PRODUCTION OF METHANE FROM PALM OILL MILL EFFLUENT USING MEMBRANE ANAEROBIC SYSTEM

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ABSTRACT

Palm oil mill effluent (POME) is a highly polluting wastewater that pollutes the environment if discharged directly due to its high chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS) and biological oxygen demand (BOD). The transformation of the palm oil mill effluent (POME) to methane gas by membrane anaerobic system (MAS) was evaluated. The membrane used in the system is a cross flow ultra filtration membrane (UF). The untreated water or the retentate was recycled back into the anaerobic reactor. 20 liter of raw material of palm oil mill effluent (POME) were used and the pH, biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS) and volatile suspended solids (VSS) are determined before and after the anaerobic digestion. There is a huge decrease in value of BOD, COD, TSS and VSS in permeate compared to the POME from the reactor before and after the treatment. The BOD of permeate on the 7th day is 612 mg/L whereas the COD is 320 mg/L. The pH of the POME inside the reactor is maintained in from 6.5 to 7.5 to induce methanogenic reaction, instead of acidogenic reaction. About 86% of methane gas released during the anaerobic digestion.

Keywords:

POME; MAS; Anaerobic; Treatment; COD; BOD; Methane; TSS; VSS

ABSTRAK

Sisa kilang kelapa sawit (pome) merupakan sisa yang sangat mencemarkan alam sekitar jika dibuang terus kerana 'chemical oxygen demand' (COD), 'total suspended solids' (TSS), 'volatile suspended solids' (VSS) dan 'biological oxygen demand' (BOD) yang tinggi.Dalam kajian ini, sistem membran anaerobik (MAS) digunakan untuk memproses sisa kilang kelapa sawit (pome). Transformasi dari sisa kilang kelapa sawit (pome) ke gas metana dalam sistem membran anaerobik (MAS) telah dinilai. Membran yang digunakan dalam sistem aliran 'cross-flow ultrafriltration membrane' (UF). Air tidak dirawat atau retentat akan dikitar semula kembali ke reaktor anaerobik. 20 liter bahan mentah yang sisa kilang kelapa sawit (pome) digunakan dan pH, 'chemical oxygen demand' (COD), 'total suspended solids' (TSS), 'volatile suspended solids' (VSS) dan 'biological oxygen demand' (BOD) telah ditetapkan sebelum dan selepas pencernaan anaerobik. Ada penurunan besar nilai BOD, COD, TSS dan VSS berbanding dengan pome dari reaktor sebelum dan selepas tindakbalas anaerobik. BOD dari permeat pada hari ke-7 adalah 612 mg / L manakala COD adalah 320 mg / L. PH dari pome didalam reaktor dikekalkan di antara 6.5-7.5 untuk menggalakkan reaksi metanogen dan bukan reaksi acidogenic. Sekitar 86% gas metana dilepaskan selama pencernaan anaerob.

Katakunci:

POME; MAS; Anaerobik; Rawatan; COD; BOD; Metana; TSS; VSS

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LIST OF ABBREVIATIONS

COD	-	Chemical Oxygen Demand
BOD	-	Biological Oxygen Demand
TSS	-	Total Suspended Solids
VSS	-	Volatile Suspended Solids
MAS	-	Membrane Anaerobic System
POME	-	Palm Oil Mill Effluent
NGV	-	Natural Gas Vehicle
mg	-	milligram
%	-	percent
L	-	liter

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Environmental pollution is one of the greatest challenges human beings face in the twenty-first century. We are also faced with consequences of climate change, increase global demand for fossil fuels, energy insecurity, and continuous exploitation of limited natural resources. The traditional approach of pollution control, which focuses on ridding pollutants from a single medium, that is, transformation of pollutants from liquid to solid or gas phase and vice versa, is no longer a desirable option. It has become enormously to direct research efforts towards sustainable methods that not only alleviate environmental pollution, but also ease the stress on depleted natural resources and growing energy insecurity. The most cost-effective and sustainable approach is to employ renewable energy technology.

In the recent years, there has been considerable interest in developing countries in the use and application of biogas. This interest is mainly due to a number of factors. Firstly, the escalating cost of fossil fuels, and the decreasing availability of renewable sources of fuel, i.e, petroleum, has forced many developing countries to look more at renewable energy technology, i.e. solar, wind and biomass based technologies such as biogas, power alcohol and gasifiers. Of these techniques, biogas has one of the lowest financial inputs per Kwh of output.

Secondly, since biogas mimics natural environmental cycles, nutrients such as nitrogen, phosphorous and potassium are conserved in the process and can be recycled back to the land in the form of slurry. This is in contrast to the burning of biomas where most of the nutrients are lost.

Thirdly, through the digestion of animal manures and nightsoil, biogas has the potential considerably reducing the plant, animal and human pathogens. This breaks the cycle of reinfection and leads to considerable improvement in public health. Finally, since biogas is a clean burning fuel, its use in domestic application can reduce the incidence of eye and lungs problem commonly encountered with the use of smoky fuels, i.e. firewood and coal. Furthermore, biogas is an extremely versatile technology and can utilize a wide variety of organic feedstocks, i.e. animal manures, nightsoil (human faeces), agricultural residues, aquatic plants and organic industrial wastes.

Anaerobic digestion of organic wastes and by products from agriculture and the food industry is a process known for many years and is widely used for waste stabilization, pollution control, improvement of manure quality and biogas production. Anaerobic digestion a process that exhibits many advantages: It can convert a disposal problem into a profit centre, it allows agricultural crops to be converted into a valuable fuel and it can reduce mineral fertilization demand by nutrient recovery. Therefore, anaerobic digestion has become a key method for both waste treatment and the production if renewable fuels.

1.2 RESEARCH BACKGROUND AND PROBLEM STATEMENT

1.2.1 Problem Statement

Currently, the world is using fossil fuels such as oil, natural gas and coal as the main source of energy. However, the international crisis in the Middle East, rapid depletion of fossil fuels and as well as climate changes has driven the world towards the renewable energy which are abundant, untapped and environmentally friendly. Malaysia has abundant biomass resources especially from the industries.

This paper will focus on palm oil mill effluent (POME) as the source of the renewable energy for the generation of methane which can be used as the source of energy in various fields.

There are two problems in the considerations of solving in the course of this project. The main consideration is actually environmental pollution. Environmental pollution will be the problem to be solved. Disposal of wastes in the environment will give negative effect to the Mother Nature. Therefore, the present study converts these wastes into useful products in this case methane, which can be used as a burning fuel and source of energy. For instance, methane can be used in vehicles (NGV).

Secondly, the depletion of fossil fuels will be the second problem to be solved. Currently, the world uses fossil fuels as one the main energy source. Current scenario such as the Middle East crisis and the depletion of fossil fuels has opened the eyes of the world that the supplies of these fossil fuels are not forever. Therefore, this study will divert the world towards the renewable energy such as biomass.

1.2.2 Objective

The objectives of this research are:

1. To evaluate the anaerobic transformation of palm oil mill effluent (POME) to methane gas in a membrane anaerobic system (MAS).
2. To experimentally assess the factors influencing anaerobic digester performance such as pH.

1.2.3 Scope of Study

A survey shows very limited or almost no work on producing methane gas from palm oil effluent (POME) using membrane anaerobic system (MAS).A high percentage of palm oil mill effluent release from the industry creates a need to do more research and study on this field where to convert wastes into energy. To accomplish the objectives of this research:

1. A laboratory digester was scaled membrane anaerobic system (MAS) with an effective 20 liter volume used to treat raw palm oil mill effluent (POME).
2. The parameters that will be considered in this research are :
    - pH
    - Chemical Oxygen Demand (COD)
    - Biological Oxygen Demand (BOD)
    - Total Suspended Solids (TSS)
    - Volatile Suspended Solids (VSS)

CHAPTER 2

LITERATURE REVIEW

2.1 ANAEROBIC DIGESTION

Scientific interest in the manufacturing of gas produced by the natural decomposition of organic matter, was first reported in the 17th century by Robert Boyle and Stephen Hale, who noted that flammable gas was released by disturbing the sediment of streams and lakes. In 1808, Sir Humphry Davy determined that methane was present in the gases produced by cattle manure. The first anaerobic digester was built by a leper colony in Bombay, India in 1859. In 1895 the technology was developed in Exeter, England, where a septic tank was used to generate gas for the sewer gas destructor lamp, a type of gas lighting. Also in England, in 1904, the first dual purpose tank for both sedimentation and sludge treatment was installed in Hampton. In 1907, in Germany, a patent was issued for the Imhoff tank, an early form of digester (Fergusen, T. & Mah, R., 2006).

Through scientific research anaerobic digestion gained academic recognition in the 1930s. This research led to the discovery of anaerobic bacteria, the microorganisms that facilitate the process. Further research was carried out to investigate the conditions under which methanogenic bacteria were able to grow and reproduce. This work was developed during World War II where in both Germany and France there was an increase in the application of anaerobic digestion for the treatment of manure (Fergusen, T. & Mah, R., 2006).

Anaerobic digestion is by far the most common process for dealing with wastewater sludge containing primary sludge. Primary sludge contains large amounts of readily available organics that would induce a rapid growth of biomass if treated aerobically. Anaerobic decomposition produces considerably less biomass than aerobic processes. The principal function of anaerobic digestion, therefore, is to convert as much of the sludge as possible to end products such as liquids and gases, while producing as little residual biomass as possible (Caye *et al.*, 2008).

Wastewater sludge contains a wide variety of organisms, and thus requires a wide variety of organisms for its decomposition. The literature relating to anaerobic sludge digestion often divides the organisms into broad groups, the acid formers and methane formers. The acid formers consist of facultative and anaerobic bacteria and include organisms that solubilize the organic solids through hydrolysis. The soluble products are then fermented to acids and alcohols of low molecular weight. The methane formers consist of strict anaerobic bacteria that convert the acids and alcohols, along with hydrogen and carbon dioxide, to methane (Caye *et al.*, 2008). The process flow is shown in the figure below:

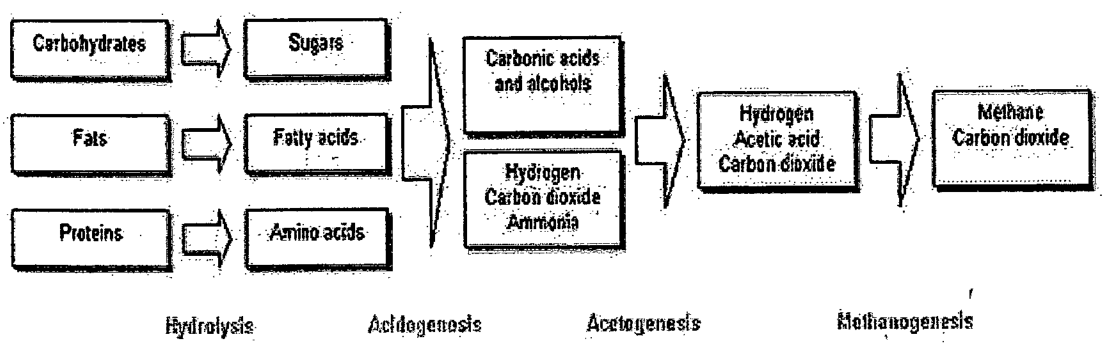

Figure 2.1: The Key Process Stages of Anaerobic Digestion (Ajit *et. al.*)

2.2 PALM OILL MILL EFFLUENT (POME)

In the process of palm oil milling, POME is generated through sterilization of fresh oil palm fruit bunches, clarification of palm oil and effluent from hydrocyclone operations. POME is viscous brown liquid with fine suspended solids at pH ranging between 4 and 5. The characteristics of POME could be referred to the Data for Engineers. Direct discharge of POME into the environment is not encouraged due to the high values of COD and BOD. Furthermore, with the introduction of effluent discharge standards imposed by the Department of Environment in Malaysia, POME has to be treated before being released into the environment (R.Borja *et. al.*, 1995; P.E.Poh *et, al*,. 2009).

POME is made up of about 95-96% water, 0.6-0.7% oil and 4-5% total solid, including 2.4% suspended solids, which are mainly debris from palm mesocarp. No chemicals are added during the production of palm oil, thus it is a nontoxic waste. Upon discharge from the mill, POME is in the form of highly concentrated dark brown colloidal slurry of water, oil and fine cellulosic materials. Due to the introduction of heat (from a process called sterilization) and vigorous mechanical processes, the discharge temperature of POME is approximately 80-90 °C (Mohd. Ali *et, al*,.). The chemical properties of POME are in the table below:

Table 2.1: Chemical Properties of Palm Oil Mill Effluent (POME)

Chemical Property	Average	Range
pH	4.2	3.4-5.2
BOD (mg/L)	25,000	10,250-43,750
COD (mg/L)	50,000	15,000-100,000
Oil & Grease (mg/L)	6000	150-18,000
Ammoniacal Nitrogen (mg/L)	35	4-80
Total Nitrogen (mg/L)	750	180-1400
Suspended solid (mg/L)	18,000	5000-54,000
Total Solid (mg/L)	40,000	11,500-78,000

Apart from the organic composition, POME is also rich in mineral content, particularly phosphorus (18 mg/L), potassium (2270 mg/L), magnesium (615 mg/L) and calcium (439 mg/L) (Shahrakbah *et. al.,* 2005).

2.3 METHANE

Methane is a colorless, odorless gas with a wide distribution in nature. It is the principal component of natural gas, a mixture containing about 75% CH_4, 15% ethane (C_2H_6), and 5% other hydrocarbons, such as propane (C_3H_8) and butane (C_4H_{10}). The "firedamp" of coal mines is chiefly methane. Anaerobic bacterial decomposition of plant and animal matter, such as occurs under water, produces marsh gas, which is also methane (Scifun.Chem.Wisc).

At room temperature, methane is a gas less dense than air. It melts at –183°C and boils at –164°C. It is not very soluble in water. Methane is combustible, and mixtures of about 5 to 15 percent in air are explosive. Methane is not toxic when inhaled, but it can produce suffocation by reducing the concentration of oxygen inhaled. A trace amount of smelly organic sulfur compounds (*tertiary*-butyl mercaptan, $(CH_3)_3CSH$ and dimethyl sulfide, CH_3–S–CH_3) is added to give commercial natural gas a detectable odor. This is done to make gas leaks readily detectible. An undetected gas leak could result in an explosion or asphyxiation (Scifun.Chem.Wisc).

The energy released by the combustion of methane, in the form of natural gas, is used directly to heat homes and commercial buildings. It is also used in the generation of electric power. During the past decade natural gas accounted for about 1/5 of the total energy consumption worldwide (Wim *et, al,.* 2009).

Natural gas occurs in reservoirs beneath the surface of the earth. It is often found in conjunction with petroleum deposits. Unfortunately, this reservoir is coming to depletion. One day, one of the main sources of energy which is methane will deplete. Therefore, production of methane from the biomass especially from the palm oil mill effluent (POME) ensures to continuity of usage of methane as one of the main sources of energy (Wim *et, al,*. 2009).

2.4 ANAEROBIC DIGESTION AND METHANE PRODUCTION

Methane is produced during the anaerobic catabolism of organic substances. This process is very common in nature. It has been estimated that 1 to 1.5 percent of the carbon liberated as atmospheric carbon dioxide, by the mineralization of organic substances, reaches the atmosphere first as methane which is converted via CO_2 to CO by hydroxyl radicals (OH). Rice fields, sediments of lakes, ponds and puddles, salt marshes, estuaries, sandy lagoons, sewage digesters and the rumen of more than 10 ruminants on the earth are various sources of methane. In such anaerobic locations organic substrates are first fermented to acetate, carbon dioxide and molecular hydrogen. It is these products of the primary and secondary breakdown that are utilized by the methane producing bacteria (methanogens). Besides, these natural sources, natural gas is also rich in methane. It is about 85 percent methane (CH_4). The table below shows the production of biogas from various organic wastes.

Table 2.2: Production of Biogas from Various Organic Wastes (Ajit *et. al.*)

Nature of Organic Substance	Methane Production
Biomass (*Calotropis procera*)	2.9 to 3.6 liter biogas per day (56 – 59% methane)
Napier grass (in presence of micronutrients)	0.7 liter per day
Rabbit waste	127.00 liter/kg VS
Rabbit waste + tomato plant wastes	0.115 m^3/kg VS
Cow paunch manure	442 liter/mg TVS
Pea-shells	220 liter/kg TS
Cattle dung	120 liter/kg TS(40=hrt)
Night soil	69.72 liter/kg VS (Methane = 73%)
Tomato wastes	0.42 m^3/kg/VS
Apple pomace	155.6 liter/kg TS
Cauliflower and raddish waste	150.7 liter/kg TS
Rotten cabbage	217.6 liter/kg TS
Wheat straw	360 liter/kg TS
Rice straw	487 liter/kg TS
Mirabilis leaves	418 liter/kg TS
Cauliflower leaves	520 liter/kg TS
Ipomea fistula leaves	507 liter/kg TS
Dhub grass	282 liter/kg TS
Banana peeling	460 liter/kg TS
Boiled rice	0.294 m^3/kg VS added
Cooked meat	0.482 m^3/kg VS added
Fresh cabbage	0.277 m^3/kg VS added

2.5 MICROBIOLOGY AND BIOCHEMISTRY OF ANAEROBIC TECHNOLOGY

2.5.1 Microbes Involved in Methane Production

The methanogens belongs to a special group of bacteria strictly anaerobic in nature. On the basis of these and other difference within the prokaryotes, the methanogens are assigned to the achaebacteria. They differ from other bacteria not only by their type of metabolism but also by a number of characteristic features in the composition of their cell constituents. They lack a typical peptidoglycan skeleton. *Methanococcus* has only a protein envelope, a peptide sheath is found in *Methanospirillum*, whilst the cell wall of *Methanosacrina barkeri* consists of a polysaccharide composed of uronic acids, neutral sugars and amino sugars. The methanogenic bacteria are not subject to growth inhibition by penicillin (Ajit *et. al.*).

Almost all the shapes known in the eubacteria can be found in the methanogens:

cocci	-	*Methanococcus venniellii*
rods	-	*Methanobacterium formicicum*
shortrod	-	*M. ruminantium*
	-	*M. arboriphilicum*
sprillia	-	*Methanospirillum hungatti*
coccal packets	-	*Methanosarcina barkeri*
filaments	-	*Methanothrix soehngenii*
squaretype	-	*Methanoplanus limicola*

Besides these, there are mesophilic and thermophilic species (*Methanobacterium thermoautotrophicum, Methanothermus fervidus*). Six families have been distinguished already and the number or known species and genera are constantly increasing (Ajit *et. al.*).

2.5.2 Organics Conversion in Anaerobic System

The transformation of complex macromolecules, for example, proteins, carbohydrates (polysaccharides), lipids present in wastewater, or solids into end products such as methane and carbon dioxide is accomplished through a number of metabolic stages mediated by several groups of microorganisms. Figure 2.2 illustrates the schematics of the various steps and the bacterial groups involved in anaerobic digestion of complex wastes.

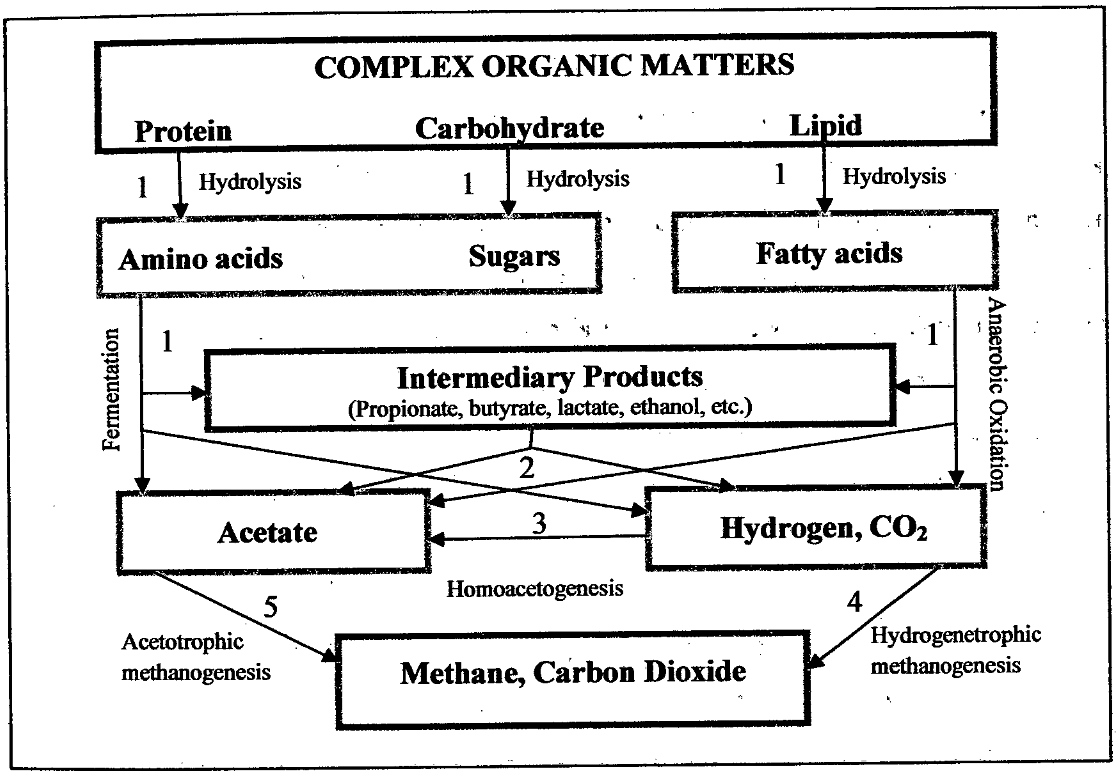

Figure 2.2: Conversion Steps in Anaerobic Digestion of Complex Organic Matter. (The Number Indicates the Group of Bacteria Involved in the Process) (Gujer *et,al,*. 1983)