Decomposition Mechanism of Insoluble Organics by DC Water Plasma at Atmospheric Pressure

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Abstract: The decomposition mechanism of 1-Decanol as an insoluble organic by DC water plasma with a mist generator was investigated in this study. The decomposition mechanism was discussed based on the analysis of generated gas and effluent liquid. A decomposition rate of over 99% and a total organic carbon (TOC) removal rate of more than 96% were achieved. This study provides a practical tool for the treatment of insoluble organics. This study also offers a potential solution for the treatment of hazardous waste.

Keywords: thermal plasma, waste treatment, insoluble organics, emulsion

1.Introduction

The increased attention in studying thermal plasma technology for hazardous waste treatment due to its high energy density and high temperature, oxidation, and reduction atmosphere in accordance with the required chemical reaction, and rapid quenching rate $(10^5-10^6 \text{ K s}^{-1})$.

Direct current (DC) water plasma is a lightweight plasma generation system without a requirement for inert gas supply, pressure-controlled and cooling-controlled units. The water plasma torch is generated by only water as plasma gas. The water plasma is highly destructive and energy efficient in a short period. Therefore, this technique provides a new incentive for waste treatment by thermal plasmas.

Insoluble oily wastewater is discharged from many industrial activities such as machining, cosmetic production, food processing, plating, etc. The oily wastewater is usually in the form of an o/w emulsion. The complexity of the physicochemical characteristics of o/w emulsions makes oily wastewater more challenging to be treated compared to other types of wastewater. The low biodegradability of insoluble oily wastewater leads to poor performance in traditional biological treatment processes [1]. Then thermal plasma treatment technology shows great potential for treating emulsion wastewater. The treatment of typical oily emulsion wastewater was demonstrated using water plasma in this study.

2. Experiment

2.1 Emulsion preparation

The o/w emulsion can be described as a collection of tiny droplets of oil dispersed in water. Surfactant prevents suspended droplets from coalescing and breaking the emulsion. The hydrophilic–lipophilic balance (HLB) of surfactant is a measure of the degree to which it is hydrophilic or lipophilic. In the case of nonionic surfactants, o/w emulsions are formed using nonionic surfactants with HLB values between 8 and 18. Nonionic surfactant Tween 20 was chosen to maintain o/w emulsion in this study due to its appropriate HLB value of 16.7. The utilization of nonionic surfactant can avoid the contaminant from elements like Na, S, and P that are commonly present in ionic surfactants. The concentrations of 1-decanol used for the formation of emulsion to be decomposed were 5–15 g/L, which were 0.06–0.17 mol%.

The molar ratio of Tween 20 to 1-decanol is 1:77.46, by which a stable emulsion can be easily obtained.

The emulsions were obtained by mixing 1-decanol and Tween 20 dispersed separately in the aqueous phase, stirring at 40°C for 1 hour, followed by ultrasonic treatment for 10 minutes.

2.2 Plasma treatment

A schematic diagram of the experimental apparatus used in this experiment is shown in **Fig. 1**. Disintegration of emulsions with a water plasma device with a current of 6.0 A. The exhaust gas was analyzed by a gas chromatograph (GC-14B, Shimadzu) equipped with a thermal conductivity detector. The effluent liquid was analyzed by HPLC (V-550, Jasco, Japan) and GC-MS (GCMS-TQ8040NX, Shimadzu). The total organic carbon (TOC) was analyzed by a TOC analyzer (TOC-L, Shimadzu).

The TOC removal rate was calculated as

$$TOC \ removal \ rate \ = \frac{T_0 - T_1}{T_0}$$
(1)

where T_0 is the initial TOC value of 1-decanol emulsion before decomposition (mg/L), T_1 is the TOC value of the effluent liquid after decomposition (mg/L).

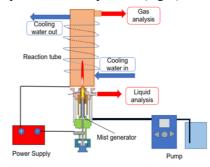


Fig. 1. Experimental setup of water plasma system with a mist generation.

Table 1. Experimental conditions	
Operation pressure [kPa]	101.3
Arc current [A]	6.0
Arc voltage [V]	110 - 140
Electrode gap distance [mm]	2
Plasma supporting gas	1-decanol emulsion
1-decanol concentration [mol%]	0.06, 0.12, 0.17
Molar ratio of Tween 20 to 1-decanol [-]	1:77.46

3.Result and Discussion

The generation rates of gas and liquid effluents are summarized in **Fig. 2**. The feed rate and liquid generation rate decreased with concentration increase. This is because the mist was more difficult to be generated at high concentration emulsion. In contrast, the gas generation rate curve did not change significantly. This is because the proportion of carbon increased although the generation of mist became more difficult with the increase in the concentration of 1-decanol.

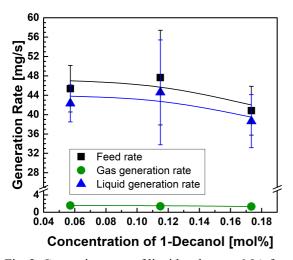


Fig. 2. Generation rates of liquid and gas at 6.0A from different concentration emulsion

The generated gas composition and TOC removal rate during 1-decanol decomposition are shown in **Fig. 3**. The effluent gases were H₂ (61.0-63.0%), CO₂ (6.5-9.3%), CO (25.0-30.0%), and CH₄ (2.2-2.6%). The composition of effluent gas was stable as the concentration of 1-decanol increased. The increase in the concentration of 1-decanol resulted in a higher percentage of CO, this is because of the higher content of carbon.

The decomposition rate and TOC removal rate are summarized in **Fig. 4**. The decomposition rate of 1-decanol was determined to exceed 99.99% because 1-decanol was not detected by HPLC. Removal rates of TOC higher than 96.5% were achieved. Formaldehyde and acetic acid detected by HPLC were the main by-products in the effluent liquid. The oxidation reaction of O radicals and OH radicals led to the formation of formaldehyde and acetic acid. The TOC removal rate increased with an increase in concentration. This may be due to the lower amount of 1-decanol in the mist at a high concentration of 1-decanol.

The GC-MS analysis revealed the presence of two enol compounds 4-penten-1-ol and 5-hexen-1-ol. The long-chain alcohol structure was easily broken into shorter-chain alcohol during the decomposition process. Then these shorter-chain alcohols reacted with OH radicals or O radicals to form enol. The fracture point of the C–C bond in the long-chain alcohol is assumed to be in the middle because other fragments were not detected [2].

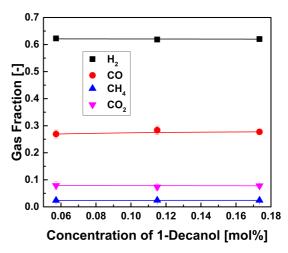


Fig. 3. Composition of effluent gas at 6.0A from different concentration emulsions

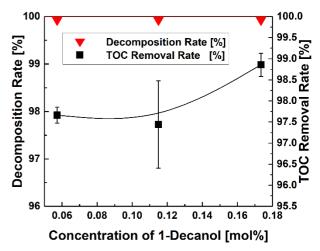


Fig. 4. Decomposition rate and TOC removal rate at 6.0A from different concentration emulsion

3.Conclusion

The insoluble organic 1-decanol was removed by water plasma with a mist generator. Effective decomposition of 1-decanol was obtained at 0.06–0.17 mol%. Analysis of the effluent provided a preliminary explanation of the mechanism of 1-decanol decomposition in the water plasma system. The presence of large amounts of hydrogen and carbon monoxide in the generated gas has the potential to be converted into clean energy through further treatment. This study provides an idea for solving the problem of oily wastewater containing large amounts of insoluble organics.

4. References

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- [2] M. R. Harper et al., Combustion and Flame, 158(1), 16–41 (2011)