IOP Conference Series: Materials
Science and Engineering

PAPER • OPEN ACCESS

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To cite this article: K Cahyari *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **358** 012001

IOP Conf. Series: Materials Science and Engineering **358** (2018) 012001 doi:10.1088/1757-899X/358/1/012001

Biohydrogen Production from Pineapple Waste: Effect of Substrate Concentration and Acid Pretreatment

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Abstract. Biohydrogen is the ultimate choice of energy carrier in future due to its superior qualities such as fewer greenhouse gases emission, high energy density (142 kJ/gram), and high energy conversion using a fuel cell. Production of biohydrogen from organic waste e.g. pineapple waste offers a simultaneous solution for renewable energy production and waste management. It is estimated that pineapple cultivation in Indonesia generated more than 1 million ton/year comprising of rotten pineapple fruit, leaves, and stems. Majority of this waste is dumped into landfill area without any treatments which lead to many environmental problems. This research was meant to investigate the utilization of pineapple waste i.e. peel and the core of pineapple fruit and leaves to produce biohydrogen through mesophilic dark fermentation (30℃, 1 atm, pH 5.0). Effect of dilute acid treatment and substrate concentration was particularly investigated in these experiments. Peel and core of pineapple waste were subjected to fermentation at 3 various substrate concentration i.e. 8.8, 17.6 and 26.4-gram VS/liter. Meanwhile, pineapple leaves were pretreated using dilute acid (H_2SO_4) at 0.2, 0.3 and 0.4 N and followed by dark fermentation. Results show that the highest yield of biohydrogen was obtained at a substrate concentration of 26.4-gram VS/liter both for peel and core of the waste. Pretreatment using dilute acid (H_2SO_4) 0.3 N might improve fermentation process with a higher yield at 0.8 ml/gram VS. Hydrogen percentage in biogas produced during fermentation process was in the range between 5 – 32% of volume ratio. In summary, it is possible to utilize pineapple waste for production of biohydrogen at an optimum substrate concentration of 26.4-gram VS/liter and acid pretreatment (H_2SO_4) of 0.3 N.
Keywords: hydrogen, fermentation, pineapple waste, core, peel, leaf

1. Introduction

Hydrogen is the cleanest energy carrier to substitute conventional fossil fuel for the betterment of the environment. It emits fewer greenhouses gases, more energy efficient conversion up to 49.7% through fuel cell platform, higher energy densities, and it is renewable [1]. The most feasible and common method to generate hydrogen is through water electrolysis, only if there is sufficient free excess electricity supply generated from solar [2], hydropower, wind, geothermal or else [3, 4]. However, recent studies show that the ratio of energy input-to-energy output through the electrolysis method is still high indicating that this method has negative energy balance. On the other hand, there is a more promising method to produce hydrogen from organic waste with least amount of energy input i.e. dark fermentation [5]. This production of hydrogen via dark fermentation process exploits microbial community to metabolize organic matter into volatile fatty acids along with electron transfer to hydrogenase to convert a proton into hydrogen (H_2). This method is influenced by many factors e.g.

type and concentration of substrate, temperature, pressure, pH, indigenous chemical inhibitors, organic loading rate, hydraulic retention time and reactor configuration [6, 7].

Pineapple waste comprises of peel and core of the fruit, leaves, and the stem is produced from cultivation and industrial processing of pineapple fruit. It leaves behind some portion of waste comprising of those components in huge quantities. This waste is commonly dumped in open area without any proper treatment creating environmental problems such as bad odors, health-related problems, contamination, and global warming. Pineapple fruit is produced more than 1.8 million tons/year in Indonesia of which some portion turned into waste as rotten fruit [8]. Core, peel, and crown of pineapple fruit become waste during processing of pineapple fruit in many fruit industries. Moreover, leaves and pseudo-stem of pineapple plant are considered as waste since they are commonly treated through open-air combustion to reduce its volumetric quantity. Therefore, it is estimated that more than 1 million tons of pineapple waste are generated every year.

Physio-chemical characteristics of pineapple waste have been reported in many previous types of research. Peel of the pineapple fruit has contents of 75 – 80% moisture, 35% cellulose, 19,7 hemicellulose, 16% lignin, 4.7% total ash, 0.46% total fat, 23.71% total crude fiber, and 0.33% total proteins [9]. It also contains of 27.08% total carbohydrate, 1.9 mg/kg magnesium, 26.096 mg/kg potassium, and 298.184 mg/kg zinc [10]. Leaf of pineapple plantation which has been decorticated contained 70.98% alpha cellulose, 15.34% hemicellulose, 4.9% lignin, 0.96% fats and waxes, 3.0% pectin matter and 0.95% total ash [11]. Extraction of a crude waste mixture of pineapple parts namely crown, peel and core using two-stage ultrafiltration (75 kiloDaltons (kDa) or 7.5 nm of pore size and 10 kDa membrane filters) showed bromelain enzyme activity of 129.4$\pm$23.0 Casein Digestion Unit (CDU) per ml extract or 76.1$\pm$9.5 CDU/milligram protein [12]. Saccharification of core and peel of pineapple fruit using microwave pretreatment (270 W, 15 minutes) and boiling pretreatment (100℃, 10 minutes) could deliver sugars yield of 35 gram/kilogram fresh waste of peel and 30 gram/kilogram fresh waste of core, respectively. Moreover, pretreatment heat at high pressure with an autoclave (121℃, 205.24 kPa, 30 minutes) could generate higher sugars yield of 60 and 50 gram/kilogram fresh waste of peel and core, respectively [13]. This research was meant to investigate the utilization of pineapple waste namely peel and core of the fruit as well as leaves of pineapple trees as raw material for biohydrogen production. Particularly, it investigated the effect of substrate concentration and concentration of dilute acid pretreatment.

2. Materials and Method

2.1. Feedstock

Peel and core of pineapple fruit were collect from local fruit market in Yogyakarta Province, Indonesia. Leaves of pineapple tree were collect from local farming in the province. Those materials were cut and ground individually to reduce the size in the range of 1-5 mm in diameter, thereafter stored at cold room (5℃, 1 atm) prior to the experimental run, called as feedstock.

2.2. Inoculums

Hydrogen-producing microorganisms were originally from the residual sludge of cows dung biogas plant followed with acidic pretreatment at pH 5.0 for 24 hours and heat-shock treatment (95℃, 45 min).

2.3. Experimental procedures

The experiment was conduct using 120 ml serum vial bottles as a bioreactor. Peel and core of pineapple were subject into dilute acid pretreatment using 0.3 N H_2SO_4 solution at 60℃ for 30 minutes. The solid fraction of pretreated feedstock of peel and core was individually weighted and introduced into bioreactor at 4, 8, and 12 grams, added with 20 ml of inoculums,10 ml buffer solution, and distilled water. The bioreactor was then closed and sealed using butyl rubber stopper and aluminum cap, followed by N_2 gas flushing for 3 minutes. Fermentation was carried out at pH 5.0, 30℃ and 1 atm. Dilute acid pretreatment of pineapple leaves was conducted through submerging of the feedstock at 0.2, 0.3 and 0.4 N of sulfuric acid (H_2SO_4) at 60℃ and 30 minute's exposure time. Thereafter, the solid fraction of the feedstock was subject to the fermentation experiment procedure. Each experiment was conduct in duplicate.

2.4. Analysis
Hydrogen content was analyzed using gas chromatography, which equipped with molecular sieve 5A column and thermal conductivity detector with injection, oven and detector temperatures at 50℃, 80℃, and 80℃, respectively. Helium gas was used as a gas carrier at volumetric flowrate 40 ml/min. Meanwhile, physio-chemical properties namely moisture content, total solid (TS), volatile solid (VS) and ash measured based on the standard method of waste and wastewater analysis according to American Public Health Association (APHA) [14].

3. Results and Discussion
Dark fermentation of organic waste occurs through complex metabolic pathways according to the simplified equation in (3.1) and (3.2) [15]. When glucose is the main substrate, the highest hydrogen yield is 4 mol H_2/mol glucose or equivalent to 498 ml STP H_2/gram glucose theoretically. However, when pineapple waste (peel, core, and leaves) is utilized as a substrate, those materials contain a non-readily fermentable substrate for hydrogen-producing microorganisms to digest and produce hydrogen. It has to be pre-treated to unleashed organo-polymeric structures into fermentable sugars, called as saccharification process. Method to conduct this process was through dilute acid pre-treatment using sulphuric acid (H_2SO_4) at various concentration of 0.2, 0.3, and 0.4 N.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \quad (3.1)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2(CH_2)_3COOH + 2H_2 + 2CO_2 \quad (3.2)$$

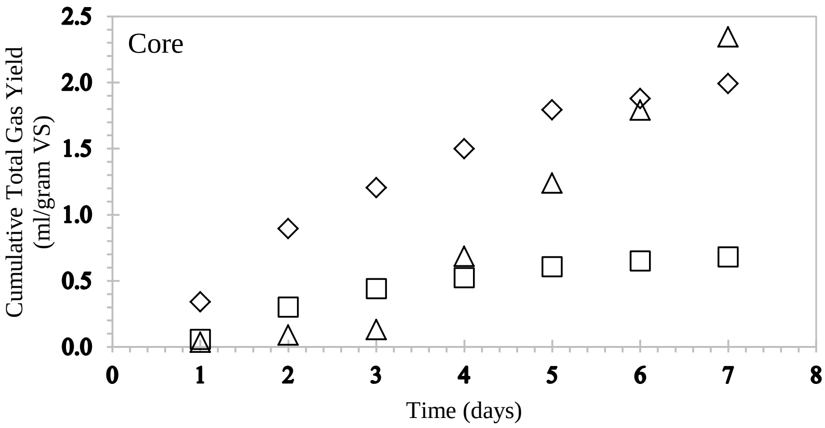

Figure 1. Total gas yield of pineapple fruit core at substrate concentration (□ 8.8 gram VS/liter, ◊ 17.6, Δ 26.4)

Profile of cumulative total gas yield during dark fermentation of pineapple fruit core at a substrate concentration of 8.8, 17.6 and 26.4-gram VS/liter was illustrated in Figure 1. It was noticed that the highest yield was achieved at a substrate concentration of 26.4-gram VS/liter corresponding to a yield of 2.4 ml STP/gram VS. It indicated that the higher concentration of substrate, the higher quantity of the organic compound which can be metabolized to produce more hydrogen. Meanwhile, a lower concentration of substrate of 8.8-gram VS/liter culture produced lower yield due to the limited quantity of carbon source for the microorganism to grow and metabolite.

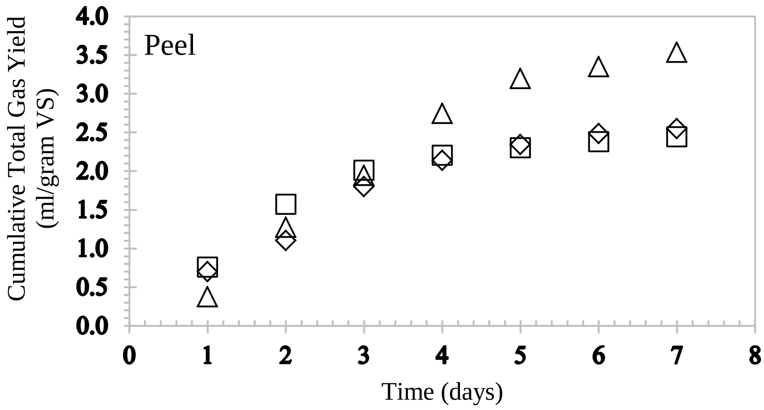

Figure 2. Total gas yield of pineapple fruit peel at substrate concentration (□ 8.8 gram VS/liter, ◊ 17.6, Δ 26.4)

Profile of total gas yield production from fermentation of pineapple peel at substrate concentration 8.8, 17.6 and 26.4-gram VS/liter culture was depicted in figure 2. A similar pattern of the gas production between peel and core was noticed in this experiment. It was demonstrated that the higher substrate concentration, the higher total gas production. Furthermore, the highest yield was also achieved at a substrate concentration of 26.4-gram VS/liter culture with a yield of 3.5 ml STP/gram VS. When higher substrate concentration introduced into fermentation, more bromelain enzymes was also added. It was reported that crude waste mixture of pineapple peel and core contain 129 - 153 CDU/ml extract [16]. Bromelain is proteolytic enzymes which can act as antimicrobial agents toward the majority of the microbial community of bacteria in dark fermentation [17]. In this experiment, the effect of bromelain as antimicrobial agents was not demonstrated as inhibiting agent toward biohydrogen production up to substrate concentration of 26.4-gram VS/liter culture.

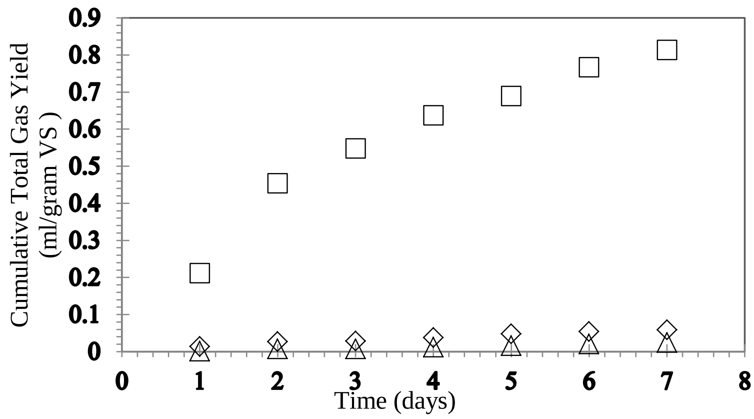

Figure 3. Profile of total gas yield of pineapple leaves fermentation at acid concentration of pre-treatment (□ 0.2 N, ◊ 0.3 N, Δ 0.4 N)

Figure 3 demonstrates profile of total gas yield from the fermentation of pineapple leaves with dilute acid pre-treatment at a various acid (H_2SO_4) concentration of 0.2, 0.3 and 0.4 N. The highest yield was achieved at pre-treatment condition of 0.3 N H_2SO_4 with total gas yield 0.8 ml STP/gram VS. This yield is considered lower compare to the yield from the fermentation of core and peel due to its higher content of cellulose and hemicellulose. It indicated that dilute acid pre-treatment was not able to provide a significant quantity of fermentable sugars from cellulose and hemicellulose to be digested by hydrogen-producing microorganisms. When limited carbon source is introduced into dark fermentation, it affects the effectiveness of microbial metabolism to grow and produce hydrogen properly. It is suggested to improve acid pre-treatment condition for increasing the concentration of fermentable sugars. Analysis of hydrogen percentage of the total gas produced was conducted with results value in the range between 5 to 32% volume ratio of hydrogen.

4. Conclusion

It is possible to produce biohydrogen from pineapple waste (peel, core, and leaf). This method can solve both environmental problems of the waste and generation of renewable energy source. Substrate concentration and acid pre-treatment affect biohydrogen production with the optimum condition at 26.4-gram VS/liter substrate concentration and 0.3 N H_2SO_4 acid pre-treatment. Total gas yield of peel fermentation was higher than that of core corresponding to 3.5 ml STP/gram VS with hydrogen content in the range between 5 to 32 % volume ratio.

Acknowledgment

Authors acknowledge the Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Islam Indonesia for providing financial support.

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