Decomposition of water-insoluble organic waste by water plasma at atmospheric pressure

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Abstract. The water plasma was generated in atmospheric pressure with the emulsion state of 1-decanol which is a source of soil and ground water pollution. In order to investigate effects of operating conditions on the decomposition of 1-decanol, generated gas and liquid from the water plasma treatment were analysed in different arc current and 1-decanol concentration. The 1-decanol was completely decomposed generating hydrogen, carbon monoxide, carbon dioxide, methane, treated liquid and solid carbon in all experimental conditions. The feeding rate of 1-decanol emulsion was increased with increasing the arc current in virtue of enhanced input power. The generation rate of gas and the ratio of carbon dioxide to carbon monoxide were increased in the high arc current, while the generation rate of solid carbon was decreased due to enhanced oxygen radicals in the high input power. Generation rates of gas and solid carbon were increased at the same time with increasing the concentration of 1-decanol, because carbon radicals were increased without enhancement of oxygen radicals in a constant power level. In addition, the ratio of carbon dioxide to carbon monoxide was increased along with the concentration of 1-decanol due to enhanced carbon radicals in the water plasma flame.

1. Introduction
Thermal plasma technology has been receiving attention as an advanced waste treatment method [1, 2]. The thermal plasma provides high temperature over thousands degrees and a large amount of chemically active species to decompose any kinds of non-degradable materials easily. Especially, gases used as an energy source such as hydrogen and carbon monoxide are synthesized in the thermal plasma treatment of organic wastes when oxygen radicals are existing in the thermal plasma flame by supplying oxygen or steam as the plasma forming gas [3-5]. In order to take advantage of abundant oxygen, hydrogen and hydroxyl radicals in the organic waste treatment process, a unique direct current (DC) arc water plasma torch has been introduced recently [4-7]. Besides the radicals that promote chemical reactions of the waste decomposition and the syngas production, the water plasma torch has benefits of high thermal efficiency and simple system because evaporated water is directly used as plasma supporting gas and coolant. Therefore, the water plasma is believed as a promising method to treat organic waste.

Although thermal plasma flame has high temperature, it also has a steep temperature gradient. In order to utilize the high temperature of arc discharge region, water-soluble organic waste can be supplied as a plasma forming liquid for the water plasma in a solution state [4]. On the contrary, water-insoluble waste is unfeasible to be used as plasma forming material directly. The emulsion including water-insoluble organic compound was used as plasma forming liquid instead of pure water...
in this work. As a model organic waste, 1-decanol (C\textsubscript{10}H\textsubscript{22}O) which is widely used in agricultural chemicals was mixed with water uniformly with the help of Tween60 (C\textsubscript{64}H\textsubscript{126}O\textsubscript{26}) surfactant. With the 1-decanol emulsion, the demonstration of water plasma treatment of water-insoluble organic waste was conducted in the present work. Effects of the arc current and 1-decanol concentration on the gas and liquid products were investigated to understand the characteristics of 1-decanol emulsion treatment with the water plasma.

2. Experimental Setup

2.1. Water plasma system

The schematic diagram of the water plasma system used in this work is depicted in figure 1. The 1-decanol emulsion filled in a liquid reservoir is transferred to the arc discharge region through a liquid absorber. High heat flux from the DC arc plasma evaporates transferred emulsion, and then the emulsion is supplied to plasma forming gas. Therefore, 1-decanol is directly decomposed in the high temperature region of the arc plasma. Decomposed substance reacts further with abundant radicals in the plasma flame generating treated gases. The generated gas was analysed by a quadrupole mass spectrometry (QMS, Dycor-Proline, AMENETEK) and a gas chromatography (GC, GC-8ATP, Shimadzu). Condensed solid carbon and liquid were generated on the wall of a cooling reactor. The treated liquid was collected through a hole on the reactor bottom and analysed by a total organic carbon (TOC) analyser (TOC-V CSN, Shimadzu) and a high-performance gas chromatography (HPLC, pump: U-986, Jasco, column thermostat: CO-966, Jasco) with an ultraviolet-visible detector (UV-975, Jasco).

![Figure 1. Schematic diagram of the water plasma system for the decomposition of 1-decanol emulsion.](Image)

The water plasma torch was operated at atmospheric pressure and the electrode gap distance was fixed at 2 mm because the arc length has a strong effect on the arc voltage and input power level. The
arc current and the concentration of 1-decanol were controlled from 5 to 7 A and from 0.10 to 0.50 mol%, respectively, in order to investigate their effects on the water plasma decomposition of 1-decanol emulsion. The average arc voltage was in the constant level of 100 V even in the change of the arc current and 1-decanol concentration. Therefore, the input power was increased with increasing the arc current, while it was not changed in different 1-decanol concentration. Table 1 shows operating conditions of the water plasma torch and 1-decanol emulsion.

Table 1. Operating conditions for the water plasma torch and 1-decanol emulsion

| Water Plasma Torch          |                  |
|----------------------------|------------------|
| Arc current                | 5, 6, 7 A        |
| Average arc voltage        | 100 V            |
| Electrode gap distance     | 2 mm             |
| Operating pressure         | 101.3 kPa        |

| 1-Decanol Emulsion         |                  |
|----------------------------|------------------|
| Concentration              | 0.10, 0.25, 0.50 mol% |
| Tween60 : 1-decanol        | 1.0 : 26.5        |

2.2. Preparation of 1-decanol emulsion
A surfactant micelle has a hydrophilic group on one side and a hydrophobic group on the other side. Therefore, the surfactant can mix water-insoluble oil with water. In this work, Tween60 surfactant, 1-decanol and distilled water were mixed together to prepare 1-decanol emulsion. The composition ratio of 1-decanol to Tween60 was fixed at 26.5 to 1.0. The 1-decanol emulsion was stirred for 1 hour for the uniform dispersion of 1-decanol in water. Figures 2 (a) and (b) show the 1-decanol emulsion before the water plasma treatment and the generated liquid after the water plasma treatment. The decomposition rate and organic carbon removal rate were evaluated by comparing those two liquids.

Figure 2. (a) Raw 1-decanol emulsion with 0.5 mol% and (b) generated liquid from the water plasma treatment.
2.3. Calculation of generation rates

In order to evaluate generation rate of solid, liquid and gas products, the balances of total substances and carbon are used as follows:

\[ F_r = \frac{M_0 - (M_r + M_a)}{\text{Time}} = G_s + G_l + G_g \]  

(1)

\[ F_r x_r = G_s x_s + G_l x_l + G_g x_g \]  

(2)

In equation (1), \( F_r \) is the feeding rate of the 1-decanol emulsion and \( G_s, G_l \) and \( G_g \) means generation rates of solid, liquid, and gas products, respectively. Masses of raw liquid before treatment \( (M_0) \), remained liquid in the reservoir after treatment \( (M_r) \), absorbed liquid after treatment \( (M_a) \) and operating time \( (\text{Time}) \) were used to evaluate the feeding rate of 1-decanol emulsion. \( x_r \) in the left hand side of equation (2) is carbon mass fraction in the feeding liquid. Likewise, \( x_s, x_l \) and \( x_g \) denote carbon mass fractions in the generating solid, liquid and gas products, respectively. Mass fractions of carbon in liquid and gas were measured by TOC analyser and GC, respectively. The generation rate of gas \( (G_g) \) was measured by a soap film flowmeter, and then the generation rate of liquid \( (G_l) \) was derived from equations (1) and (2) with the assumption of pure solid carbon product \( (x_s = 1) \) as follows:

\[ G_l = \frac{F_r (1 - x_r) - G_g (1 - x_g)}{1 - x_l} \]  

(3)

Finally, the generation rate of gas was calculated based on equations (2) and (3) as follows:

\[ G_g = F_r x_r - G_l - \frac{F_r (1 - x_r) - G_g (1 - x_g)}{1 - x_l} \]  

(4)

3. Results and discussion

Generation rates of gas, liquid and solid products by changing the arc current are presented in figure 3. The concentration of 1-decanol was fixed at 0.5mol% in the experiment for the arc current. The feeding rate shows a tendency to increase with increasing the arc current, because the input power level which is proportional to the arc current determines the evaporation rate of 1-decanol emulsion. The gas generation rate depicted as the gap between circle and diamond symbols in figure 1 is increased with increasing the arc current, while the generation of solid carbon is decreased at the same time. These results are explained by enhanced oxygen radicals in the high arc current condition. The high input power of the water plasma dissociates large number of water molecules resulting in the production of radicals. Among produced radicals, oxygen radicals actively react with carbon radicals that are dissociated from 1-decanol producing carbon oxides. Therefore, the gas generation rate is increased reducing the solid carbon in the high arc current condition.

Figure 4 shows the effects of 1-decanol concentration on the generation rates at the fixed arc current of 7 A. Different to the change of the arc current, both of gas and solid generation rates are increased with increasing the concentration of 1-decanol. Since the input power level was constant in the change of 1-decanol concentration from 0 to 0.5mol%, the number of oxygen radicals is also expected to be constant. Carbon radicals in the plasma flame, however, are increased with increasing the content of 1-decanol in the feeding liquid. Therefore, larger number of oxygen radicals reacts with
abundant carbon radicals in the high 1-decanol concentration, and the rest carbon is converted to solid carbon on the inner wall of the cooling reactor.

![Figure 3](image)

**Figure 3.** Generation rates of gas, liquid and solid products according to the arc current at the fixed 1-decanol concentration of 0.5 mol%.

![Figure 4](image)

**Figure 4.** Generation rates of gas, liquid and solid products according to the concentration of 1-decanol at the fixed arc current of 7 A.
Generated gas species were monitored by QMS during the decomposition of 1-decanol by the water plasma. The main species are hydrogen, carbon monoxide and carbon dioxide as shown in figure 5. The QMS patterns were hard to distinguish even though the arc current and 1-decanol concentration were changed. Therefore, GC was used for the quantitative analysis on the generated gas product. Small amount of methane less than 0.1mol% was measured by GC in addition to hydrogen and carbon oxide gases. In the whole experimental conditions, the mole fractions of hydrogen and carbon monoxide were about 60mol% and 30mol%, respectively.

In order to investigate oxidation characteristics in the decomposition of 1-decanol with the water plasma, the mole fractions of each carbon oxides in the gas product were compared. The ratio of carbon dioxide to carbon monoxide is plotted in figures 6 and 7 based on GC measurement data. The value of carbon dioxide to carbon monoxide is increased with increasing the arc current, while that is decreased with increasing the concentration of 1-decanol. In the arc current change, enhanced oxygen radicals in the high current promote the generation of carbon dioxide. On the other hand, increased carbon radicals in the high 1-decanol concentration prefer to produce carbon monoxide rather than carbon dioxide. These oxidation characteristics for carbon oxide according to the arc current and 1-decanol concentration are in good agreement with results of the gas and solid generation rates in figures 3 and 4.

In HPLC analysis on the treated liquid, 1-decanol was not detected in the whole experimental conditions. Since a strong 1-decanol peak was found at 9.1 min in HPLC measurement for the raw feeding emulsion, the complete decomposition of 1-decanol was achieved by the water plasma treatment. The TOC that is expected to come from water-soluble byproducts, however, was measured by TOC analyzer. The TOC removal rates were evaluated with the measured TOC values for the raw 1-decanol emulsion ($n_{C,0}$) and for the treated liquid ($n_{C,l}$) as follows:

$$
\eta_{TOC} = \frac{n_{C,0} - n_{C,l}}{n_{C,0}} \times 100
$$

Figure 5. Analysis of the generated gas species by QMS in different arc current.
As shown in figures 8 and 9, most carbons in the 1-decanol emulsion are removed by the water plasma treatment. This result means that the water plasma system can be effectively applied for the purification of contaminated water with organic wastes. The removal rate of TOC is increased with increasing the arc current as shown in figure 8, because enhanced oxygen radical promotes the generation of carbon oxide gases than water-soluble organic byproducts. Meanwhile in the change of 1-decanol concentration, the TOC removal rate does not have a distinct tendency. Therefore, oxygen radicals in the water plasma are believed as a major factor to control TOC level in the treated liquid.

**Figure 6.** The ratio of CO$_2$ to CO according to the arc current at the fixed 1-decanol concentration of 0.5mol%.

**Figure 7.** The ratio of CO$_2$ to CO according to the concentration of 1-decanol at the fixed arc current of 7 A.

**Figure 8.** The removal rate of TOC in the generated liquid according to the arc current at the fixed 1-decanol concentration of 0.5mol%.

**Figure 9.** The removal rate of TOC in the generated liquid according to the concentration of 1-decanol at the fixed arc current of 7 A.
4. Conclusion

Water-insoluble 1-decanol in emulsion state was completely decomposed in the water plasma. Oxygen radicals in the water plasma are increased with increasing the arc current and input power. Therefore, the gas generation rate, the ratio of carbon dioxide to carbon monoxide and TOC removal rate are increased in the high arc current conditions, while the solid carbon generation is decreased at the same time. Different to the increase of the arc current, carbon radicals are enhanced with increasing the concentration of 1-decanol in the raw liquid. For this reason, both of gas and solid carbon generation rates are increased with increasing the concentration of 1-decanol. At the same time, the ratio of carbon dioxide to carbon monoxide is decreased due to relatively large amount of carbon radicals in the water plasma. Because the removal rate of TOC is mainly influenced by the population of oxygen radicals that are controlled by the input power level, the change of 1-decanol concentration does not have a significant effect on the TOC removal rate. Available organic wastes in the water plasma treatment are extended to water-insoluble materials through the present work. In addition, the role of oxygen radicals and carbon radicals were clarified in the water plasma treatment of organic wastes.

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