposal for the training of technical microbiologists at the Technical University in Vienna.

Programme proposal for the designer of the pilot plant:

Note: In this case please contact VOGELBUSCH GES.M.B.H.,
1050 Wien, Blechturmgasse 11.
Austria.
According to my information, VOGELBUSCH is ready to receive the training of a designer of the Pilot-Plant:

e.g. - practice in the projetion of the fermentation-plant
and
- lay-out of the Plant a.s.o.
- choice of the suppliers
- price calculation.

Should this trial plant meet the requirement of technique and Infrastructure, you can be sure that the start-up is in 1988.
At scale-up problems help is necessary.

S U M M A R Y

The efforts of NIST, the assistance of experts, and the financial support of UNIDO,built the foundation for the basis Know-how to produce citric acid in the industrial scale.
The national requirement of citric acid is approx 2.000 metric tons per year.
At present only a small plant with a capacity of 3.000 metric tons/year is planned.
According to sugar industry (especially Victorias Milling, discussed during my visit 1985), it does not exclude the erection of a plant with a capacity of 10.000 m.t./year.
As raw material blackstrap molasses, sweet water, raw or refined sugar is recommended. By the scaling-up it must be helped.

Supposing that the Pilot-plant conforms with the stand of technique, start-up will become realistic at the beginning of next year.

PRELIMINARY PROGRAMME FOR THE TECHNOLOGISTS

(RECOVERY AND PURIFICATION OF CITRIC ACID)

1. The Removing of Mycelium

1.1 Filtration of fermentation liquor by means of filter aid and without filter aid

2. Precipitation of Citric Acid as Calcium Citrate

2.1 Model Trials

2.1.1 With and without addition of Alkali Ions

2.1.2 Effect of Temperature on the Quality of Citrate

2.1.3 Effect of Time on the Quality of Citrate

2.1.4 Crystal Structure of Precipitation

2.1.5 Purity of Calcium Citrate

2.2. Trials with Fermentation Liquor

2.2.1 - 4 See 2.1.1 - 3

3. Decomposition of Calcium Citrate by Sulphuric Acid

3.1 Determination of the End Point of the Decomposition of Calcium Citrate by Menas of Conductivity Measurement

3.2 Determination of Sulphuric Acid Express in System Citric Acid, Sulphuric Acid, Calcium Sulphate, Water

4. Ion Exchange and Decolourizing of Crude Citric Acid Liquor

4.1 Cation Exchange

4.2 Anion Exchange

4.3 Decolourizing by REsin

4.4 Decolourizing by Granulated and Pulverized Acitve Carbon

4.4.1 Determination of the absorption Activity of Active Carbon

4.5 Estimation of the quality of the Citric Acid Liquor after Ion Exchange and Decolourizing

5. Effect of the Crystallization on the Quality of Citric Acid Distribution of the Impurities in two crystalls and Mother Liquor

THE PROGRAMME PROPOSAL FOR THE

MICROBIOLOGIST FERMENTOLOGIST

(AT N I S T)

1. The Genus Aspergilus

1.1 Characters

1.2 Habitus (description and morphology)

1.3 Cultivation (culture media, conditions of cultivations, isolation techniques, removal of induvidual spore)

2. Aspergillus niger

2.1 Characters

2.2 Habitus

2.3 Selection ability to the citric acid fermentation

2.4 Propagation of high efficient spores

2.5 Preservation and storage of cultures and spores

2.6 Security precautions for the handling with spores

2.7 Physical health injurities

3. Laboratoy course

3.1 Microscopic technique

3.2 Fermentation

3.2.1 Aeration of the mash (oxygen transfer and K, a value) in the stirred fermenter and in the bubble column)

3.2.2 Spent air analyse (CO2, O2)

3.3 Handling and keeping of pH and PO2 sterisable electrodes.