

Ozonation of styrene in the flue gas from fiberglass reinforced plastics manufacturing facility: Laboratory and on-site studies

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Abstract—Styrene is a typical volatile organic compound (VOC) emitted from various sources that is considered hazardous due to its toxicity and strong odor. Many technologies have been developed to control VOCs, including plasma, catalytic, and thermal oxidation. In this study, styrene, one of the typical VOCs, was decomposed by ozone (O₃) in laboratory and on-site systems. In a laboratory reactor, the styrene conversion efficiency in the reaction was determined under different temperatures, inlet styrene concentrations, and [O₃]/[styrene] mole ratios. The styrene conversion efficiency decreased as the reaction temperature increased and was higher at higher mole ratios. A complete conversion was obtained in the laboratory system at room temperature, and 58.3% styrene conversion efficiency was achieved in the on-site system.

Keywords: Styrene, Ozone, On-site System, Volatile Organic Compound (VOC), Decomposition

INTRODUCTION

Volatile organic compounds (VOCs) are emitted from various industrial sources, including petroleum refining, automobile manufacturing, shipbuilding, furniture manufacturing, footwear, pharmaceuticals, packaging, and printing [1-3]. They can cause adverse health effects and also have environmental consequences, so effective removal technologies are essential to meet clean air standards [2,4-7]. Many technologies have been used to destroy VOCs, including thermal incineration, adsorption, and catalytic/plasma oxidation [4,8-13].

Styrene is a typical VOC and a widely used alkene, typically ranging from 0.06 to 45 ppb in the ambient atmosphere due to emissions from anthropogenic sources, such as adhesives, solvents, tobacco smoke, and automobile exhaust [9-12]. Styrene is odorous and harmful to human health, with potential carcinogenic and mutagenic properties, as well as causing damage to the central nervous and reproductive systems [13-15]. Styrene emission easily occurs in the fiberglass reinforced plastics (FRP) lamination process, and the indoor styrene concentration of workplace is regulated to 20 ppm or less for workers [21].

Ozonation is one of the most effective technologies to control gas phase pollutants [17-20]. The ozonolysis of unsaturated hydrocarbons in atmospheric chemistry is known as the Criegee mechanism [14,26,27]. Zhang et al. examined styrene removal with an AC/DC streamer corona plasma system in air and found that the reaction between ozone (O₃) and styrene molecules proceeded at a rapid rate [28]. Nguyen et al. degraded styrene in a plasma catalytic system and found that the O₃ formed by the plasma played an important role in styrene oxidation [4]. Ghavami et al. reported

that catalytic ozonation is an efficient process for removing VOCs at low reaction temperatures, and was more effective than catalytic oxidation in an advanced oxidation process [29]. An oxidation process using O₃ is considered to be an attractive pollution control option due to its high oxidant capacity and electrophilic characteristics [23,30,31]. However, the ozone is sensitive against temperature and collision with other components and can be decomposed to oxygen (Eq. (1)). Therefore, ozonation was mainly studied at room temperature [10-12,26,32].



Tuazon et al. examined the gas-phase reactions of styrene with O₃ at room temperature and identified formaldehyde (HCHO) and benzaldehyde (C₆H₅CHO) as the two major products of the styrene-O₃ oxidation system, with respective molar yields of 37±5% and 41±5%, while carbon monoxide (CO: 7±2%), carbon dioxide (CO₂: 4±2%), benzoic acid (C₆H₅COOH: ~1%), and formic acid (HCOOH: 1-2%) were found to be minor products [32]. Based on the hazardous substances data bank (HSDB), the solubility of styrene is 0.31 g/L (25 °C). However, the solubility of main products such as HCHO and C₆H₅CHO is 400 g/L (20 °C) and 6.95 g/L (25 °C), respectively, considerably higher than that of styrene. Na et al. investigated the O₃ reaction with the olefinic double bonds of styrene to generate secondary organic aerosol (SOA) formation and proposed that 3,5-diphenyl-1,2,4-trioxolane and a hydroxyl-substituted ester were the major aerosol-forming products in the styrene ozonolysis system [15]. Based on these previous studies, it is possible that styrene emissions can be reduced by a combined styrene-O₃ reactor and wet scrubber system, where products such as HCHO, C₆H₅CHO, and SOA can be captured. However, there have been few industrial on-site studies of styrene ozonation, whereas there has been much research conducted on styrene distribution in ambient air and laboratory-scale ozonation [10,12-15,33].

In this study, ozonation of styrene in an industrial flue gas was

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conducted. The basic concept was that ozonation products such as HCHO and C_6H_5CHO can be easily removed by a wet scrubber due to their higher solubility compared to styrene, and SOA can also be eliminated physically. As a preliminary test, the effects of the O_3 /styrene ratio, styrene concentration, and reaction temperature on styrene conversion efficiency were determined in a laboratory-scale reactor. The reaction temperature was varied to 250 °C due to the on-site flue gas condition, which was emitted from regenerative thermal oxidation system.

To determine the on-site ozonation efficiency, O_3 was injected into the flue gas emitted from a work place ventilation system of FRP manufacturing company located in Daejeon, Korea, that was required to install a flue gas styrene control system in addition to its existing wet scrubbing system due to civil complaints regarding odors.

MATERIALS AND METHODS

1. Laboratory-scale Reactor and Procedure

Fig. 1 is a schematic diagram of a laboratory-scale reactor made of a stainless steel tube (0.02-m i.d.×0.4-m length), which was placed inside a horizontal electrically heated furnace. The temperature was controlled by a K-type thermocouple at the center of the stainless steel tube reactor. Styrene was injected into the reactor together with nitrogen gas (N_2) through a mass flow controller. The styrene concentration was varied from 10 to 45 ppm, which was controlled by altering the gas flow rate of the 50-ppm styrene and N_2 mixture. Ozone was produced by a plasma O_3 generator (Ozonetech Corp., Daejeon, South Korea), and a 1-2% O_3/O_2 mixture was injected into the reactor through a mass flow controller. The reaction tempera-

Table 1. Experimental condition of the laboratory-scale reactor

Reaction temperature	(°C)	25-250
Styrene concentration	(ppm)	10-45
$[O_3]/[styrene]$ ratio	(-)	1-10

ture was varied from room temperature to 250 °C, and the mole ratio of $[O_3]/[styrene]$ was varied from 1.0 to 10.0. The experimental condition is shown in Table 1.

After the reactors were heated to preset temperatures with N_2 carrier gas, 50-ppm styrene- N_2 mixture was fed into the tube reactor and the styrene concentration was measured at the entrance and exit of the reactor. After the styrene concentration was stabilized at the initial set value, ozone was introduced and sampling of product gases was performed 3-4 times for each reaction condition to obtain an average value.

The initial and produced gases were sampled and analyzed by a gas chromatograph-mass spectrometer (GC-MS: 7890D-5975C; Agilent Technology, Santa Clara, CA, California, USA) equipped with an Agilent 19091P-Q04 (30 m×320 μm ×20 μm) column, and GC-pulsed discharge detector equipped with GS-Q (30 m×530 μm ×20 μm) and molesieve (30 m×530 μm ×20 μm) columns. The styrene conversion efficiency (%) was calculated as follows [4]:

$$\text{Styrene conversion (\%)} = \left(1 - \frac{\text{Styrene in flue gas}}{\text{total styrene fed}} \right) \times 100 \quad (2)$$

2. On-site System

Fig. 2 shows the on-site ozonation test facility. Ozone was injected to the flue gas at 2 m before the wet scrubber. Based on the laboratory-scale results, O_3 was injected at a flow rate of 2.7 L/min

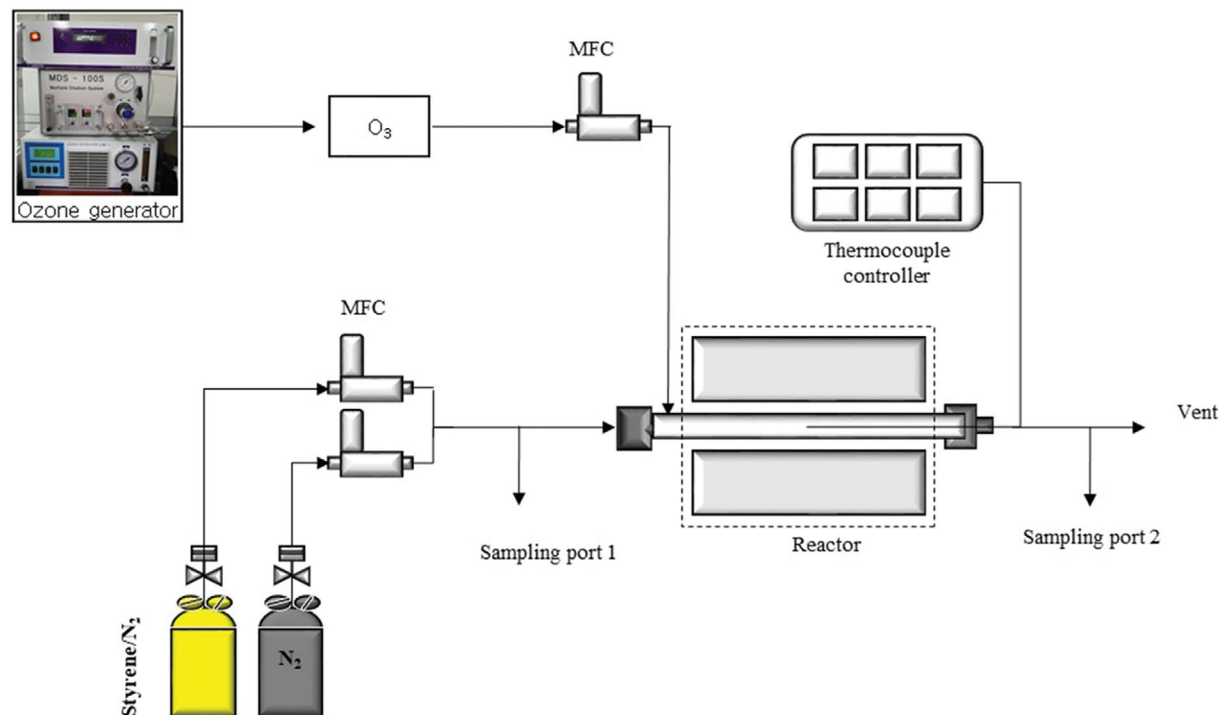


Fig. 1. Schematic diagram of the laboratory-scale reactor.



Fig. 2. On-site test facility.

($[O_3]/[styrene]=5$) by the O_3 generator (Ozonetech Corp.). The original flue gas and the flue gas after O_3 injection were sampled from the stack and analyzed by the same GC-MS used for the laboratory-scale reactor samples.

RESULTS AND DISCUSSION

1. Laboratory-scale Reactor

To investigate the effects of reaction temperature, styrene concentration, and mole ratio on styrene conversion efficiency, a styrene- O_3 reaction was conducted in a laboratory-scale reactor. Fig. 3 shows the effects of temperature on conversion efficiency at a 30-ppm styrene concentration. Conversion efficiency decreased as the reaction temperature increased and was higher at the higher mole ratio due to the promotion of styrene decomposition. At the mole ratio of 5.0, the conversion efficiency was 100% at room temperature and 100 °C. At the mole ratio of 3.0, styrene was completely converted at room temperature. The conversion efficiency decreased from 100% at room temperature to 20% at 200 °C. However, at the mole ratio of 1.0, the conversion efficiency decreased

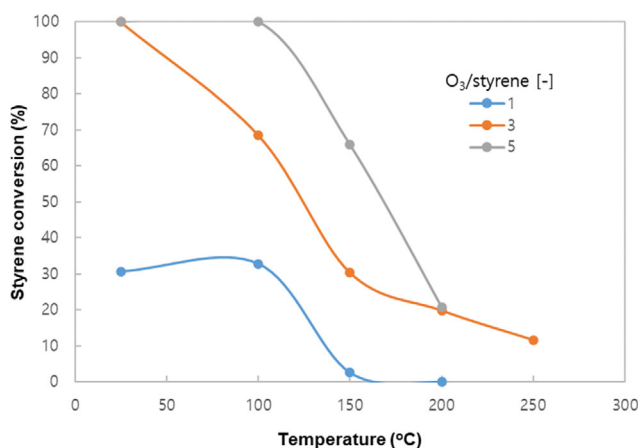


Fig. 3. Effect of reaction temperature on styrene conversion at different $[O_3]/[styrene]$ mole ratios and 30-ppm styrene concentration.

from 31% at room temperature to 0% at 200 °C.

This was in agreement with the results of earlier studies. Alibolandi et al. reported that the increase of temperature contributes to the decomposition of O_3 [33]. Batakliiev et al. reported that the half-life of O_3 was reduced substantially as the reaction temperature increased [34]. Zhang and Pagilla reported that a high initial $[O_3]/[hydrogen\ sulfide\ (H_2S)]$ mole ratio in the inlet stream resulted in greater H_2S removal in an O_3 oxidation experiment at any given

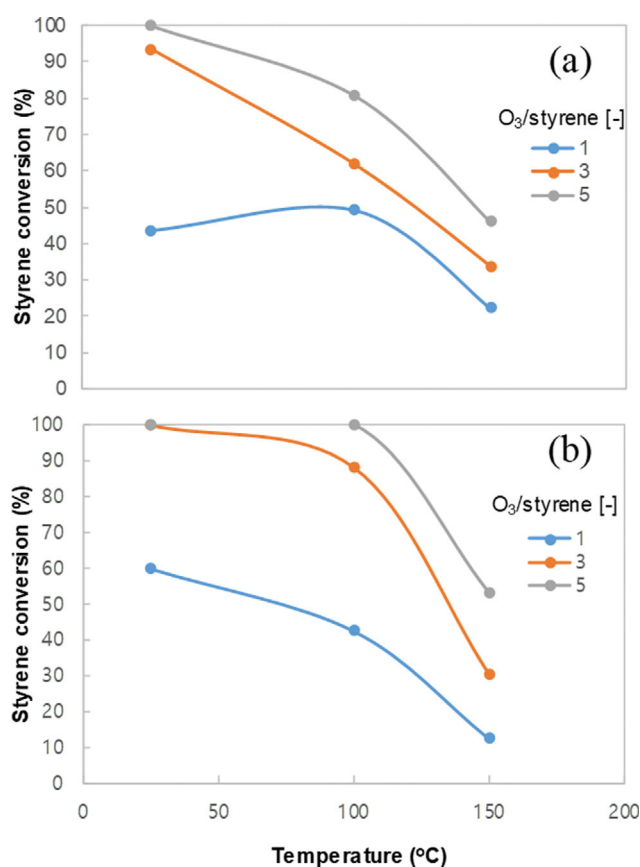


Fig. 4. Effect of reaction temperature on conversion efficiency for the styrene concentrations of (a) 10 ppm and (b) 45 ppm.

initial H_2S concentration [35].

Fig. 4 shows the conversion efficiency for the 10- and 45-ppm styrene concentrations. The conversion efficiency decreased as the reaction temperature increased from room temperature to 150 °C. At 10 ppm, styrene was completely converted only at room temperature and a mole ratio of 5.0. At 45 ppm and a mole ratio of 5.0, styrene was completely converted at room temperature and 100 °C, and conversion efficiency was higher than at 10 and 30 ppm.

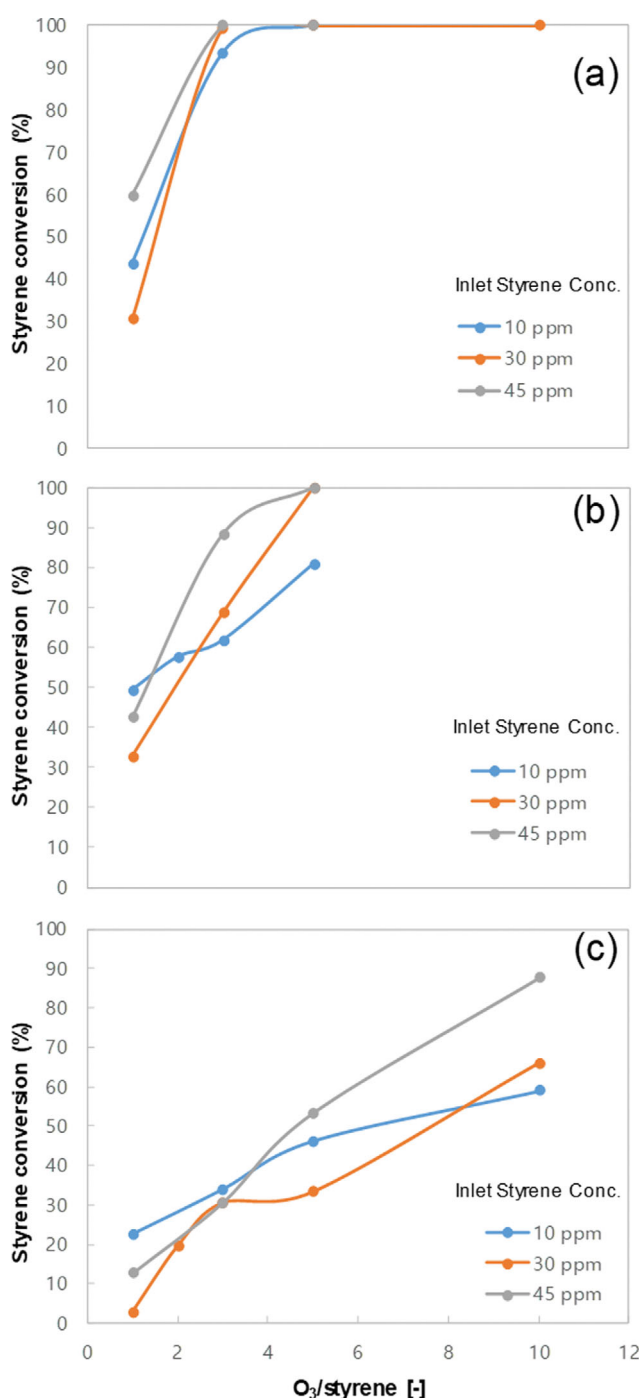


Fig. 5. Effect of the $[\text{O}_3]/[\text{styrene}]$ mole ratio on conversion efficiency at different styrene concentrations. (a) Room temperature, (b) 100 °C, and (c) 150 °C.

Fig. 5 shows the effects of the mole ratio on conversion efficiency, which increased as the $[\text{O}_3]/[\text{styrene}]$ mole ratio increased due to the promotion of the reaction. Regardless of the reaction temperature, conversion efficiency was higher at the higher styrene concentration. In Fig. 5(a), at room temperature, styrene was completely converted at the mole ratio of 3.0 for both the 30- and 45-ppm concentrations. At the mole ratio of 1.0, the conversion efficiency was 31% and 60% at 30 and 45 ppm, respectively, and then reached 100% at the mole ratio of 3.0.

However, at 10 ppm, the styrene conversion efficiency was 93.4% and 100% at the mole ratio of 3.0 and 5.0, respectively. Fig. 5(b) presents conversion efficiency at 100 °C. Conversion efficiency increased as the $[\text{O}_3]/[\text{styrene}]$ mole ratio increased; however, the rate of increase was lower than that shown in Fig. 5(a). Styrene was completely destroyed at both 30 and 45 ppm. The conversion efficiency at 45 ppm and mole ratio of 1.0 was 42.5%, with an increase to 100% at the mole ratio of 5.0. Fig. 5(c) shows the conversion efficiency at 150 °C. The conversion efficiency increased as the $[\text{O}_3]/[\text{styrene}]$ mole ratio increased, as shown in Fig. 5(a) and (b). However, styrene was not completely destroyed at the maximum $[\text{O}_3]/[\text{styrene}]$ mole ratio of 10.0. The conversion efficiency at 45 ppm and mole ratio of 1.0 was 12.5%, with an increase to 87.8% at the mole ratio of 10.0.

Fig. 6 summarizes all of the results of the styrene- O_3 experiments. Styrene conversion efficiency was increased as the $[\text{O}_3]/[\text{styrene}]$ mole ratio increased and the temperature decreased. The styrene conversion efficiency was higher at higher styrene concentrations of inlet gas in this system [35]. Room temperature was the optimal condition for the laboratory system in this study, and a $[\text{O}_3]/[\text{styrene}]$ mole ratio of at least 5.0 was necessary at 100 °C. Above 100 °C, the styrene conversion efficiency was limited even at the highest $[\text{O}_3]/[\text{styrene}]$ mole ratio [34].

Fig. 7 shows the effects of mole ratio on the $\text{C}_6\text{H}_5\text{CHO}$ concentration in the product gas. Fig. 7(a) shows that at room temperature, the $\text{C}_6\text{H}_5\text{CHO}$ concentration decreased as the $[\text{O}_3]/[\text{styrene}]$

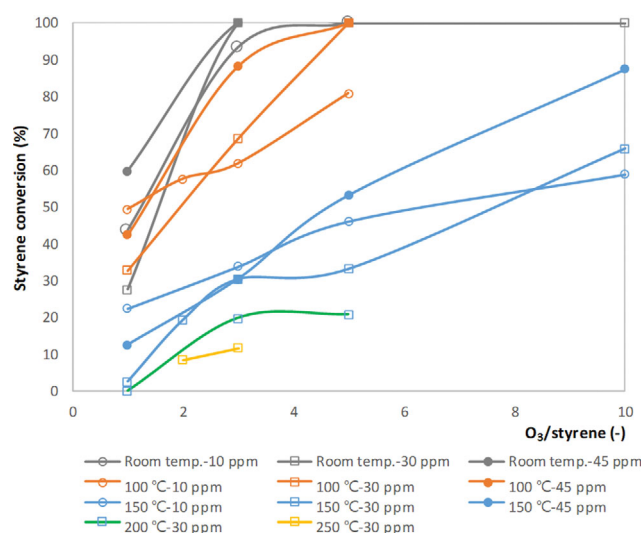


Fig. 6. Effect of the $[\text{O}_3]/[\text{styrene}]$ mole ratio on conversion efficiency at different styrene concentrations and reaction temperatures.

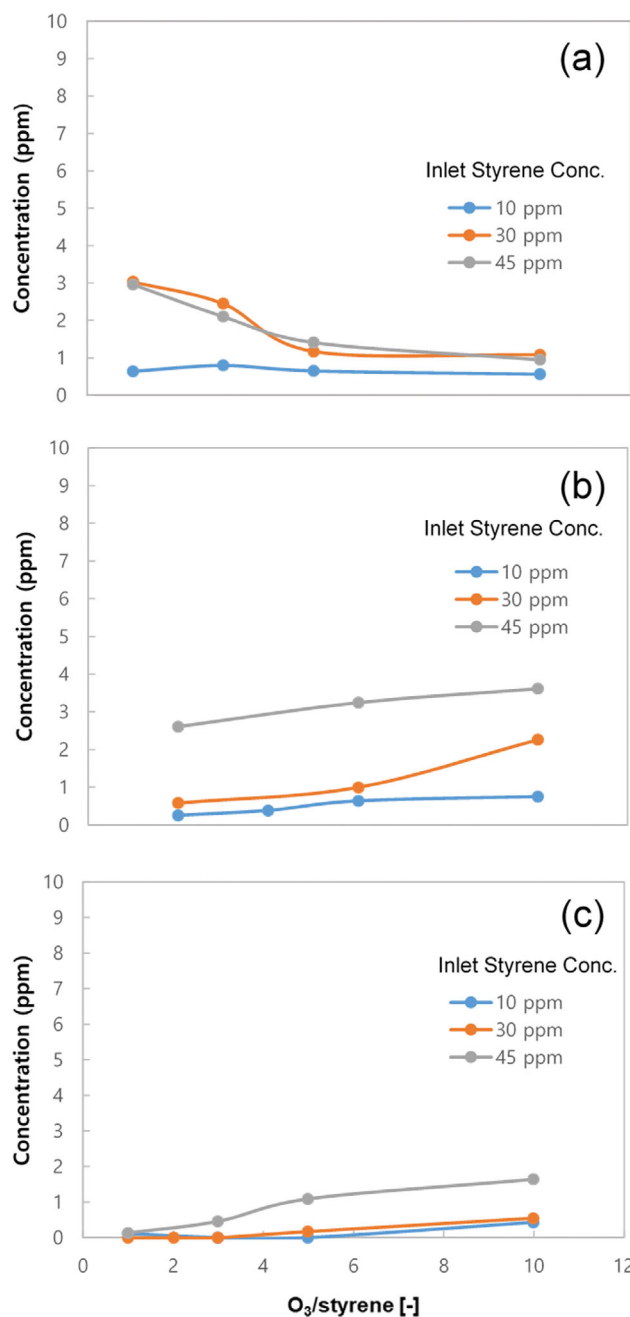


Fig. 7. Effect of the $[O_3]/[styrene]$ mole ratio on the C_6H_5CHO concentration at different styrene concentrations. (a) Room temperature, (b) 100 °C, and (c) 150 °C.

mole ratio increased. As shown in Fig. 5(a), the styrene conversion efficiency was high at room temperature compared to the other temperature conditions, and O_3 reactivity was sufficiently high compared to other temperature conditions. Therefore, it is likely that C_6H_5CHO could be easily produced and converted by the excessive O_3 [36]. However, at 100 °C and 150 °C, the C_6H_5CHO concentration increased as the $[O_3]/[styrene]$ mole ratio increased due to the promotion of styrene conversion.

2. On-site System

In this study, an on-site test was performed on the flue gas pro-

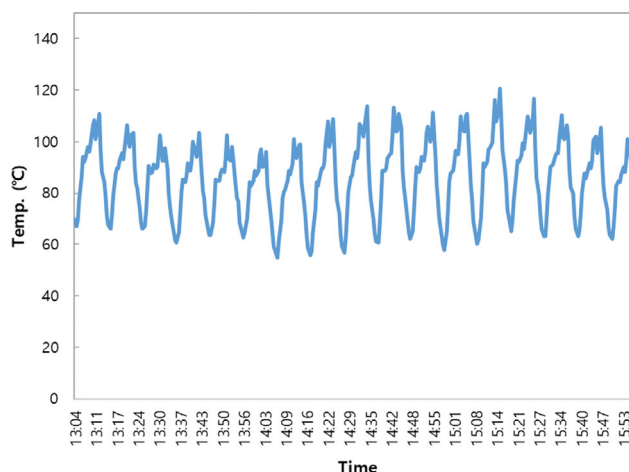


Fig. 8. Temperature of the on-site flue gas.

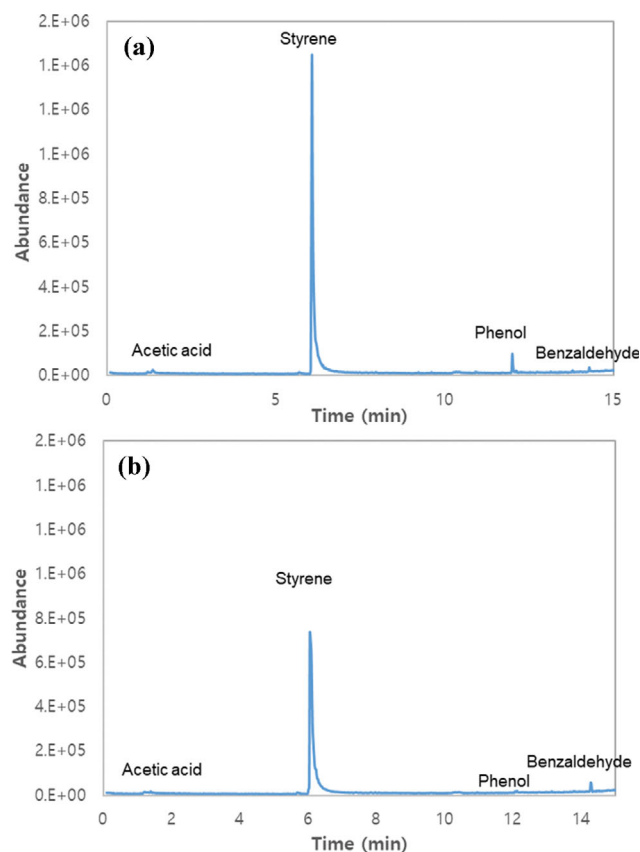


Fig. 9. Gas chromatography-mass spectrometry analysis of flue gas (a) before and (b) after ozonation.

duced in a commercial plant. As can be seen in Figs. 3 and 4, the temperature was the most important reaction condition controlling the styrene- O_3 reaction. Therefore, the temperature of the on-site flue gas was continuously monitored. The on-site flue gas temperature is shown in Fig. 8 and the temperature varied from around 60 °C to 120 °C.

To study styrene decomposition in the on-site flue gas, O_3 was injected at a flow rate of 2.7 L/min ($[O_3]/[styrene]$ mole ratio=5).

The results from the stack flue gas analysis before and after O₃ injection are shown in Fig. 9. Fig. 9(a) shows the styrene concentration of the original on-site flue gas; the main compound in the original flue gas was styrene, with a concentration of 6 ppm. Several minor compounds were also identified, including phenol (C₆H₆O), C₆H₅CHO, and acetic acid (CH₃COOH). Fig. 9(b) shows the GC-MS analysis results of the flue gas after O₃ injection; styrene was present at 2.5 ppm, with the same minor compounds as in the original flue gas, and there were no typical peaks for other byproducts, except CH₃COOH, C₆H₆O, and C₆H₅CHO. Based on these results, the styrene conversion efficiency was calculated to be 58.3%. Based on the laboratory-scale result (Fig. 5), the styrene conversion efficiency at 10 ppm and the [O₃]/[styrene] mole ratio of 5.0 was 80% and 46% at 100 °C and 150 °C, respectively. Therefore, under on-site conditions, the styrene conversion efficiency agreed with the preliminary test results from the laboratory-scale reactor.

CONCLUSIONS

Ozonation of styrene was investigated in a laboratory-scale tube reactor and on-site system. At all of the initial styrene concentrations in this study, the styrene conversion efficiency was 100% at room temperature with a [O₃]/[styrene] mole ratio of 5.0 in the laboratory-scale reactor. The styrene conversion efficiency decreased as the reaction temperature increased due to the reduction in O₃ reactivity, and was higher at higher mole ratios due to the promotion of the styrene-O₃ reaction. A 58.3% styrene conversion efficiency was achieved in the on-site study due to the high temperature range of the on-site flue gases (60–120 °C), and no other byproducts were detected except CH₃COOH, C₆H₆O, and C₆H₅CHO, which were also detected in the original flue gases.

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