

**CHEMICAL OXYGEN DEMAND (COD) REDUCTION EFFICIENCY AND
KINETIC EVALUATION OF ANAEROBIC DIGESTION PROCESS OF PALM
OIL MILL EFFLUENT (POME) IN ANAEROBIC BENCH SCALE REACTOR
(ABSR)**

WONG YEE SHIAN

UNIVERSITI SAINS MALAYSIA

2007

**CHEMICAL OXYGEN DEMAND (COD) REDUCTION EFFICIENCY AND
KINETIC EVALUATION OF ANAEROBIC DIGESTION PROCESS OF PALM
OIL MILL EFFLUENT (POME) IN ANAEROBIC BENCH SCALE REACTOR
(ABSR)**

by

WONG YEE SHIAN

**Thesis submitted in fulfillment of
the requirements for the degree
of Master of Science**

November 2007

ACKNOWLEDGEMENTS

With great honor, I wish to express my sincere appreciation to my main supervisor, Prof. Mohd. Omar AB. Kadir for his excellent, patient guidance, infinite suggestions and help throughout this research work. I am also very grateful to my co-supervisor, Dr. Norli Ismail for her valuable guidance, advice and comments to complete this thesis.

I would also like to show my gratitude to the Dean of School of Industrial Technology for the support and research facilities available in the school. The financial support by USM Graduate Assistant allowance is gratefully appreciated. I would like to wish thanks to the administrative staff and technicians in the school for their valuable help. Sincere thanks are also extended to all the lab assistants of the Environmental Technology division especially En. Sadali and En. Fadzli for their assistance in handling the equipment in the laboratory. Special mention is due to MALPOM Industries SDN BHD for allowing me to collect the POME wastewater. I also would like to record my gratitude to Ms Shalima, Ms Ling Yu Lang, Ms Hazana, Ms Ang Paik Imm, Mdm Asyirah, Ms Kavita, Mr Azizi Che Yunus, Mdm Harlina and others for their support and encouragement.

Last but not least, I also would like to express my deepest gratitude to my parents, Mr Wong Kok Bing and Madam See Cheng Luan for their unconditional love, patience, understanding and support through the study.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	i
TABLE OF CONTENTS	ii
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF PLATES	xi
LIST OF SYMBOLS	xii
LIST OF ABBREVIATION	xiii
ABSTRAK	xiv
ABSTRACT	xvi
CHAPTER ONE: INTRODUCTION	
1.1 Introduction	1
1.2 Statement of Problem	4
1.3 Objectives of Study	7
1.4 Scope of the Study	7
1.5 Organization of the Thesis	9
CHAPTER TWO: LITERATURE REVIEW	
2.1 Palm Oil Industry in Malaysia	11
2.1.1 History and Development of Palm Oil Industry	11
2.1.2 Standard Wet Mill Process and Generation of Residues of Oil Palm	12
2.1.3 Palm Oil Mill Effluent (POME)	16
2.2 Palm Oil Mill Effluent Wastewater Treatment	17
2.2.1 Pond Treatment System	17
2.2.2 Anaerobic ponds	18
2.2.3 Facultative Ponds	19
2.2.4 Aerated Ponds	20

2.3 Anaerobic Digestion Process	22
2.3.1.0 Acidogenic bacteria	24
2.3.1.1 Methanogenic bacteria	25
2.3.1.2 Hydrogen Producing Acidogenic Bacteria	26
2.3.2 Factor influencing anaerobic digestion process	29
2.3.2.1 Effect of pH variations	29
2.3.2.2 Effect of temperature	30
2.3.2.3 Effect of hydraulic retention time	31
2.3.2.4 Effect of solids retention time	31
2.3.2.5 Effect of organic loading rate	32
2.3.2.6 Effect of toxic materials	32
2.3.2.7 Effect of food to microorganism ratio	33
2.3.2.8 Effect of nutrients addition	33
2.4 Bio-Kinetic model development	34
2.4.1 Formulation of model	34
2.4.1.1 Mass balance	35
2.4.1.2 Rate equation	38
CHAPTER THREE: MATERIAL AND METHODOLOGY	
3.1 Wastewater Source	40
3.1.1 Wastewater Sampling and Characterization	40
3.2 Experimental Set-up	41
3.2.1 Bench-Scale System Configuration	41
3.2.2 ABSR Sampling Procedure	42
3.3 ABSR Operation	42
3.3.1 Acclimatization of ABSR	42

3.3.2 Performance Study of ABSR	43
3.3.3 Determination of kinetic Coefficients	44
3.4 Analysis of Sample	45
3.4.1 pH and Temperature	45
3.4.2 Total solids (TS)	45
3.4.3 Volatile Solids/ Total Volatile Solids (VS/TVS)	46
3.4.4 Mixed Liquor Suspended Solids	46
3.4.5 Mixed Liquor Volatile Suspended Solids (MLVSS)	48
3.4.6 Chemical Oxygen Demand (COD)	49
3.4.7 Biochemical Oxygen Demand (BOD)	50
3.4.8 Oil and Grease (O & G)	51
3.4.9 Total Nitrogen (TN)	52
3.4.10 Ammonia Nitrogen (NH ₃ -N)	53
3.4.11 Alkalinity	54
3.4.12 Volatile Acidity	54

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Wastewater Characteristics	56
4.2 Acclimatization phase of ABSR	57
4.2.1 pH variation during acclimation process of ABSR	57
4.2.2 Microbial growth variations during acclimation process of ABSR	59
4.2.3 COD variations during acclimation process of ABSR	61
4.2.4 Alkalinity and VFA:AIK variations during acclimation process	63
4.3 Performance study of ABSR at difference HRT	65
4.3.1 Performance study at 60 days of HRT	66
4.3.1.1 pH variations during 60 days of HRT	66

4.3.1.2 Biomass variations in the ABSR during 60 days of HRT	67
4.3.1.3 Alkalinity and VFA:AIK variations during 60 days of HRT	69
4.3.1.4 COD of effluent and removal efficiency during 60 days of HRT	71
4.3.2 Performance study at 50 days of HRT	72
4.3.2.1 pH variations during 50 days of HRT	72
4.3.2.2 Biomass variations in the ABSR during 50 days of HRT	74
4.3.2.3 Alkalinity and VFA:AIK variations during 50 days of HRT	75
4.3.2.4 COD of effluent and removal efficiency during 50 days of HRT	77
4.3.3 Performance study at 40 days of HRT	79
4.3.3.1 pH variations during 40 days of HRT	79
4.3.3.2 Biomass variations in the ABSR during 40 days of HRT	80
4.3.3.3 Alkalinity and VFA:AIK variations during 40 days of HRT	81
4.3.3.4 COD of effluent and removal efficiency during 40 days of HRT	83
4.3.4 Performance study at 30 days of HRT	85
4.3.4.1 pH variations during 30 days of HRT	85
4.3.4.2 Biomass variations in the ABSR during 30 days of HRT	86
4.3.4.3 Alkalinity and VFA:AIK variations during 30 days of HRT	88
4.3.4.4 COD of effluent and removal efficiency during 30 days of HRT	89
4.3.5 Performance study at 20 days of HRT	91
4.3.5.1 pH variation during 20 days of HRT	91
4.3.5.2 Biomass variations in the ABSR during 20 days of HRT	92
4.3.5.3 Alkalinity and VFA:AIK variations during 20 days of HRT	94
4.3.5.4 COD of effluent and removal efficiency during 20 days of HRT	95

4.3.6 Performance study at 10 days of HRT	97
4.3.6.1 pH variation during 10 days of HRT	97
4.3.6.2 Biomass variations in the ABSR during 10 days of HRT	98
4.3.6.3 Alkalinity and VFA:Alk variations during 10 days of HRT	99
4.3.6.4 COD of effluent and removal efficiency during 10 days of HRT	101
4.3 Steady state performance of ABSR	102
4.3.1 Volatile fatty acid as acetic acid and pH	104
4.3.2 Alkalinity and VFA:Alk ratio fraction in the ABSR	105
4.3.3 Anaerobic digestion process efficiency of ABSR	107
4.4 Determination of bio-kinetic coefficients	111
4.4.1 Specific substrate utilization rate of ABSR	112
4.4.2 Y_G , b , $r_{x, \max}$, k_s , μ_{\max} and Θ_c kinetic analysis	114
4.5 Application of research result to existing scale	120
CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS	
5.1 Conclusions	122
5.2 Recommendations	124
REFERENCES	126
APPENDICES	136

LIST OF TABLES

	Page
2.1 Characteristics of palm oil mill effluent (POME)	16
4.1 Characteristics of palm oil mill effluent (POME)	56
4.2 Experimental results obtained under steady state condition at six different HRT (mean values)	103
4.3 Performance of various systems of treating POME	109
4.4 Experimental results at six different HRT for kinetic analysis (mean values)	110
4.5 Specific substrate utilization rate, r_x for SCOD and VFA under steady state at various HRT (mean value)	111
4.6 Summarize data for kinetic coefficients of ABSR	115
4.7 Kinetic coefficients in different type of reactor for the treatment of POME wastewater	118
4.8 Predicted effluent BOD and COD with recommended volume of pond for the treatment of POME wastewater to the existing scale	119

LIST OF FIGURES

	Page	
2.1	Schematic diagram of palm oil extraction process	15
2.2	Scheme of degradation process of anaerobic digestion	23
2.3	Degradation of each organic component by three groups of bacteria in the anaerobic digestion process.	28
2.4	Scheme of completely mixed ABSR	35
3.1	Sampling spot of the wastewater studied	41
4.1	pH variation of anaerobic bench scale reactor (ABSR) during acclimation process	58
4.2	Microbial growth of the ABSR during acclimation process	59
4.3	COD concentration of effluent and removal efficiency of ABSR during acclimation process	61
4.4	Alkalinity and VFA:Alk of ABSR during acclimation process	63
4.5	pH variation of ABSR during 60 days of HRT	66
4.6	Biomass variation in the ABSR during 60 days of HRT	67
4.7	Alkalinity and VFA:Alk ratio fraction of the ABSR during 60 days of HRT	69
4.8	Effluent COD and COD removal efficiency of ABSR during 60 days of HRT	71
4.9	pH variation of ABSR during 50 days of HRT	73
4.10	Biomass variations of ABSR during 50 days of HRT	74
4.11	Alkalinity and VFA:Alk ratio fraction of ABSR during 50 days of HRT	76
4.12	Effluent COD and COD removal efficiency of ABSR during 50 days of HRT	77
4.13	pH variation of ABSR during 40 days of HRT	79
4.14	Biomass variation in the ABSR during 40 days of HRT	80

4.15	Alkalinity and VFA:Alk ratio fraction of ABSR during 40 days of HRT	82
4.16	Effluent COD and removal efficiency of ABSR during 40 days of HRT	83
4.17	pH variation of ABSR during 30 days of HRT	85
4.18	Biomass variation in the ABSR during 30 days of HRT	86
4.19	Alkalinity and VFA:Alk ratio fraction of ABSR during 30 days of HRT	88
4.20	Effluent COD and COD removal efficiency of ABSR during 30 days of HRT	90
4.21	pH variation during 20 days of HRT	91
4.22	Biomass of the ABSR during 20 days of HRT	93
4.23	Alkalinity and VFA:Alk ratio fraction of ABSR during 20 days of HRT	94
4.24	Effluent COD and COD removal efficiency of ABSR during 20 days of HRT	96
4.25	pH variation during 10 days of HRT	97
4.26	Biomass of ABSR during 10 days of HRT	98
4.27	Alkalinity and VFA:Alk ratio fraction of ABSR during 10 days of HRT	100
4.28	Effluent COD and COD removal efficiency of ABSR during 10 days of HRT	101
4.29	Effluent COD, SCOD and VFA under steady state condition on various hydraulic retention times	103
4.30	Effluent VFA as acetic acid concentration and pH under steady state condition on various hydraulic retention times	104
4.31	Alkalinity and VFA:Alk ratio fraction of ABSR under steady state condition on various hydraulic retention time	106
4.32	COD and SCOD removal efficiency of ABSR under steady state condition on various hydraulic retention time	107

4.33	Specific substrate utilization rate, r_x of SCOD and VFA variations under steady state at various HRT	113
4.34	Determination of growth yield, Y_G and specific biomass decay, b for the substrate of SCOD	116
4.35	Determination of growth yield, Y_G and specific biomass decay, b for the substrate of VFA	116
4.36	Determination of maximum specific substrate utilization, $r_{x,max}$ and saturation constant for substrate, k_s for the substrate of SCOD	117
4.37	Determination of maximum specific substrate utilization, $r_{x,max}$ and saturation constant for substrate, k_s for the substrate of VFA	117

LIST OF PLATES

	Page
4.1 Image of scum layer of ABSR at high, middle and low HRT: (a) High HRT (60 and 50 days) (b) Middle HRT (30 and 40 days) and (c) Low HRT (20 and 10 days)	108

LIST OF SYMBOLS

Y_G	Growth yield
b	Specific biomass decay
D	Dilution rate, (day^{-1})
$r_{x,\text{max}}$	Maximum specific substrate utilization
K_s	Saturation constant for substrate
μ_{max}	Maximum specific biomass growth rate
Θ_c	Critical retention time
$\Delta G_o'$	Gibbs free energy change value
S	Substrate concentration in the reactor
Q	Flow rate
S_1	Influent substrate concentration
S_2	Effluent substrate concentration ($S_2 = S$),
V	Reactor volume
r_x	Specific substrate utilization rate
r_v	Substrate utilization rate per volume
t	Time
X	Biomass concentration in the reactor, mg/l
μ	Specific biomass growth rate
w/v	Weight over volume

LIST OF ABBREVIATION

ABSR	Anaerobic Bench Scale Reactor
Alk	Total Alkalinity
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CPO	Crude Palm Oil
EQA	Environmental Quality Act
FFB	Fresh Fruit Bunches
HRT	Hydraulic Retention Time
MPOB	Malaysia Palm Oil Board
MPOPC	Malaysia Palm Oil Promotion Council
NH ₃ -N	Ammonia Nitrogen
O & G	Oil and Grease
OLR	Organic Loading Rate
POME	Palm Oil Mill Effluent
SRT	Solid Retention Time
SS	Suspended Solid
TN	Total Nitrogen
TS	Total Solid
TVS	Total Volatile Solid
VFA	Volatile Fatty Acid
VSS	Volatile Suspended Solid

**KECEKAPAN PENGURANGAN KEPERLUAN OKSIGEN KIMIA (COD) DAN
PENILAIAN KINETIK UNTUK PROSES PENCERNAAN ANAEROBIK UNTUK
AIR SISA KILANG KELAPA SAWIT DALAM REAKTOR ANAEROBIK
BERSKALA KECIL (ABSR)**

ABSTRAK

Keberkesanan pengurangan COD pengolahan air sisa kilang kelapa sawit dalam reaktor anaerobik secara skala makmal telah dijalankan dengan pelbagai jenis aliran yang terdiri daripada 0.63, 0.76, 0.95, 1.27, 1.9 dan 3.8 liter air sisa kilang kelapa sawit untuk setiap hari kajian. Sehubungan dengan itu, data aliran yang dinyatakan di atas adalah menyerupai masa tahanan hidraul dengan 60, 50, 40, 30, 20 dan 10 hari. Dalam masa yang sama, kajian parameter kinetik telah dijalankan dalam keadaan yang konsisten melalui pelbagai jenis nilai pencairan (D) dari 0.017 sehingga 0.1 hari⁻¹. Parameter kinetik yang telah dikaji adalah merangkumi pekali pertumbuhan (Y_G), pekali kematian (b), pekali penguraian sisa maksimum ($r_{x,max}$), pekali halaju separa (k_s), kadar pertumbuhan maksimum (μ_{max}) dan masa tahanan hidraul genting (Θ_c).

Kajian penilaian prestasi telah menunjukkan pengolahan air sisa kilang kelapa sawit melalui proses anaerobik adalah sangat berkesan terhadap pelbagai masa tahanan hidraul (HRT). Kecekapan penyingkiran COD telah dilaporkan berada dalam julat 85.41% dan 66.38% untuk masa tahanan hidraul daripada 60 hari hingga 10 hari. Sementara itu, kandungan biojisim reaktor anaerobik telah dilaporkan dalam julat 18418 dan 28694 mg MLVSS/l untuk julat masa tahanan hidraul yang sama. Kandungan pH dan bebanan alkali reaktor anaerobik didapati

semakin merosot daripada 8.55 hingga 7.64 dan 18320 hingga 12772 mg CaCO₃/l dalam julat masa tahanan hidraul 60 hari sehingga 10 hari.

Dua jenis parameter air sisa seperti SCOD dan VFA (asid asetik) daripada air sisa kilang kelapa sawit telah dipilih dalam kajian penilaian parameter kinetik melalui proses anaerobik. Beberapa model enapcemar teraktif seperti persamaan keseimbangan jisim, persamaan tindak-balas penguraian air sisa dan model Monod telah digunakan dalam kajian penilaian parameter kinetik. Penilaian parameter kinetik berasaskan SCOD telah dilaporkan seperti: Y_G (14.368 gVSS gSCOD⁻¹), b (0.2069 hari⁻¹), μ_{max} (0.148 hari⁻¹), K_s (3.8915 g SCOD l⁻¹) dan Θ_c (6.76 hari). Manakala, penilaian parameter kinetik berasaskan VFA (asid asetik) telah dilaporkan seperti: Y_G (16.474 gVSS gCH₃COOH⁻¹), b (0.0544 hari⁻¹), μ_{max} (0.084 hari⁻¹), K_s (0.2179 g CH₃COOH l⁻¹) dan Θ_c (11.9 hari).

CHEMICAL OXYGEN DEMAND (COD) REDUCTION EFFICIENCY AND KINETIC EVALUATION OF ANAEROBIC DIGESTION PROCESS OF PALM OIL MILL EFFLUENT (POME) IN ANAEROBIC BENCH SCALE REACTOR (ABSR)

ABSTRACT

The COD reduction efficiency of ABSR for the treatment of POME wastewater was conducted by a series of continuous experiments using feed flow-rates of 0.63, 0.76, 0.95, 1.27, 1.9 and 3.8 liters of raw POME per day, which correspond to the hydraulic retention time (HRT) of 60, 50, 40, 30, 20 and 10 days. Simultaneously, the experiments were performed using different dilution rates (D) ranging between 0.017 and 0.1 day⁻¹ under steady state condition to determine the kinetic coefficients such as: growth yield (Y_G), specific biomass decay (b), maximum specific substrate utilization ($r_{x,max}$), saturation constant for substrate (k_s), maximum specific biomass growth rate (μ_{max}) and critical retention time (Θ_c). The kinetic coefficients were evaluated from the common type of model as mass balance, rate equation reaction and the most popular model of Monod equation.

The performance study showed that the treatment of POME wastewater could be treated effectively through ABSR at different HRT. The COD removal efficiency was in the range of 85.41% and 66.38% between 60 days and 10 days of HRT. Besides, the biomass concentration of ABSR was between 18418 and 28694 mg MLVSS/l. Moreover, the pH level and total alkalinity of the ABSR were reduced from 8.55 until 7.64 and 18320 until 12772 mg CaCO₃/l, respectively from the HRT of 60 days until 10 days.

In the experiment of kinetic coefficients determination, two different influent substrates as SCOD and VFA (acetic acid) were selected. The evaluated kinetic coefficients based on SCOD basis were in the range of values: Y_G (14.368 gVSS gSCOD⁻¹), b (0.2069 day⁻¹), μ_{max} (0.148 day⁻¹), K_s (3.8915 g SCOD l⁻¹) and Θ_c (6.76 day), respectively. Concurrently, similar kinetic coefficients evaluated based on VFA as acetic acids were: Y_G (16.474 gVSS gCH₃COOH⁻¹), b (0.0544 day⁻¹), μ_{max} (0.084 day⁻¹), K_s (0.2179 g CH₃COOH l⁻¹) and Θ_c (11.9 day), respectively.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Malaysia is the largest producer and exporter of crude palm oil (CPO). The production of crude palm oil reached 15 million tones in the year 2005 from 14 million tones in the previous year (MPOB, 2006). This amount will continuously increase in proportion to the world demand of edible oils seeing as palm oil already is bio-diesel product. Although the palm oil industry is the major revenue earner for our country but it has also been identified as the single largest source of water pollution source due to the palm oil mill effluent (POME) characteristic with high organic content and acidic nature.

In palm oil mills, liquid effluent is mainly generated from sterilization and clarification processes in which large amounts of steam and hot water are used (Zinatizadeh et al., 2006). For every ton of palm oil fresh fruit bunch, it was estimated that 0.5-0.75 tones of POME will be discharged (Yacob et al., 2006). In general appearance, palm oil mill effluent (POME) is a yellowish acidic wastewater with fairly high polluting properties, with average of 25,000 mg/l biochemical oxygen demand (BOD), 55250 mg/l chemical oxygen demand (COD) and 19610 mg/l suspended solid (SS). This highly polluting wastewater can cause several pollution problems and also create odor problems to the neighborhoods of the mills such as a nuisance to the passers-by or local residents and river pollution. Thus, there is need to prevent environmental pollution due to the increase of crude

palm oil production. The Malaysian government therefore enacted the Environmental Quality Act (EQA 1974) (Prescribed Premises) (Crude Palm Oil) Regulations in 1977 with its amendment in 1982. Section 18 (1) and 19 of the act which relate to palm oil mill processing industry, has thereafter, set parameter limits for the discharge of POME into the environment as shown in the appendix A.

Over the past 20 years, the technique available for the treatment of POME in Malaysia has been basically biological treatment, consisting of anaerobic, facultative and aerobic pond systems (Chooi, 1984; Ma, 1999). The pond system has been applied in our country for POME treatment since 1982 (Ashhuby et al., 1996). Most of the pond system that has been applied for the treatment of POME in Malaysia was classified as waste stabilization pond. The configuration of this system consists of essentially a number of ponds of different functions such as anaerobic, facultative and aerobic ponds. Thus, anaerobic ponds are one of the most effective treatments that are being applied in Malaysia either in pond system or close digesting tank systems to treat highly concentrated POME wastewater. This is because the anaerobic process has considerable advantages such as (a) it demands less energy, (b) sludge formation is minimal, (c) unpleasant odors are avoided, and (d) anaerobic bacteria efficiently break down the organic substances to methane (Rincon et al., 2006).

Anaerobic digestion may be defined as the engineered methanogenic anaerobic decomposition of organic matter. It involves different species of anaerobic microorganisms that degrade organic matter (Cote et al., 2006). In the anaerobic process, the decomposition of organic and inorganic substrate is carried out in absence of molecular oxygen. The biological conversion of the organic substrate occur in the mixtures of primary settled and biological sludge under anaerobic condition followed by hydrolysis, acidogenesis and methanogenesis to convert the intermediate compounds into simpler end products as methane (CH₄) and carbon dioxide (CO₂) (Gee and Chua, 1994; Guerrero et al., 1999). Therefore, the anaerobic digestion process offers great potential for rapid disintegration of organic matter to produce biogas that can be used to generate electricity and save fossil energy (Linke, 2006).

Nowadays, the anaerobic pond systems are designed depending on a few common parameters such as hydraulic retention time (HRT), solids retention time (SRT), influent and effluent concentrations, sludge age and others; however the behavior or kinetic factor is not taken into consideration. Moreover, the literature survey showed that there is lack of information related to the biological kinetic (bio-kinetic) coefficients for anaerobic stabilization pond system of POME wastewater.

Bio-kinetic coefficients are useful tools to obtain information on the rate of microbial growth and consumption of substrate, which is essential to determine the volume of the reactor and understanding well the process control through system simulation. Meanwhile, the bio-kinetic coefficients also play an important role to illustrate the development of microorganism and substrate balances, the prediction of effluent concentration, the development of process design factors and the effects of kinetic coefficients on the process of design, performance, and stability (Metcalf and Eddy, 2003). Throughout this research, an anaerobic bench scale reactor (ABSR) was operated continuously at different hydraulic retention time (HRT) in order to evaluate the performance and to define the bio-kinetic coefficients of anaerobic biodegradation process.

1.2 Statement of Problems

As mentioned earlier, large quantities of POME wastewater are produced from the crude palm oil extraction process. This large amount of wastewater if discharged untreated into freshwater, estuarine and marine ecosystems may alter aquatic habitats, affect aquatic life and adversely impact human health. However, the treatment of wastewater is always a burden and costly for many industrialists. Therefore, a new and effective approach in wastewater treatment technology should be developed to comply with stringent environmental regulations on the quality of the effluent entering receiving waters.

In relation to that, several POME wastewater treatment plants have been successfully operated but majority of the plants are still struggling to observe the Malaysian discharge standards under Environmental Quality Act (EQA 1974) (Prescribed Premises) (Crude Palm Oil) Regulations in 1977. Most of the palm oil mill industries are facing a common problem; an under designed wastewater plant to cope with ever growing production. Though installation of higher capacity plant and new alternative treatment system such as membrane technology will be an alternative but it always involves a high cost. In practice, it has been observed that all industries prefer simple, low cost wastewater treatment technology especially ponds or lagoon systems.

Throughout this research study, the studies would be focused on the anaerobic pond system since anaerobic digestion process is the first treatment of waste stabilization pond system for POME wastewater. The anaerobic ponds have been available for the treatment of POME wastewater in Malaysia for the past 20 years. One of the major problems of the anaerobic pond system is that it occupies vast area of land and requires relatively long hydraulic retention time (HRT), up to 66 days for effective performance (Ashhuby et al., 1996). Long HRT is the major problem for most palm oil mill industries due to their high production capacity, resulting in a number of mills not strictly observing the specific retention times in the anaerobic pond system. Moreover, there are signs that the anaerobic ponds systems are failing due to lack of de-sludging.

Therefore, this research study is required to investigate the performance of anaerobic pond system through laboratory anaerobic bench-scale reactor (ABSR) over various hydraulic retention times to treat POME wastewater. Moreover, for better understanding of process control of anaerobic digestion process, it is necessary to evaluate the kinetic coefficients for the anaerobic pond system. Thus, the results of the study could provide a firm scientific and engineering basis to design a new anaerobic pond system or revamp the existing anaerobic pond system of POME wastewater.

Nowadays, the literature is abound with results of research on advanced anaerobic treatment such as high rate up-flow anaerobic sludge fixed film (Zinatizadeh et al., 2006), modified anaerobic baffled reactor (Faisal and Unno, 2001), membrane anaerobic system (Fakhrul and Noor, 1999) and anaerobic hybrid digester (Borja et al., 1996) for the treatment of POME wastewater but there is scarcity of information in the literature about the anaerobic pond system.

1.3 Objectives of the Study

This research aims to scrutinize the performance and kinetic coefficients of POME wastewater in the anaerobic bench-scale reactor which operates as an anaerobic stabilization pond system. There are two specific objectives:

- a) To observe the performance of the anaerobic bench scale reactor effect by hydraulic retention time (HRT).
- b) To determine the kinetic coefficients of anaerobic biodegradation process base on anaerobic stabilization pond system for cleaning up wastewater derived from the production of palm oil.

1.4 Scope of the Study

The treatment of POME wastewater is in demand due to the pollution problems created from the high volume of wastewater generated by the palm oil mill industry. The anaerobic digestion process is the main focus in this study. The approach is to treat POME wastewater under various hydraulic retention time (HRT) in the anaerobic bench scale reactor (ABSR). The ABSR operates based on the anaerobic stabilization pond system. The performance and kinetic coefficients of the ABSR are examined between the range of HRT as 60, 50, 40, 30, 20 and 10 days.

The performance of the ABSR monitored based on the chemical oxygen demand (COD) removal efficiency at each batch of HRT as mentioned above. Besides, the samples from ABSR were also collected and subjected to the analysis of the following parameters such as feed and effluent of the total and soluble COD, ABSR pH, feed and effluent volatile fatty acid (VFA), ABSR total alkalinity, ABSR suspended solid (SS) and volatile suspended solid (VSS) for the purpose of performance study at each batch of HRT. Therefore, the screening of the best or most suitable HRT can be defined from the performance study of ABSR for the treatment of POME wastewater.

Another part of the research contributes to determination of the kinetic coefficients for the treatment of POME wastewater in the anaerobic stabilization pond system. The kinetics constant of the anaerobic digestion process is a useful tool to be able to describe and to predict the performance of the system. In this study, the ABSR is continuously operated until steady state condition at each batch of HRT is reached in order to determine the kinetics constant. Two influent substrates of SCOD and VFA as acetic acids are selected to analysis the kinetic coefficients of ABSR.

The kinetic coefficients of ABSR includes values for growth yield (Y_G), specific biomass decay (b), maximum specific substrate utilization ($r_{x,max}$), saturation constant for substrate (k_s), maximum specific biomass growth rate (μ_{max}) and critical retention time (Θ_c) are evaluated by using laboratory-scale

experiments. The common type of model such as mass balance, reaction rate equation and the most popular model of Monod equation of anaerobic digestion process is applied through laboratory-scale experiment to evaluate the kinetic coefficients.

1.5 Organization of the Thesis

This thesis consists of five chapters. A brief introduction on the status of the palm oil mill industry; POME wastewater characteristic; regulatory enforcement towards the discharge of effluent; environmental issues of POME wastewater; anaerobic digestion process and kinetic coefficients are given in Chapter one (Introduction). This chapter also includes problem statements that give some basis and rationale to identify the research direction to be followed in this study. The objectives of the study are stated together with the scope of the research to be covered. Moreover, the organization of the thesis is also given in the last section of the chapter.

Chapter two (literature review) covers the review of the history of palm oil industry; processes of crude palm oil production; POME wastewater characteristic and pond treatment system. This chapter also presents the detailed information and specific topics relevant to anaerobic digestion process and kinetic coefficients model development that been used in this study.

Chapter three (Material and methodology) describes in detail the materials and chemicals used in the present study. This is followed by the detailed experimental procedures which include anaerobic bench scale study about the performance study, kinetic coefficients determination and the analysis of sample.

Chapter four (Results and discussion) outlines two main studies. The acclimatization phase of anaerobic bench scale reactor (ABSR) is carried out at the beginning of the study. In the first study, the performance of ABSR over various range of HRT between 60 days and 10 days is carried out to monitor the operating condition such as pH, biomass, total alkalinity, ratio fraction between volatile fatty acid and alkalinity, effluent COD and COD removal efficiency. Moreover, the kinetic coefficients of the ABSR are determined from the steady state condition of each batch HRT is carried out in the second part of study.

Chapter five (Conclusions and recommendations) give conclusions and recommendations from the current study. The conclusions are based on the results obtained toward the objectives of this study. This is followed by the recommendations and suggestions for the future studies in this related field.

CHAPTER TWO

LITERATURE REVIEW

2.1 Palm Oil Industry in Malaysia

2.1.1 History and Development of Palm Oil Industry

The oil palm tree (*Elaeis guineensis*) originated from West Africa where it was grown wild and later developed into an agriculture crop. It was first introduced to Malaysia in the early 1870's as an ornamental plant. In the year 1917, the first commercial planting took place at Tennamaran Estate in Selangor, laying the foundation for the vast oil palm plantations and palm oil industry in Malaysia (MPOPC, 2006). According to Wang et al. (2004), the plantation of oil palm increased from a mere 400 hectares to 54000 hectares from the year of 1920 to 1960.

Later in the 1960's, the government introduced land settlement schemes for planting oil palm as a means to eradicate poverty for the landless farmers and smallholders. The oil palm plantations in Malaysia were largely based on the estate management system and small holders scheme (MPOPC, 2006). In 1996, the oil palm plantation area stood at a staggering 2.6 million hectares (MPOB, 2006).

The Malaysian oil palm industry recorded a mixed performance in the year of 2005. The year had been an eventful for the Malaysian palm oil industry as the National Biofuel Policy was announced by the Government in August 2005 to spur the development of the biofuel industry in Malaysia. In relation to that, the total oil palm agricultural estate increased by 4.5% or from 174,000 hectares to 4.0 million hectares in 2005 (MPOB,2006). Meanwhile, the production of crude palm oil continued to increase for seven consecutive years reaching 15.0 million tones in 2005 (MPOB, 2006).

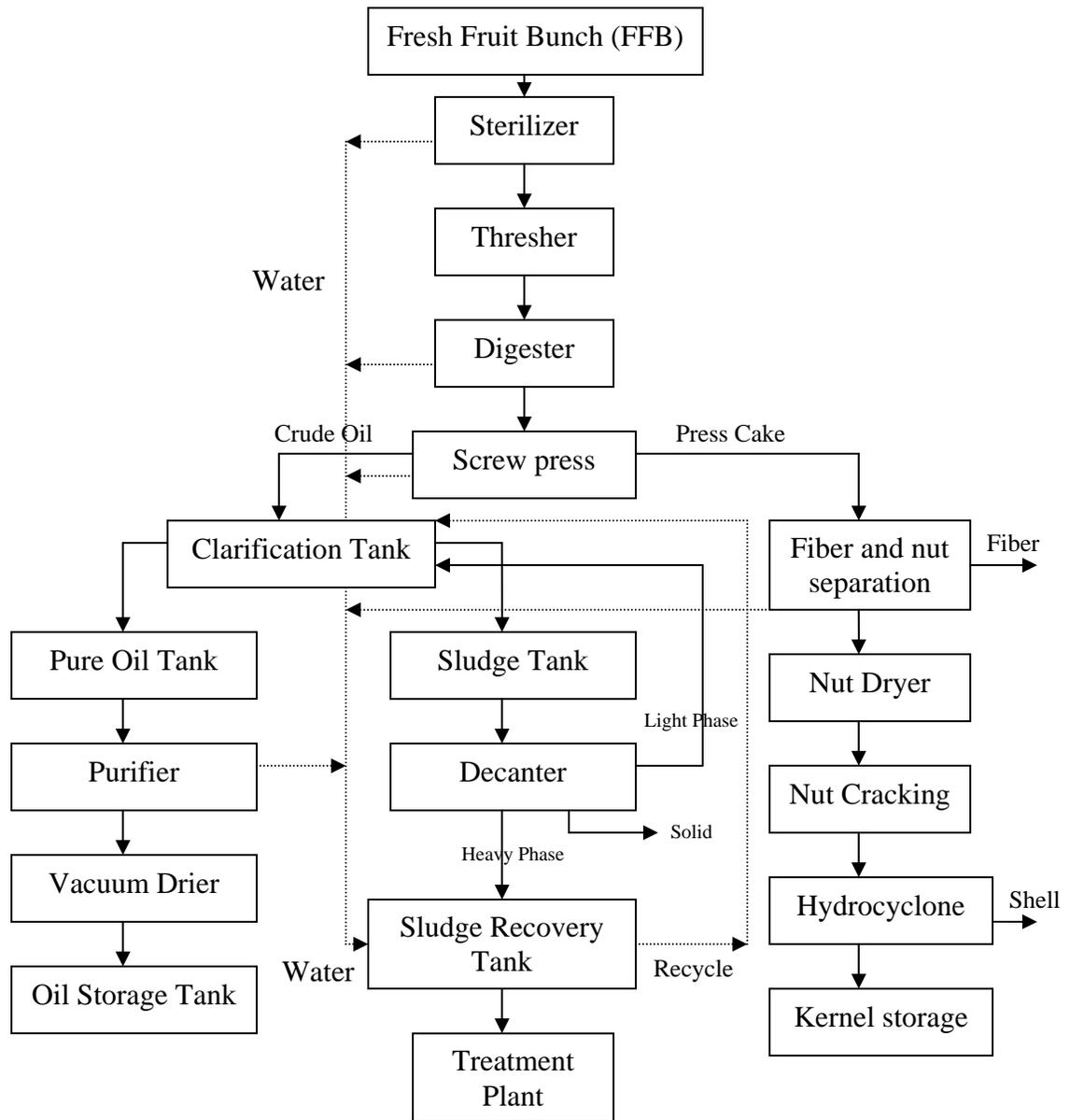
2.1.2 Standard Wet Mill Process and Generation of Residues of Oil Palm

Palm oil mills with wet milling processing are accounted as major production of crude palm oil (CPO) in Malaysia. The Malaysia Palm Oil Board or MPOB (2006) reported that about 380 mills were in operation with total capacity of 79.74 million tones of fresh fruit bunches (FFB). Generally, 2.5 tones Palm Oil Mill Effluents (POME) was generated by each ton of crude palm oil produced (Rahman et al., 1996). The Figure 2.1 illustrates the flow diagram of palm oil extraction and typical process for POME produced fraction. Bunches of oil palm fruits harvested in the palm oil estate are sent to the palm oil mill for processing. The capacity of a large scale mill ranges from 10 to 60 tones FFB/hr. The FFB harvested from the oil palm plantation have to be processed immediately to prevent poor quality of CPO due to the increase of free fatty acid content.

On arrival, the FFB are subjected to steam-heat treatment in the horizontal sterilized for around 1 hour with the temperature of about 140°C and pressure at 40 psi. This process is to soften the oil palm fruits so that it easily detaches from the stalk while threshing. Duration, temperature and pressure of sterilization sometime are dependant on the age and growth of the FFB. The detached fruits are further softened with steam in digesters. The digester mashes the fruits and then is passed through the screw press where the oil and the juice from the fruits are extracted. The crude palm oil which is compressed may contain approximately 48% oil, 45% water and 7% solids.

Crude palm oil is then sent to clarifier tank while the fiber and nut retrieved during the screw press process are sent to the fiber and nut separation section. Fiber is used as fuel for boiler to produce superheated steam which is used to generate electricity through turbine generators. Furthermore, the nut is cracked to separate the kernel and shell. The kernel is collected while the hard shell is sent to boiler as fuel. Some of the water in this crude palm oil slurry is actually steam condensate from the sterilization, digestion and screw pressing where steam was injected into the respective machinery to maintain the high temperature required throughout the milling process.

Crude palm oil is then sent to the clarification tank and hot water is further added to the crude oil slurry to reduce the viscosity so that the oil will cream to the surface. The underflow from the lower section of the clarification tank is channeled to the sludge tank for settling purpose and to centrifuge to remove as much of the solids and water. This watery phase or sludge is discharged and any oil found here constitutes as oil loss as it is discharged as effluent. These effluents are then mixed with other wastes as sludge effluent and are sent for treatment before being discharged to environment. The lighter phase from the sludge recovery tank, which consists of oil and water, are recycled to the clarification tank. The creamed palm oil from the surface of the clarification tank is then skimmed and further purified, dried and sold as crude palm oil to the refinery for further processing (Chow and Ho, 2000).



Sources: MALPOM Industries Sdn Bhd, (2006)

Figure 2.1: Schematic diagram of palm oil extraction process

2.1.3 Palm Oil Mill Effluent (POME)

A large quantity of water is required for the oil extraction process. For every ton of oil palm fresh fruit bunch, it is estimated that 0.5-0.75 tons of POME will be discharged (Yacob et al., 2006). POME is a colloidal suspension, which contains 95 – 96% of water, 0.6 – 0.7% of oil and grease and 4 – 5% of total solids (Ma, 2000). It is a thick brownish liquid and is discharged at a temperature between 80 and 90°C (Ahmad et al., 2005). Meanwhile, POME is considered as one of the most polluting agro-industrial residues due to its high organic load. This highly polluting wastewater can create odor problems to the neighborhood of the mills, a nuisance to the passers-by or local residents and river pollution. Table 2.1 shows the refined characteristic of POME from literature.

Table 2.1 Characteristics of palm oil mill effluent (POME)

Parameter	Concentration (mg/l)
pH	4.0 – 5.0
Oil and grease	4000 - 6000
BOD 3-days, 30°C	25000
COD	50000
Total solids	40500
Suspended solids	18000
Total volatile solids	34000
Ammoniacals nitrogen	35
Total nitrogen	750
Phosphorus	180
Potassium	2270
Calcium	439
Boron	7.6
Iron	46.5
Manganese	2.0
Copper	0.89
Magnesium	615
Zinc	2.3

Source: Ahmad et al., (2005)

2.2 Palm Oil Mill Effluent Wastewater Treatment

The treatment employed for POME in Malaysia follows to a large extent and the principles of biochemical operations. Three different types of treatment systems were adopted and these include: a) open tank digester and extended aeration system (Lim et al., 1984), b) closed anaerobic digester and land application system (Ma, 1999), and c) pond treatment system (Lim et al., 1984). The choice of treatment systems depends to a large extent on the company's preference, location of the mill and availability of useable land. However, the pond treatment system was the most popular as it was adopted by more than 85% of the mills in Malaysia nowadays (Ma, 1999). Therefore, the discussions would be limited to this treatment system, since this research study was focus on the anaerobic pond system.

2.2.1 Pond Treatment System

Ponds have been widely used as a method of sewage disposal since the ancient times (Gray, 1992). Most of the pond systems that have been applied for the treatment of POME in Malaysia are classified as waste stabilization pond. According to Arceivala (1998), stabilization pond is similar to an activated sludge process but differ in the following ways: Stabilization ponds have i) long retention period, ii) low loading rate, iii) less active microbial biomass, and iv) less mixing and agitation where the particulate solids were settled and formed sludge layer in which the anaerobic process breakdown occurs. The configuration of the pond system consists of essentially a number of ponds of different functions such as

anaerobic, facultative and aerobic ponds, which are made up of earthen structures with no lining (Ma, 1999).

2.2.2 Anaerobic ponds

There has not been significant anaerobic pond research in the past three decades (Hanson and Yoon, 2001). Some research efforts had in the past been directed towards the assessment of the treatment capacity of anaerobic ponds and understanding their behavior; such efforts include the works of Oswald, (1963, 1968); van Eck and Simpson, (1966); Parker and Skerry, (1968). According to Hanson and Yoon (2001), all earlier reports showed that the anaerobic pond has characteristic behavior similar to high-rate anaerobic reactor with respect to treat high strength wastewaters.

Anaerobic ponds for POME treatment consist of at least two ponds connected in series to other ponds. The raw POME is channeled into the anaerobic pond from the sludge recovery tank. Anaerobic pond system is very effective in the treatment of effluents with high strength, biodegradable organic contents (BOD>500) generated in large quantities by agricultural and food industries (Gray, 1992). Anaerobic ponds are usually designed with deeper basins than the other ponds in order to reduce the surface area to volume ration thereby minimizing re-aeration (since oxygen transfer through the air-water interface is undesirable) and heat loss (Gray, 1992). The anaerobic ponds for POME treatment in Malaysia are usually 5-7 meters in depth (Chooi, 1984). Three zones

can be identified in the pond, which includes: the scum layer, the supernatant layer and the sludge layer (Kosaric, 1992). Anaerobic reaction takes place in the sediment include solubilization of biodegradable particulate matter followed by acidogenesis, acetogenesis and methanogenesis (Rajbhandari and Annachhatre, 2004).

Generally, anaerobic ponds are used as preliminary treatment for high strength organic wastes, and for partial stabilization of the waste, before secondary treatment took place. Organic loading was considerably reduced and the retention time needed was generally long (Ashhuby et al., 1996). The organic loading for POME treatment varies from 0.2-0.35 kg BOD/m³/day with a minimum of 30 days HRT (Ma, 1999).

2.2.3 Facultative Ponds

Facultative ponds are characterized by having an upper aerobic and a lower anaerobic zone with active purification occurring in both (Gray, 1992). As the digested effluent enters the basin from the anaerobic pond, the settleable and flocculated colloidal matter settles to the bottom to form a sludge layer where organic matter is decomposed anaerobically (Rajbhandari and Annachhatre, 2004). The remainder of the organic matter, which is either soluble or suspended, passes into the body of the water where decomposition was mainly aerobic or facultative and rarely anaerobic (Gray, 1992). Aerobic and facultative bacteria are the primary decomposers although fungi may be present in the pond system. The

fungus is presented because of the high pH caused by the photosynthetic activity of the algae (Arrceivala et al., 1970). The dominant bacteria found are of the genera *Pseudomonas*, *Achromobacter* and *Flavobacterium*. The soluble degradation products such as ammonia, organic acids, and inorganic nutrients are also released and subsequently oxidized aerobically in the water layer. Facultative ponds are much shallower than the anaerobic ponds, and usually 1-1.5 meters in the depth in order to maintain dissolved oxygen in the basin. Depth above the upper limit may cause some odor problem due to excessive anaerobiosis, while depth below 0.7 m will encourage growth of rooted aquatic weeds, which may not only damage the lining of the pond and hinder circulation but also attract mosquitoes and other flies (Gray, 1992). The retention time of facultative ponds depended on load, depth, evaporation rate, and loss by seepage, but are shorter than anaerobic ponds. The HRT for POME treatment is between 8-16 days (Ashhuby et al., 1996).

2.2.4 Aerated Ponds

The aerated ponds are used as tertiary treatment process for improving the effluent quality from secondary biological process (Grady et al., 1999). Effluent quality is improved by removing the suspended solids, ammonia, nitrate, phosphate concentration and also the number of enteric microorganisms. There are two types of aerated ponds exist: the aerobic pond and the aerobic-anaerobic pond. In the aerobic pond, all the solids are in suspension so that the concentration of the effluent suspended solids will be equal to the suspension of

solids in the basin. On the other hand, in aerobic-anaerobic pond, the degree of turbulence maintained insures uniform distribution of oxygen throughout the basin but is usually insufficient to maintain all the solids in suspension so that some solids are settled at the bottom of the basin to undergo anaerobic decomposition. For the fact that the deposited solids undergo anaerobic decomposition, the net sludge is not too much and is required only for periodic de-sludging. About 70% to 90% of BOD removal efficiency will be achieved for aerobic pond system but the effluent may contain relatively high concentration of suspended solids which gave the turbid appearance. Therefore the installation of settling tank or shallow pond for removal of solids should be carried out after aerobic pond system.

The aerated pond used in the treatment of POME in Malaysia could be described as aerobic-anaerobic pond system. The current aerated pond contained high concentration of suspended solids and the turbid appearance of the effluent from the pond have to undergo to the next settling pond before final discharge. However, some of the aerobic ponds of POME treatment are equipped with mechanical surface aerators for oxygen supply. The hydraulic retention times for recovery tank, acidification, anaerobic, facultative and aerobic ponds are 1, 4, 45, 8 and 8 days respectively (Ashhuby et al., 1996; Ma, 1999). For the purpose of cost minimization, many oil palm mills in Malaysia do not apply the aerated pond because of energy consumed in operating the aeration pump. In these cases, the HRT for the facultative pond system was increased to 16 days. The pond system

has however been reported to be reliable, stable and capable of producing good final quality effluent (Chan and Chooi, 1982; Chooi, 1984).

2.3 Anaerobic Digestion Process

The anaerobic digestion process stabilizes a wide variety of organic materials and concurrently produces methane from the digestion process. Various kinds of organic materials such as sewage sludge, municipal solid waste, industrial wastewater and agriculture waste are degraded and ultimately converted into methane (CH₄) and carbon dioxide (CO₂) in the anaerobic digestion process (Annachhatre, 1996). Microorganisms are used under anaerobic condition (absent of oxygen) in the anaerobic digestion to convert organic solids to other compounds (Raymond, 1974).

Anaerobic digestion is usually the basic biological treatment process for high organic strength wastewater, since it results's in limited production of stabilized sludge compared to the conventional aerobic treatment. The anaerobic digestion of organic waste has been performed for about a century and has the advantage over aerobic treatment process because of its high organic removal rates, low energy requirement, low sludge and energy production (Angenent et al., 2004). Fig 2.2 illustrates the scheme of the anaerobic digestion process. At first, the complex materials such as polysaccharides, proteins and neutral fats is hydrolyzed into the component monomers of monosaccharides, amino acids, and long chain fatty acids by the extra cellular enzymes (Step A). These monomers are

then fermented to intermediates such as volatile fatty acids as acetate, propionate and butyrate acids and also hydrogen gas (Step B). Therefore, these intermediates are ultimately converted to methane gas (Step C) (Gee and Chua, 1994; Toprak, 1994; Guerrero et al., 1999).

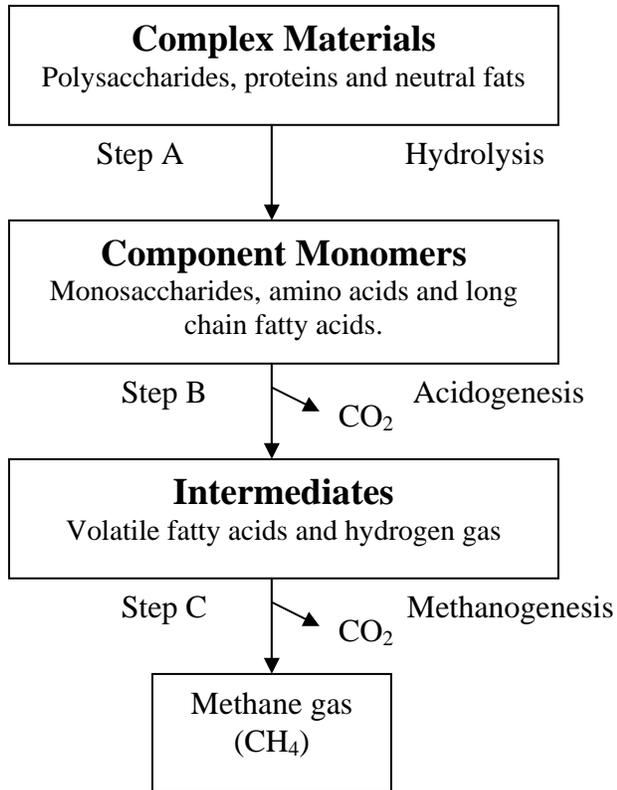


Figure 2.2: Scheme of degradation process of anaerobic digestion.

Several nomenclatures have been proposed for these three steps. Basically, the step of A, B and C are usually named hydrolysis, acidogenesis and methanogenesis. Respectively, the hydrolysis phase is sometimes regarded as a part of the acidogenesis phase (Rajbhandari and Annachhatre, 2004). Toerien and Hattingh (1969) named the step A and B as non-methanogenic phase and the step C as methanogenic phase because of the hydrogen gas as compound other than acids are formed in the step B. Moreover, Speece R. E. (1996) called the step A and B as the constant BOD phase and step C as BOD reduced phase because only the methane formation occurred in the step C brought out the reduction of BOD or COD through the process. Throughout the anaerobic digestion, the organic materials in the solids state were liquefied in the step A. Besides, the soluble organic matters were gasified at step C.

The reaction in the acidogenesis phase was conducted by a group of bacteria called acidogenic bacteria, while the methanogenic bacteria and hydrogen producing acidogenic bacteria were responsible for the methanogenesis phase (Chynoweth et al., 1999).

2.3.1.0 Acidogenic bacteria

A group of acidogenic bacteria includes various kinds of bacteria which ferments the organic materials and produces organic acids in the anaerobic digestion. The number of strains of acidogenic bacteria that occur in the anaerobic digester was too much as been reported in the literature but only a small