Complete Oxidation of Volatile Organic Compounds (VOCs) Using Plasma-Driven Catalysis and Oxygen Plasma

H.H. Kim*, A. Ogata, S. Futamura
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

Abstract — The decomposition of volatile organic compounds (VOCs) was investigated using a flow-type plasma-driven catalysis (PDC) system and a cycled system. In the flow-type PDC reactor a trade-off relation was observed between the formation of nitrogen oxides and the decomposition of VOCs. Complete decomposition of VOC to CO₂ was achieved with the cycled system without forming CO, aerosol, and any nitrogen oxides. The oxygen-partial pressure dependence of different catalysts on the decomposition of benzene and toluene was investigated. The influence of VOC concentration and the temperature of oxygen plasma on the equivalent energy in the cycled system will be also discussed.

Keywords — Nonthermal plasma, plasma-driven catalysis (PDC), VOC, oxygen plasma, enhancement factor

1. INTRODUCTION

Volatile organic compounds (VOCs) have high vapor pressure under normal conditions, so they can be easily vaporized into the atmosphere. Two important VOCs-related environmental issues in urban area are the photochemical smog and the secondary aerosol formation. Many of VOCs are known as carcinogenic, teratogenic and mutagenic. The key driving force of environmental market is the environmental policy of government (i.e. policy-driven market) rather than technology or demand (technology/demand-driven market). Emission standards and regulations are getting stringent in many countries over the world. There is, therefore, an urgent need to develop more effective and inexpensive techniques for the treatment of VOCs.

In Japan, new regulation of VOC emission has been started in April 2006 to achieve 30% reduction of the total VOCs emission by 2010 compared to that of 2000 (1.85 million tons/year). More accelerated movements towards the reduction of toxic chemicals have been noticed by European Union (EU, REACH; registration, evaluation and authorization of chemicals) and United Nations (UN, GHS; globally harmonized system of classification and labeling of chemicals). The upcoming new regulations of REACH may bring out big change on the environmental market (i.e. policy-driven market) rather than technology or demand (technology/demand-driven market). Emission standards and regulations are getting stringent in many countries over the world. There is, therefore, an urgent need to develop more effective and inexpensive techniques for the treatment of VOCs.

Factors to be solved before the industrial use of the NTPs for the abatement of VOCs are the reduction of energy consumption (i.e. high energy efficiency), less NOX formation) and good material balance. One of the recent remarkable trends in the NTP application for air pollution control is the combination of NTP with catalyst in either configuration of single-stage [6-8] or two-stage [9-11]. The authors have been investigated the decomposition of VOCs using a plasma-driven catalysis (PDC) system, and demonstrated the effectiveness of the PDC in terms of energy efficiency, product selectivity and carbon balance [12-15].

Table 1 summarizes the differences between the conventional NTP alone processes and the PDC system. Both the plasma alone and the PDC system are not influenced by gas hourly space velocity (i.e. residence time) because the characteristic time of plasma chemical reactions is usually much more shorter than the gas residence time. One important characteristics of the PDC system that we focused on in this work is the influence of oxygen partial pressure on the decomposition efficiency [16]. In contrast to the plasma alone processes, the decomposition efficiency of VOC linearly increased with oxygen partial pressure in the PDC reactor packed with 2 wt% Ag/TiO₂ catalyst. In addition to the decomposition efficiency, the selectivity of CO₂ also remarkably enhanced with oxygen partial pressure. On the other hand, this strong influence of oxygen partial pressure on the decomposition efficiency of VOC is not observed in the NTP alone processes regardless of the type of plasma reactors [17-19]. Based on the highly oxygen partial pressure-dependent property of the PDC system, a cycled system of adsorption and the decomposition of adsorbed VOCs using oxygen plasma has been proposed. The expected advantages of this cycled process include high energy efficiency, high CO₂ selectivity and no formation of nitrogen oxides.

In this work, the decomposition of benzene and toluene was investigated using a flow-type PDC reactor and a cycled system. The oxygen partial pressure-dependent characteristics of different catalysts (~ 4 wt% Ag/TiO₂ and 0.5 wt% Pt/γ-Al₂O₃) were evaluated using a new parameter of enhancement factor. The optimum range of plasma-catalyst process according to the gas flow rate and the concentration of VOCs will be also discussed.

Corresponding author: Hyun-Ha Kim
e-mail address: hyun-ha.kim@aist.go.jp

Originally presented at ISNTPT-5, June 2006
Revised: October 29, 2006, Accepted: January 23, 2007
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Plasma alone</th>
<th>PDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetics*</td>
<td>First-order</td>
<td>Zeroth-order</td>
</tr>
<tr>
<td>( \eta(%) = (1 - \exp(-kE \cdot \text{SIE})) \times 100 )</td>
<td>( \eta(%) = \frac{kE \cdot \text{SIE}}{C_0} \times 100 )</td>
<td></td>
</tr>
<tr>
<td>GHSV</td>
<td>No influence</td>
<td>No influence</td>
</tr>
<tr>
<td>( O_2 ) content</td>
<td>No influence</td>
<td>Large influence</td>
</tr>
<tr>
<td>Carbon balance</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Aerosol</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>IP vs DRE</td>
<td>Highly related</td>
<td>Unrelated</td>
</tr>
</tbody>
</table>

* The rate constant \( k_E \) is referred to as energy constant. The unit for first-order and zeroth-order are \( \text{LJ}^{-1} \) and \( \text{ppm} \cdot \text{L}^{-1} \), respectively.

### II. EXPERIMENTAL

#### A. Reactor and Method

Figure 1 shows the conceptual diagrams of (a) the flow-type PDC reactor and (b) the cycled system for the complete destruction of VOCs. In the flow-type PDC reactor, catalysts are packed inside the reactor and directly activated by a plasma application. There is a trade-off relation between the degree of VOCs decomposition and the NOx formation. So the determination of the maximum applicable specific input energy (SIE) is important in the flow-type PDC reactor. On the other hand, nitrogen oxides are formed in the cycled system because the plasma is only turned on under oxygen environment. The cycled process is based on the highly oxygen content-dependent behavior of the PDC system for the decomposition of benzene [16]. In the adsorption mode, VOCs was removed by adsorption without plasma application. When the catalyst bed reached a saturated adsorption, then the catalyst bed purged with oxygen before applying oxygen plasma to decompose the adsorbed VOCs. For the measurement purpose, the regeneration mode was operated with oxygen flow of 5~8 L/min. A small additional PDC reactor was set downstream of the main PDC reactor to decompose the desorbed VOC just after the \( O_2 \) plasma was turned on. In practical case, it will be beneficial to operate the regeneration mode in closed system after purging the catalyst bed with oxygen. Since the main goal of the current work is to find the dependence of various catalysts on the oxygen partial pressure, most of the experiments were done with the flow-type PDC reactor at 100 °C. The flow-type system consisted of the PDC reactor (quartz tube of 13 mm in inner diameter and 200 mm in effective length), AC power supply, and measurement system. In the case of cycled system, the adsorption mode was operated at room temperature. The regeneration mode was operated at room temperature or 100 °C to see the temperature influence on the energy efficiency. A Fourier transform infrared (FITR) spectrometer (Perkin Elmer, Spectrum One) was used for the gas measurements of both the reactants and products.

#### B. Electrical Measurement

Discharge power of the PDC reactor was measured using the automated V-Q Lissajous program (Insight Co. ver 1.71) [15]. A condenser (about 100 nF) was connected in series to the ground line of the plasma reactor. The charge \( Q \) (i.e. time-integrated current) was measured with a 10:1 voltage probe. Specific input energy \( (P/Q)_f \) is the ratio of discharge power \( (P_{	ext{dis}} \text{ in watt}) \) to gas flow rate \( (Q_f \text{ in L/min}) \).

\[
\text{SIE (J/L)} = \frac{P_{	ext{dis}}}{Q_f} \times 60
\]  

(1)

In the case of the cycled operation equivalent specific input energy \( (\text{SIE}_{eq}) \) was introduced to evaluation the energy consumption.

\[
\text{SIE}_{eq} (J/L) = \frac{(P_{	ext{dis}})_{\text{Ads}}}{(Q_{\text{Ads}})_f} \times \frac{T_{\text{day}}}{T_{\text{Ads}}} \times 60
\]  

(2)
Fig. 2. Temperature increase in the PDC reactor as a function of specific input energy.

Here, \( (P_{dis})_{ave} \) and \( (Q_{ads}) \) indicate the average discharge power of oxygen plasma for the decomposition of adsorbed VOC and gas flow rate during the adsorption, respectively. \( T_{Oxy} \) and \( T_{Ads} \) indicate the period of oxygen plasma and adsorption, respectively.

### III. RESULTS AND DISCUSSION

Figure 2 shows the temperature increase as a function of SIE at the outlet of PDC reactor packed with 1 wt% Ag/TiO\(_2\) catalysts. The real gas temperature inside the PDC reactor depends on the SIE and the position. There was a temperature gradient along with the flow direction, so the maximum temperature was measured at the outlet of the PDC reactor. The temperature data shown in Figure 2 indicate the maximum temperature found in the PDC reactor. A good linear function was observed between the temperature increase and the SIE.

\[
[Temp]_{outlet} = [Temp]_{inlet} + 0.35[SIE]
\]

Helium dilution test exhibited almost the same trend with the \( N_2 \) dilution case. Considering the thermal decomposition of benzene on the Ag/TiO\(_2\) catalyst starts above 200 °C [13], it is quite clear that the thermal catalytic reaction play a minor role in the PDC reactor.

Figure 3 shows the decomposition of benzene and toluene using the flow-type PDC reactors. The decomposed amounts of benzene was found to be determined by the SIE regardless of its inlet concentration. Benzene of 110 ppm was completely decomposed with about SIE of 120 J/L. The decomposition of toluene also showed a similar trend with the benzene case. The inlet concentration had little influence on the decomposed amount of toluene. The key factor determining the decomposed amount of toluene was SIE. These simple relationship between the SIE and the removed amount of VOCs render the SIE as designing and scaling parameter of the PDC system. When the type and the concentration of VOC are given, one can easily grasp how much energy is necessary to decompose it using the flow-type PDC system.

Figure 4 shows the formation of NO\(_2\) and N\(_2\)O during the decomposition of benzene and toluene using the flow-type PDC reactors. As long as the NTP is applied in air-like mixtures, the formation of N\(_2\)O is unavoidable [20-22]. Although the flow-type PDC system can decompose 200 ppm of benzene or more, for example, complete conversion of VOCs is counterbalanced by the formation of nitrogen oxides. As was also reported on the decomposition of halomethanes using BaTiO\(_3\) packed bed reactor [23], the type of VOCs or the catalysts had no influence on the formation of NO\(_2\) and N\(_2\)O. In both cases of benzene and tolene, the formation of NO\(_2\) increased quadratically, while the N\(_2\)O exhibited a linear increase. The formation of NO\(_2\) became significant as the SIE became larger than about 100 J/L. This observation indicates that the flow-type PDC reactor should be operated at SIE below about 100 J/L to suppress the formation of nitrogen oxides. The concentration of VOCs (benzene and toluene), which can be removed by the PDC reactors with SIE of about 100 J/L, may range below 100 ppm. Judging from the experimental results in Figs 3 and 4 in terms of decomposition efficiency of VOC and the formation of nitrogen oxides, the optimum concentration region of the flow-type PDC system ranges below about 100 ppm.

Figure 5 shows the influence of oxygen partial pressure on the decomposition of benzene and toluene using the PDC reactors packed with different catalysts. In the case of benzene removal using the TiO\(_2\) catalysts the decomposition efficiency increased linearly with oxygen partial pressure regardless of the loading amount.
of Ag (0–4 wt%). Although there was difference in the degree of enhancement, the decomposition efficiency of toluene was also increased with the oxygen partial pressure. An enhancement factor was newly introduced to evaluate the potential of each catalysts for the cycled system. The enhancement factor (EF) is defined as the ratio of decomposition efficiency of VOC with respect to the O₂ partial pressure at the same SIE.

\[
EF = \frac{\eta_{\text{Oxygen}} - \eta_{\text{Air}}}{[O_{2}]_{\text{Oxygen}} - [O_{2}]_{\text{Air}}} \times 100
\]  

(4)

Here, \(\eta_{\text{Oxygen}}\) and \(\eta_{\text{Air}}\) indicate the decomposition efficiency of VOCs in oxygen and in air, respectively. Since the cycled system is operated in pure oxygen, the larger the EF value, the higher the potential of catalyst for the cycled system. The physical meaning of the enhancement factor is the slope of decomposition efficiency of VOC with respect to O₂ partial pressure at a given SIE. The enhancement factors with the Ag/TiO₂ catalyst were 100 and 61 for the decomposition of benzene and toluene, respectively. The enhancement factor with the Pt/γ-Al₂O₃ catalyst for toluene decomposition was about 6.7. These results clearly indicate that the selection of catalyst having a large EF is a very important factor determining the performance of the cycled system.

Figure 6 shows the required energy for the complete decomposition of benzene using the cycled system. Oxygen plasma completely oxidized the adsorbed benzene to CO₂, which is impossible with the conventional NTP alone processes or the flow-type PDC system. The SIE$_{eq}$ for the decomposition of adsorbed benzene largely depended on the inlet concentration. The higher the benzene concentration, the larger the SIE$_{eq}$ for the complete decomposition of adsorbed benzene. These results can be explained by the zeroth-order kinetics of the PDC system [10, 11]. In the zeroth-order kinetics, the
amount of VOC decomposition is determined by SIE rather than the concentration of benzene. These observations indicated that the cycled system is more effective in treating dilute VOCs than the high concentration. Our preliminary data indicated that the SIE$_{eq}$ to achieve complete decomposition of 60 ppm and 205 ppm benzene were about 150 J/L and 310 J/L, respectively. It should be noted that these values are the required energy for the total oxidation of benzene to CO$_2$, which is impossible with the flow-type PDC reactors. One of the reasons for the larger SIE$_{eq}$ compared to that of the SIE with the flow-type PDC reactor is the use of additional PDC reactor used in the regeneration mode [16]. This additional PDC reactor will not be necessary if the regeneration mode is operated in closed system, which may lead to the reduction of energy consumption. Temperature during the regeneration mode did not affect the SIE$_{eq}$ within the tested conditions. The data obtained at room temperature and 100 ºC fell on single line. Further reduction of SIE$_{eq}$ can be possible by optimizing the plasma parameters of the regeneration mode and the use of proper adsorbent/catalyst. The key factor for the further enhancement and optimization of the cycled system is to seek proper catalyst materials having large enhancement factor as well as a large adsorption capability. 

For practical point view, it is very important to know the advantages and the limitations of different VOCs control technologies for the selection of best method for a given condition. Figure 7 shows the cost-effective and technically feasible Q$_f$–[C] ranges for the major VOCs control technologies together with the NTP technology. The fundamental framework of this Q$_f$–[C] map is based on the data reported by Dyer and Mulholland in 1994 [24], and later it was extended to the halogenated VOCs [25]. The solid circles in the figure indicate the commercialized plasma-catalyst facilities in Japan. It is clear from the figure that each technology has advantages and drawbacks according to the flow rate and concentration. Generally, gas residence time is an important parameter determining the degree of removal efficiency in most of chemical reactors, so do in the pollution control devices shown in Figure 7 except for NTP process. Since the NTP is an energy-dependent process, the overall efficiency is mostly determined by the energy input to the system rather than the residence time (i.e. reactor size). Therefore, the [C] is more important factor than the Q$_f$ in the plasma process. The upper concentration limit may depend on the gas flow rate, the type of VOCs, and NOx formation as well. Up to medium scale application, NTP process can be applied for the three-digit concentration (roughly less than 200 ppm). At large scale, where the flow rate exceeds about 200 m$^3$/min, the optimum concentration may be reduced to two-digit range. In contrast to the important role of catalyst type on the CO$_2$ selectivity, the type of catalyst had little influence on the decomposition efficiency in the flow-type PDC reactors [12]. On the other hand, the cycled system is expected to have higher concentration limit than that of the flow-type PDC system due to the adsorption. This adsorption step may also render the cycled system effective because there is a large variation of VOCs concentration over the operation period in many chemical facilities.

**IV. CONCLUSION**

The decomposition of benzene and toluene has been investigated using the flow-type PDC reactor and the cycled system. The key findings in this study can be summarized as follows.

1) The outlet temperature of the PDC reactor linearly increased with the specific input energy.

2) In the case of flow-type PDC reactors, a trade-off relation was found between the formation of nitrogen oxides and the decomposition of VOCs. The formation of NOx limits maximum applicable specific input energy to about 100 J/L in the flow-type PDC system. Therefore, the application of the flow-type PDC system may be limited to the processing of dilute VOCs (concentrations below 100 ppm).

3) In the cycled system, the energy required for the complete oxidation of benzene increased with the inlet concentration. The type of catalyst largely affect the EF. Temperature did not influence on the required energy of the oxygen plasma for the complete decomposition of benzene.

4) The feasible Q$_f$–[C] map of NTP technology was presented based on the data of current study and the commercialized facilities. The energy-dependent characteristic of the NTP process may widen the optimum range of Q$_f$, but limit the concentration. For large-scale application, the optimum concentration may reduced to 2-digit range.

**ACKNOWLEDGMENT**

This work was partly support by MEXT; Grand-in-Aid for Young Scientist (A) (16681007).

**REFERENCES**