Fuel Production and Materials Synthesis by In-liquid Plasma

Shinfuku Nomura 1
1Graduate school of Science and Engineering, Ehime University, Japan

Abstract. The in-liquid plasma process has been utilized to produce fuel gases from various liquids such as hydrocarbon and alcohol liquids, electrolytes, waste oil, biomass solutions, including glucose and cellulose, as well as to synthesize Zn, ZnO, WO3, Mg(OH)2 nanoparticles and diamonds. Using this technology, zero-emission hydrogen generation could become possible because it enables liquids to be directly broken down by plasma, making possible the decomposition of waste substances while producing useful materials. The application of the in-liquid plasma process for hydrogen production, decomposition of biomass, and synthesis of materials has already produced significant results. These highlight data will provide new information on “in-liquid plasma application.

1. Introduction
These Various methods have been proposed to date for discharge phenomena in liquids, such as DC / AC, pulse, high frequency, microwave, equilibrium plasma, non-equilibrium plasma, and so on. These discharge phenomena are called pulse or arc discharge in liquid, in-liquid plasma, solution plasma etc., depending on the discharge form and discharge method [1-4]. We call plasma in liquid “in-liquid plasma”, using microwave (primarily 2.45 GHz MW) or high frequency radio generation (13.72 MHz or 27.12 MHz RF) [5]. The generated plasma is called MW in-liquid-plasma and RF or High Frequency (HF) in-liquid plasma. In-liquid plasma is used broadly to refer to plasma in liquid. The reason we use plasma in these frequency bands is that they generate a gas phase plasma process for which most of the know-how regarding its application has been accumulated so far. Using this method, plasma generate bubbles within which the pressure is up to 200 times that of atmospheric while the surrounding liquid remains at room temperature and normal pressure [6-8]. In addition a supercritical state can be generated allowing its application range to be diversified. By using this reaction field, waste can be rendered harmless, decomposed, and materials can be synthesized.

Here, we will discuss a variety of applications of the in-liquid plasma method such as for hydrogen production from waste liquids or non-edible biomass, nanoparticle production for use in batteries and printed electronics.

2. Hydrogen production by the in liquid plasma process
2.1 Decomposition of hydrocarbon-based liquids
When plasma is generated in hydrocarbons, a chemical reaction is created that reaches 3500 K in atmospheric pressure which produces hydrocarbons hydrogen and solid carbon by thermal decomposition [9]. This technology can decompose various substances and recover hydrogen as a fuel gas. In the case of MW in-liquid plasma, it is relatively easy to generate in-liquid plasma simply by installing electrodes to increase the electric field strength in a conventional MW oven [9,10]. Table 1 shows the gas generation rate and the volume percentages of component gasses obtained by decomposition of hydrocarbon-based liquids using the in-liquid plasma process.

For hydrocarbons such as n-dodecane (C12 H26), ideally it would be decomposed into hydrogen and solid carbon (13 moles hydrogen gas and 6 moles solid carbon), but in actuality, in addition to the
target hydrogen gas, other hydrocarbon components such as methane gas and acetylene are generated. Since hydrocarbon-based liquids naturally contain a large amount of hydrogen, a method for safe storage and use of hydrogen is necessary. To that end, development of a compound called organic hydride is under way \cite{11}. Oxides, such as CO and CO$_2$, are also generated when hydrocarbons are decomposed. The contents of the decomposition products depends on the components of the liquid, but for hydrocarbons or alcohols, 50% to 90% of the decomposition products is hydrogen gas, with the remainder being hydrocarbon components and solid carbon. While in-liquid plasma can be used as a recycling technology to make hydrogen from waste oil, energy is required for hydrogen production. From the viewpoint of extracting hydrogen from waste and using it as energy, EPR$_{H_2}$ the input energy to recoverable energy ratio \cite{12, 13}, is found to be 0.16 for engine oil and 0.52 for methanol decomposition as is calculated by the following Eq.(1). Since energy is required to generate plasma, it naturally becomes 1 or less.

$$\text{EPR}_{H_2} = \frac{n_{H_2} \times \Delta H_{H_2}}{P}$$ (1)

Here, $n_{H_2}$ is the gas production rate of H$_2$ (mol / s), $\Delta H_{H_2}$ is the heat of combustion of hydrogen (J / mol), $P$ is input power of MW (W)

When water is pyrolyzed by plasma, hydrogen and oxygen are generated (part of the generated oxygen is dissolved in water, so that the ratio of the generated gas does not exactly become 2:1), the gas production rate $\nu$ is slower than other hydrocarbons and alcohol liquids. Comparisons of the gas production rate are shown in Table 1 where it can be seen that the in-liquid plasma method has a hydrogen gas production rate that is 30% - 100% that of the electrolysis of alkaline water. \cite{9, 11-15}. Since the product gas from decomposition is not purely 100% hydrogen, a separation and recovery system is required for application to fuel cells. At present application of this method for large scale generation of hydrogen is not practical unless the gas production rate during decomposition is increased by several orders or the hydrogen purity is greatly improved. In order to apply this method to an actual machinery, it is necessary to develop a process such that total EPR becomes 1 or greater by advancing methods to recover usable solid carbon components or other valuable resources produced in the decomposition process.

2.2. Steam reforming experiment

The steam reforming method of natural gas is a technology established for commercially producing large amounts of hydrogen and is described by an endothermic reaction of Eq. (2) and a shift reaction of Eq. (3).

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2, \quad \Delta \text{H}_{298 \text{K}} = +206 \text{kJ/mol} \quad (2)$$

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2, \quad \Delta \text{H}_{298 \text{K}} = -41 \text{kJ/mol} \quad (3)$$

| Table 1. Composition gasses and components for hydrogen production by various in-liquid plasma methods |
|---------------------|-----------------|--------|------|------|------|------|------|
| Liquid | Method | Input power (W) | $\nu$ (ml/s) | H$_2$ | O$_2$ | CO | CH$_4$ | CO$_2$ | C$_2$H$_6$ | C$_2$H$_4$ |
| Engine oil | MW | 700 | 10.9 | 82.0 | 0.2 | 0.6 | 1.8 | 0.1 | 13.4 | 1.9 | 0.16 |
| n-dodecane \cite{9} | MW | 750 | 35.7 | 74.0 | 0.0 | 0.0 | 2.0 | 0.0 | 20.0 | 2.0 | 0.45 |
| Methanol | RF | 200 | 12.6 | 64.8 | 0.0 | 32.2 | 1.8 | 0.3 | 0.9 | 0.1 | 0.52 |
| Cellulose (20 wt\%) \cite{15} | RF | 150 | 0.3 | 45.6 | 13.1 | 17.4 | 1.2 | 18.1 | 0.3 | 4.3 | 0.01 |
| Cellulose (40 wt\%) \cite{15} | RF | 150 | 3.1 | 36.8 | 0 | 31.9 | 1.7 | 25.2 | 0.7 | 3.8 | 0.10 |
| Pure water | RF | 200 | 0.39 | 82.4 | 17.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.02 |
| n-dodecane with Steam \cite{10} | MW | 250 | 12.5 | 73.8 | 0 | 12.9 | 2.5 | 0 | 6.8 | 3.9 | 0.47 |
| Water-oil interface \cite{14} | RF | 250 | 5.3 | 62 | 0 | 23 | 3 | 2 | 6 | 4 | 0.32 |
From 1 mol of methane gas and 2 moles of water, 4 moles of hydrogen and 1 mol of carbon dioxide are produced. Therefore, the hydrogen production energy per 1 mol is significantly lower than that by electrolysis of water. By introducing water to oil decomposition when using the in-liquid plasma and inducing a steam reforming reaction, the amount of hydrogen generated is increased. The water may be introduced into the plasma reaction field directly from a cavity inside the electrode as shown in Fig. 1 (a) or by generating plasma near the interface between oil and water as shown in Fig. 1 (b). As shown in Fig. (a), water is supplied from the inside of the hollow electrode and becomes steam due the plasma which results in the generation of 12.9% of CO.

In addition, as shown in Fig. 2, this reaction increases the hydrogen gas production rate up to 1.4 times as compared to that without steam supply [13]. The comparison of with and without water steam in n-dodecane shown in Table 1 indicates that there was no difference in hydrogen purity, which means that the amount of hydrogen produced increased by steam introduction. However, for the method of Fig. 1, no shift reaction of CO and H₂O described in Eq. (3), which is found in the methane steam reforming method, was confirmed. Although the amount of steam supplied to the reaction field is small, MW absorbed by water as the amount of water passing through the electrode increases, the generation of plasma itself was difficult for 2.45 GHz MW plasma. On the other hand, in Fig. 2 (b), since RF of 27.12 MHz is used, there is no influence of water absorption, and when the tip of the electrode is installed on the lower water side, the influence of adhesion of carbon components to the electrode can be prevented. In this case, CO₂ is generated with hydrogen generation of about 60 to 71%, and the shift reaction can be confirmed. However, the amount of CO₂ generated is as small as 2%, conversely, it means that water is thermally decomposed, and the gas production rate during decomposition decreases.

Fig. 3 shows a chemical equilibrium diagram when the ratio of n-dodecane and water is (a) 10: 1 and (b) 1: 100. The gas temperature of the plasma at atmospheric pressure is about 3500 K. When water is not sufficiently supplied, only CO is generated, however, in (b), where the ratio of water is increased,
the generation of CO2 becomes conspicuous. Although the generation of CO and CO2 depends on the amount of water in the reaction field, water is thermally decomposed within the plasma. When the amount of water is increased, energy is consumed for water decomposition. Therefore, in order to take advantage of the steam reforming reaction, it is necessary to adjust the amount of water supplied to the reaction field to optimize the steam reforming reaction.

(a) \( \text{C}_{12}\text{H}_{26} \cdot \text{H}_{2} \text{O} = 10:1 \)

(b) \( \text{C}_{12}\text{H}_{26} \cdot \text{H}_{2} \text{O} = 1:100 \)

Figure 3. Thermal equilibrium composition of the mixture of \( n \)-dodecane and water \([14]\)

2.3 Decomposition of cellulose
The results for the decomposition experiments carried out on cellulose powder are also shown in Table 1 and Fig. 4 for comparison. The amount of gas generated changes greatly depending on cellulose concentration. Since cellulose is insoluble, at a concentration of 27 wt% and below, the cellulose powder is dispersed in water. As the concentration of the cellulose increases, the relative amount of water decreases, so the diameter of the powder grains becomes smaller. Since cellulose is a nonvolatile substance, it does not enter into bubbles created by the heat of plasma evaporating the surrounding water. Therefore, decomposition of cellulose is an indirect decomposition of OH radicals existing around the bubble. At 30 wt%, the cellulose grains containing water (hydrated cellulose particles) are pushed out of the plasma region due to the pressure of bubble created by plasma generation and air gaps form in the plasma region without returning to their original positions due to the contact resistance between the particles with large diameter grains. Hence, the plasma cannot reach the cellulose grains containing water.

At 40 wt% and above, the cellulose enters a state of high viscosity, and the discharge of the plasma comes into direct contact with the cellulose powder, and the generation gas significantly increases. The fluidity disappears at 50 wt%, when the contact with the plasma is continued for an extended time resulting in the carbonization of the contact surface of cellulose and plasma. It may be possible to directly gasify cellulose itself using thermal plasma such as direct current arc discharge, however, the decomposition mechanism varies depending on the weight ratio of the substances dispersed in water for decomposition \([12]\).

Figure 5 shows a summary of the hydrogen production rate in the form of EPR of Eq. (1) under various conditions. It is lowest in water, higher for cellulose and engine oil, and over 50% for methanol. Results for cellulose dispersed in an acid solvent such as diluted sulfuric acid or sodium hydroxide are shown in Fig. 5. In these solutions, the hydrogen production is larger than when cellulose powders are dispersed in water at the same weight ratio (20 wt%) \([12]\). The ions in the electrolyte collide with the electrode, resulting in emission of secondary electrons and the plasma region increases. The effect of sodium hydroxide is particularly remarkable.

Even with the same saccharide, monosaccharide glucose dissolves in the liquid, so it can be decomposed by plasma. When used in combination with ultrasound, decomposition is promoted and ultrasonic irradiation has a beneficial effect on plasma decomposition of saccharides \([17]\).
2.4 Effect of catalyst introduction and type of catalyst

Because in-liquid plasma is generated within bubbles in the liquid, decomposition rates improve when bubbles are held in place by control plates installed above the electrodes as shown in Figs. 6 and 7. The effect of the shape and material of plates are summarized in Fig. 6. The use of copper or nickel for the electrode, and solid copper, solid nickel, porous ceramics, porous bronze and porous nickel for the control plate, have been investigated as to the effect of catalytic reaction. The gas generation rate for each combination of plate and electrodes have been compared. When the plate is placed above the electrode, the hydrogen production rate increases by 2.5 to 3.6 times [16]. The most effective device configuration in this experiment is a nickel electrode combined with a nickel porous plate. Separately, plasma decomposition of water was carried out under these configurations, however almost no differences were found for the combinations of these materials. The effect of nickel appears for methanol decomposition but not for water decomposition. However, the simple installation of a bubble control plate made of catalytic metal in in-liquid plasma reaction field improves the decomposition rate for compounds other than water. It is effective to construct the material of the electrode and plate from catalytic metals.

![Figure 4](image1.png)

Figure 4. Gas production rate obtained by plasma decomposition of cellulose [15]

![Figure 5](image2.png)

Figure 5. Energy yield of in-liquid plasma in various media [9,12,15]
3. Synthesis of metallic nanoparticles by in-liquid plasma

The synthesis mechanism of nanoparticles is obtained through processes of evaporation of metal by plasma which aggregates near the gas-liquid interface and precipitates out. At this time, the nanoparticles exist in a dispersed state in the liquid. The synthesis method of nanoparticles by in-liquid plasma is basically realized by inserting the raw metal to be converted into the plasma. If a metal with a low melting point is used for the plasma electrode, the electrode itself can be evaporated and it can be recovered, but then, since the condition of the plasma changes as the electrode is damaged, it is not suitable for synthesis of nanoparticles. Therefore, as shown in Fig. 7, there is a method for introducing metal as a thin wire into the plasma [18].

Nanoparticles of interest can be synthesized depending on the type of raw material and liquid utilized. The synthesis of nanomaterials by in-liquid plasma has been reviewed in detail in reference (3). For example, ZnO nanoparticles are synthesized by injecting zinc into plasma in pure water, whereas Zn particles are synthesized in plasma in ethanol [19]. It is generally known that ZnO nanoparticles become flower-type crystals [19], while Zn assumes a hexagonal crystal structure [20], however, after detailed analysis, Zn turned out to be cubic in liquid plasma (See Fig. 8).

It is believed that there is a severe quenching effect or intense temperature gradient in the reaction field of plasma submerged in liquid that makes it easier for a cubic structure to form, but this mechanism has yet to be clarified. Metal reduction by plasma can also be applied to recycle metal oxides after use such as Zn and Mg used as negative active materials in batteries [21]. However, the method for reducing a large amount of metal oxide depends on how best to bring these metals into contact with the plasma reaction field. Separately, there is already a method of reducing zinc oxide by using RF dielectric heating [22].

Table 2 summarizes the production of nanoparticles using in-liquid plasma including laser ablation. Compared with the laser ablation method, the in-liquid plasma method is much more effective, and it is convenient that nanoparticles can be recovered in a state of being dispersed in the liquid. A method for precisely controlling the particle diameter by controlling various plasma parameters has not yet been established. Synthesis of low-melting-point metal nanoparticles such as Sn or Cu by plasma in liquids has been reported [26].

4. Conclusion

At the gas-liquid interface exposed to the in-liquid plasma, active species are generated in which electrons are excited into various orbits. This environment can be used for a variety of purposes. For
example, phenol can be synthesized in a single process by reacting benzene at the plasma interface in water \[27\]. This reaction is a simple one in which OH is bonded to the benzene ring. However, in the standard chemical process, this requires a plurality of processes using an acid catalyst and such. Whereas when in-liquid plasma is used, the radical reaction occurs as a simple chemical reaction. One of the advantages of decomposition and synthesis by plasma in liquid is that the expensive catalysts and microorganisms necessary for the chemical reaction processes for organic synthesis and decomposition of substances difficult to decompose are no longer required. This would eliminate the reliance on the use rare metals for radical reactions. We believe that it is important to be able to convert to a process that does not require rare metals even in fuel production and material synthesis processes using plasma in the future.

Fig. 7 Synthesis of nanoparticles by in-liquid plasma

Fig. 8 TEM image of zinc nanoparticles: (a) flower-type nanoparticles \[19\], (b) cubic zinc nanoparticles

Table 2

| Particles     | Target | Liquid            | Productivity (g/hour) | Efficiency (μg/J) | Electrical source          |
|---------------|--------|-------------------|-----------------------|-------------------|---------------------------|
| Mg(OH)\(_2\) [18] | Mg     | Water             | 66                    | 80.2              | MW: 160W                  |
| Zn/ZnO [18]   | Zn     | Water             | 14                    | 20.4              | MW: 135W                  |
| Ag [18]       | Ag     | Water             | 0.8                   | 0.74              | MW: 220W                  |
| Zn [20]       | Zn     | Ethanol, Menthol  | 3.3                   | 2.6               | MW: 250W                  |
| ZnO [24]      | -      | Zn(CH\(_3\)COO)\(_2\) | 4.2                  | 1                 | MW: 800W                  |
| Zn/ZnO [25]   | Zn     | Tetrahydrofuran   | 0.016                 | 5                 | YAG laser 125 mJ/pulse    |
|               |        |                   |                       |                   | Repetition rate: 5kHz     |
|               |        |                   |                       |                   | MW: 220W                  |
| WO\(_3\) [23] | W      | Water             | 15.5                  | 13.65             |                           |

Synthesis of nanoparticles by plasma in liquid
References

[1] Bruggeman P J, etal., 2016 Plasma Sources Sci. Technol. 25 053002
[2] Yang Y, Cho Y I , Friedman A, 2012 Plasma Discharge in Liquid, CRC Press, ISBN 9781138074958
[3] Horikoshi S and Serpone N, 2017 RSC Adv. 7 47196
[4] Tsuchida A, Shimamura T, Sawada S, etal., 2018 Radiation. Phys. Chem. 147 53
[5] Nomura S, Toyoda H, Mukasa S, Takahashi Y, Maehara T, Kawashima A, and Yamashita H, 2008 Appl. Phys. Express, 1 046002
[6] Nomura S, Mukasa S, Toyoda H, Miyake H, Yamashita H, Maehara T, Kawashima A and Abe F, 2011 Plasma Sources Sci. Technol. 20 034012
[7] Kawashima A, Nomura S, Toyota H, Takemori T, Mukasa A and Maehara T, Nanotechnology, 2007 18 495603
[8] Rahim I, Nomura S, Mukasa S, Toyota H, 2015 Appl. Therm. Eng., 90 120
[9] Nomura S, Toyoda H, Mukasa S, Yamashita H, Maehara T, and Kawashima A, 2009 J. Appl. Phys., 106 073306
[10] H. Toyota, S. Nomura, S. Mukasa, International Journal of Materials Science and Applications, 2 (2013) 83
[11] Alhumaidan F, Cresswell D, and Garforth A, 2011 Hydrogen Storage in Liquid Organic Hydride, Energy Fuels, 25 4217
[12] Tange K, Nomura S, Mukasa S, Toyota H, Syahrial F, 2016 J. Jpn. Inst. Energy. 95 1105
[13] Moctar A A, Nomura S, Mukasa S, Toyoda H, Kawamukai K, 2017 J. Jpn. Inst. Energy. 96 86
[14] Yamane R, Nomura S, Kawamukai K, Mukasa S, Toyoda H, 2017 54th National Heat Transfer Symposium of Japan, CD-ROM H144 (in Japanese).
[15] Rahim I, Nomura S, Mukasa S, etal., 2015 Journal of Power and Energy Engineering, 3 28
[16] Shiraiishi R, Nomura S, Mukasa S, Nakano R, Kamatoko R, 2018 Int. J. Hydrog. Energy, 43 4305
[17] Syahrial F, Nomura S, Mukasa S, Toyota H, Okamoto K, 2015 Int. J. Hydrog. Energy, 40 11399
[18] Hattori Y, Nomura S, Mukasa S, Toyota H, Inoue T, Usui T, 2013 Journal of Alloys and Compounds, 578 148
[19] Saito G, Nakasugi Y, Yamashita T, Akiyama T, 2014 Applied Surface Science, 290 419
[20] Hattori Y, Mukasa S, Toyota H, Inoue T, Nomura S, 2010 Materials Letters, 65 188
[21] Amaliyah N, Mukasa S, Nomura S, Toyota H, Kitamae T, 2015 Mater. Res. Express, 2 025004
[22] Mukasa S, Udaka Y, Matsuzawa K, Doi N, Toyota H, Nomura S, 2017 J. Jpn. Inst. Energy, 96 357
[23] Hattori Y, Mukasa S, Toyota H, Inoue T, Nomura S, 2011 Mater. Chem. and Phys., 131 425
[24] Yonezawa T, Hyono A, Sato S, Ariyada O, 2010 Chem. Lett., 39(7) 783
[25] Wagener P, Schwenke A, Chichkov B N, Barcikowski S, 2010 J. Phys. Chem. C, 114 7618
[26] Saito G, Wan Omar Sidiq Bin Wan Mohd Azman, Nakasugia Y, Akiyama T, 2014 Advanced Powder Technology, 25 1038
[27] Agung M, Nomura S, Mukasa S, Toyota H, Otsuka K, 2017 Plasma Sci.& Technol. 19, 055503