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Decomposition of Waste Organic Solvents by Liquid-Phase Atmospheric Pressure Microwave Plasma Generated Using Carbon Felt Pieces Impregnated with NaCl

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The decomposition of organic solvents was divided into three periods: LPSD, LPAPMP, and APMP. We found that the generation behaviors of LPAPMP were different due to the relative permittivity of the solvents, however, LPAPMP generation is effective for decomposing each of the organic solvents.

Industrial liquid waste containing organic solvents is often harmful to human health. For this reason, it is important to develop a useful method for removing toxic and harmful organic solvents from mixtures. Several chemical processes for removing hazardous organic solvents from liquid waste have already been proposed.[1–4] Recently, considerable attention has been given to a decomposition method for hazardous organic solvents that utilizes atmospheric pressure plasma induced by microwave irradiation in the liquid phase.[5–11] Our previous study revealed that carbon felt impregnated with metal salts (CF/metal salts) worked effectively to generate atmospheric pressure microwave plasma (APMP).[12,13] Gaseous toluene in air was completely decomposed by APMP.[13] We also succeeded in generating microwave plasma attributed to metal salts even in the liquid phase (LPAPMP) in a similar manner, and liquid toluene was smoothly decomposed.[14] In this study, the generation behaviors of LPAPMP in various organic solvents were investigated, and decomposition of the organic solvents was examined. Here, toluene and methanol were used as models of waste organic solvent.

To obtain CF/NaCl pieces, CF pieces made of rayon fibers calcined at 2500 °C were immersed in 2% NaCl aqueous solution, then removed and dried. A 2.45-GHz and 100-W microwave generator (Chronix Giken Co., Ltd.) was used as a microwave source. A reactor tube containing three CF/NaCl pieces (ca. $5 \times 5 \times 10$ mm each) and 10 cm^3 of solvent was placed in an elliptical chamber (Chronix Giken Co., Ltd.). N_2 gas flowed through the reactor tube, condenser, and trap

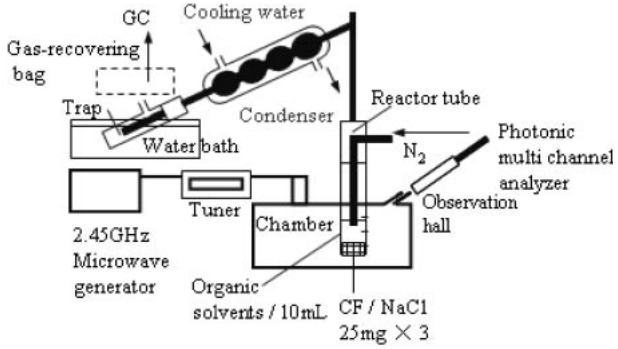

Figure 1. Experimental apparatus for decomposing organic solvents by microwave irradiation using CF/NaCl pieces.

for 8 min, and was collected in the terminal gas-recovering bag. The flow rate was 1 $dm^3\,min^{-1}$ (SATP). Inert N_2 gas was supplied to prevent explosive reactions. Unreacted solvents were condensed and recovered by a trap on a water bath. Any gaseous products and solvents escaping from the trap were recovered completely by a terminal gas-recovering bag (Figure 1). The microwave generator was switched on as soon as N_2 gas started to flow, and microwave energy was continuously input to the reactor tube for the prescribed time. The temperature of the solvent was measured by a thermocouple as soon as possible when the microwave generator was turned off. Recovered gases were analyzed by gas chromatography (Shimadzu Co., Ltd.: type GC12A with a packed column, SHINCARBON-ST) and gas chromatography-mass spectrometry (Shimadzu Co., Ltd.: type QP5050 with a capillary column, DB-1). Emission spectra were measured and analyzed using a photonic multi-channel analyzer (Hamamatsu Photonics Co., Ltd.: type PMA 11). Solid products were analyzed by X-ray diffraction (Rigaku Co., Ltd., type RINT 2000).

Typical changes in the emission spectrum and the temperature of the solvent during microwave irradiation are shown in Figure 2 (Figure 2A for toluene and Figure 2B for methanol). Figure 2A suggests that the microwave irradiation period can be divided into three parts.[14] In the initial period, about 100 s, emission spectroscopy over wavelengths longer than 600 nm, weak emission spectra at 468, 514, and 388 nm were observed. The spectrum may be attributed to C_2 and CN radicals,[15] which were generated by faint electrical discharge sparked between CF/NaCl pieces in the solvent, i.e., the liquid-phase spark discharge (LPSD), making the temperature of liquid toluene increase. In the second period, from about 100 s to about 140 s, a sharp emission spectrum at 589 nm was observed, as well as a weak emission spectrum attributed to CN radicals. The spectrum may be attributed to sodium D transitions: $3^2P_{1/2} \rightarrow 3^2S_{1/2}$ (589.6 nm) and $3^2P_{3/2} \rightarrow 3^2S_{1/2}$ (589.0 nm).[13] It was considered that LPAPMP was generated since CF/NaCl was still in the liquid solvent in this period. The temperature of the solvent had already reached the boiling point. In the third period, from about 140 s to about 180 s, a sharp and strong emission spectrum at 589 nm was observed. It was considered that APMP was generated since the solvent had evaporated out of the reactor tube.

Figure 2B for methanol suggests that the microwave irradiation period can be also divided into three parts. However, there are some differences between toluene and methanol in

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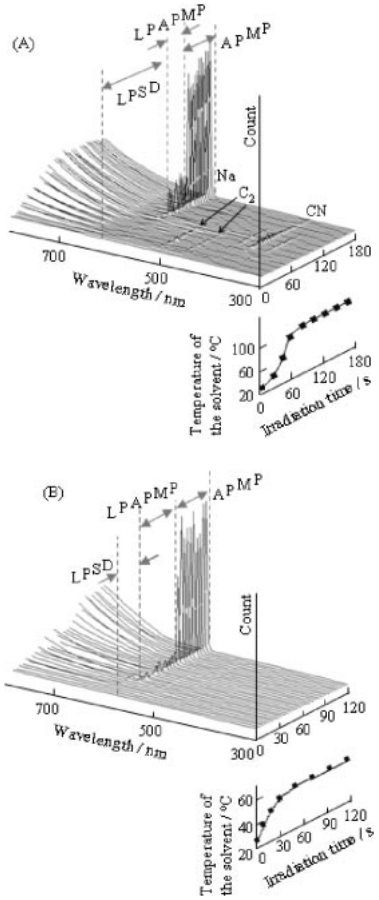

Figure 2. Emission spectral changes and temperature of the solvents through runs: toluene (A) and methanol (B).

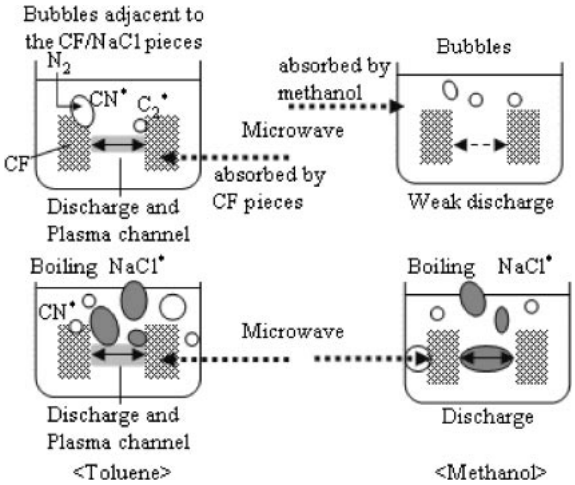

Figure 3. LPAPMP generation mechanism in toluene or methanol.

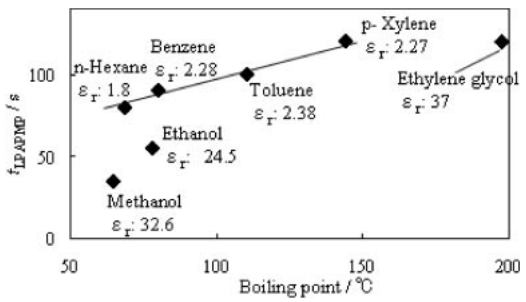

Figure 4. Relationships between t_{LPAPMP} in some solvents and the boiling points of some solvents.

the generation of LPAPMP. For instance, toluene required ca. 100 s of microwave irradiation to generate LPAPMP, whereas methanol required ca. 40 s. And, in regards to the emission spectra over wavelengths longer than 600 nm, the intensity of methanol was significantly weaker than that of toluene. Furthermore, emission peaks attributed to C_2 and CN radicals were not observed in this case.

To explain these results, the following scenario is conceivable for the LPAPMP generation mechanism (Figure 3). Toluene is less capable of absorbing microwave energy because of its small relative permittivity (ε_r: 2.38). Instead, CF/NaCl pieces preferentially absorb it to generate LPSD between the CF/NaCl pieces. Plasma channels are formed by the discharge,[3,9] however, disappear through cooling by the liquid solvent. Therefore, C_2 radicals may be generated in the vapor bubbles at the hot surface of CF/NaCl pieces. When such bubbles contain carrier N_2 molecules, CN radicals may form in the bubbles. And, when the temperature of the whole solvent reaches the boiling point and stable vapor bubbles contact with plasma channels, LPAPMP may be generated in bubbles containing NaCl vapor. The plasma may spread out the vapor phase over the CF/NaCl pieces. Accordingly, it is considered that microwave irradiation time necessary for LPAPMP generation (t_{LPAPMP}) is associated with the boiling point of the solvent. Relationships between t_{LPAPMP} in some solvents and the boiling points are shown in Figure 4. The result indicates that in regards to solvents of small relative permittivity (i.e. hexane, benzene, toluene, and *p*-xylene), the two are associated.

In contrast, as methanol has a larger ε_r (32.8), it absorbs the microwave energy, it prevents the CF/NaCl pieces from absorbing the energy, and LPSD is hardly generated. Therefore, the intensities of emission over wavelengths longer than 600 nm are weaker than toluene and emission peaks attributed to C_2 and CN radicals are not observed. Liquid methanol can be heated by direct absorption of microwave energy. When the temperature reaches the boiling point, and a stable vapor phase is formed between CF pieces, CF/NaCl pieces are able to absorb the microwaves, and discharges, NaCl evaporation, and plasma are generated in the vapor phase. It is considered that microwave irradiation time necessary for LPAPMP generation may be associated with not only the boiling point but also the relative permittivity of the solvent (Figure 4).

After each 8-min run, substances recovered by the reactor tube, trap, and gas-recovering bag were analyzed. In the reactions of toluene, hydrogen and hydrocarbons including acetylene, 2,4-hexadiyne-3-yne, and ethylene were detected as well as toluene in the reactor tube, trap, or the gas-recovering bag. Soot was deposited on the internal wall surfaces of the reactor. Only the XRD pattern of NaCl was observed in the soot. This fact indicates that the deposited carbon was amorphous and contained NaCl originated in CF/NaCl pieces. In the reactions of methanol, methanol, hydrogen, carbon monoxide, and a

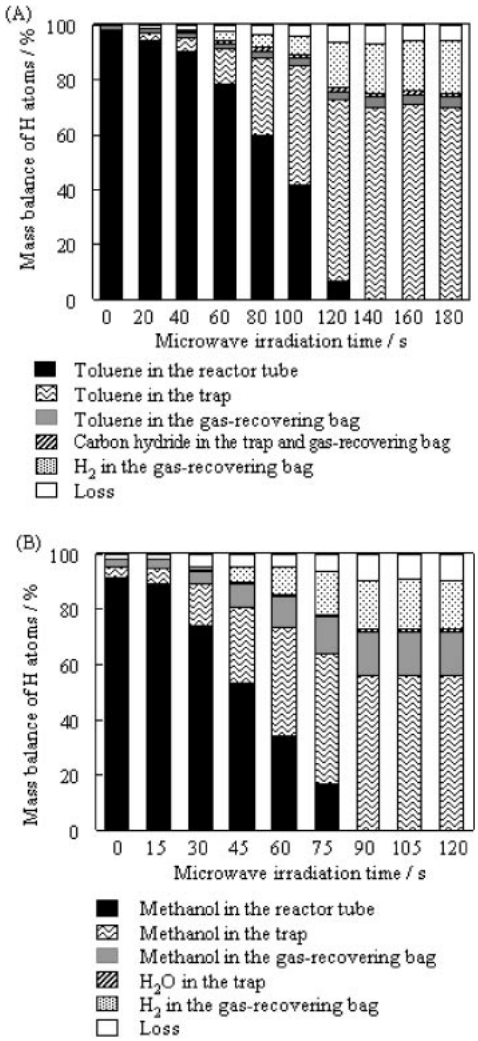

Figure 5. Mass balance of H atoms before and after microwave irradiation: toluene (A) and methanol (B).

small amount of water were detected.

For qualitative discussion, mass balances of H atoms before and after microwave irradiation for various times are shown in Figure 5 for both toluene (A)[14] and methanol (B). The symbol H_o represents the entire amount of H atoms bonding to the solvent molecules, which was estimated from the amount of the solvents put in the reactor tube: toluene, 0.75 mol and methanol, 0.99 mol. The symbol H represents the amount of H atoms of each substance recovered from each part (the reactor tube, trap, and the gas-recovering bag) of the experimental apparatus after each run. In Figure 5, the ordinate shows the mass balance of hydrogen atoms: $H/H_o \times 100\%$.

These results show that the mass balances are almost perfect in every run, although unknown losses somewhat increase as the yield of hydrogen becomes larger. The main cause of the loss may be the adsorption of the solvent on the walls of the apparatus that include the reactor tube and so on.

Changes in the ratio of the decomposed amount of solvent to the decreased amount of liquid solvent in the reactor tube (R_{dec}) with time are shown in Figure 6. The decomposed amount of solvent was estimated from the amounts of H_2 and H_2O (Figure 5), and, the decreased amount of liquid solvent was estimated from the difference between the initial amount of solvent and the amount of solvent remaining in the reactor tube after each run (Figure 5). These results indicate that in the first period when LPSD is generated, the R_{dec} of both solvents are low, in the second period when LPAPMP is generated, the R_{dec} of both solvents are high. From these results, it is found that decomposition of the solvent is accompanied by evaporation of liquid solvent in this system, however, when LPAPMP is generated, the ratio between the decomposition and the evaporation leans to the decomposition independently of relative permittivity of the solvents. The reason is thought to be that LPAPMP spreads out liquid phase and contacts with the organic solvents for a long time and the organic solvents are decomposed effectively. Conclusively, it is clarified that the LPAPMP generation is important to decompose the liquid organic wastes.

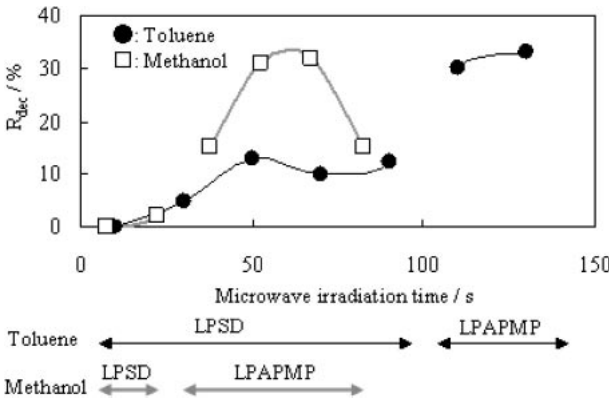

Figure 6. Changes in the ratio of the decomposed amount of the solvent to decreased amount of the liquid solvent (R_{dec}) with time (solvent: (●) toluene, (□) methanol).

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