

**TREATABILITY OF PALM OIL MILL EFFLUENT (POME) USING BLACK
LIQUOR IN AN ANAEROBIC TREATMENT PROCESS**

by

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LIST OF SYMBOLS

%	Percent
μ	Micro
=	Equal to
>	More than
\pm	Plus minus
\approx	Around
\geq	More or equal with
<	Less than
>>	Much more than

LIST OF ABBREVIATION

AFFR	Anaerobic fixed-film reactor
ANOVA	Analysis of variance
AOX	Adsorbable organic halide
APHA	America Public Health Association
ASBR	Anaerobic sequencing batch reactor
BL	Black liquor
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CPO	Crude palm oil
CSTR	Continuous stirred tank reactor
DO	Dissolved oxygen
DOE	Department of Environment, Malaysia
FFB	Fresh fruit bunch
GHG	Green house gas
HDPE	High density polyethylene
HRT	Hydraulic retention time
MLVSS	Mixed liquor volatile suspended solids
MPN	Most probable number
MPOB	Malaysia Palm Oil Board
NH ₃ -N	Ammonia nitrogen
O&G	Oil and grease
OLR	Organic loading rate
P	Probability
PC	Personal computer
POME	Palm oil mill effluent
ppm	Part per million

ppmv	Part per million by volume
SCOD	Solubilised chemical oxygen demand
SFB	Solubilised POME with palm fibre and commercialised bacteria
SFP	Solubilised POME with palm fibre and digested POME
SKB	Solubilised POME with palm kernel shell and commercialised bacteria
SKP	Solubilised POME with palm kernel shell and digested POME
SS	Suspended solids
TCD	Thermal conductivity detector
TCOD	Total chemical oxygen demand
TN	Total nitrogen
TPAD	Temperature-phased anaerobic digestion
TS	Total solids
TVS	Total volatile solids
UAF	Up-flow anaerobic filter
UASB	Up-flow anaerobic sludge blanket
US EPA	United State Environment Protection Agency
USA	United State of America
VFB	Synthetic wastewater with palm fibre and commercialised bacteria
VFP	Synthetic wastewater with palm fibre and digested POME
VKB	Synthetic wastewater with palm kernel shell and commercialised bacteria
VKP	Synthetic wastewater with palm kernel shell and digested POME
VOC	Volatile organic carbon
VS	Volatile solids
VSS	Volatile suspended solids
w/v	Weight over volume

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LIST OF PUBLICATIONS & SEMINARS

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- 2 Nik Norulaini, N. A., Ling, Y. L., Norli, I. and Mohd. Omar, A. K. (2006). Effect of chemical pulping black liquor addition on thermophilic anaerobic digestibility of palm oil mill effluent (POME). Malaysian Research Group International Conference, 19-21 June, University of Salford, UK.
- 3 Norli, I., Ho, C. M. and Ling, Y. L. (2006). Anaerobic digestion of mixed chemical pulping and palm oil mill effluent in suspended growth anaerobic digester. International Conference on Green and Sustainable Innovation, 29 Nov – 1 Dec, Chiang Mai, Thailand.

Kebolehrawatan Efluen Kilang Kelapa Sawit dengan Menggunakan Likuor Hitam Secara Proses Anaerobik

ABSTRAK

Kebolehrawatan efluen kilang kelapa sawit (POME) dalam pelbagai keadaan operasi telah dijalankan. Satu kajian skala makmal telah dijalankan pada suhu termofilik (55°C) untuk menilai dan membanding kesan dua jenis media, benih dan substrat yang berlainan terhadap kebolehrawatan POME secara anaerobik. Pengurangan keperluan oksigen kimia (COD) dipantau untuk menilai kesan media, benih dan substrat terhadap persembahan sistem ini. Penyingkiran COD sebanyak 59.9% telah dicapai daripada kepekatan awal 9.30 g COD/L dalam reaktor POME terlarut yang mengadungi benih daripada POME yang terurai dan tempurung isirung kelapa sawit sebagai media. Keterlarutan dengan cara penambahan natrium hidroksida (NaOH) pada suhu, pH dan masa rawatan yang berbeza dikaji untuk menentukan keadaan terbaik bagi menyediakan POME terlarut supaya dapat meningkatkan keberkesanan rawatan POME secara anaerobik. Keberkesanan penyingkiran COD meningkat sebanyak 5.9% daripada 40.9% sebelum rawatan kepada 46.8% selepas ia dirawat pada pH 10, suhu 120°C selama 90 minit. Kebolehrawatan POME yang ditambah likuor hitam secara anaerobik dikaji dalam reaktor semi selanjat dalam keadaan termofilik (55°C) dan mesofilik (35°C). Kebolehrawatan POME dan POME yang ditambah likuor hitam (2.5% hingga 20% mengikut isipadu) dibandingkan. Penyingkiran COD untuk masa tahanan 5 hari dan 10 hari diuji untuk menilai kesan masa tahanan terhadap persembahan reaktor. Proses anaerobik dalam keadaan termofilik lebih berkesan berbanding dengan keadaan mesofilik semasa merawat POME and POME yang ditambah dengan likuor hitam. Keputusan eksperimen menunjukkan bahawa penyingkiran COD sebanyak 87.2% boleh dicapai dalam reaktor POME pada kadar muatan organik (OLR) 8.30 g COD/L/hari manakala penyingkiran COD dalam reaktor POME yang mengandungi likuor hitam adalah sebanyak 78.9%

pada OLR 8.67 g COD/L/hari dalam keadaan termofilik. Pengeluaran spesifik gas metana untuk POME pada keadaan termofilik adalah daripada 0.124 kepada 0.066 L_{CH_4}/g_{COD} apabila OLR diubah daripada 8.30 kepada 16.00 g COD/L/hari. Pengeluaran spesifik gas metana untuk POME yang ditambah likuor hitam berada dalam lingkungan 0.130 kepada 0.223 L_{CH_4}/g_{COD} dan 0.072 kepada 0.105 L_{CH_4}/g_{COD} apabila kandungan likuor hitam ditambah daripada 2.5% kepada 10% untuk 10 hari dan 5 hari masa tahan. POME dengan penambahan 20% likuor hitam hanya mencapai 0.059 dan 0.018 L_{CH_4}/g_{COD} bagi OLR 7.06 dan 14.30 g COD/L/hari.

Treatability of Palm Oil Mill Effluent (POME) Using Black Liquor in an Anaerobic Treatment Process

ABSTRACT

Treatability studies of POME in various operational conditions were studied. A laboratory study was carried out at thermophilic temperature (55°C) to assess and compare the effect of two types of media, seeding and substrate on the anaerobic digestibility of (palm oil mill effluent) POME. Chemical oxygen demand (COD) reduction was monitored to evaluate the effect of media, seeding and substrates on the system performance. The COD removal was up to 59.9% from the initial COD concentration of 9.30 g/L that was achieved from the digested POME digester with palm kernel shell as a media, and fed with solubilised POME. Sodium Hydroxide (NaOH) solubilisation at different temperature, pH and treatment time was studied to determine the best condition for POME solubilisation in order to improve the POME treatability by anaerobic digestion process. The COD removal efficiency increased 5.9% from 40.9% prior solubilisation to 46.8% after solubilisation at pH 10, temperature 120°C and retention time 90 minutes. The feasibility of anaerobic digestion treating POME with addition of chemical pulping black liquor was studied in semi-continuous fed digesters under thermophilic (55°C) and mesophilic (35°C) condition. The anaerobic digestibility of raw POME and POME with addition of chemical pulping black liquor (2.5% to 20% by volume) was compared. The chemical oxygen demand (COD) reduction for hydraulic retention time (HRT) of 5 days and 10 days were examined to evaluate the effect of HRT on the performance of digesters. Thermophilic anaerobic process was more effective than mesophilic process to treat either raw POME or POME with addition of black liquor. The experiment resulted that COD reduction up to 87.2% can be achieved in raw POME digester at OLR 8.30 g COD/L/day and the COD reduction in black liquor added digester was 78.9% at OLR 8.67 g COD/L/day under thermophilic condition. The specific methane gas yielded from raw POME at thermophilic condition

was 0.124 to 0.066 L_{CH_4}/g_{COD} when the OLR was altered from 8.30 to 16.00 g COD/L/day. The specific methane gas yielded from POME with addition of black liquor was ranged between 0.130 to 0.223 L_{CH_4}/g_{COD} and 0.072 to 0.105 L_{CH_4}/g_{COD} when the black liquor content was altered from 2.5% to 10% at 10 days and 5 days HRT respectively. POME with addition of 20% black liquor only achieved 0.059 and 0.018 L_{CH_4}/g_{COD} with OLR 7.06 and 14.30 g COD/L/day respectively.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Operating a successful business as well as concern for the environment does not always go hand in hand. Wastewater treatment often incurs high non-profitable cost in an industry that reduces the company profit. The cost for wastewater treatment could be reduced either by reducing the wastewater generation or enhance the treatment efficiency. The concept of transforming waste to energy makes waste treatment seem more appealing and cost-effective.

1.1.1 Palm Oil Industry in Malaysia

Oil Palm was first introduced to Malaysia in year 1875 as an ornamental plant (DOE, 1999). Malaysia has the most ideal climate conditions for growing oil palm. The growth of the palm oil industry in Malaysia has been phenomenal over the last 4 decades. Nowadays Malaysia is the world's largest producer and exporter of palm oil. Approximately 14.96 million tonnes of crude palm oil (CPO) was produced in the year 2005 which increased by 4.7% from 13.98 million tonnes in the year 2004 (MPOB, 2006). Nevertheless, palm oil industry is one of the most pollution generating agro-industry in Malaysia. The three main sources of POME are steriliser condensate, hydrocyclone waste and clarifier sludge. For a well-controlled conventional oil palm mill, about 0.9 m³, 0.1 m³ and 1.5 m³ of steriliser condensate, clarifier sludge and hydrocyclone waste are generated for each tonne of crude palm oil produced (Borja *et al.*, 1996). The mixed POME is characterised by low pH (average 4.0), high chemical oxygen demand COD (60-90 g/L) and high suspended solids SS (20-40 g/L).

An increasingly stringent environmental regulations in view of the government's commitment to the conservation of the environment and increased public awareness of pollution problems caused the palm oil industries facing tremendous challenges as POME is a highly pollutant effluent. The biological ponding system or the lagoon system is developed rapidly as typical POME treatment system in Malaysia. Methane gas is a by-product from POME treatment by anaerobic ponding system. However, the gas emitted caused air contamination as methane gas is a green house gas. On the other hand, the methane gas produced from the POME treatment has a great potential as a renewable energy source if the gas is properly collected and can earn carbon emission credit.

1.1.2 Waste to Energy

The energy utilization has been ever increasing worldwide. Malaysia's demand of energy is relatively high in comparison with most developed countries such as Japan and USA (Yusoff, 2006). The limitation of fossil fuels resources and the destructive effects of consuming these energies on the environment have increased interest all over the world in the use of renewable energy sources. The interest in renewable energy also is driven by the goal of minimising the emission of CO₂ that results from the burning of fossil fuels. Renewable energy technologies offer the promise of clean, abundant energy gathered from self-renewing resources such as the sun, wind, earth and plants. These resources can be used to produce electricity for all economics sectors, fuel for transportation and heat for buildings and industrial processes (Bull, 2001). Biomass is one of the renewable energy sources besides hydraulic power generation, solar energy and others. Biomass is abundantly available in the environment especially in the form of agricultural wastes and municipal wastes. Today the most economical biomass fuels for generating electricity come from the organic by products of food, fibre, forest and animal manure (Rahman, 2003).

Biomass can be converted into electricity in one of several processes. The majority biomass is applied as boiler fuel to generate the steam which can turn a turbine to generate electricity. Biomass can also be used with coal to produce electricity in an existing power plant. Biomass can also be converted to a fuel gas that can then be used in a piston-driving engine, high-effective gas-turbine generator or a fuel cell and can be integrated into industrial manufacturing plants for power, heat and cooling needs.

1.2 Rationale for the Proposed Project

Anaerobic digestion is one of the most feasible treatments for high strength organic waste. Although biological treatment is the most favorable POME treatment in Malaysia, an anaerobic biological system has difficulties of start-up procedure, which can be time-consuming and unproductive. The ponding system normally requires long retention time in excess of 20 days. The major problem of anaerobic treatment lies in the inconsistency of effluent and the establishment of the most suitable microbial population for the waste to be treated. Besides that, the growth rates of anaerobic microorganisms tend to be slow especially methanogens.

Since methanogens prefer to grow in a surface film, attached film bioreactor has the potential to retain a more active methanogenic population. Thus, it would be interesting to study the potential use of palm fibre and palm kernel shell as the microbial support growth in anaerobic digestion of POME. Normally the palm fibre and palm kernel shell are the byproduct of palm oil extraction are used as solid fuels for steam boilers. Nevertheless the burning of these solid fuels associated with the emission of dark smoke and the carry over of partially carbonized fibrous particulates due to incomplete combustion of fuels (Yusoff, 2006). The study will lead to an alternative use of palm fibre and palm kernel shell.

The biological solubilisation of organic substrate of POME will occur in the anaerobic process where hydrolysis, acidogenesis and methanogenesis is taking place (Gee and Chua, 1994). The biological solubilisation requires proper maintenance, close monitoring and time consuming. Hydrolysis is an important step to control the anaerobic process rate in treating organic wastes (Rittmann and McCarty, 2001). By introducing a pretreatment unlike the usual method, the POME will have more of a short chain fatty acid and an increase in the retention time of methane producing bacteria, while the overall operation time could be shortened compared to conventional ponding system. Alkaline treatment of organic material was reported to induce swelling of particulate organic, making the cellular substances more susceptible to enzymatic attack (Baccay and Hashimoto, 1984; Vlyssides and Karlis, 2004).

The wastewater generated from pulping process is called black liquor. Black liquor is the most polluting stream in pulp and paper mill. Black liquor is dark in colour with high pH, BOD, COD and suspended solid. Generally black liquor is burnt in conventional boilers to recover the pulping chemicals and generate biomass energy. Black liquor gasification is a promising alternative for recovery of energy and chemicals from black liquor in the pulp and paper industry because the organic fraction of black liquor comes from biomass and the degradable products that are dissolved in alkaline pulping liquor. Black liquor is now proposed to be used in this study as an alkaline source to solubilise the POME and as a degradable organic source with the goal to reduce the chemical cost for pH adjustment and reuse black liquor to reduce the environmental pollution impact for pulp and paper industry. The pH correction in industrial applications incurs higher production cost when treating large amounts of wastes (Neves et al., 2006).

1.3 Objectives

In general, the research aims to study the influence of solubilisation on anaerobic treatability of palm oil mill effluent (POME) for a feasible and cost-effective anaerobic treatment technology that can be applied in the palm oil industries. There are three specific objectives in order to meet the goal:

- a) To evaluate the application of an existing palm oil waste on thermophilic anaerobic digestibility of POME.
- b) To determine the best condition for NaOH solubilisation of POME.
- c) To evaluate the influence of different ratios of black liquor and POME on thermophilic and mesophilic anaerobic digestibility and biogas production.

1.4 Research Outline

A general review of palm oil mill effluent (POME) characteristics and the POME treatment technologies was first carried out. This was followed by a refined review of the literature on anaerobic digestion process to gain thorough understanding for the commencement of the laboratory and experimental aspects of the project. The optimum pH condition for the anaerobic study was obtained from previous studies in the literature.

In line with first specific objective of the project, the effect of media, microbial seeding and substrate on thermophilic anaerobic digestibility of POME was studied. Palm oil waste such as palm fibre, palm kernel shell, anaerobic digested sludge from anaerobic pond in palm oil industry was used in this study. The influence of raw substrate and solubilised substrate on anaerobic digestibility was compared to evaluate the importance of sample pretreatment.

Optimum operating condition for waste solubilisation was easily found in literature. However, the study of POME solubilisation is lacking. Thus the effect of pH,

temperature and treatment time on POME COD and volatile solid solubilisation was studied with the equipment available in laboratory to determine the best solubilisation condition for POME. The anaerobic digestibility of solubilised POME at the best operating condition was studied using the best media and seeding from the previous work (Nik Norulaini et al., 2005).

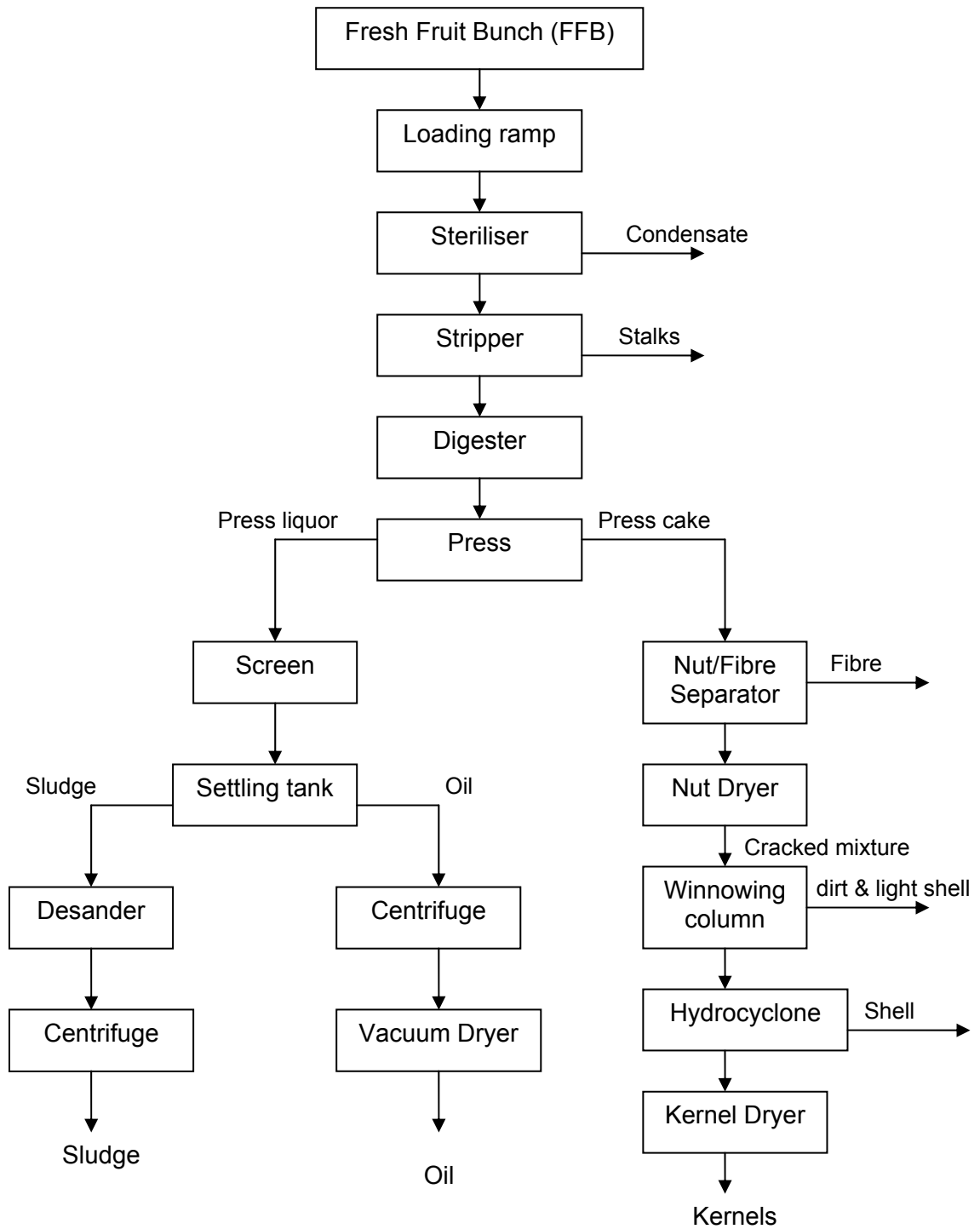
The alkali consumed in the solubilisation process can be costly. Black liquor was used as an alternative alkali source in this study in order to reduce the operational cost. Black liquor was added to POME in different ratios and the influence of black liquor addition on COD removal efficiency and biogas production was studied.

CHAPTER TWO

LITERATURE REVIEW

2.1 Palm Oil Mill Processing

The conventional palm oil extraction process is depicted in Figure 2.1. Crude palm oil (CPO) is extracted from the mesocarp of fresh fruit bunch (FFB). Approximately 225 kg CPO is obtained from 1000 kg of processed FFB (DOE, 1999). The capacity of a large scale mills range from 10 to 60 tonnes FFB/h. The FFB harvested from the oil palm plantation have to be process immediately to prevent poor quality CPO due to increased free fatty acid content. FFB is subjected to steam-heat treatment in horizontal sterilisers at a pressure of 3 kg/cm² and a temperature of 140°C for 75 to 90 minutes. Sterilisation facilitates FFB for mechanical stripping and preconditioning of the nuts to minimise kernel breakage (Maycock, 1990). After sterilisation the FFB is fed to a rotary drum-stripper where the fruits are separated from the spikelet. The fruits are then mashed in the digester under steam heated condition with temperature around 90°C. Twin screw presses are generally used to press out the oil from the digested mashed fruits under high pressure. Incomplete oil extraction can increase the effluent COD content substantially. CPO from the presses consists of a mixture of palm oil (35%-45%), water (45%-55%) and fibrous material in varying proportions (DOE, 1999). The CPO is directed to the clarification tank and the temperature is maintained at about 90°C to enhance oil separation. The clarified oil is then passed through a high speed centrifuge and vacuum dryer before storage. The oily fibre and nuts from the press cake are conveyed to a nut and fibre separator with a strong air current induced by a suction fan. The nuts are sent to a nut cracker and further to a hydrocyclone to separate the shell from the kernel. The kernel is dried to below 7% moisture in order to prevent the growth of mould for a longer storage time.



Source: Ma, 1999

Figure 2.1 Schematic flow of conventional palm oil extraction process

2.1.1 Palm Fibre and Palm Kernel Shell

Each tonne of processed FFB produces 140 kg of oil palm mesocarp fibre and 60 kg of oil palm kernel shell (Mahlia et al., 2001). The chemical composition on dry basis of palm fibre and palm kernel shell is tabulated in Table 2.1. Normally the palm fibre and palm kernel shell are used as solid fuels for steam boilers. Nevertheless the burning of these solid fuels associated with the emission of dark smoke and the carry over of partially carbonised fibrous particulates due to incomplete combustion of fuels lead to air pollution (Yusoff, 2006).

Table 2.1 Chemical compositions on dry basis of mesocarp fibre and palm kernel shell

Element	Fibre (%)	Shell (%)
H	6.0	6.3
C	47.2	52.4
S	0.3	0.2
N	1.4	0.6
O	36.7	37.3
Ash	8.4	3.2

Source: Mahlia et al., 2001

2.1.2 Palm Oil Mill Effluent (POME)

POME is considered as one of the most polluting agro-industrial residues due to its high organic load. POME is in the form of highly concentrated dark brown colloidal slurry of water, oil and fine cellulose materials from sterilisation and clarification stages. POME is a colloidal suspension of 95-96% water, 0.6-0.7% oil and 4-5% total solids (Ma, 2000). In general 1 tonne of POME will be generated from every 2 tonnes of FFB processed from the mill (Yacob et al., 2005). Characteristics of POME from literature are tabulated in Table 2.2.

Table 2.2 Characteristics of untreated palm oil mill effluent (POME)

Parameter	Concentration*
pH	4.7
Temperature	80 - 90
BOD 3-day, 30°C	25,000
COD	50,000
Total Solids	40,500
Suspended Solids	18,000
Total Volatile Solids	34,000
Ammoniacal-Nitrogen	35
Total Nitrogen	750
Phosphorus	18
Potassium	2,270
Magnesium	615
Calcium	439
Boron	7.6
Iron	46.5
Manganese	2.0
Copper	0.89
Zinc	2.3

* All parameters in mg/l except pH and temperature (°C)
Source: Ma, 1999

Table 2.3 shows the parameter limits for water course discharge of POME according to Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977.

Table 2.3 Parameter limits for watercourse discharge for palm oil mill effluent

Parameter	Limits of discharge*
pH	5.0 - 9.0
Temperature	45
BOD 3-day, 30°C	100
COD	-
Total Solids	-
Suspended Solids	400
Oil and Grease	50
Ammoniacal-Nitrogen	150**
Total Nitrogen	200**

* All parameters in mg/l except pH and temperature (°C)

** Value of filtered sample

Source: EQA 1974 (Act 127) and Subsidiary Legislation, 2002.

2.1.3 Palm Oil Mill Effluent Treatment

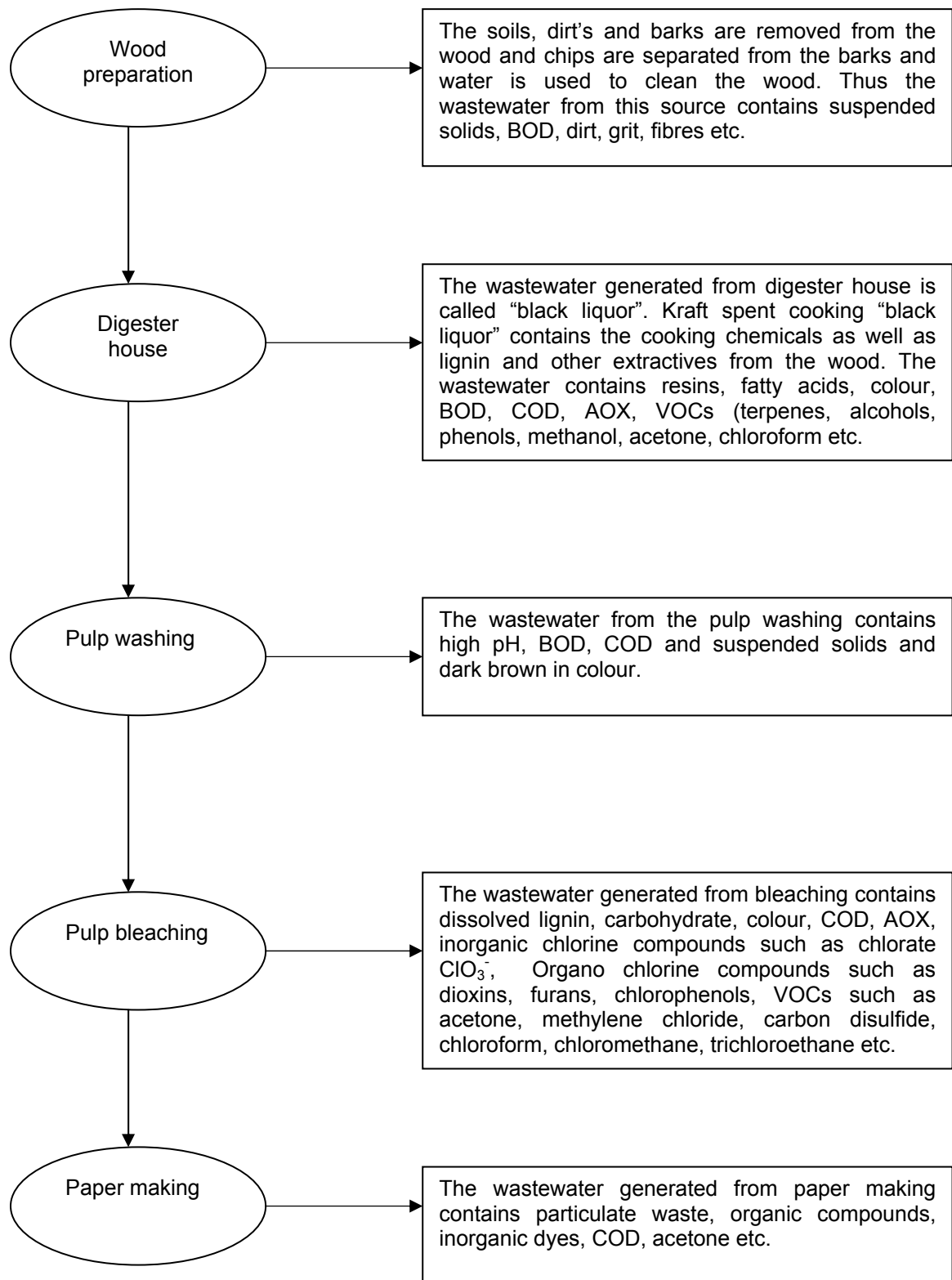
The biological ponding system or the lagoon system has developed rapidly as a typical POME treatment system in Malaysia. More than 85% of the palm oil mill use solely lagoon system for POME treatment (Yeoh, 2004; Tong and Jaafar, 2004; Najafpour et al., 2006). This system consists of deoiling ponds, anaerobic, facultative and aerobic ponds. The ponding system normally requires long retention time in excess of 20 days and the biogas is released into the atmosphere. According to Yacob et al. (2005), an average of 36% methane gas is emitted into the atmosphere from open tank digester. The methane gas produced by open tank digester and lagoon system is 35% and 45% respectively as studied by Shirai et al. (2003). The methane emission from the palm oil and rubber industry are the largest green house gas (GHG) source in Malaysia. Carbon emission credit can be earned for reducing GHG emission.

Various POME treatments were studied in order to meet the stringent water course discharge regulation. POME treatment using membrane technology with physical chemical pretreatment showed a reduction in turbidity, COD and BOD up to 100%, 98.8% and 99.4% respectively (Ahmad *et al.*, 2003). Two-stage up-flow anaerobic sludge blanket system (UASB) could work efficiently up to 30 g COD/L/day whilst methane yield and COD reduction greater than 90% (Borja *et al.*, 1996). COD removal efficiencies greater than 94% obtained in single stage anaerobic tank digester and single stage anaerobic ponding system after 10 days of retention time (Ugoji, 1997). A work carried out by Borja and Banks (1995) showed COD removals higher than 90% in both anaerobic filter and anaerobic fluidized bed reactor at loading of 10 g COD/L/day. COD removal up to 88% was obtained with 55h HRT using attached growth on a rotating biological contactor (Najafpour et al., 2005). A 95% COD reduction was achieved using treatment of tropical marine yeast with 2 days retention time (Oswal et al., 2002).

The anaerobic digestion systems are being increasingly used in wastewater treatment especially in agro-industry because they do not require high energy demanded as in aerobic biological treatment, produce less waste sludge and they can be easily restarted after months of shut down (Beccari et al., 1996). The potential of producing methane, a biogas as a by-product make this method is even more attractive. As cited by Yacob et al. (2005), the end product of the anaerobic digestion of POME is a mixture of biogas (65% CH₄, 35%CO₂ and traces of H₂S) from laboratory studies and approximately 28m³ of biogas can be obtained from 1 tonne of POME.

2.2 Pulp and Paper Mill Wastewater

Pulp and paper mill wastewater has also been considered as one of the most polluting agro-industrial residues. The primary source of fibres used in pulp and paper mill is wood. Major constituents in woods are cellulose, hemicellulose, lignin and extractives that are hard to biodegrade (Vadodaria, 1999). Pulp and paper mill wastewater is produced from wood preparation, pulping process, pulp washing, screening, washing, bleaching, and paper machine and coating operations (Pokhrel and Viraraghavan, 2004). Effluents generated by pulp and paper mill are associated with certain major problems; the dark color of effluent reduced the penetration of light therefore affecting benthic growth and habitat. The dark color is attributable to lignin and its degradation products. Persistent, bio-accumulation and toxic pollutants are present in the effluents. Effluents also contribute to adsorbable organic halide (AOX) load in the receiving water that contaminate remote parts of seas and lakes (Sumathi and Hung, 2004). Pollutant from various sources of pulping and paper making process is shown in Figure 2.2.



Source: (US EPA, 1995; Pokhrel and Viraraghavan, 2004)

Figure 2.2 Pollutant from various sources of pulping and papermaking

Pulping is the initial stage of the paper making industry. The main objective of the pulping process is to separate the cellulose fibres in as free form as possible. The pulping process can be categorised into mechanical, chemical and thermal pulping or the combination of these treatments. Mechanical pulping methods use mechanical pressure, disc refiners, heating and mild chemical treatment to yield pulp. Chemical pulping of wood is commonly carried out according to Kraft (sulfate) or sulfite process. Wood chips are cooked at 340-350°F and 100-135 psi in liquor containing sodium hydroxide, sodium sulfite and sodium carbonate. Kraft pulping promotes cleavage of various ether bonds in lignin and the degradable products that are dissolved in alkaline pulping liquor. This wastewater both generated by adding alkali or acid is dark brown in color and usually been called as black liquor. Black liquors generated from Kraft pulping consist of ligninolytic compounds, saccharides acids, solvent extractives and low-molecular-weight organic acids (Sumathi and Hung, 2004).

2.2.1 Pulping Wastewater Treatment

Alkaline pulping liquors are problematic for anaerobic treatment as the pollutants are not readily degradable and toxic to methanogenic population. Anaerobic biodegradability and toxicity to methanogens are strongly dependent on wastewater characteristics. Characteristics of wastewater generated from various processes depend upon the type of process, wood materials, process technology applied, management practices, internal recirculation of the effluent for recovering and amount of water used in particular process.

Various pulping wastewater treatment had been studied. The anaerobic digestion of black liquor generated from cereal straw using soda pulping achieved 55% COD removal at the optimum organic loading rate (OLR) of 8.0 kg/m³/day. The biogas production and the methane yield were 11 dm³/day and 71% respectively (Grover et al., 2001). OLR above 8.0 kg/m³/day inhibited methanogenic activity. Anaerobic-

aerobic treatment with upfront effluent recirculation was studied by Kortekaas et al. (1998) to treat hemp stem wood black liquor. This treatment yielded 72% and 97% COD and BOD removal respectively at OLR of 3.6 g COD/L/day. Anaerobic treatment of black liquor obtained from a mixture of bagasse, rice and wheat straw yielded 71% COD reduction and 80% methane with addition of 1% w/v glucose while in the absence of glucose only 33% COD reduction was achieved (Ali and Sreekrishnan, 2000). An average COD removal efficiency of 80% was achieved in up-flow anaerobic sludge blanket (UASB) system treating black liquor from Kraft pulp plant (Buzzini and Pires, 2002). COD removal of $73\pm 10\%$ was achieved in an aerobic sequencing batch reactor operated at 45°C for the degradation of bleached Kraft pulp mill effluent (Tripathi and Allen, 1999). In the filtration of black liquor with straw as raw material, approximately 80% and 90% lignin retention was achieved with microfiltration and ultrafiltration membranes system respectively (Liu et al., 2004).

2.3 Anaerobic Digestion Process

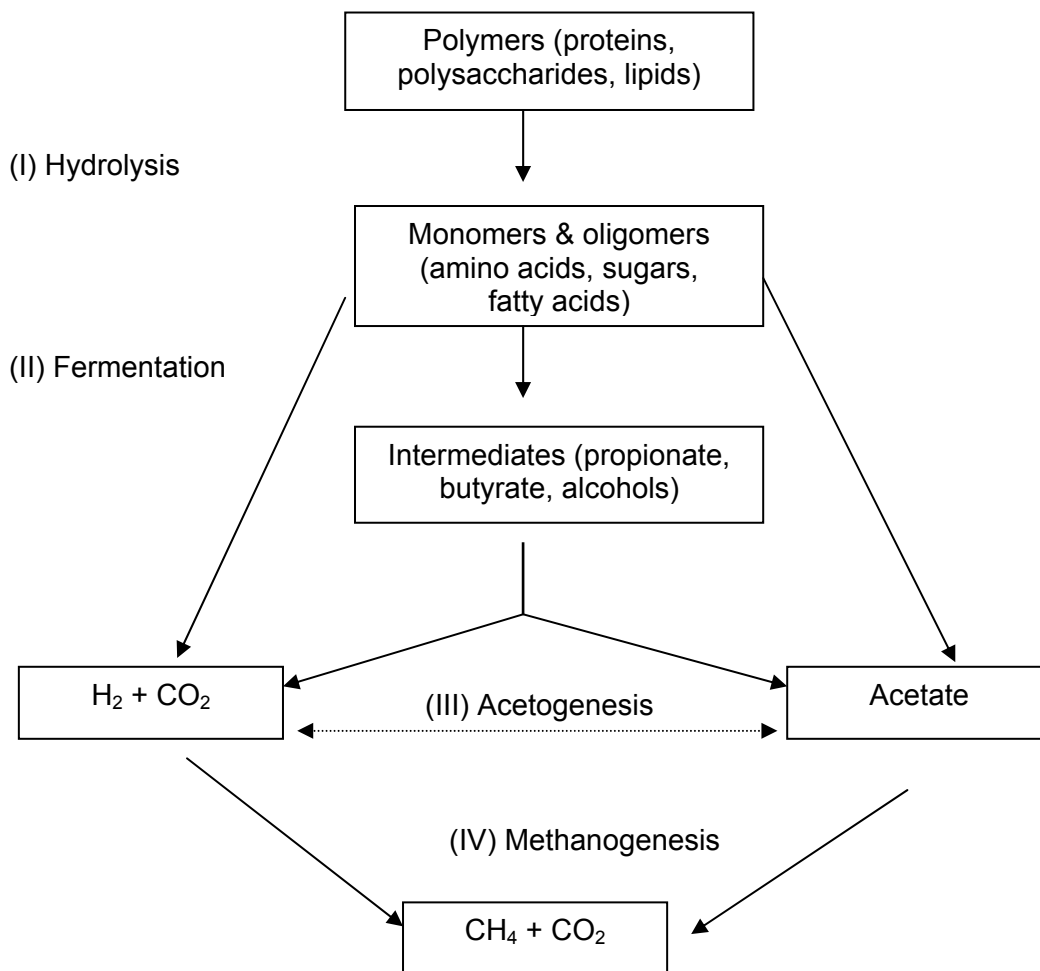
The anaerobic digestion is a versatile biochemical process and is being increasingly used to treat agricultural wastes. Anaerobic digestion is a multistage biochemical process in which complex organic substances are fermented by microorganisms in the absence of oxygen and the presence of anaerobic microorganisms. Methanogenic anaerobic digestion of organic waste has been performed for about a century and is advantages over aerobic treatment process because of its high organic removal rates, low energy requirement, low sludge production and energy production (Angenent et al., 2004). In general, anaerobic digestion occurs in four major stages, hydrolysis, fermentation, acetogenesis and methanogenesis. Each step involves different microbial population. Pathway in methane fermentation of complex waste is depicted in Figure 2.3.

In the first stage of hydrolysis, the polymeric organic materials are hydrolysed to monomers such as glucose, fatty acids and amino acids by hydrolytic bacteria. The hydrolysis process is of significant importance in high organic waste and may become rate limiting. Solubilisation involves hydrolysis process where the complex organic matter is hydrolysed into soluble monomers. Fats are hydrolysed into fatty acids or glycerol; proteins are hydrolysed into amino acids or peptides while carbohydrates are hydrolysed into monosaccharides and disaccharides. The hydrolysis reaction can be expressed as below (Gray, 2004):

Fats → long chain fatty acids, glycerol

Proteins → amino acids, short-chain peptides

Polysaccharides → monosaccharides, disaccharides

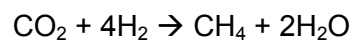
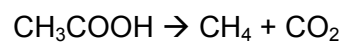


Source: Angenent et al., 2004

Figure 2.3 Pathways in methane fermentation of complex waste

In fermentation stage, the hydrolysed products are converted to volatile fatty acids, alcohols, aldehydes, ketones, ammonia, carbon dioxide, water and hydrogen by the acid-forming bacteria. The organic acids formed are acetic acid, propionic acid, butyric acid and valeric acid. Volatile fatty acids with more than four-carbon chain could not be used directly by methanogens (Wang et al., 1999). Those organic acids are further oxidised to acetic acid and hydrogen by obligatory hydrogen-producing acetogenic bacteria through a process called acetogenesis. Acetogenesis also includes acetate production from hydrogen and carbon dioxide by acetogens and homoacetogens. Sometimes the acidogenesis and acetogenesis stage is combined together as one stage.

Finally the methane gas is produced in two ways. One is conversion of acetate to carbon dioxide and methane by acetotrophic organisms and another is reduction of carbon dioxide with hydrogen by hydrogenotrophic organisms (Verma, 2002; Hutňan et al., 1999). Predominant methanogens in biogas reactors is limited to *Methanobacterium*, *Methanothermobacter*, *Methanobrevibacter*, *Methanosarcina* and *Methanosaeta* (formerly *Methanothrix*) (Sekiguchi et al., 2001). The methanogenesis reaction can be expressed as below:



Reactions for the different bioprocess strategies were tabulated in Table 2.4.

Table 2.4 Reactions for the different (bio) process strategies

Biotic or abiotic process	Reaction
Hydrogen fermentation to acetic acid	$C_6H_{12}O_6 + 2H_2O \leftrightarrow 4H_2 + 2CH_3COOH + 2CO_2$
Hydrogen fermentation to butyric acid	$C_6H_{12}O_6 \leftrightarrow 2H_2 + CH_3CH_2CH_2COOH + 2CO_2$
Fermentation to ethanol	$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2$
Propionic acid production with hydrogen	$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O$
Ethanol production with hydrogen	$CH_3COOH + H_2 \leftrightarrow CH_3CH_2OH + H_2O$
Syntrophic propionic acid oxidation	$CH_3CH_2COOH + 2H_2O \leftrightarrow CH_3COOH + 3H_2 + CO_2$
Syntrophic butyric acid oxidation	$CH_3CH_2CH_2COOH + 2H_2O \leftrightarrow 2CH_3COOH + 2H_2$
Syntrophic acetic acid oxidation	$CH_3COOH + 2H_2O \leftrightarrow 4H_2 + 2CO_2$
Hydrogenotrophic methanogenesis	$4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O$
Acetoclastic methanogenesis	$CH_3COOH \leftrightarrow CH_4 + CO_2$
Methane formation from glucose	$C_6H_{12}O_6 \leftrightarrow 3CH_4 + 3CO_2$
Catalytic methane conversion to syngas	$CH_4 + H_2O \leftrightarrow 3H_2 + CO$
Catalytic gas-shift reaction	$CO + H_2O \leftrightarrow H_2 + CO_2$
Hydrogen fuel cell	$2H_2 + O_2 \leftrightarrow 2H_2O + \text{electricity}$
Methane fuel cell	$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O + \text{electricity}$
MFC	$C_6H_{12}O_6 + 6O_2 \leftrightarrow 6CO_2 + 6H_2O + \text{electricity}$
Cellulose bioconversion	$[-C_6H_{11}O_6^-]_n + aH_2O \leftrightarrow bCH_3COOH + cCH_3CH_2OH + dCO_2 + eH_2$
Polyhydroxyalkanoates formation	$aC_6H_{12}O_6 + bO_2 \leftrightarrow [-COOH(CH_2)_3COO^-]_n + cH_2O$
Dyes formation	$[-C_6H_{11}O_6^-]_n + aNH_3 + bH_2O \leftrightarrow cC_{23}H_{26}O_5 + dC_{22}H_{27}O_5N + eC_{21}H_{22}O_5$

Source: Angenent et al., 2004

2.3.1 Anaerobic Digestion Systems

Anaerobic digestion occurs in various reactor modes such as continuously stirred tank reactor, batch reactor, semi-continuous, sequencing batch reactor. In order to enhance the anaerobic digestion performance, new methods like two-phase or two-stage anaerobic process, attached-growth anaerobic process and high rate anaerobic digestion system were introduced. Anaerobic sequencing batch reactor (ASBR), up-flow anaerobic sludge blanket (UASB) was applied in the high-rate anaerobic system. Five conditions should be met to enable an anaerobic reactor system to handle high space loading rate (Lettinga, 1995). The high retention of viable sludge in the reactor under operational conditions is imperative. Viable bacteria biomass must have sufficient contact with the wastewater and sufficiently acclimatised. The size of biofilm should remain relatively small and the accessibility of the organisms inside the biofilm should be high. Ultimately the success depends on the favorable environmental condition for all required organisms inside the reactor under all imposed operational

conditions. According to Chen and Shyu (1996), the order of volumetric methane production rates was up-flow anaerobic filter (UAF) > UASB > baffled > continuous stirred-tank reactor (CSTR).

2.3.1.1 Single-stage and Two-stage System

In conventional anaerobic digestion process, acidification and methanogenesis take place in a single reactor system (single-stage) and there is a delicate balance between acidogens and methanogens because both groups differ widely in terms of physiology, nutritional needs, growth kinetics and sensitivity to environmental conditions (Demirel and Yenigün, 2002). The aim for two-phase anaerobic digestion process is to separate the acid and methane fermentation phases for determining and satisfying optimum environmental conditions for each type microbial population in two separate reactors (Demirel and Yenigün, 2006). A major limitation of anaerobic digestion of fruit and vegetable wastes in one stage system is a rapid production of volatile fatty acids attributed to pH decreased during acidification which stressed and inhibited the activity of methanogenic bacteria (Bouallagui et al., 2004). Conditions that are favorable to the growth of acid-forming bacteria such as short HRT and low pH are inhibitory to the methanogens. A two-phase process can optimise the condition for hydrolytic acidogenic groups of bacteria as well as for the acetogenic and methanogenic groups (Ince, 1998). The pH during the acidogenic phase usually maintained at 5.5 to 6.0 and HRT less than 5 days while in the methanogenic phase the pH was maintained at pH greater than 7.0 (Ince, 1998; Raynal et al., 1998; Demirel and Yenigün, 2002; Bouallagui et al., 2004). As a consequence, higher treatment efficiency and better process stability can be attained by two-phase process with an overall organic matter removal greater than 87% at 17 days HRT (Raynal et al., 1998), 96% of the total COD was converted to biomass and biogas (Bouallagui et al., 2004).

2.3.1.2 Anaerobic Sequencing Batch Reactor (ASBR)

Anaerobic sequencing batch reactor was developed to better handle high suspended solids wastewater. The ASBR bioreactor operates in four-step cycle in a single reactor (Ratusznei et al., 2000; Zaiat et al., 2001; Angenent et al., 2004). The first stage is the feeding process where wastewater is fed into the reactor with settled biomass. The wastewater and biomass are mixed intermittently in reaction process. This follow by settling of biomass and lastly effluent is withdrawn from the reactor. Advantages of the ASBS system are better solids retention, efficient operating control, high organic matter removal efficiency, simple operation and absence of settling tank (Ratusznei et al., 2000). A very short start-up and 86% COD removal was observed in Ratusznei et al. study (2000) treating 0.5 L synthetic substrate containing 485 mg/L COD per cycle with 8 hours each cycle.

2.3.1.3 Up-flow Anaerobic Sludge Blanket (UASB)

Approximately 60% of the thousands anaerobic full-scale treatment facilities worldwide are now based on the UASB design concept (Angenent et al., 2004). The excellent sludge retention in UASB system is based on bacterial sludge entrapment in or between sludge particles and bacterial immobilisation by a mechanism of bacteria self agglomeration and bacteria attachment to support material present in the sludge (Lettinga, 1995). According to Agrawal et al. (1997), 81±5% COD removal was obtained at an HRT of 9 hours for a synthetic wastewater containing 300 mg/L COD. COD removal efficiency greater than 90% was achieved in UASB reactor treating potato leachate at organic loading rate (OLR) of 6.1g COD/L/day at 2.8 days HRT (Parawira et al., 2006). The anaerobic methane generation for the cheese whey study was found to be 424 ml CH₄/g COD at relatively short HRT with a COD removal efficiency of 95-97% at influent COD concentration of 42700±141 - 55100±283 mg/L in UASB reactor (Ergüder et al., 2001).

2.3.1.4 Attached-growth System

Low growth rate of anaerobic microorganisms has encouraged the development of various techniques for their immobilisation within bioreactors so as to retain the viable bacteria biomass in the reactor. Buffering capacity is greater in the reactors with support material (Björnsson et al., 1997). Attached-growth reactors developed include fluidised bed, fixed-bed, fixed-film, and anaerobic biofilter. The anaerobic fixed-film reactor (AFFR) treating a synthetic wastewater with 3000 mg/L COD could recover from the inhibition due to shock loading and resumed normal operation within eight days (Chua et al., 1997). The AFFR was packed with 1cm in diameter of fire expanded clay spheres. COD removal up to 98.1% was achieved in the study at 5 days HRT. Fluidised-bed reactors offer many advantages to the anaerobic digestion process. Microbial biomass was attached on the support thus provided high concentration of biomass as consequence been not easily washed out from the reactor. AFFR enables high mass transfer, no plugging, channeling or gas hold-up. The biomass support can be fabricated to a specific application to enhance performance (Borja et al., 2000). COD removal efficiency of 98.3-80.0% was achieved in AFFR with saponite as bacterial support at OLR between 0.6 and 9.3 g COD/L/day and HRT between 20.0 and 1.1 days. Polyurethane was used as packing media in anaerobic filter treating rubber thread wastewater. The specific biogas yielded from this study was ranged between 0.25 to 0.069 L_{CH_4}/g_{COD} added when the organic loading rate was altered 2.0 to 14.0 g COD/L/day respectively (Agamuthu, 1999). Anaerobic digestion of acidic petrochemical wastewater using CSTR with plastic net biomass support material achieved 95% COD reduction and biogas production of about 8L/L/day at OLR 20.0 kg COD/m³/day and at HRT as low as 1.5 days. Reactor without support particles could only treat the wastewater above a 5-day HRT and at OLR of 5 kg COD/m³/day with feed pH 6.0 (Ramakrishna and Desai, 1997). Anaerobic digestion of acidic petrochemical wastewater in up-flow fixed-film reactor achieved 90-95% COD reduction and methane yield of 0.450 m³/kg COD/day added at OLR of 21.7 kg COD/

m³/day and the operating temperature of 37°C (Patel and Madamwar, 2002). Straw was used as biofilm carrier in the two-stage anaerobic digestion of crop residues and achieved 73-50% COD removal at OLR from 2.4-25 g COD/L/day (Andersson and Björnsson, 2002).

2.3.2 Anaerobic Digestion Operational and Environmental Conditions

Anaerobic digestion especially the methanogenesis process is very sensitive to the operational condition than aerobic process. Thus the process control measures are of critical importance which guard against process instability of anaerobic digestion. Some of the major parameters are discussed in the following section.

2.3.2.1 pH

Anaerobic microbial especially the methanogens are sensitive to the acid concentration in the reactor and inhibited by acidic condition. In methanogenesis stage, the concentration of ammonia increases and the pH value can increase to pH above 8.0 and once methane production is stabilised, the pH level stays between 7.2 and 8.2 (Verma, 2002). At pH 6.0, anaerobic degradation rate significantly decreases as temperature decreases. Lipids are not degraded at pH 6.0 but are completely degraded at pH 8.5 (Beccari et al., 1996). Study by Horiuchi et al. (2002) reported that the product spectrum in the acid reactor strongly depended on the culture pH. Butyric acids were formed under acidic and neutral condition while acetic acids and propionic acids were the main products under the basic condition. The control of reactor pH to obtain interested acids for methane production would improve the treatment performance and stability. Acetic and butyric acids are favorable substrates for methanogens while low level of propionic acids will minimise the inhibition growth of methane-forming bacteria (Yang et al., 2004).

2.3.2.2 Temperature

There are three major temperature ranges in the anaerobic digestion processes. Psychrophilic is operated below 25°C, mesophilic range is between 25°C to 40°C and the optimum is at 30°C to 35°C. The thermophilic is operated at temperature greater than 45°C (El-Mashad et al., 2004). The main contributions of the thermophilic anaerobic process are higher stability for solids reduction, higher biogas production, improvement of the energy balance of the treatment plant, high resistance to foaming, less odour and high effect of destroying pathogens in the thermophilic digesters (Zábranská et al., 2002). Faecal coliform concentration in mesophilic and thermophilic reactor was 10^2 - 10^4 MPN/g and 10^0 MPN/g respectively as reported by Riffat et al. (1998). One of the imperative parameter for anaerobic treatment is operating temperature that selects the dominant bacterial flora and determines microbial growth rate (Patel and Mandawar, 2002). Biogas production from the thermophilic anaerobic digestion treating fruit and vegetable wastes was higher on average than psychrophilic and mesophilic by 144% and 41% respectively (Bouallagui et al., 2004). Temperature-phased anaerobic digester was developed with combination of mesophilic and thermophilic process to enhance the treatment performance. In general, the temperature-phased anaerobic digestion (TPAD) involves a two-stage reactor system with the first stage operated at thermophilic condition and the second stage at mesophilic condition. More than twenty full-scaled TPAD systems have been set up in the United States for the treatment of wastewater sludge (Sung and Santha, 2001).

2.3.2.3 Mixing

Conventional anaerobic digestion process applied continuous stirred-tank reactor (CSTR). Mixing was reported to have benefits such as to promote close contact between raw and digested sludge, to maintain uniform temperature and solids mixture in order to prevent accumulation of inhibiting substances, to discourage scum

formation, settlement of grit, dense solids and to encourage release of gas (Gray, 2004). Agitation helps to reduce the particle size as digestion process and to release biogas from the mixture (Karim et al., 2005). Ahn and Forster (2002) reported that completely mixed system is more sensitive at any temperature. Kim et al. (2002) hypothesised that non-mixing reactor has closer microbial consortia proximity than others. Floating layer of solids was formed in resulted lack of sufficient mixing in low solids digesters. Unmixed digester showed a quicker start-up than the mixed digesters and exhibited higher methane yield than continuous mixed digesters (Karim et al., 2005).

2.3.2.4 Organic Loading Rate (OLR)

Organic loading rate is a measure of the anaerobic digestion biological conversion capacity. The substrate fed above the optimum OLR results in low biogas yield and organic matter removal due to accumulation of inhibiting substances like volatile fatty acids (Verma, 2002). At high OLR, methanogenic cannot consume hydrogen and resulted in increased of hydrogen partial pressure concomitantly decreased the methane yield (Patel and Madamwar, 2002). According to Yu and Fang (2000), carbohydrate degrades at all loading rates but degradation for protein and lipids decreased with increase in loading.

2.3.2.5 Retention Time

Performance of anaerobic digestion process is affected primarily by the retention time. HRT had significant effect of distribution of effluent products. HRT for anaerobic digestion varies with different technologies, process temperature and waste composition (Verma, 2002). The control of HRT is critical to the successful enrichment of hydrolytic acidogenic bacteria in the first stage of a two-stage reactor. The biodegradability of three major constituents in dairy wastewater increased with HRT following the order of carbohydrates > proteins > lipids (Fang and Yu, 2000).