Optimum Conditions for Effective Decomposition of Toluene as VOC Gas by Pilot-Scale Regenerative Thermal Oxidizer

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Abstract—Regenerative Thermal Oxidizer (RTO) is one of the best solutions for removal of Volatile Organic Compounds (VOC) from industrial processes. In the RTO, VOC in a raw gas are usually decomposed at 950-1300 K and the combustion heat of VOC is recovered by regenerative heat exchangers charged with ceramic honeycombs. The optimization of the treatment of VOC leads to the reduction of fuel addition to VOC decomposition, the minimization of CO₂ emission and operating cost as well.

In the present work, the thermal efficiency of the RTO was investigated experimentally in a pilot-scale RTO unit using toluene as a typical representative of VOC. As a result, it was recognized that the radiative heat transfer was dominant in the preheating process of a raw gas when the gas flow rate was relatively low. Further, it was found that a minimum heat exchanger volume to achieve self combustion of toluene without additional heating of the RTO by fuel combustion was dependent on both the flow rate of a raw gas and the concentration of toluene. The thermal efficiency calculated from fuel consumption and the decomposed toluene ratio, was found to have a maximum value of 0.95 at a raw gas mass flow rate of 1810 kg h⁻¹ and honeycombs height of 1.5m.

Keywords—Regenerative Heat Exchange, Self Combustion, Toluene, Volatile Organic Compounds.

I. INTRODUCTION

VOC are often used as solvents in many industrial processes such as painting, printing and laminating. However, as a consequence of their utilization, aromatic and chlorinated hydrocarbons are widely discharged into the environment. For example, an amount of 101,736 tons of toluene was discharged in FY 2006 in Japan and this amount represented the largest amount among the target chemicals [1]. In general, VOC are considered to be responsible for various health problems due to the generation of photochemical oxidants and SPM (Suspended Particulate Matter) from VOC [2].

As a countermeasure of VOC emission, Japanese air pollutant control law had been revised in May 2004 and more rigorous measures were taken to prevent the release of VOC to the atmosphere [3]. Concentrations of VOC in exhaust gases of driers, paint booth, industrial cleaning as well as VOC storage tank, were targeted by the revised regulation which is in accordance with regulations in other countries such as Council Directive 1999/13/EC and Clean Air Act Amendments of 1990 [4]. For example, total hydrocarbons concentration permitted in exhaust gases of a drier for a gravure printing was set to 700 ppmC. Regarding the treatment of VOC from printing dryer and laminator, etc., various methods on the recovery or thermal decomposition of VOC have been in practical use. For VOC recovery, the methods on PSA (Pressure Swing Adsorption) [5] and membrane separation [6] have been used to recover mainly a single species of VOC from exhaust gases. However, in general, the exhaust gas discharged from industrial processes contains different kinds of VOC, which may cause a lot of energy consumption for the separation and recovery of the desired VOC. Meanwhile, among the decomposition methods for VOC treatment, there are several methods in use; combustion, chemical agents, plasma [7] and biochemical decomposition [8]. In particular, the combustion method is widely used for the treatment of VOC such as toluene, ethyl acetate, methyl ethyl ketone, etc. In the combustion method, a RTO is known as an effective device for the oxidative decomposition of the majority of VOC, in terms of high thermal efficiency, robustness and economical merit. Further, the RTO covers a wide range of VOC concentration.

Generally it is considered that the efficiency of VOC treatment in the RTO is affected by the concentration of VOC, the residence time and the temperature of a raw gas to be treated, etc. Among these operation factors, flow rates and VOC concentration of a raw gas are of primary significance. However, so far, there have been only few reports which gave the guideline for the optimum operation of an RTO to accomplish a higher thermal efficiency as well as high decomposition efficiency for VOC treatment. Therefore, in the present work, the thermal efficiency and the thermal performance of an RTO during the oxidative decomposition of VOC was studied in a pilot-scale RTO unit using toluene as VOC, and the optimum conditions for a higher thermal efficiency as well as a cost-effective design of the RTO were
discussed.

II. PROCEDURE FOR EXPERIMENTS

A. Operation Principle of Regenerative Thermal Oxidizer

An illustrative diagram of a typical RTO is shown in Fig. 1. The RTO consists of a set of two heat exchange columns where ceramic honeycombs are charged as heat storage/regeneration media. These two heat exchangers are connected to a combustion chamber on the top of the unit.

The raw gas containing VOC is made flow into heat exchanger “A” which has stored the remainder of combustion heat for VOC decomposition, by operating V01 and V04 valves open, while V02 and V03 valves are closed. In the first step of operation, the raw gas receives the heat stored in the heat exchanger “A” during preheating period and enters the combustion chamber. When, the preheated raw gas enters the combustion chamber, VOC undergo oxidative decomposition and the treated gas of a higher temperature leaves the combustion chamber. Thereafter, the treated gas free from VOC flows into heat exchanger “B” where the honeycombs are heated up storing the exhaust heat from the combustor, and leaves the RTO.

In the second step, a direction of the raw gas flow in the RTO is reversed by opening V02 and V03 valves, with V01 and V04 valves closed. When the raw gas enters heat exchanger “B” where the combustion heat of VOC has been stored in the honeycombs in the former step, the raw gas recovers the heat from the honeycombs and is preheated before entering the combustion chamber. After VOC in the raw gas had been decomposed in the combustion chamber, the treated gas enters heat exchanger “A”. Thus, one cycle of cyclic operation of VOC treatment in the RTO is completed.

B. Experiments

As shown in Fig. 1, the raw gas was sucked into the RTO by an exhaust fan operated by a frequency controller. The mass flow rate \( W \) (kg\(h^{-1}\)) was measured by a mass flow meter. A LPG burner was used to keep the gas temperature in the combustion chamber at a given value (973-1173 K). The LPG consumption was measured by a gas flow meter, and the combustion heat caloric value of LPG \( Q_c \) (kJ\(h^{-1}\)) was calculated from the consumption and heating value of LPG.

As a typical representative of VOC, toluene was used in this study and was supplied to the RTO by a spray nozzle. The mass flow rate of the supplied toluene was monitored, and the concentration of toluene in the raw gas and the treated gas was measured by an FID gas chromatograph. The combustion heat caloric value of toluene \( Q_t \) (kJ\(h^{-1}\)) was calculated from the supplied toluene flow rate and the heating value of toluene \( AH \) (kJ\(mol^{-1}\)).

Table I shows the specification of the ceramic honeycombs used in the present study. A cross section of each heat exchanger was 0.36 m², and ceramic honeycombs were charged up to a given height \( H \) (0.9 - 1.5 m) in both heat exchangers.

The combustion chamber and the heat exchangers were insulated around the inside of the outer walls, so that the heat loss from the combustion chamber and the heat exchangers by heat conduction, heat convection and heat radiation, \( Q_h \) (kJ\(h^{-1}\)) from the RTO could be lowered.

The gas temperatures at measuring points indicated in Fig. 1 were measured by K-type thermocouple. In Fig. 1, \( T_i \) (K) is the temperature of the raw gas in the inlet duct of the RTO and \( T_e \) (K) is the gas temperature in the combustion chamber, and \( T_a \) (K) is the temperature of the treated gas in exhaust dust. The calorific values of \( Q_r \), \( Q_o \) and \( Q_i \) (kJ\(h^{-1}\)) are those of the gas at each temperature of \( T_i \), \( T_e \) and \( T_a \). The calorific value, \( Q_o \) (kJ\(h^{-1}\)) shown in Fig.1 is that of charged or discharged heat in the heat exchanger. The calorific value of \( Q_o \) charged in the heat exchanger is equal to the calorific value regenerated for preheating the raw gas, in the steady-state condition.

In the experiment, the ambient air was introduced into the RTO for about 2 hours to start up the RTO and the main valves (V01 - V04) were switched continuously at a given interval, \( t_1 \). During this operation, the gas temperature in the combustion chamber was slowly heated up to a given temperature by a LPG burner. When a stable state condition of the RTO was achieved, the raw gas containing toluene was introduced into the RTO and the treatment of the raw gas was started.

The experimental conditions were as follows; the gas
temperature in the combustion chamber was set to a value from the a temperature range of 973 to 1273 K and the mass flow rate of the raw gas was in the range of 1090 to 2550 kg·h⁻¹. The time interval of switching the main valves to change the direction of gas flow was set to a value from 60 to 180 s.

C. Temperature Efficiency \( \eta_T \)

The temperature efficiency \( \eta_T \) is practically used to evaluate the heat exchange performance of various heat exchangers, since it can be calculated only from the temperatures of a high temperature fluid and a low temperature fluid at the inlet and the outlet. The \( \eta_T \) of typical heat exchangers is calculated by (1) [10]-[11].

\[
\eta_T = \frac{T_{hi} - T_{ho}}{T_{hi} - T_{ci}}
\]  

(1)

where, \( T_{hi} \) is the temperature of a high temperature fluid in the inlet of heat exchanger, \( T_{ho} \) is the temperature of a high temperature fluid in the outlet of heat exchanger and \( T_{ci} \) is the temperature of a low temperature fluid in the inlet of heat exchanger.

As shown in Fig.1, the sensible heat of the treated gas leaving the combustion chamber at \( T_c \) was stored in the honeycombs while the treated gas was flowing downward heat exchanger “B”, and the treated gas was discharged as exhaust gas at \( T_o \). After heat exchanger “B” was heated up and kept at a prescribed temperature, the raw gas at the temperature of \( T_i \) was allowed to flow into heat exchanger “B”, so that the raw gas could be preheated in heat exchanger “B”. When the temperature efficiency is adapted to the RTO system, (1) is replaced by (2).

\[
\eta_T = \frac{T_e - T_o}{T_e - T_i}
\]  

(2)

In the operation of RTO, the temperature of the exhaust gas, \( T_e \), changed with time, which meant that the \( \eta_T \) value calculated by (2) was dependent on time. For example, variation of \( T_e, T_o \), and \( T_i \) at \( t_v = 120 \text{ s} \) is shown in Fig.2. In the present work, the overall \( \eta_T \) value of RTO was calculated using average gas temperatures of \( T_e, T_o \) and \( T_i \) as expressed in (3). As shown in Fig.2, \( T_e, T_o \), and \( T_i \) can be assumed to be constant, and then (3) is simplified as (4).

\[
\eta_T = \frac{\frac{1}{t_v} \int_{t_0}^{t_v} T_e(t)dt - \frac{1}{t_v} \int_{t_0}^{t_v} T_o(t)dt}{\frac{1}{t_v} \int_{t_0}^{t_v} T_e(t)dt - \frac{1}{t_v} \int_{t_0}^{t_v} T_i(t)dt}
\]  

(3)

\[
T_c = \frac{1}{t_v} \int_{t_0}^{t_v} T_o(t)dt
\]  

(4)

Heat exchange characteristic of the honeycombs was evaluated using the \( \eta_T \) calculated by (4).

D. Thermal Efficiency \( \eta_H \)

As expressed in (4), a decrease in the temperature of the exhaust gas, \( T_o \), led to an increase of temperature efficiency \( \eta_T \). However, at a higher temperature level, the heat loss such as the radiation heat loss, \( Q_r \), should not be neglected, since as a radiation heat loss from heat exchanger surface increases, \( \eta_T \) increases due to a decrease in \( T_o \). To estimate the radiation heat loss, \( Q_{r} \), the enthalpy balance in the RTO during the steady-state condition was considered. In accordance with the energy conservation law, the enthalpy values of the raw gas \( Q_i \) and the exhaust gas from the RTO \( Q_o \), and the calorific values of \( \text{VOC}, Q_c \), and \( \text{LPG}, Q_L \) are related as expressed in (5).

\[
Q_o + Q_L = Q_i - Q_c + Q_r
\]  

(5)

In the case that the concentration of VOC is low, the combustion heat of LPG is required to provide heat to raise the temperature of the raw gas from \( T_i \) to \( T_e \). On the other hand, when VOC concentration is high, the heat supply to the RTO by LPG combustion is not necessary. Furthermore, when the concentration of VOC is high enough providing an excess amount of combustion heat to the RTO, the surplus heat should be removed from the RTO, so that \( T_e \) may be kept within a safe temperature level for a commercial operation of RTO. In the present work, such an operation condition will not be discussed, since the surplus heat can not be removed from the combustion chamber of the present RTO unit.

The thermal efficiency \( \eta_H \) of the RTO can be expressed by (6), in accordance with its definition.

\[
\eta_H = \frac{Q_{co}}{Q_c - Q_r}
\]  

(6)
As shown in Fig. 1, the raw gas at the temperature of \( T_i \) is heated by the regenerative heat stored in the honeycombs and attains \( T_c \) by the combustion heats of toluene and LPG. These enthalpy values are related to (7).

\[
Q_e = Q_i + Q_{co} + Q_v + Q_L \tag{7}
\]

When (8) is replaced by (7) and substituted for (6), \( \eta_H \) is calculated by (9) using \( Q_e \) and \( Q_L \).

\[
Q_{co} = Q_e - Q_i - (Q_v + Q_L) \tag{8}
\]

\[
\eta_H = 1 - \frac{Q_o + Q_L}{Q_e - Q_i} = 1 - \frac{Q_o - Q_i}{Q_e - Q_i} \tag{9}
\]

III. RESULTS AND DISCUSSION

A. Effect of Gas Temperature on VOC Decomposition Efficiency

Fig. 3 shows the experimental results on the decomposition efficiency of toluene and the yield of by-products obtained in the temperature range of \( T_c = 973 \) to 1173 K, at the mass flow rate \( W = 2180 \text{ kg·h}^{-1} \) and the time interval \( t_f = 120 \text{ s} \). The concentration of toluene in the raw gas was kept in the range of 100 to 400 ppm.

As shown in Fig. 3, the raw gas at the temperature of \( T_i \) is heated by the regenerative heat stored in the honeycombs and attains \( T_c \) by the combustion heats of toluene and LPG. These enthalpy values are related to (7).

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Q_e = Q_i + Q_{co} + Q_v + Q_L \tag{7}
\]

When (8) is replaced by (7) and substituted for (6), \( \eta_H \) is calculated by (9) using \( Q_e \) and \( Q_L \).

\[
Q_{co} = Q_e - Q_i - (Q_v + Q_L) \tag{8}
\]

\[
\eta_H = 1 - \frac{Q_o + Q_L}{Q_e - Q_i} = 1 - \frac{Q_o - Q_i}{Q_e - Q_i} \tag{9}
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\eta_H = 1 - \frac{Q_o + Q_L}{Q_e - Q_i} = 1 - \frac{Q_o - Q_i}{Q_e - Q_i} \tag{9}
\]

B. Effect of Height of Honeycombs and Mass Flow Rate on \( \eta_T \) and \( \eta_H \)

As shown in Fig. 3, toluene was completely decomposed above 1073 K. Then, at a constant gas temperature in the combustion chamber of \( T_c = 1073 \text{ K} \), the effect of height of ceramic honeycombs \( H \) and the mass flow rate \( W \) on the temperature efficiency \( \eta_T \) and the thermal efficiency \( \eta_H \) was studied and the results are shown in Fig. 4.

As shown in Fig. 4, \( \eta_T \) increased from 0.92 to 0.96 and \( \eta_H \) increased from 0.92 to 0.95 when \( H \) was increased from 0.9 to 1.5 m at \( W = 1810 \text{ kg·h}^{-1} \). Moreover, \( \eta_T \) increased from 0.90 to 0.95 when \( W \) was decreased from 2550 to 1090 kg·h\(^{-1}\) at \( H = 0.9 \text{ m} \). On the other hand, \( \eta_H \) increased from 0.91 to 0.92 when \( W \) was decreased to 1810 kg·h\(^{-1}\) at \( H = 0.9 \text{ m} \). But, when \( W \) was further decreased, the value of \( \eta_H \) decreased.

The heat transfer performance of honeycombs was improved, so that an increase in \( H \) or a decrease in \( W \) led to increase in the residence time of the gas in the honeycombs. Thus, an increase in \( \eta_H \) with a decrease in \( W \) at a constant height of honeycombs was also predicted. But \( \eta_H \) had a maximum value at \( W = 1810 \text{ kg·h}^{-1} \).

This phenomenon can be explained by the effect of the heat radiation loss, \( Q_r \). The total enthalpy for heating the raw gas from \( T_i \) to \( T_c \) decreases proportionally to a decrease in \( W \). Further, a ratio of enthalpies of both toluene and LPG to the total enthalpy for heating the raw gas decreased. On the other hand, the enthalpy of both toluene and LPG in order to make up the radiation heat loss, \( Q_r \) was a constant. This is because \( Q_r \) was almost independent on \( W \) at a constant temperature of \( T_c \). Therefore, when the mass flow rate \( W \) was low, the combustion heats of toluene and LPG were mostly lost in the form of \( Q_r \), and \( \eta_H \) decreases.
C. Effect of Residence Time on $\eta_T$ and $\eta_H$

As seen in Fig. 4, the temperature efficiency $\eta_T$ and the thermal efficiency $\eta_H$ were affected by the mass flow rate of treated gas $W$ and the height of ceramic honeycombs $H$. From this result, it was considered that $\eta_T$ and $\eta_H$ were dependent on the space velocity or the residence time of the gas in the honeycombs. Hence, the residence time of the treated gas, $t_R$ was defined by (10).

$$t_R = \frac{3600 \times V}{F}$$

(10)

where, $V$ is the volumetric volume of honeycombs in the heat exchanger, $F$ is the volumetric flow rate of the raw gas at the average gas temperature $T_{ave}$ in the heat exchanger. The values of $V$ and $F$ are expressed by (11) and (12), respectively.

$$V = A \times H \times O_s$$

(11)

$$F = \frac{W \times T_{ave}}{T_{c}}$$

(12)

where, $A$ is a cross section of the honeycombs 0.36 m$^2$, $O_s$ is an open space of the honeycombs 0.625, $\gamma$ is the specific gravity of the raw gas 1.293 kg·m$^{-3}$ at 273 K.

Fig. 5 shows the effect of the residence time of the treated gas, $t_R$ on the efficiencies of $\eta_T$ and $\eta_H$.

As seen in this figure, $\eta_T$ increased almost linearly from 0.90 to 0.98 when $t_R$ increased from 0.15 to 0.58 s at each honeycombs height of $H=0.9, 1.2$ and 1.5 m. It was found that $\eta_T$ is almost independent on $H$ at a constant $t_R$. On the other hand, $\eta_H$ took the maximum value a constant height of $H$ when $t_R$ was increased. The value of $t_R$ which gave the maximum value of $\eta_H$ was increased from 0.21 to 0.35 s when $H$ was increased from 0.9 to 1.5 m. From these results, it can be said that the amount of heat recovered from honeycombs was increased with an increase in the residence time of the raw gas. However, as already explained on the reason of the decrease in $\eta_H$ value in Fig. 4, the radiation heat loss from the RTO became relatively large when the mass flow rate was increased.

D. Effect of Time Interval on Thermal Efficiency

As was shown in Fig. 2, the treated gas temperature at the outlet of the duct $T_o$ changed from 323 to 372 K with time at each interval of $t_V=120$ s. Based on this, it is considered that $T_o$ and thermal efficiency $\eta_H$ should vary with the change in $t_V$. Fig. 6 shows the effect of $t_V$ on $\eta_H$ and $T_o$.

As seen in this figure, when $t_V$ was changed from 60 to 180 s, the minimum value of the temperature of $T_o$ decreased from 327 to 318 K, and the maximum value of the temperature of $T_o$ increased from 355 to 389 K. In addition, the thermal efficiency $\eta_H$ decreased only slightly, although the time-averaged value of $T_o$ increased from 337 to 347 K. When $t_V$ was increased, the temperature of the upper part of honeycombs approaches the gas temperature in combustion chamber $T_c$ and then the heat transfer from the treated gas to honeycombs is reduced.

E. Optimization of Honeycombs for Self Combustion

As was shown in the previous section, the maximum value of the thermal efficiency $\eta_H$ was obtained at $W=1810$ kg·h$^{-1}$ and $\eta_H$ increased with an increase in $H$. In an optimum RTO operation, the shortage of calorific value for a stable combustion of toluene in the raw gas was provided by heat exchanger when LPG combustion was not used ($Q_L=0$). Hence, the minimum concentration $C$ of toluene in the raw gas to achieve self combustion can be calculated from (13), in terms of calorific value of combustion $Q_L$, heat value of toluene $\Delta H$ and mass flow rate of the gas $W$ at $H=0.9, 1.2$ and 1.5 m.
\[ C = \frac{Q_v}{\Delta H} \times \frac{22.4 \times \gamma}{W} \times 10^3 \]  
(13)

\[ \eta_r = (1 - \eta_H) \times (Q_v - Q_{lo}) \]  
(14)

where, \( \eta_r \) is calculated from (14), which was replaced by (9) on the assumption that \( \eta_r \) was equal to 0.

Fig. 7 shows the relation between the calculated value of \( C \) and the height of honeycombs at \( W = 1810 \) kg·h\(^{-1}\). It was found that toluene concentration of 530 ppm in the raw gas was necessary for self combustion at \( H = 0.9 \) m and this concentration decreased to 340 ppm due to the increase in \( \eta_H \) from 0.92 to 0.95 when \( H \) was increased up to 1.5 m. However, if an excess amount of honeycombs is charged in the heat exchangers, the pressure drop in heat exchangers increases, which leads to a deterioration in cost effectiveness of RTO. Thus, based on these findings, it is possible to determine an optimum height of honeycombs for self combustion of toluene in the raw gas.

Fig. 7 Toluene concentration in the raw gas necessary for self combustion

\[
(W = 1810 \text{ kg·h}^{-1}, \ T_c = 1073 \text{ K}, \ t_v = 120 \text{ s})
\]

IV. CONCLUSION

In the present work, the thermal efficiency of the RTO was investigated using a pilot-scale RTO unit for effective decomposition of toluene. As a result, it was recognized that the heat transfer of honeycombs depended only on the residence time of the gas in the honeycombs. In addition, the optimum value of the raw gas mass flow rate was determined to be 1810 kg·h\(^{-1}\) in this RTO unit. As for the gas mass flow rate lower than 1810 kg·h\(^{-1}\), it was considered that the majority of combustion heat of toluene and LPG was used to compensate the radiation heat loss. Finally, it was found that when the height of honeycombs decreased from 1.5 to 0.9 m, a minimum concentration of toluene to achieve self combustion without additional heating increased from 340 to 530 ppm at an optimum mass flow rate of 1810 kg·h\(^{-1}\).