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ORIGINAL ARTICLE

Plasma generation for hydrogen production from banana waste

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Abstract
Agricultural and forestry wastes, which primarily consist of cellulose, hemicellulose, and lignin, are currently being utilized as a significant energy resource. Banana waste is an abundant source of biomass in Indonesia. In this study, through plasma generation in banana waste using pure water, lignocellulose contents were decomposed into various gas products. Pseudo stem and true stem from banana waste were used to compare hydrogen production rates and product gas percentages. The result shows that hydrogen production rate increased up to 49% from 13.30 to 25.93 mmol/s for banana true stem and 11% from 17.43 to 19.66 mmol/s for banana pseudo stem as the initial concentration increased, and the highest hydrogen production rate at 25.93 mmol/s was found from banana pseudo stem at 3 wt% initial concentration. Energy payback ratio varies from a low of 17 to a high of 37% for banana true stem and 25 to 27% for banana pseudo stem. Hydrogen yield and hydrogen selectivity as high as 70.7% and 98.8% were determined when using banana pseudo stem. Hydrogen yield and hydrogen selectivity tend to decrease as the initial concentration increases.

Keywords Banana · Waste · Plasma · Renewable · Energy

1 Introduction

The depletion of fossil fuels along with environmental pollution problems is currently two vital issues that must be dealt with to ensure global sustainable development. In many developed countries, hydrogen is listed in the energy development strategy for the future energy. Among other renewable energy sources, hydrogen is a high-energy fuel (122 MJ/kg), which is three times higher than hydrocarbon fuels [1]. When using hydrogen as a fuel, it only leaves water behind and no traces or residue that would negatively affect the nature or human life [2–4]. Although, the process of producing hydrogen might release emissions and the use of hydrogen in other sectors also contributes significant CO_2. Hydrogen (H_2) as energy carrier is currently primarily derived from natural gas and petroleum, but it also can be economically produced from biomass.

Biomass is an important energy resource and largely available throughout the world. In recent years, there has been an increasing amount of literature on hydrogen production from biomass. Tea waste as an agricultural waste produced hydrogen with a maximum hydrogen yield determined to be 3.55 mol H_2 per kilogram of tea waste at gasification conditions of 850 °C, with a 15-min reaction time and 20 wt% K_2CO_3 catalyst ratios [2]. Other studies have considered hydrogen production from canola meal, wheat straw, and timothy grass using the supercritical water gasification method. It was found that canola meal has a higher hydrogen yield and higher heating value (HHV) because its lignin and ash contents are lower than that of wheat straw and timothy grass [5]. Four types of agricultural waste (corn stalk, rice straw, wheat straw, and peanut shell) were investigated for H_2 production using steam gasification with CaO addition. It has been found that there is a significant relationship between the type of biomass with the H_2 yield, which is also closely related to volatility and carbon content of the biomass material [6].

Agricultural and forestry wastes, which primarily consist of cellulose, hemicellulose, and lignin, are currently being utilized as another significant energy resources. A number of

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studies have examined hydrogen production using biomass models such as chemical cellulose and lignin. In an investigation into the supercritical water gasification method using lignin and cellulose with various catalysts, it was found that the highest hydrogen yield was observed from lignin at 2.86 mmole/g using a K_2CO_3 catalyst [5]. The effect of temperature on hydrogen production from cellulose concluded that the maximum hydrogen yield was 19.02 mmole H_2/g cellulose under hyper-thermophilic temperatures [7]. Hydrogen also could be produced from cellulose through pyrolysis catalytic reforming [8].

Among other tropical fruits, banana is known as the most prominent fruit that consumed worldwide. Due to population growth along with the increase in cultivated area and productivity, there was a higher demand resulting in an increase in banana production. Among the banana-producing countries, Indonesia is included in the top ten countries that accounts for approximately 74.5% of total world banana production [9]. After harvesting banana bunches from trees, a large amount of waste such as leaves, banana stems, and banana peels remains, since the banana plant cannot be harvested again. The high content of cellulose in the banana pseudo stem has been found to have promising potential for many applications [10]. The presence of cellulose, hemicellulose, and lignin was determined by chemical analysis of pseudo stem sheaths. It was found that lignocellulose constitutes about 60–85% on the dry weight of the banana pseudo stem [11]. The banana pseudo stem is composed on average of cellulose 47%, hemicellulose 13%, holocellulose 55%, lignin 13%, ash 8.2%, and extractives 3.05% [12]. Another study reported both banana pseudo stems and fruit bunch stems had a high amount of lignocellulose which is more than 85 wt% of their dry weight along with higher holocellulose, hemicellulose, lignin, and extractive contents and thermal stability of around 150 °C [13]. Production of hydrogen together with methane was reported from banana peels using two-phase anaerobic fermentation [14].

Development of in-liquid plasma application has led to great success in various fields such as nanoparticle production [15, 16], decomposition of clathrate hydrates, [17, 18] methane hydrate [19, 20], coir fiber treatment [21], and hydrogen production from glucose [22] due to the high temperature and high electron density that plasma provides either at atmospheric and higher pressure [23]. Plasma heats the surrounding liquid causing evaporation and generating a plasma-filled bubble [24].

The in-liquid plasma method has been applied to produce hydrogen from a glucose solution and cellulose suspension by 27.12 MHz RF with and without ultrasonic irradiation [22], using a batch-type breakdown device and a funnel-shaped device [25] and using various types of reagents such as H_2SO_4 and NaOH [26]. Other research on the decomposition of cellulose has been conducted using hydrothermal decomposition [27] and thermal decomposition [28]. Most cellulose decompositions are conducted using chemical cellulose powder.

In this study, cellulose is directly decomposed from the banana waste using radio frequency (RF) in-liquid plasma. Two types of biomass sources from the banana plant such as banana pseudo stem and true stem powder were used to compare gas production rates and gas percentages produced from the decomposition of cellulose content in the biomass. Pseudo stem is a part of the banana plant that consists of concentric layers of leaf-petiole sheaths, composed of long fibers, whereas true stem is the inner part of pseudo stem layers.

2 Experiment and procedures

Plasma was generated using a radio-frequency (RF) of 27.12 MHz. A schematic of the experimental set-up used in this work is shown in Fig. 1.

2.1 Schematic diagram of the experimental set-up

Plasma was generated at the tip of an electrode composed of a copper rod 3 mm in diameter enveloped by a glass pipe with an outer diameter of 6 mm and an inner diameter of 4 mm as a dielectric substance and inserted at the bottom of a polycarbonate reactor vessel. The inner and outer diameters of the reactor vessel were 55 mm and 60 mm, respectively. To generate plasma in-liquid, the impedance and input power were adjusted together by a matching box.

Banana pseudo stem and banana true stem were cut into small pieces and air-dried for approximately a week in the sun and then pulverized into a size of about 50 µm. The particle size distribution of banana waste powder was measured by 270 mesh test sieves.

The initial concentrations of banana waste powder solution were prepared at 0.5, 1, and 3 wt%. Eighty milliliters of pure water and banana waste powder were poured into the reactor vessel. The pressure of the reactor vessel was reduced to 0.02 MPa using an aspirator to allow plasma generation. After plasma was stable, aspirator was turned off. Then, in-liquid plasma was generated at an RF input power of 0.2 kW at atmospheric pressure. The power values were calculated by subtraction of the reflected power from the forward power. The reflected power, which can be determined from the monitor of the RF generator, was maintained constant at the lowest value possible. Plasma generation time was varied from 8 to 11 min for 200 ml of gas collection with five replications for each initial concentration.

The gas produced was collected from the top of the reactor vessel using the water displacement method after the pressure reached the atmospheric pressure. The collected gas was then transferred to a sealed glass syringe, and the concentration of

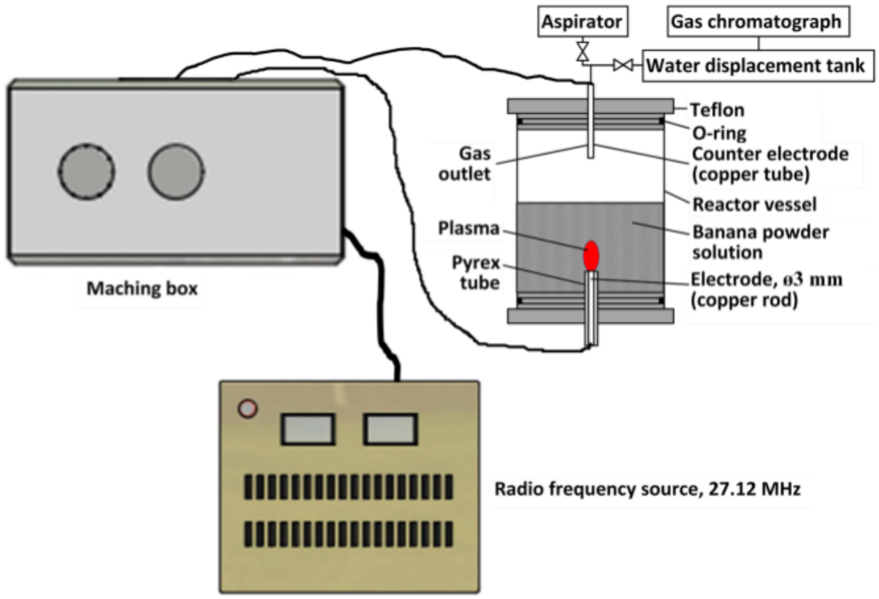

Fig. 1 Experimental apparatus

the product gas was determined by a gas chromatograph (GC-14A Shimadzu). Argon gas was used as the carrier gas with a flow rate of 0.5 ml/s, and the head pressure was 152 kPa.

3 Results and discussion

To determine the hydrogen production rate, the in-liquid plasma treatment of banana wastes was carried out at 0.5%wt, 1%wt, and 3%wt initial concentrations. More initial concentration was difficult to conduct due to the liquid becoming darker, and the plasma generation is difficult to observe. As seen in Fig. 2, the hydrogen production rate increased up to 49% from and 11% for banana true stem and banana pseudo stem with respectively as the

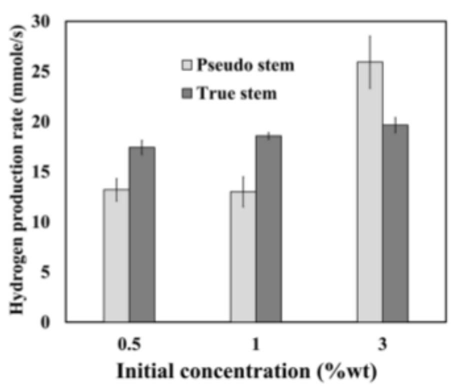

Fig. 2 Hydrogen production rate of banana waste with initial concentration variation. Error bars represent 95% confidence level

initial concentration increased. These results match those observed in previous studies of cellulose decomposition using the in-liquid plasma method with pure water and Na_2SO_4 reagent [26]. The decomposition of water molecule by plasma can produce OH radicals that indirectly decompose lignocellulose content in banana waste. It is assumed that more initial concentration resulted in a probability of lignocellulose content existing near plasma increased. The rate of gas is an average for 20 min after atmospheric pressure is obtained.

At 0.5 wt% and 1 wt% of initial concentration, a higher hydrogen gas production rate was observed for banana true stem; however, at 3 wt%, banana pseudo stem shows higher hydrogen gas production rate. The highest hydrogen production rate at 25.93 mmole/s was found from banana pseudo stem at 3%wt initial concentration. In the previous study, when no biomass addition in pure water was observed using the same apparatus, a 7-mmole/s of hydrogen gas was produced [24]. The hydrogen production rate was increased up to 73% when banana waste was decomposed. Several studies show that the composition of the inner cores of true stem and pseudo stem is quite different. Pseudo stems have higher cellulose and low lignin content than true stem [11, 29, 30]. The proportion of cellulose to lignin is assumed to contribute to hydrogen decomposition from cellulose. Lignin fills the space between cellulose and hemicellulose, and the higher lignin content may make some intra and inter-molecular hydrogen bonds difficult to break.

The energy payback ratio (EPR) of hydrogen was measured based on production rate data. EPR is the ratio of total energy produced during a system, divided by the energy

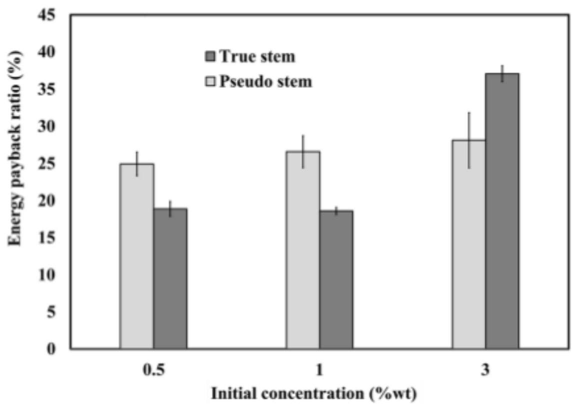

Fig. 3 Energy payback ratio of hydrogen with initial concentration variation. Error bars represent 95% confidence level

required to build it. A high ratio indicates a favorable environmental performance. Calculation of the EPR is shown in the Eq. (1) [26].

$$EPR_{H_2} = \frac{n_{H_2}\ x\ \Delta H_2}{P} x\ 100\% \quad (1)$$

nH_2 is the gas production rate of H_2 (mole/s), ΔHH_2 is the standard heat of combustion of H_2 (kJ/mol), and P is the input power (kW). The EPR H_2 from the decomposition of banana waste by RF in-liquid plasma at variation of initial concentration is shown in Fig. 3. The highest $EPRH_2$ of 37% was obtained at 3 wt% of the banana true stem. From the decomposition of cellulose using radio frequency plasma, 8% of $EPRH_2$ was obtained using 20wt% of cellulose and 1 mol/dm^3 of NaOH reagent [26], while maximum EPR of H_2 of 47% was achieved when hydrogen was produced from n-dedocane using steam reforming in-liquid plasma method [31]. Compared with other fuel, the EPR of coal, fission, wind, and deuterium-tritium fusion electrical power plants are 11%, 16%, 27%, and 23% respectively [32].

The gas percentage of hydrogen (H_2), oxygen (O_2), carbon dioxide (CO_2), methane (CH_4), and also byproducts such as acetylene (C_2H_2) and ethylene (C_2H_4) in banana true stem and banana pseudo stem were detected at a variation of initial concentration using gas chromatography as shown in Table 1.

Higher gas percentages of hydrogen and oxygen were found in banana pseudo stem. Previous studies have shown elemental analyses of banana waste that are in accordance with the result of this study. It was found that pseudo stems have a higher hydrogen content than true stems [13]. However, hydrogen percentage in pseudo stem and true stem was decreased as initial concentration increases, which is described in Table 1.

The H_2 selectivity was calculated following Eq. (2) [33].

$$H_2\ \text{selectivity}\ (\%) = \frac{\text{Moles of } H_2}{\text{Sum of moles of } CO, CO_2, \text{ and } CH_4} \times 100\% \quad (2)$$

In Figs. 4 and 5, the cumulative hydrogen yield and hydrogen selectivity as a function of the initial concentration using banana pseudo stem and banana true stem can be seen. Hydrogen yield and hydrogen selectivity tend to decrease as the initial concentration of increases. The highest hydrogen yield was 70.7% and 67.3% in banana pseudo stem and true stem respectively, while hydrogen selectivity was 98.8% and 96.4% at 0.5wt% initial concentration. These results are comparable with the decomposition of glucose solution using RF in-liquid plasma with and without ultrasonic vibration [25]. Higher initial concentration means there is proportionally less water present. Plasma is generated within bubbles due to the highest temperature at the center of the bubbles, and the decomposition process was indirectly occurred via decomposition of water molecules. It was observed that banana pseudo stem and banana true stem coat the surface of the bubble as the initial concentration increase. It is assumed that this condition will prevent the decomposition of water. If banana waste covered the bubble, there was a lack production of active radical that causes the decomposition of cellulose by water molecule

Table 1 Gas percentage of banana waste with 95% of confidence level

Initial concentration (%wt)	Content of gas						
	H_2	O_2	CO	CH_4	CO_2	C_2H_2	C_2H_4
True stem							
0.5	67 ± 7	27 ± 5	1 ± 0.5	1 +0.3	4 ± 2	0	0
1	60 ± 9	23 ± 4	2 ± 1	0.1 ± 0.2	7 ± 1	9 ± 4	0
3	65 ± 5	13 ± 1	5 ± 2	5 ± 2	12 ± 3	0.3 ± 0.1	0
Pseudo stem							
0.5	71 ± 3	23 ± 1	1 ± 0.8	0.4 ± 0.3	4 ± 3	0	0
1	63 ± 4	27 ± 6	1 ± 0.1	3 ± 2	6 ± 1	0	0
3	65 ± 6	17 ± 3	6 ± 2	1 ± 0.2	12 ± 1	0.005 ± 0.02	0.04 ± 0.03

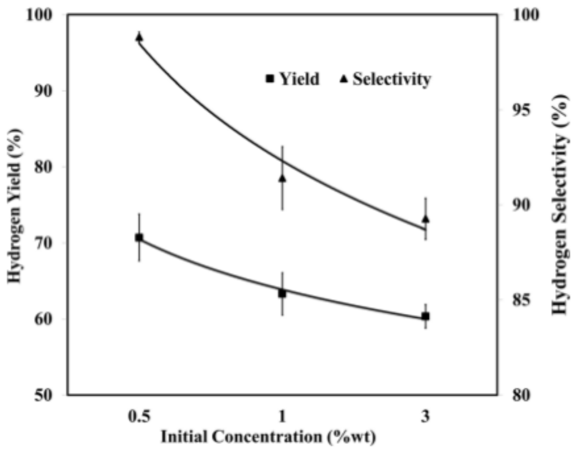

Fig. 4 Hydrogen yield and selectivity of banana pseudo stem with 95% of confidence level

is not maximum resulted in reduced hydrogen formation. Previous study identified that generation of radio frequency plasma in water will produce H_2O_2, which is more specifically produced inside the bubbles surrounding the plasma. The H_2O_2 production amount has an alternation with the OH radical production amount. This has an important effect on the decomposition of organic matter [34].

Comparing with other methods, the significance of this work is to produce hydrogen energy from banana waste by in-liquid plasma method in a short time without using a catalyst. In order to increase the amount of initial concentration and to continue hydrogen production process, further improvement apparatus is needed by circulating the banana waste solution. By using this circulating method, the observation of plasma generation becomes easier. The fermentation method requires 10 days to produce hydrogen yield at 19.02 mmole H_2/g [4], while the gasification method with catalyst from tea waste and cellulose model produces hydrogen yield at 3.55 mol H_2/kg in 15 min and 23 mmole H_2/g in

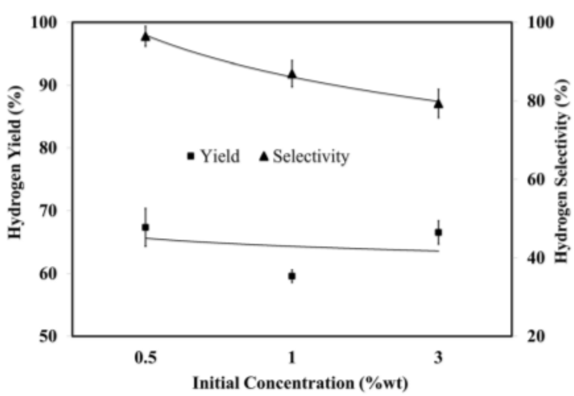

Fig. 5 Hydrogen yield and selectivity of banana true stem with 95% of confidence level

50 min, respectively [2, 5]. However, this method can produce hydrogen yield at 13.20 mmole H_2/g in an average of 12 min.

4 Conclusion

In this paper, the results for hydrogen production from various banana wastes using the in-liquid plasma method have been presented. A comparison of banana waste type on hydrogen gas production rates and gas composition has been investigated using a gas chromatograph. Banana pseudo stem has a higher hydrogen production rate at 3wt% of initial concentration resulting in a higher energy payback ratio. Maximum hydrogen yield and hydrogen selectivity was determined to be 70.7% and 98.8% respectively when using banana pseudo stem at 0.5wt% initial concentration. Finally, the in-liquid plasma method can be considered a promising hydrogen resource from banana waste as a renewable energy source.

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