EFFECT OF THE ORGANIC LOADING RATE ON THE PERFORMANCE OF MESOPHILIC AND THERMOPHILIC ANAEROBIC DIGESTION OF PALM OIL MILL EFFLUENT

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by

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LIST OF ABBREVIATIONS

Abbreviation	**Description**
AT	Ambient temperature
BOD	Biochemical oxygen demand
CCD	Central composite design
CDM	Clean Mechanisms Development
COD	Chemical oxygen demand
CPO	Crude palm oil
CSRT	Continuous stirred tank reactor
EB	Executive Board
EFB	Empty fruit bunch
F/M	Food-to-microorganisms ratio
FFA	Free fatty acids
FFB	Fresh fruit bunch
GHG	Greenhouse gases
HRT	*Hydraulic retention time*
L.H.V.	Lower heating value
MB	Microbial biomass
MDS	Mineral dissolved solids
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
MPOB	Malaysia Palm Oil Board
MS	Mineral solids
MS_s	Mineral solids of the treated effluent supernatant

MSS	Mineral suspended solids
O & G	Oil and grease
ODM	*Organic dry matter*
OLR	Organic loading rate
$PCOD_e$	Particular chemical oxygen demand of mixed effluent
$PCOD_s$	Particular chemical oxygen demand of treated effluent supernatant
POME	Palm oil mill effluent
SA	Specific activity
SCOD	Soluble chemical oxygen demand
$SCOD_e$	Soluble chemical oxygen demand of mixed effluent
SMA	Specific methane activity
TCOD	Total chemical oxygen demand
$TCOD_e$	Total chemical oxygen demand of mixed effluent
$TCOD_s$	Total chemical oxygen demand of treated effluent supernatant
TDS	Total dissolved solids
TKN	*Total Kjeldahl Nitrogen*
TS	Total solids
TS_s	Total solids of the treated effluent supernatant
TSS	Total suspended solids
UNFCCC	United Nation Framework Convention on Climate Change
TVFA	Total volatile fatty acids
VDS	Volatile dissolved solids
VFA	Volatile fatty acids
VS	Volatile solids

VS_s	Volatile solids of the treated effluent supernatant
VSS	Volatile suspended solids
WAS	Waste activated sludge

LIST OF SYMBOLS

Symbol	Description
ΔX_i	Step size
μ	Specific growth rate
μ_{max}	Maximum growth rate
∞	Infinity
A	Kinetic parameter
B_{CH4}	Methane yield coefficient (based on organic load)
B_o	Ultimate methane yield coefficient (based on organic load)
C	Contois empirical constant
e	Emission
E_A	Volumetric daily energy production rate
exp	Experimental data
e/yr	Emission per year
f	Recovery factory (for TVFA)
F	Volumetric substrate removal rate
g	Gravity force
k	Hydrolyzed substrate transport rate coefficient
K	Kinetic parameter (Chen-Hashimoto equation)
kGy	Kilo gray
K_h	Hydrolysis rate coefficient
kHz	Kilo Hertz
K_s	Half-saturation constant for hydrolyzed substrate
m	Biomass maintenance coefficient

MHz	Mega Hertz
M_V	Volumetric methane production rate
pred	Predicted data
Q	Flow rate
R	Refractory coefficient
r^2	Regression coefficient (linear)
R^2	Regression coefficient (non-linear)
S'	Limiting substrate concentration
S	Effluent biodegradable substrate concentration
S_h	Hydrolyzed substrate concentration
S_o	Influent biodegradable substrate concentration
S_r	Influent refractory substrate concentration
S_T	Total substrate concentration in the effluent
S_{To}	Total substrate concentration in the influent
STP	Standard temperature and pressure
S_u	Intracellular substrate concentration
T	Sum of squares
t	Time
t	Ton
V	Volume
W	Watt
X	Microbial (biomass) concentration
Y	Biomass yield coefficient
Y	Response
Y_{CH4}	Methane yield coefficient (based on organic utilized)

yr	Year
θ	Hydraulic retention time (HRT)

Kesan kadar bebanan organik terhadap prestasi pencernaan anaerobik secara mesofilik dan termofilik bagi efluen kilang kelapa sawit

ABSTRAK

Projek ini dilakukan bagi menyelidik prestasi pencernaan anaerobik secara mesofilik dan termofilik bagi efluen kilang kelapa sawit (POME). Pada mulanya, kekat enapcemar telah diadaptasikan pada suhu mesofilik and termofilik sebelum permulaan pencernaan anaerobik. Penghasilan CH_4 yang kerap pada kedua-dua suhu menunjukkan bahawa bacteria anaerobik telah mengadaptasi POME dengan baik. Selepas itu, kasan kadar bebanan organik terhadap pencernaan anaerobik secara mesofilik dan termofilik telah dikaji. Prestasi pencernaan secara mesofilik dan termofilik adalah hampir sama semasa OLR $\leq$ 4.0 g COD/L/day. Purata biodegradasi POME dalam reaktor mesofilik dan termofilik adalah 77.14 % and 80.35 % masing-masing. Reaktor termofilik lebih bercekap kerana kadar penghasilan CH_4 maksimumnya (1.940 L CH_4/L/day) adalah 53 % lebih tinggi daripada reaktor mesofilik (1.267 L CH_4/L/day). Pekali hasil metana bagi kedua-dua reaktor didapati menurun apabila OLR ditingkatkan kerana kehilangan biomass secara beransur-ansur. Kepekatan efluen substrat (S_T), kadar penyinkiran substrat (F) dan kadar penghasilan metana (M_V) dapat diramal melalui model kinetik umum. Parameter-parameter bio-kinetik (A, R, μ_m, K_s dan B_o) bagi pencernaan mesofilik adalah 0.0419, 0.1729, 0.0756 day^{-1}, 0.2774 g/L and 0.322 L CH_4/ g COD_{added}; manakala bagi pencernaan termofilik adalah 0.0342, 0.1428, 0.1130 day^{-1}, 0.2610 g/L and 0.3136 L CH_4/g COD_{added}. Nilai A yang rendah menunjukkan sistem tersebut lebih sesuai untuk peringkat hidrolisis dalan percernaan anaerobik.

Effect of the organic loading rate on the performance of mesophilic and thermophilic anaerobic digestion of palm oil mill effluent

ABSTRACT

This project investigates the performance of mesophilic and thermophilic anaerobic digestion of palm oil mill effluent (POME). First, the scum-sludge mixture was acclimatized at mesophilic and thermophilic temperature prior the start-up of anaerobic digestion. The rapid CH_4 production under both temperatures implied the anaerobic bacteria well adapted to POME. Later, the effect of organic loading rate (OLR) on anaerobic digestion of POME was investigated. The performance of mesophilic and thermophilic digestions were similar when OLR was $\leq$ 4.0 g COD/L/day. The average biodegradability of POME in mesophilic and thermophilic reactors was 77.14 % and 80.35 % respectively. Thermophilic reactor is more efficient because its maximum CH_4 production rate (1.940 L CH_4/L/day) was 53 % higher than mesophilic reactor (1.267 L CH_4/L/day). The methane yield coefficient (Y_{CH4}) observed in both reactors was decreased with the increase of OLR because of the gradual lost of biomass. The effluent substrate concentration (S_T), volumetric substrate removal rate (F) and volumetric methane production rate (M_V) could be predicted using the generalized kinetic model. The estimated bio-kinetic parameters (A, R, μ_m, K_s dan B_o) for mesophilic digestion is 0.0419, 0.1729, 0.0756 day^{-1}, 0.2774 g/L and 0.322 L CH_4/ g COD_{added}; for thermophilic digestion is 0.0342, 0.1428, 0.1130 day^{-1}, 0.2610 g/L and 0.3136 L CH_4/g COD_{added}. Low value of A implied the batch-fed systems are more suitable for the hydrolysis step in anaerobic digestion.

CHAPTER ONE

INTRODUCTION

1.1 Palm Oil Industry in Malaysia

The Malaysian palm oil industry has grown over the past few years to become the world's second largest producer of crude palm oil (CPO) (MPOB, 2010). Also, Malaysia is the second largest exporters of palm oil which contributed to 45 % of the world's palm oil exportation. In year 2009, the total exports of oil palm products, consisting of palm oil, palm kernel oil, palm kernel cake, oleo-chemicals, biodiesel and finished products have achieved total export earnings of RM 49.59 billion (MPOB, 2010). This industry served as the backbone of Malaysian economy and has significantly increased the living standard of its population (Lam and Lee, 2011). Palm oil is even used to produce renewable energy - biodiesel. The current development of palm oil industry in Malaysia is summarized in Table 1.1.

Table 1.1 Palm oil industry development in year 2009 (MPOB, 2010)

Parameters	**Value**
Oil palm planted area, hectares	4691160
Fresh fruit bunch yield, tonnes/hectare	19.20
Number of palm oil mill (in operation)	416
Total mill capacity, tonnes/year	99658600
Oil extraction rate, %	20.49
CPO yield, tonnes/hectares	3.93
Annual CPO production, tonnes	17564937
Total export earnings, RM	49.59 billion

Malaysia has adopted a wet process for palm oil milling since the dry process is unsuitable for use in large-scale productions (Prasertsan and Prasertsan, 1996). It is estimated that 5 to 7 tonnes of water are required to produce one tonne of CPO, and more than 50 % of this water ends up as palm oil mill effluent (POME) (Wu et al., 2009). Therefore, the production of such huge amount of CPO results in even larger amount of POME in which case in year 2009 alone, around 44 million m^3 of POME was generated and the figure is expected to rise every year.

1.2 Bioenergy Production from POME

The effective treatment of POME is a big challenge to the palm oil industry because releasing untreated POME directly to surface watercourse will led to serious environmental pollution. Previously, ponding system is the most popular treatment of POME in Malaysia (Ma and Augustine Ong, 1985). A baseline study of methane emission from anaerobic ponds of POME treatment showed that the methane content was between 35.0 % and 70.0 %, with average emission of 54.4 % CH_4 (Yacob et al., 2006). POME is recognized not because of the large quantity generated but more significant as a type of high organic strength wastewater. The industry has started to look into new sources of incentives which may be derived from the Clean Development Mechanism (CDM) under Kyoto Protocol 1997, if efforts to reduce CH_4 emission from POME treatment systems were to be implemented (Tong and Jaafar, 2004). The mechanism had a dual purpose of assisting the non-Annex I Parties in achieving sustainable development and also assisting the Annex I Parties (developed countries) in achieving compliance with their quantified greenhouse gases (GHG) emission commitments (Hassan et al., 2009). CDM could be used as a platform to demonstrate and disseminate new and modern bio-energy technology with low investment risks and enhanced project's cost-efficiency (Hassan et al., 2009). As at the end of March 2009, there were 12 CDM projects on methane recovery and utilization registered with the Executive Board (EB) United Nation Framework on Climate Change (UNFCC). These projects will contribute to the sustainability of development from many aspects of environment and economy. The energy recovery and utilization system will reduce the uncontrolled emissions of methane and the demand on fossil fuels. Thus, the displacement of fossil fuels by methane will decrease the emission of GHG as well as reducing the operating and maintenance costs in palm oil mills (Hassan et al., 2009).

Tong and Jaafar (2004) have proved that POME anaerobic digester technology could offer an attractive energy source recovery while concurrently reducing GHG emission. The cost-benefit analysis by Yeoh (2004) also demonstrated high energy potential of POME with short investment payback period. Thus, the palm oil industry could earn carbon credits as revenue and recover energy by the utilization of methane gas as renewable energy from the anaerobic digestion of POME (Poh and Chong, 2009).

1.3 Rationale for the Proposed Project

The rising worldwide utilization of fossil fuels has increasingly threatened the world stability. The negative effects of global climate change, world energy conflicts and energy source shortages are observed at all levels of the society, i.e. locally, regionally and globally (Kothari et al., 2010). A lot of research and development are going to solve the local, regional and global problems. Most of the researchers show their reliance on renewable energy technologies for sustainable development and long lasting life on this planet earth for their daily energy needs through waste-to-energy routes, which do not cause negative societal impacts (Kothari et al., 2010).

Environmental concern is always ignored by industries because the construction, operation and maintenance costs of wastewater treatment plant may be cut back the industry profit. These costs could be return by integrate waste treatment and renewable energy technologies. Anaerobic digestion is one of the major waste-to-energy options which minimizing environmental pollution and meeting the demand of energy for various purposes. The biogas (CH_4) produced may be utilized for combined heat and power production or for transport fuel production. The potential revenue from CH_4 enriched biogas when replacing petrol is higher than that for replacing diesel (Murphy et al., 2004). The high organic strength of POME makes it become one of the potential renewable energy resources to attain sustainability and for switch over to waste-to-energy routes.

According to Wu et al. (2010), the anaerobic suspended growth digester for POME is operated under mesophilic condition. However, it would be advantageous to carry out the anaerobic digestion under thermophilic temperature with the POME temperature varying between 45 to 70 °C (Poh et al., 2010; Wu et al., 2010). The methane yield and production rates of thermophilic digester were higher than those obtained from mesophilic digester. As said by Gannoun et al. (2007), the thermophilic reactor produced a higher chemical oxygen demand (COD) removal and biogas yield than mesophilic reactor, and could sustain this at high organic loading rate (OLR). The increased energy requirement was believed to be compensated by the increased methane production (Fannin, 1987). It is generally recognized that higher temperature promote higher reaction rates during anaerobic digestion, thus allowing lower hydraulic retention time (HRT) and higher organic loading rate (OLR) without reduction in conversion efficiency (Fannin, 1987). However, Poh et al. (2009) stated higher OLRs will reduce COD removal efficiency in wastewater treatment. The biogas production will increase with OLR until a stage when methanogens could not metabolize quick enough to transform acetic acid to CH_4. It is practically difficult to alter the characteristics of wastewater. Therefore, the operating temperature and OLR of wastewater treatment plant are two common but important control parameters which significantly affects the process efficiency. In order to maximize the CH_4 production, more researches should be focus on determination of optimum operating condition for anaerobic digestion.

1.5 Objectives

In general, this study aims to investigate the performance of anaerobic digestion of POME using partial-mixed semi-continuous laboratory reactor operated at both mesophilic and thermophilic temperatures. It is vital to develop a flexible wastewater treatment system with energy recovery that can be applied in the palm oil industries in order to reduce its environmental impact to surface water and atmosphere. There are three specific objectives in order to meet the goals:

i. To investigate the feasibility of conversion of scum-sludge mixture into inoculum seed for start-up of mesophilic and thermophilic anaerobic digestions;

ii. To evaluate the effect of OLR on the performance (in terms of biodegradability and CH_4 production) of mesophilic and thermophilic anaerobic digestions of POME; and

iii. To estimate the bio-kinetic parameters (A, μ_m, K_s, B and R) in mesophilic and thermophilic anaerobic digestions of POME at the corresponding OLR.

CHAPTER TWO

LITERATURE REVIEW

2.1 Crude Palm Oil Production and Sources of Water Pollution

In Malaysia, the wet palm oil milling process is the most standard and typical way of extracting palm oil. This process requires about 5 to 7 tonnes of water for each tonne of crude palm oil produced, thus giving rise to the main source of wastewater known as palm oil mill effluent (POME). The palm oil milling process is similar for all the mills throughout the country. Figure 2.1 shows the stages involved in the typical processing of crude palm oil and the source of POME. Details of the palm oil mill processes are explained and summarized in previous literatures (Ma and Augustine Ong, 1985; Prasertsan and Prasertsan, 1996; Mahlia et al., 2001; Hassan et al., 2006; Wu et al., 2010).

2.2 Palm Oil Mill Effluent (POME)

As mentioned in Figure 2.1, POME mainly originated from sterilizer condensate, separator sludge from clarification and hydrocyclone wastewater. Under proper mill operation and management, about 0.9 m^3 of the first source of POME, sterilizer condensate is generated for each tonne of crude palm oil produced. In the other hand, the bottom sludge from clarification tank is sent to a sludge separator or centrifuge where approximately 1.5 m^3 of sludge waste is obtained per tonnes of crude oil produced. The third source of POME, washing water of the hydrocyclone is about 0.1 m^3 per ton of crude palm oil produced. Therefore, approximately 2.5 m^3 of POME is generated per tonne of crude palm oil produced under typical operation processes (Ma and Augustine Ong, 1985).

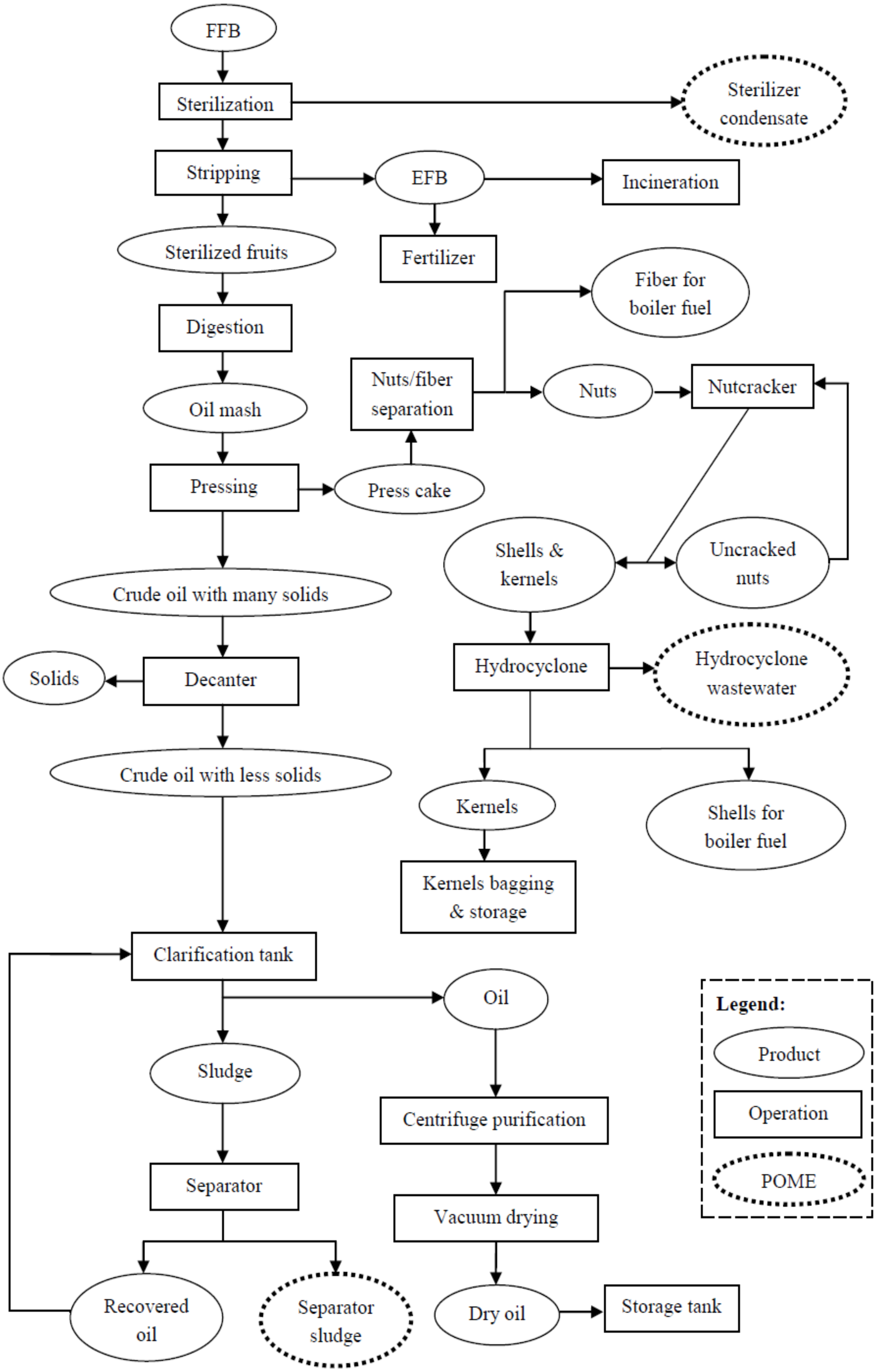


Figure 2.1 Flow diagram of a typical processing of crude palm oil and the source of POME

POME, when fresh, is a thick brownish colloidal mixture of water (95 to 96 %), oil (0.6 to 0.7 %), and total solids (4 to 5 %), including suspended solids (2 to 4 %), which are mainly debris from palm mesocarp. The discharge temperature of POME is 80 to 90 °C due to the introduction of heat from sterilization and vigorous mechanical processes (Hassan et al., 2006). It is important to note that no chemicals are added in the oil extraction process therefore making POME nontoxic to the environment. But the direct discharge of POME into watercourses will make serious environmental problems due to its high biological oxygen demand, BOD (62500 to 69215 mg/L), chemical oxygen demand, COD (95465 to 112023 mg/L), oil and grease (O&G) (8845 to 10052 mg/L), and total solids, TS (68854 to 75327 mg/L) (Choorit and Wisarnwan, 2007). It is 100 times as polluting as domestic sewage (Ma and Augustine Ong, 1985). The properties of POME vary widely and depend on the processing techniques, quality control of individual mills, age or type of fruit, crop seasons and other factors (Hassan et al., 2006; Poh et al., 2010; Wu et al., 2010). The characteristics of POME in previous researches are shown in Table 2.1.

The particulate fraction in POME included colloidal rod-like particles of macrofibrils, raphide particles and plant cell debris, the last being the major component. Together they contributed slightly less than 50% to the pollutant level of the effluent (Ho and Tan, 1983). Lignocelluloses are the main recalcitrant organic material found in POME (Saifuddin and Fazlili, 2009). It is known that the enzymatic hydrolysis of lignocelluloses is limited by its polymeric structures thus attribute a possible barrier to the successful anaerobic treatment of POME (Wu et al., 2010). The particulates fractionated from POME along with the corresponding details are shown in Figure 2.2. Besides that, about 30 % of the total solvent-extractable oil in POME existed as free oil droplets where the rest is almost completely associated with the particulate fraction (Ho et al., 1984).

Table 2.1 The characterization of POME in previous researches

References / Parameters	Borja and Banks, 1993	Borja et al., 1995a	Borja et al., 1996b	Chin et al., 1996	Mustapha et al., 2003	Choorit and Wisarnwan, 2007	Zhang et al., 2008	Poh et al., 2010
pH	4.9	4.6	4.4	4.4	4.6	4.66	4.8	4.86
TCOD	65000	48200	30600	67000	58000	100600	79723.2	79000
SCOD	-	-	-	-	-	-	-	36200
BOD	-	-	-	28000	-	65427	-	49000
TS	-	-	31200	54000	45000	68858	67200	43300
VS	-	-	24300	-	-	-	-	42600
TSS	22800	15200	10800	31800	23200	46213	49300	39100
VSS	18100	11800	8100	-	20800	-	35935	-
VFA	-	4300	-	1000	-	4335	2287	18000
TKN	855	-	365	1000	920	1493	873.6	930
Oil and grease	-	-	-	-	-	8845	17410	14700
Proteins	-	1120	-	-	-		-	-
Fats	-	4500	-	-	-	-	-	-
Cellulose	-	950	-	-	-	-	-	-
Hemicellulose	-	540	-	-	-	-	-	-
Lignin	-	-	-	-	-	-	-	1700
Starch	-	650	-	-	-	-	-	-
P	160	-	110	-	-	-	277.7	-
Fe	470	-	205	-	-	-	61.17	-
S	140	-	60	-	-	-	400	-
SO_4	-	-	-	-	-	-	-	5
Ca	497	-	220	-	-	-	607.3	-
Na	14	-	4	-	-	-	87.92	-
K	1160	-	510	1500	-	-	5533	-
Mg	390	-	170	-	43.4	-	1065	-
Cu	2	-	1	-	1.8	-	5.08	-
Zn	13	-	6	-	4.7	-	6.83	-
Mo	0.5	-	0.1	-	-	-	-	-
Co	0.03	-	0.007	-	-	-	-	-
Mn	1.5	-	0.6	-	6.9	-	8.572	-
Ni	2.8	-	1.2	-	-	-	-	-
Al	197	-	120	-	-	-	6.299	-
B	2	-	0.9	-	-	-	-	-
Ba	0.6	-	0.3	-	-	-	0.4802	-
Si	125	-	55	-	-	-	99.67	-
Sn	-	-	-	-	-	-	3.669	-
Pb	-	-	-	-	12.4	-	-	-
PO_4	-	-	-	140	775	-	-	-
NO_3	-	-	-	-	62.5	-	-	-
Cl	-	-	-	-	900	-	-	-

Unit for all parameter is mg/L except pH

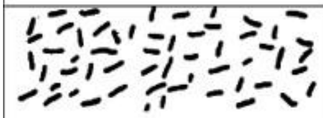
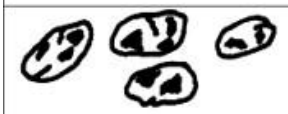
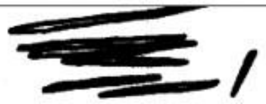
Pictorial representation of fractions	*Centrifugal force*	*Dimensions*	*Weight percentage, w/w (Wet)*	*Characteristics*
	112 *g*	Length: 2.23 ± 0.52 μm Width: 0.59 ± 0.03 μm	0.12 – 0.15	Rod-like particles of colloidal dimensions
	40 *g*	Length: 10 – 40 μm Breadth: 10 – 40 μm	1.50 – 2.40	Plant cell debris: ruptured cell-walls and cell debris with entrapped oil drops
	28 *g*	Length: 50 – 150 μm Breadth: 50 – 130 μm		
	10 *g*	Length: 50 – 130 μm Diameter: 2.0 – 3.0 μm		Crystal-like particles with long and needle shape at both ends
	Normal gravity	Not determined	0.04 – 0.07	Fiber and sand

Figure 2.2 Centrifugal fraction of POME
Source: Wu et al. (2009)

2.3 Conventional Treatment System of POME - Ponding System

Ponding system is the common treatment system which has been adopted in more than 85 % of palm oil mills to treat POME (Ma and Augustine Ong, 1985). A typical ponding system requires a vast area to accommodate a series of ponds to achieve the desired characteristic for discharge to meet local standard (Table 2.2). The system may be comprised of different facilities such as de-oiling tank, holding/equalization ponds, acidification pond, anaerobic, facultative and algae (aerobic) ponds but the number and size of tanks/ponds varies according to the capacity of palm oil mill. It is cheap to construct, by excavating the earth and only a layer of clay lining is needed (Hassan et al., 2006). The anaerobic ponds are usually 5 to 7 m deep, the facultative anaerobic ponds are about 1.5 m deep while the aerobic ponds requires shallower depth of approximately 0.5 to 1 m (Ma and Augustine Ong, 1985; Hassan et al., 2006), the effective hydraulic retention times (HRT) of 45, 20 and 14 days, respectively. In order to meet the requirement of DOE, the ponding system is normally operated at low rate with organic loading of 0.2 to 0.35 kg BOD/m^3.

Table 2.2 Parameter limits for watercourse discharge

Parameters[a]	Discharge standard (1-1-1984 and thereafter)
Temperature, °C	45
pH	5.0 – 9.0
Oil and grease	50
BOD_3[b]	100
Suspended solids	400
Total nitrogen	200[c]
Ammonical nitrogen	150[c]

[a] All parameters are in mg/L except temperature and pH.
[b] Sample is incubated for 3 days at 30 °C.
[c] Value of filtered sample.
Source: Lam and Lee, 2011

The treated POME flows under gravity using a sideways tee-type subsurface draw-off system in between the different stages of the ponding system. Figure 2.3 shows a simple pond system layout which consists of an oil separator, a wastewater pump, a lift station, and 8 functioning ponds arranged in series (Chin et al., 1996).

Figure 2.3 illustrated a two-phase operation where acidification phase is separated from the methanogenic phase (Ma and Augustine Ong, 1985). The effluents of the first two ponds of the treatment facilities were acidic but the pH continued to increase to greater than 8 for the final effluent (Chin et al., 1996). Investigation by Yacob et al. (2006a) showed that the anaerobic pond had average CH_4 composition of 54.4 %, ranging from 35.0 to 70.0 %, whereas the emission rate was averaged at 1.5 L/min/m^2, ranging from 0.5 to 2.4 L/min/m^2. The severe fluctuations were due to the palm oil mill operations and seasonal cropping of oil palm (Poh et al., 2010). It is quite difficult to control and monitor the ponding system due to its size and configurations.

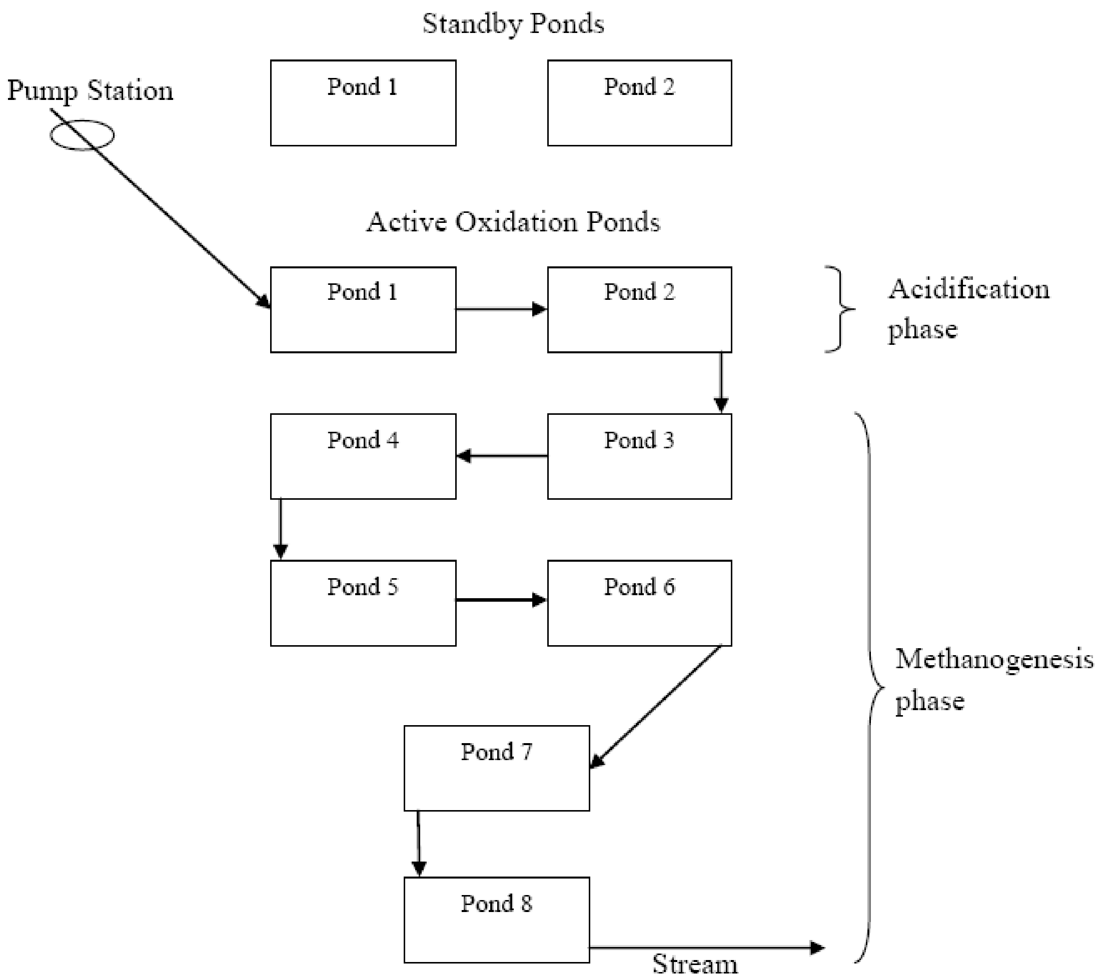


Figure 2.3 Schematic diagram of POME ponding system
Source: Adapted from Chin et al. (1996)

As a result of low organic loading rate, localized mixing through rising bubbles that bring sludge to the surface was the only mixing observed in the anaerobic pond (Yacob et al., 2006a). This type of passive mixing is always inadequate where dead spots or short circuiting in the ponding system are common. The poor mixing system plus the presence of oil and grease in POME leads to the formation of scum, islands of solid that can be seen floating at the surface of anaerobic pond. Other operating problems are the accumulation of sludge that shallowed the ponds depth with the sludge and scum will be clumping together inside the pond therefore significantly lowering the treatment efficiency by reducing the treatment capacity as well as HRT (Chin et al., 1996; Hassan et al., 2006). Regular desludging by means of submersible pumps or excavators is necessary to recover the treatment efficiency. The removed sludge can be used as fertilizer after it is being dewatered and dried.

2.4 Anaerobic Digestion

Anaerobic digestion is the biodegradation of complex organic matters under the absence of oxygen. It is a time consuming process as the bacterial consortia responsible for the biodegradation requires time to acclimatize to the new environment before they start to consume on organic matters to reproduce (Poh and Chong, 2009). The degree of biodegradation as well as biogas quality can be affected in various ways including type of digester, operating condition, influent substrate characteristic etc. There is a sequence of reactions involved in the bioconversion of organic matters into methane, carbon dioxide and water: i) hydrolysis, ii) acidogenesis, iii) acetogenesis and iii) methanogenesis. The overall anaerobic digestion process is shown in Figure 2.4.

Hydrolysis is a process where high molecular weight polymeric component (organic polymers), e.g., carbohydrates, proteins or lipid are hydrolyze by means of the hydrolytic extracellular enzymes, into smaller molecules and simple water soluble compounds, such as simple sugar, alcohols, amino acids and fatty acids. In acidogenesis, these hydrolytic intermediates are further broken down into water soluble organic end products, mainly short chained fatty acids, carbon dioxide and hydrogen by the same fermentative bacteria that responsible for the hydrolysis, displacing the process into the cell itself. After that, the intermediates from previous step are further digested by acetogens to produce largely acetic acid as well as carbon dioxide and hydrogen. The acetogenesis can only take place at a low concentration of hydrogen. Due to that, acetogens live in symbiosis with methanogens, where hydrogen and carbon dioxide will be utilized by hydrogenotrophic methanogens while acetic acid will be utilized by acetotrophic methanogens to generate biogas (methane) as final product. Methanogenics are strictly anaerobic because the present of oxygen will inhibit their metabolisms or mortifies the microorganisms.

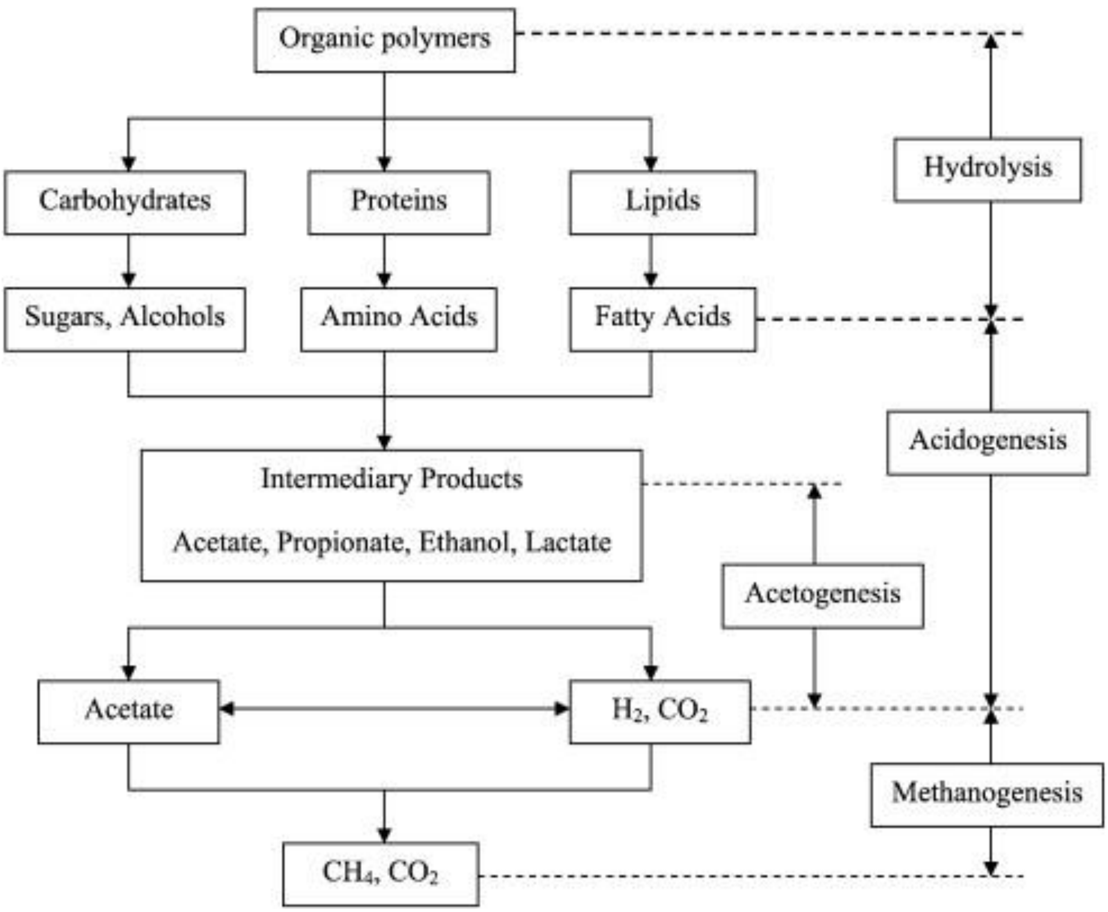


Figure 2.4 Flow chart of anaerobic digestion
Source: Lam and Lee (2011)

The substrate composition is a major factor affecting the biogas yield and its production rate. The specific biogas yields and qualities of carbohydrates, lipids and proteins are shown in Table 2.3. Based on the research by Yacob et al. (2006a), approximately 28 m^3 of biogas, mainly consist of methane and carbon dioxide in 65:35 ratio, generated from every tonne of POME. The biogas may contain traces of water vapour, hydrogen sulphide (H_2S) or hydrogen which influence the selection of technologies for cleaning and utilizing of biogas (Pesta, 2007). It is known that methane is one of the GHG with its global warning potential twenty one times more potent than carbon dioxide. However, methane is not captured in POME treatments that have been applied either as open ponding systems or open digesting tank systems. This makes the overall processes not environmental friendly and contributed the highest impact towards the climate change (Lam and Lee, 2011).

Table 2.3 Specific biogas yield and qualities of substrates main components

	Gas yield (L/kg ODM)	CH_4 (% by vulume)	CO_2 (% by volume)	Calorific value (kWh/kg ODM)
Carbohydrates	790	50	50	4.0
Lipids	1250	68	32	4.9
Proteins	700	71	29	8.0

Source: Pesta (2007)

Previous investigations on anaerobic digestion of POME were conducted using various types of reactor. Table 2.4 summarized the performance of various reactors treating POME in previous studies. It is clear that the COD removal efficiency of anaerobic digestion is significantly affected by the reactor design, HRT and influent substrate concentration. Thus, these variations complicated the direct comparison of the reactors performance. But it may serve as a reference for those reactors operated under similar conditions.

Table 2.4 Performance of various reactors treating POME

Type of reactor	HRT, days	Influent COD, g/L	OLR, g COD/L/day	COD removal, %	Reference
Up-flow anaerobic sludge fixed film bioreactor	1.5	26.21	17.47	90.2	Najafpour et al., 2006
		34.73	23.15	89.5	
Anaerobic hybrid digester	3.5	56.6	16.2	92.3	Borja te al., 1996a
		65	18.6	77.9	
Up-flow anaerobic sludge blanket	4	42.5	10.63	96	Borja and Banks, 1994a
Modified anaerobic baffled reactor	3	16	5.33	77.3	Faisal and Unno, 2001
Immobilized cell bioreactor	6.2	6.9	11.13	96	Borja and Banks, 1994b
Up-flow anaerobic sludge fixed film bioreactor	1.5	34.725	23.15	89.6	Zinatizadeh et al., 2006
Continuous flow, completely mixed reactor	50.0	48.2	0.964	83.4	Borja et al., 1995a
	25.0	48.2	1.928	78.2	
	12.5	48.2	3.856	67.0	
	8.3	48.2	5,784	52.9	
Semi-commercial closed digester	10.7	111.11	10.0	97.5	Sulaiman et al., 2009
Expended granular sludge bed reactor	2	79.723	17.5	91	Zhang et al., 2008
Continuous stirred tank reactor	7[a]	95.465	12.25	71.10	Choorit and Wisarnwan, 2007
	5[b]	95.465	17.01	70.32	

[a] mesophilic

[b] thermophilic

Source: adapted from Zinatizadeh et al. (2006)

2.4.1 Success Case Study – Full-Scale Anaerobic Digestion of POME

Keck Seng (M) Berhad revealed one of the successful reported cases in implementing the closed system of POME anaerobic digester. The generated biogas was captured and it had been utilized efficiently. The continuous fed and complete mixed system has been operated over 18 years practically without any interruptions or failure in daily operation. The digester (operating temperature was not mentioned) with volumetric feeding rate of 400 m^3/day of POME has been estimated to generate total biogas of 11200 m^3/day with CH_4 generated approximately 62.5 % (7000m^3). The biogas generated had been utilized for steam boilers and high-pressure heaters for the palm oil refinery and a total amount of RM 1.46 million was saved in terms of diesel and medium fuel oil as reported in year 2002. The total methane captured and utilized as boiler fuel has been estimated to be about 1407 t/yr. In terms of GHG emission avoided, this quantity converts to 29547 t CO_2 e/yr (Tong and Jaafar, 2004). Besides that, as at the end of March 2009, there were 12 methane recovery CDM projects in Malaysia registered with the Executive Board (EB) of United Nation Framework Convention on Climate Change (UNFCCC) (Hassan et al., 2009).

2.5 Factors Influencing Anaerobic Digestion Performance

Adequate control is required to prevent digester failure since a lot of factors affect the performance of anaerobic digestion. The major factors that significantly influence the digester performance in POME treatment including pH, volatile fatty acids (VFA), operating temperature, hydraulic retention time (HRT), organic loading rate (OLR), inoculum, mixing and feeding mode (Fannin, 1987).

2.5.1 pH

The efficiency of anaerobic digestion in terms of pollutant removal and biogas production is highly depending on the pH stability. Previous investigations has reported that excellent performance of anaerobic digester occurred in pH range of 6.5 to 8.0 (Borja et al., 1995b; Borja et al., 2002; Hu et al., 2002; Borja et al., 2005; Rincom et al., 2008a). Although the pH may be affected by the digester operating conditions and characteristics of the feeding substrate, the anaerobic microbial community showed tolerance at pH near to neutral. Borja et al. (1995b) observed that similar influence of pH in mesophilic and thermophilic conditions which optimal working pH range of anaerobic digester was between 6.6 and 7.8. However, the decreasing of pH value due to volatile acids accumulation has made the system failure consequently and drastically reduced the CH_4 production as well as COD removal.

2.5.2 Volatile Fatty Acids (VFA)

VFA is the most important and main intermediates produced during the anaerobic digestion of complex polymeric components in the hydrolysis and acidogenesis processes. It is the main precursor for biogas production by methanogens. The concentration of VFA in anaerobic digester is determined by their rate of production and their rate of removal (Fannin, 1987). Accumulation of high concentration of VFA will result in decrease of pH, acidification, inhibit methanogenic metabolisms therefore leading to failure of the anaerobic process. The utilization of VFA by methanogens will increase the pH value. Thus, the concentration of total VFA can be considered as essential control parameters in liquid phase and indicators to the performance of anaerobic digestion.

2.5.3 Operating Temperature

Most reactor operate at either mesophilic temperatures or thermophilic temperatures, with optima at 35 °C and 55 °C respectively although anaerobic digestion can take place at psychrophilic temperature below 20 °C (Borja et al., 2002). POME is discharged at temperatures about 80 to 90 °C (Najafpour et al., 2006) but the effluent temperature may be different depends on the crop seasons as well as mill operation (Poh et al., 2010). The high discharge's temperature makes anaerobic treatment of POME at both mesophilic and thermophilic temperatures feasible. In Malaysia anaerobic treatments of POME are usually conducted at mesophilic temperature range. A few researches have been conducted to examine the feasibility of treating high organic strength wastewater in the thermophilic temperature range such as olive mill wastewater (Borja et al., 1995b) and POME (Borja and Banks, 1993; Borja et al., 1995a; Choorit and Wisarnwan, 2007). These studies demonstrated the successful of thermophilic anaerobic digestion. Choorit and Wisarnwan (2007) reported similar COD reduction and methane yield in mesophilic and thermophilic reactors at the same OLR and HRT. However, Borja et al. (1995) observed that higher methane production was obtained in thermophilic reactor in comparison to mesophilic reactor. The anaerobic digestions process exhibited a different finding in each case. It is possibly due to the different characteristics of wastewater used and also a variation in each system configuration.

The effect of temperature, OLR and HRT on anaerobic digestion of high strength wastewater has been investigated by a few researchers. Borja et al. (1995b) found that the methane yield coefficient was 28 % higher in the thermophilic process in comparison to the mesophilic conditions. Choorit and Wisarnwan (2007) also reported that at same OLR, the process in thermophilic reactor was more stable compared to process in the mesophilic reactor. Therefore, the thermophilic digesters are able to tolerate higher OLR, operate at shorter HRT and generate more methane (Borja et al., 1995b; Choorit and Wisarnwan, 2007). Nevertheless, the temperature fluctuation should be minimized because thermophilic digesters could only tolerate temperature change of 0 ± 0.80 °C and that the volatile acids concentration were always more than twice as high as those in mesophilic digesters (Fannin, 1987).

2.5.4 Hydraulic Retention Time (HRT)

The HRT in anaerobic digesters is determined by calculating the number of days required for displacement of the mixture volume of the culture (Fannin and Biljetina, 1987). The HRT of a digester is reduced by increasing the loading rate. As result, the increasingly large amount of slow-growing methanogenic bacteria washed out of the system will led to a decreased conversion efficiency, lower methane yield as well as greater digester instability.

2.5.5 Organic Loading Rate (OLR)

OLR is another important operating condition (except temperature) which controls the effectiveness of treatment process. Higher OLR shorten the anaerobic treatment time as well as reduced reactor volume. OLR is related to substrate concentration and HRT, treatment of high substrate concentration with short HRT reduces the contact time of substrate and biomass. Thus, the balance between these two parameters is necessary to obtain a good anaerobic performance (Poh and Chong, 2009). Many studies have proved that the COD removal efficiency in anaerobic treatment system was reduced at higher OLR (Borja et al., 1995a; Borja et al., 1995b; Borja et al., 2004; Rincon et al., 2006; Choorit and Wisarnwan, 2007; Rincon et al., 2008a; Rincon et al., 2009; Rincon et al., 2010). However, the methane production was kept increasing with OLR until a maximum level was achieved, where further increase of OLR led to reduce generation of methane and accumulation of volatile fatty acids (Borja et al., 1995a; Borja et al., 1995b; Borja et al., 2004; Rincon et al., 2006; Rincon et al., 2008a; Rincon et al., 2009; Rincon et al., 2010).

2.5.6 Inoculum

In previous lab-scale experiments, inoculum was introduced into digester since the microorganism population in wastewater might be too low to initiate anaerobic digestion (Borja et al., 1995a; Hu et al., 2002; Borja et al., 2003; Mustapha et al., 2003; Yacob et al., 2006b; Choorit and Wisarnwan, 2007; Rincon et al., 2008a; Rincon et al., 2008b; Rincon et al., 2009; Zhang et al., 2008). An active inoculum can be obtained from existing digester thus minimized time for bacteria cultivation (Borja et al., 1995a; Hu et al., 2002; Borja et al., 2003; Rincon et al., 2008a; Rincon et al., 2008b; Rincon et al., 2009). However, an acclimatization period and nutrient supplement may be required for the microorganism adaption to new environment, especially for those treating different substrate (Hu et al., 2002; Borja et al., 2003; Rincon et al., 2008a; Rincon et al., 2008b; Rincon et al., 2009). Sludge from existing digester treating similar substrates was used to facilitate the adaptation of microorganisms in anaerobic treatment, reducing the acclimatization period as well as the HRT (Borja et al., 1995a; Rincon et al., 2003; Yacob et al., 2006b; Rincon et al., 2008a). Besides that, the sludge from anaerobic pond can be used for adaptation to anaerobic treatment (Mustapha et al., 2003; Choorit and Wisarnwan, 2007).

2.5.7 Feeding and Mixing Mode

Mixing of the digester contents can be carried out in different ways depending on the reactor design and substrate characteristics. The common method of mixing employed is propellers mixing. To achieve adequate mixing and to prevent the need for moving parts within the reactor, the recirculation of biogas through the bottom of the reactor or hydraulic mixing by recirculation of the digestate with a pump can be used (Ward et al., 2008). Besides that, periodical feeding also may give a minimal mixing effect.

Usually, the continuous feeding and continuous/complete mixed system (Borja et al., 1995a; Borja et al., 1995b; Rincon et al., 2008a; Rincon et al., 2008b) were used to evaluate the performance of the anaerobic reactor for treating wastewater, and to determine the optimum organic loading rate (OLR). Furthermore it is useful for the kinetic study of the anaerobic process. Some studies on lab-scale reactor has applied a semi-continuous feeding system (Choorit and Wisarnwan, 2007; Rincon et al., 2010) as it is more feasible to control and monitor the process.

The contents of most anaerobic reactor are completely mixed to ensure the intimate contact between microorganisms and organic matters, prevent precipitation of denser particles and release the biogas bubbles trapped in the medium which ultimately results in enhanced anaerobic digestion. Therefore, previous lab-scale anaerobic reactors reported mostly were operated in continuous mixing mode (Borja et al., 1995a; Borja et al., 1995b; Borja et al., 2003; Borja et al., 2005; Rincon et al., 2008a; Rincon et al., 2008b; Rincon et al., 2009; Rincon et al., 2010; Senturk et al., 2010).

However, continuous mixing was not necessary for good performance because process inhibition was only observed at higher OLR (Stroot at al., 2001). Kim et al.

(2002) reported that the non-mixing anaerobic reactors showed a higher gas production indicating that non-mixing reactor configuration has closer microbial consortia proximity than others. Sulaiman et al. (2009), who has conducted an anaerobic digestion of POME in semi-commercial closed digester tank, also reported that vigorous mixing shall inhibit CH_4 production and caused high concentration of total volatile fatty acids (TVFA) in the system. Furthermore, Stafford (1982) reported no improvement in gas yield for mixing speed between 140 and 1000 rpm, but a slight reduction in biogas production at higher speeds were observed. It is possibly due to shear forces that is separating the hydrolytic bacteria from their polymeric substrates. Mixing appears to inhibit the syntrophic oxidation of volatile fatty acids, possibly by disrupting the spatial concurrence of syntrophic bacteria and their methanogenic partners (Stroot at al., 2001). In addition, mixing systems not only affect the anaerobic efficiency but are often expensive to install, maintain and operate. Although many lab-scale investigations showed excellent performance of the completely mixed anaerobic reactor at agitation speed ranged from 70 to 260 rpm (Borja et al., 1995a; Borja et al., 1995b; Borja et al., 2003; Borja et al., 2005; Choorit and Wisarnwan, 2007; Rincon et al., 2008b; Rincon et al., 2009; Rincon et al., 2010; Senturk et al., 2010), but high speed continuous mixing systems seems to be impractical in conventional digester tank since the operating volume may be up to a few thousand cubic meter as stated by Tong and Jaafar (2004). Therefore, an efficient mixing system is advantageous in terms of productivity and cost effective (Ward et al., 2008).

2.6 Kinetic study of Anaerobic Digestion

Process modelling is a useful tool for describing and predicting the performance of anaerobic digestion systems. In early kinetic studies, the growth of mixed cultures in complex organic wastes was assumed to be similar to the growth of a pure culture utilizing simple substrates (Chen, 1987). Therefore, Monod type kinetic models have been widely applied to describe the process kinetics of continuous multicultural anaerobic digestion (Borja et al., 1995a). In the Monod equation, the specific growth rate is expressed only as a function of the concentration of the limiting substrate in the reactor.

$$\mu = \frac{\mu_{\max} S'}{Ks + S'} \tag{2.1}$$

However, the effluent substrate concentration is not independent of the substrate concentration entering the reactor when pure or heterogeneous cultures were used (Hu et al., 2002). Besides that, for those substrates that are inhibitory to the microorganisms at high concentration, such as volatile acids, the Monod kinetic equation was again to be non-predictable (Chen, 1987).

In the models proposed by Contois, specific growth rate (μ) is considered a function of the growth-limiting nutrients in both input substrate and effluent by use of an empirical constant (*C*) related to the microbial concentration (*X*) and the limiting substrate concentration (*S'*), thus:

$$\mu = \frac{\mu_{\max} S'}{CX + S'} \tag{2.2}$$

This model has general acceptability and account for bacterial growth in both batch and continuous bacterial cultures (Contois, 1959). On this basis, Chen and Hashimoto developed kinetic models for substrate utilization and methane production