OPTIMIZATION OF BIOHYDROGEN FROM PALM OIL MILL EFFLUENT (POME) USING IMMOBILIZED BIOMASS

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ABSTRACT

Worldwide energy system utilized fossil fuels as the source of combustion. However, it cannot be sustainable and decreases from time to time. Exploration of a new sustainable energy has been conducted around the word in order to replace conventional fossil fuels. Hydrogen has been considered as a potential fuel for the future since it is carbon-free and oxidized to water as a combustion product. There are several methods to produce hydrogen. Either from mushroom cultivation waste, sweet potato or many more organic wastes in order to generate fermentative hydrogen production. In this study, Palm Oil Mill Effluent (POME) was used as a substrate carbon source. The optimization of hydrogen production using polyethylene glycol (PEG) immobilized sludge was investigated by using a batch test. It was found that a maximum hydrogen production rate that can be produce by immobilized sludge was 339 mL/L-POME/h at the optimal amount of biomass (10 mg VSS/ g bead), pH 6.5 and PEG concentration (10% w/v). Therefore, immobilized biomass and PEG really helps to maintain a higher cell density. More importantly, it not only enhanced hydrogen production but can also tolerate with the harsh environment and produce hydrogen at wide range of pH. The present results indicate that potential of PEG- Immobilized sludge for large scale operations and play an important role in stable and continuous hydrogen production.

ABSTRAK

Sistem tenaga di seluruh dunia mengggunakan bahan api fosil sebagai sumber pembakaran. Walau bagaimanapun, ia tidak boleh berterusan dan berkurangan dari semasa ke semasa. Penerokaan tenaga mampan baru telah dilaksanakan di seluruh dunia untuk menggantikan bahan api fosil konvensional. Hidrogen telah dianggap sebagai bahan api yang berpotensi pada masa akan datang kerana ianya bebas karbon dan di oksidakan kepada air sebagai hasil pembakaran. Terdapat beberapa kaedah untuk menghasilkan hidrogen. Sama ada dari sisa penanaman cendawan, kentang manis atau pelbagai lagi bahan buangan yang lebih organik untuk menjana pengeluaran hidrogen melalui penapaian. Dalam kajian ini, bahan buangan dari Kilang Minyak Sawit (POME) telah digunakan sebagai sumber karbon. Pengoptimuman pengeluaran hidrogen menggunakan polietilena glikol (PEG) telah dikaji dengan menggunakan ujian kelompok. Di dalam kajian ini, kadar pengeluaran hydrogen yang paling maksimum yang boleh dihasilkan adalah 339 mL / L-POME / h pada jumlah biomas (10 mg VSS / g manik), pH 6.5 dan kepekatan PEG (10% w/v). Jesteru itu, biomas bergerak dan PEG benar-benar membantu untuk mengekalkan kepadatan sel yang lebih tinggi. Tambahan pula, ia bukan sahaja meningkatkan pengeluaran hidrogen malahan ianya amat bersesuaian dengan persekitaran yang sukar dengan menghasilkan hidrogen pada pH yang pelbagai. Keputusan ini menunjukkan bahawa potensi kumbahan PEG amat bersesuaian untuk operasi berskala besar dan memainkan peranan penting dalam pengeluaran hidrogen yang stabil dan berterusan.

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LIST OF SYMBOLS

m	Mass of biomass
mg	Milligram
ml	Milliliter
kg	Kilograms
L	Liter
v	Volume of sample
^0C	Degree Celsius
$\%$	Percent

LIST OF ABBREVIATIONS

BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DOE	Department of Environment
EFB	Empty Fruit Brunches
FFB	Fresh Fruit Brunches
NaOH	Sodium Hydroxide
OLR	Organic Loading Rate
PEG	Polyethylene glycol
POME	Palm Oil Mill Effluents
SRT	Solid Retentian Time
TSS	Total Suspended Solid
UASB	Upflow Anaerobic Sludge Blanket

CHAPTER 1

INTRODUCTION

1.1 Background to the study

Worldwide energy system utilized fossil fuels as the source of combustion. However, it cannot be sustainable and decreases from time to time. Exploration of a new sustainable energy has been conducted around the word in order to replace conventional fossil fuels. Hydrogen is the viable as an alternative source because water is the sole end product after combustion that considered as clean energy. Besides that, Hydrogen also has high energy content, clean, recyclable and has high conversion efficiency.

Hydrogen can be produced from many different sources, and different ways. Some of the researches utilize mushroom cultivation waste (Chyi et al., 2012), sweet potato (Chen et al., 2012), and many more organic waste in order to generate fermentative Hydrogen production. While according to Bi ca´kova and Straka (2012), Hydrogen also can be produced form steam reforming of natural gas, electrolysis of water, gasification of coal and mainly is from fossil fuels.

Hydrogen can be produced by various physical, chemical and biological methods that shown in Table 1.1.

Table 1.1: Hydrogen production technologies used today

Technology	**Feed stock**
Steam reforming	Hydrocarbons
Autothermal reforming	Hydrocarbons
Plasma reforming	Hydrocarbons
Aquesous phase reforming	Carbohydrates
Ammonia reforming	Ammonia
Partial oxidation	Hydrocarbons
Biomass gasification	Biomass
Photolysis	Sunlight + water
Dark fermentation	Biomass
Photo fermentation	Biomass + sunlight
Microbial electrolysis cells	Biomass + electricity
Alkaline electrolyzer	H_2O + electricity
PEM electrolyzer	H_2O + electricity
Photo-electrochemical water splitting	H_2O + heat
Thermo-chemical water splitting	H_2O + sunlight

Due to the rising amount of waste material, research in the area of biohydrogen has increased in the last few decades. Biological processes have been used since it reduces the energy costs and costs for the transport of the initial raw material. Hydrogen production by microorganism can be divided into two main categories which are anaerobic fermentative bacteria under dark condition (dark fermentation) or photosynthetic bacteria and algae under light condition and the other (photo-fermentation).

15.2 million tons of waste water know as palm oil mill effluent (POME) have been produce annually by the palm oil industry in Malaysia that can be use as a source for fermentative hydrogen production.

Table 1.2: Chemical characteristics of palm oil mill effluent used in this study

Parameter	Concentration (mg/l)	Range
Biochemical Oxygen Demand (BOD)	14 496	10 000 - 44 000
Chemical Oxygen Demand (COD)	56 942	16 000 - 100 000
pH	4.2	3.4 - 5.2

The Malaysian palm oil industry is one of the main industries in Malaysia and has grown rapidly over the years. According to Wu et al., (2008) 13 million tons of crude palm oil has been produced and amounts of palm oil mill effluent (POME), estimated at nearly three times the quantity of crude palm oil. Hwang et al., (1978) summarizes this by stating that the largest pollution load into the river is caused by the palm oil mill industry by discharging POME directly into the river.

Optimization of biohydrogen is a process of producing hydrogen biologically which is normally by algae, bacteria or from waste organic material. According to Ueno et al., (1996) there are a lot of advantages by hydrogen production such as less energy, sustainable and eco-friendly.

Most of the study applied suspended-cell system to produce hydrogen but it is ineffective. So, by using biomass immobilization that can be defined as keeping the whole cells of agriculture waste in an insoluble phase, which allows the free exchange of solutes from and towards the biomass, while at the same time isolating the cells from their surrounding medium in order to improve operational characteristics of hydrogen production.

This study will determine the effect of biomass amount on hydrogen production by immobilized cell. Also, the effect pH variation on hydrogen production of immobilized cell in PEG beads. Lastly, the effect of polyethylene glycol (PEG) concentration on the hydrogen production. In this study, I will used of immobilized biomass to optimize the

hydrogen production from POME. The tables/charts of effect of varies above will be established to shown the hydrogen production from POME.

1.2 Potential Adverse Environmental Impacts of Palm Oil Industry

As Malaysian palm oil industry has seen unprecedented growth in the last few decades to emerge as the leading agricultural industry in the country, it causes the potential for adverse environmental impacts. Due to this rapid transformation of natural forests to the farming area, there are causes typical environmental problems associated with plantation agriculture. Like soil erosion, water pollution due to application of fertilizers and pesticides and agriculture runoff. This is echo with a study by Department of Environment (1999) that in the processing of the oil palm crop or fresh fruit brunch it may causes adverse impact on the pollution of the country's surface water.

Normally palm oil mills are located close to river area that can provide them with water supply. Ahmad et al., (2003) concedes that the palm oil extraction required a large quantity of water to run the process of extraction. In addition, palm oil mills typically located within the estates that far into the interior of the country. Because of the location, normally the discharge POME will pollute the water streams and rivers due to the lack of supervision from the authority.

According to Ngan (2002) Malaysia has 360 palm oil mills. Therefore, the estimated annual production of palm oil mill effluent (POME) would be higher. Nevertheless, the high contents of organic matter, suspended components, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and others can cause depletion of oxygen and other related effect. Hence, it causes severe pollution to waterways. Hence, treatment processes need to be carried out before it can be discharge into the river and water stream.

1.3 Problem Statement

In order to overcome energy crisis and global climate change, hydrogen has been proposed as an alternative energy source by using a POME. Continuous operation on suspended-cell system often encounters problem of biomass washout at high dilution rate, recycling the biomass back to the reactor has to be used to maintain sufficient cell density for high hydrogen production. Therefore, this research will use immobilized biomass and PEG as additional merits to maintain a higher cell density in order to increase hydrogen production.

1.4 Research Objectives

The purposes of this study are as follows:

1.4.1 To determine effect of biomass load on hydrogen production by immobilized cell.

1.4.2 To determine the effect pH variation on hydrogen production of immobilized cell in PEG beads.

1.4.3 To determine the effect of polyethylene glycol (PEG) concentration on hydrogen production.

1.5 Scope of study

Raw Palm Oil Mill Effluent (POME) has been collected from the tank of the palm oil mill at Lepar Hilir Pahang and has been used as the carbon source for hydrogen production. Using POME as waste water, the effluent taken has been tested to get the Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and pH for characteristic of POME.

There were three vary that need to be consider during this study. The first thing is the amount of biomass, pH variation and PEG concentration, in order to differentiate the hydrogen production from POME.

Meanwhile, there were two stages of process in the laboratory's experimental which is the first, need to determine the characteristic of the POME without processing the POME. Then the second stage is to determine the amount of hydrogen production from varies effect. After the experiment done, the data collect use for characterized the characteristic of the POME and to determine the amount of hydrogen production using POME.

1.6 Expected outcomes

By doing this study, I will prove that POME can be use as a source of Hydrogen production and I will explore the effect of various parameters such as biomass load, variation of pH, and lastly PEG concentration, on hydrogen production from POME by using immobilized biomass. During the course of experiments the produces hydrogen was examined at designed time period and presented in graphs/tables form. Unintentionally, it can increase production of hydrogen due to the various parameter determined.

1.7 Significance of study

The significant of study of this study are:

1. By using immobilized biomass, it maintained a high cell concentrations and long retention time of biomass in order to produce more hydrogen.

2. Cell can be reuse back without the costly processes of cell recovery and cell recycles.

3. Can prevent cell elimination during cell washout at high dilution rates.

4. Besides that, this study will help to establish a suitable parameter and favourable micro-environmental conditions for cells to overcome the lower yield of hydrogen production from POME. For example, cell-cell contact, nutrient-product gradients and pH gradients that can resulting in better performance of the biocatalysts (higher yields, growth and production rates) of hydrogen.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The non- renewable energy is reducing as the world population is expending and so is the demand for energy resources such as coal, petroleum, gasoline and metal cores. Lin and Chen (2006) states that, as the reserves of oil and gas are being depleted, fossil fuel has become main energy source used and causes global atmospheric pollution problems during its combustion. This is echo with Lin and Lay (2003) finding that the burning of fossil fuels (coal, natural gas, oil, petroleum) in different sectors contributes to the emission of greenhouse gases, such as carbon dioxide (CO_2), and other waste gases are the main causes of ozone layer depletion, global warming, climate change and acid rain.

David and Richard (2009) mentions that since this problem has risen all over the world, a lot of research has been carried out to utilize biomass as alternative renewable resource. Kajan et al., (2012) later summarizes that biomasses is a potential renewable energy sources to displace conventional fossil fuels.

2.2 Hydrogen Overview

Symbol of H in a periodic table and atomic no of 1 is a chemical element known as Hydrogen. At standards temperature and pressure hydrogen is a colorless, odorless, nonmetallic, univalent, tasteless, highly flammable diatomic gas (H_2). With an atomic mass of 1.00794 g/mol, hydrogen is the lightest element.

The result of a study by Debabrata and Nejat (2008) found that hydrogen is an ideal energy carrier of the future because hydrogen is a clean, recyclable and has high conversion efficiency. This is echo with Naim et al., (2008) finding. Other than that, Radjaram and Saravanane (2011) found that, hydrogen is widely produced and have high energy yielding (122 kJ/g) nature.

When hydrogen is used as a fuel, water is the sole end product after combustion that can be recycled again to produce more hydrogen that considered as clean energy. With regards to Nielsen et al., (2001) Biohydrogen derived from renewable energy sources, environmental friendly and clean bio-energy replacement for fossil fuels. It also can be produced by less energy-intensive processes.

2.2.1 Application of Hydrogen

Due to the broad application and ecological aspects, hydrogen production has become a subject of interest for many global companies. According to study by Bi ca´kova and Straka (2012), hydrogen is used mainly for chemical industries for the production of methanol and ammonia and in the refining industry. Other than that, hydrogen has been used in a food and beverage industries as a hydrogenating agent in order to increase the level of saturation of unsaturated fats and oils like margarine product.

Large quantities of hydrogen are needed by the engineer and car manufacturers for using hydrogen gas as an efficient and viable car fuel. By reacting hydrogen with oxygen, water and electricity will be produce. The chemical energy of hydrogen is converted by a combustion method used to power a range of new alternate fuel vehicles which is hydrogen gas. In the near future, hydrogen will become a significant fuel which can solve the local problems connected with an air quality.

Other than used as a power source, hydrogen gas also used in metallurgical industry. In order to obtain a reducing atmosphere, hydrogen will mix with inert gases like heat treating steel and welding. During welding, hydrogen gas will be used as a shielding gas. More, the combination of hydrogen gas and nitrogen gas can be applied as a protective atmosphere for applications such as brazing or bright annealing. Since hydrogen has a high thermal conductivity, is has been used as the rotor coolant in electrical generators at power stations.

Apart from its use as a reactant, Hydrogen has wide applications in physics. It is used as a rotor coolant in electrical generators especially at large power station due to its high thermal conductivity and low friction resistance. While for liquid Hydrogen is used in as a rocket fuel that has propelled the space shuttle. Since Hydrogen is lighter than air, (1/15th of the density of air), it was once widely used as a lifting agent in balloons and airships.

2.2.2 Hydrogen production

The production of Hydrogen can be regenerate from different energy sources and variety ways. For example, water, nuclear, renewable, and mainly is from fossil fuels. The production of Hydrogen gas generated by stem is considered as expensive, energy exhaustive and not environmental friendly. Therefore as stated by Wang and Wan (2009), biological process is less energy intensive and more eco-friendly compared to conventional chemical method.

There were many research has been conducted in order to optimize the production of Hydrogen gas as well as to preserve our environment. Lakhveer et al., (2012) indicates that currently, about 98% of hydrogen comes from fossil fuel which is the highest one. Worldwide, 48% production of hydrogen from natural gas or steam reforming of hydrocarbon, 30% from oil, 18% from coal, and the remaining 4% via water electrolysis. While, Sompong et al., (2007) mentions that many researches using organic wastes and wastewater as substrates, employing mixed microflora in order to improve the hydrogen production yield.

Vijayaraghavan and Ahmad (2006) suggest that among all the sources to generate hydrogen, biomass seemed to be best options as it takes care of the degradation of the waste and yield hydrogen as a by-product. Through Khan et al., (2010) studies, reveals that Malaysia itself is a tropical country involving in agricultural sectors. So, we have a variety of biomass residue produced from oil palm, rice, sugarcane, wood industry and municipal solid waste as shown in Figure 2.1.

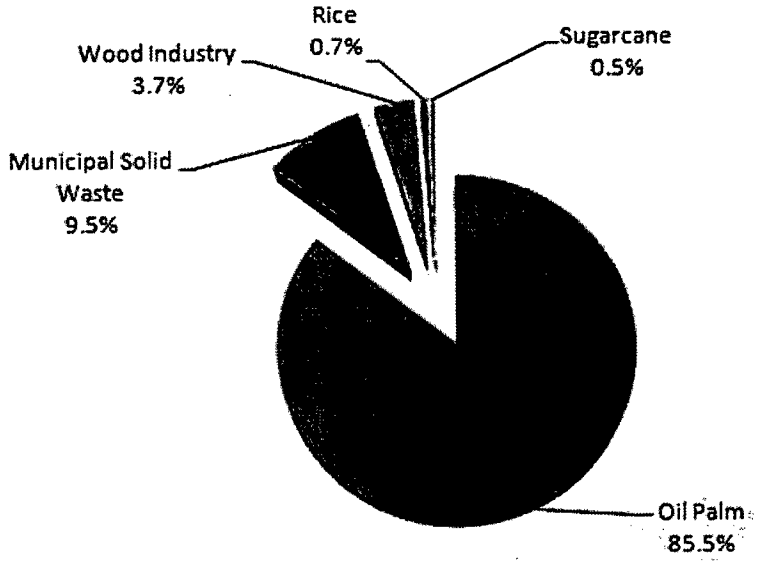

Figure 2.1: Different biomass produced in Malaysia

(Source: Khan et al., 2010)

Based on study by Turker et al., (2008) one of the alternative methods to produce Hydrogen is a biological process. Hydrogen can be produce through a wide range of approaches that include dark fermentation, light driven photo fermentation, direct biophotolysis and indirect biophotolysis. This is echo with a study by Levin et al., (2004) stated that to generate hydrogen by using biological process is a new area of technology development that offer a lot of advantages and more safe to the environment.

Nath et al., (2001) indicates that major advantages of Dark fermentation are high rate of cell growth, operation without light source and no oxygen limitation problems that presented as a promising route of biohydrogen production compared to photosynthetic routes. Therefore, numerous work and attempt have been made by the researches to generate hydrogen like from dairy waste (Babu et al., 2010), wheat straw (Chu et al., 2011), municipal solid waste (Lay et al., 1999) and many more.

2.3 Wastewater

Wastewater is used water discharged by domestic residences, commercial properties, industry, agriculture and other sources which often contains some waste substances and contaminants that result from the mixing of wastewater from different sources. Wastewater may contain waste substances and inorganic material that will infiltrate through the soil and contaminated water, runoff and groundwater.

Saifuddin and Fazlili (2009) advocates that wastewater output come from many branches of agriculture and food industries such as dairy, edible oil, fat refining, slaughter house, wool scouring and meat processing plants. Content of organic matter available in wastewater is one of a caused of pollution as well as total amount of wastewater production.

With regard to wastewater, Renoua et al., (2008) stipulate that, there are a lot environmental issues that concern about wastewater treatment. Since these problems become an issue, requirement has been set for the level of removal of various pollutants in treated water by legislation.

Therefore, effective wastewater treatments need to be conducted to control the wastewater discharge into the clean water body. Seng (1980) mentions that, good housekeeping, conservation of water usage, integrated treatment system design, accurate process control, and dose supervision and operation will help to treat wastewater.

2.4 Palm Oil

Figure 2.2: Immature palm trees

Malaysia is comprised with plenty natural resources and bears a favorable climate for commercial cultivation of crops like rubber and palm oil. Malaysia also has become the world's largest producer and exporter of palm oil and its products since this industry grown rapidly over the years. Yusoff and Hansen (2007) indicates that in 2003 more than one-third of the total cultivated area in Malaysia and 11% of the total land area which is 3.79 million hectares of land has been use for oil palm cultivation.

As a whole, palm oil industry contributes significantly towards the increased standard living among Malaysians. Wu et al., (2010) advocates by states that this industry provides employment opportunities to agricultural workers in estates as well a source of livelihood to rural families in government land schemes and private small holders. Lim and Teong (2010) emphasize that after the announcement of Fifth Fuel Policy under Eighth Malaysia