UNIVERSITI PUTRA MALAYSIA

CONTINUOUS PRODUCTION OF ORGANIC ACIDS FROM PALM OIL MILL EFFLUENT AND KITCHEN GARBAGE

PHANG LAI YEE

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By

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Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in the Faculty of Food Science and Biotechnology Universiti Putra Malaysia

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Specially dedicated to,

My beloved parents, sisters, friends
and Kum Cheng,

For their invaluable love, sacrifices,

and wishing me all the best……….

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman: Associate Professor Dr. Mohd. Ali Hassan

Faculty: Food Science and Biotechnology

Waste materials such as palm oil mill effluent (POME) and kitchen garbage or refuse can be used as raw materials for organic acids production. In this study, POME and blended kitchen garbage were separately fed continuously into an anaerobic fermentation system in which they were converted to organic acids namely acetic, propionic, butyric and lactic acids, depending on the experimental conditions and type of microorganisms involved in the anaerobic treatment.

The effect of two types of neutralizer, $CaCO_3$ and NaOH, on anaerobic treatment of POME was examined. The POME treatment was stabilized at pH5.0-5.5 when $CaCO_3$ was used to adjust the pH. Subsequently, anaerobic treatment of POME was performed at pH 5.0–5.5 with sludge recycle system. The major organic acids produced were acetic (5.0-5.6 g/L), propionic (2.0-2.6 g/L) and butyric acids (2.3-3.3 g/L). Higher amount of butyric acid (average 2.8 g/L) was produced at pH 5.0. The sludge solids in the treated POME were separated by freezing-thawing technique and recycled into the reactor. More than 87% of the suspended solids in the treated POME were removed by this method. However, the clarified solution

still contained more than 20,000 mg/L of total solids. Total microbial population stabilized at 10^8 cfu/mL in the reactor but reduced to 10^6 cfu/mL in the dewatered sludge upon freezing and thawing. The organic acids were fractionated to obtain more concentrated organic acids (22.4 g/L).

In the case of kitchen garbage, *Lactobacillus rhamnosus* converted the carbohydrates to lactic acid with more than 87% selectivity. Glucoamylase with the activity of 60 U/mg was added during the fermentation at a dosage of 300 mg/L to enhance the hydrolysis of organic materials. Three sets of experimental conditions were studied, i.e. at pH 6.8 with RT 5 days, pH 5.5 with RT 5 days and pH 5.5 with RT 2.5 days which produced an average lactic acid concentration of 42 g/L, 53 g/L and 50 g/L respectively. The residual glucose and total sugars at steady state were less than 1 g/L and 20 g/L respectively. The optical purity of L-lactic acid obtained was more than 90% under the optimum condition of pH 5.5 with RT 2.5 days.

Abstrak thesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

PENGHASILAN ASID ORGANIK SECARA BERTERUSAN DARI EFLUEN KILANG KELAPA SAWIT DAN BAHAN BUANGAN DAPUR

Oleh

PHANG LAI YEE

Febuari 2001

Pengerusi: **Profesor Madya Dr. Mohd. Ali Hassan**

Fakulti: **Sains Makanan dan Bioteknologi**

Bahan sisa seperti efluen kilang kelapa sawit (POME) dan sisa makanan dari dapur boleh menjadi bahan mentah untuk penghasilan asik organik. Dalam kajian ini, POME dan sisa makanan dari dapur yang telah dihancurkan disuapkan secara berterusan ke dalam sistem anaerobik di mana bahan sisa tersebut ditukar kepada asid organik seperti asid asetik, propionik, butirik dan laktik, bergantung kepada keadaan ujikaji dan jenis mikroorganisma yang terlibat dalam rawatan anaerobik tersebut.

Kesan bahan penimbal ($CaCO_3$ dan NaOH) terhadap rawatan anaerobik POME telah dikaji. Rawatan POME mencapai kestabilan pada pH 5.0-5.5 apabila $CaCO_3$ digunakan untuk mengawal pH. Seterusnya, rawatan POME dijalankan pada pH 5.0-5.5 dengan sistem kitar semula sisa enapcemar. Asid organik utama yang dihasilkan ialah asid asetik (5.0-5.6 g/L), propionik (2.0-2.6 g/L) dan butirik (2.3-3.3 g/L). Jumlah asid butirik yang dihasilkan pada pH 5.0 adalah lebih tinggi, iaitu 2.8 g/L (purata). Pepejal sisa enapcemar dipisahkan dari POME terawat dengan

mengguna teknik penyejukbekuan diikuti oleh pencairan. Teknik ini telah dapat memisahkan lebih daripada 87% bahan terampai dari POME yang dirawat. Walau bagaimanapun, larutan cairan masih mengandungi lebih daripada 20,000 mg/L bahan pepejal. Populasi mikroorganisma dalam reaktor mencapai kestabilan pada 10^8 unit koloni terbentuk/mL tetapi populasi mikroorganisma dalam sisa enapcemar (untuk dikitar semula) menurun ke 10^6 unit koloni terbentuk/mL selepas penyejukbekuan dan pencairan. Pembahagian asid organik dilakukan untuk memekatkan asid organik kepada 22.4 g/L.

Untuk sisa makanan dari dapur, *Lactobacillus rhamnosus* menukarkan karbohidrat dalam sisa dapur kepada asid laktik dengan daya pemilihan melebihi 87%. Glukoamilase yang berkepekatan 300mg/L digunakan semasa fermentasi untuk menggalakkan penguraian bahan organik. Tiga keadaan ujikaji telah dijalankan semasa fermentasi itu pada pH 6.8 dengan 5 hari masa tahanan, pH 5.5 dengan masa tahanan 5 hari dan pH 5.5 dengan 2.5 hari masa tahanan. Kepekatan purata asid laktik masing-masing ialah 42 g/L, 53 g/L dan 50 g/L. Baki kandungan glukosa dan jumlah gula adalah kurang daripada 1 g/L dan 20 g/L masing-masing. Ketulenan optikal L-asid laktik yang dicapai melebihi 90% pada keadaan optima, iaitu pada pH 5.5 dengan masa tahanan 2.5 hari.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

AN	-	Ammoniacal nitrogen
BOD	-	Biological oxygen demand
C/N	-	Carbon to nitrogen ratio
$CaCO_3$	-	Calcium carbonate
CMA	-	Calcium magnesium acetate
COD	-	Chemical oxygen demand
COD/N	-	Chemical oxygen demand to nitrogen ratio
COD/P	-	Chemical oxygen demand to phosphorus ratio
CODsol	-	Soluble chemical oxygen demand
CODtot	-	Total chemical oxygen demand
D	-	Dilution rate
D(-)-LDH	-	D(-)-lactate dehydrogenase
HPLC	-	High performance liquid chromatography
HRT	-	Hyraulic retention time
I	-	Iodide
MeI	-	Methyl iodide
MeOH	-	Methanol
NaOH	-	Sodium hydroxide
NH_4OH	-	Ammonium hydroxide
POME	-	Palm oil mill effluent
Rh	-	Rhodium
RT	-	Retention time
SRT	-	Solid retention time

SS	-	Suspended solids
TKN	-	Total Kjeldahl nitrogen
TN	-	Total nitrogen
TS	-	Total solids
t_d	-	Doubling time
VS	-	Volatile solids
μ	-	Specific growth rate

CHAPTER I

INTRODUCTION

Anaerobic treatment process has long been popular in the wastewater treatment field. However, it has been mainly employed to stabilize the suspended organic material and to provide a source of energy. Accordingly, large amount of literature materials exists on the anaerobic digestion, most of it dealing with the overall rate-limiting methanogenic phase. Less attention has been paid to the acid phase, the process by which waste particulates are solubilized and fermented to volatile acids.

It was reported that the volatile fatty acids (VFA's) produced during anaerobic digestion of sludge have ten times commercial value than the methane produced subsequently (Jones, 1986). Volatile fatty acids such as acetic acid, lactic acid, propionic acid and higher acids could be used as chemical feedstocks. Besides, petroleum-based feedstocks have reached such high prices that interest is increasing in the bioconversion of renewable materials to replace fossil raw materials as a source of the oxychemicals feedstocks production, such as acetic acid. Thus, controlled biochemical production has attractive economic incentives associated with it.

Acetic acid is one such compound that is used extensively as an intermediate in manufacturing vinyl acetate, cellulose acetate, dimethyl terephthalate, chloroacetic acid and various acetate esters. Demand for acetic acid is forecast to increase nearly 2% per annum to 4.2 billion pounds in the year 2004, valued at $ 1.1 billion (USADATA, 2000). A newer industrial use of acetic acid is to produce acetate deicers, including calcium magnesium acetate (CMA) as a noncorrosive road deicer (Huang, 1998) and potassium acetate and sodium acetate as airport runway deicers. These acetate deicers are environmentally friendly.

There is also increased interest in lactic acid production due to its wide range of application areas (food, pharmaceutical, plastic, textile industry, etc). As an example, biodegradable plastics made of poly(lactic) acid have the potential to greatly expand the market for lactic acid due to the environmental issue of plastic wastes disposal.

In wastewater treatment applications, these soluble organic products from acidogenic activity can be used as energy and carbon sources for microorganisms carrying out other processes, such as biological phosphorus removal or 2-stage biological nitrogen removal (Barnard, 1983).

Waste materials generally require treatment before being discharged to the environment. This is mainly due to its polluting characteristic, i.e. high BOD value. The BOD can be a good source of raw material for biological processes if optimum operation conditions are applied. Utilization of waste materials in fermentation process is based on the concept of resource recovery and utilization while still achieving the objective of pollution control. Hence, it can be expected that producing organic acids such as acetic acid and lactic acid by the fermentation of palm oil mill effluent and kitchen garbage or refuse will become commercially attractive.

Palm oil mill effluent (POME) has been known as the most highly polluting agro-waste in Malaysia. Rapid growth and development of palm oil industry in Malaysia has at the same time led to the production of tremendous amount of wastes. POME with its high BOD value (20,000-30,000mg/L) is commonly treated by anaerobic ponding system and open tank digesters which normally require long residence times in excess of 20 days. Recently, our research group has studied the feasibility of integrating organic acids production from POME within its conventional wastewater treatment system as part of a zero emission system for the palm oil mill (NorAini *et al.*, 1999).

Kitchen garbage or refuse is another organic substance that can be subjected to biological treatment for organic acids production, particularly for lactic acid production under controlled conditions. Kitchen garbage is a food-based material that contains carbohydrates, proteins and lipids. These compounds are essential for the growth of microorganisms to synthesize desired products. In the developed countries such as Japan, segregation of wastes according to different criteria e.g. combustible and non-combustible material, recyclable materials (bottle, cans, newsprint and paper), has been adopted in the whole country. Kitchen refuse is classified as combustible material which is usually subjected to incineration. However, owing to the environmental pollution problem, again appropriate method of handling this organic waste has to be developed.