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

FAIR USE POLICY

CONTACT

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

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

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

15724

July 1986

RESTRICTED

ENGLISH

INDUSTRIAL CHEMICALS FROM INDIGENOUS CARBOHYDRATE

RAW MATERIALS (SUCRO-BASED CHEMICALS)

ST/PHI/81/001

PHILIPPINES

Technical Report*

Mission 2-20 March 1984

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

Based on the work of Mohammed Y. Yassein
consultant in fermentation technologies

United Nations Industrial Development Organization
Vienna

* This document has been reproduced without formal editing.

325

CONTENTS

1. INTRODUCTION

The consultancy was carried out on behalf of UNIDO, to evaluate work being done and to facilitate progress towards pilot plant scaling-up, and exploitation at a commercial scale. The consultancy involved briefing and debriefing at UNIDO Headquarters in Vienna and field work at UPLB in Manila. The duration of the consultancy was nine working days. The state of the sub-project C, in terms of results obtained and the attitude and technical competence of the staff involved, was assessed. Laboratory procedures and techniques used for the production and fermentation technology of simple organic chemicals are described.

The project was evaluated in terms of the technical performance of the individual project and assessed in terms of programme controls, inputs and outputs. The programme, while in its infancy, can be considered relevant to the establishment of a sucrochemical industry in the Philippines in so far as it will achieve the following objectives:

1.1 Lessen the country's dependence on imported petrochemicals;
1.2 Intensify the search for producing these products from renewable sources;
1.3 Encourage and promote foreign exchange earnings;
1.4 Generate employment opportunities;
1.5 Increase the value of agricultural products and by-products;
1.6 Promote the development of agro-based industries and technical co-operation among developing countries (TCDC) in this field;
1.7 Presence of abundant by-products and wastes of the sugar cane industry and other fermentable raw materials;
1.8 Identify a selection of chemical products from indigenous sources through microbiological processes;
1.9 Assess the technical and economic feasibility of existing processes for the production of the selected chemicals;
1.10 Develop manpower for science and technology;
1.11 Infrastructure improvement.
1.12 Enhance the national capability by training scientists and engineers.

1/13 Promote TCDC through appropriate twinning arrangements.

1/14 Promote investment for the production of sucro-based chemicals.

For the above reasons, the government of the Philippines attaches high priority to the project.

The project is headed by a project Director with a coordinating staff, having its office at the NSTA. The staff are :

Project Director : Ms.Lydia G.Tansinsin

Coordinating staff: Ms. Teresita M. Valdez
Ms. Hermelina H.Bion
Ms.Isabelita H.Lino.
Ms.Alice A. Bustamante

The project consists of four sub-projects, two of which contain four studies (project-A and project-C) and are being undertaken at the University of the Philippines at Los Banos and the other two at the NIST. The four sub-projects are :

Sub-project- A : Single-cell protein (SCP) production from Agro-Industrial By-products and Residues (UPLB).

Sub-Project-B : Production of Dextran and Fructose(NIST).

Sub-project-C : Biotechnological production of Simple Organic Chemicals (UPLB).

Sub-project-D : Improvement in the Microbiological Production of Complex Organic Acids, in particular Citric Acid, Gluconic Acid and Itaconic Acid (NIST).

This technical report concerns an assessment of the sub-project-C" Biotechnological production of Simple Organic Chemicals". (University of the Philippines at Los Banos).

Project Leader : Dr. Carlito R. Barril

Study 1 : Development of Continuous-Flow Fermentation for Ethanol production.

Study Leader : Dr. Ernesto J. Del Rosario

Study 2 : Ressessment of the Acetone-Butanol Fermentation process.

Study Leader : Dr. William G. Padolina.

Study 3 : Improvement of Acetic Acid Fermentation process

Study Leader : Dr. Ann Maureen Ramirez.

Study 4 : Polyhydric Alcohols from Saccharine Materials.

Study Leader : Prof. Conchita A. Orillo.

2- SCHEDULE OF ACTIVITIES

2/1 VIENNA :

Briefing and debriefing with Dr. M. Maung, Industrial Operations Division, and administrative staff at UNIDO headquarters.

2/2 MANILA :

On the first day March 5, 1984, a meeting with Dr. C. R. Barril, Project Leader of the sucro-based project took place. During this meeting, an extensive review of sub-project-C was given by him. All the studies were visited and progress and problems encountered were discussed. The staff was given a range of experiments and tasks to carry out, all associated with the sub-project-C. The objective of this was two fold . Firstly, it would be used for an improvement of the technical capability of the researchers. Secondly, it exposed them to the range of techniques and experiments required for a successful research program on the production of simple organic chemicals. The execution of each experiment was carefully supervised and talks on practical and theoretical aspects of simple organic chemicals production were given on an individual basis while the work was going on.

On March 9 . courtesy call to Dr. Emil Q. Javier , Director-General of NSTA, who is also the Chancellor of UPLB. He would greatly appreciate any assistance which can be provided in terms of obtaining information from the Egyptian Government on the transfer of the Egyptian technology and experience in the commercial operation of an integrated sucro-chemical solvent plant, and particularly for acetone, butanol, ethanol, acetic acid, ethyl acetate, butyl acetate, yeast and thinner. On the same day visit to BIOTECH. and

IRRI were payed. The consultancy involved two seminars; one at BIOTECH; and the other at the Institute of Chemistry. On March 16, preliminary discussion at NSTA, Bicutan with Ms. Lydia Tansinsin National Project Director. Ms. Tansinsin welcomed the technical co-operation among devleoping countries and the transfer of the Egyptian technology and experience to the Philippines. Also there was a courtesy call to Dr. Quintin L. Kintanar, Deputy Director-General NSTA. On March 19, return to Vienna.

3 - PREVIOUS WORK

The simple organic chemicals studied within the Sucro-based Chemicals project were acetone, butanol, ethanol, acetic acid and polyhydric alcohols. The simple organic chemicals were produced either aerobically or anaerobically. Various strains(all known producers) had been tested. Promising results were obtained on a laboratory scale.

3.1 Equipment

Fermentation equipment and distillation apparatus is not available. It was found that the laboratory was lacking in glassware, chemicals and other equipment. The lack of equipment, supplies and materials was considered as one of the major problems encountered by the project research staff. These problems must be tackled if the project is going to be seriously considered for scale up to pilot plant and production scale.

Project staff confirmed that arrangements have been made to get the necessary equipment.

3.2 General impression

All staff involved in fermentation research were also given a general lecture on fermenter design and operation. The staff involved in the sucro-based chemicals were technically competent.

The staff currently engaged in the production of simple organic chemicals will be responsible on different activities such as:

3.2.1. Isolation, identification, purification, selection and maintenance of local strains to be used in the production of simple organic chemicals from different biological sources, because the most promising results have been obtained with locally developed strains.

3.2.2. Evaluation of the optimum environmental conditions (medium, temperature, incubation period, ect.) of the different cultures used for the production of the simple organic chemicals.

3.2.3 Development of a process for the recovery and purification of strains.

3.2.4 Evaluation of suitable raw materials and substrates.

3.2.5 Use of standard mutation technique, U.V., X-ray and mutating agents.

3/2/6 Effect of medium constituents; i.e.

3/2/6/1 Optimum sugar concentration.

3/2/6/2/ Optimum nitrogen (organic and inorganic) source and its concentration.

3/2/6/3 Optimum initial pH.

3/2/6/4 Optimum size of inoculum.

3/2/6/5 Optimum temperature.

3/2/7 Determination of the residual sugar and the concentration of products in the fermented worts.

3/2/8 Raw material storage and preparation.

3/2/9 Investigation on effect of successive transfer.

3/2/10 Scaling up of production to the pilot plant level

3/2/11 Determination of other production requirements for fermatation.

3/2/12 To conduct physical and chemical characterization of simple organic chemicals.

3/2/13 To conduct economic feasibility studies on the process developed for the production of simple organic chemicals.

3/3 <u>Technical Cooperation among Development Countries(TCDC)</u>

If this project is to be scaled up to production stage, high producing strains must be developed. Most of those are available locally. Molasses and rice bran are by far the most common cheaper raw materials for industrial production of simple organic chemicals. Funds should be made available to carry out the fermentation under standard environmental conditions.

Acetic acid can be produced by fermentation of dilute alcohol mashes through 24-36 hours using the Frigns Acetator which is highly aereated. It is used to produce vinegar containing 10-12% acetic acid. The major problems encountered during the production of this product at UPLB were:

3/3/1 Shortage of vital equipments.

3/3/2 Unavailability of butyl acetate.

3/3/3 The administrative and technical support for the study is insufficient.

3/3/4 Technical services are almost nil.

3/3/5 There are some aspects of the study that are not within the technical ability of the workers.

Also it is noticed that, the production cost of one liter of solvent (2:1 butanol-acetone) is too high-about $ 29.00. It was pointed out that their estimated production cost is very high compared to produchin obtained by the Egyptian plant. Low rate of production will greatly increase the costs, but the low production yield arose also from the poor efficiency of technical processes. This could be improved in various ways, including

the transfer of the Egyptian technology and experience to Philippine. A major indirect benefit of the transfer of the Egyptian technology and experience in the commercial operation of an integrated plant for production of simple organic chemicals has been the development of a scientific research training capability at Los Banos. Egypt and Philippines have similar conditions in terms of resources and experience in the commercial operation of an integrated plant for the production of acetone, butanol, ethanol acetic acid, ethyl acetate, butyl acetate, yeast and thinner will be no major problem. Philippines can obtain the know-how and plant designs as well as take over testing from Egypt for the production of acetone, butanol,ethanol,acetic acid, ethyl acetate, butyl acetate,,yeast and thinner from molasses and rice bran by fermentation. We in Egypt would certainly welcome this within the frame of technical cooperation among developing countries (TCDC).

Egypt and Philippines have an abundant supply of these carbohydrate and protein raw materials which may be obtained from the sugar and rice industries. These raw materials can be converted in different fermenting plants to industrial chemicals.

4. Pilot Plant

A severe lack of experience in fermentation technology was observed caused by the absence of a small pilot plant, although, this is of signigicant importance for a successful outcome of the project. It is proposed to design a small pilot plant of 1000 L capacity including all glasswares, chemicals and equipments which were all set aside for the sub-project-C during the consultancy.

The pilot plant must be supllied with the necessary utilities such as steam, water, electricity, compressed air etc., and must allow a full range of studies as follows:

4/1 Test process under realistic conditions, and its optimisation.

4/2 Supply quantities of material for test.

4/3 Carry out economic and engineering studies.

4/4 Develop a team skilled in general plant oepration.

and in the development of microbiological processes if large scale is aimed at.

The time period required for the design, procurement and construction of the pilot facility is estimated to take a minimum of six months. Start-up of the pilot plant is anticipated to occur in early 1985; so it should be possible to confirm the viability of the process within six months to one year from start-up, i.e. by the end of 1985 or early 1986.

The water used for the preparation of the pilot plant mashes must be potable i.e. clear, colourless, odourless, bacteriologically clean and without sediments of suspended particles. It must be as much as possible free of chlorine and other compounds which will damage microorganisms and calcium and copper ions.

The operation of a pilot plant usually requires a skilled team of workers and outside help could well be sought. Assistance is required to train a group of workers in plant operation and to build up an experienced team of workers in the bacteriological-fermentation area.

The workers have produced a useful assessment of the project. Project appraisal and discussion on the proposed restructuring and scale-up of the industrial fermentation programme took place on a number of occasions. Also some of the nutritional requirements had been worked out, leading to media which favour simple organic chemicals production. It is hoped to work on a larger scale in the near future after the results of experiments from the pilot plant scale will be obtained.

5. PROJECT ACHIEVEMENTS AND CONSTRAINTS

Considerable progress has been made in streamlining the laboratory procedures and techniques used for the production of simple organic chemical solvents as mentioned before.

5.1 Acetone - Butanol production:

5.1.1 The experimental work performed to date was limited to some screening studies.

5.1.2 Preliminary tests were performed with four strains (three obtained from Dr. C.T. Calam, and the fourth from MIT) an one substrate, molasses.

5/1/3 Many investigations included heat shock, incubation period and incubation temperature.

5/1/4 Some data were obtained by using gas-liquid chromatography. These data should be treated with caution because the gas-liquid chromatography gives a rough idea on the concentration in the solvents only.

5/2 Acetic Acid production

5/2/1 Various local and imported strains of Acetobacter were tested

5/2/2 A local bacteria isolate was also tested.

5/2/3 Vinegar starter cultures, from NIST and from an ethanol substrate

5/2/4 Test results have been erratic and inconsistant.

5/2/5 There has been very little work performed towards the production of glacial acetic acid.

5/2/6 Laboratory scale extractions with ethyl acetate were reported. The extraction step is considered not to present any serious difficulties.

5/2/7 The azeotropic distillation step has not been attempted yet because of the unavailability of butyl acetate.

5.3 Ethyl Alcohol Production

The project has fully achieved its specific goals within the scope of the UNFSSTD programme.

6. RESULTS

The results of the technical consultancy evaluations are:

The efficiency of project activities, organization and execution was evaluated and relevance and effectiveness of project outputs were assessed.

The programme was evaluated in terms of infrastructure development, potential socio-economic impact in the Philippines and recommendations for future actions.

Information was shared on the commercial operation of the Egyptian integrated simple organic chemicals and fermentation plant for ketones, alcohols and esters of acetic acid, using molasses and rice-bran.

Plans for a larger scale plant were discussed.

It was agreed that the value added products enhanced the project.

Methods were suggested for isolation and purification of micro-organisms used in the production of simple organic chemicals.

Advice was given on how to obtain higher - yielding strains, capable of converting molasses to simple organic chemicals at a higher rate.

Shortcomings were discussed in detail to provide a basis for future assistance, if required.

It appeared that specific tasks which require skills and experience were not available locally within the programme.

Information was given on a number of practical points, such as the suitable time for heat shock, and other modifications, also on ways to improve asepsis and working conditions generally, also on the storage of cultures.

The development of a scientific infrastructure for the conduction of microbiological research, and the establishment of awareness of potentials for converting products and by-products of the sugarcane industry into locally viable, industrial organic chemicals was discussed.

Methods for isolating micro-organisms producing simple organic chemicals were investigated.

7. RECOMMENDATIONS

7.1 More expert consultancy would be very helpful for the entire programme.

7.2 It is necessary to set up a small pilot plant 1 m^3 capacity to gain valuable experience in the production of simple organic chemicals and also through fermentation and to study its industrial scale operation.

7.3 Further research, training and transfer of experience in the areas of microbiology and process research are still required.

7.4 The equipment is presently lacking for performing laboratory experiments with recycling of the main process stream. So the necessary equipment needed for the process research studies should be acquired as soon as possible.

7.5 A programme of staff seminars and discussion groups should be implemented. This would not only build up the confidence of the researchers, but would also improve project planning.

7.6 There is an urgent need for better experimental designs, performance goals definition, product specification and description, as well as project planning and implementation.

7.7 Cheaper raw materials for substrates should be identified.

7.8 Development of a commercially viable production process for simple organic chemicals requires a different mix of skills and training than the current investigators have who are principally interested in microbiology.

7.9 The preparation of sound feasibility studies should be given priority.

7.10 A temperature controlled area (25°C) should be provided for the incubators so that the working temperature during the growth of culture is 32-33°C.

7.11 One day excess is given to the fermentation period to ensure that enough time is given for the micro-organisms to act on the substrate.

7.12 A number of strains must be tested on the plant, possibly with minor modifications to medium and inoculum preparation, so as to find one modification to medium and inoculum preparation, so as to find one capable of reaching the desired production level.

7.13 Laboratory work must be extended to the isolation of new strains from different sources so as to provide a basis for plant tests.

7.14 A plant house should be built to cultivate beans and other legumes on samples of soil.

7.15 The inoculation of cultures must be done under completely aseptic conditions.

7.16 The fermenters should be of high quality stainless steel, with mirror finish inside, to facilitate cleaning after fermentation.

7.17 Laboratory tests should be extended to include tests under adverse or subcptimal conditions and in the pilot plant trials are also desirable, and it is usually necessary to pick out strains for plant use which sho good results under these conditions. The testing may take a long time, until good strains are obtained, but there is no means of avoiding this.

7.18 The strains are very sensitive to variation of conditions hence a wide range should be tested in the plant; once a good strain is found, it must be carefully retained and preserved in soil culture for future use.

7.19 The procedure used at Los Baños is adequate, though it is preferable to use the inoculating room with double doors and sterilized by the ultraviolet lamps to give high efficiency to culture work and to provide a better margin of safety against infection.

7.20 Further process research studies are necessary to optimize the fermentation synthesis conditions with the strains developed.

7.21 The concentration of the solvents can be determined by distillation of the broth, and titrated it against sodium thiosulphate and barium hydroxide to obtain the amount of acetone and butanol respectively. The gas-liquid chromatography is mainly used to make sure that the selected strains were actually producing acetone and butanol. A rough idea of teh concentration of solvents could be obtained from the height of the peaks.

7.22 It should be possible to produce glacial actic acid if ethyl acetate can be obtained easily and butyl acetate on a large scale by establishing an esterification unit to produce ethyl and butyl acetate from ethanol production, butanol (produced from acetone-butanol fermentation production) and acetic acid (produced from acetic acid fermentation production), i.e., all chemicals are produced locally.

7.23 The air used in acetic acid production was not of the kind recommended. It has severe lack in sterility, affecting seriously the production of acetic acid. In addition to this, there had been a series of power failures, and no satisfactory air pumps are available.

7.24 The staff need to gain practical experience with the technology of industrial fermentation under commercial operation, therefore mutual visits between the workers of Chemical Factories Hawamdia, Egypt and the staff of sub-project C is recommended to enhance the entire fermenter operations.

7.25 The transfer of Egyptian technology, experience and know-how should be taken into consideration by the Government of the Philippines as soon as possible to accelerate the follow-up of the project.