Effects of background-gas composition on phenol decomposition by pulsed-discharge plasma above a water surface

By-products from phenol by the exposure of pulsed-discharge plasma above a phenol aqueous solution are investigated, and the effects of background-gas composition on phenol decomposition by the pulsed plasma exposure above a water surface are examined. When Ar is used as a background gas, catechol, hydroquinone and 4-hydroxy-2-cyclohexene-1-on are produced. When O₂ is used as a background gas, CO₂, CO, catechol, hydroquinone, formic acid, maleic acid, succinic acid and 4,6-dihydroxy-2,4-hexadienoic acid are produced. When Ar-O₂ mixture is used as a background gas, by-products, produced in O₂, are produced, and the quantities of the products tend to be proportional to the mixture ratio of O₂.

1. Introduction

Water pollution by persistent organic pollutants and volatile chlorinated organic compounds is serious problem. Species, having high oxidation potential, such as OH, H₂O₂ and ozone, can be produced when pulsed-discharge plasma is generated above or in water, and those species have potential to decompose the pollution, water treatment techniques using a pulsed discharge have attracted attention. In this work, we minutely investigate the by-products of phenol decomposed by pulsed-discharge plasma generated above a phenol aqueous solution when Ar, O₂ and Ar-O₂ mixture are used as a background gas, and deduce decomposition processes of phenol from the by-products. Further, we investigate effects of background gas composition on phenol decomposition.

2. Experimental apparatus and procedure

A needle electrode and a water bath electrode, made of stainless steel, are placed in a cylindrical discharge chamber made of acrylic resin, having 140 mm in inner diameter and 100 mm in height. The needle electrode is 1.5 mm in diameter and 19 mm in length, and the water bath electrode, which is earthed, is 119 mm in inner diameter and 12 mm in depth, having 0.13 L in capacity. 70 g of phenol aqueous solution with a concentration of 3000 ppm is poured into the water bath, and the distance between the needle electrode and the surface of the phenol aqueous solution is fixed at 4 mm. Ar and O₂, the purities of which are 99.99% and 99.5 %, respectively, are used as a background gas, and it is fed into the discharge chamber at a constant flow rate of 1 L/min. The mixture ratios of the background gas are Ar:O₂=100:0, 95:5, 90:10, 50:50 and 10:90.

Liquid samples are taken before and after the plasma exposure, and they are analyzed by a Gas Chromatograph Mass Spectrometer (Shimadzu, GCMS-QP2010 Plus, column: DB-17ms). Further, off-gas from the discharge chamber is analyzed by a Fourier Transform Infrared Spectrophotometer (Shimadzu, FTIR-8900).

3. Results and Discussion

In a previous work [1], it is found that catechol, hydroquinone and 4-hydroxy-2-cyclohexene-1-on are produced from phenol when Ar is used as a background gas, and that formic acid, maleic acid, succinic acid, 4,6-dihydroxy-2,4-hexadienoic acid, catechol and hydroquinone are produced from phenol when O₂ is used as a background gas. Also, CO₂ and CO are found in the off-gas from the discharge chamber only when O₂ is used as a background gas. Also, CO₂ and CO are found in the off-gas from the discharge chamber only when O₂ is used as a background gas.

Figure 1 shows the decomposition process of phenol when Ar is used as a background gas. No ozone production is observed, so that OH radicals generated in the plasma can initiate the decomposition of phenol. Also, 4-hydroxy-2-cyclohexene-1-on is detected in this work, it is likely that phenol is converted into 4-hydroxy-2-cyclohexene-1-on at first by the reaction with OH radical, and that 4-hydroxy-2-cyclohexene-1-on is converted into catechol and hydroquinone. Since catechol and
gas.

**Fig. 1.** Decomposition process of phenol when Ar is used as a background gas.

Hydroquinone can be produced through another process, which is not clarified, because catechol and hydroquinone are detected when Ar-O2 mixture gas is used as a background gas, at which no 4-hydroxy-2-cyclohexene-1-on is produced. Figure 2 shows the decomposition process of phenol when pure O2 is used as a background gas. Since ozone is produced when O2 is used as a background gas, phenol is probably decomposed into 4,6-dihydroxy-2,4-hexadienoic acid by 1,3-dipolar addition reaction with ozone. Further, 4,6-dihydroxy-2,4-hexadienoic acid is decomposed into oxalic acid, maleic acid and succinic acid by O3, and oxalic acid is probably decomposed into formic acid, CO2 and CO.

**Fig. 2.** Decomposition process of phenol when O2 is used as a background gas.

**Fig. 3.** Concentration of O3 and by-products as functions of mixture ratio of Ar-O2

**References**

