Investigation on the Effects of Ultrasonic Irradiation and Sodium Hydroxide on Decomposition of Cellulose Using RF Plasma in Liquid for Hydrogen Production at Atmospheric Pressure

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(Received January 26, 2017)

There is an imperative need to explore new technologies for hydrogen energy production without sacrificing life and environment. A 27.12 MHz radio-frequency plasma in liquid was used to decompose cellulose suspension for hydrogen production. The experiment was conducted to investigate the effects of sodium hydroxide and ultrasonic irradiation pretreatment. Molar concentration of sodium hydroxide was varied to 0.001 M, 0.01 M and 0.1 M and ultrasonic irradiation time was varied between 15 and 60 minutes in order to observe the hydrogen production rate and hydrogen yield. Hydrogen production had no significant enhancement at lower than 0.01 M sodium hydroxide. On the other hand, the hydrogen production rate increased dramatically to 23.0 µmol/s at 0.1 M sodium hydroxide. Typical optical emission spectrum of 0.001 M sodium hydroxide solution showed that radical species including OH (281.1 nm), H_{β} (486 nm), H_{α} (656.3 nm) and O (777 and 845 nm) were generated which are very beneficial in attacking and decomposing organic molecules for hydrogen production. The highest production rate was obtained at 30 minutes of pretreatment. A longer than 30 minutes pretreatment with ultrasonic irradiation reduced the hydrogen production rate. Thus, ultrasonic irradiation pretreatment between 15 and 30 minutes was the potential condition for hydrogen production without sacrificing greenhouse gases effect.

Key Words

Ultrasonic irradiation, Sodium hydroxide, Plasma in liquid, Cellulose, Hydrogen

1. Introduction

The continued growth of global energy demand and depending on fossil fuels as primary energy will increasingly cause global green-house effect and pollutants that will cause climate change effect. Thus, there is an imperative need to explore new technologies for energy efficient without sacrificing life and environment. Renewable energies are the fastest growing source of world energy consumption due to number of factors. Estimation of theoretical potential of biomass energy for 2050 shows about 3500 EJ/year energy is available in the world. Conventional pyrolysis and gasification are promising technologies that have been employed for energy recovering from biomass conversion. However, the gas produced from both methods contains tar and char that cause various problems in the follow-up processes. Thus, in recent years, many researchers have been trying to focus on biomass energy conversion assisted by plasma discharge technology for higher temperature and heating rate as well as reducing unwanted tar and char compound.

In our previous study, results showed that hydrogen production rate, yield and purity was greater at 20 wt% for decomposition of glucose solution by RF in-liquid plasma with 29 kHz and 1.6 MHz ultrasonic transducer. The results showed that acoustic streaming effect from 1.6 MHz ultrasonic transducer enhanced the hydrogen production rate while agitation effect from 29 kHz ultrasonic enhanced hydrogen yield and purity.

More recently, applications of ultrasonic irradiation have been widely used as an advanced oxidation process.
Ultrasonic irradiation on aqueous solutions generates high and low pressure waves that cause the formation of micro bubbles and bubble collapse in exposed liquids. This process is called cavitation. Bubble collapse leads to high temperature and pressure and hence, many organic compounds in solutions are degraded by physical and chemical effects. An employing ultrasonic as a pretreatment process has been extensively investigated by many researchers.

Thus, in this study a newly developed radio frequency plasma in liquid with ultrasonic irradiation pretreatment process was employed to decompose cellulose suspension as a model of biomass for sustainable hydrogen energy. Effects of molar concentration of sodium hydroxide and pretreatment with ultrasonic irradiation on hydrogen production rate and hydrogen yield were investigated.

2. Experiment

The experimental apparatus is schematically shown in Fig. 1. Decomposition of cellulose suspension for hydrogen production was conducted using RF plasma in liquid at atmospheric pressure.

An electrode consisting of a 3 mm diameter copper rod enveloped by a glass pipe as a dielectric substance to avoid energy loss was inserted at the bottom of polycarbonate reactor vessel. An aspirator was used to expel the air inside the reactor vessel before plasma discharge. In order to discharge a plasma, the pressure of the reactor vessel was reduced to 0.01-0.02 MPa using an aspirator.

Plasma was discharged at the tip of the electrode instantly after impedance and input power of the 27.12 MHz RF generator was simultaneously adjusted by matching box. The input power was 150 W. The input 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.

Cellulose suspension was mixed with 0.001 M, 0.01 M and 0.1 M of sodium hydroxide. The volume of the solutions were prepared for 120 mL and initial concentration of 20 wt%. Cellulose powder was provided by Wako Chemical Industries, Japan.

The ultrasonic irradiation was used for pretreatment process prior to decomposition of cellulose with RF plasma in liquid. A 29 kHz horn-type ultrasonic transducer was attached at the top of the reactor vessel 26 mm from the tip of the electrode. The input power of the transducer was adjusted to 15 W by using a function generator. During the pretreatment process, irradiation time of ultrasonic was varied between 15 and 60 minutes.

The gas produced was collected from the top of the reactor vessel using a gas-tight glass syringe and the concentration of the produced gas was determined with 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. Temperatures for the column, injection and thermal conductivity detector were 40°C, 50°C and 50°C, respectively.

Plasma emission was diagnosed in situ to observe the active radical species and atoms formation. A multichannel spectral analyzer (Hamamatsu PMA-11) was positioned at the side wall of reactor vessel close to the plasma zone. The scanning wavelength range of the analyzer was 200-900 nm with average values for 5 repetitions over a sampling time of 0.5 seconds.

3. Results and discussions

3.1 Effect of Molar Concentration

The experiment for hydrogen production from cellulose suspension in various molar of sodium hydroxide solvents was carried out at atmospheric pressure plasma in liquid generated by an RF generator.

Fig. 2 shows the production rate of hydrogen produced from decomposition of cellulose suspension in various molar concentration of sodium hydroxide. The gas production rate is calculated from the average the total volume and the time exposed to plasma of the gas produced at certain molar concentration.

The figure obviously demonstrated that no significant increment of hydrogen production rate at lower than 0.01 M sodium hydroxide. On the other hand, the hydrogen production rate increased dramatically to 23.0 µmol/s at
0.1 M sodium hydroxide.

Cellulose is β-(1-4)-linked polymer of D-glucopyranosyl and does not melt before thermal degradation due to strong intra- and intermolecular hydrogen bonding. Decomposition of cellulose suspension in sodium hydroxide using RF plasma in liquid cause swelling of cellulose which increase the internal surface of the cellulose and decreases both the polymerization degree and crystallinity of cellulose. Alkali has a capability to disrupt the structure of cellulose and breaks the linkage \(^\text{17}\). Thus, a higher molar concentration of sodium hydroxide lead to more disruption of cellulose structure and susceptible to be attacked by radical species produced from RF plasma in liquid. Hence, a higher hydrogen production rate was produced as shown in Fig. 2.

### 3.2 Plasma Emission Spectrum

In the field of plasma chemistry, emission spectrum plays an important method for plasma diagnostic. Fig. 3 shows the typical optical emission spectrum of 0.001 M sodium hydroxide solution. The figure shows that radical species including OH (281.1 nm), H\(_\beta\) (486 nm), H\(_\alpha\) (656.3 nm) and O (777 and 845 nm) were generated. OH and H radicals were formed due to the dissociation of water molecules during plasma irradiation process \(^\text{18} - \text{20}\). These radical species are very beneficial in attacking and decomposing organic molecules for hydrogen production \(^\text{21}\). Interestingly, a strong Na-D line was observed due to the decomposition of sodium hydroxide by plasma in liquid, hence emitted strong yellow light \(^\text{22}\). It is believed that OH and H radicals attacked and decomposed cellulose molecules for hydrogen and byproducts gases production.

### 3.3 Effect of Ultrasonic Irradiation

The experiment was continued for investigation on the effect of ultrasonic irradiation pretreatment. Ultrasonic irradiation was employed as a pretreatment method for decomposition of cellulose in sodium hydroxide solvent for hydrogen production. The experiment was conducted at 0.1 M sodium hydroxide of cellulose suspension due to higher hydrogen production rate obtained.

Cellulose suspension was pretreated at 15 W and 25 kHz of ultrasonic irradiation for 15, 30 and 60 minutes prior to decomposition process by plasma in liquid. Fig. 4 shows the hydrogen production rate obtained at those conditions. The figure obviously shows that a longer pretreatment with ultrasonic irradiation reduced the hydrogen production rate. The highest production rate was obtained at 30 minutes of pretreatment. The decreased of hydrogen production rate was correlated with the byproduct gases yield obtained as shown in Fig. 5.

Fig. 5 shows that apart from hydrogen (H\(_2\)), carbon monoxide (CO), methane (CH\(_4\)) and carbon dioxide (CO\(_2\)) were also detected. In addition, oxygen (O\(_2\)), acetylene (C\(_2\)H\(_2\)) and ethylene (C\(_2\)H\(_4\)) were also observed but were neglected due to small amount. Both figures illustrated that pretreatment with ultrasonic irradiation enhanced the hydrogen production rate but potentially reduced byproduct gases yield.
gases at specific irradiation time. When critical irradiation time reached, the byproduct gases production surpassed the hydrogen production.

The effect of ultrasonic irradiation is to decrease intra and intermolecular ordering in cellulose, due to the breakdown of the system of intermolecular hydrogen bonds and to chemical transformation of the polymer. Ultrasonic irradiation in liquid cause the formation and subsequent collapse of bubbles. This phenomena is defined as cavitation. Rapidly collapsing cavitation bubbles induce high pressure gradients and high local velocities of liquid layers in their vicinity resulting in shear forces that are capable of breaking the chains of polymers. Exposure to irradiation of ultrasonic resulted to scission of cellulose macromolecules. This is the mechanochemical action of ultrasound on cellulose. Thus, cellulose molecules were more susceptible to be attacked by the radical species.

Ultrasonic irradiation time has a remarkably influence on the morphology and structures of certain organic compounds. Further increase of the irradiation time would possibly damage the cellulose structure. The damage on organic compounds due to a longer irradiation time has been reported by some researchers. Thus, the increment of byproduct gases yield was presumed due to the degradation of cellulose into a much lower molecular weight fraction and therefore resulted in production of more carbon monoxide, methane and carbon dioxide than hydrogen. Consequently, the hydrogen production rate decreased.

Fig. 6 shows the correlation between hydrogen production rate and byproduct gases rate with and without ultrasonic irradiation pretreatment. The figure illustrated that ultrasonic irradiation pretreatment enhanced hydrogen production and reduced byproduct gas production. Pretreatment between 15 and 30 minutes were the potential conditions for hydrogen production without sacrificing greenhouse gases effect. It was obviously showed that the decrease of hydrogen production at longer ultrasonic irradiation time because of higher production of byproduct gases as previously discussed.

4. Conclusion

In this study, investigation on the effects of sodium hydroxide and ultrasonic irradiation pretreatment on decomposition of cellulose suspension for hydrogen production was carried out. Production of hydrogen had no significant increment at lower than 0.01 M sodium hydroxide. On the other hand, the hydrogen production rate increased dramatically to 23.0 µmol/s at 0.1 M sodium hydroxide. Typical optical emission spectrum of 0.001 M sodium hydroxide solution showed that radical species including OH (281.1 nm), Hβ (486 nm), Hα (656.3 nm) and O (777 and 845 nm) were generated. It is believed that OH and H radicals attacked and decomposed cellulose molecules for hydrogen and byproducts gases production. A longer pretreatment with ultrasonic irradiation reduced the hydrogen production rate. The highest production rate was obtained at 30 minutes of pretreatment. Ultrasonic irradiation enhanced the hydrogen production rate but potentially reduced byproduct gases at specific irradiation time. When critical irradiation time reached, the byproduct gases production surpassed the hydrogen production.
Pretreatment between 15 and 30 minutes were the potential conditions for hydrogen production without sacrificing greenhouse gases effect.

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