Doctoral Thesis

Hydrogen Energy Production from Biomass-derived Polysaccharides using Radio Frequency In-Liquid Plasma

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September 2016

Acknowledgement

There a number of people who give their support and contributions throughout this long and arduous process of earning a doctorate and writing a dissertation which is certainly not done singlehandedly.

Praise to Allah SWT, The Almighty with His willing and guidance for establishing me to complete my PhD study. Boundless love and special appreciation to my beloved mother, Hjh Nelly Zulyati Binti Jais and father, Hj. Syahrial Bin Rusli for their infinite guidance, pray and support in my life. I am privileged for having my beloved wife, Syafrah Binti Shukri, who is always by my side, loving, encouraging and keep patient during this endeavor.

I would like to express my deep gratitude and sincere appreciation to my supervisor, Professor Dr. Shinfuku Nomura who expertly guided me through my PhD journey and who shared the knowledges of three years discovery. I also would like to express my thanks to my second and third

supervisor, Professor Dr. Hiromichi Toyota and Professor Dr. Nakahara, respectively for providing advices throughout my PhD journey. Special thanks to Senior Assistant Professor Dr. Shinobu Mukasa for his great support and patience at all times.

This acknowledgement would not be complete without mentioning my research colleagues, Kei Okamoto and Kazuyuki Tange. It was a great pleasure working with them. Their excellence ideas and help are really appreciated. Special thanks to all the Heat and Mass Transfer Laboratory members as well. Further, I would like thank to all Malaysian community in Ehime for their great moral supports.

Finally, I would like to acknowledge the financial, academic and technical support of Universiti Teknikal Malaysia Melaka, Ministry of Higher Education of Malaysia and the staffs, particularly in the award of a Skim Latihan Akademik IPTA that provided necessary financial support for me and family during the study.

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Chapter 1

General Introduction

1.1 Background Study

Plasma is a partially or fully ionized gas consisting of electrons, free radicals, ions and neutrons [1]. Plasma are generated by supplying energy to a neutral gas causing the formation of charge carriers [2]. Traditionally, plasma chemical systems are categorized in two major types: thermal and non-thermal plasma, in terms of electronic density or temperature [3]. Thermal plasma is associated with sufficient energy and temperature at high operating pressure to allow plasma constituents to be in thermal equilibrium. This type of plasma is found, for example, in plasma arcs and radio frequency inductively coupled plasma discharges. Non-thermal plasma is characterized by lower pressures, less power use and operating at effectively low temperature. Glow, radio frequency and microwave plasma are found in non-thermal plasma.

Plasma is generally generated within a gas. However, the application of strong electric fields in liquid has been studied for many years due to its importance in electrical transmission processes and its practical applications in biology, chemistry and electrochemistry [4]. Recently, much attention has been given to liquid-phase electrical discharges for wastewater treatment and carbon nanotubes as well as for environmentally benign chemical processes.

Electrical discharge observed in liquids are initiated in the gas phase-in bubbles that are either formed due to local heating of liquid or other mechanism [5] or are directly injected into liquid [6]. Based on the plasma distribution, electrical discharges above liquid surface, direct electrical liquid discharges and discharges in bubbles/vapor in liquids are the three main groups of electrical discharges with liquid [4].

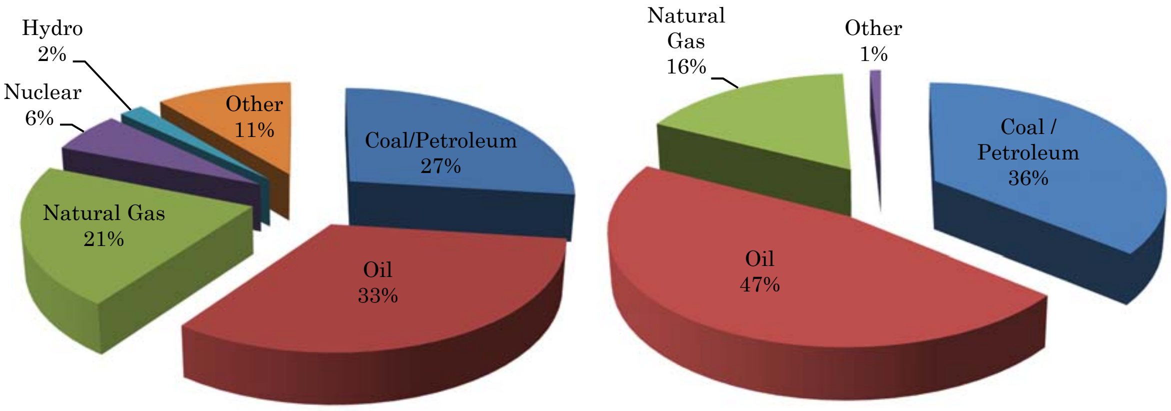
Non thermal atmospheric pressure plasma in liquid has been extensively investigated due to their low temperature properties, controllability of various agents such as radicals, ions, UV and electric field and offers high selectivity and energy efficiency in plasma reactions [7], [8]. Therefore, plasma discharges in liquid have been received a lot of attention in various fields. Synthesis of artificial diamond [9], carbon nanotube [10], nanoparticle [11], water treatment [12], medical application [13] and surface modification [14] are those applications that have been widely investigated. In addition plasma discharge for renewable energy is an emerging field leading for sustainable future development [15].

Plasma in-liquid is generated by applying direct voltage or high frequency voltage to a submerged electrode [16]. Plasma in liquid generation is depended on the electrode configuration and power sources. Nomura et al. have demonstrated the ignition of stable plasma in a liquid hydrocarbon exposed to a combination of ultrasonic waves and microwave radiation [17]. Plasma is generated inside bubbles or around the bubble boundary in the liquid [18]. The temperature of plasma in water is estimated to be 4000 – 4500 K [19]. Moreover, the formation of OH and H radicals via dissociation, ionization and vibrational/rotational excitation of water by electrical discharge leads to the plasma oxidation [20].

1.2 Problem Statement

It is widely acknowledged that dependence on fossil fuels as the main energy source led to global energy crisis and environmental problems, that is fossil fuels depletion and pollutant emission [21]. Some researchers predict that the global consumption of energy will triple in the next thirty years [22]. The impact to the environment will be significant if fossil fuels still be used as the main energy at high rates. **Fig. 1.1** presents world's primary energy supply and the resulting carbon dioxide (CO_2) emission shares by energy source.

Fossil fuels deposits are limited, either physically or economically. Thus, it is considered that fossil fuels are finite and non-renewable natural resources. Fossil fuels are created over millions of year correspondently due to the accumulation and transformation of organic debris in a specialized environment deposition. As originating from simple fact that fossil fuels take millions of years to accumulate, it is impossible for the rate of creation to keep up with the rapid rate of extraction. Generally, if the rate of extraction is faster than rate of replenishment the resource will ultimately be depleted [23].



(a) (b)

Fig. 1.1 World's total primary energy source (a) and CO_2 emissions by energy source (b) in 2010 [24]

Fossil fuels will remain as the backbone of the world's energy supply. Furthermore, global dependence on fossil energy will result about an associated problem, namely associated emissions. Approximately 70% of all anthropogenic greenhouse gas (GHG) emissions derive from the energy sector as shown in **Fig. 1.2** [25]. Combustion of fossil fuels plays as the key factor to the build-up of CO_2 in the atmosphere and hence, contributes to the greenhouse effect, likely increase in global average temperature [26]. The concentration of CO_2 in the atmosphere has increased from approximately 277 parts per million (ppm) in 1750 to 395.31 ppm in 2013 [27].

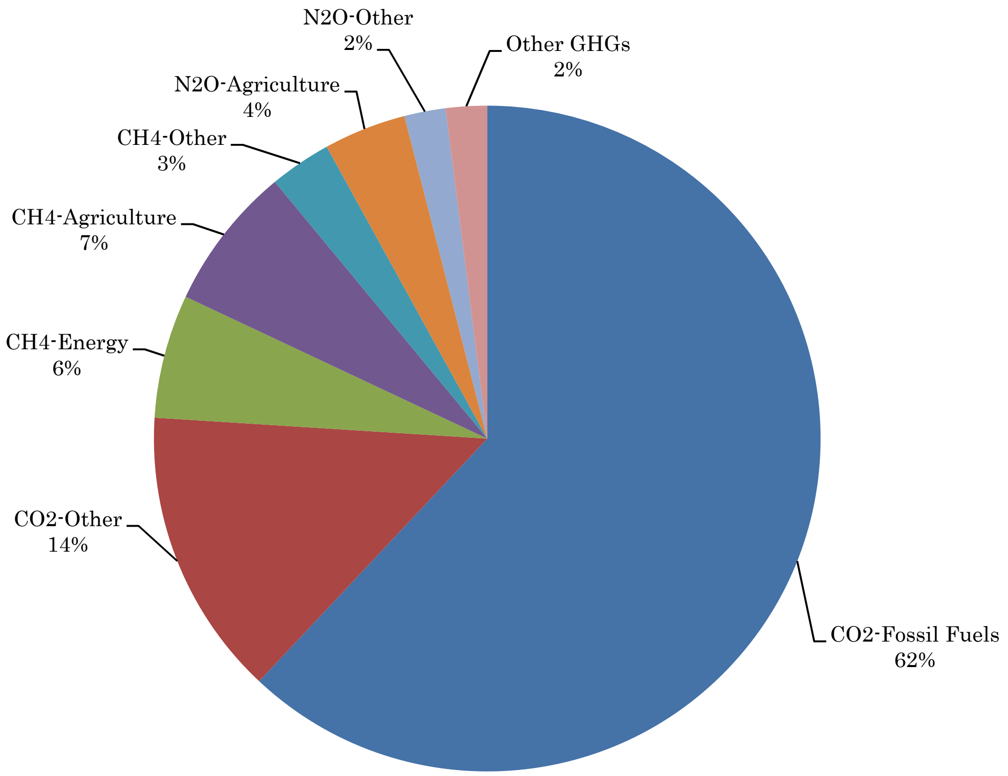


Fig. 1.2 Global anthropogenic GHG emissions by type and source [25]

Biomass is an organic that is derived from plants or animals available on a renewable basis and it is decomposable. Wood and agricultural crops, herbaceous and woody energy crops, municipal organic wastes as well as manure are classified as biomass. Biomass is abundance in the universe and woody biomass was estimated to satisfy 18% of world primary energy consumption in 2050 [28]. Energy extracted from biomass and waste is seen as one of the dominant alternative renewable energy source due to the guaranteed power generation from the sources, unlike other types of renewable energy such as solar energy and wind energy[29]. In 2010, woody biomass stated roughly 9% of world primary energy consumption and 65% of world renewable primary energy consumption [28].

Thus, a drastic movement to more secure, clean and diversified alternative energy source could be a successful strategy to reduce and eliminate GHG emissions and meet the future sustainable energy needs. Compared to other alternatives, hydrogen is the lightest, simplest and most plentiful of all chemical elements in the universe as it can be generated from clean and green sources. Even though it is not a primary source, hydrogen becomes an attractive energy carrier when split from other elements by using a source of energy. Hydrogen is carbon free and hence environmentally friendly since its combustion only produces water as byproduct [30]. In addition, hydrogen has high energy content per mass compared to fossil fuels (**Table 1.1**).

Table 1.1 Energy contents of different fuels [31]

Fuel	Energy content (MJ/m^3)
Hydrogen	120.0
Liquefied natural gas	54.4
Propane	49.6
Aviation gasoline	46.8
Automotive gasoline	46.4
Automotive diesel	45.6
Ethanol	29.6
Methanol	19.7
Coke	27.0
Wood (dry)	16.2
Bagasse	9.6

1.3 Purpose and Procedure of This Study

The purpose of this study is the application of radio-frequency plasma in liquid with and without ultrasonic vibration for hydrogen production from saccharides. Due to the energy crisis, severe environmental effect from greenhouse gases emission and abundance amount of biomass in the universe, the clean and carbon-free energy is a mandatory for future sustainable life. Furthermore, there have insufficient fundamental research on plasma discharge in liquid by using radio-frequency with and without ultrasonic vibration for hydrogen production from biomass-derived saccharides.

In Chapter 2, the potential of biomass-derived hydrogen energy and overview of biomass were discussed. Furthermore, the production routes of hydrogen production from biomass which were classified as thermo chemical conversion and biological conversion, was briefly discussed.

In Chapter 3, radio-frequency plasma in liquid was used for hydrogen production by decomposing glucose solution and cellulose suspension with and without ultrasonic irradiation. By applying ultrasonic vibration to a liquid, cavitation bubbles, microjets, acoustic streaming or hotspots are generated by the nonlinearity of the sound. It is well-documented that these phenomena can enhance chemical reactions, heat transfer and plasma generation in a liquid [32]. The purpose of this study is to decompose glucose solution and cellulose suspension with and without 29 kHz horn-type ultrasonic transducer and 1.6 MHz piezoelectric transducer. The gas production rate and enhancement ratio were compared for each device.

In Chapter 4, the detailed mechanism of decomposition of glucose solution by 27.12 MHz radio-frequency in-liquid plasma with and without ultrasonic vibration for hydrogen production was investigated. Two types of ultrasonic transducers, a lower range frequency, 29 kHz horn-type ultrasonic transducer and a higher range frequency, 1.6 MHz piezoelectric transducer, were used to irradiate ultrasonic vibration in the solution. In order to clarify the mechanism, the spectrum emissions of pure water and glucose solution were studied to observe the effectiveness of decomposition process. In addition, higher and lower frequency ranges of ultrasonic vibration were compared as to their effect on the behavior of hydrogen production rate, hydrogen yield, hydrogen purity and hydrogen production efficiency.

Finally, Chapter 5 describes the summaries of the studies.

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Chapter 2

Biomass as a Clean Energy

2.1 Introduction

The global energy consumption is seemly to greatly increase faster than was expected. It was recorded that global energy consumption was growing from 10,557 million tons of oil equivalent (Mtoe) in 2004 to almost 23% of the energy consumption which had reach 12,928 Mtoe in 2014 [1]. Fossil fuels covered 86% of total energy consumption followed by hydroelectricity and nuclear energy which account for only 7% and 4%, respectively. However the share of renewable energy is very small with only

3%.

The continued use of fossil fuels to meet the majority of global energy demand will significantly contribute to the concentration of carbon dioxide (CO_2) in the atmosphere and raising the climate change issue [2]. Moreover, a limited reserve of petroleum is rapidly becoming scarcer and expensive. Thus, one most promising alternative energy source is vital toward a sustainable future life.

Hydrogen is one of the dream fuels for future sustainable energy. It is not a primary energy that exists freely in nature. As the electricity, hydrogen is in a form of secondary energy that has to be manufactured. The majority of the researchers recognize that hydrogen plays as a promising alternative energy carrier in the future [3], [4]. Thus, bioenergy or biohydrogen which is derived from biomass has a great attention these days for renewable and clean energy source.

2.2 Overview of Biomass

Biomass as a carbon neutral source of energy is an organic matter which is derived from plants as a result of photosynthesis. It is stored source

Table 2.1 Typical characteristic of cellulose, hemicellulose and lignin in biomass [6]

Component	Percent dry weight (%)	Description
Cellulose	40 - 60	A high-molecular-weight (10^6 or more) linear polymer of β-gycosidic linkage. These chains are stable and resistant to chemical attack
Hemicellulose	20 – 40	A mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose and uronic acid. Relatively easy to be hydrolyzed into basic sugars
Lignin	10 - 25	A biopolymer rich in three-dimensional, highly branched polyphenolic constituents that provide structural integrity to plants. Amorphous with no exact structure. More difficult to be dehydrated than cellulose and hemicellulose

of solar energy in the form of chemical energy. This energy can be extracted when the bonds between adjacent carbon, hydrogen and oxygen molecules are broken by various thermo-chemical and biological processes. The formation of non-renewable fossil fuels such as oil, coal and natural gas is originated from ‘ancient’ biomass that have been transformed through microbial anaerobic degradation and metamorphic geological changes over millions of years [5].

Biomass is a kind of natural polymer, which is generally composed of cellulose, hemicellulose, lignin, lipids, proteins, simple sugars and starches. The three major constituents among these compounds are cellulose, hemicellulose and lignin as shown in Table 2.1 [6].

2.3 Hydrogen Production Routes from Biomass

A lot of factors influence the choice of conversion method such as the type and quantity of biomass feedstock, the desired form of energy, i.e. end-use requirements, environmental standards, economic conditions and project specific factors. The potential biomass conversion to energy is undertaken using two main process technologies which are thermo-chemical and biological [7].

Thermo-chemical conversion encompasses of combustion, pyrolysis, gasification, liquefaction and plasma discharge. On the other hand, biological conversion consists of digestion and fermentation.

2.3.1 Thermo Chemical Conversion

Thermo-chemical conversion processes mainly comprise of combustion, pyrolysis, gasification and liquefaction [8], [9]. Basically, the conversion processes are divided into two approaches. The first approach is the gasification of biomass and its conversion to hydrocarbon products. The second approach is to liquefy biomass directly by high-temperature pyrolysis, high-pressure liquefaction, ultras pyrolysis or supercritical extraction. All of these processes are focusing on conversion of waste biomass to energy rich useful products. The conversion processes are adopted depends on the type and quantity of biomass feedstock, environmental standards, economic conditions and project specific factors [10].

2.3.1.1 Combustion

The biomass is directly burnt in the presence of oxygen to convert the chemical energy stored in biomass into useful heat and electricity with the assistance of a steam cycle. Co-combustion of biomass in coal fired power plants is an especially attractive process due to high conversion efficiency of these plants. Net bio-energy conversion efficiencies of biomass combustion power plants range from 20% to 40% [11]. Biomass feedstocks with water contents up to maximum 60% are possible to be used for combustion process [12]. The biomass combustion process exhibits serious environmental impact to the nature. NO makes 90 – 95 % of the total NO_x emitted from the combustion of fossil fuels and biomass [13].

2.3.1.2 Pyrolysis

Pyrolysis is thermal destruction of organic matrix that takes place in the absence of oxygen. Pyrolysis is basic thermo-chemical process for biomass conversion to obtain an array of solid, liquid and gas products. Depending on the reaction temperature and residence time, pyrolysis can be categorized into fast pyrolysis, intermediate pyrolysis and slow pyrolysis. Fast pyrolysis is a process operates at very high heating rates, very high heat transfer rates and short hot vapor residence times of typically less than 2 s [14]. It particularly favors the formation of high grade bio-oils products, but suppress the formation of solid chars [15].

2.3.1.3 Gasification

Gasification is carried out through partial thermal oxidation of biomass to produce high proportion of gaseous products (CO_2, water, carbon monoxide, hydrogen and gaseous hydrocarbons), small quantities of char (solid products), ash and condensable compounds (tars and oils) [16]. It is normally carried out at high temperature over 700 ^{0}C [17]. The syngas (CO and H_2) produced can be used as feed gas for Fischer-Tropsch and methanol synthesis [18]. Formation of tar with concentration ranges from 5 to 75 g/N m3 in fluidized-bed gasifiers is remarkably above the maximum allowed for gas turbines and diesel engines [19]. Tar is a complex mixture of condensable aromatic compounds [20]. The characteristics of tar that can easily condense and polymerize into more complex structure in engines, heat exchangers and filters leads to high maintenance cost and low process efficiency.

2.3.1.4 Direct Liquefaction

Direct liquefaction is conducted at low temperature (250 – 450 ^{0}C) and high pressure (50 – 200 atm) using a catalyst to obtain water-insoluble bio-liquid [21]. The yield of gaseous, liquid and solid from direct liquefaction of biomass depends on numerous parameters. Lignin content of the biomass, solvent, catalyst and atmosphere are listed as the impact of chemical parameters, while temperature, pressure, mass ratio of solvent to biomass (S/B), concentration of the homogenous catalyst and residence time are considered as the impact of physical parameters [22].

Liu et al [23] concluded that liquefaction products were greatly affected by the type of solvent. Jena et al [24] reported the thermochemical liquefaction for production of bio-crude from *Spirulina platensis* at various temperature (200 – 380 ^{0}C). Bio-crude produced at 350 – 380 ^{0}C had similar properties to that of petroleum crude with energy density of 34.7 – 39.9 MJ kg^{-1}. Sun et al [25] observed the Fe and Na_2CO_3 catalyst's effect on direct liquefaction of paulownia. The maximum heavy oil yield was found to be 36.34% with Fe catalyst and the minimum solid residue yield was obtained when Na_2CO_3 was employed as catalyst. However, the heavy oil produced is tarry lump that caused the liquefaction process trouble in handling [26].

2.3.1.5 Plasma Discharge

Plasma is generated when adequate energy is supplied to a neutral gas to cause charge production. Operating at low neutral gas temperature, while the electron temperature can be much higher, are the main reasons why plasma discharge was acknowledged as one of the potential methods in biomass conversion process. Recently, plasma gasification and plasma pyrolysis were greatly investigated for hydrogen production [27], [28].

Plasma gasification is an effective method for solid waste and hazardous waste treatment for energy production. Through plasma gasification process, biomass is decomposed into high calorific value syngas such as hydrogen and carbon monoxide, used as fuel or chemical. A DC plasma torch is well developed technology that has two electrodes to produce an arc. The arc is generated by transmitting a high electric current between the electrodes in the presence of a working gas flowing between them and taking advantage of its low electrical conductivity to dissipate energy resulting in localized high enthalpy and high temperature fields [29]. Electron is dissociated from the molecules at high temperature and hence, producing ionized gas stream (plasma) [30], [31]. The formation of a large amount of radicals, electrons, ions and excited molecules in the system resulting to substantially high reaction rates and allow reactions to proceed at lower temperature condition.

2.3.2 Biological Conversion

Biological biomass conversion technologies are fermentation and anaerobic digestion [7]. Anaerobic digestion has been successfully applied for energy production from variety of wet biomass feedstocks such as organic domestic and industrial wastes, manure and sludge [32]. The biomass is directly converted to a mixture of methane and carbon dioxide biogas by bacteria in an anaerobic environment. Anaerobic biodegradation can be divided into four main phases : hydrolysis, acidogenesis, acetogenesis and methanogenesis [33].

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Chapter 3

Hydrogen Production from Glucose and Cellulose Using Radio Frequency In-Liquid Plasma and Ultrasonic Irradiation

3.1 Introduction

Hydrogen is well-known as an alternative secondary energy. With the weakening of resolve towards world energy conservation and the increasing evidence of the detrimental effect of global greenhouse effect for humankind, sources of clean and alternative renewable energy are gaining increasing attention for future energy production. Recently there has been much international attention toward the development of hydrogen production technologies as a solution to this current dilemma and as a way to stabilize world energy demand. Steam reforming, partial oxidation and biomass gasification are the primary technologies that have been developed and implemented. The advantage of steam reforming is that no oxygen is required. However it must be performed at high temperatures of 700 to 900^{O}C and produces unwanted greenhouse gasses. Similarly, the partial oxidation process operates at the same high temperature level as steam reforming and additionally requires a catalyst in order to reduce the temperature and avoid the formation of coke. Reviews of the technologies developed for hydrogen production are presented by Holladay et al. [1].

On the other hand, development of plasma technology has been applied with great success in various fields [2]–[7]. The application of plasma technology for synthesis of diamond [8], nanoparticles [9], carbon nanotubes [10], surface modifications [11], decomposition of gaseous pollutants [12], medical treatment [13] and such has been widely investigated. Recently, there has been a significant increase in the development of this plasma technology for the production of hydrogen gas from direct electric (DC) water plasma [14], microwave plasma [15], gliding arc discharge [16], dielectric barrier discharge [17], thermal and non-thermal plasma and corona discharge [18]–[20] due to the high temperature and high electron density it provides at atmospheric pressure. However, less emphasis has been given to experimental study of hydrogen production from biomass and municipal wastes utilizing radio frequency (RF) in-liquid plasma.

RF in-liquid plasma is a process in which plasma is generated inside a bubble produced by evaporation of a surrounding liquid by the heat of plasma. Basically, a copper electrode and a brass electrode are used as the lower and upper electrodes respectively. An RF generator and tuner are used together to increase input power and reduce reflected power respectively until breakdown occurs. After breakdown, plasma appears as a violet region surrounded by a bubble. The bubbles occur due to evaporation of water heated by RF input power before the occurrence of breakdown. Under the assumption that plasma in water is at thermal equilibrium, the temperature of the plasma is estimated to be 4000-4500 K using the theory of spontaneous emission [21], [22]. Since in-liquid plasma produces such high temperatures of several thousand Kelvin which in turn produces reactive radical species such as H, O and OH, investigation into its use for hydrogen production through decomposition of waste oil and other such organic liquids as well as methane hydrate has been successfully conducted [23]–[25].

In this study, RF in-liquid plasma was used for hydrogen production by decomposing glucose solution and cellulose suspension with and without ultrasonic irradiation applied. By applying ultrasonic vibration to a liquid, cavitation bubbles, microjets, acoustic streaming or hotspots are generated by the nonlinearity of the sound. It is well-documented that these phenomena can enhance chemical reactions, heat transfer and plasma generation in a liquid [26]. The purpose of this study is to observe the decomposition of glucose solution with and without application of ultrasonic vibration by a 29 kHz horn-type ultrasonic transducer and 1.6 MHz piezoelectric transducer and then to compare any enhancement of the gas production rate for each device.

3.2 Experiment

The experimental apparatus is schematically shown in **Fig. 3.1**. Radio-frequency (RF) in-liquid plasma was generated at tip of the electrode.

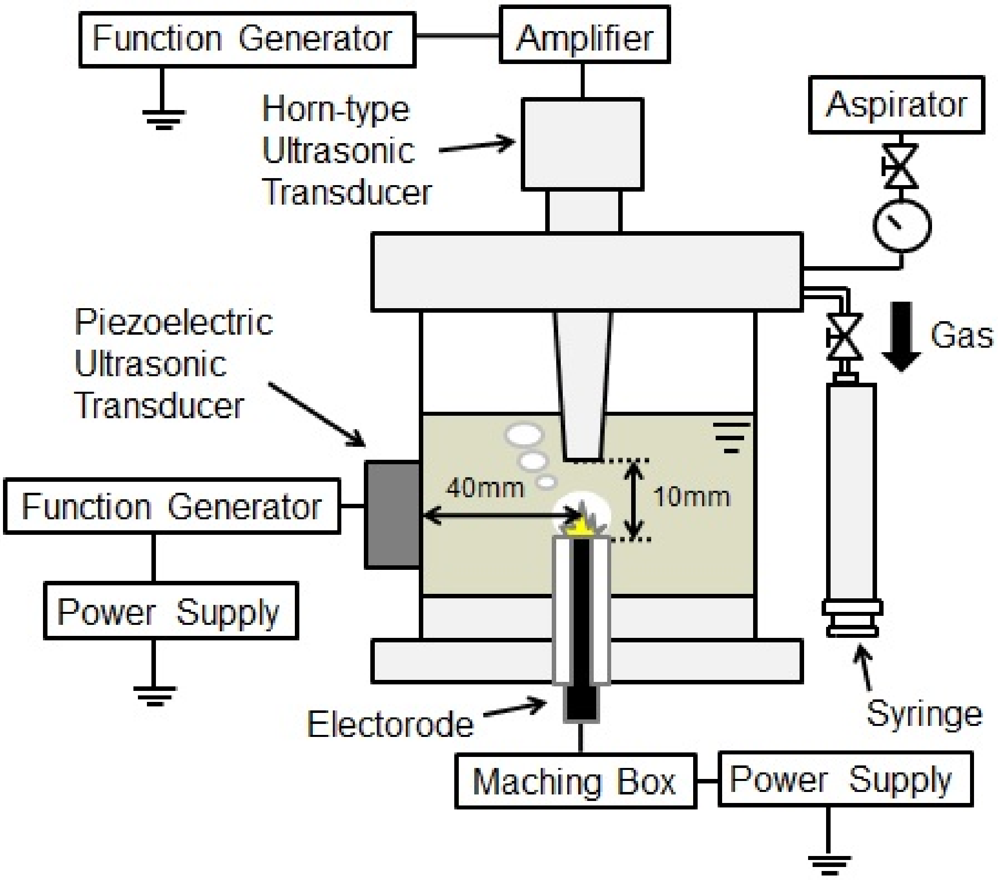


Fig. 3.1 RF in-liquid plasma and ultrasonic transducer experimental apparatus

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 was 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. In order to generate plasma in liquid, the impedance and input power were adjusted together by a matching box and 27.12 MHz RF generator.

A 29 kHz horn-type ultrasonic transducer was attached at the top of the reactor vessel 10 mm from the tip of the electrode. In the presence of 29 kHz ultrasonic irradiation, the input power of the transducer was adjusted to 30 W by using a function generator. Additionally, a 1.6 MHz piezoelectric transducer was attached to the side wall of the reactor vessel with the input power fixed at 30 W. The distance between the transducer and electrode was 40 mm. The position of each transducer was fixed.

120 mL of pure water, glucose solution and cellulose suspension were poured into the reactor vessel. The initial concentrations of glucose solution were prepared at 0.5, 1.0, 5.0, 10.0, 20.0 and 50.0 wt% while the cellulose suspension varied among 0.5, 1.0, 5.0, 10.0 and 20.0 wt%. The pressure of the reactor vessel was reduced to 0.01-0.02 MPa using an aspirator to expel the air. In-liquid plasma was generated at an RF input power of 150 W with ultrasonic irradiation and at 180 W without ultrasonic irradiation 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.

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 ^{O}C, 50 ^{O}C and 50 ^{O}C, respectively.

Experiments under the same condition were conducted three times. The averaged difference of the results was always less than 10%.

3.3 Results and Discussions

3.3.1 Decomposition of glucose

The experiment for hydrogen production from glucose solution was carried out at atmospheric pressure in-liquid plasma generated by an RF generator. Two types of ultrasonic transducers were used, a 29 kHz horn-type ultrasonic transducer and a 1.6 MHz piezoelectric transducer in order to analyze the hydrogen production rate. The incident power of RF was

180 W when ultrasonic irradiation was not applied and 150 W when ultrasonic irradiation was applied. The power of the ultrasonic transducers was 30 W.

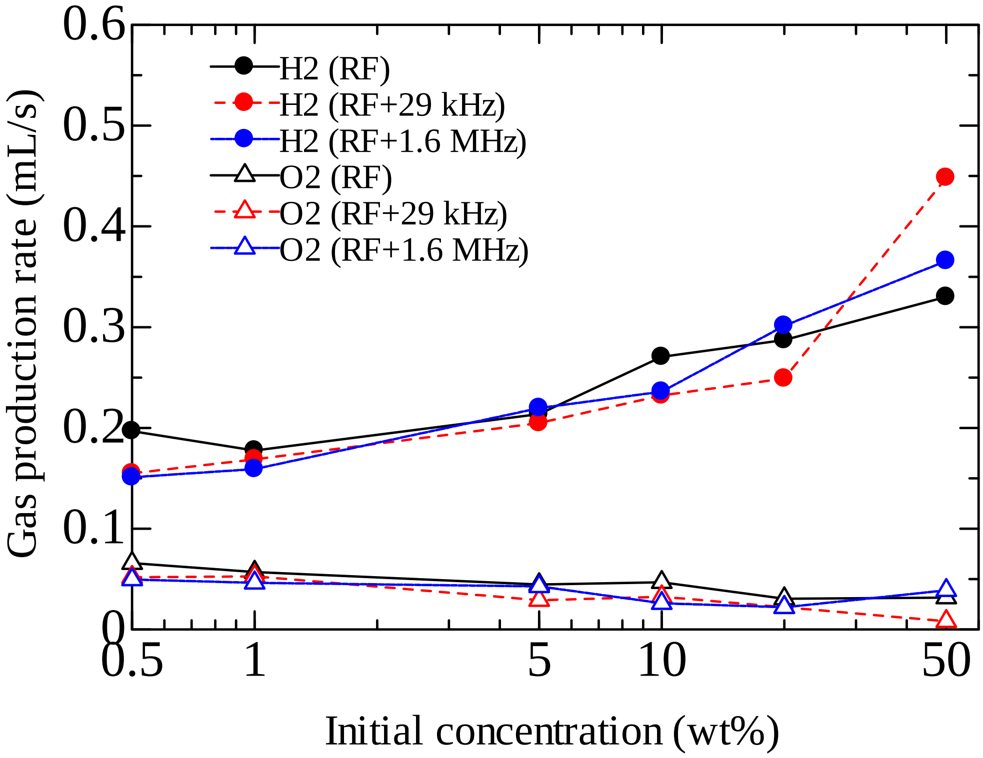


Fig. 3.2 Decomposition of glucose solution: Main gas production rates as a function of initial condition using RF in-liquid plasma with and without ultrasonic irradiation

Fig. 3.2 shows the production rates of the main gasses produced from decomposition of glucose solution as a function of the initial concentration.

The volume of gas produced was 50 mL after exposure to RF in-liquid plasma for 10 minutes with and without ultrasonic irradiation applied. The gas production rate is calculated from the average of the percentage of each gas produced, the total volume and the time exposed. Initially, the production rate of hydrogen was lowest at 0.5 wt% but there was an upward trend beyond 0.5 wt%. For decomposition with RF in liquid plasma only, there was a significant production increase of 60% between 0.5 wt% and 10 wt%. The rate then increased steadily upward, reaching a level of around 0.3 mL/s.

The production rate of hydrogen for decomposition by RF in-liquid plasma using the 29 kHz horn-type ultrasonic transducer increased slightly between 0.5 wt% and 20 wt%, but then, interestingly, it climbed sharply to 0.45 mL/s at 50 wt%. Meanwhile, decomposition by RF in-liquid plasma using the 1.6 MHz piezoelectric transducer rose steadily and at 20 wt% it had the highest rate of the three methods.

Meanwhile, the production rate of oxygen decreased slowly with an increased initial concentration. At the same initial concentration, there were no significant production rate differences between decomposition by RF in-liquid plasma with and without ultrasonic irradiation applied.

Glucose is a monosaccharide of the aldehyde group obtained most readily by the hydrolysis of starch or cellulose. It is obtained from high molecular polysaccharides. Additionally, glucose has characteristics which are soluble but non-volatile. As shown in the figure, the hydrogen production rate of glucose decomposed by RF in-liquid plasma with ultrasonic irradiation applied was almost always higher than that without application of ultrasonic irradiation at initial concentrations beyond 20 wt%. The molecules of glucose were decomposed by the plasma and radical species were produced. The high production rate occurred due to ultrasonic atomization induced by the high frequency ultrasonic irradiation.

Ultrasonic atomization is a phenomenon resulting from the formation of fine droplets released from the liquid which is vibrating due to the ultrasonic irradiation. Capillary wave hypothesis and cavitation hypothesis are the two hypotheses that best explain the ejection of the droplets from a vibrating surface. Capillary wave hypothesis suggests that a capillary wave formed on the vibrating liquid surface consisting of crests and troughs. A large number of droplets were ejected from the crests by overcoming the surface tension force, which is less than half the wavelength of the capillary wave [27]. Lang [28] reported that ultrasonic atomization involves the rupture of capillary surface waves and the subsequent ejection of the wave peaks from the surface as particles, and that an increase in the frequency of ultrasound decreases the wavelength of the capillary wave, consequently reducing the droplets size.

However, cavitation hypothesis suggests that droplets are formed by the cavitation caused by the expansion and contraction of cavitation nuclei due to the compression and rarefaction cycles of the ultrasonic waves. The phenomenon of cavitation occurs at a micro level which cannot be observed visually on the surface of the atomizer, but can be deduced from the fact that the droplets ejected from vibrating surface of the atomizer likely have much higher velocities due to energy dissipation during the cavitational event. This can be explained based on the facts that cavitation causes the formation of cavities near the surface of the atomizer and liquid film, with the rapid growth and final implosive collapse of these cavities resulting in the release of quantum energy locally. Substantially, the ejected droplets have higher velocities in comparison to the induced droplet ejection velocity from capillary wave propagation [27].

Thus, it is believed that capillary wave hypothesis and cavitation hypothesis occurred during the decomposition of glucose. The glucose solution was atomized into finer droplets and ejected from the crests of the surface of glucose solution by overcoming the surface tension forces. The ejected droplets with high velocities obtained by the energy dissipation during cavitational event entered into a bubble generated by the liquid evaporating around the plasma due to the heat of the plasma. The maximum temperature of the bubble is expected to be from approximately 3500 to 4300 K. The highest temperature is at the center of the bubble where the plasma is generated in liquid. In this heated area which is approximately 90% of the maximum temperature, H and O radicals are found to be dominant [29], [30]. Consequently, the glucose molecules were decomposed due to the high temperature inside the bubble with radical species being generated in the liquid. H and OH radicals were produced during decomposition of water by plasma [29],[31] and cavitation bubbles [32].

3.3.2 Decomposition of cellulose

The experiment on hydrogen production from cellulose suspension was carried out in the same manner as that for the decomposition of glucose solution. In this experiment, the initial concentration was varied up to 20 wt%.

Cellulose is from a group of polysaccharides, whose substances have high molecular weights of more than 1,000,000. They are widely found in nature and are completely insoluble in liquids [33]. Furthermore, cellulose in wood has a high crystallinity and a low specific surface area.

Fig. 3.3 illustrates the production rate of hydrogen from cellulose suspension as a function of initial concentration. The hydrogen production rate fluctuated but, in general, tended to increase slightly beyond initial concentrations of 10 wt%. The hydrogen production rate from cellulose suspension by RF in-liquid plasma without ultrasonic irradiation was higher throughout the varied initial concentrations than that with ultrasonic irradiation. There was a decrease to the lowest point at 10 wt% but then there was a dramatic increase after 10 wt%.

Similarly, the hydrogen production rate for decomposition by RF in-liquid plasma using the 29 kHz horn-type ultrasonic transducer fluctuated at the beginning and decreased to the lowest point at 5 wt%.

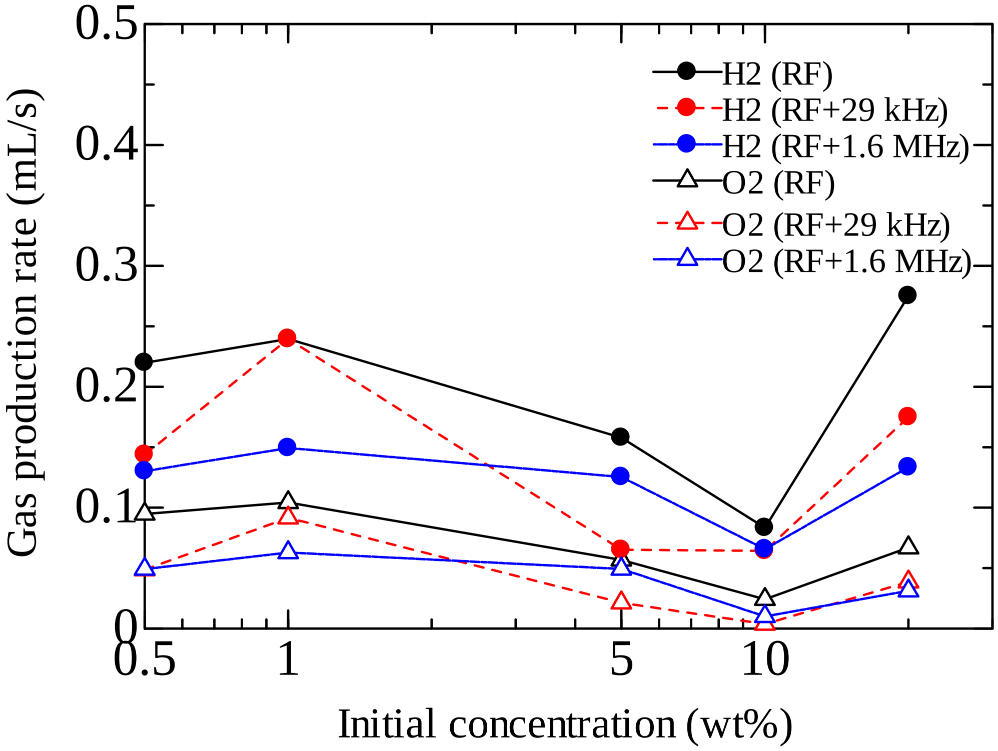
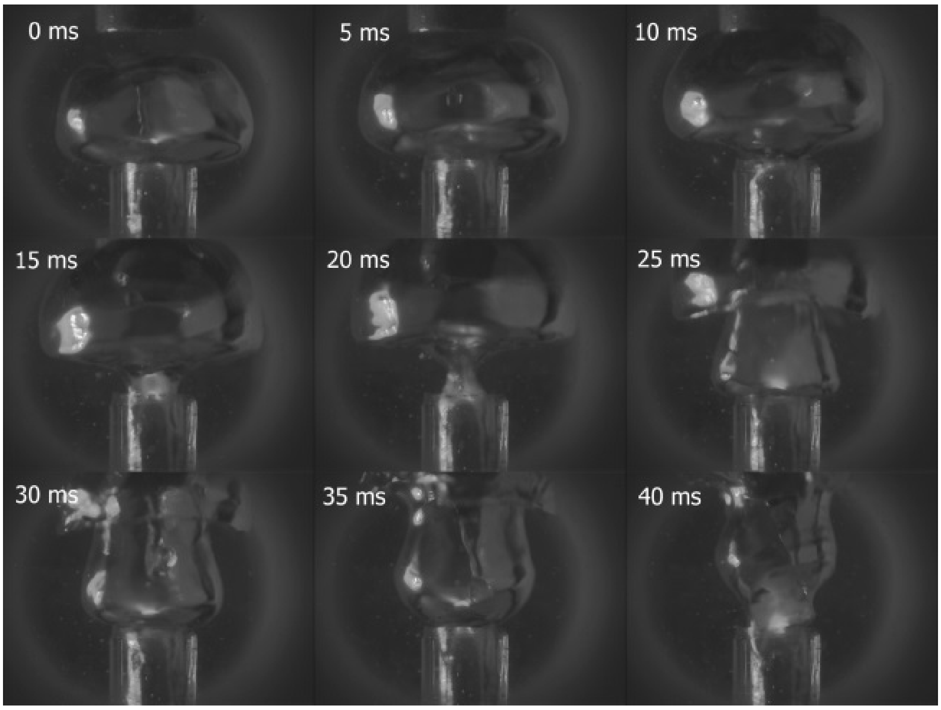


Fig. 3.3 Decomposition of cellulose suspension: Main gas production rate as a function of initial condition using RF in-liquid plasma with and without application of ultrasonic irradiation

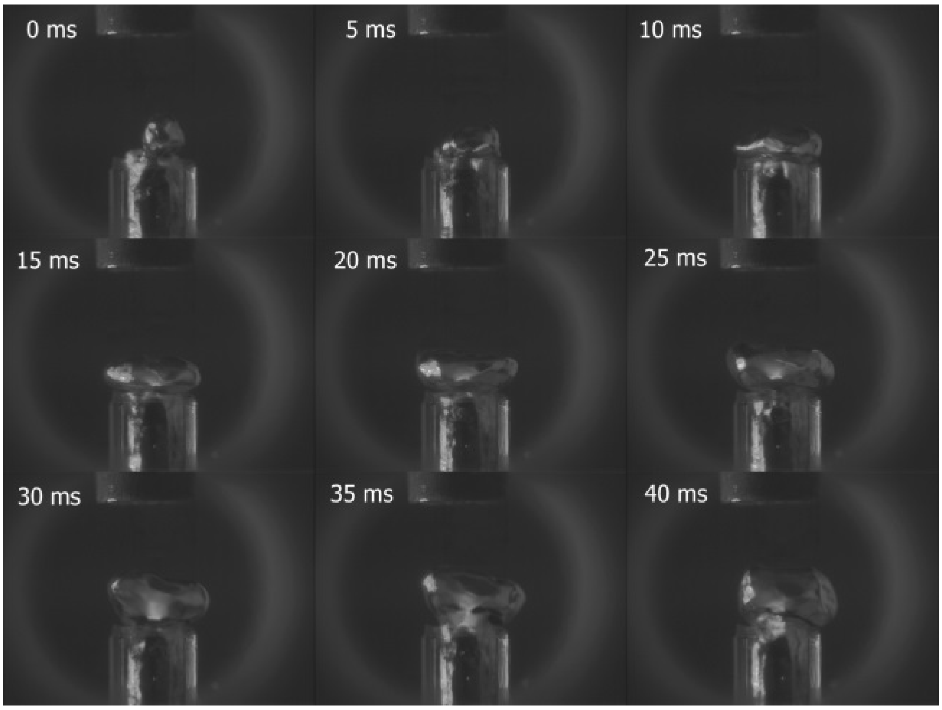
Then, the production rate remained stable at 0.06 mL/s at the initial concentration of 10 wt% and increased steadily at 20 wt%. Meanwhile, the hydrogen production rate for decomposition of RF in-liquid using the 1.6 MHz piezoelectric transducer was relatively stable through the varied initial concentration of suspension although there was a slight decrease at 10 wt%.

Fig. 3.3 shows clearly that most of the hydrogen production rates fluctuated at initial concentrations less than 10 wt% and started to increase at 10 wt%. At 0.5 wt% of cellulose, the results are almost the same as that of pure water without cellulose. Therefore, it is inferred that only the decomposition of water occurred while little if any decomposition of cellulose occurred. Moreover, the cellulose might act to prevent the decomposition of water at wt% of 10 or less because of its stability. The decomposition of cellulose will not occur directly by the plasma, because cellulose is nonvolatile and remains in the liquid water in spite of evaporation 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 concentration. If the concentration of cellulose increases more, the decomposition of cellulose will occur by hydroxyl radicals which are produced by the decomposition of water. This is because the hydroxyl radicals reach the surface of the bubble more easily without colliding with the water molecules in the bubble.

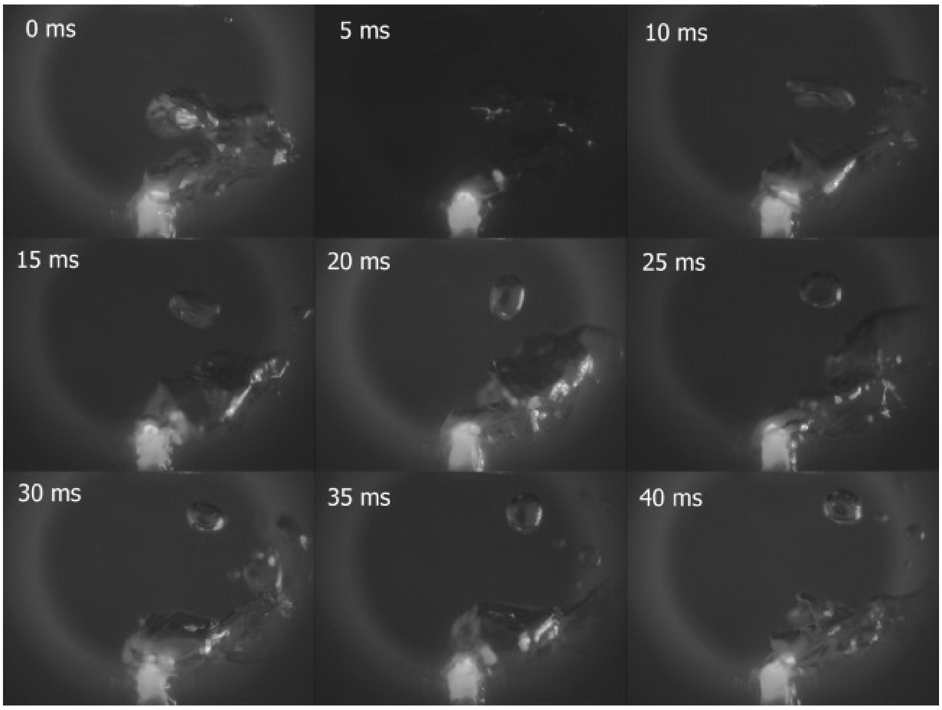
3.3.3 Bubble pattern



a) RF only



b) RF with 29 kHz ultrasonic



c) RF with 1.6 MHz ultrasonic transducer

Fig. 3.4 Sequential images of bubble pattern captured by high-speed camera

In order to investigate the details of what was happening to the bubbles when RF was irradiated with and without application of ultrasonic irradiation, a high-speed camera was used, capturing 200 pictures in 0.1 s. The differences in the pattern of the bubble growth when plasma was generated inside a bubble by radio-frequency (RF) with and without application of ultrasonic irradiation by the 29 kHz horn-type ultrasonic transducer or the 1.6 MHz piezoelectric transducer are shown in **Fig. 3.4**. “Single-period” bubbles appeared when RF only was applied as shown in

Fig. 3.4(a) [29]. A spherical bubble was generated and grew at the tip of the electrode and separated from the electrode due to buoyancy. Similar bubbles appeared subsequently and the actions were repeated almost regularly. Likewise, a similar pattern of bubbles was observed in **Fig 3.4(b)**. Interestingly, **Fig. 3.4(c)** shows a non-uniformity bubble pattern occurred when the 1.6 MHz piezoelectric transducer was turned on. Sinusoidal signals were excited from the transducer which generated a time harmonic acoustic field inside the fluid that propagated perpendicular to the flow direction and disrupted the uniformity of the “single-period” bubbles. Stable plasma continued to be generated at the tip of the electrode. This is believed to have occurred due to acoustic streaming. Langevin acoustic radiation pressure was propagated by an acoustic wave. Thus, it is believed that in addition to ultrasonic atomization as reported earlier, acoustic streaming was also an influence on the decomposition of glucose molecules by plasma inside a bubble. The induced acoustic streaming provides a high mass flux to the bubble at the tip of the electrode. Thus, the bubble was attached near to the tip of the electrode and hence evaporates easily due to buoyancy. The mechanism on how the acoustic streaming influenced the decomposition of glucose will be investigated in future.

3.4 Conclusion

In this study for future alternative energy sources, hydrogen gas was produced from glucose solution and cellulose suspension by 27.12 MHz RF in-liquid plasma with and without ultrasonic irradiation being applied. The production rate of hydrogen from decomposition of glucose solution by RF in-liquid plasma with ultrasonic irradiation applied was higher than that without ultrasonic irradiation. However, no enhancement effect of hydrogen production rate was found for the decomposition of cellulose suspension by RF in-liquid plasma with ultrasonic irradiation. In addition, high-speed camera imagery of the pattern of bubble generation by RF with the 1.6 MHz piezoelectric transducer indicated that acoustic streaming had been occurring. This raises the prospect of investigating the mechanism of acoustic streaming on plasma inside a bubble for future research.

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Chapter 4

Synergetic Effects of Radio-frequency (RF) In-Liquid Plasma and Ultrasonic Vibration on Hydrogen Production from Glucose

4.1 Introduction

One of the major challenges faced by the world today is to provide sustainable energy while at the same time protecting the environment from greenhouse gas (GHG) emissions. The high global dependence on fossil fuels as a primary energy source is rapidly resulting in exhaustion of the finite fossil fuel supply in addition to causing a serious environmental crisis throughout the world. In response to the mentioned problems, intense and continuous effort has been invested into the investigation and production of clean and renewable alternative energy sources for a sustainable future lifestyle. Hydrogen shows great promise for being such an energy source. Besides its abundance throughout the universe, hydrogen provides a quantity of thermal energy per unit weight that is three times that of petrol [1].

Hydrogen can mainly be extracted from various sources such as fossil fuels, biomass and water [2]. Among all current technologies for hydrogen production, almost 80 to 85% of the world's total hydrogen is derived by steam reforming of natural gas followed by coal gasification, and only 4% generated from water electrolysis [3]. Steam reforming of natural gas produces low purity hydrogen, high air emission and requires high temperature that may promote carbon formation [4,5]. The gasification process, with a sustained low thermal efficiency produces tar as a by-product at even high temperature of 800 to 1000^{O}C [6]. Both of these technologies directly or indirectly utilize fossil fuels. Electrolysis is essentially the conversion of electrical energy to chemical energy for hydrogen production and oxygen as a useful byproduct. However, it only accounts for a small amount of the world's hydrogen production at the moment.

Recently, non-thermal plasma technologies have been suggested as promising methods of producing hydrogen due to their relatively low energy requirement [7]. Moreover, they have the capacity to induce physical and chemical reaction within gases at relatively low temperatures due to their non-equilibrium properties. The electron temperatures of non-thermal plasma can reach 1 – 10 eV while the gas temperature remains as low as room temperature [8]. Yan et. al. conceded that the glow discharge plasma electrolysis technique has a potential for producing hydrogen and formaldehyde simultaneously from methanol solutions [9]. Jasinski and his colleagues identified that microwave plasma sources have high potential for hydrogen production from hydrocarbon conversion [10]. Meanwhile Kim et. al. successfully applied a plasmatron reformer to increase the concentration of the hydrogen in product gas [11].

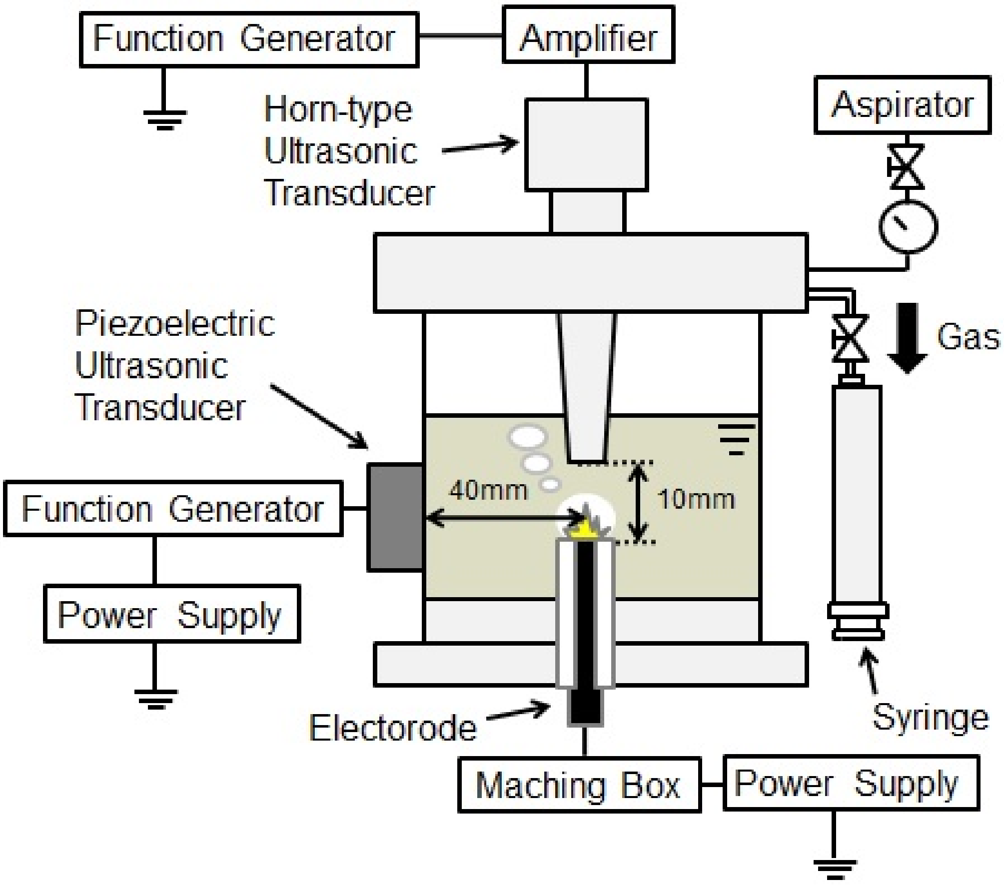
Besides, in-liquid plasma was first inspired by Nomura and Toyota when they succeed in depositing diamond-like carbon 9000 times faster than gas-phase plasma by applying plasma within bubbles created in a *n*-dodecane irradiated simultaneously by ultrasonic waves and microwaves [12]. The plasma is generated inside bubbles produced by the evaporation of surrounding liquid heated by plasma [13]. The electron temperature of plasma in water is approximately between 4000 and 4500 K [14]. Since in-liquid plasma is generated in a liquid that provides cooling effect, the plasma can be maintained without damaging the electrode or substrate [15]. The existence of radical species such as H radicals and hydroxyl radicals inside the bubbles seems more favorable for higher reaction rates than those for conventional gas-phase plasma [16].

In previous work, an initial study of decomposition of glucose solution and cellulose suspension for hydrogen production using RF in-liquid plasma with and without ultrasonic vibration was carried out in order to compare any enhancement of the gas production rate for each device [17]. It was clarified that the enhancement of hydrogen production rate from glucose decomposition was due to the atomized glucose molecules being fed into the plasma in a bubble with acoustic streaming providing a high mass flux to the bubble which resulted in evaporation of the bubble due to buoyancy. There was no enhancement of the hydrogen production rate observed for decomposition of cellulose suspension with ultrasonic irradiation applied.

In this study, the detailed mechanism of decomposition of glucose solution by 27.12 MHz radio-frequency in-liquid plasma with and without ultrasonic vibration for hydrogen production was investigated. Two types of ultrasonic transducers, a lower range frequency, 29 kHz horn-type ultrasonic transducer and a higher range frequency, 1.6 MHz piezoelectric transducer, were used to irradiate ultrasonic vibration in the solution. In order to clarify the mechanism, the spectrum emissions of pure water and glucose solution were studied to observe the effectiveness of decomposition process. In addition, higher and lower frequency ranges of ultrasonic vibration were compared as to their effect on the behavior of hydrogen production rate, hydrogen yield, hydrogen purity and hydrogen production efficiency.

4.2 Experiment

Radio-frequency (RF) of 27.12 MHz was generated with and without application of ultrasonic vibration from a 29 kHz horn-type ultrasonic transducer and a 1.6 MHz piezoelectric transducer in order to investigate the effects of ultrasonic vibration on the mechanism of hydrogen production from glucose decomposition. A schematic and photograph of the experimental set-up used in this work is shown in **Fig. 4.1(a,b)**.



(a) Schematic diagram of experimental set-up

(b) Photograph of the experimental set-up

Fig. 4.1 RF in-liquid plasma and ultrasonic transducer experimental apparatus (a) schematic diagram, (b) photograph

Plasma was generated at the tip of a 3 mm diameter copper electrode inserted in a liquid solution at atmospheric pressure. The copper electrode was encased in a glass pipe as a dielectric substance to avoid energy loss. The impedance and power absorption were adjusted simultaneously by a matching box and RF generator in order to generate plasma in liquid. The power absorbed by RF to generate plasma in-liquid was 150 W, as calculated by subtraction of the reflected power from the generated power.

A 29 kHz horn-type ultrasonic transducer was attached at the top of the reactor vessel at a distances of 10 mm from the electrode. The input power was fixed at 30 W. Furthermore, a 1.6 MHz piezoelectric transducer with 40 W of input power was affixed to the side wall of reactor. The distance between transducer and electrode was 40 mm.

In this study, 120 mL of glucose solution with an initial concentration up to 20 wt% was used. The gas produced was drawn out of the apparatus by a gas-tight glass syringe 10 min after the reaction reached atmospheric pressure. The specific reaction time is calculated when the syringe is filled with 50 mL of product gas. The equation of the hydrogen production rate is shown below.

$$H_2\ (\mu mol/s) = (H_2\ \text{yield}\ \%\ \text{x}\ 50\ \text{mL})/[22400\ \text{mL} \times \text{specific reaction time (s)}] \quad (1)$$

Then, gas produced from decomposition of the glucose was analyzed using a gas chromatograph (GC-8A Shimadzu). Argon gas was used as the carrier gas with a flow rate of 34 mL/min with a head pressure of 600 kPa. Temperatures for the column, injector and detector were 60, 160 and 160^{O}C, respectively.

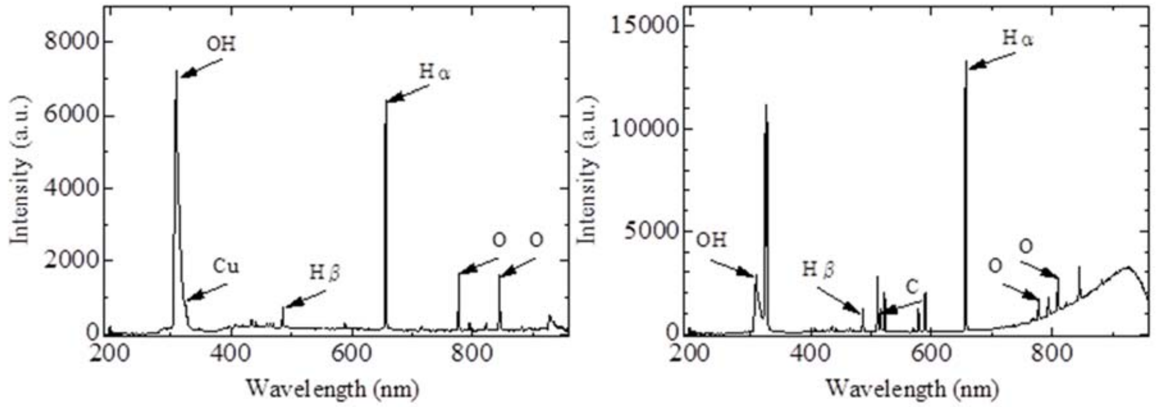
The emission spectrum of the plasma induced by RF was measured using a multichannel spectral analyzer Hamamatsu PMA-11 C7473-36 and the values used are the average values for 5 repetitions over a sampling time of 0.5 seconds.

4.3 Results and Discussions

4.3.1 Plasma emission spectrum

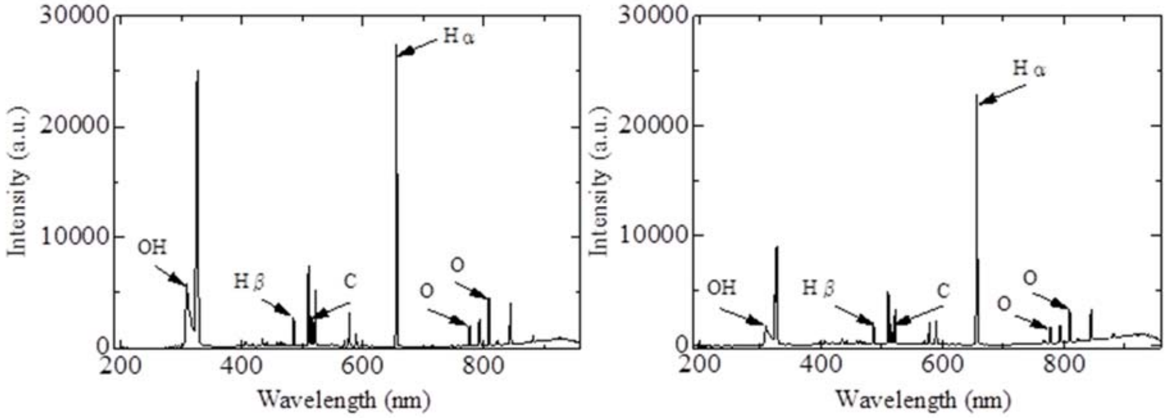
Emission spectroscopy is one of the most important methods for plasma diagnostics. **Fig. 4.2(a)** shows the typical optical emission spectrum for decomposition of pure water by RF in-liquid plasma. It shows that decomposition of pure water generates radicals species including OH (281.1 nm), H_β (486 nm), H_α (656.3 nm), and O (777 and 845 nm). The water molecules are believed to be dissociated into OH radicals and H atoms according to the dissociation reaction [18]–[20]. These radical species in water RF in-liquid plasma are very beneficial for decomposition of glucose. In addition, due to the erosion of the copper electrode in water RF in-liquid plasma, an emission line of Cu atoms is also observed.

Fig. 4.2(b-d) show typical optical emission spectrums for glucose



a) RF : Pure water

(b) RF : Glucose



(b) RF+29 kHz : Glucose

d) RF+1.6 MHz : Glucose

Fig. 4.2 Optical emission spectrum of (a) RF in-liquid plasma pure water, (b) glucose decomposition by RF in-liquid plasma, (c) RF in-liquid plasma with a 29 kHz ultrasonic transducer and (d) RF in-liquid plasma with a 1.6 MHz piezoelectric transducer decomposition by RF in-liquid plasma, RF in-liquid plasma with a 29 kHz ultrasonic transducer and RF in-liquid plasma with a 1.6 MHz piezoelectric transducer, respectively. Active species of C atoms are observed in the emission spectra in addition to OH, H and O. Undoubtedly, the existence of active C species during the decomposition of glucose functions as precursors or intermediaries for other components in the gas product. In fact, the intensity of active C species was greater in RF in-liquid plasma with ultrasonic vibration applied by both the 29 kHz and the 1.6 MHz piezoelectric transducer compared to that of RF in-liquid plasma alone.

4.3.2 Hydrogen production

The experiment was carried out by generating in-liquid plasma by RF at atmospheric pressure with and without ultrasonic vibrations. The initial concentration of glucose solution was varied up to 20 wt%. The power absorption of RF was maintained constantly at 150 W, as calculated by subtraction of the reflected power from generated power.

As a preliminary study, pure water and glucose solution at low initial concentrations of 0.5 wt% were decomposed by RF in-liquid plasma both with

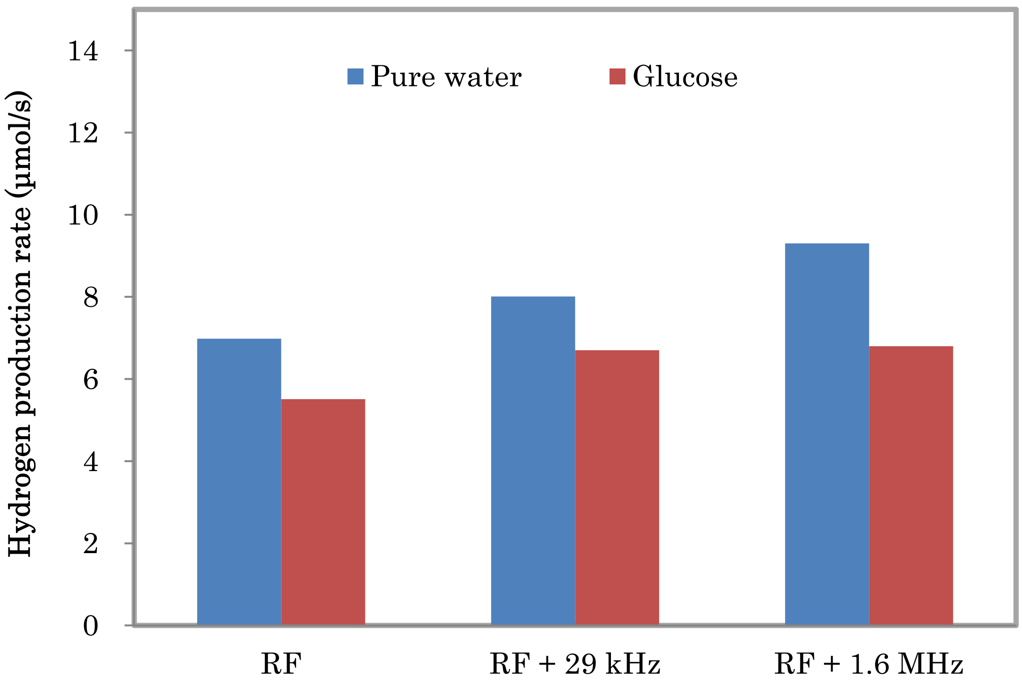


Fig. 4.3 Comparison of hydrogen production rate between pure water and glucose at an initial concentration of 0.5 wt%

and without application of ultrasonic vibrations to observe the effect of ultrasonic vibration on hydrogen production rate as shown in **Fig. 4.3**. It is clearly indicated that the utilization of ultrasonic vibrations enhances hydrogen production rate in both cases. The hydrogen production rate increased 15 to 35% and 20 to 25% for RF in-liquid plasma with ultrasonic vibrations applied for the decomposition of pure water and glucose, respectively.

Though the hydrogen production rate of decomposition of pure water is higher compared to the glucose solution, biomass represents a highly versatile and renewable resource. It amounts to 15% of the world's primary energy consumption and is considered the fourth largest energy source for the world [21]. Utilization of biomass as alternative energy source would be quite beneficial.

Since there is an enhancement of the hydrogen production rate, the study on effect of ultrasonic vibration was continued at higher initial concentration up to 20 wt%. **Fig. 4.4** illustrates the hydrogen production rate as a function of the initial concentration of glucose using RF in-liquid plasma with and without application of ultrasonic vibrations from the 29 kHz ultrasonic transducer and 1.6 MHz piezoelectric transducer. As can be seen, the hydrogen production rate increases as the glucose initial concentration increases for both cases. For the same initial glucose concentration, the utilization of ultrasonic vibrations showed an enhancement of the hydrogen production rate. Moreover, enhancements of 11% and 30% were achieved for the 29 kHz ultrasonic transducer and 1.6 MHz piezoelectric transducer, respectively at the highest initial concentration. Significant enhancement was also achieved for lower initial concentrations as previously described.

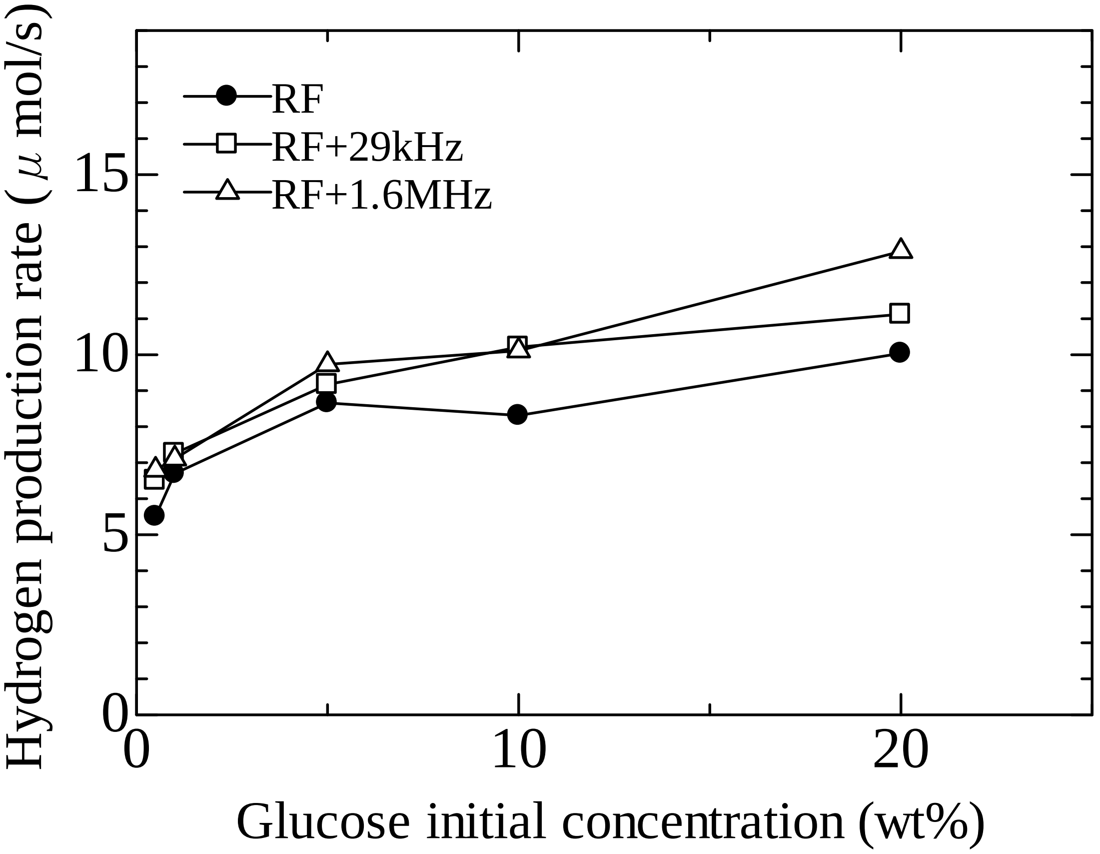


Fig. 4.4 Hydrogen production rate

Fig. 4.5 shows the cumulative hydrogen yield as a function of glucose initial concentration from decomposition of glucose solution using RF in-liquid plasma with and without application of ultrasonic vibrations from the 29 kHz ultrasonic transducer and 1.6 MHz piezoelectric transducer. The hydrogen yield tends to decrease as the glucose initial concentration increases. In spite of the decrease, the hydrogen yield was higher for RF

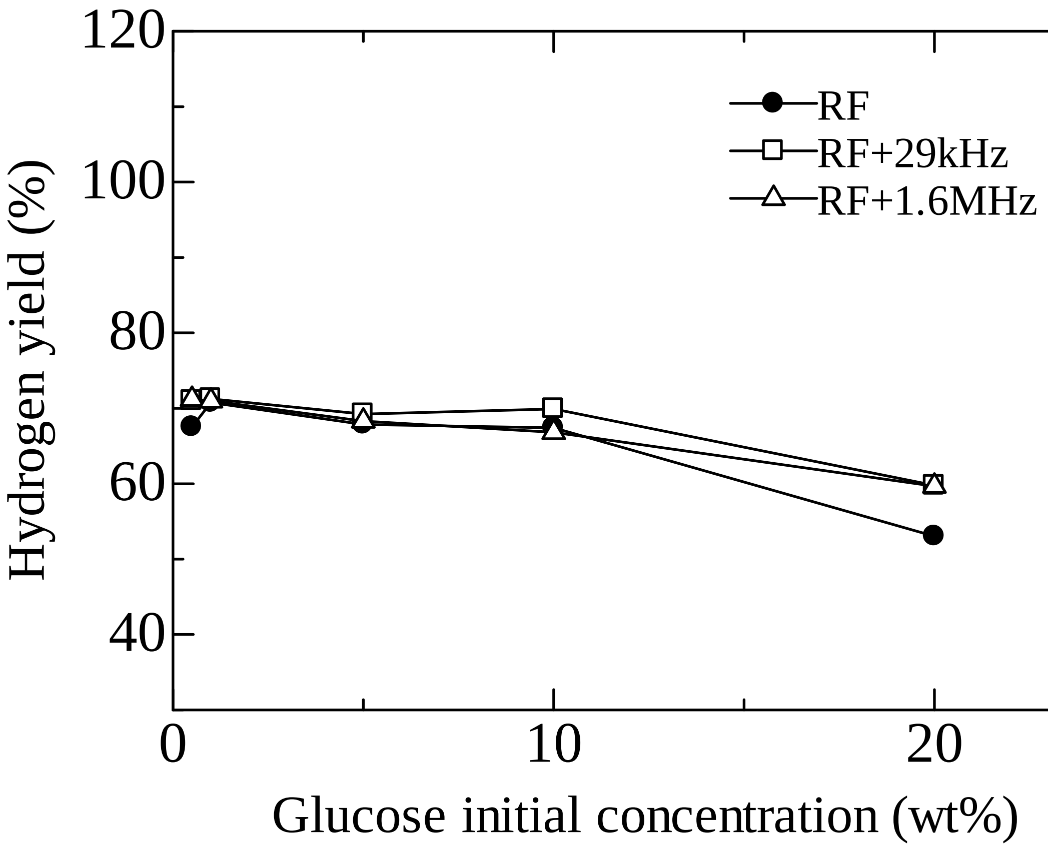


Fig. 4.5 Hydrogen yield

in-liquid plasma with ultrasonic vibrations than that without ultrasonic vibrations especially at an initial concentration of 20 wt%. The highest hydrogen yield obtained was 72% at an initial concentration 1.0 wt% for RF in-liquid plasma with ultrasonic vibrations applied by the 29 kHz ultrasonic transducer. These results are comparable to other biomass gasification methods [22].

The decomposition of glucose solution by using RF in-liquid plasma

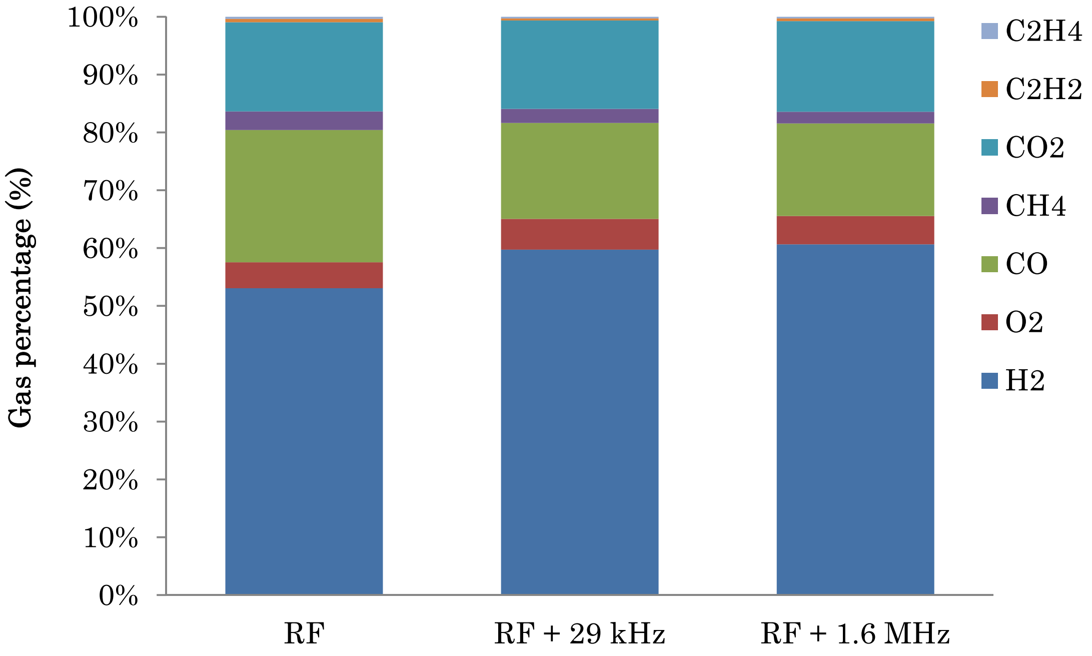


Fig. 4.6 Gas produced from decomposition of glucose solution at an initial concentration 20wt%

both with and without ultrasonic vibrations also produced byproducts as detected by gas chromatograph. **Fig. 4.6** shows that apart from hydrogen (H_2), oxygen (O_2), carbon monoxide (CO), methane (CH_4), carbon dioxide (CO_2), acetylene (C_2H_2) and ethylene (C_2H_4) were also detected.

As can clearly be seen in **Fig. 4.6**, the hydrogen gas increased when ultrasonic vibration was applied at an initial concentration 20 wt% which was similarly described in **Fig. 4.5**. On the other hand, while there was no increase in oxygen, methane or carbon dioxide, carbon monoxide actually

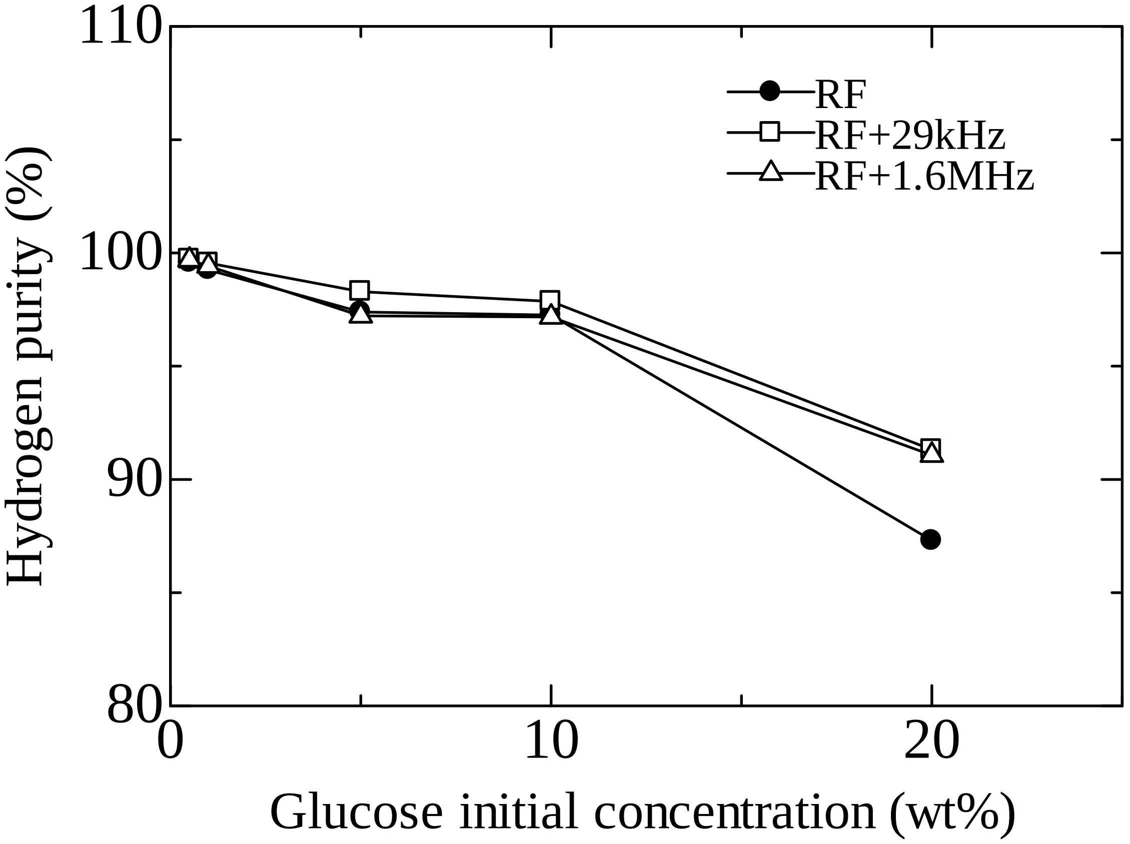


Fig. 4.7 Hydrogen purity

decreased. Since the percentages of acetylene and ethylene were very small, they could be considered negligible.

The hydrogen purity decreases with an increase of the glucose initial concentration as shown in **Fig. 4.7**. The hydrogen purity is defined as the number of H_2 molecules detected in the product gas, normalized by the total number of H atoms in the byproducts. Throughout all initial concentrations, the hydrogen purity increased when ultrasonic vibration was applied. The RF in-liquid plasma with 29 kHz ultrasonic transducer shows a slightly higher enhancement than that of RF in-liquid plasma to which 1.6 MHz piezoelectric transducer was applied between initial concentration of 5 and 10 wt%. The highest enhancement ratio was 5% and 4% for RF in-liquid plasma with the 29 kHz ultrasonic transducer and RF in-liquid plasma with the 1.6 MHz piezoelectric transducer, respectively at an initial concentration of 20 wt%.

The results of this experimental work demonstrate that utilization of ultrasonic vibrations on RF in-liquid plasma for the decomposition of glucose solution enhances the hydrogen production rate, hydrogen yield and hydrogen purity. However, the enhancements depend on the type of ultrasonic vibration used. A higher hydrogen production rate was observed for the 1.6 MHz piezoelectric transducer over that of 29 kHz ultrasonic transducer, this was reversed for hydrogen yield and hydrogen purity.

It is fully understandable that most of the OH and H radicals formed from dissociation reaction of water in the cavitation bubbles react with glucose molecules and hence, produce hydrogen gas and byproducts.

Formation of active C species atoms in the emission spectrum as shown in **Fig. 4.2(b-d)** also suggests that glucose molecules were decomposed into intermediary and final products. The higher intensity of active C species atoms for RF in-liquid plasma with ultrasonic vibration than that for RF in-liquid plasma alone suggests that continued ultrasonic vibration enhances the chemical reaction [23]. This could indicate that the decomposition of glucose was affected by chemical effects due to the formation of radicals produced from dissociation of water molecules [24].

The higher hydrogen production rate obtained when using RF in-liquid plasma irradiated with the higher range frequency ultrasonic vibrations, from the 1.6 MHz piezoelectric transducer as compared to that of lower range frequency ultrasonic vibrations, from the 29 kHz ultrasonic transducer is due to acoustic streaming which provides a high mass flux to the bubble and hence the bubble evaporates easily due to buoyancy as previously described in [17].

Higher hydrogen yield and hydrogen purity for the 29 kHz ultrasonic transducer than that of the 1.6 MHz piezoelectric transducer could be due to the agitation effect of the ultrasonic vibrations themselves. The agitation of the bubbles enhanced the heat transfer coefficient and chemical reaction resulting in a greater hydrogen yield and hydrogen purity [25]. If a single cavitation bubble is considered, the larger shock waves and microjets that occurred during the cavitation event broke the chains of the glucose molecules. Consequently, the broken glucose chains were decomposed by the plasma inside the bubble [26], [27]. This phenomenon is called the mechanochemical action of ultrasonic vibration. Moreover, the higher collapse temperature for lower ultrasound frequency leads to a faster OH radical production rate which decomposes glucose molecules for hydrogen production [28]. Additionally, the lower OH intensity in glucose solution than that in pure water as shown in **Fig. 4.2** indicates that a higher solution viscosity may reduce the intensity of cavitation and result in a decreased hydrogen yield and hydrogen purity [29].

4.3.3 Hydrogen production efficiency

The hydrogen production efficiency of the RF in-liquid plasma decomposition process must be considered an important factor because this is not just a measure of the decomposition of glucose process for hydrogen production but also a measure of energy efficiency, which relates to any future commercial value. Thus, **Fig. 4.8** illustrates the hydrogen production efficiencies for RF in-liquid plasma with and without application of ultrasonic vibrations for hydrogen production. The hydrogen production efficiency is defined as the output energy versus input energy. The energy in the outlet stream is defined as the molar flow of hydrogen multiplied by the lower heating value of hydrogen and the input energy is defined as the electric power for the plasma generation.

In this experiment, the hydrogen production efficiency increased as initial glucose concentrations increased. Cumulatively, however, the hydrogen production efficiency is relatively low for RF in-liquid plasma with ultrasonic vibrations applied compared to RF in-liquid plasma without ultrasonic vibration due to the higher total input power required to induce ultrasonic vibration along with RF. This is true for most cases except for decomposition of glucose 20 wt% by RF in-liquid plasma with application of ultrasonic vibrations by the 1.6 MHz ultrasonic transducer which was 7% higher than that without ultrasonic vibrations.

It is well known that the pH of the aqueous solution affects the

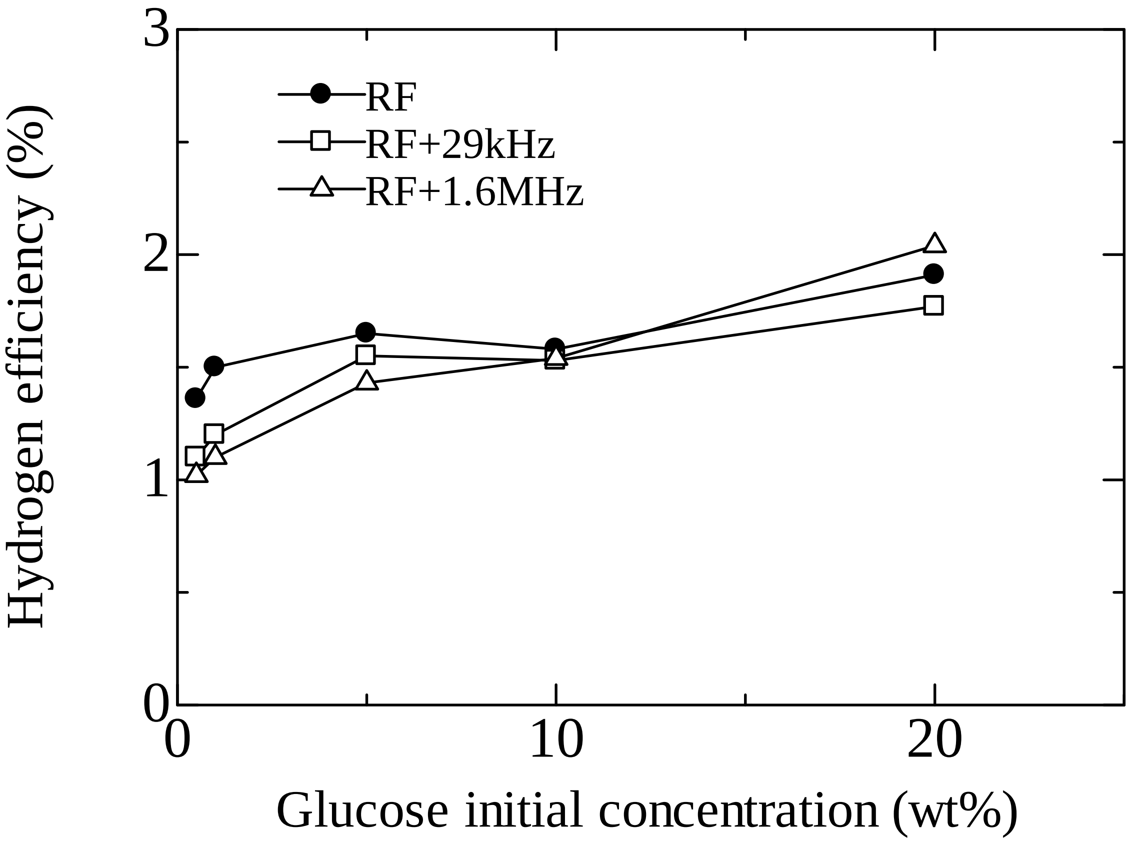


Fig. 4.8 Hydrogen production efficiency

oxidation processes. Previous studies agree that the decoloration of dye using photolysis process is more effective at low pH values than that at high pH values [30]. The obtained results in this study show that the initial pH values of glucose solutions up to 20 wt% were 6. It was then found that after the decomposition processes by RF in-liquid plasma with and without ultrasonic vibration, the pH values of the glucose solutions were reduced to 3 for all solutions examined. The increases of hydrogen production efficiency as shown in **Fig. 4.8** could be explained by the fact that decreases of the pH favor the formation of H_3O^+ ions and hydroxyl radicals in the water due to the electronic and ionic bombardment [31]. Formation of hydroxyl radicals enhances the oxidation process.

The hydrogen yield is a major challenge that must be improved in the future in order to enhance the hydrogen production efficiency of RF in-liquid plasma with ultrasonic vibration. Though the hydrogen production efficiency is low for RF in-liquid plasma with ultrasonic vibrations, this process does not use any catalyst for hydrogen production making it possible to be considered as a promising technique in the future.

4.4 Conclusion

This early finding of mechanism of hydrogen production stimulated extensive interests in RF in-liquid plasma with ultrasonic vibration. The process of RF in-liquid plasma with and without ultrasonic vibrations induced formation of OH and H radicals that are important for decomposition of glucose molecules. Formation of C atoms in the emission spectrum clarified that glucose molecules were decomposed into hydrogen gas and byproducts.

The hydrogen production rate was enhanced 11% and 30% for RF in-liquid plasma with ultrasonic vibrations applied by the 29 kHz ultrasonic transducer and the 1.6 MHz piezoelectric transducer, respectively at an initial concentration of 20 wt%. The average enhancement ratios of hydrogen yield obtained were 5% and 3% for RF in-liquid plasma with the 29 kHz ultrasonic transducer and the 1.6 MHz piezoelectric transducer, respectively. The hydrogen purity was enhanced by 5% and 4% for RF in-liquid plasma with the 29 kHz ultrasonic transducer and with the 1.6 MHz piezoelectric transducer, respectively at an initial concentration of 20 wt%.

The enhancement of the hydrogen production rate, hydrogen yield and hydrogen purity depends on the types of the ultrasonic vibration used. A higher range frequency, 1.6 MHz piezoelectric transducer enhanced the hydrogen production rate. On the other hand, a lower range frequency, 29 kHz ultrasonic transducer enhanced the hydrogen yield and hydrogen purity of the glucose decomposition. A combination of acoustic streaming and agitation effect from both higher and lower range frequencies of ultrasonic vibration could possibly be applied for better hydrogen production process.

Consideration of hydrogen production efficiency is one of the most important factors when evaluating the hydrogen production process. Though the hydrogen production efficiency of RF in-liquid plasma with ultrasonic vibrations was generally lower than that without ultrasonic vibrations except at an initial concentration of 20 wt% for RF in-liquid plasma with application of ultrasonic vibrations by the 1.6 MHz ultrasonic transducer which was 7% higher than that without ultrasonic vibrations, it still can be considered as a promising technique for hydrogen production in the future.

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Chapter 5

General Summary

In this research, the fundamental study was conducted to produce hydrogen gas from polysaccharides, the abundant compounds in the universe, as a sustainable fuel for future. Glucose solution and cellulose suspension were decomposed by using 27.12 MHz radio-frequency in-liquid plasma with and without ultrasonic vibration.

In Chapter 3, the experimental study found that the production rate of hydrogen from decomposition of glucose solution by RF in-liquid plasma with ultrasonic irradiation applied was higher than that without ultrasonic irradiation. However, no enhancement effect of hydrogen production rate was found for the decomposition of cellulose suspension by RF in-liquid plasma with ultrasonic irradiation. In addition, high-speed camera imagery of the pattern of bubble generation by RF with the 1.6 MHz piezoelectric transducer indicated that acoustic streaming had been occurring. This raises the prospect of investigating the mechanism of acoustic streaming on plasma inside a bubble for future research.

The detailed mechanism of decomposition of glucose solution by 27.12 MHz radio-frequency in-liquid plasma with and without ultrasonic vibration for hydrogen production was investigated in Chapter 4. The findings of mechanism of hydrogen production stimulated extensive interests in RF in-liquid plasma with ultrasonic vibration. The process of RF in-liquid plasma with and without ultrasonic vibrations induced formation of OH and H radicals that are important for decomposition of glucose molecules. The enhancement of the hydrogen production rate, hydrogen yield and hydrogen purity depends on the types of the ultrasonic vibration used. A higher range frequency, 1.6 MHz piezoelectric transducer enhanced the hydrogen production rate. On the other hand, a lower range frequency, 29 kHz ultrasonic transducer enhanced the hydrogen yield and hydrogen purity of the glucose decomposition. A combination of acoustic streaming and agitation effect from both higher and lower range frequencies of ultrasonic vibration could possibly be applied for better hydrogen production process. The hydrogen production efficiency of RF in-liquid plasma with ultrasonic vibrations was generally lower than that without ultrasonic vibrations but it still can be considered as a promising technique for hydrogen production in the future.