

DIOXINS FORMATION IN A GASIFICATION AND REFORMING PROCESS WITH CATALYST FOR THE PURPOSE OF HYDROGEN PRODUCTION

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Introduction

The pyrolysis-gasification process, applied in combination with the reforming process, is one of the anticipated systems for waste disposal and resource recovery in the near future. However, various byproducts potentially harmful to the environment and to the next stage use may arise from the process, because it usually takes place in a strictly oxygen deficient atmosphere. Hydrocarbons, such as simple alkane and aromatic compounds, are known to be formed.

In this respect, little information exists with regard to the formation of dioxins that is PCDD/PCDF and Co-PCBs. The formation of dioxins is expected to be hard to occur because of the low O₂ atmosphere. However, the low temperature operation of the gasification process may have the potential to generate a variety of trace constituents from pyrolysis or the partial oxidation condition. The objective of this study is to investigate the formation and behavior of dioxins during the gasification and reforming process for solid waste. Emphasis was placed on the effect of temperature on the behavior and also the effect of the catalyst.

Materials and Methods

Solid waste samples

Three kinds of solid waste were used in the experiment. The composition of the samples is shown in Table 1. Waste wood was obtained from a pulled down wooden building, the main source being Japanese cedar. Since Chlorine and sulfur amount in this material was therefore very low. Refuse derived fuel (RDF) includes kitchen waste and miscellaneous matters, so Cl and S content were relatively high. As refuse paper and plastic fuel (RPF) was made from plastics with high hydrogen content, the amount of H was slightly high. These samples were crushed and sieved to a particle size of several millimeters, adequate for the feeding in the experiment.

Table 1 Element composition of solid waste samples used (Values are on a dry basis)

Sample	Description	C	H	O	Cl	S
		[wt %]	[wt %]	[wt %]	[wt %]	[wt %]
Waste wood	Collected from a pulled down house	51.4	5.9	40.7	<0.01	<0.02
RDF	Made from municipal solid waste	45.4	6.4	34.3	0.4	0.1
RPF	Made from paper and plastic waste	50.6	8.1	33.0	0.04	0.05

Two kinds of catalyst were used, namely a steam reforming catalyst containing Ni and CaO, supported by Al₂O₃, and a Ti-V catalyst designed for dioxin decomposition.

Apparatus and experimental

Gasification and reforming experiments were conducted using the apparatus as shown in Fig. 1. This consisted of two reactors, a gasifier and a reformer, made of stainless steel in series; the inside diameter of both reactor being 50 mm and the length around 1500 mm. After the reactors were preheated to the desired temperature (600 – 850 °C), the feedstock was introduced into the gasifier with/without steam and a little oxygen, and further

Thermal processes

nitrogen was added as a carrier, usually in the amount of 20 l/min. The generated gas was passed to the reformer where the catalyst bed was made, and further channeled to the catalytic layer in the case of dioxin decomposition during the experimental runs.

Gas sampling and analysis

Gas sampling was done at two or three points. They are after the gasifier or before the reformer (A), after the reformer (B) and after the dioxin decomposition catalyst (C) respectively. Although carrier nitrogen was added, the exhausted gas volume was essentially a small amount because of the pyrolysis process, meaning a volume of 1 – 1.5 m³ gas or less was sampled for the determination of dioxins.

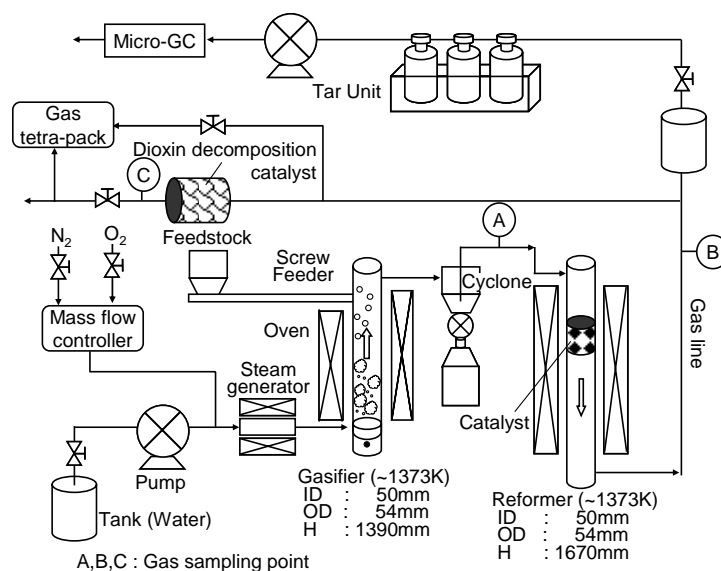


Fig. 1 Experimental apparatus and gas sampling point

Results and Discussions

Dioxins in the gasification and reforming process running

Table 2 shows the process data of the gasification/reforming operation and the concentrations of dioxins. This

Table 2 Results of process data and dioxins measurement

Run No.	Feedstock	Temperature [°C]	S/C ^{a)} [-]	O ₂ conc. [vol%]	Catalyst	Dioxins [ng/m ³ _{N@12%O₂}] at each sampling point ^{b)}		
						A	B	C
1	Waste wood	600	1.7	0.5-0.6	Ni	200 (5.1)	130 (4.9)	— ^{c)}
2		650	1.6	0.4-0.6		80, 89 (1.7, 1.9)	26, 18 (1.1)	—
3		700	1.7	0.3-0.4		130 (4.6)	5.1 (0.25)	—
4		750	2.1	0.4-0.5		79, 230 (1.5, 6.6)	2.8, 12 (0.076, 0.19)	—
5	RDF	750	1.8	0.5-1.9	Ni/CaO	540 (1.3)	44 (0.54)	—
6	Waste wood/RDF mixture (40/60)	650	2.5	0.5-1.5		460 (5.0)	170 (4.4)	—
7		750	1.8	0.7-1.8		300 (4.5)	11 (0.16)	—
8		850	1.7	1.1-1.3		49 (1.0)	14 (0.041)	—
9	RDF	650	1.8	0.5	Ni/CaO, Ti/V	—	9.5 (0.1)	17 (0.13)
10		750	1.9	0.2		—	2.4 (0.0059)	2.1 (0.039)
11		750	0.92	0.7		—	19 (0.10)	6.8 (0.066)
12		850	1.8	0.5-2.1		11 (0.12)	2.8 (0.049)	4.2 (0.055)
13	RPF	650	0.92	0.5-1.9	Ni/CaO, Ti/V	46 (0.36)	3.6 (0.026)	4.8 (0.027)
14		850	0.92	0.3-0.5		12 (0.077)	1.2 (0.009)	0.28 (0.0017)

a) Steam/Carbon ratio (mol/mol)

b) The number in parentheses shows the toxic equivalent ([ng-TEQ/m³_N]). In runs 2 and 3, experiments under the same conditions were performed twice.

c) Measurement was not conducted.

process aims to produce hydrogen as a new energy source from waste biomass at relatively low temperature by using the performance of the catalyst. The generated hydrogen is anticipated to be applicable to fuel cells in future. As a result, gas containing hydrogen at a concentration exceeding 50% by volume was successfully obtained and temperature was identified as the most important factor for hydrogen production. The catalyst worked effectively in producing much more hydrogen than the non-catalyst condition and the use of the catalyst was effective in reducing the temperature necessary for approaching the same hydrogen yield¹, namely about 200 °C.

Dioxins were detected in the concentrations of 79–230 ng/m³@12%O₂ (1.5–6.6 ng-TEQ/m³_N) at point A when using waste wood as a feedstock. Considering that the exhausted gas was diluted by the carrier gas, these values are fairly high, despite the low O₂ conditions. In the next reforming process, those compounds were decomposed, possibly by both effects of the residence in a high temperature atmosphere and of the catalytic performance. However, the Ni catalyst used in the reformer would not be very effective for dioxin decomposition and temperature may be rather effective in reducing dioxins.

The result of Run 5 using RDF was relatively different to the others. The toxic equivalent of pyrolysis gas of the sample (1.3 ng-TEQ/m³_N) was small compared to the dioxin concentration of 540 ng/m³@12%O₂. The TEQ value is usually around 2% of the gas concentration value. This was because the concentration of Co-PCB, at 500 ng/m³@12%O₂, and the ratio to the concentration of PCDD/PCDF were significantly high compared to usual incineration flue gas. The cause will be examined, considering the contamination of RDF sample used.

This effect of temperature was seen and clearly demonstrated in Fig. 2, where results suggest that temperatures of over 700 °C are necessary to decompose dioxins to sufficiently low levels for environmental concerns. The same tendency was observed from the results regarding the waste wood/RDF mixture (Run 6-8) and the result of Run 8, conducted at the highest temperature of 850 °C, showed a fair reduction.

From Runs 9-14, dioxin concentrations seemed to be relatively low compared to the runs using waste wood although measurement at sampling point A was not done for Runs 9-11. There may remain some points to discuss concerning the contribution of chlorine in the RDF sample and further investigation is needed.

The Ti/V catalyst for dioxins decomposition seemed not to be effective in reducing dioxins. This might be due to the fact that the concentration of dioxins at the inlet of the catalyst bed (B) was so low and the residence time of

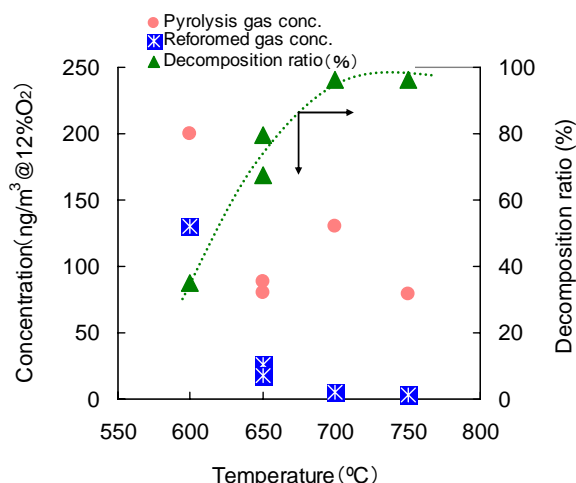


Fig. 2 Effect of temperature on the decomposition of dioxins in the case of experiments using waste wood.

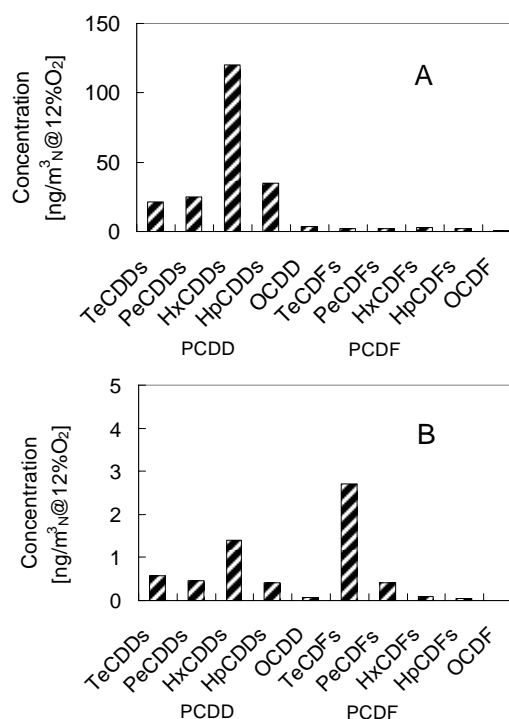


Fig. 3 Homologous distributions of pyrolysis gas sampled at point A and reformed gas at B, based on the result of the second run in Run 4

gas in this experiment was rather short (<1 s) due to the limitation of the equipment design.

Characteristics of the PCDD and PCDF patterns

The homologous distribution of PCDD and PCDF is brought up to clear the formation behavior. Figure 3 shows a typical distribution of PCDD and PCDF for the pyrolysis gas sampled at A and its reformed gas at B in case of the second run at 750 °C of waste wood. The pattern of A was very characteristic and PCDD homologues, mainly HxCDD, except OCDD were dominant. The same pattern was observed in the other analyzed results regarding waste wood. The fact suggests that the formation stems from incomplete oxidative reactions during pyrolysis. Oxygen contained in waste wood, amounting to about 40 wt%, may contribute to this reaction. However, the pattern differed significantly from the reported homologous distribution in the pyrolysis of industrial plastic shredder material². The ratio of $\sum PCDF/\sum PCDD$ for TeCDD/F to OCDD/F ranged from 30–200 in that report. On the contrary, PCDD was much more than PCDF in terms of pyrolysis gas and the ratio $\sum PCDD/\sum PCDF$ ranged from 22–28 in this study. This may be relevant to the kind of feedstock.

The change in patterns from pyrolysis to catalytic treatment in the case of RPF feedstock was shown in Fig. 4. PCDD constituents in pyrolysis gas were totally reduced during reform. However, only the TeCDFs in PCDF were found to be difficult to eliminate, and the congeners remained in the next catalytic process as a whole. The fact suggests that PCDD generated in pyrolysis are easily transformed during thermal reforming processes. The discussion conducted beforehand that catalytic decomposition was not effective can be shown here.

The composition regarding Co-PCB was also characteristic and a typical result was shown in Fig.5. The congener pattern of Co-PCB in gas in the case of using RDF resembled an industrial PCB product that has a feature whereby the compounds of #118, #115 and #77 were dominant congeners³. Further investigation, including the analysis of feedstock, is necessary to clarify the details.

References

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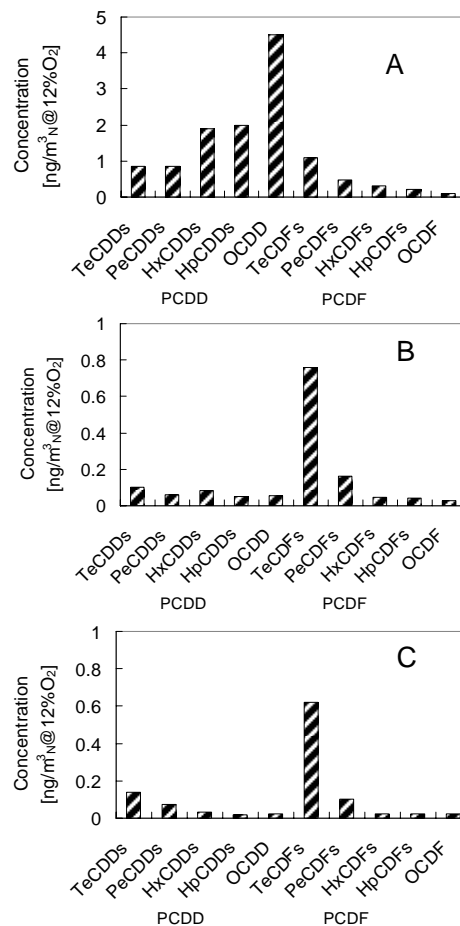


Fig. 4 Homologous distributions of PCDD/PCDF sampled at A, B and C (Run 13)

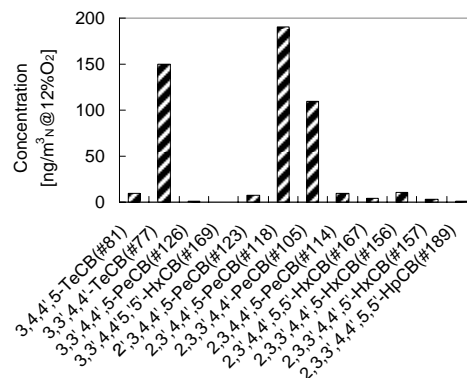


Fig. 5 Typical congener pattern of Co-PCB in gas (Run 5)