

Hydrothermal Gasification of Palm Shell Biomass for Synthesis of Hydrogen Fuel

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Production of hydrogen has been widely practiced to produce a CO₂-neutral green fuel that can substitute for fossil fuel. One of the alternative ways in producing such fuel is to utilize biomass by the hydrolysis process. In this study the effects of reaction times (10 to 70 min), reaction temperatures (180 to 260 °C), and biomass to water mass ratio (1:1 to 1:9) were evaluated relative to the hydrolysis of palm shell particles in a low temperature (below 300 °C) hydrolysis process. Palm shell biomass was hydrolyzed in distilled water, and the gaseous products (bio-syn gas) generated were comprised of H₂ and CO₂, with small amounts of carbon monoxide and methane.

Keywords: Hydrolysis; Biomass; Palm shell; Bio-syn gas; Hydrogen

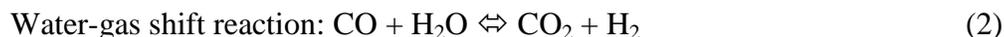
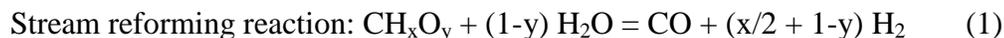
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INTRODUCTION

Non-renewable energy resources such as petroleum-based fuels have become a major concern globally, due to their finite availability and the environmental concern of increased levels of carbon dioxide in the atmosphere. Nowadays, an alternative way has emerged that produces combustible gases by using hydrolysis of biomass in hot compressed water. This approach has the added advantage of being CO₂-free.

Hydrolysis of biomass is a hydrothermal gasification process that is being investigated as an energy recovery from biomass. Hot compressed water (above 200 °C) is used as the reaction medium, whereby it exhibits excellent properties. The dielectric constant of water decreases very strongly, and at this stage it has the properties of a non-polar solvent. All gases and most organic substances dissolve completely in water, making a homogeneous reaction that decreases the mass transfer resistance between phases. This enables a quick and almost complete hydrothermal gasification of biomass into gaseous products with minimum of char formation (TABH 2002; Kruse 2005). The process is suitable for wet biomass with moisture higher than 50 wt% and thus reduces the costs related to energy consumption for drying as a pretreatment of biomass. Biomass consists of the polymers cellulose, hemicellulose, and lignin. In the hydrolysis reaction, biomass is hydrolyzed into intermediate compounds (*i.e.* glucose/fructose). This is followed by production of gaseous products that mainly consist of hydrogen (H₂) and carbon dioxide (CO₂), with small amounts of methane (CH₄) and carbon monoxide (CO). The major interest of this paper is the production of hydrogen gas for energy generation due to its clean and efficient nature as an energy source. Mechanisms can be summarized in terms of the following reactions (Yan *et al.* 2006; Schmieder *et al.* 2000):



Oil palm shell biomass, a residue of palm oil refining, is one of the abundant sources and potential alternatives of biomass in Malaysia, which is considered to be the world's second largest producer and exporter of palm oil after Indonesia. In Malaysia, the palm oil industry generated about 53 million tons of these residues in 2010 and it is increasing annually by 5% (Mohammed *et al.* 2011). With this significant volume of residue generated, it can be converted into high density and high value fuels. The main components of palm shell are cellulose, hemicelluloses, and lignin, with typical elemental proportions of 49.74 wt% carbon, 5.32 wt% hydrogen, 0.08 wt% nitrogen, 44.86 wt% oxygen by difference, and 0.16 wt% sulfur (Abnisa *et al.* 2011). However, the characteristics vary depending on the source of palm shell. Present applications of palm shell include charcoal, activated carbon, direct using for burning, and energy recovery. Nowadays interest in the use of oil palm biomass for energy recovery is increasing.

In fact, hydrogen gas can be produced using biomass. Such hydrogen can be directly used in engines and fuel cells (Balat and Krtay 2010). Ultimately, hydrogen gas as a fuel provides zero carbon emissions. Biomass-derived hydrogen can be regarded as a clean, renewable energy source that could preserve the environment and improve energy security. It is an environmental friendly fuel, with high energy capacity and a low heating value (LHV), which is 2.4, 2.8, and 4 times greater than that of methane, gasoline, and coal, respectively. It produces only water as a by-product of combustion (Khan *et al.* 2010). Besides that, hydrogen can be used in fuel cells for generation of electricity, for transportation, and stationary application. High energy yield (122 kJ/g) makes it more favorable in energy produced application. The consumption of hydrogen contributes 400 to 500 billion Nm³ in current total annually worldwide. The present utilization of hydrogen is equivalent to 3% of the energy consumption, and it has a 5 to 10% growth rate per year. Only a small portion of this hydrogen is used for energy purposes (Balat and Krtay 2010).

In this paper, the main objective is to utilize biomass palm shell as a raw material by producing qualitative bio-syn gases as fuel in hot compressed water. It is crucial to convert biomass palm shell into high density and high value fuels of hydrogen gas by investigating the effect of process variables in the hydrolysis process.

EXPERIMENTAL METHODS

Experimental Set-up

Experiments were conducted using a 1000 mL stainless steel 316 laboratory high pressure autoclave batch reactor, as shown in Fig. 1. It was fabricated to achieve a maximum temperature up to 500 °C and a maximum pressure up to 100 bar, with a pressure sensor that measures the internal pressure of the reactor and Inconel rupture disc 600 that is designed to burst at a pressure of 100 bar. A Bourdon type pressure gauge is mounted on the reactor as well. The reactor was heated by ceramic heater (132 ID x 120

Ht) with a maximum of 2250 W. A 6-blades turbine stirrer with 100 to 1450 RPM rotational speed and 0.1865 kW power rating was used for stirring to allow uniform mixing during the reaction. Heating temperature, stirring power, and set value of pressure can be controlled by a control panel right beside the reactor. At the same time, they can also be controlled by using SCADA software on a computer that is connected to the control panel. A stainless steel thermocouple was fitted into a stainless steel sheath thermowell, which is used to measure the internal temperature of the reactor. The reactor was well equipped with a cooling coil that cools the reactor by circulating water when the reaction is finished. Another cooling water jacket was used in cooling the instruments and fittings of the reactor. The reactor was mounted with two gas charging valves. One gas inlet charging valve was connected with nitrogen for purging action, while another outlet charging valve was used for gas sampling. The gas sampling system was comprised of a stainless steel tube attached at the end of the gas outlet charging. It was connected to a mounted heat exchanger via a solenoid valve that was designed to open when the pressure exceed the set pressure value to vent out excess pressure and close when pressure is below set pressure value. The gas sample was collected at the end of the heat exchanger through a braided hose connected to Tedlar gas sampling bag. Gas samples were analyzed using gas chromatograph 6890N (online) with detector type TCD, 250L. It was equipped with two columns; an HP Plot Q column 1 was used for the analysis of CO₂, and an HP Molsieve 54 column 2 was used for analysis of H₂, N₂, CH₄, and CO. Helium was used as a carrier gas with average velocity of 55 cm/sec. The oven temperature was operated at 40 °C isothermally during analysis.

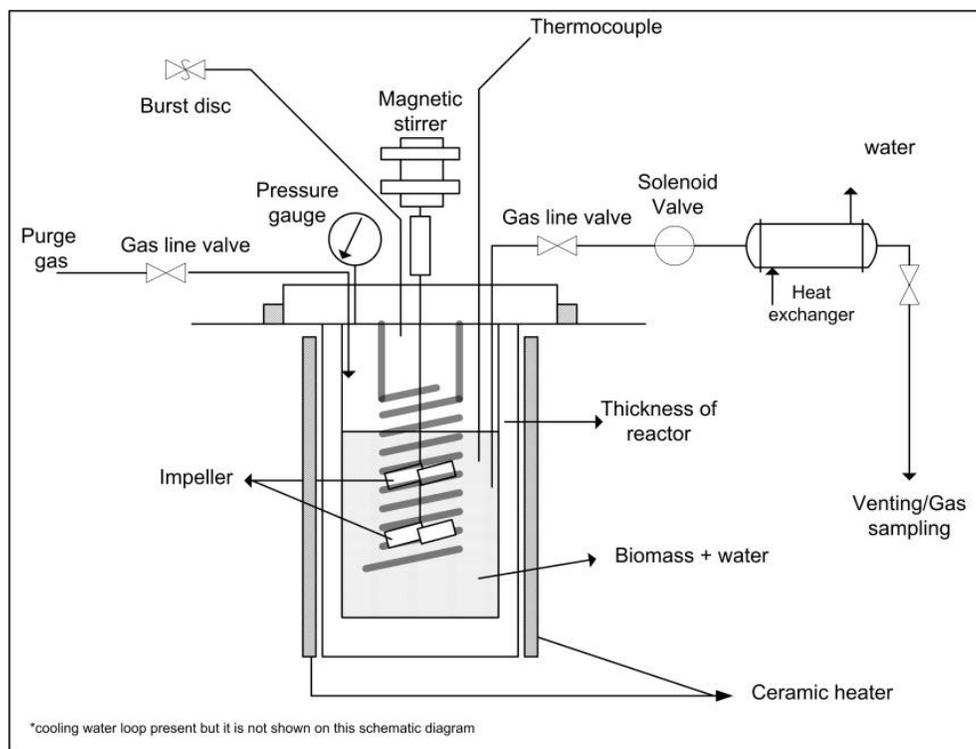


Fig. 1. Schematic diagram of autoclave reactor for hydrolysis of palm shell

Experimental Procedures

Subcritical hydrothermal liquefaction of palm shell was carried out by charging the 1L autoclave reactor at 80 vol% loading. Maximum loading was determined with 800 g of a combination of dried palm shell and distilled water. Nitrogen gas was purged into the reactor for 5 min at a pressure of 3 bar. When the reactor was ready it was clamped properly. It was then pressurized with nitrogen gas up to 10 bar to avoid vaporization of water during heating. After pressurizing, stirring power was set to 400 rpm, and the reactor was heated by setting a preliminary set temperature value in which a 20 °C tolerance was used for the temperature to overshoot to the desired set temperature. Since the reactor was fully sealed, there was an increase of pressure corresponding to the equilibrium pressure at the particular temperature when heating. From the pre-test, the pressure reached nearly 80 bar when temperature reached 270 °C. Therefore, a maximum of 260 °C was set as maximum allowable temperature for safety purposes and giving allowance space for pressure to continue to increase when the reaction was held for certain time period.

Experiments were divided into three parts. The first part of the experiment (A) was conducted to determine the effect of reaction time on gaseous products with constant temperature and biomass to water mass ratio. This was done by using a temperature of 220 °C, a 1:5 biomass to water mass ratio, and a varying residence time from 10 to 70 min. Reaction time represented the reaction time held for the reaction to happen once the reactor was heated to the desired temperature. The second part of experiment (B) involved varying the temperature in the range 180 °C to 260 °C to study the influence of temperature on the yield of gaseous products using the experimental reaction time obtained and biomass to water mass ratio. Finally, further experiments (C) were conducted to study the effect of wet content to the gaseous products yield. This was done by using the experimental reaction time and reaction temperature obtained and changing the biomass to water mass ratio from 1:1 to 1:9.

During the reaction, the cooling loop system for the instruments was opened until the experiment ended. At the end of an experiment, the heating process was stopped and the reactor was cooled with the water coil of the reactor to bring the system down to room temperature. It was advised that a rapid decrease in temperature can minimize the solubilization of gas in the water. Gas product was extracted at 70 °C and collected by using a gas sampling bag. This was to ensure that no water vapor was collected inside the sampling bag and to avoid contamination. Liquid and solid products that remained inside the reactor were collected and stored at the end of the experiment. To validate the data, each experiment was repeated in 3 to 5 replicates, and the average result was taken as the final yield.

Table 1(a). Particle Size Distribution of Palm Shell

Particle size (µm)	Percentages (%)
<500µm	6.1
500<x<1000µm	5.5
1000<x<1400µm	4.8
1400<x<2000µm	8.9
2000<x<2500µm	5.9
x>2500µm	68.8

Table 1 (b). Ultimate Analysis of Malaysian Palm Shell

Composition of palm shell	C (%)	H (%)	N (%)	O (%)
	36.7	4.63	0.49	58.06

RESULTS AND DISCUSSION

Physical and Chemical Properties of Palm shell

Palm shell from a local palm oil mill source was dried in an oven at 105 °C until its mass remained constant. The sample was ground and sieved into various size ranges, where its percentage distribution was as shown in Table 1 (a). From physical observation, grinding produced a major portion of particle size within 4,000 µm to 8,000 µm. It has been reported that particle sizes between 4,000 µm and 10,000 µm are sufficient to overcome heat and mass transfer limitations at a reasonable grinding cost (Akhtar and Saidina 2011). Table 1 (b) shows the ultimate analysis of palm shell. Significant amounts of carbon and hydrogen were found in the sample.

Effect of Residence Time on Synthesis of Bio-Syn Gases

From Fig. 2 it is apparent that the yield of gases increased linearly with reaction time until a certain reaction time was reached. Prolongation of the reaction did not influence the yield of gases. In other words, an increase of time no longer improves the hydrolysis reaction. In fact, some components can only be hydrolyzed at higher temperatures. Therefore, a 50 min reaction time was chosen, a point beyond which prolongation did not affect the gas yield significantly. Similar results reported by Boukis *et al.* (2005) indicate that gasification efficiency increases linearly with reaction time until reaching a particular reaction time in a tubular reactor, and prolongation of the reaction time does not affect the gas yield. Reaction time is crucial to yield the maximum products without prolongation. In fact, prolonged time will increase the cost of heating and lead to undesired reactions. It is expected that during the hydrolysis reaction, decomposition of intermediate products to form gaseous products will compete with dehydration and ring closure to furfural derivatives or phenols, leading to char formation (Kruse *et al.* 2003).

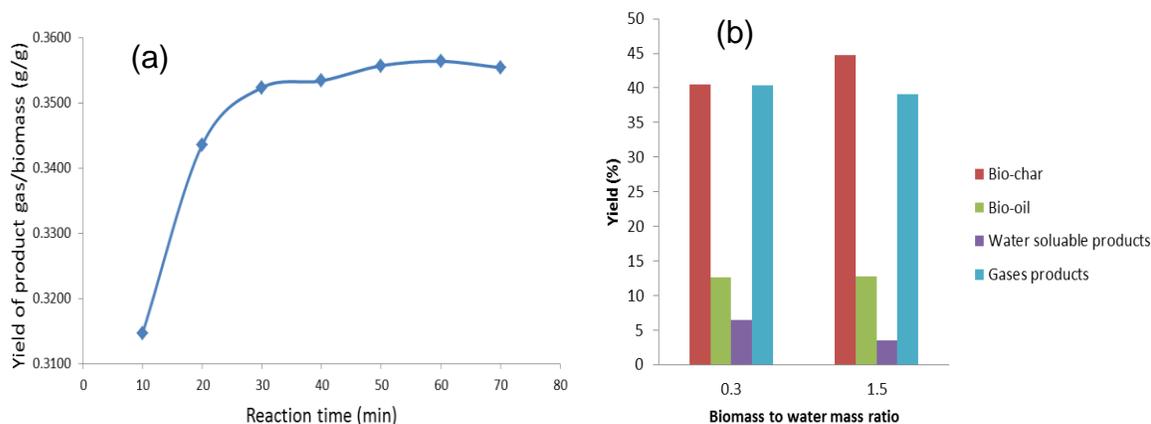


Fig. 2. (a) Yield of product gas/biomass against reaction time at 220 °C and biomass to water mass ratio of 1:5; **(b)** Different productions composition of hydrolysis process at different biomass to water mass ratio with reaction time 60 min and temperature 220 °C

Figure 3 shows that the most abundant gaseous product was CO₂. It increased initially and remained almost constant after 40 min, and the increment may be due to the water gas shift reaction in which CO was converted to CO₂. Gas content of H₂ decreased initially and remained constant after 40 min along with the reaction time. CO and CH₄ were significantly lower compared to other gaseous products. From the result, it was shown that prolonged residence time does not have much effect on the yield of gaseous products. This is quite similar to the result reported by Savage *et al.* (2011), who used lignin as feedstock within a residence time of 0 to 40 min at 600 °C. Results showed increased formation of H₂ and decreased formation of CO, simply due to water gas shift formation. Prolongation of the reaction time did not increase the H₂ yield significantly (Savage *et al.* 2011). Significant changes in gaseous products can be observed when biomass is hydrolyzed near to the supercritical temperature, as it is believed that within the temperature range 200 °C to 250 °C, cellulose was only hydrolyzed to form water-soluble product and a lesser amount of these intermediate products were gasified to gaseous products at low temperature (Azadi *et al.* 2009). Williams and Onwudili (2006) also reported that at the lower temperature below 330 °C, the main reaction is hydrolysis of the biomass to produce water-soluble products.

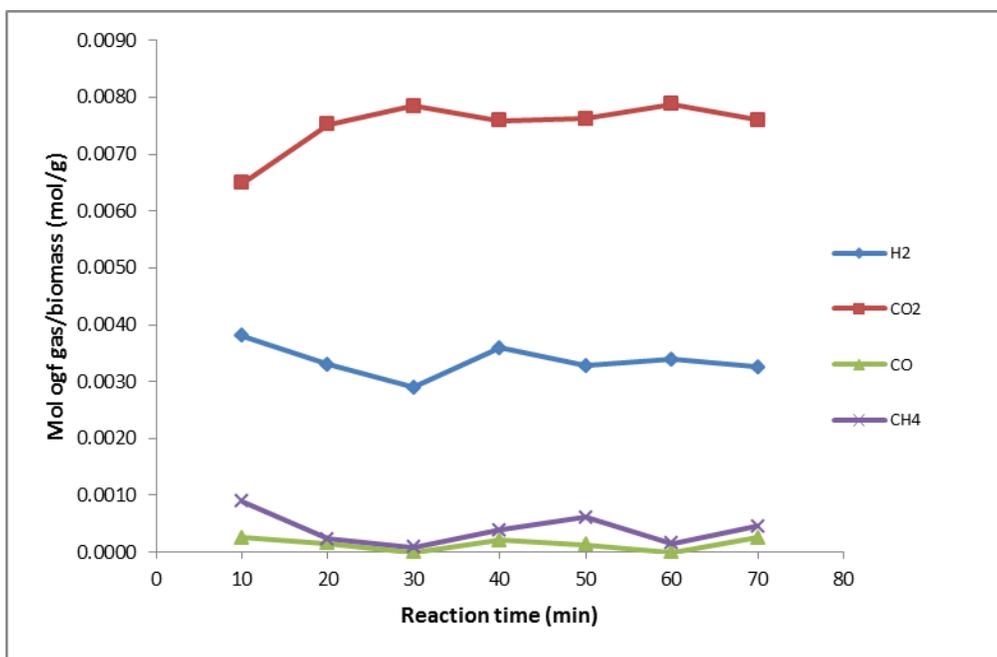


Fig. 3. Molar fraction of gaseous products in relation to time at temperature of 220 °C and biomass to water mass ratio of 1:5

Effect of Reaction Temperature on Synthesis of Bio-Syn Gases

Figure 4 shows that production of gaseous products, H₂, CO₂, CO, and CH₄ were thermodynamically reactive. Higher temperatures lead to higher reaction rates and higher temperatures favor the free radical reaction that generally leads to gas formation. The results show that the production of hydrogen was more favorable when temperature began to increase. This resulted from a water gas shift reaction which is more favored at higher temperature, where CO is converted to H₂ and CO₂.

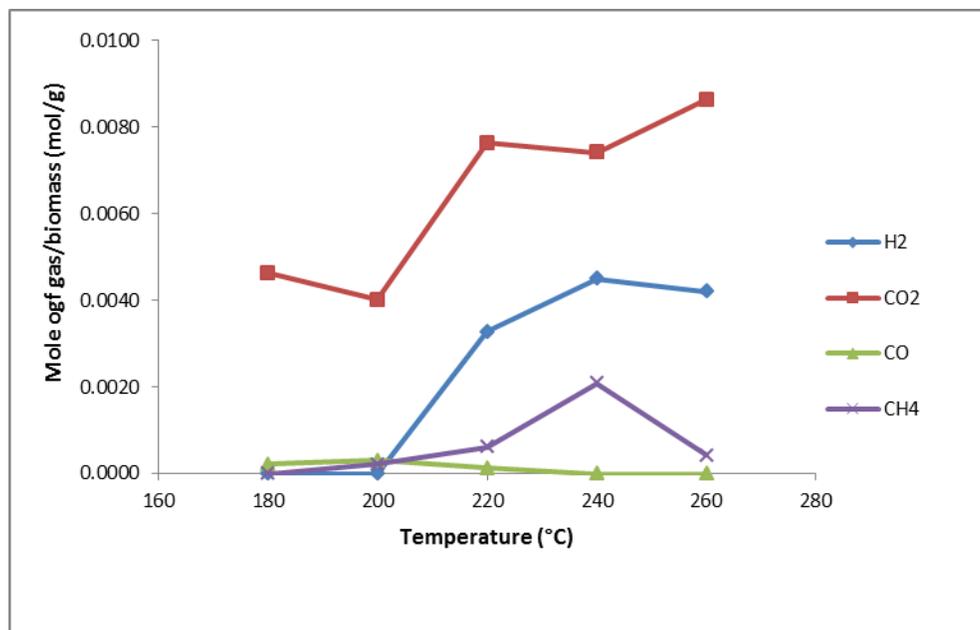


Fig. 4. Mole of gaseous products in relation of temperature at reaction time of 50 min and biomass to water mass ratio of 1:5

A similar trend for CH₄ was observed when higher temperature favored the methanation reaction and the amount of CH₄ increased. However, at the higher temperature of 260 °C, a reverse methanation reaction was observed, leading to an increase of CO₂ while H₂ remained more or less the same. This proved that low temperature hydrolysis did not ensure complete equilibrium reaction, whereas at high temperature a complete equilibrium reaction could occur. The effect of reaction temperature could be further investigated with higher temperature (near or above supercritical temperature), as from the viewpoint of thermodynamics, a higher reaction temperature is crucial for production of gas hydrogen (Guo *et al.* 2010). Under such conditions water is in a supercritical state and it exhibits complete solubilization behavior for organic and inorganic substances (Yusman 2007). Current studies show that hydrothermal gasification with supercritical water gives a promising result, with higher gasification efficiencies and higher yield of gas H₂ (Khan *et al.* 2010). A temperature of 240 °C was selected for the subsequent experiments due to the fact that H₂ remained almost constant and the selectivity of H₂ was higher. A higher amount of CH₄ and a lower amount of CO₂ was also observed at this particular temperature.

Effect of Biomass/Water Mass Ratio on Synthesis of Bio-Syn Gases

Figure 5 shows very clearly that the yield of H₂ increased sharply when there was high water content over the biomass. This followed the Le Chatelier's principle that the formation of 1 mol of H₂ and CO₂ requires 1 mol of H₂O in this reaction, and this reaction was thermodynamically more preferable at high water content (Kruse *et al.* 2003). At low temperature hydrothermal gasification, lower temperature offered a high selectivity towards H₂ in the water gas shift reaction. A similar result was obtained by Hashaikeh *et al.* (2005) in gasification of glucose in hot compressed water, whereby gas production was shifted towards H₂ production at low temperatures instead of CO₂. Besides that, a decrease of CO₂ and an increase of CH₄ were observed, and this may due

to the forward methanation reaction occurring at high water content of biomass. A trend was observed whereby CO increased when biomass was hydrolyzed at higher water content as well, and this may be due to the fact that CO₂ was converted backward into CO in the water gas shift reaction. In investigating the effect of water content of biomass, a high concentration of biomass also leads to a situation where gasification becomes more difficult, resulting in low amounts of gaseous products generated (Guo *et al.* 2010).

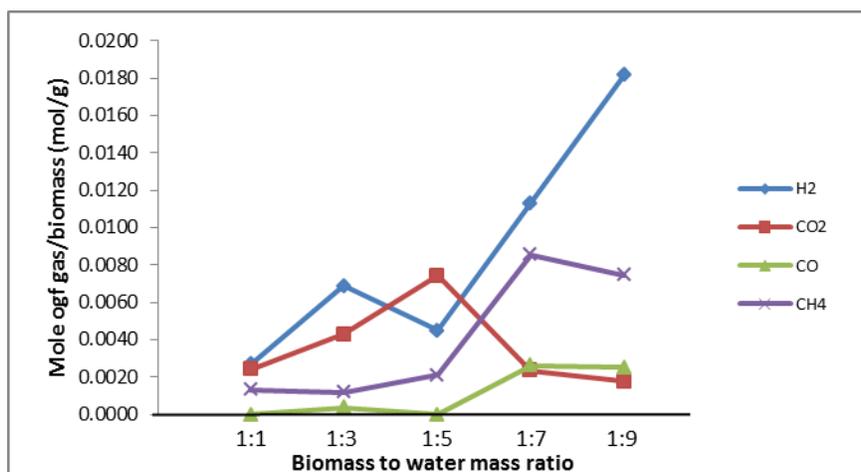


Fig. 5. Mole of gaseous products in relation of biomass to water mass ratio at reaction time of 50 min and temperature 240 °C

CONCLUSIONS

In this study the parameters of residence time, reaction temperature, and biomass to water mass ratio were selected as the process variables that can alter the hydrothermal gasification efficiency and the yield of bio-syn gaseous products. Experiments were conducted to find out the effect of the selected parameters on hydrolysis to produce a significant yield of hydrogen gas. It was shown that bio-syn gas containing H₂, CO₂, CO, and CH₄ can be generated by hydrothermal gasification of palm shell, whereby CO₂ and H₂ are dominant in the bio-syn gas. The results showed maximum conversion of biomass by hydrolysis gasification at an optimum reaction time of 50 min. Production of bio-syn gases was thermodynamically reactive, which was shown by the fact that the gaseous products changed with reaction temperature. Higher temperature was preferable for H₂ production. Hydrogen gas generation was favored when palm shell was hydrolyzed at higher water content and, less gaseous products were generated when a higher concentration of biomass was present. Bio-syn gases composition changed with changes of reaction temperature, which was consistent with the water gas shift reaction and the methanation reaction. Finally, this study provided preliminary research on hydrogen gas production by hydrolysis of palm shell.

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