

COMPARISON OF DECOMPOSITION CHARACTERISTICS BETWEEN AROMATIC AND ALIPHATIC VOCs USING ELECTRON BEAM

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Abstract

The removal efficiency of n-decane ($C_{10}H_{22}$) by electron beam was the highest among aliphatic VOCs of concern, and that of n-hexane (C_6H_{14}), n-butane (C_4H_{10}), and methane (CH_4) followed. On the other hand, in terms of aromatic VOC decomposition efficiencies, benzene (C_6H_6) decomposition was the lowest and that of toluene (C_7H_8), ethylbenzene (C_8H_{10}), and p-xylene (C_8H_{10}) were similar. It was also found that there was increase in by-product (untreated VOC, CO, CO_2 , O_3 , and other compounds) formation as well as all VOC removal efficiencies. It was demonstrated that the removal efficiency of VOC increased as its concentration decreased and the irradiation dose increased. In addition, low removal efficiency was observed because helium was relatively stable compared to the other gases, and nothing but electrons produced by electron accelerator reacted with VOC. It was also found that relative humidity had some effects on the decomposition rates of VOC. The removal efficiency at the 100 % RH condition was slightly higher than that at 7.4 % RH (dry condition) due to OH radical formation.

1. INTRODUCTION

Volatile organic compounds (VOCs) have been well-documented as one of the most important ozone (O_3) precursors. Many countries have concerns about reducing VOCs because they have adverse effects on human health as carcinogenic and toxic substances [1, 2]. There are many different conventional techniques to control VOCs emissions from a variety of industrial processes. They are carbon adsorption, absorption, catalytic oxidation, thermal incineration, and biotreatment [3, 4]. The method of VOC removal by electron beam (EB) irradiation has been taken into account as one of the most recent novel technologies [1, 5, 6]. EB process can be operated economically for the low VOC concentrations diluted in high volume flows at room temperature [7, 8]. The EB operation time is quite short because the electrons are generated during 10^{-18} ~ 10^{-12} seconds and interact with the gas molecules. Besides, this reaction produces free radicals and ions during 10^{-8} ~ 10^{-1} seconds. In this study, the degradation characteristics of n-hexane were mainly investigated for different concentrations, background gases (oxygen, nitrogen, air, and helium), absorbed doses (kGy, kJ/kg), and relative humidities (RH) using electron beam irradiation. In addition, the decomposition rates of saturated aliphatic VOCs (methane, n-butane, n-hexane, and n-decane) were compared, and those of aromatic and aliphatic VOC were also compared.

2. EXPERIMENT

An electron beam accelerator (1 MeV, maximum power 40 kW, ELV4 type) was used for electron beam irradiation. One liter of oval tedlar reactors (SKC, USA) were used in order to control hexane under various background gases, different concentrations, and absorbed doses during the batch treatment. The hexane decomposition system using EB irradiation is depicted in FIG. 1 and FIG. 2. The absorbed dosage was operated in the range of 2.5 to 10 kGy. Different concentrations (140, 300, and 600 ppmC) of reactors with various background gases were put onto a conveyor system and passed under the scanning window of the electron accelerator at a speed of 10 m/min.

A GC/FID (HP5890 Series II, Hewlett Packard, USA) was used to make quantitative analysis of the samples. The GC column was HP-1 ($25m \times 0.32mm \times 0.52\mu m$). Sampling was conducted using adsorbent trap (Carbopack B / CarboxenTM 1000) for the qualitative analysis. GC/MSD (Clarus 500, Perkin Elmer, USA) coupled with thermal desorber (Aerotrap 6000, Tekmar, USA) was also employed. The sample trap was then desorbed using helium (25 mL/min) at 250°C for 5 min with the desorbed material collected in a cryotrap at -150°C. The hexane samples were transferred to a cryofocus trap at -150°C through a transfer line held at 190 °C. Finally, the chemicals concerned were

Working Material

injected into a GC capillary column DB-1 ($50\text{m} \times 0.32\text{mm} \times 5.0\mu\text{m}$). A CO/CO₂ analyzer (Gas Data PAQ, UK) was adopted to measure the amount of CO and CO₂. The relative standard deviation (RSD) obtained from the quantitative analysis turned out to be less than 7.6 %.

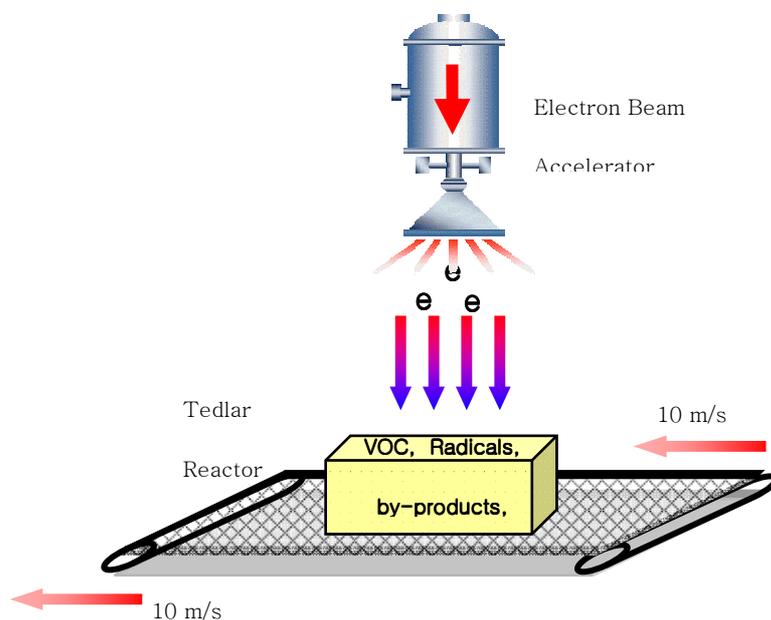


FIG. 1. VOC decomposition using electron beam technique (Batch system).

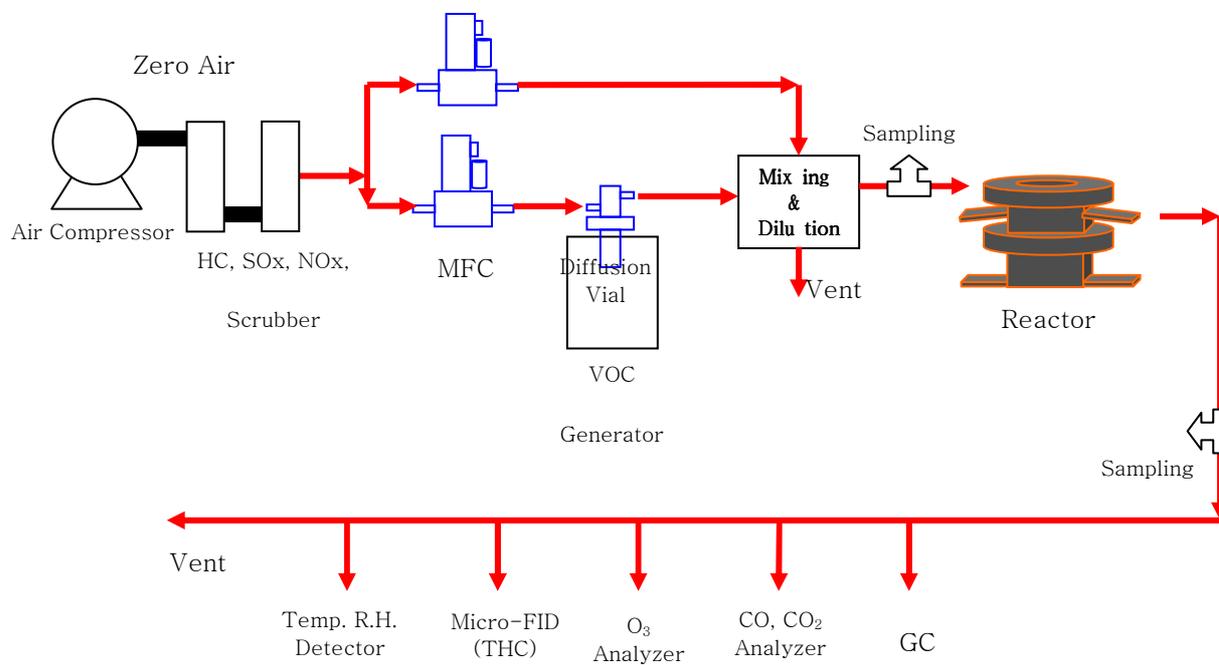


FIG. 2. VOC decomposition using electron beam technique (Continuous flow system).

3. RESULTS AND DISCUSSION

3.1. Effects of the background gas

Approximately 140 ppmC of hexane mixed with ultra-high purity He, N₂, O₂, and Air atmosphere was controlled by EB irradiation in order to determine the mechanism of hexane decomposition. Fast moving primary electrons interact with the background gas molecules, and this reaction produces ions, electron-ion pairs, and free radicals through ionization and excitation processes. Major free radicals are OH•, HO₂•, O•, N• and H•. These primary and secondary activated species rapidly react with VOCs. FIG 3 suggests that the hexane removal efficiency (49 % at 10 kGy) under helium atmosphere should be considerably lower than that under the other gases (95~98 % at 10 kGy). The low removal efficiency is expected because helium is relatively stable compared to the other gases, and nothing but electrons produced by electron beam react with hexane. The removal efficiency when mixed with oxygen, nitrogen, and air atmospheres was much higher than that of helium. In general, the decomposition efficiency of hexane (140 ppmC) under the He, N₂, O₂, and Air atmosphere increased as the absorbed dose increased.

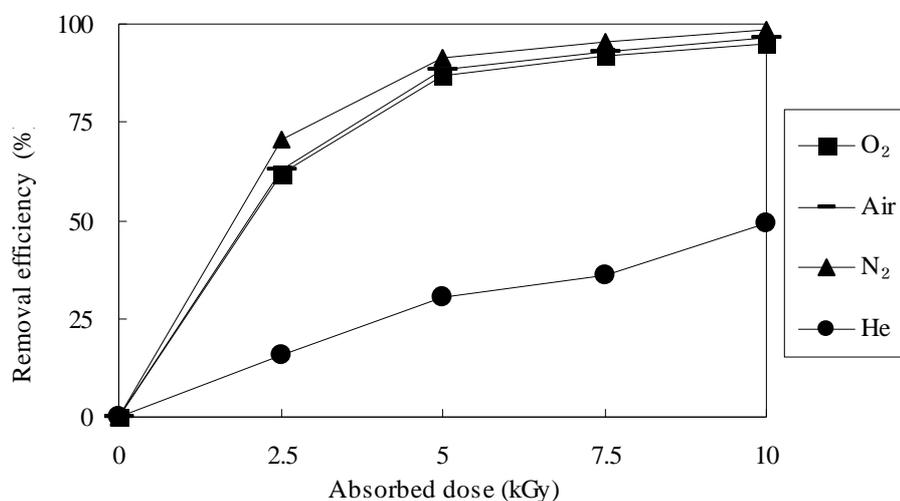


FIG. 3. Removal efficiency of Hexane (140 ppmC) by background gases.

3.2. Effects of the initial concentration and humidity

The decomposition characteristics of hexane at various concentrations in an air atmosphere are seen in FIG. 4. It was found that the removal efficiency of hexane increased with a decrease in initial concentration. In the range of 2.5 to 10 kGy, the removal efficiencies at 140, 300, and 600 ppmC were 63~96%, 46~88%, and 23%~50%, respectively. This trend of hexane degradation agrees with those of previous studies [7, 8].

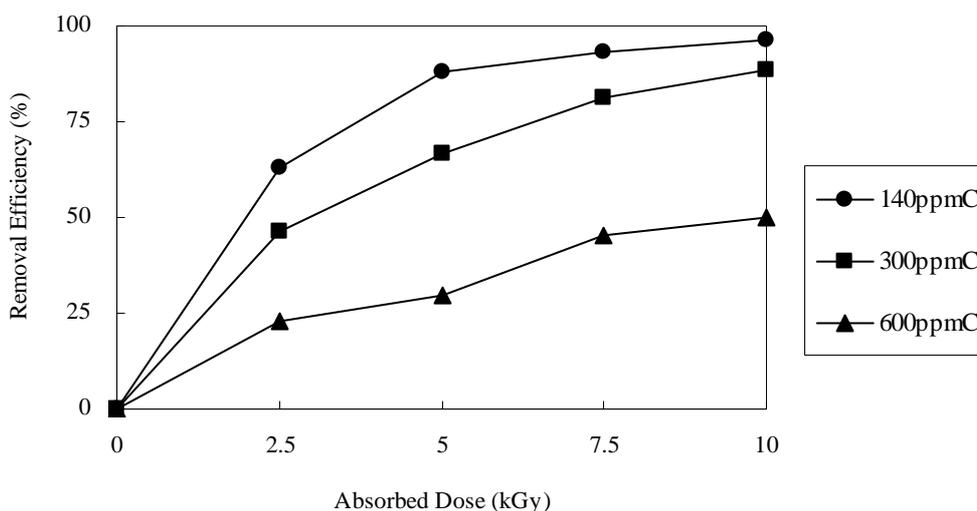


FIG. 4. Hexane removal efficiency with respect to concentrations.

The removal efficiency of hexane with respect to relative humidity (RH) inside the reactor is presented in FIG. 5. If H₂O (water vapor) is added to the air environment while using EB irradiation, the chemical reaction rate becomes faster because of OH radical formation. Therefore, it was found that there was a 2 to 6 % removal difference between 50 and 100 % RH conditions. More extensive studies on humidity effects need to be carried out in the future to get a more clear understanding of this OH radical effect.

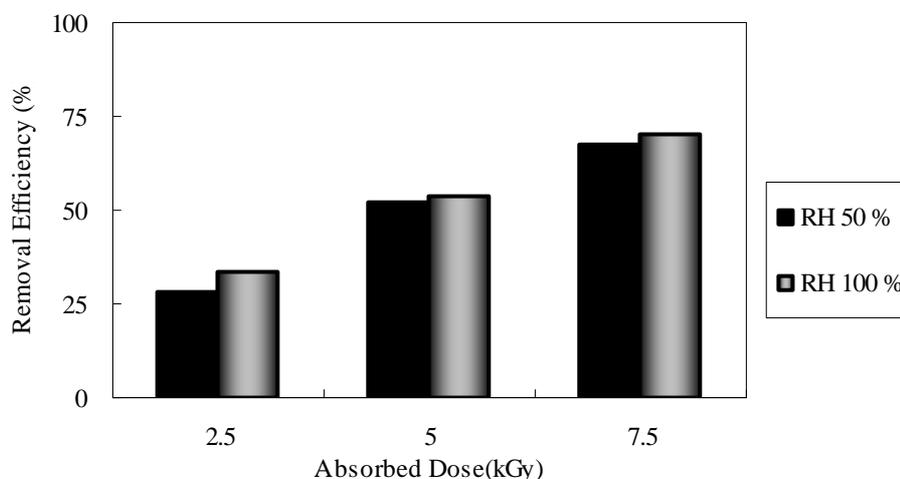


FIG. 5. Hexane removal efficiency by relative humidity (RH).

3.3. Formation of carbon monoxide (CO) and carbon dioxide (CO₂)

Concentrations of carbon monoxide (CO) and carbon dioxide (CO₂) generated by EB irradiation are shown in FIG. 6 and 7. Although both CO and CO₂ concentrations increased in proportion to the dosage increment, slight differences between two initial hexane concentrations were observed. This can be explained through carbon mass balance because the initial hexane concentrations were low.

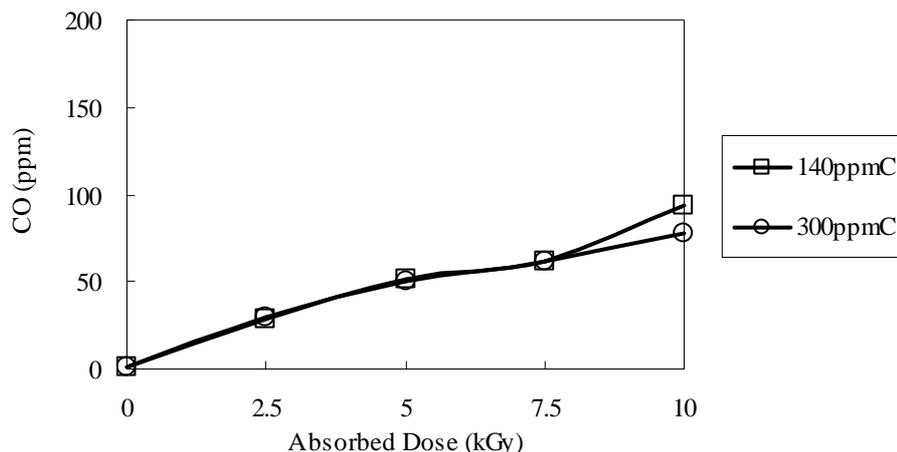


FIG. 6. Variations of CO concentration at various doses and two different hexane levels.

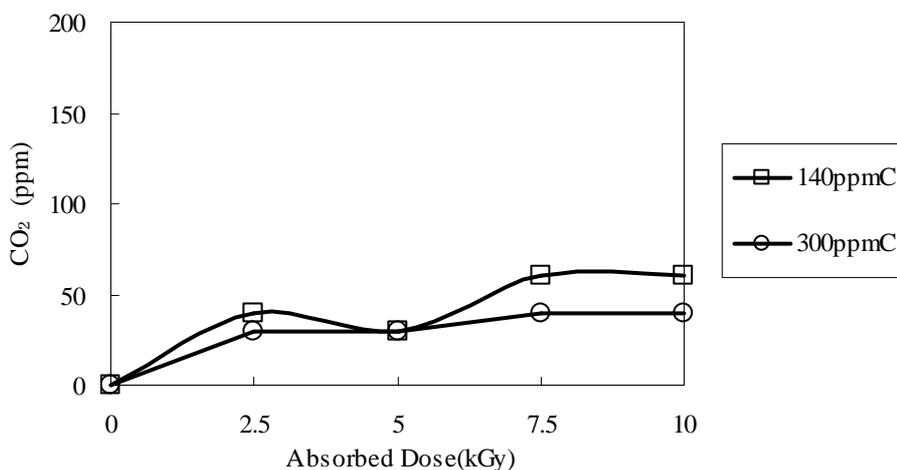


FIG. 7. Variations of CO₂ concentration at various doses and two different hexane levels.

3.4. Comparison of hexane and aliphatic VOCs decomposition

The removal efficiencies were compared with respect to absorbed doses in order to study the decomposition characteristics hexane and aliphatic VOCs. The decomposition rate of methane was very low as 8 % and of n-decane was almost 100 % at 10kGy. The rate of aliphatic VOCs appears to be increasing depending upon number of carbon. As an aliphatic VOC removal result, the removal efficiency of n-decane(C₁₀H₂₂) by electron beam was the highest and that of n-hexane(C₆H₁₄), n-butane(C₄H₁₀), and methane(CH₄) followed.

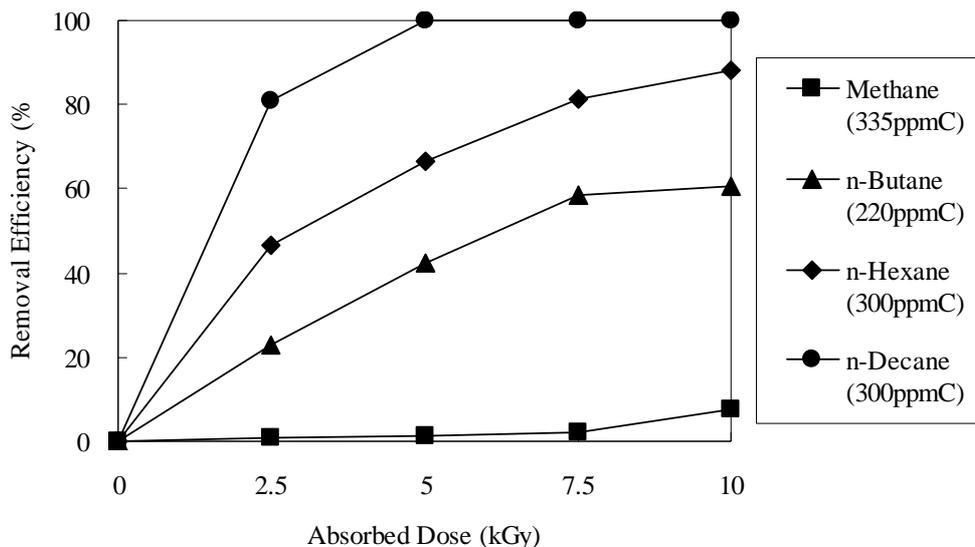


FIG. 8. Variations of aliphatic VOCs removal at various doses.

3.5. Comparison of hexane and aromatic VOCs decomposition

In terms of aromatic VOC decomposition efficiencies, benzene decomposition was the lowest and that of toluene, ethylbenzene, and p-xylene was similar. The decomposition rate of hexane as aliphatic VOC was as higher as 15 % compared to that of toluene at 10kGy. Comparing reaction rate constants with OH radical for hexane(5.36×10^{-12}) and toluene(5.96×10^{-12}), these values were similar, however decomposition rate of hexane was higher than that of toluene. This suggested that aromatic VOC with benzene ring should be more difficult to decompose than aliphatic VOC with a series of carbon chain although they have similar reaction rate constants with OH radical.

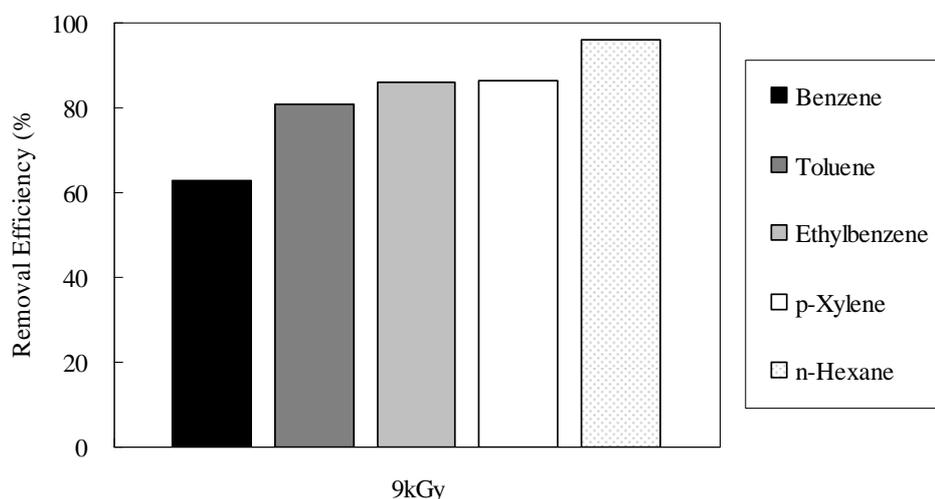


FIG. 9. Comparison of hexane and aromatic VOCs at 9kGy (initial concentration: 130ppmC ~ 140ppmC).

4. CONCLUSION

The application of a novel control technique using electron beam irradiation has been studied to control hexane contained in various background gases (helium, nitrogen, oxygen, and air). This study demonstrated that the removal efficiency of hexane increased as its concentration decreased and the irradiation dose increased. The maximum hexane removal efficiencies at 10 kGy were 98.4, 96.4, 95.2, and 49.1 %, respectively with nitrogen, air, oxygen, and helium atmospheres. Additionally, the maximum hexane decompositions at the initial concentrations of 140, 300, and 600 ppmC were determined to be 96.4, 88.3, and 49.9 %, respectively. It was also found that relative humidity (RH) had some effects on the decomposition characteristics of hexane. The removal efficiency at the 100 % RH condition was slightly higher than that at 50 %. As an aliphatic VOC removal result, the removal efficiency of n-decane(C₁₀H₂₂) by electron beam was the highest and those of n-hexane(C₆H₁₄), n-butane(C₄H₁₀), and methane(CH₄) followed. On the other hand, in an aromatic VOC decomposition efficiency, benzene(C₆H₆) decomposition was the lowest and those of toluene(C₇H₈), ethylbenzene(C₈H₁₀), and p-xylene(C₈H₁₀) were similar. Further comparison studies on the degradation characteristics of other aliphatic and aromatic VOC under continuous flow system should be performed to determine more characteristic control parameters.

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