Analysis of hexadecane decomposition by atmospheric microplasma

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Abstract— **Atmospheric microplasma has a potential to be one of the technology used to purify the indoor air. In this study, we examined the removal of hexadecane by using it. The removal energy efficiency of hexadecane was evaluated to 0.069 g/Wh. Several products were generated with the plasma process and were analyzed by detector tubes, Fourier transform infrared spectroscopy (FTIR) and gas chromatograph - mass spectrometer (GC-MS). According to the products analysis, CO_2, O_3, N_2O and various kinds of alkenes were found after the plasma process.**

I. INTRODUCTION

People spend long time inside buildings thus indoor air quality (IAQ) is an important element to people's health. Specifically, smell, fine particles and chemical substances became an issue [1]-[9]. Therefore many technologies of purifying indoor air are studied. Plasma is known as one of the technologies. Plasma discharge in air generates O_3, some active species and UV. These are useful for decomposing chemical substances or sterilizing bacteria.

In this study, target of removing was hexadecane ($C_{16}H_{34}$) [10]-[13]. It is one of the semi-volatile organic compounds (SVOC) [14], and is present in the gasoline for the diesel engine [15], [16]. It comes from outside with air mixed with the exhaust gas to indoor. It causes bad smell or affects the respiratory organs. Large molecular weight substances such as hexadecane are not easy to remove, since it has many carbon-carbon bonds. The bond is strong and, it has low chemical reaction. Therefore we have carried out a removal process by plasma. During this process, various products were measured and analyzed by using detecting tubes, FTIR and GC-MS.

II. MICROPLASMA ELECTRODE

Figure 1 shows the microplasma electrode system used in this study. It consisted of two electrodes which have the aperture ratio of 41.5 % and are coated with dielectric. Electrodes were faced each other with a 30 μm gap in between and fixed at periphery by resin. Plasma was generated between the two electrodes, and the gas was processed while passing through the holes [17]-[19]. Discharge starting voltage was 400 V_{0-p} in air.
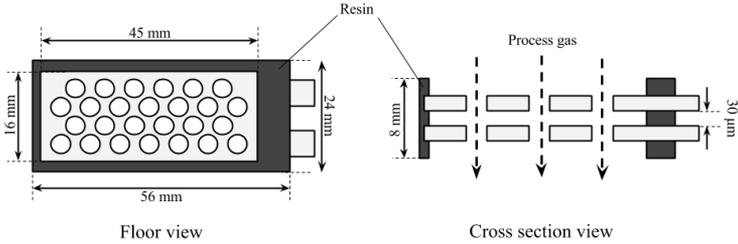
Fig. 1. Microplasma electrode.

Figure 2 shows measurement circuit of the electrode system. The electrode was energized by a 27 kHz sine wave AC from a neon transformer [17]. Applied voltage was controlled using a slide transformer.
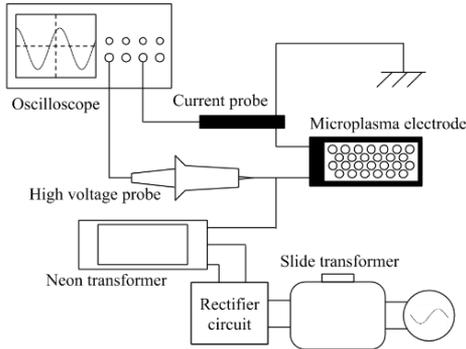
Fig. 2. Measurement circuit.

Figure 3 shows the waveforms of voltage and current when the electrode was energized at 550 V_{0-p} in air. Because of plasma generation, some spikes could be observed in the waveform of current.
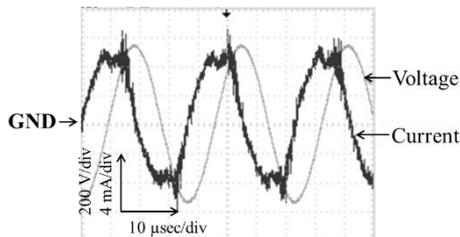
Fig. 3. Waveform of voltage and current.

Figure 4 shows electric power consumption while electrodes were energized and various gases were used as discharge gas. In case of argon, plasma discharge started at lower voltage than in the case of other gases.
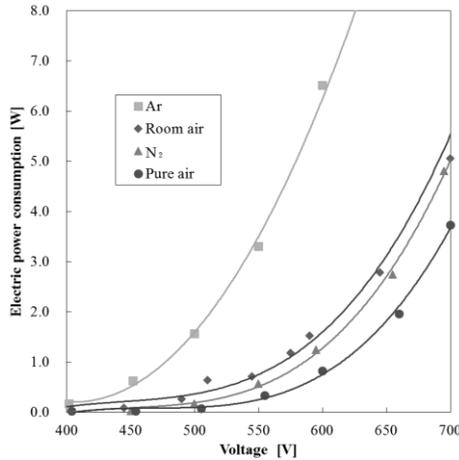
Fig. 4. Electric power consumption.

III. MEASUREMENT OF HEXADECANE

The process of removing of hexadecane by the electrode was following:

1. Setting of the electrode in small chamber (11.4 l) and closing it.
2. Hexadecane was vaporized in the chamber to produce about 3000 ppm of gas phase of hexadecane.
3. 450 V_{0-p} was applied to the electrode for 120 minutes.

All the gases utilized in the study (pure air, N_2, and Ar) were from the gas cylinder (G3 grade). Amount of removed hexadecane was evaluated by FTIR.

Figure 5 shows the spectrum before and after 120 minutes of the plasma processing. Vibrational band belonging to hexadecane was decreased and that of CO and of N_2O were increased. Other bands could not be distinguished because of many overlapped spectra of present molecules.
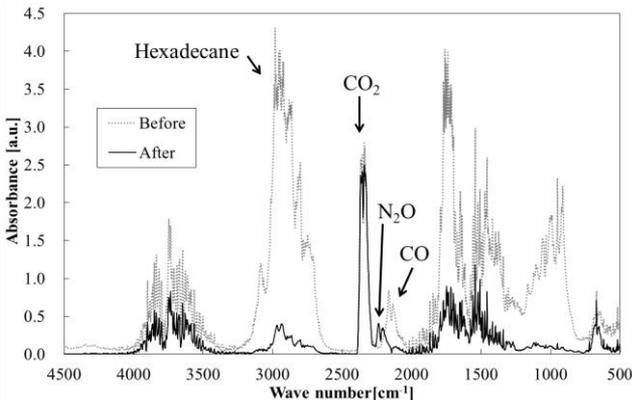
Fig. 5. The spectrum before and after 120minutes plasma processing.

Figure 6 shows the spectrum before and after vaporizing the hexadecane in the chamber. Generally observed alkanes or alkenes are shown by the arrows in the upper part of Figure 6. Various kinds of alkane or alkene were generated with vaporizing hexadecane.
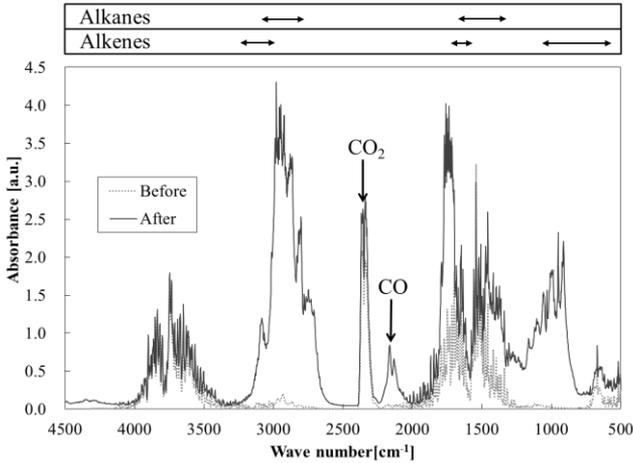
Fig. 6. The spectrum before and after vaporizing of hexadecane.

Figure 7 shows spectrum before and after 120 minutes without the plasma processing in the chamber (after this section this is defined as "natural decay"). Hexadecane was decreased without the plasma processing after vaporization because it condensed on walls of the chamber.
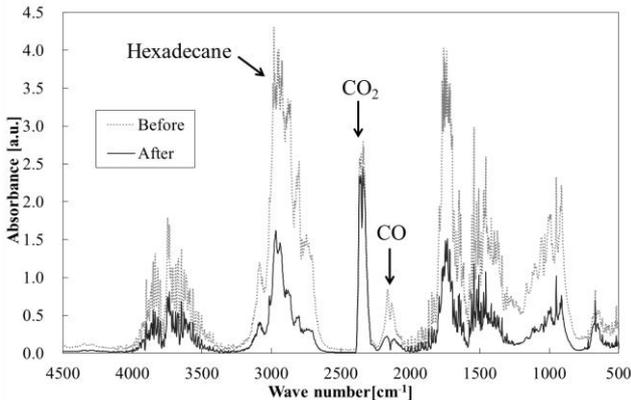
Fig. 7. The spectrum before and after 120minutes without the plasma processing.

The maximum peak in 2984-2833 cm^{-1} was used for estimating the hexadecane concentration.

Figure 8 shows the concentration of hexadecane dependent on processing time. Hexadecane concentration after the plasma processing was lower than after the natural decay. Initial concentration of 3000 ppm was decreased to 105 ppm after the 120 min of processing. A decrease to 950 ppm occurred also by the natural decay, thus removal of hexadecane was promoted by the plasma process. The removal energy efficiency of hexadecane was evaluated to be 0.069 g/Wh.
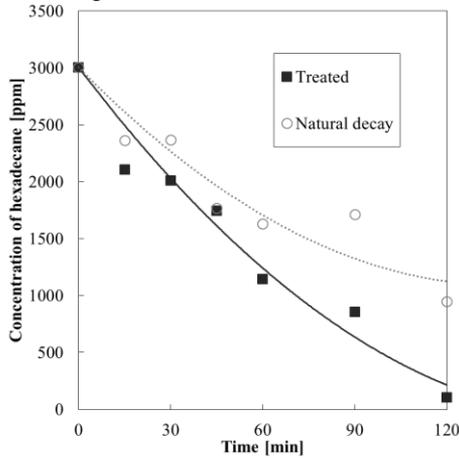
Fig.8. The concentration of hexadecane with processing time.

IV.   MEASUREMENT OF BY-PRODUCTS

For analyzing the by-products, the removal process was examined while using argon, nitrogen and air without H_2O.

The concentration of O_3, H_2O, CO and CO_2 were measured by using detecting tubes. These could not be exactly measured by FTIR because of many overlapped bands.

Figure 9 shows the concentration change of various products. The concentration of O_3 and CO_2 was increased, and that of H_2O and CO was not changed with the processing time.
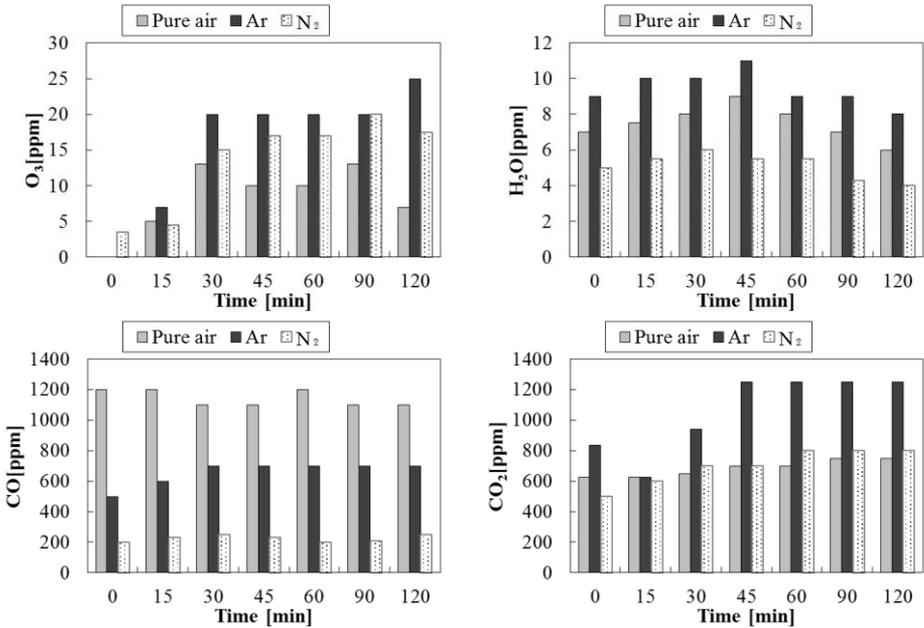
Fig. 9. The concentration of by-products for various times of plasma processing.

According to FTIR measurements, various alkane or alkene were generated during the plasma processing. It was analyzed by using GC-MS for more detail measuring. Measurements, were carried out with the following four patterns:

- Natural decay (it was only evaporated hexadecane).
- The plasma process in the pure air.
- The plasma process in the Ar.
- The plasma process in the N_2.

Concentrations of alkanes and alkenes in the chamber were measured by GC-MS. The amount of the substances were evaluated using the maximum value of extracted each mass chromatograms from total chromatograms.

The results of GC-MS measurements are shown in Figures 10-13. Figures 10 and 11 show the maximum value of each alkane mass chromatograms before and after 120 minutes. In figures 12 and 13 are shown the maximum number of each mass chromatograph in case of alkene before plasma process and after 120 minutes of treatment. Note that in figures 11 and 13, that were not any plasma treatment for "natural decay". Alkanes and alkenes which have 4-17 carbons were detected in the measurement. In figures 10 and 12, less amount of almost all substances was measured while the process gases were Ar and N_2. However, these results were opposite after 120 minutes of plasma processing, as it is shown in figures 11 and 13. In addition to it, some of them decreased less than by natural decay in spite of using the plasma discharge. These was considered to occur because of the higher amount of products which were obtained from the hexadecane decomposition by the plasma processing than the amount of decrease by natural decay.
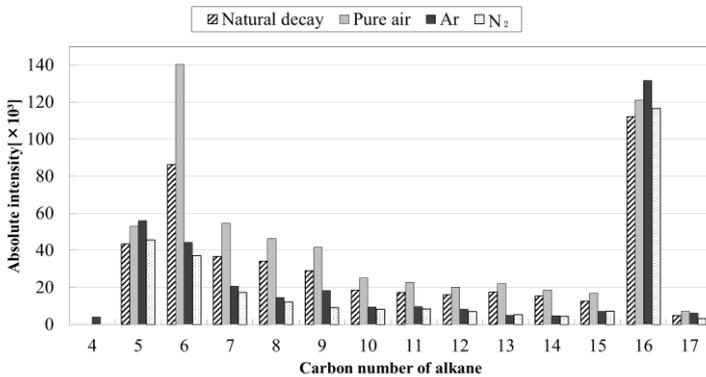
Fig. 10. The maximum value of each alkane mass chromatograms
(The elapsed time 0 minutes).
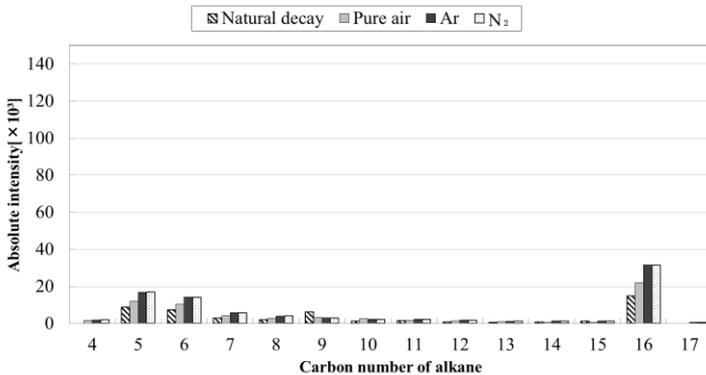
Fig. 11. The maximum value of each alkane mass chromatograms
(The elapsed time 120 minutes).

V. DISCUSSION

It was confirmed that N_2O, O_3, CO_2, various alkanes and alkenes were generated by the decomposition process of hexadecane. It is generally known that N_2O and O_3 are generated by plasma discharge in air [20]. Also CO_2 and other hydrocarbons were found by using gas detecting tubes as the final products from decomposed hexadecane [21], [22].

Hexadecane has many carbon single bonds, and there was considered that the carbon bonds could be cut by the active species generated by the microplasma. The chemical substances which have less carbon atoms were formed as intermediate products [23], [24]. The bonds were cut several times, and finally substances such as CO_2 were obtained [25].
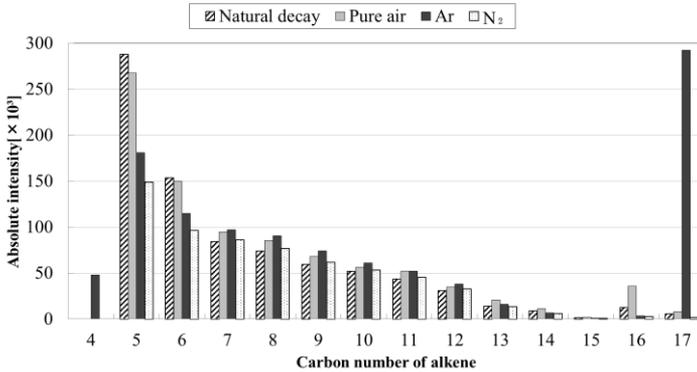
Fig. 12. The maximum value of each alkene mass chromatograms
(The elapsed time 0 minutes).
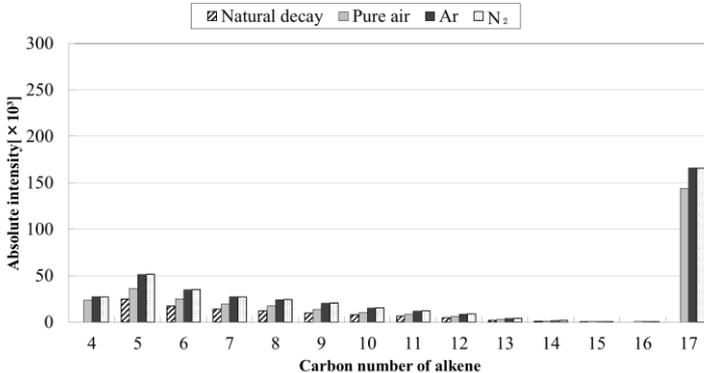
Fig. 13. The maximum value of each alkene mass chromatograms
(The elapsed time 120 minutes).

VI. CONCLUSION

From the process of decomposing hexadecane by microplasma and analyzing their intermediate and final products, the following results were obtained:

(1) A decrease in the concentration from 3000 ppm of hexadecane to 105 ppm was obtained after 120 minutes of plasma processing. In the case of natural decay, the concentration of hexadecane decreased to 950 ppm after 120 minutes. Amount of hexadecane was decreased by the plasma processes over the amount of natural decay.

(2) One of the final product of hexadecane decomposition was CO_2. In addition, various alkanes and alkenes were formed during the decomposition process. These intermediate products' concentrations were also decreased similarly to the hexadecane after the plasma processing.

VII. REFERENCE

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