

Decomposition of Pharmaceuticals and Personal Care Products by Water Plasma with Mist Generation

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Abstract: *N, N*-diethyl-*m*-toluamide (DEET) and Caffeine (CAF) were decomposed by water plasma with mist generation at atmosphere pressure. The effect of arc current on the decomposition was discussed in detail. Decomposition rates of the DEET and CAF were improved with an increase of arc current up to 93.7% and 99.8%, respectively. Major effluent gases were H₂, CO₂, CO, and N₂. The plasma temperatures were over 5000 K. A possible decomposition pathway was deduced based on the identification of intermediate products.

Keywords: Water plasma, PPCPs, DEET, Caffeine, decomposition mechanism

1. Introduction

Pharmaceuticals and personal care products (PPCPs) have raised significant attention for therapeutic and beauty, including a broad range of medicines, cosmetics, and detergents for both humans and veterinary [1]. However, they have been widely detected in rivers, groundwater, urban areas, and even in drinking water around the world due to immense use and continuous discharge. Moreover, some PPCPs may cause ecological harm, such as endocrine disruption and the development of antimicrobial resistance [2].

N, N-diethyl-*m*-toluamide (DEET) and Caffeine (CAF) used as a primary insect repellent and psychoactive legal drug are the most frequently detected PPCPs. For example, DEET was the most abundant PPCPs in landfill leachates in the Yangtze River Delta, China [3]. Also, CAF was the highest concentration ranging from 3 to 11 mg L⁻¹ in the seawater of many countries such as the USA, Australia, Portugal, and Japan [4]. Thus, an improved water treatment technique for the removal of DEET and CAF is very essential.

Water thermal plasma has been considered as one of the most promising waste treatment. This is because water molecule offers higher plasma enthalpy and thermal conductivity than commonly used plasma gases such as N₂, O₂, and Ar. Moreover, highly reactive radicals such as H, O, and OH accelerate the chemical reactions, produce a large amount of syngas like H₂ and CO, and finally suppress by-product formation. Phenol as an organic waste was successfully decomposed with a high decomposition rate of over 99% in our previous work [5].

The decomposition of DEET and CAF using the DC water plasma with mist generation was experimentally investigated in this study. The qualitative and quantitative analysis for the effluent gas and liquid including the decomposition rate were investigated. Furthermore, intermediate products were identified, by which the decomposition pathway was proposed.

2. Experimental

2.1. Experimental setup

The diagram of the water plasma system for DEET and CAF decomposition is shown in Fig. 1. The generated mist is directly supplied to the discharge area and subsequently heated and dissociated. Then, water plasma is discharged. Then, the mist is evaporated in the arc discharge, and the

produced hot gases can be rapidly quenched in the reaction tube and separated into the gaseous, liquid, and solid phases. In particular, the mist and evaporation of water in the torch can cool the anode, thus the torch can be run without a cooling device, carrier gas system, and further pressure regulator. The water plasma system thus can be used as a light-portable system providing high energy efficiency.

The concentrations of DEET and CAF solutions were 2 g/L and 20 g/L; the solution volume was set at 55 mL; the applied arc current was 6.0 A, 7.5 A, and 9.5 A; plasma discharge time was for 10 min at atmospheric pressure; Experiment at each arc current was conducted at least three times for reproducibility.

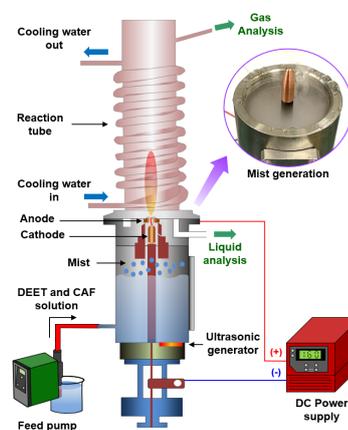


Fig. 1. Schematic diagram of water plasma system with mist generation for DEET decomposition.

2.2. Effluent gas and liquid analysis

The effluent gas was qualitatively and quantitatively analyzed by gas chromatography with a thermal conductivity detector (GC-TCD) (GC-14B, Shimadzu, Japan) and a Shin-carson ST 50/80 packed column. Pure Ar gas (>99.999%) was used as the carrier gas.

The UV-Vis absorption spectra for effluent liquid after DEET decomposition were monitored over wavelengths of 190–900 nm by UV-Vis spectrophotometer (V-550, Jasco, Japan). The absorbance changes for DEET were measured at 286 nm.

The concentration of CAF was determined by high performance liquid chromatography (HPLC) (V-550,

Jasco, Japan) at a wavelength of 294 nm with a UV detector (UV-975) and an Inertsil ODS-3V C18 column. The mobile phase was acetonitrile and ultrapure water (75:25) at 40 °C with a flow rate of 0.8 mL/min.

The mineralization was measured using a total carbon organic analyzer (TOC-L, Shimadzu, Japan).

2.3. Decomposition rate and mineralization

The decomposition rates of DEET and CAF, and TOC removal rate were calculated as listed by Eqs. (1)–(3):

$$\text{DEET decomposition rate (\%)} = \frac{I_o - I}{I_o} \times 100 \quad (1)$$

$$\text{CAF decomposition rate (\%)} = \frac{c_o - C}{c_o} \times 100 \quad (2)$$

$$\text{TOC removal rate (\%)} = \frac{T_o - T}{T_o} \times 100 \quad (3)$$

where I_o and I are the measured peak intensities of DEET for the initial DEET solution and the effluent liquid, respectively. C_o and C are the CAF concentrations for the initial CAF solution and the effluent liquid. T_o and T are the TOC values of initial solutions and the effluent liquids for DEET and CAF.

2.4. Spectroscopic diagnostic and plasma temperature

Optical emission spectra (OES) were measured to identify the excited species using an optical emission spectrometer (iHR550, HORIBA Jobin Yvon, Japan). The optical fiber was fixed to the nozzle exit and 45 cm away from the nozzle exit. The excitation temperatures were calculated by the Boltzmann plot through H_α and H_β atom lines [6].

2.5. Identification of intermediate products

Intermediate products (IPs) formed in DEET and CAF decomposition were identified using a high-resolution quadrupole time of flight mass spectrometer (QTOF-MS) (micrOTOF-Q III, Bruker, USA). The spectra were obtained in the positive ion mode by electrospray ionization (ESI) and the m/z range was from 50 to 1000. The eluent consisted of methanol and ultrapure water (50:50) and the flow rate was 1.0 mL/min.

3. Results and Discussion

3.1. Effect of arc current on the decomposition.

The generation rates in liquid, gas, and solid are shown in Fig. 2, where the solid generation rate was calculated via mass balance [7]. The generation rates in the liquid and gas including the feed rate increased, whereas that of the solid decreased with an increase of arc current from 42.3 to 39.6 $\mu\text{g/s}$. This is due to an increase of total input power at a higher arc current causing not only strong Joule heating but also dissociation of water molecules. Therefore, arc current has a significant influence on the oxidative environment. The same tendency was also confirmed in the CAF decomposition.

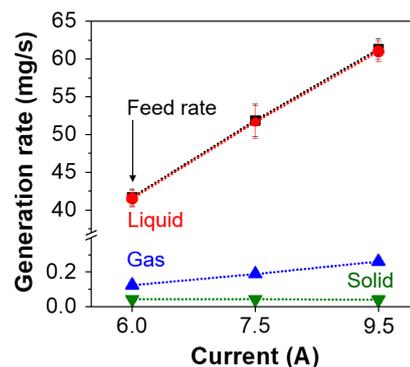


Fig. 2. Generation rates for liquid, gas, and solid during the decomposition of 2 g/L DEET at different arc currents.

3.2. Analysis of effluent gas

The main effluent gases are H_2 (45.3–55.5%), CO_2 (11.2–12.7%), CO (14.0–15.5%), and N_2 (17.8–27.9%) in DEET decomposition. The mole fractions of H_2 and CO_2 gradually increased, whereas those of CO and N_2 showed a decreasing tendency as arc current increased. This result is attributed to higher evaporation and dissociation of water molecules at an increased arc current as discussed in the previous section. On the other hand, H_2 (40.9–49.2%), CO_2 (10.0–10.2%), CO (19.3–21.3%), and N_2 (19.3–29.8%) were obtained in CAF decomposition. Here, the amounts of H_2 and CO_2 were higher in the DEET decomposition compared to those in the CAF decomposition. This is considered to be a relatively lower concentration of DEET (2 g/L) and the resultant higher radical reaction from H_2O evaporation and dissociation.

3.3. Analysis of effluent liquid

The decomposition rates and TOC removal rates at various arc currents are presented in Fig. 3. With the increasing arc current, the removal rates were improved in not only the TOC reduction rate but also in the decomposition rate for DEET and CAF decompositions; thus, the oxidation was enhanced at higher input energy.

The decomposition rate of CAF is higher than that of DEET, showing the highest decomposition rates of 99.8% and 93.7%, respectively. This may be attributed to the stable molecular structure of the benzene ring in DEET molecule by the delocalized π bonding [8].

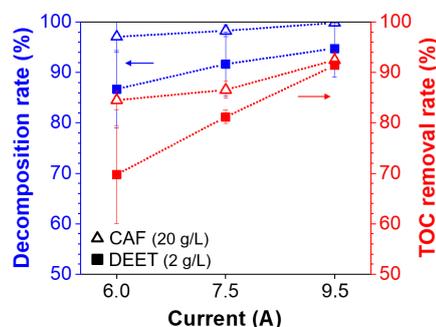


Fig. 3. Effect of arc current on decomposition and TOC removal rates.

3.4. Reactive species and plasma temperature

OES spectra were achieved to not only identify excited species but also calculate plasma temperature. Excited species such as C (247.9 nm), OH (306.4 nm), Cu (318.5 nm), CH (388.8 nm), H δ (408.2 nm), H γ (434.0 nm), H β (486.1 nm), and O (777.9 and 845 nm) were examined in all conditions. OH, H, and O radicals could be originated from the electron collisions as well as the thermal dissociation of H $_2$ O molecules. In particular, the emission intensities of H, OH, and O increased with an increase in arc current, proving that a higher reactive environment was achieved due to high input energy.

As seen from Fig. 4, the plasma temperature increased with an increase of arc current in a range of 6700–8700 K and 5800–7700 K in DEET and CAF decomposition, respectively. Therefore, the increased input power caused by a higher arc current obviously prompts not only plenty of reactive species but also higher temperature, resulting in finally a higher decomposition rate. On the other hand, the plasma temperature was higher in DEET decomposition than that in CAF decomposition. This is because more energy was consumed to decompose highly concentrated CAF solution.

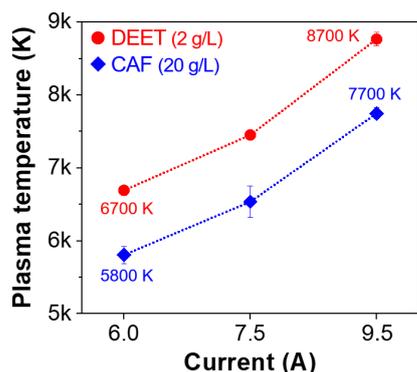


Fig. 4. Plasma temperature at different arc current.

3.5. Decomposition mechanism

The results on the detected intermediates with different values of m/z are shown in Fig. 5. The peaks of DEET and CAF molecules were dramatically decreased in all cases after decomposition, indicating that a high degree of decomposition was achieved. Moreover, the possible 17 IPs and 11 IPs were postulated in DEET and CAF decompositions, respectively. The main decomposition pathways for DEET and CAF are presented in Fig. 6 and discussed.

As shown in Fig. 6(a), IP D1 may be formed through electron dissociation and hydroxylation. First, C–N bond having low bond energy is fragmented via electron impact due to high electron energy density in the arc column [9]. Then, hydroxylation preferentially occurs for IP D1 due to high oxidizing power, which was detected at near 350 nm range of wavelength in the UV–Vis absorption spectrum. Subsequently, the 5C in DEET molecule having the largest negative charge (-0.78) in the benzene ring can be attacked by the electrophilic characteristic of \cdot OH, followed by the

ring opening and the formation of IP D2 [10]. For further reaction, IP D3 can be formed through the removal of the amine group due to the feeble C–N bond by oxygenation. Finally, gases are formed as final products through further oxidation.

IP C1 can be formed via the electron impact and further \cdot O from the arc region in CAF decomposition as shown in Fig. 6(b). The imidazole ring opening could be likely to take place via the electron impact due to low average local ionization energy near the 9N [11]. \cdot O could be immediately attached for the generation of the aldehyde group, followed by further oxidation into the carboxyl group while generating CO $_2$ and H $_2$ O. IP C1 eventually evolved to a further oxidized product noted as IP C2 together with pyrimidine ring opening. IP C2 could react more with radicals to produce more short-chain organic compounds and finally would derive micromolecules and/or gaseous.

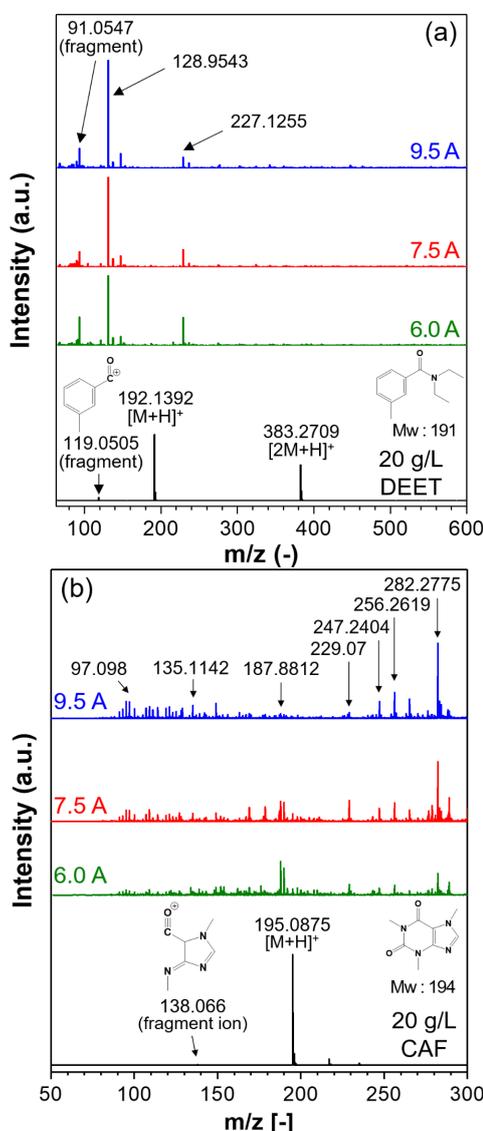


Fig. 5. ESI-MS spectra in the positive mode for effluent liquids of (a) DEET and (b) CAF at different currents.

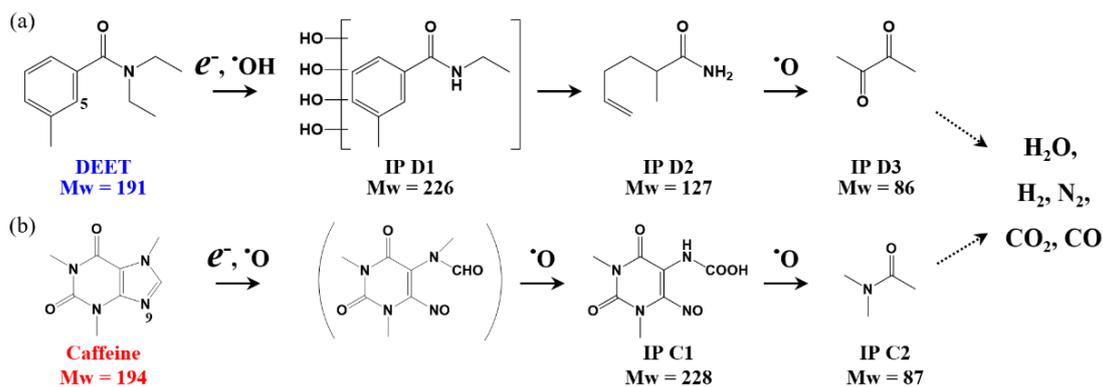


Fig. 6. Proposed decomposition mechanism for (a) DEET and (B) CAF.

4. Conclusion

Water plasma with mist generation has proved high performance in the decomposition of PPCPs. The highest decomposition rates of 93.7% and 99.8% were obtained at an arc current of 9.5 A in the decomposition of DEET and CAF, respectively. The contents of H_2 and CO_2 increased at a higher arc current due to an enhanced oxidative environment. Based on the intermediate products identified in ESI-MS, the decomposition mechanism was proposed, where electronic dissociation brought about an important factor for the ring opening at the early stage of decomposition. In conclusion, water plasma could be a powerful tool for processing further harmful wastewater.

5. References

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