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Effect of Pretreatment by Sulfuric Acid on Cellulose Decomposition Using the In-Liquid Plasma Method

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Hydrogen energy is the most promising source of sustainable energy under development. The decomposition of cellulose suspension for hydrogen production by using a 27.12 MHz in-liquid plasma was carried out at atmospheric pressure. Various types of reagents, such as 1 mol/dm³ H₂SO₄, 1 mol/dm³ NaOH and 0.333 mol/dm³ Na₂SO₄, were used and compared as to the rate of gas production. Cellulose dispersed in acid liquids is decomposed indirectly by active radicals by the plasma. The highest hydrogen production rate was obtained by employing 1 mol/dm³ NaOH. The gasification rate of cellulose suspension was determined from the increase of C atoms in the product gas. When 1 mol/dm³ NaOH was used, the rate was 7 times greater than that for pure water. It was found that carbon atoms in the product gas is indicative of the decomposition rate of the cellulose suspension.

水素エネルギーは、最も有望で持続可能な発展途中のエネルギーである。27.12 MHz の液中プラズマを用いたセルロース懸濁液の分解が大気圧下で行われた。1 mol/dm³ H₂SO₄, 1 mol/dm³ NaOH, 0.333 mol/dm³ Na₂SO₄ が溶媒として使用され、気体生成速度の比較を行った。酸の溶液の中に分散したセルロースはプラズマによる活性種によって、間接的に分解される。1 mol/dm³ NaOH を用いたとき、もっとも高い水素生成速度が得られた。セルロース懸濁液の気体化の速度は、生成した気体に含まれている炭素原子の増加によって決められる。1 mol/dm³ NaOH を用いたとき、気体生成速度は純水の7倍であった。生成気体に含まれる炭素原子の数はセルロース懸濁液の分解速度を示すものである。

Key Words

Hydrogen, Radio-frequency, In-liquid plasma, Cellulose, Acid

1. Introduction

Currently many researchers are working to develop clean and renewable alternative energy sources due to the reduction of fossil fuels reserves, the serious damage from greenhouse gases (GHGs) and the rapid growing of worldwide energy needs¹⁾. Hydrogen energy is the most promising energy carrier for sustainable development. The dominant benefits of hydrogen as an alternative energy carrier consist of reduction of global greenhouse gas emission, reduction of urban air pollutants, security

of energy supply through the diversification of energy production and increase in the efficiency of hydrogen fuel cell technology²⁾. If hydrogen energy is to be considered as the clean energy source for the future, a novel generation technology will be necessary to meet the increase in demand.

Biomass is the first- fuel ever used by humankind and one of the most abundant renewable resources in the world contributing about 10 to 15% of today's world energy demand³⁾. Biomass is versatile fuel that can be the source of biogas, liquid fuels and electricity. Biomass energy is carbon neutral in that it is derived from plants, a stored source of solar energy in the form of chemical energy through the process of photosynthesis⁴⁾. It can be released when the chemical bonds between adjacent carbon, hydrogen and oxygen molecules are broken by various thermochemical and biological energy conversion processes⁵⁾.

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The conversion of plant material into a suitable form of energy, for instance, electricity or fuel can be achieved using a number of various routes⁶⁾. Pyrolysis and gasification of renewable biomass energy have been found to be the most favorable thermo-chemical conversion processes for hydrogen production⁷⁾. It was found that conventional pyrolysis and gasification produces not only useful fuel gases, char and chemicals but also byproducts such as fly ash, NO_x, SO₂ and tar⁸⁾. This leads to severe operational problems such as clogging and blockage in fuel lines, filters and engines when the tar in the product gases condenses at low temperatures. Hence, the investigation of new processes that can reduce the production of tar is of utmost importance.

Plasma is a clean technique that has great application potential for treating various types of hazardous wastes⁹⁾. It is a more or less ionized produced gas mainly by electric fields, which consist of a mixture electrons, ions, neutral particles and so on¹⁰⁾. Plasma enhances chemical reaction rates¹¹⁾ since in plasma it is possible to instantaneously form strong radical species such as H, O, OH, HO₂, etc¹²⁾. The formation of UV radiation in plasma discharge also has been suggested to be a cause of effective degradation¹³⁾. Among the plasma discharge processes, radio-frequency (RF) plasma in liquid has great potential, but until recently has received little attention for biomass conversion. With this method, the low liquid temperatures and high molecular density of liquid in comparison to those of gases provide great appeal for application in low-temperature environments and to generate higher reaction rates^{14) 15)}. The electron temperature of RF in-liquid plasma is estimated to be in the range between 3300 and 4800 K¹⁶⁾. Since cellulose, one of the basic constituents in biomass, is nonvolatile, it cannot enter the bubbles containing plasma. With the application of in-liquid plasma, the cellulose is not directly decomposed by the plasma, but rather is decomposed indirectly by the active radicals created by the plasma¹⁷⁾.

The purpose of this research is to convert cellulose in electrolyte solution into hydrogen gas by using RF in-liquid plasma. The conductivity of solutions is important parameter for in-liquid plasma. The size of plasma increases with conductivity because it leads to a reduction of RF power loss in water. The decomposition efficiency of the organic matter by in-liquid plasma changes depending on the conductivity of solutions¹⁸⁾. Some electrolytic solutions such as 1 mol/dm³ NaOH containing many OH⁻ ions, 1 mol/dm³ H₂SO₄ containing many H⁺ ions, and 0.333 mol/dm³ Na₂SO₄ containing many Na⁺ ions and SO₄²⁻ ions were used as the solvents of cellulose to promote the

reaction for cellulose decomposition.

2. Experimental and procedures

A schematic diagram of apparatus for decomposition of a cellulose suspension is shown in Fig. 1. A 3.0 mm diameter copper electrode was inserted vertically from the bottom of reactor. An aluminum tube, used as a dielectric substance to avoid energy loss, enveloped the electrode. A counter electrode was attached to the top of the reactor and fixed at 26.0 mm from the tip of the copper electrode.

The experimental procedures were as follows. Initially, the pressure of the reactor was reduced to 0.01-0.02 MPa using an aspirator. In this condition, power input from a 27.12 MHz radio-frequency (RF) generator and impedance were simultaneously adjusted by a matching box. Plasma was discharged at the tip of electrode instantly after electric breakdown. The discharge power was 150 W and the AC voltage was 200 V, as calculated by subtraction of the reflected power from the input power.

In this experiment, the three solutions used as a reagent were 1 mol/dm³ H₂SO₄, 1 mol/dm³ NaOH and 0.333 mol/dm³ Na₂SO₄. Pure water was used as a control reagent. These reagents were used to enhance the gas production rate from decomposition of cellulose suspension by RF in-liquid plasma. Cellulose powder passed through a 38.0 μm mesh (catalogue number 034-22221) provided by Wako Pure Chemical Industries, Japan was employed as the source material. The experiments were performed at initial cellulose contents of 0.5, 10.0 and 20.0 wt%.

The pressure increased due to the gas generation and reached atmospheric pressure. Then the produced gas was drawn out of the apparatus by an air-tight glass syringe. The gas production rate was measured at one

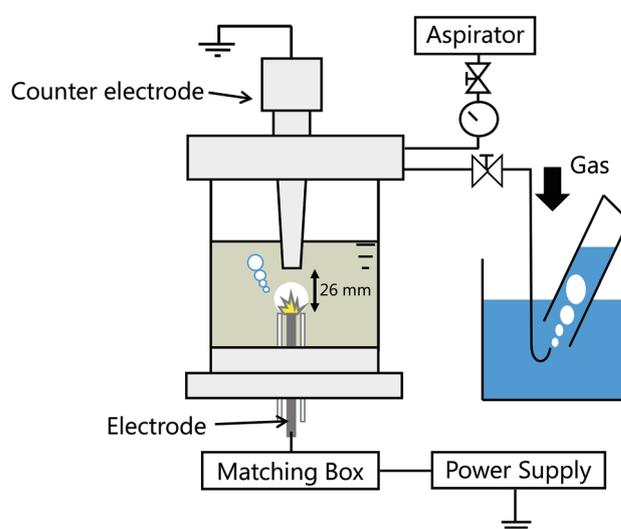


Fig. 1 Experimental set-up

minute intervals. Then, the produced gas was analyzed using a gas chromatograph (GC-8A Shimadzu). Argon was used as the carrier gas.

3. Results and discussion

As a preliminary study, gas production from a cellulose suspension decomposed by RF in-liquid plasma using $0.333 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ reagent was compared to that employing pure water. As shown in Fig. 2, with $0.333 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ the gas production rate was increased by a maximum of 5 times in comparison to that using pure water at an initial cellulose content of 20.0 wt%. The decomposition of cellulose will not occur directly by the plasma, because cellulose is nonvolatile. OH radicals are produced in the plasma via the decomposition of water molecules¹⁸⁾. It is assumed that OH radicals decompose cellulose by strong oxidation power. When pure water was used and the content of cellulose was 10.0 wt%, the gas production rate was found to be lower than when 0.5 wt% of cellulose was used. It is thought that the cellulose might act to prevent the decomposition of water. The evaporated water is fed into the plasma, and decomposed by the plasma. The amount of the evaporation is reduced by the cellulose covering the surface of the bubble, and thus the production rate decreases with an increase of the cellulose concentration¹⁷⁾. When the content of cellulose was 20.0 wt%, it is assumed that the decomposition of cellulose occurred easily due to probability of cellulose existing near plasma increased. When $0.333 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ is used as a reagent, the gas production rate increased as the initial cellulose content increases. The conductivity of $0.333 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ is higher than pure water and RF power loss is low. So, plasma was generated efficiently.

The experiment was then conducted at an initial

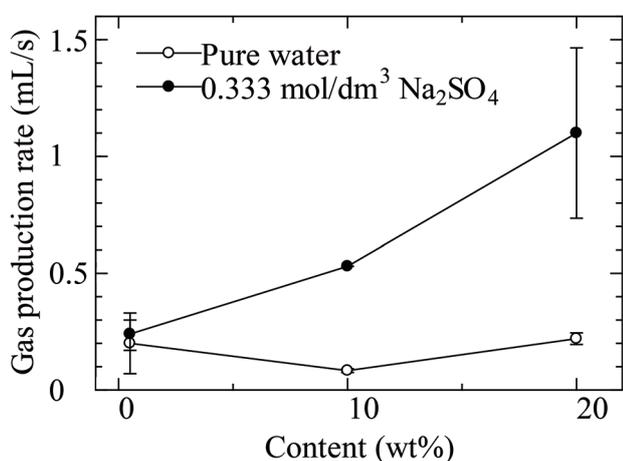


Fig. 2 Gas production rate by cellulose content

cellulose content of 20.0 wt% employing various types of reagents. Fig. 3 shows the rate of produced gas from decomposition of cellulose suspensions at an initial cellulose content of 20.0 wt% employing pure water, $0.333 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$, $1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ and $1 \text{ mol/dm}^3 \text{ NaOH}$ as reagents. As can be seen in figure, employing reagents for cellulose decomposition enhanced the gas production rate compared to pure water. The effects of $1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ and $0.333 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ reagents on gas production rate are less significant in comparison to $1 \text{ mol/dm}^3 \text{ NaOH}$ reagent. However, when $1 \text{ mol/dm}^3 \text{ NaOH}$ reagent was used, the gas production rate dropped over time. Decomposition using $1 \text{ mol/dm}^3 \text{ NaOH}$ as a reagent had a significant effect on the gas production rate. Here, since the $0.333 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ was used in present study, if molar concentration increases, the gas production rate may be enhanced. The molarity of solutions is a topic of future discussion.

The gas production rates from decomposition of cellulose suspensions by RF in-liquid plasma in various types of reagents at an initial cellulose content of 20.0 wt% are shown in Fig. 4. The rate of gas is an average for 20.0 min after atmospheric pressure is obtained. By using $1 \text{ mol/dm}^3 \text{ NaOH}$ as a reagent, the hydrogen production rate was 6 times as high as that of pure water.

$0.333 \text{ mol/dm}^3 \text{ Na}_2\text{SO}_4$ and $1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ reagents were 4 times as high as that of pure water. However, utilization of reagents for the decomposition of cellulose suspension leads to formation of some unwanted byproducts such as carbon monoxide (CO) and carbon dioxide (CO_2). The amount of methane (CH_4) and acetylene (C_2H_2) produced can be neglected due to their too small amounts.

EPR (energy payback ratio) was measured in order to define economical production of H_2 . Equation (1) shows

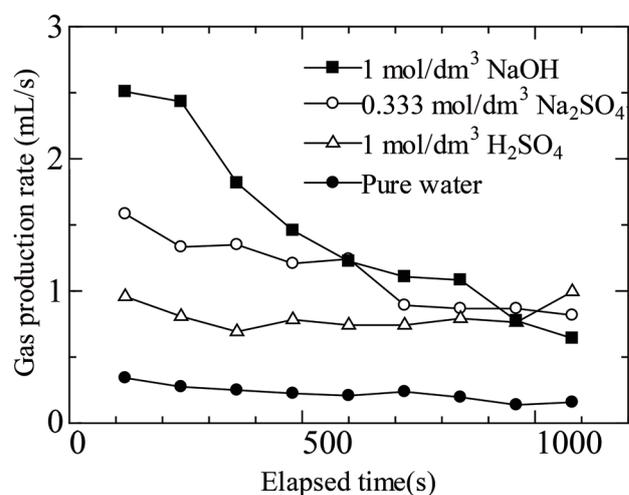


Fig. 3 Gas production rate for each solvent at an initial cellulose content of 20 wt%

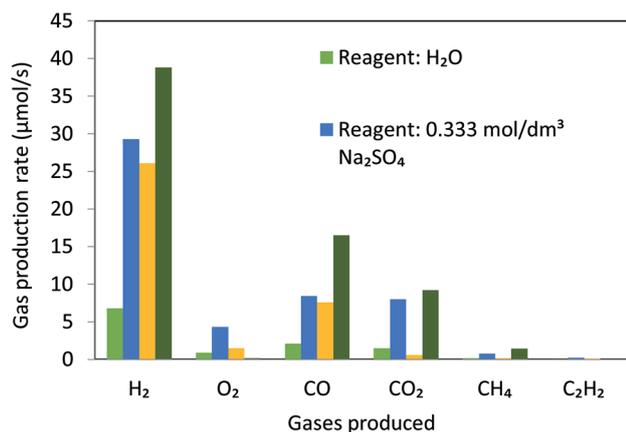


Fig. 4 Gas production rate at an initial cellulose content of 20 wt%. The rate of gas is an average for 20 min after atmospheric pressure is obtained

the calculation of EPR:

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

n_{H_2} is the gas production rate of H₂ (mol/s), ΔH_{H_2} is the standard heat of combustion of H₂ (J/mol), and P is the input power (W). The rate of gas is an average for 20 min after atmospheric pressure is obtained. The EPR_{H_2} from decomposition of cellulose suspensions by RF in-liquid plasma in various types of reagents at an initial cellulose content of 20 wt% is shown in Fig. 5. The highest EPR_{H_2} was obtained when using 1 mol/dm³ NaOH, then decreased in the order, 0.333 mol/dm³ Na₂SO₄, 1 mol/dm³ H₂SO₄, with the lowest case being pure water.

A well-known property of cellulose is that, by itself, it is insoluble in water due to the multiplicity and strength of the hydrogen bonds formed between cellulose chains in fibrils. It is these intra- and intermolecular hydrogen bonds that make cellulose insoluble in water. By using NaOH, He *et al.* proved that NaOH was capable of breaking some intra- and intermolecular hydrogen bonds through complex reaction¹⁹. Thus it was expected that using 1 mol/dm³ NaOH would lead to the degradation of cellulose and make cellulose more susceptible to be attacked by radical species produced from RF in-liquid plasma compared to using 1 mol/dm³ H₂SO₄ and 0.333 mol/dm³ Na₂SO₄. The radical species produced by RF in-liquid plasma includes OH, H and O atoms^{20,21}.

In order to determine the degree of decomposition of cellulose suspension, the carbon gasification rate were measured. The rate is an average for 20.0 min after atmospheric pressure is obtained. The carbon gasification was determined by the total number of C atoms produced as carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄) and acetylene (C₂H₂). Fig. 6 shows the carbon

gasification rate through the decomposition process of cellulose in pure water, 0.333 mol/dm³ Na₂SO₄, 1 mol/dm³ H₂SO₄ and 1 mol/dm³ NaOH reagents. The amount of C atoms produced during decomposition of cellulose suspension using 1 mol/dm³ NaOH reagent was 7 times higher than that of pure water alone. The rates for 0.333 mol/dm³ Na₂SO₄ and 1 mol/dm³ H₂SO₄ reagents were only 4.5 times and 2.3 times higher than that of pure water, respectively. This shows that carbon gasification rate of cellulose suspension in 1 mol/dm³ NaOH reagent is higher than the others. Fig. 7 shows the relationship between the hydrogen production rate and the quantity of carbon atom in the product gas. The hydrogen production rate tends to rise as the quantity of carbon atoms in the product gas rise. This result suggests that a greater amount of hydrogen can be obtained by the gasification of cellulose with in-liquid plasma.

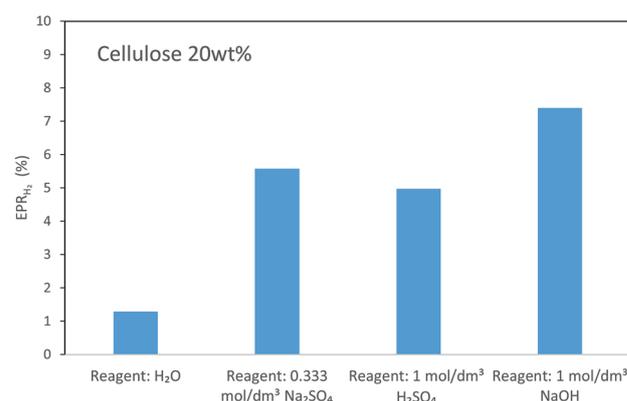


Fig. 5 EPR_{H₂} at an initial cellulose content of 20 wt%. The rate of gas is an average for 20min after atmospheric pressure is obtained

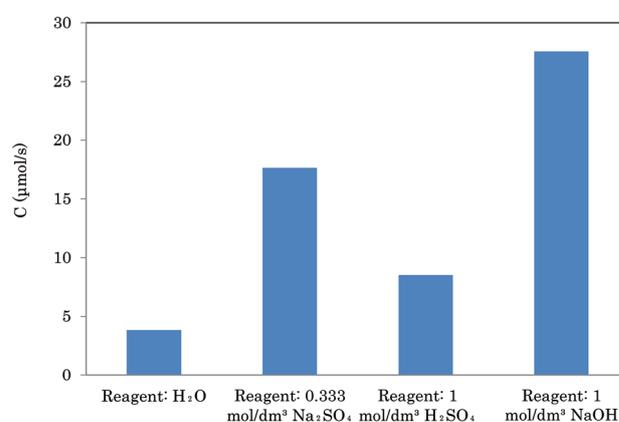


Fig. 6 Carbon gasification rate at an initial cellulose content of 20 wt%. The carbon gasification rate is an average for 20min after atmospheric pressure is obtained

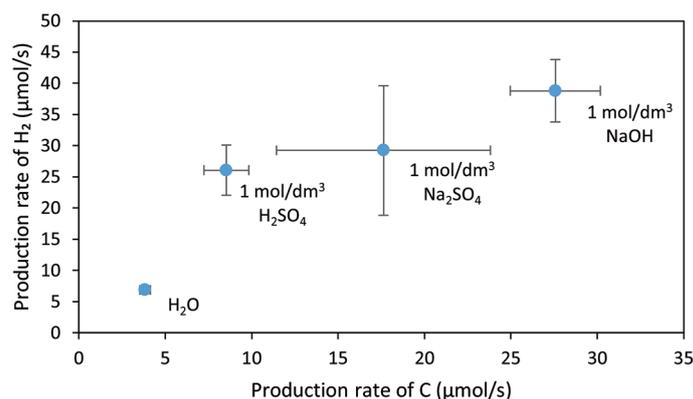


Fig. 7 The relationship between the hydrogen production rate and the quantity of carbon atom in the product gas. Here, the error bar shows all experimental data

4. Conclusion

Decomposition of cellulose suspension in liquids, such as 1 mol/dm³ NaOH, 1 mol/dm³ H₂SO₄, 0.333 mol/dm³ Na₂SO₄ and pure water, was carried out using 27.12 MHz in-liquid plasma and the gas production rates were measured. When 0.333 mol/dm³ Na₂SO₄ is employed, the gas production rate by in-liquid plasma was enhanced as the initial cellulose content was increased. The highest hydrogen production rate was obtained when using 1 mol/dm³ NaOH, then decreased in the order, 0.333 mol/dm³ Na₂SO₄, 1 mol/dm³ H₂SO₄, with the lowest case being pure water. The hydrogen production rate from 1 mol/dm³ NaOH was increased by 7 times over that from pure water. The highest EPR_{H_2} was obtained when using 1 mol/dm³ NaOH, then decreased in the order, 0.333 mol/dm³ Na₂SO₄, 1 mol/dm³ H₂SO₄, with the lowest case being pure water. The hydrogen production rate tends to rise as the quantity of carbon atoms in the product gas rise.

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