



## Photocatalytic decomposition of mobile-source related pollutants using a continuous-flow reactor

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### Abstract

This study evaluated the application of a continuous-flow photocatalytic reactor for the control of two mobile-derived pollutants, methyl-tertiary butyl ether (MTBE) and naphthalene, present at in-vehicle levels. Variables tested for this study included the hydraulic diameter (HD), stream flow rate (SFR), relative humidity (RH), and feeding type (FT). The fixed parameters included contaminant concentration, ultraviolet light source, and the weight of TiO<sub>2</sub>. In all experimental conditions the adsorption process reached equilibrium within 30 to 180 min for the target compounds, and the outlet concentrations of the photocatalytic oxidation (PCO) reactor while operating reached a steady state within 60 to 180 min. The degradation of the target compounds was dependent on RH, HD, FT, or SFR. The PCO system exhibited high degradation (up to nearly 100% for certain conditions) and mineralization efficiencies of target compounds, suggesting that this system can effectively be employed to improve indoor air quality. Moreover, it was confirmed that trichloroethylene at urban-ambient level also could enhance the degradation efficiency of naphthalene when applying the PCO technology inside vehicles.

**Key words:** in-vehicle level; methyl-tertiary butyl ether; naphthalene; trichloroethylene

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### Introduction

Methyl-tertiary butyl ether (MTBE) has received increasing amounts of attention in relation to in-vehicle exposure (Lioy et al., 1994; Lee and Jo, 2002). The addition of MTBE to gasoline reduces the CO concentrations by 10%–15% (Mannino and Etzel, 1996). However, the addition of MTBE can elevate the in-vehicle MTBE levels, thereby increasing the vehicle occupants' exposure to this compound (Lioy et al., 1994; Lee and Jo, 2002). Exposure to MTBE is of particular concern because of its toxicity and is potentially linked to ailments such as headaches, dizziness, irritated eyes, and nausea (Mehlman, 1998).

In contrast to MTBE, little information is available for in-vehicle exposure to naphthalene (Batterman et al., 2002). Nevertheless, naphthalene is the most abundant of the polycyclic aromatic hydrocarbons in both gasoline and diesel fuels (Marr et al., 1999). Non-combusted fuels and the conversion of 2-methylnaphthalene in the fuel to naphthalene are the major sources of naphthalene in vehicle emissions (Rhead and Pemberton, 1996). Naphthalene has been classified as a hazardous air pollutant by the United States Environmental Protection Agency (USEPA, 2003).

Potential in-vehicle exposure to MTBE and naphthalene and their health effects require the development of control

strategies inside vehicles. It has already been reported that photocatalytic oxidation (PCO) can result in significant reduction of MTBE (In et al., 2006; Araña et al., 2008), naphthalene (Ohno et al., 2001), and other compounds in air and water environments (Suzuki et al., 1993; Hager et al., 2000; Pichat et al., 2000; Chapuis et al., 2002; Liu et al., 2004; Bertinchamps et al., 2006; Hu et al., 2007; Zhao et al., 2007). The degradation of the organic compounds occurs as a result of reactions with molecular oxygen or with hydroxyl radicals and super-oxide ions formed after the initial production of highly reactive electrons and hole pairs when the TiO<sub>2</sub> was ultraviolet (UV)-irradiated. Consequently, rather than transferring pollutants from the gas phase to the solid phase, PCO provides a reduction of absolute toxicity as the gaseous products from the complete PCO of toxic hydrocarbons are carbon dioxide and water (Chatterjee and Dasgupta, 2005; Bouzaza et al., 2006).

However, much less information on the PCO of air pollutants associated with non-occupational indoor air quality is available in the existing literature, whereas many previous studies have dealt primarily with concentrations in the low to high ppm range, which is typical of chemical process stream concentrations (Zhao and Yang, 2003; Ao and Lee, 2004). Extrapolations of oxidation performance data collected at concentrations much higher than the

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intended application may not be valid. The current study evaluated the feasibility of applying PCO technology to control two mobile-source related pollutants, MTBE and naphthalene, at low concentrations associated with in-vehicle air quality issues employing a continuous flow reactor. The addition of trichloroethylene (TCE) to the PCO system can promote the PCO of certain low photo-efficiency volatile organic compounds (VOCs) for ppm level (Luo and Ollis, 1996; d'Hennezel and Ollis, 1997; Jo and Park, 2004; Young et al., 2008). Therefore, it is suggested that the TCE of urban-ambient-ppb levels penetrating into vehicle cabins can also influence the degradation efficiency of in-vehicle level MTBE and naphthalene when applying the PCO technology. This assertion was also examined in the present study.

## 1 Methods

The PCO reactors employed during the course of this study had an annular geometry. The reactor consisted of a Pyrex tube coated on the inner surface with a thin film of TiO<sub>2</sub> (20% Degussa P-25 slurry) photocatalyst, which has a primary particle diameter of 300 Å, a surface area of 50 m<sup>2</sup>/g and a crystal distribution of 70% anatase and 30% rutile. The Pyrex surface to be coated was first etched with a 5 mol/L sodium hydroxide solution at 100°C. An aqueous suspension containing 5% Degussa P-25 TiO<sub>2</sub> was introduced to the Pyrex inner-surface. The coated reactor was dried for an hour at room temperature and then baked for 30 min at 450°C. After poorly adhered TiO<sub>2</sub> particles were rinsed off with distilled water, the sequence was repeated until a coating smooth and opaque to UV was achieved. Then, a cylindrical UV light source was inserted inside the glass tube and served as the inner surface of the annular reactor. The gas was flown through the annular region. Moreover, the reactor was designed to direct the flow of incoming air normally to the UV light to increase air turbulence inside the reactor, thus enhancing the distribution of target compounds onto the catalytic surface of the reactor.

Four parameters were evaluated for the PCO efficiencies: hydraulic diameter (HD, defined as the inside diameter of the annular reactor tube minus the outside diameter of the lamp), stream flow rate (SFR), relative humidity (RH), and feeding type (FT). Three different HDs (5, 20 and 45 mm) were tested. The range of SFR investigated was 0.4–3.0 L/min, which is comparable to that reported previously by Obee (1996). Measurements of SFR were carried out using identical rotameters (0–10 L/min) calibrated against a dry test meter (3000-020C, URG Corp., USA). Humidity is an important variable since photocatalytic technology should be applicable to the wide humidity range encountered in real in-vehicle environments. Accordingly, the RH range for these experiments was 10%–90% (10%–20%, 30%–40%, 50%–60%, and 80%–90%) that cover dried and humidified environments. The RHs were adjusted by passing zero-grade air through a humidification device in a water bath (HAAKE W26, Cole-Parmer Inc., USA). The RHs were measured just

**Table 1** Representative operating parameters for the current PCO study

Parameter	Representative value
RH (%)	50%–60%
HD (mm)	20.0
SFR (L/min)	2.0
FT	Mixture of target compounds
UV light source	8-W fluorescent black light
Input concentration (ppbv)	
MTBE	25
Naphthalene	10
TCE	45
Weight of catalyst film (mg/cm <sup>2</sup> )	0.5

prior to the PCO reactor inlet using a humidity meter (Thermo Recorder TR-72S, T&D Co., Japan). The RH was increased from low to high to cover the range shown. The PCO degradation efficiencies of MTBE and naphthalene were also determined to examine the effects of FT. For each parameter test, other parameters were all fixed to their representative values (Table 1). RH was within the American Society of Heating, Refrigerating and Air-Conditioning (ASHRAE) comfort range (50%–60%). The representative HD was 20 mm. The fixed SFR was 2 L/min, which provides a face velocity of 10.6 cm/sec for the representative HD. In the range above 10 cm/sec the effects of mass transfer are negligible (Obee, 1996). The representative FT was a mixture of the three target compounds. The UV radiation was supplied by an 8-W fluorescent black light with a maximum spectral intensity 352 nm. The UV light intensity was measured at the distance from the UV lamp equal to half of HD using a Black-Ray radiometer (Model J-221, UVP Inc., USA). The concentrations surveyed were associated with in-vehicle MTBE (Lee and Jo, 2002), personal air naphthalene (Edwards et al., 2005), or ambient air TCE (Chan et al., 2002) quality issues: 25 ppb of MTBE; 10 ppb of naphthalene; and 45 ppb of TCE. Little information is available for in-vehicle naphthalene and TCE concentrations. The desired concentrations were achieved through the use of a syringe pump (Model 210, KdScientific Inc., USA). The weight of the TiO<sub>2</sub> film coated inside the reactor was 0.5 mg/cm<sup>2</sup>. The temperature measured outside the PCO reactor was between 49 and 56°C. It was assumed that this temperature variation would not be significant enough to result in experimental discrepancies.

A series of concentration measurements of the target compounds were done at the outlet of the PCO reactor prior to and after turning on the UV lamp. For these measurements, the catalyst was pretreated for several hours by forcing zero-grade air flow through the illuminated photocatalytic reactor. The catalyst pretreatment was performed after the reactor outlet humidity level reached equilibrium. When no contamination with the target compounds was measured in the PCO reactor, the target compounds were introduced. After the adsorption process between the TiO<sub>2</sub> catalyst and target compounds reached equilibrium, as indicated by equality between the inlet and outlet concentrations, the UV lamp was turned on. Control tests using an uncoated Pyrex reactor and a UV intensity of 5.8 mW/cm<sup>2</sup> (highest level used) had no effect on the pollutant

concentration. The CO concentrations were measured at the PCO reactor inlet and outlet during the course of the experiment using a CO monitor (CMCD-10P, Gastec Co., Japan). In addition, the outlet CO<sub>2</sub> concentrations were measured when the UV lamp was on and off, using a CO<sub>2</sub> analyzer (Model 360Z, Advanced Pollution Instrumentation, Inc., USA). This experiment was conducted with 1 ppm of each target compound. The other experimental parameters were all fixed to their representative values.

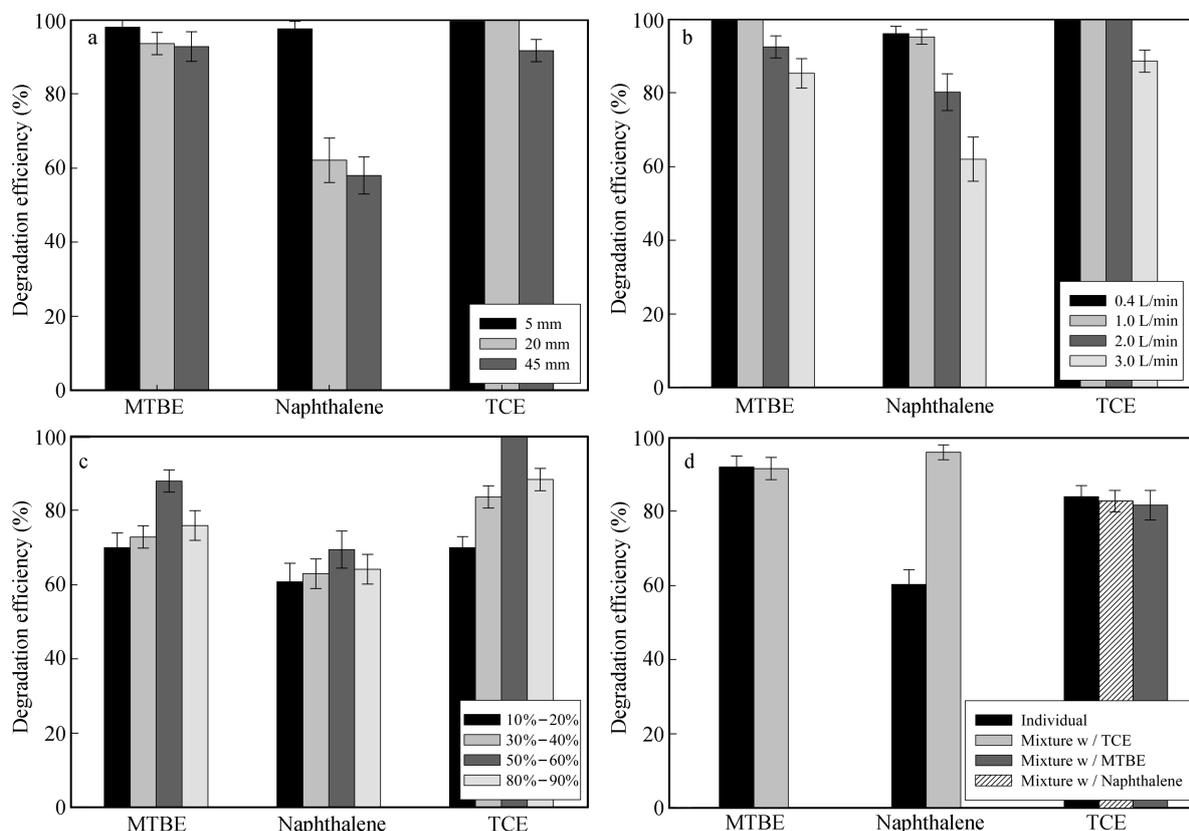
The target VOC compounds in the air stream were collected by filling an evacuated 5 L Tedlar bag at a constant flow rate. Air from this bag was then drawn through a sorbent trap containing 0.2 g Tenax TA and 0.2 g Carboxen 569 using a constant flow-sampling pump (Model I.H, A.P. Buck Inc., USA). Sampling time varied from 1 to 5 min depending on the flow rate. All samples were taken at ambient room temperature (19–25°C). The target compounds collected on the sorbent trap were analyzed by coupling a thermal desorption system (Model Aerotrap 6000, Tekmar Inc., USA) to a gas chromatograph (Model 3400CX, Varian Inc., USA) with a flame ionization detector using a 0.32-mm-i.d. by 60-m-length fused silica column (SPB-5, Supelco Co., USA). Since the peak areas for other compounds on the GC chromatogram were not significantly high, they were not quantified.

The quality assurance/quality control program for the measurements of VOCs included laboratory blank traps and spiked samples. At the beginning of the day, a laboratory blank trap was analyzed to check for any

trap contamination; however, no trap contamination was identified. An external standard was analyzed daily to check the quantitative response. When the quantitative response differed by more than 20% from that predicted by the specified calibration equation, a new calibration equation was determined. The method detection limits were 1.3, 1.5, and 3.8 ppb for MTBE, naphthalene, and TCE, respectively.

## 2 Results and discussion

The effects of HD, SFR, RH, and FT on the PCO degradation efficiencies of the target compounds were evaluated (Fig. 1). The experiments were repeated three times for each experimental condition, and the repeated experiments showed very similar patterns. Thus, average values are presented for all experimental conditions. The concentration series measured prior to turning on the UV lamp show that for all experimental conditions the adsorption process reached equilibrium within 30 to 180 min for the target compounds, as indicated by the similarity between the inlet/outlet pollutant concentrations. In addition, the series of concentrations measured after turning on the UV lamp indicate that the outlet concentrations of the PCO reactor reached a steady state within 60 to 180 min after the UV lamp was turned on. Accordingly, the inlet concentrations measured prior to turning on the UV lamp were compared with the outlet steady-state concentrations to evaluate the PCO degradation efficiencies of the target chemicals.



**Fig. 1** Degradation efficiencies of MTBE, naphthalene, and TCE for three different hydraulic diameters (HDs) (a), four different stream flow rates (SFRs) (b), different relative humidity (RH) ranges (c), and different feed type (FT) conditions (d). Error bars represent standard error.

## 2.1 Effects of HD on PCO degradation

Three reactors with different HDs (5, 20, and 45 mm) were tested as regards the PCO efficiencies for the three target compounds (MTBE, naphthalene, and TCE). To avoid the reactor residence time effect on degradation efficiencies, tests were conducted using the same residence time (5 sec) for the three reactors by adjusting the SFR to 0.4, 2.3 and 7.8 L/min for 5, 20 and 45 mm HDs, respectively. Figure 1a presents the degradation efficiencies of the target chemicals for three reactors with different HDs. Regardless of the HDs, the degradation efficiencies were nearly 100% for MTBE and TCE. As a result, the effect of light intensity was not distinguishable for these compounds. Previous studies (Mohseni, 2005; Araña et al., 2008) also reported that photocatalytic systems with TiO<sub>2</sub> (Degussa P-25) could effectively degrade and mineralize these compounds. Araña et al. (2008) suggested that MTBE degradation starts with reactions with hydroxyl radicals. For TCE, chlorine radicals trigger a chain reaction, which accelerates the degradation of TCE and its intermediates on the surface and in the bulk phase (Fu et al., 1995; Driessen and Grassian, 1998). Similarly, Stevens et al. (1998) reported that various types of TiO<sub>2</sub> reactors resulted in complete, steady-state conversions of lower concentrations of carbonyl compounds. In contrast, the degradation efficiency for naphthalene decreased as HD increased: the degradation efficiency was nearly 100%, 78%, and 66% for the 5, 20, and 45 mm HD reactor, respectively. The lower degradation efficiency of naphthalene is likely due to a slower photocatalytic degradation rate as compared to other organic compounds like TCE (Ireland et al., 1995). As the distance of the catalyst from the light source increased with increasing HD, the decrease in light intensity appeared to be the most obvious reason for the drop in the PCO of naphthalene. The UV radiation intensities measured in this study were 5.8, 3.8 and 2.2 mW/cm<sup>2</sup> for the 5, 20 and 45 mm HDs, respectively. The effect of UV radiation intensities is supported by previous studies (Peral and Ollis, 1992; Obee and Brown, 1995; Tsoukleris et al., 2007). Obee and Brown (1995) reported that the oxidation rate of toluene and formaldehyde increased with an increase in UV intensity. In addition, Peral and Ollis (1992) reported identical results in the PCO study of acetone, 1-butanol, butyraldehyde, formaldehyde, and *m*-xylene. Additionally, bulk mass transport of the target compounds from the gas-phase to the surface of the catalyst particle due to convection and diffusion is an important heterogeneous catalytic reaction process (Obee and Brown, 1995; Van Gerven et al., 2007). The flow rate employed in this study was increased with increasing reactor volume to give the same residence time. Therefore, mass transfer would increase with the lower face velocity for the larger HD, thereby causing more PCO efficiency for the 45 mm HD reactor. Nevertheless, the current results suggest that the mass transfer effects did not exceed the light intensity effects on the PCO efficiency of naphthalene.

## 2.2 Effects of SFR on PCO degradation

SFR, which is related to residence time and face velocity in reactors, was tested for the degradation efficiencies of the target compounds using the reactor with a 5-mm HD. Figure 1b shows the degradation efficiencies of three target compounds for four different flow rates (0.4, 1.0, 2.0, and 3.0 L/min). For the two lowest flow rates (0.4 and 1.0 L/min), the degradation efficiencies were nearly 100% for the entire target compounds. Similar degradation efficiency was observed even at the highest flow rate for both MTBE and TCE. However, the degradation efficiency of naphthalene was 78% and 70% for the flow rates of 2.0 and 3.0 L/min, respectively, suggesting that flow rate is an important parameter for the application of TiO<sub>2</sub> photocatalytic technology for cleansing naphthalene. The lower degradation efficiency of naphthalene for the high flow rate is possibly caused by an insufficient reactor residence time or mass transfer due to high flow rate. The residence time, which were calculated by dividing the reactor volume by flow rate, were 5.1, 2.0, 1.0, and 0.7 sec for the flow rates of 0.4, 1.0, 2.0, and 3.0 L/min, respectively. On the other hand, Obee and Brown (1995) reported that the face velocity influenced the mass transfer of formaldehyde, toluene and 1,3-butadiene. However, once face velocity exceeds 10 cm/sec, the effects of mass transfer are negligible (Obee and Brown, 1995; Van Gerven et al., 2007). In the present study, the face velocities were 4.9, 12.3, 24.5, and 36.8 cm/sec for the flow rates of 0.4, 1.0, 2.0, and 3.0 L/min, respectively. Accordingly, the bulk mass transport effect would be insignificant for lower degradation efficiency of naphthalene at the two highest flow rates.

## 2.3 Effects of RH on PCO degradation

Figure 1c presents the degradation efficiencies of the three target compounds for four different RH ranges that cover typical ambient air humidity ranges. The degradation efficiencies of MTBE and TCE were close to 100% for the RH range of 50% to 60%, which is within the ASHRAE comfort range. This result is consistent with the results of Stevens et al. (1998), who reported complete, steady-state conversions of lower concentrations of carbonyl compounds. However, the degradation efficiencies of all target compounds decreased at the other RH ranges tested in the present study. These results appear to be due to the effect of the hydroxyl radical population on the catalyst surface or the competitive adsorption between water and the contaminant on the catalyst surface (Zhao and Yang, 2003). The drop in the PCO efficiency with decreasing humidity is probably due to a decrease in the hydroxyl radical population on the catalyst surface (Zhao and Yang, 2003). This PCO dependence on humidity was also reported for *m*-xylene (Peral and Ollis, 1992). The drop in the PCO efficiency at the highest RH range (80% to 90%) tested in this study is likely the result of competitive adsorption between water and the contaminant on the catalyst surface.

## 2.4 Effects of FT on PCO degradation

The PCO degradation efficiencies for the two FTs (individual and mixed target compound feeds) were compared to examine the interrelationship between MTBE and TCE, and between naphthalene and TCE. Figure 1d presents the degradation efficiencies of target compounds measured for two FTs. Since the PCO degradation efficiency was close to 100% for both MTBE alone and for MTBE and the TCE mixture, the enhancement of MTBE conversion in MTBE-TCE mixed feeds was unclear. TCE conversion remained near 100% during both the MTBE-TCE and the naphthalene-TCE mixture test. However, the conversion efficiencies of naphthalene were elevated with a mixed feed compared to an individual feed. The naphthalene conversion efficiency was near 100% for the mixed feed, while it was 70% for the individual feed. The present result, obtained for low naphthalene feed concentrations (ppb levels) is also consistent with previous findings for high feed concentrations of several other compounds (ppm levels) (Sauer et al., 1995; d'Hennezel and Ollis, 1997; Jo and Park, 2004; Young et al., 2008). d'Hennezel and Ollis (1997) demonstrated that TCE promotes the PCO degradation efficiency of aromatic VOCs. Meanwhile, Sauer et al. (1995) reported that two other chlorinated olefins, perchloroethylene (PCE), and trichloropropene, exhibit high photo-efficiencies for individual conversions, and when each is fed with toluene, the conversion of the latter is raised to 100%. Young et al. (2008) suggested that the function of the added sensitizer (TCE) is to provide the radicals required to initiate chain-propagated degradation of the pollutant. A subsequent mechanism will involve a new activation path for toluene, i.e., a chain transfer from the active chlorine in the chlorocarbon oxidation chain.

## 2.5 Mineralization efficiencies and potential byproducts

The mineralization efficiencies ( $R$ ) of target compounds were calculated as follows (Coronado et al., 2003):

$$R = ((C_{\text{CO}_2,\text{on}} - C_{\text{CO}_2,\text{off}}) / nC_{\text{in}}) \times 100\% \quad (1)$$

where,  $C_{\text{CO}_2,\text{on}}$  and  $C_{\text{CO}_2,\text{off}}$  (ppm) are quasi-steady-state  $\text{CO}_2$  concentrations measured at the outlet of photocatalytic reactor when the UV lamp was on and off, respectively;  $n$  is the number of carbon atoms that target compounds contain; and  $C_{\text{in}}$  is the inlet concentration (ppm). The mineralization efficiencies of MTBE, naphthalene, and TCE were 62%, 53%, and 70%, respectively (Table 2). Similar to the photocatalytic degradation rates, the mineralization efficiencies of MTBE and TCE were higher than that for naphthalene, and they were comparable with those of previous studies (Avila et al., 1998; Sánchez et al., 1999; Araña et al., 2008).

**Table 2** Mineralization efficiencies ( $R$ , %) of three target compounds

Compound	$C_{\text{in}}$ (ppm)	$C_{\text{CO}_2,\text{on}}$ (ppm)	$C_{\text{CO}_2,\text{off}}$ (ppm)	$R$ (%)
MTBE	1	3.5	0.4	62
Naphthalene	1	5.7	0.4	53
TCE	1	1.8	0.4	70

In order to examine whether the PCO application significantly added to the indoor CO level, the CO concentrations were measured simultaneously with the VOC concentrations at the PCO reactor outlet during the course of each test. The CO levels measured during the PCO processes were elevated up to 0.6 ppm, thereby indicating that some CO was generated as a result of the oxidation reaction of surface-bound reactants and adsorbed intermediates. These results are consistent with those of a previous study (Jacoby et al., 1996), where it was reported that some portion of benzene was converted to CO. Nevertheless, considering that the Occupational Safety and Health Administration (OSHA) eight-hour exposure limit for CO in the workplace is 35 ppm, under the conditions relevant to the use of PCO, the elevated CO concentrations would be negligible to indoor CO levels. In addition, several previous studies (Fu et al., 1995; Obee and Brown, 1995; Blanco et al., 1996; d'Hennezel et al., 1998) have reported that the PCO of many VOCs did not produce any detectable byproduct in the reactor effluent. However, it is noteworthy that other byproducts such as phosgene, dichloroacetylene chloride, and trichloroacetylene chloride can be formed during the course of PCO of TCE and PCE (Nimlos et al., 1993; Bellobono, 1995; Wang et al., 2002; Feiyan et al., 2002; Mohseni, 2005). Therefore, further studies are suggested to examine the formation of phosgene and other potential byproducts under the studied conditions. If phosgene is determined in harmful levels, the use of a modified  $\text{TiO}_2$ , such as metal-doped  $\text{TiO}_2$ , might be helpful for their further degradation (Bellobono, 1995; Jung and Park, 2000; Mohseni, 2005; Ou and Lo, 2007).

## 3 Conclusions

The present study evaluated the technical feasibility of the application of  $\text{TiO}_2$  photocatalytic technology for cleansing MTBE and naphthalene in the low concentrations commonly associated with in-vehicle air quality issues. The present finding demonstrates that the degradation of the target compounds is dependent on humidity, HD, or SFR, and that the PCO system can effectively be employed to improve indoor air quality. Moreover, it was confirmed that the TCE of the urban-ambient level also could enhance the degradation efficiency of naphthalene when applying the PCO technology inside vehicles. These abilities, combined with operational attributes such as a low pressure drop across the reactor and ambient temperature operation, can make the PCO reactor an important tool in the effort to improve in-vehicle air quality. However, the HDs of the PCO reactor and SFRs should be considered for better degradation efficiencies in the application of  $\text{TiO}_2$  photocatalytic technology for cleaning in-vehicle air. Meanwhile, it is noteworthy that since previous studies reported the formation of phosgene and other potential byproducts during PCO processes of TCE, further studies are suggested to examine the formation levels of these byproducts under the experimental conditions similar to the present study.

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