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Enhancement of batch biohydrogen production from prehydrolysate of acid treated oil palm empty fruit bunch

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ABSTRACT

Carbohydrates from hydrolyzed biomass has been a potential feedstock for fermentative hydrogen production. In this study, oil palm empty fruit bunch (OPEFB) was treated by sulfuric acid in different concentrations at 120 °C for 15 min in the autoclave. The optimal condition for pretreatment was obtained when OPEFB was hydrolyzing at 6% (w/v) sulfuric acid concentration, which gave the highest total sugar of 26.89 g/L and 78.51% of sugar production yield. However, the best conversion efficiency of OPEFB pretreatment was 39.47 at sulfuric acid concentration of 4%. A series of batch fermentation were performed to determine the effect of pH in fermentation media and the potential of this prehydrolysate was used as a substrate for fermentative hydrogen production under optimum pretreatment conditions. The prehydrolysate of OPEFB was efficiently converted to hydrogen via fermentation by acclimatized mixed consortia. The maximum hydrogen production was 690 mL H_2 L^{-1} medium, which corresponded to the yield of 1.98 $molH_2/mol_{xylose}$ achieved at pH 5.5 with initial total sugar concentration of 5 g/L. Therefore, the results implied that OPEFB prehydrolysate is prospective substrate for efficient fermentative hydrogen conducted at low controlled pH. No methane gas was detected throughout the fermentation.

1. Introduction

Hydrogen gas is well known to be a recyclable, clean and high-energy fuel with minimum pollution towards the environment. Hydrogen gas can be used as electricity through fuel cells and also an important energy carrier [27]. Conventionally, hydrogen gas is produced by costly chemical processes such as steam reforming and water electrolysis [37]. In contrast, biological hydrogen is generated from biomaterials that are abundant, sustainable and most importantly rich in

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carbohydrate, such as biomass and agricultural waste, via eco-friendly process [18].

The Malaysian palm oil industry is growing rapidly and quickly becoming a significant agriculture-based industry in this country. According to Wu et al. [48], the total productions of crude palm oil in 2008 and 2009 were 17,734,441 and 16,044,874 tonnes, respectively. Oil palm empty fruit bunch (OPEFB) is the major solid waste produced after the crude palm oil is extracted from the fresh fruit palm. It is estimated that about 15 million tonnes of OPEFB is produced per annum [30]. Generally, OPEFB is commonly used for making compost, however in current practice; they are distributed back to the plantation for mulching purposes. This activity is performed in an open system, which contributes to environmental pollution as it emits methane and carbon dioxide.

OPEFB consists of three main polymeric components i.e., cellulose, hemicellulose and lignin. The holocellulosic material composes 60–70% of cellulose and hemicellulose. OPEFB has higher content of lignocellulosic material compared to other type of commodity biomass such as sugarcane bagasse, rice straw, sorghum straw and corn cobs [25]. Therefore, pretreatment is required to open up the plant cell wall and break up the lignocellulose structure, thus making the carbohydrates more accessible to either acid or enzyme in subsequent hydrolysis [49]. Generally, pretreatment of biomass can be carried out by mechanical or chemical pretreatment. Chipping and grinding are often used as mechanical pretreatment while steam explosion, hydrothermal, acid and alkaline pretreatment are some examples of chemical pretreatment [6,17]. Dilute sulfuric acid pretreatment is one of the most extensively studied pretreatment methods. It results in an effective hydrolysis of hemicellulose constituents into mono and disaccharide sugars and a reduction in the crystallinity of cellulose [49]. Previous studies reveal that, most hemicellulose in lignocellulosic biomass is solubilized during this acid pretreatment producing xylose as the main sugar in the prehydrolysate and exposing lignin and cellulose for subsequent hydrolysis [19,28]. In addition to xylose, other by-products such as glucose, acetic acid and furfural are also present in small amount in the hydrolysis product [30]. Nonetheless, acetic acid and furfural are claimed to be inhibitors for microorganisms in subsequent fermentation. The presence of these compounds causes inhibition during fermentation process as it affects to the change of cell morphology or ultimate death of the microorganism [30]. However, formation of these inhibitors can be reduced by manipulating the concentration and temperature of pretreatment process [33].

Dark fermentation uses fermentative bacteria to breakdown carbohydrate rich substrates to hydrogen and other products such as acids and alcohols [46], in which waste biomass is generally rich in carbohydrate. Biological hydrogen produced from various types of waste biomass, such as food waste, sewage sludge and palm oil mill effluent, has been widely investigated [2,47]. Previous studies show that fermentative hydrogen production can be performed in the presence of carbohydrate rich hydrolyzate as the substrate. However, there was little information on hydrogen production from OPEFB biomass hydrolyzate which is composed mainly of simple carbohydrate. Typically, the fermentation of biomass hydrolyzate, that uses wastewater sludge as inoculums, is influenced by parameters such as pH, temperature and substrate specificity [38]. The perception of the hydrogen production under different operational condition is extraordinarily narrowed, particularly with the use of mixed culture. Fermentative hydrogen production by mixed culture in different operating conditions substantially alters the rates of hydrogen production, metabolite by-product, substrate removal and biomass growth [35]. Many studies have shown that pH is crucial to the hydrogen production, due to the effect on the hydrogenase activity and metabolism pathways [12]. Thus, it is critical to control pH at the desired optimum range to maintain and to avoid inhibition on hydrogen production or microbial population shift, resulting in cessation of hydrogen production [20]. The reported optimal initial pH value for hydrogen production is conflicting, varying from pH 4.0 to 9.0 under controlled batch fermentation. This might happen due to the difference type of inoculums used, substrate and range of studied pH [43].

Research on the utilization of biomass hydrolyzate as carbon source in fermentation process and the preparation of hydrolyzate from various pretreatment are gaining more attention recently. Chu et al. [8], hydrolyzed cotton cellulose with 55% sulfuric acid and produced sugar yield of 73.9%. The biomass hydrolyzate was used as substrate for hydrogen fermentation with hydrogen yield of 0.98 molH_2/mol reducing sugar at 35 °C and pH 8.2. Chang et al. [6], employed dilute acid pretreatment to hydrolyze rice straw resulting in 66.37 g/L reducing sugar and the hydrogen yield of 5.28 mmol/g rice straw. Fangkum and Reungsang [13], applied high temperature (121 °C) with 1% sulfuric acid to hydrolyze sugarcane bagasse and obtained a yield of 11.28 g/L total sugar. The sugars were used for batch fermentation with hydrogen yield of 0.84 molH_2/mol total sugar, operated at the initial pH 6.5 and initial total sugar concentration 10 g/L. Datar et al. [11], performed steam explosion with the addition of 1.2% sulfuric acid to hydrolyze the corn stover into sugars, and produced sugar yields of 21.8% and 15.7% respectively without addition of acid. The highest hydrogen production rate was achieved at 8.49 mmol/L/h obtained from the fermentation of the hydrolyzed sugar at 35 °C and pH 5.5.

In this study, we aimed to enhance the sugar conversion of OPEFB by manipulating acid concentrations in the pretreatment process. Then, we measured and employed both pentose and hexose sugars from OPEFB prehydrolysate as fermentation media, where palm oil mill effluent sludge's microbial consortia were used to produce hydrogen in fermentation process. The influence of the pH was investigated for high hydrogen rate in batch mode of fermentation conducted for 24 h. The fermentation's by-products such as total volatile fatty acids were also analyzed to gain more information on the microbial communities in hydrogen fermentation.

2. Material and methods

2.1. *Preparation of inocula*

In this study, the palm oil mill waste sludge was obtained from wastewater treatment plant at Sri Ulu Langat Palm Oil Mill, Dengkil, Selangor. A mixture of sludge containing mixed culture and distilled water in ratio of 1:1 was initially prepared by filtering the sludge using a sieve with mesh size of 1 mm to