# The Formation and Decomposition of Dioxins on the Exhaust Gas of a Fluidized Incinerator

Kenji Toyoda, Takeichi Kondo, Minoru Asai, Masanobu Naito, Shigeki Abe and Yoshio Takeuchi, Ishikawajima-Harima Heavy Industries Co. Ltd., 1-Shin-Nakahara-cho, Isogo-ku, Yokohama, 235 Japan

## Abstracts

Homogeneous non-catalytic rate parameters (pre-exponential factor and activation energy) were determined by the minimization calculation from the temperature changing data of the blank test on a fluidized incinerator.

Heterogeneous catalytic rate parameters were determined on the simultaneously occurring condition of homogeneous and heterogeneous reactions.

## Introduction

Nowadays, the dioxins of the exhaust gases on waste incinerators must be controlled under the 0.1 ng-TEQ/$m^3$ in European countries. The same regulated value is adopted by the Environmental Health Bureau in Japan.

The basic analysis of dioxins rate process is acquired a great importance in order to eliminate dioxins from the exhaust gases. So the basic experiments and analysis were carried out.

## Experimental Methods

RDF containing chlorine was burned by using an advanced fluidized-bed swirl incinerator (20 ton/day).[1),2)] The RDF was prepared from the photographic paper laminated by vinyl chloride resin.

The exhaust gas from the incinerator were branched at the induced draft fan(IDF) into the catalytic tester shown in Fig. 1. On the tester the four reactors were set and they were made from silica glass. Three kinds of catalysts were packed in the reactors and blank tests were done on the remaining reactor. One catalyst(A) mainly contains noble metals and alumina. The other two(A,B) mainly contain vanadium and titanic oxide. The same sizes are utilized on the all catalysts.

The size at the cross section is square 35x35mm. Its length is 490mm.

Alumina cement was packed between the catalyst and the glass wall of the reactor in order to prevent bypass flow.

The connecting tube from IDF to the tester is long in comparison with the reactor. The tube is divided into three zones. The sizes of the zones are shown in Table 1. The volume of the zones and their temperatures were considered on the rate analysis of dioxins homogeneous reactions.

For dioxins analysis gases were collected at the IDF and the inlet and outlet of the reactors. Dioxins analytic values of the inlet were coincide with those of outlet, so gas sampling at the inlet was omitted at the forward experiments.

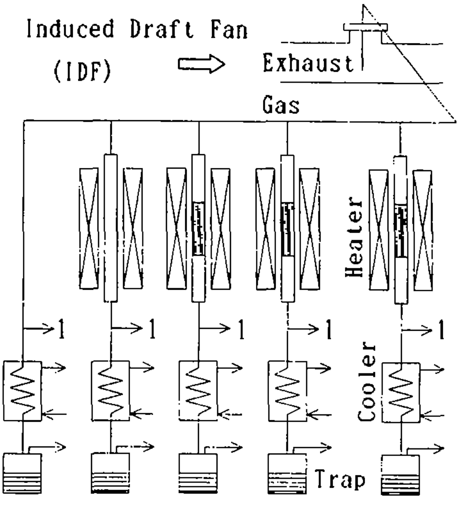


Fig.1 A catalytic tester

Table 1 The size of tube from IDF to the tester

| | Position | Inner Diameter mm | Length mm |
|---|---|---|---|
| I | IDF to P | 53.5 | 23500 |
| P | Preheater | 53.5 | 2000 |
| H | Heating zone | 53.5 | 1500 |
| R | Reactor | 72.1 | 1100 |

## Rate Analytical Methods

It is mentioned in mainly new reports that dioxin reactions must be considered under the complex reaction paths.

But few quantitative analysis studies are present.[3)]

So for the trial those studies this time the following two reactions are considered.

precursor $\rightarrow$ dioxin (i-1)

$r_1$, $r'_1$

$r_1$[mol/(ml·s)] $r'_1$[mol/(ml-cat·s)]

dioxin $\rightarrow$ light toxic materials (i-2)

$r_2$, $r'_2$

$r_2$[mol/(ml·s)] $r'_2$[mol/(ml-cat·s)]

The reaction rates $r_1$, $r'_1$ are zero order equations if the concentration change of precursor is small in the reactor. In the case the next equations are given.

$r_1=k_1$ (1) $r'_1=k'_1$ (2)

If the decomposition rates of $r_1$, $r'_1$ are typical first order rates, the next equations are given.

$r_2=k_2f_{DXN}$ (3) $r'_2=k'_2f_{DXN}$ (4) $f_{DXN}$:mol fraction of DXN[-]

The rate constant k is expressed as Arrhenius' equation $k=A\exp(-E/RT_K)$.
Firstly the homogeneous rate profile is calculated by using the data of the blank test.
At the time the next equation is used.

$$\frac{dF_{DXN}}{d\xi}=(r_1+r_2)\varepsilon V \qquad (5)$$

$F_{DXN}$:mol flow rate[-]
$\xi$ :dimension-less length[-] $\xi=0$ inlet $\xi=1$ outlet
$\varepsilon V$ :void volume[ml] $\varepsilon$ :void fraction[-]

From more than four data by changing temperature between 140℃ and 250℃ the following value S was calculated.

$$S=\sum_{i=1}^{N}(f_{data}-f_{cal})_i^2 \qquad (6)$$

$f_{data}$:experimental mol fraction of i-th
$f_{cal}$ :calculated value from eq.(5)

Four parameters $A_1,E_1,A_2,E_2$ were set at the minimum value of S by the minimization technique(simplex method).[4)]
Secondly $f_{cal}$ is calculated on heterogeneous catalytic reaction rate by the following equation. Four parameters $A'_1,E'_1,A'_2,E'_2$ were similarly set by the minimization of S.

$$\frac{dF_{DXN}}{d\xi}=(r_1+r_2)\varepsilon V+(r'_1+r'_2)V_{cat} \qquad (7)$$

$V_{cat}$:catalyst volume[ml]

**Results and Conclusions**

The example of the calculated rate parameters of PCDDs and PCDFs are shown in Table 2 and Table 3. The calculated rate parameters on the homogeneous non-catalytic condition is shown in Table 2. The catalytic parameters is shown in Table 3. The following conclusions are obtained from Table 2 and Table 3.

(1) Catalytic rate constants is $10^2 \sim 10^3$ times larger than those of homogeneous reactions on the all cases of PCDDs and PCDFs.

(2) Catalytic rate constants of a noble metal catalyst(A) is lager than those of vanadium catalysts(B,C) at high temperature(250℃), but is smaller than those of B,C at low temperature(140℃) on PCDDs and PCDFs. The activity of B is almost equal to that of C.

Table 2 The rate analysis of dioxins on the homogeneous condition
Total flow rate in the reactor $F_T$=50 l/min(dry base) $H_2O$:30mol% $O_2$:12mol%

| DXN / rate / Run | PCDDs | | | | PCDFs | | | |
|---|---|---|---|---|---|---|---|---|
| | formation | | decomposition | | formation | | decomposition | |
| | $A_1$ | $E_1$ | $A_2$ | $E_2$ | $A_1$ | $E_1$ | $A_2$ | $E_2$ |
| | mol/(ml·sec) | cal/mol | mol/(ml·sec) | cal/mol | mol/(ml·sec) | cal/mol | mol/(ml·sec) | cal/mol |
| Blank test | 0.310e+02 | 0.444e+05 | 0.776e-06 | 0.459e+01 | 0.286e+01 | 0.432e+05 | 0.518e-06 | 0.482e+01 |

Table 3 The rate analysis of dioxins on the heterogeneous condition
Same conditions in Table 1.

| DXN / rate / Run | PCDDs | | | | PCDFs | | | |
|---|---|---|---|---|---|---|---|---|
| | formation | | decomposition | | formation | | decomposition | |
| | $A'_1$ | $E'_1$ | $A'_2$ | $E'_2$ | $A'_1$ | $E'_1$ | $A'_2$ | $E'_2$ |
| | mol/(ml·sec) | cal/mol | mol/(ml·sec) | cal/mol | mol/(ml·sec) | cal/mol | mol/(ml·sec) | cal/mol |
| A cat. | 0.106e-03 | 0.233e+05 | 0.461e+06 | 0.177e+05 | 0.884e-11 | 0.741e+04 | 0.176e+00 | 0.299e+04 |
| B cat. | 0.319e-07 | 0.161e+05 | 0.803e+03 | 0.122e+05 | 0.212e 11 | 0.738e+04 | 0.553e 01 | 0.251e+04 |
| C cat. | 0.797e-07 | 0.171e+05 | 0.101e+05 | 0.142e+05 | 0.106e-11 | 0.791e+04 | 0.167e-02 | 0.415e+03 |

## Literature cited


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