

Role of CH, CH₃, and OH Radicals in Organic Compound Decomposition by Water Plasmas

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Abstract: Decomposition mechanisms of organic compounds and role of generated intermediates in water plasmas were investigated by the comparative study on the basis of the experimental results of decomposition of organic compounds such as acetone, methanol, ethanol, and glycerine. Larger amount of CH₃ radical were generated during acetone and ethanol decomposition, then leading to C₂H₂ formation as well as soot formation. In contrast, negligible amount of soot generation from glycerine decomposition even at high concentration indicated that the oxidation of CH and CH₃ was enhanced by OH radical.

Keywords: Thermal plasma, Water plasma, CH radical, CH₃ radical, OH radical.

1. Introduction

Thermal plasma waste treatment processes have attracted the most attention because of the ability of the plasma to vaporize anything and destroy any chemical bonds. Different kinds of organic wastes, such as plastic, agricultural residue, and medical waste, have been subjected to the studies of plasma pyrolysis [1-3]. The results showed that the amount of gas products can reach up to 70-80% of the feed rate of waste and contain 9-29% of H₂ and CO.

Hrabovsky et al. [4] have developed a water plasma generation device for gasification of waste. Previously, we decomposed some typical organic pollutants such as phenol in wastewater [5] and alcohols solutions [6] by direct current (DC) water plasma at atmospheric pressure. For decomposition of phenol [5], 99% of feeding carbon in phenol was mineralized to CO₂ and CO by thermal dissociation, chemical reactions, or electron impact.

In this study, the different compounds, namely methanol, ethanol, acetone, and glycerine, selected as model substance for water soluble compounds, were decomposed by the water plasma. The spectroscopic measurement of intermediate species in high temperature region have been performed and the role of CH₃, CH₂, CH, and OH radicals in water plasmas were elucidated by comparatively study of the results themselves within this study with the results of other studies.

2. Experimental

A DC water plasma system was used for organic compounds decomposition, which is the same as in [5]. After the arc ignition, water plasmas were generated by heating and ionization of steam that is produced by evaporation of water from the torch. Then, the hot produced gas and target

compounds undergo complex reactions in high-temperatures zone. In contrast to conventional thermal plasma technique, there are no necessary of additional system, then leading to a lower cost and higher energy efficiency. Hence, the capable of high decomposition efficiency for organic waste is the unique characteristic of this torch.

Solutions were introduced into the torch with a controlled feed rate after adjusting the concentration at 1mol%, 5mol%, and 10mol%. The system was operated at atmospheric pressure with an arc current of 7 A and the voltage from 110 to 150 V.

The instruments for the analysis of gas effluent include a gas chromatograph equipped with a thermal conductivity detector (GC-TCD) and a quadrupole mass spectrometer (QMS). The liquid effluent was analyzed by a total organic carbon (TOC) analyzer and a high performance chromatograph (HPLC).

3. Results and discussion

The production rates of gas, liquid, and solid for methanol, ethanol, acetone, and glycerine at different concentrations are shown in **Figures 1-3**. Herein, the solid production rate was estimated on the basis of the mass balance. The gas production rate was increased with increasing organic concentration, as shown in Figure 1. Hence, the organic compounds were useful for syngas generation because recombination of H and O can be inhibited by generating CO and CO₂.

The tendency of the liquid production was has little deference from the gas production rate, as shown in Figure 2. The liquid production rate was greatly increased with increasing the concentration from 1mol% to 5mol% for any compounds by decomposition because of the increase of feed rate.

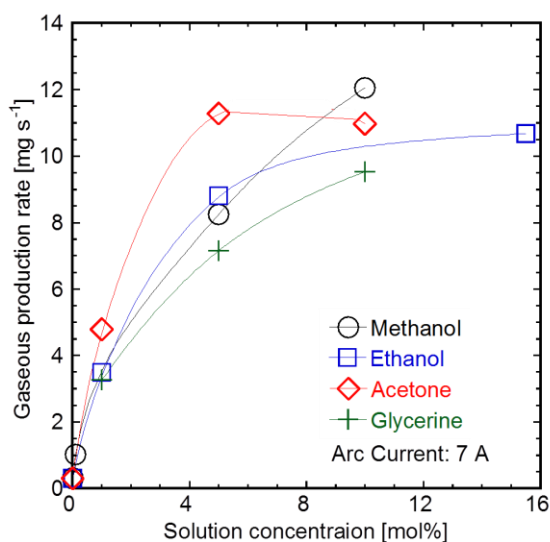


Figure 1. Effect of the concentration of different solutions on gas production rate.

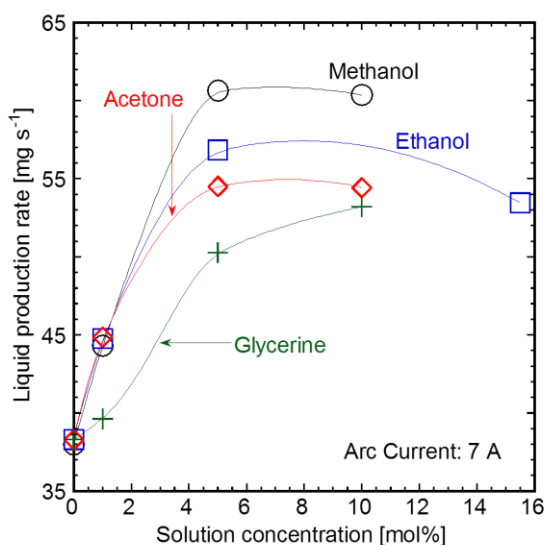


Figure 2. Effect of the concentration of different solutions on liquid production rate.

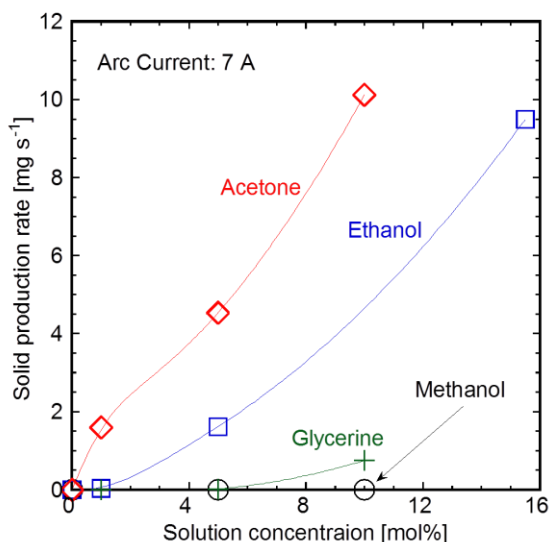


Figure 3. Effect of the concentration of different solutions on solid production rate.

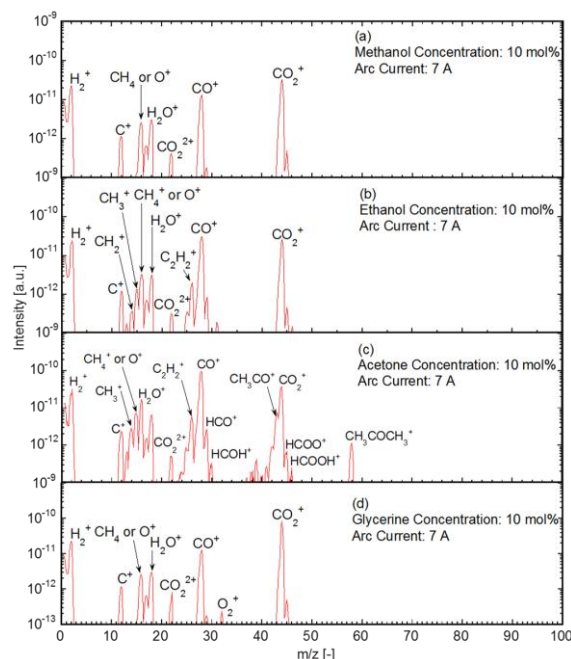


Figure 4. Mass spectra of the produced gas during the decomposition of 10mol% (a) methanol, (b) ethanol, (c) acetone, (d) glycerine solutions at 7 A.

However, as the solution concentration increases further, the liquid production rates were decreased slightly since the hot plasma gas mixtures were converted to gas and solid.

The production rates of gas and solid for the decomposition of either 5mol% of acetone or ethanol was larger in quantity than that of for the decomposition of 5mol% of methanol or glycerine, as shown in Figures 1 and 3. In contrast, the gas produced by 10mol% methanol decomposition was the largest than that from other cases because larger amount of carbons from acetone and ethanol solutions were converted into solid at high concentrations. There was negligible solid observed even decomposition of high concentration of methanol or glycerine, as shown in Figure 3.

The solid produced by acetone decomposition was analyzed using X-ray photoelectron spectroscopy (XPS) and an organic elemental analyzer. C, O, and H were detected from the solid products by the XPS. The elemental analysis results indicated that carbon/oxygen/hydrogen in solid product was 1.94/(0.51-1.41)/1 (mole ratio).

Mass spectra of the effluent gas produced by the decomposition of 10ml% of methanol, ethanol, acetone, and glycerine solutions at 7 A are shown in **Figure 4 (a)-(d)**, respectively. H_2 , C, CH_4 , H_2O , CO, and CO_2 were observed for all cases. The intensity peak of CO in Figure 4 (b) and (c) was stronger than that in Figure 4 (a) and (d). C_2H_2 was identified by the intensity peak of $C_2H_2^+(26)$ in Figure 4 (b) and (c), reflecting incomplete oxidation of ethanol and acetone in water plasmas.

The effect of glycerine concentration on

composition of the produced gas is shown in **Figure 5**. As the solution concentration increases, the concentrations of CO_2 , CO , and CH_4 slightly increased because the concentrations of C-containing species, such as CH_3 , CH_2 , CH , and C in water plasmas increase with increasing glycerine concentration. The increase of CO_2 concentration also indicated a stronger oxidation atmosphere formed at higher glycerine concentration.

The TOC concentrations of the liquid effluents produced by the decomposition of methanol, ethanol, acetone, and glycerine solutions are shown in **Figure 6**. With increasing the organic concentration in solution, the TOC was increased for methanol, ethanol and acetone, but decreased for glycerine, indicating that the structure of target compounds influences on the final products. The difference tendency obtained for glycerine was due

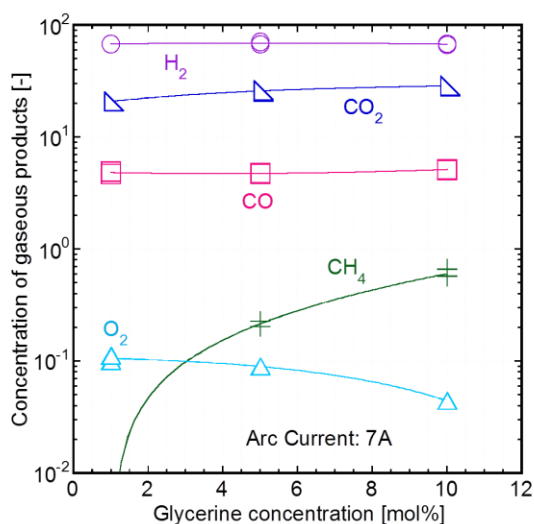


Figure 5. Major gas products for decomposition of glycerine by water plasmas at different concentrations at 7 A.

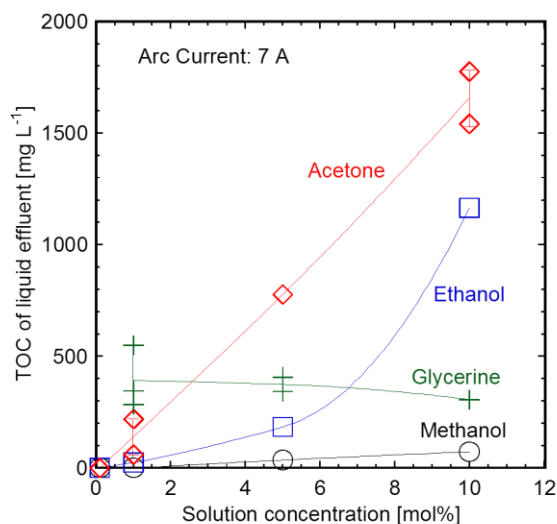


Figure 6. TOC of liquid effluent as a function of different concentrations of acetone, methanol, ethanol and glycerine solutions at an arc current of 7 A.

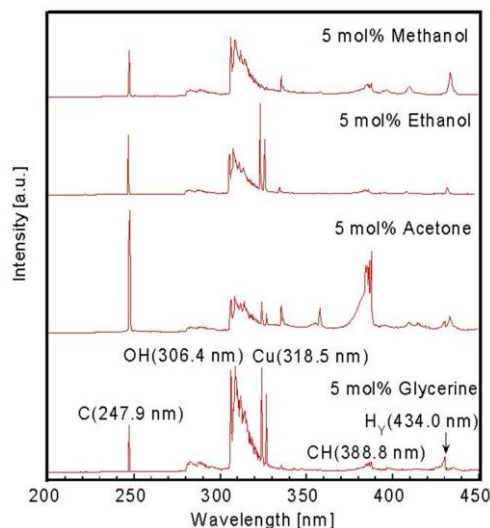


Figure 7. Optical emission spectra during decomposition of different organic solutions by water plasmas.

to OH formed in larger quantities in plasmas.

The intermediate species in water plasmas were identified by an imaging spectrometer (Jobin Yvon, iHR550). The excited species such as CH_3 (218.8 nm), C (247.9 nm), OH (306.4 nm), CH (388.8 nm), H_β (486.1 nm), and H_γ (434.0 nm) were identified from the plasma jet at nozzle exit during decomposition of 5 mol% of acetone, methanol, ethanol, and glycerine solutions, as shown in **Figure 7**. Herein, Cu (318.5 nm) originated from the anode and cathode component.

The relative intensities of $\text{CH}_3/\text{H}_\beta$, CH/H_β , and OH/H_β as a function of solution concentration for different organic compounds are shown in **Figures 8-10**, respectively. $\text{CH}_3/\text{H}_\beta$, CH/H_β , and OH/H_β were increased with the organic concentration because the amount of C-containing species such as CH_3 and CH were increased in water plasmas. Larger $\text{CH}_3/\text{H}_\beta$ for acetone was due to CH_3 structure in acetone molecular. To take into consideration of glycerine structure, the lower CH/H_β for glycerine indicated that the stronger oxidation atmospheric may formed at high glycerine concentration.

Larger OH/H_β was obtained for glycerine decomposition, as shown in **Figure 10**. The intensity ratio of OH to H_β was increased with increasing of glycerine concentration. Hence, the OH was considered to be generated not only from water but also from glycerine. The generation OH radical is an important species for the oxidation of organic intermediates because OH radical itself has a strong oxidation potential of 2.85 V. Lower TOC observed at high concentration of glycerine was considered the OH radical may have accelerated the oxidation of intermediate species.

A simplified decomposition mechanism of aqueous methanol, ethanol, acetone, and glycerine was proposed on the basis of the experimental

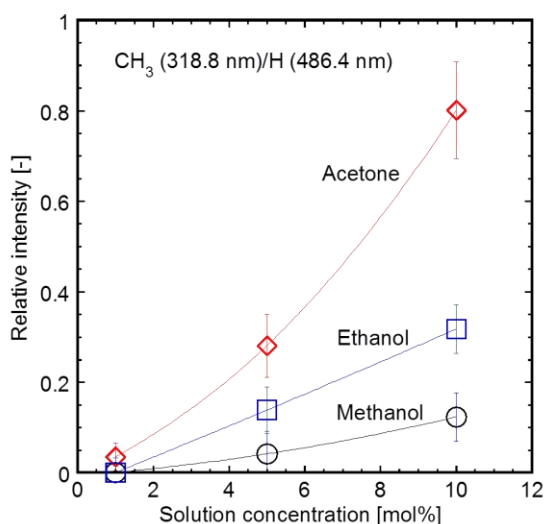


Figure 8. Effect of organic concentrations on relative intensity of CH₃ normalized by the intensity of H.

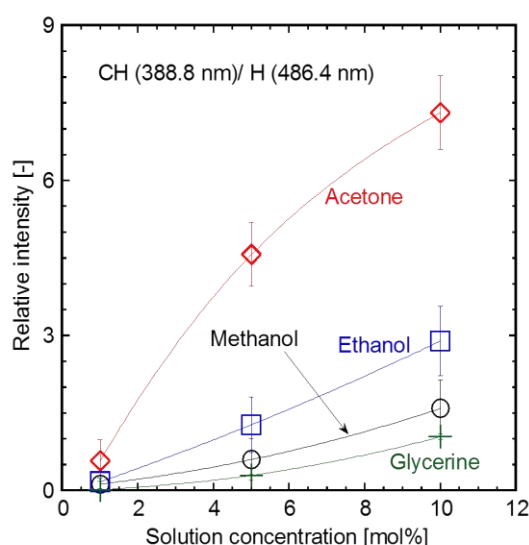


Figure 9. Effect of organic concentrations on relative intensity of CH normalized by the intensity of H.

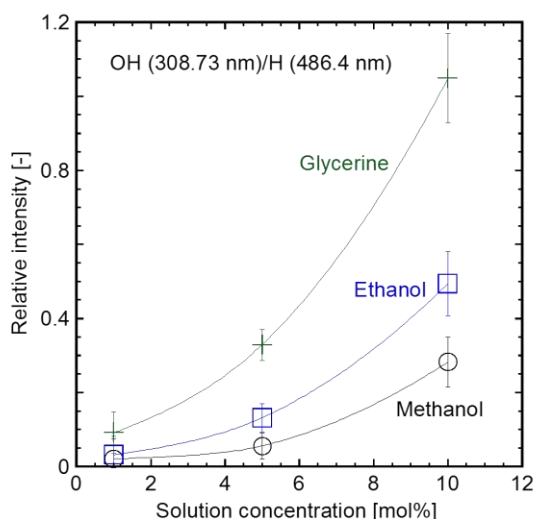


Figure 10. Effect of organic concentrations on relative intensity of OH normalized by the intensity of H.

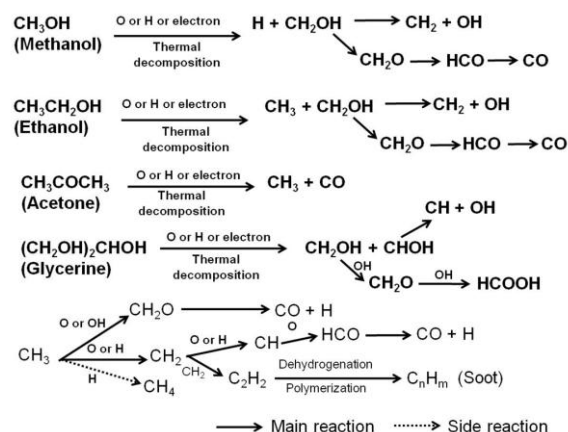


Figure 11. Decomposition mechanism of acetone, methanol, ethanol, and glycerine solutions in water plasmas.

results, as shown in **Figure 11**. The target compounds were decomposed by means of electron dissociation, thermal decomposition, oxidation and reduction. Generation of CH₃ radical was the most favorable for both of acetone and alcohols decomposition because of the weaker C-C bond. Hence, CH₃ was considered to contribute for soot formation.

4. Conclusions

Decomposition of aqueous acetone, glycerine and alcohols were performed using DC discharge at atmospheric pressure. The roles of generated active species such as CH, CH₃, and OH radicals in water plasmas were investigated; (1) larger CH₃/H was observed for both of acetone and ethanol decomposition, which lead to C₂H₂ formation as well as soot formation, (2) the smallest of CH/H observed for glycerine decomposition indicated that the CH can be easily oxidized to CO, and (3) larger OH/H was observed for glycerine decomposition even at high concentrations, indicating that the oxidation of CH and CH₃ was enhanced by OH.

Acknowledgment

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