UNIVERSITI PUTRA MALAYSIA

THE PERFORMANCE AND KINETIC STUDY OF MEMBRANE ANAEROBIC SYSTEM (MAS) IN TREATING POME

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By

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Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science in Faculty of Engineering, Universiti Putra Malaysia

November 1999

ACKNOWLEDGEMENT

I am particularly grateful to my supervisor, Assoc. Prof. Dr. Fakhru'l – Razi Ahmadun who has helped me to complete this project. Your helping word to me in my difficulties is like a switch on a railroad track- but one inch between a wreck or smooth rolling prosperity. I wish to express my deepest thank and appreciation for your invaluable guidance, keen interest, advice, unreserved assistance and encouragement throughout the period of this study. Appreciation also goes to members of my supervisory commitee, Assoc. Prof. Dr. Mohd. Ali Hassan and Assoc. Prof. Dr. Azni Idris for their kind assistance in this study.

I also wish to extend my appreciation to En. Ismail Ghani and En. Mohd. Taufik for their technical support throughout this study. To the staffs in Fakulti Kejuruteraan, I wish to express my gratitude for being so kind in helping me in many ways to complete this study.

Last but not least, I like to thank Mum, Dad, Fook, Wee, Choo and Min for their love, understanding and steadfast. Special thanks to my fiancee, May, for her patience supports and loving encouragement. To all the brothers and sisters of The Church in Kajang, thank you for your love and care during my time in UPM.

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LIST OF ABBREVIATIONS

b	Specific Microorganism Decay Rate
BLR	Biological Loading Rate
COD	Chemical Oxygen Demand
CSTR	Completely Mixed Stirred Tank Reactor
E	Substrate Utilisation Rate
HRT	Hydraulic Retention Time
k	Maximum Specific Substrate Utilisation Rate
θc	Solids Retention Time (MCRT)
K_s	Half-velocity Coefficient
MAS	Membrane Anaerobic System
MLSS	Mixed Liquor Suspended Solids
MWCO	Molecular Weight Cut-off
OLR	Organic Loading Rate
POME	Palm Oil Mill Effluent
PVC	Polyvinylchloride
S	Effluent Substrate Concentration
S_o	Influent Substrate Concentration
SEM	Scanning Electrom Microscope
SRT	Solids Retention Time
SS	Steady State
SSUR	Specific Substrate Utilization Rate
SUR	Substrate Utilization Rate
TSS	Total Suspended Solids
μ	Specific Growth Rate
μ_m	Maximum Specific Growth Rate
VSS	Volatile Suspended Solids
X	Microorganism Concentration
Y	Growth Yield Coefficient

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

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November 1999

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Faculty: Engineering

Anaerobic digestion has been proven to be the most efficient process for primary treatment of POME. However a major problem in the anaerobic wastewater treatment process is to maintain the sufficient quantity of active biomass in the reactor. In this study membrane separation technology has been applied after anaerobic digestion to increase solids retention time and improve treatment efficiency. The objectives of the study are to evaluate the overall membrane anaerobic system (MAS) treatment efficiency and the applicability of three known kinetic models on the system and determination of kinetic coefficients.

The MAS consists of a cross-flow ultrafiltration membrane (PCI Micro 240) for solid-liquid separation. Six steady states were ottained over a range of mixed liquor suspended solids of 12,681 – 30,460 mg/l. The study showed a good fitting of the Monod Model (91.1%), Contois Model (98.5%) and Chen and Hashimoto Model (95%)

for the MAS treating raw POME at organic loadings between 1.5 kgCOD/m^3/d to 6.5 kgCOD/m^3/d. The growth yield coefficient, Y, was found to be 0.604 kg VSS/kgCOD while the specific microorganism decay rate was 0.099 day^{-1}. The k values were in the range of 0.242 to 0.425 mg COD/mg VSS.d and the μ_m values were between 0.145 to 0.257day^{-1}. The Monod Model and Chen and Hashimoto Model are better than the Contois Model for solids retention time (SRT), effluent substrate concentration (S) and substrate utilisation rate (E) estimation. Both models are able to produce a good predicted S and E if the SRT ≥ 50 days. Throughout the study, the removal efficiency of COD was 83.2 to 97.97 %. The methane production rate was between 0.262 to 0.473 l/g-COD-utilised/d. The MAS treatment efficiency was greatly affected by SRT and OLRs. In this study, membrane fouling and polarization at the membrane surface played a significant role in the formation of a strongly attached cake layer limiting membrane permeability.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi sebahagian keperluan untuk ijazah Master Sains

KAJIAN PRESTASI DAN KINETIK BAGI SISTEM ANAEROBIK MEMBRAN (MAS) DALAM PERAWATAN POME

Oleh

LAI LONG SENG

November 1999

Pengerusi : **Fakhru'l-Razi Ahmadun, Ph.D.**
Fakulti : **Kejuruteraan**

Pencernaan anaerobik telah dibukti sebagai proses yang paling berkesan dalam rawatan POME. Bagaimanapun masalah utama yang dihadapi dalam rawatan air sisa anaerobik ialah penahanan biojisim yang aktif serta mencukupi dalam reaktor. Dalam pengajian ini teknologi membran telah diguna selepas pencernaan anaerobik demi meningkat masa tahanan pepejal dan mempertingkatkan keberkesanan rawatan. Objektif-objektif pengajian ialah menilai keberkesanan keseluruhan sistem rawatan anaerobik membran (MAS) dan penggunaan tiga jenis model kinetik pada sistem serta penentuan koefisien–koefisien kinetik.

Sistem ini terdiri daripada membran ultraturasan (PCI Micro 240) untuk pemisahan pepejal-cecair. Enam tahap tetap telah dicapai untuk pepejal terampai larutan campuran antara 12,681- 30,460 mg/l. Kajian menunjukkan kepadanan yang baik bagi Model Monod (91.1%), Model Contois (98.5%) dan Model Chen dan Hashimoto (95%)

untuk perawatan POME dengan MAS bagi muatan bebanan organik antara 1.5 $kgCOD/m^3/d$ dan 6.5 $kgCOD/m^3/d$. Koefisien Penghasilan Pertumbuhan, Y ialah 0.604 kgVSS/ kgCOD manakala kadar penguraian makro-organisma ialah 0.099 $hari^{-1}$. Nilai-nilai k adalah dalam julat 0.242 – 0.425 mg COD/ mgVSS.h dan nilai-nilai μ_m adalah dalam lingkungan 0.145 – 0.257 $hari^{-1}$. Model Monod dan Model Chen dan Hashimoto didapati lebih baik dibanding dengan Model Contois bagi penganggaran masa penahanan pepejal (SRT), kepekatan substrak terawat (S) dan kadar penguraian substrak (E). Untuk kedua-dua model ini dapat menghasilkan anggaran baik untk ramalan S dan E jika SRT ≥ 50 hari. Sepanjang kajian ini, kecekapan penyingkiran COD berada pada 83.2 hingga 97.97 %. Kadar penghasilan metana berada pada 0.262 hingga 0.473 l/g-COD-penggunaan/ h. Kecekapan rawatan MAS amat dipengaruhi oleh SRT dan OLRs. Dalam kajian ini, penyumbatan membran dan polarisasi pada permukaan membran memainkan peranan yang penting dalam pembentukan lapisan kek yang melekat dengan kuatnya justeru menghadkan keronggaan membran.

CHAPTER I

INTRODUCTION

Anaerobic digestion has made considerable progress in the last two decades as a result of active research in this field. This technology is recognised as a versatile biological waste treatment particularly for treating high strength organic wastewater and solids concentration. Besides that the methane-rich biogas produced as a by-product of the process is considered as a useful biofuel for power to offset the cost of the treatment.

In Malaysia, the palm oil industry is a very important agriculture-based industry. Currently there are more than 2.5 million hectares of land under oil palm cultivation and there are 280 palm oil mills and 36 active refineries (Ma, 1997). In 1994 however, besides producing 7.2 million tonnes of crude palm oil, the palm oil mills also generated about 18.0 million tonnes of palm oil mill effluent (POME) (Ma, 1995). Due to the highly polluting characteristics (Table 1) of POME, much efforts have be done to overcome this problem. In fact anaerobic digestion has been proven to be the most efficient process for primary treatment of POME and all palm oil mills have adapted this process to decrease environmental pollution (Ma, 1997).

However due to the slow growth rate of anaerobic microorganisms, therefore in this study, the combination of anaerobic treatment and membrane

Table 1: Typical Analysis of Palm Oil Mill Effluent

Parameter	Range	Mean
BOD_3, 30°C	10,250-47,500	25,000
COD	15,500-106,360	53,635
Total Solids	11,450-164,950	43,635
Suspended Solids	410-60,360	19,020
Oil & Grease	130-86,430	8,370
Ammonical-N	0-110	35
pH	3.8-4.5	4.0

All parameters are expressed in mg/l except pH
Source: Ma and Hassan (1991)

separation technology will be investigated in treating palm oil mill effluent. In fact several investigators have conducted experimental works of anaerobic membrane processes for treatment of a variety of wastewater (Fakhru'l-Razi, 1994; Ross et al., 1992; Hall et al., 1995). In this study, the experiment is carried out under six steady states and the membrane anaerobic system (MAS) inherently allows the separation of hydraulic retention time (HRT) and solid retention time (SRT), thus increase the biomass retention period in reactor.

Objectives

The objectives of this study in treating the palm oil mill effluent are:

1. To evaluate the overall MAS treatment efficiency, and
2. To evaluate the applicability of three known kinetic models on the system and determination of kinetic coefficients.

CHAPTER II

LITERATURE REVIEW

Biological Treatment

Biological treatment process has been widely used for wastewater treatment. In fact, it can be classified into two groups:

1. Aerobic processes in which the microbes use oxygen dissolved in the waste liquors.
2. Anaerobic processes in which the microorganisms do not have access to freely dissolved oxygen, nor to other energetically favorable electron acceptors such as nitrate ions. Microorganisms can use the carbon in organic molecules as the electron acceptor.

Comparison between aerobic and anaerobic processes for wastewater treatment has tended to the former because the system is more reliable, stable and better understood. However Lettinga (1996) concluded that the anaerobic processes have several clear advantages as:

- Treatment can be accomplished at very low costs, viz. the installations are relatively plain.
- Instead of consuming energy, a useful energy carrier in form of biogas is produced.

- The method can be applied at practically any place and at any scale.
- Very high space loading rates frequently can be applied in modern anaerobic wastewater treatment systems, so that the space requirements of the system are relatively small.
- The volume of excess sludge produced in anaerobic treatment generally is significantly lower compared to aerobic treatment. The excess sludge generally is well stabilized.
- Anaerobic organisms can be preserved unfed for long periods of time (exceeding one year) without any serious deterioration of their activity, while also other important characteristics of anaerobic sludge generally remain almost unaffected.
- The method can lead to the application of integrated environmental protection systems, e.g. it can be combined with post-treatment methods by which useful products like ammonia or sulfur can be removed, while in specific cases effluents and excess sludge could be employed for irrigation and fertilization or soil conditioning.

However the main disadvantages of anaerobic system is the lower rates of reaction when compared to aerobic processes. The growth rate of certain microorganisms in anaerobic processes is slightly lower but the high concentration of action biomass is an important factor in any successful treatment system. Thus the understanding of the kinetics microbiology and biochemistry of the anaerobic processes is essential in any engineering practice.

Biochemistry and Microbiology

The understanding of biochemistry and microbiology mechanisms of anaerobic digestion is important in process control and optimisation, especially during start-up and for preventing digester instability. Basically the biological conversion of complex macromolecules organic matter by anaerobic bacteria will pass through in four steps, namely hydrolysis, acidogensis, acetogenesis and methanogenesis.

First step: Hydrolysis

In this process, it involves the enzyme-mediated transformation for higher-molecular-mass compounds into compounds suitable for use as source of energy and cell carbon (Metcalf & Eddy, 1991). Haandel and Lettinga (1994) also reported that hydrolysis process involves the mediation of exo-enzyme that is excreted by fermentation bacteria. Organic polymers and lipids are hydrolyzing to basic structural building blocks such as monosaccharides, amino acids, fatty acids and related compounds as shown in Figure 1. Hydrolysis is claimed to be rate-limiting when the waste contains much insoluble material (Archer and Kirsop, 1991). In fact at lower temperature (< 20 °C), and particular for lipids, hydrolysis rate practically can be limiting for the overall rate of anaerobic digestion (Haandel and Lettinga, 1994).

Second Step: Acidogenesis

The acidogenic bacteria will ferment the breakdown products from hydrolysis to simple organic acids, mainly volatile fatty acid, alcohols, lactic acid and mineral compounds such as carbon dioxide, hydrogen, ammonia and hydrogen sulfide gas (Haandel and Lettinga, 1994). The responsible organisms are called "acid-producing" or "acid-forming" bacteria. In fact acidogens and hydrolysis bacteria are considered as one group in Sahm (1984). Metcalf and Eddy (1991) and Sahm (1984) reported that members of this group may be either strict anaerobes or facultative. It is believe that the concentration of hydrogen plays a central role in controlling the proportions of the various products from acidogenic bacteria and the acidogenic bacteria may utilize feedback control loops to stabilize the digester stability (Sahm 1984).

Third Step: Acetogenesis

The hydrogen producing acetogenic bacteria which include both obligate and facultative species can ferment organic acids larger than acetic (e.g. butyrate, propionate) and neutral compounds larger than methanol (e.g. ethanol, propanol) to hydrogen and acetate (Zeikus, 1981). Besides that the homoacetogenic bacteria can ferment a very wide spectrum of multi or one carbon compounds to acetic acids. By consuming hydrogen, homoacetogenisis lower the hydrogen partial pressure in anaerobic digestion (Zeikus, 1981). In fact the conversion of various fermentation products by obligate hydrogen producing bacteria can only be functioning if the partial pressure of hydrogen is kept low by hydrogen consuming organism (Zehnder et al., 1981).

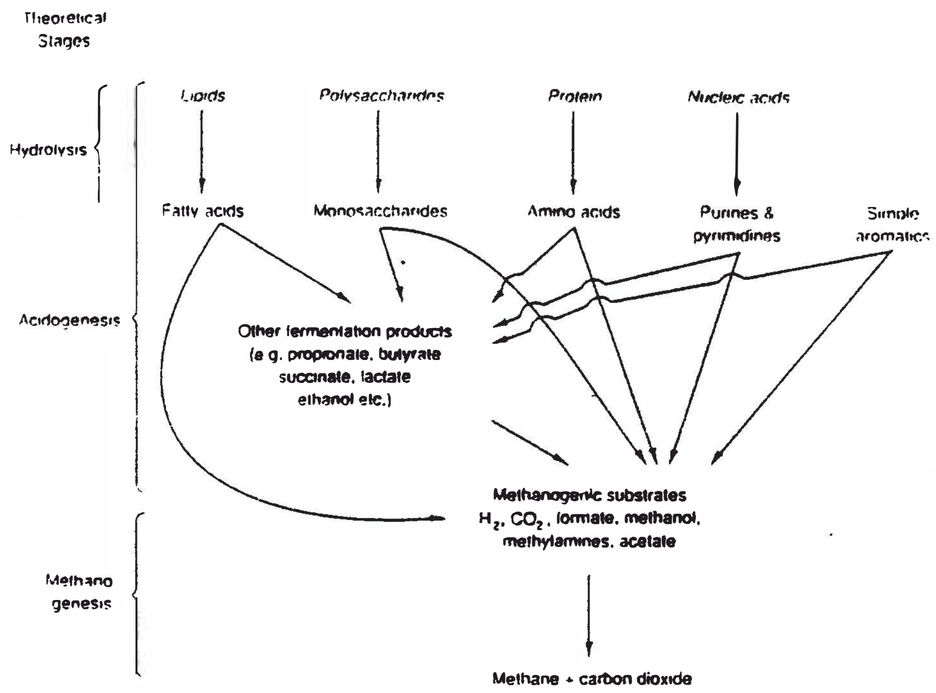

Figure 1: Schematic Diagram of the Patterns of Carbon Flow in Anaerobic Digestion (Metcalf & Eddy, 1991)

Fourth Step: Methanogenesis

In this process, hydrogen and acetate acid are converted to methane gas and carbon dioxide. The bacteria responsible for conversion are strictly anaerobes and these methanogenic bacteria are physiologically united by their requirement to form methane as final product of energy metabolism (Sahm, 1984). The growth rate of methanogenic is lower than the acid-forming bacteria, thus it takes more time for the methane bacteria to recover from inhibition or shock conditions (Corbitt, 1998). As a result their metabolism usually considered as rate limiting in the anaerobic treatment of organic waste (Metcalf and Eddy, 1991) as high treatment efficiencies can be only achieved as long as a sufficient quantity of active methanogens exist in the digester (Ince et al., 1995 and Ince et al., 1997). Methanogenic bacteria can only use a limited number of substrate for the formation of methane and the typical energy-yielding conversions of these substrates are as follow (Metcalf and Eddy, 1991):

Hydrogen	$4H_2 + CO_2 \longrightarrow$	$CH_4 + 2H_2O$
Acetate	$4\ HCOOH \longrightarrow$	$CH_4 + 3CO_2 + 2H_2O$
Formate	$CH_3COOH \longrightarrow$	$CH_4 + CO_2$
Methanol	$4CH_3OH \longrightarrow$	$3CH_4 + CO_2 + 2H_2O$
Trimethylamine	$4(CH_4)_3N + H2O \longrightarrow$	$9CH_4 + 3CO_2 + 6H_2O$

The two principal pathways involved in methane formation (Figure 2) are:

1. The conversion of hydrogen and carbon dioxide to methane and water;
2. The conversion of acetate to methane and carbon dioxide.

The methanogens are able to utilize the hydrogen produced by the acidegens because of their efficient hydrogenase. The utilisation of the hydrogen by methanogens bacteria is termed as interspecies hydrogen transfer and it remove compounds that would inhibit the growth of acidogens (Metcalf and Eddy, 1991).

According to Sahm (1984), most methanogenic bacteria prefer to oxidize H_2 and reduce CO_2 to form methane as their pathway of methanogenesis. Contrary to hydrogen, acetate is a poor substrate and the slow growth rates for acetotropic methanogenesis might be a consequence of this fact (Zehnder et al., 1981) and so far only three acetotropic methanogenic species (*Methanosarsina barkeri, Methanococcus mazei and Methanothrix soehgenii*) have been isolated in pure culture (Sahm, 1984). Thus, acetotropic methanogenesis are usually rate limiting, as their growth rate is much lower than hydrogenotrophs (Haandel and Lettinga, 1994).

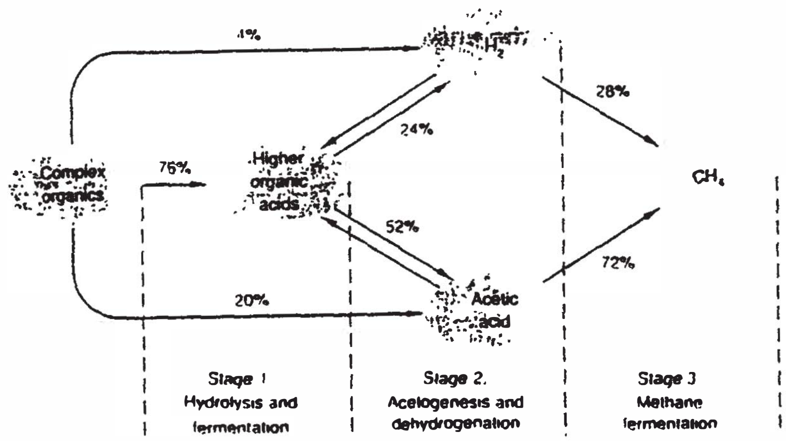

Figure 2: Steps in the Anaerobic Digestion Process with Energy Flow
(Metcalf & Eddy, 1991)

Methane fermentation phase is the most important phase because:

1. It is the only mechnism of BOD and COD removal. Waste stabilization in anaerobic is accomplished when methane and carbon dioxide is produced (Cheremisinoff, 1994a).
2. The reproduction rate for methane bacteria is low relative to other groups of bacteria. The doubling time for acidogenisis is few hour while methanogenisis under ideal condition is four days (Cheremisinoff, 1994a). Thus this step have been found to be the rate-limiting step.

3. Methanogenic bacteria are too sensitive to surrounding conditions changes compared to other anaerobes.

Anaerobic Digestion

The two types of commonly used anaerobic digesters are identified as standard-rate and high-rate reactor (Figure 3). In the standard-rate digestion process, the content of digester are usually unmixed and unheated and the detention times vary from 30 to 60 days (Metcaft and Eddy, 1991). In high-rate digester the mixing is continuous; thus the mixing provides better contact between the seeded sludge and fresh solids that have been added. Hence high-rate detention time normally is 15 days or less (Metcalf and Eddy, 1991). A combination of these two processes is known as the "two- stage process".

Several treatment systems have been developed by the palm oil industry in Malaysia. Due to the POME high organic content, it is easily amenable to biodegradation. Therefore the treatment system for POME consists essentially of anaerobic and aerobic or combination of this two biological processes. Ma and Hassan (1991) reported that the three most common and efficient wastewater treatment systems adopted by palm oil industry are ponding system, open tank digester with extended aeration and closed tank digester with biogas recovery and land application (Figure 4).

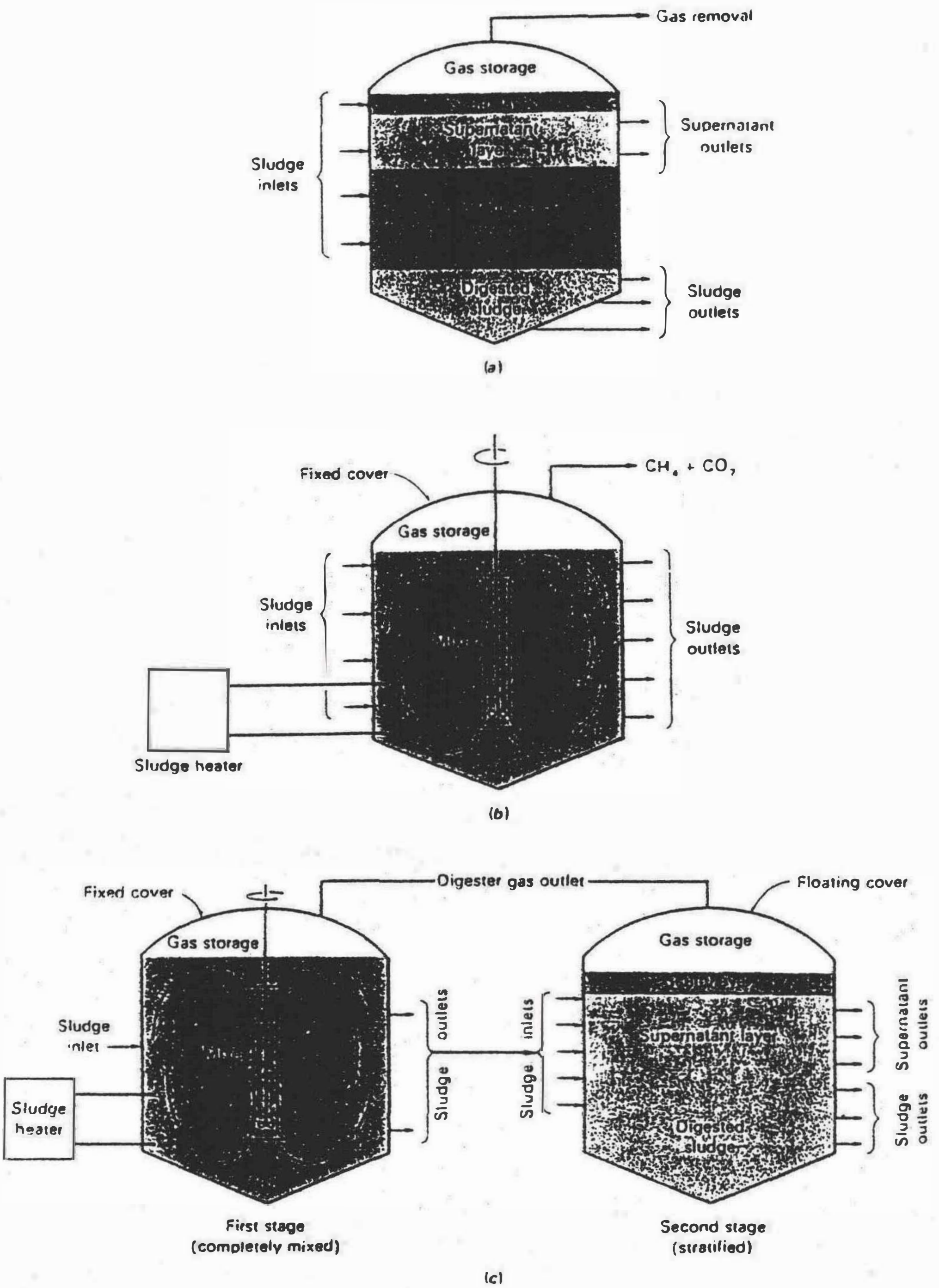

Figure 3: Typical Anaerobic Digestion: (a) Conventional Standard-rate Single-stage Process, (b) High-rate Complete-mix, Single-stage Process, and (c) Two-stage Process (Mecalf & Eddy, 1991)