Decomposition Mechanism of Sulfur- and Nitrogen-containing Liquid Waste in DC Water Plasma

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Abstract: Decomposition of N,N-dimethylformamide and dimethyl sulfoxide in simulated industrial liquid waste was demonstrated by DC water plasma. The interactions between sulfur and nitrogen were investigated. A higher sulfur content in the solution leads to a lower NO/N₂ ratio, inhibiting the formation of NO₂-N and NO₃-N. The existence of SO₃ in downstream region promotes the oxidation of CO. The detailed decomposition mechanism was discussed based on the calculation of Gibbs free energy.

Keywords: Thermal plasmas, Water plasma, DC arc discharge, Industrial liquid waste, Nitrogen-sulfur interactions

1.Introduction

Industrial processes such as pharmaceutical production and coke gasification generate a large amount of wastewater, resulting in a series of potential health issues. Nitrogen- and sulfur-containing organic compounds in industrial liquid waste are known as principal sources of pollution, as they may cause the generation of hazardous by-products, such as NO_x and H_2S , during conventional wastewater treatment processes.

Thermal plasma technologies have attracted increasing attention recently due to their advantages such as high energy densities and high temperatures. These advantages make them attractive for waste treatment, particularly the treatment of hazardous waste.

A mist-type water plasma torch was developed in our lab for the treatment of highly concentrated industrial liquid waste [1]. In the plasma torch, water or waste solution can be atomized into mist by an ultrasonic transductor and be introduced into the jet. The plasma jet can be generated from mist directly without any additional gas.

In our previous studies, the treatment of nitrogen- and sulfur-containing organic liquid waste by water plasma has been demonstrated successfully. The decomposition mechanism of typical hazardous compounds such as N,N-Dimethylformamide (DMF), pyridine and dimethyl sulfoxide (DMSO) has been discussed in detail [2-3]. Organic compounds with high concentrations of a few hundred grams per litre were treated, and high decomposition rates of more than 90% with high energy efficiency of over 40 g/kWh were achieved. Meanwhile, large amounts of H, O and OH radicals benefit the mineralization of contaminants and inhibit the formation of unwanted by-products effectively. Furthermore, the process generates large amounts of syngas, mainly consisting of hydrogen and carbon monoxide and carbon dioxide.

Recent studies have established some important features of the decomposition mechanism of N- and S-containing compounds in water plasma, however, the interactions between N and S still remain unclear. In this study, the interactions between nitrogen and sulfur in the water plasma waste treatment process were discussed under varying input power, based on the observation of plasma and the analysis of effluents.

2. Experimental

The experimental setup was illustrated in **Fig. 1**. A nontransferred water plasma torch with DC power supply was applied. The torch uses a nozzle-type anode made of copper, while the cathode was made of hafnium embedded into a copper rod. A water-cooled reaction tube was set in the downstream of plasma jet to separate the effluent into liquid and gas products. During the experiment, waste solution was pumped into the torch from the bottom, where it was atomized into mist by an ultrasonic atomizer.

Simulated liquid waste was prepared using DMF, DMSO and ethanol. The concentration of DMF was 0.25 mol/L, while different amounts of DMSO were added to provide varying relative sulfur concentrations. The experimental



Fig. 1. Schematic of experiment set up.

conditions were shown in **Table 1**. To avoid the effect of concentration, the concentration of the solution was adjusted to 40 g/L using ethanol.

Table 1. Experimental conditions

DMF ((CH ₃) ₂ NCHO) [mol/L]	0.25
DMSO ((CH ₃) ₂ SO) [mol/L]	0.1
S/N ratio [-]	0.4
Ethanol [mol/L]	0.3
Current [A]	6.0, 7.5, 9.5

Optical emission spectroscopy (OES) was applied to study the distribution of temperature and radicals in the plasma. When observing, the reaction tube was removed. The optical emission spectra were measured using an imaging spectrometer (iHR-550, HORIBA Jobin Yvon), equipped with a charge-coupled device detector (CCD). The temperature of plasma was calculated by Boltzmann plot of the relative emission intensity of Balmer series H atoms (H_{α} and H_{β}).

The gas effluent from the reactor was analysed by gas chromatography with thermal conductivity detector (GC-TCD, Shimadzu GC-14B). The concentration of sulfur dioxide (SO₂) was measured by a short-term measurement detector tube (Sulphur dioxide 5H, GASTEC). The existence of hydrogen sulfide (H₂S) was monitored by a single-gas detector (BW SOLO Lite BWS2-H-Y, Honeywell).

The liquid effluent collected from the bottom of reaction tube was analysed by a high-performance liquid chromatography (HPLC, Jassco) equipped with a UV detector (UV-975). A reverse-phase column (InerSustain AQ-C18, 250mm x 4.6mm, 5 μ m) was adopted, the mobile phase consisting of water: acetonitrile = 8:2 (v:v), with a flow rate of 1.0 ml/min. Total carbon (TC) and total organic carbon (TOC) of the liquid effluent were determined by a TOC analyser (TOC-L, Shimadzu). The concentration of sulfate ion (SO₄²⁻) was analysed by barium sulfate turbidimetry, while the concentration of



Fig. 2. Removal rate of DMF, DMSO and TOC.

sulfite ion (SO_3^{2-}) was determined by titration with sodium thiosulfate solution. Concentrations of ammonia nitrogen (NH_3-N) and nitrite nitrogen (NO_2-N) was determined using Nessler's reagent and Griess reagent respectively, with ultraviolet–visible spectroscopy.

3. Result and discussion

Removal rates of DMF, DMSO and TOC were measured with different currents, S/N ratio of the solution was 0.4. As shown in **Fig. 2**, high DMF removal rates of more than 97% were achieved, increasing with increasing current. DMSO was not detected in the liquid effluent. The high decomposition rate of DMSO can be attributed to the fact that the C-S bond in DMSO was weaker than the C-N bond in DMF. TOC in the liquid effluent consists of undecomposed DMF and carbon-containing by-products. The high TOC removal rates in higher currents indicate that increasing input power can promote the mineralization, leading to more sufficient oxidation.

Generation rates of different main gas products during the treatment was shown in **Fig. 3**. The syngas generated from the decomposition mainly consists of hydrogen,



Fig. 3. Effect of current on main gas product generation rates



Fig. 4. Effect of current on minor gas product generation rates



Fig. 5. Concentration of products in liquid effluent.

carbon monoxide, carbon dioxide and nitrogen. When increasing current, higher input power leads to higher temperature and pressure inside the torch, increasing the feed rate and thus generating more gas products. Generation rates of minor gass products were also measured, as shown in **Fig. 4**. The formation of CH₄ was negligible when the current was higher than 7.5 A, while the generation rate of NO and SO₂ increased, indicating a stronger oxidation environment.

The concentrations of by-products in liquid effluent was presented in **Fig. 5**. Sulfate ion (SO_4^{2-}) and ammonia nitrogen (NH₃-N) were identified as main conponents in the liquid effluent, with trace amount of nitrate-nitrogen (NO₃-N) and nitrite-nitrogen (NO₂-N). Sulfite (SO_3^{2-}) and sulfide (S^{2-}) were not detected in all conditions. The concentration of all by-products decreased with increasing current, indicating higher input powers can lead to more sufficient removal of contaminants. The concentrations of



NO₃-N and NO₂-N were 2 orders of magnitude smaller than the condition without DMSO addition (200–300 mg/L). The Gibbs free energy changes of possible reactions under different temperatures were calculated, as shown in **Fig. 6**. The results show that a large amount of SO₂ can be generated in the plasma flow region where temperature decreased to lower than 4,000 K (Fig. 6(a)), which can inhibit the formation of NO₃-N and NO₂-N by reacting with their precursors NO₂ and NO₃ (Fig. 6(b)) through following reactions (**Eqs. (1–3**)).

$$SO + NO_2 \rightarrow SO_2 + NO$$
 (1)

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$
 (2)

$$SO_2 + NO_3 \rightarrow SO_3 + NO_2$$
 (3)

The effect of sulfur on the conversion of carbon and nitrogen was also investigated, as shown in **Fig. 7**. The CO_2/CO ratio during the decomposition was in the range



Fig. 6. Gibbs free energy of possible reactions in water plasma (a) Oxidation of SO and SO₂;
(b) Reactions between NO_x and SO_x;
(c) Oxidation of CO by NO_x and SO_x

of 0.28–0.31, which was only 0.2 when no DMSO was added. This would be attributed to the reaction between CO and SO_3 in the downstream region of about 2,000 K (Fig.6(c))(**Eq. 4**).

$$SO_3 + CO \rightarrow SO_2 + CO_2$$
 (4)

The existence of N has less effect on the oxidation of carbon, as about 80% of N can be converted into N_2 in the plasma, with a small portion of NO (**Fig. 8**). The formation of oxidative NO₂ and NO₃ was negligible (<0.1%).

The NO/N₂ ratio during the treatment was in the range of 0.14-0.22, which was higher than 0.5 when no DMSO was added. The result shows that the existence of sulfur can suppress the formation of NO effectively, through the reduction by S, SO and SO₂ in plasma flow region (**Eqs.** (5–7)). Increasing current shows positive effects on the reduction of nitrogen, as the dissociation of S and SO radicals from DMSO were accelerated.

$$S + NO \rightarrow SO + 0.5N_2$$
 (5)

 $SO + NO \rightarrow SO_2 + 0.5N_2$ (6) $SO_2 + NO \rightarrow SO_3 + 0.5N_2$ (7)

4. Conclusions

The decomposition of DMF and DMSO in simulated industrial liquid waste was demonstrated successfully using mist-type DC water plasma torch. The interactions between sulfur and nitrogen were investigated. The existence of sulfur can suppress the oxidation of nitrogen, leading to a lower NO/N₂ ratio, and thus inhibit the formation of NO₂-N and NO₃-N. Furthermore, the existence of SO₃ in downstream region promotes the oxidation of CO. The detailed decomposition mechanism was discussed based on the calculation of Gibbs free energy.

5. Acknowledgements

This work was supported by the JST SPRING (Grant No. JPMJSP2136).

6. References

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Fig. 8. Gibbs free energy of possible radical reactions of NO in water plasma