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# Determination of Dioxins Produced through Hydrothermal Reaction of Biomass Waste, Chicken Manure

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***Abstract*—Production of hydrogen gas and/or valuable material has successfully been made from biomass wastes by hydrothermal reactions in supercritical water. However, it is expected that toxic compounds might be produced through the reactions. It is therefore significant to clarify whether toxic compounds are synthesized or not in hydrothermal reactions of biomass wastes (biowastes), particularly of biomass wastes containing hetero-atoms in organic matrices. In this work, formation of Dioxins (Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs)) was examined since Dioxins are categorized among the most toxic compounds for human being. Chicken manure was tested as a real biowaste for hydrothermal reactions, the produced compounds in the liquid and solid phases were analyzed for detection of Dioxins by GC/MS. It was confirmed that total TEQ of Dioxins produced by the hydrothermal reaction was much lower than that regulation levels in Japan and the products requires no additional post treatments.**

***Keywords-Hydrothermal reaction, supercritical water, dioxins, biowaste.***

## I. INTRODUCTION

Year by year, energy demand is increasing all around the world. Many researchers are studying on new energy resources. Hydrogen is expected to be among the most promising alternative clean fuels because of its wide applications in a variety of energy systems.

Biomass including biowastes has also been thought to be a new energy resource, because of their renewability and their possibility for fuel production [1]. Hydrogen fuel has been produced through hydrothermal reactions in sub or supercritical water which has an capability to dissolve and decompose organic compounds [2]. Hydrothermal reactions in supercritical fluid of water (Pc=21MPa, Tc=374°C) occur very rapidly and effectively, compared to conventional fermentation to produce hydrogen from various bio-wastes [3].

In our laboratory, various alkali additives have been tested for efficient hydrogen production and suppression productions of other gases in the gas phase. $Ca(OH)_2$ that is less expensive than many other additives was selected to be adequate[4]. For treatment of a large amount of bio-wastes, the reagent cost is an important factor.

However, production of pollutants by the reaction has not been studied in detail. Toxic compounds might be produced from the hydrothermal reaction of real biowastes that contains hetero-atoms such as S, P N and Cl in their organic matrices. In this study, we focused on generation of dioxins that are among the most toxic substances for human being.

We employed "chicken manure" for a test real bio-waste sample. The compounds resulting under the various experimental conditions were analyzed by GC/MS for determination of dioxins. The value of total toxic equivalent quality (TEQ) is found to be less than 0.1 pgdm$^{-3}$ of the Japanese regulation level.

## II. EXPERIMENTS

The experimental procedure conducted in this study is schematically shown in Figure 1. They are mainly composed of three portions, 1. sample preparation, 2. hydrothermal reaction, and 3. analysis of produced compounds.

### *A. Sample preparation*

Into a reactor (10 cm$^3$) made of stainless steel tube (1/2 inch o.d. x 144 mm long, Swagelok Co., Ltd), about 100 mg of sample was weighed, and 5ml of water and an aliquot amount of $Ca(OH)_2$ were added. After the remaining air in the reactor was purged by a $N_2$ flow, the reactor was set into a GC-oven (Hewlett Packard, 5890 GC) (Figure 2).

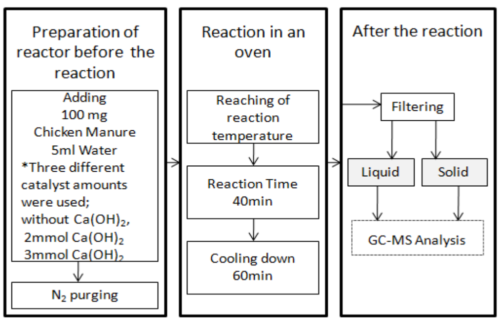


Figure 1 Experimental procedures

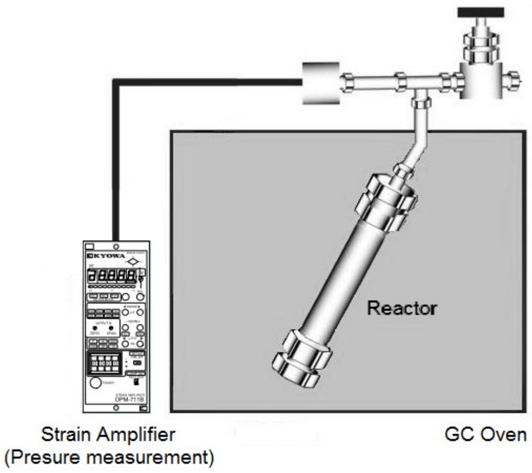


Figure 2 Experimental equipment for hydrothermal reaction

## B. *Hydrothermal reaction*

Different programmed temperatures of the reactor were available in the GC oven (Fig.2). After the temperature was reached the isothermal condition, it was kept for 40 minutes to complete the reaction. During the reaction, the pressure was monitored by the strain gauge (Fig.2). Subsequently, the reactor was cooled down to room temperature. The Dioxins in the liquid and solid phases were analyzed by GC/MS. The experimental conditions (temperatures and the amounts of additive) are listed in Table 1.

TABLE 1 EXPERIMENTAL CONDITIONS

| Run No. | Temperature [°C] | $Ca(OH)_2$ Amount [mmol] |
|---|---|---|
| 1 | 400 | 3 |
| 2 | 300 | 3 |
| 3 | 200 | 3 |
| 4 | 400 | 0 |
| 5 | 300 | 0 |
| 6 | 200 | 0 |

## C. *Analysis of Dioxins*

The substances in the liquid and solid phases produced by the hydrothermal reaction were separated into solid and liquid samples by filtration. More than 100 ml of the liquid sample was required for the determination of Dioxins by GC/MS. The reaction procedure therefore was repeated more than 20 times (5 ml x 20 = 100 ml).

Dioxin analysis was performed by a gas chromatograph combined with a mass spectrometer (GC/MS) for the resulting liquid and solid samples. An Agilent model 6890-GC interfaced with a JMS-700D double focus MS (JEOL, Japan) was used for the analysis. The GC was equipped with a SP-2331 capillary column (60m x 0.32mm i.d.) for Cl4-6 PCDDs/Fs and a HT8-PCB capillary column (60m x 0.25mm i.d.) for Cl7,8 PCDDs/Fs and Co-PCBs. The mass spectrometer was operated in the EI mode at a resolution of R>10,000 (10% valley). For the quantification of TEQ, TEF of WHO (2006) was used. 13C12-Labeled standards were added to the extracts (clean-up spike). These solutions were treated with concentrated sulfuric acid, followed by multi-layered silica gel column chromatography and activated carbon impregnated silica gel column chromatography. These treated solutions were carefully concentrated and spiked with 13C12-labeled standards (13C-1,2,7,8-T4CDF, 13C-1,2,3,4,6,8,9-H7CDF and 13C-2,3',4',5-T4CB(#70)) as syringe spike compounds. Then, the volume was adjusted to 20 $mm^{-3}$ under a nitrogen flow prior to the GC/MS analysis.

## D. *Reagents*

$Ca(OH)_2$ of analytical grade (Wako Chemical Co. Ltd, Japan) was used as the additive. Chicken manure (G.I. Ltd., Japan) was tested as the biomass waste sample.

## E. *Toxic Equivalent Quantity (TEQ)*

TEQ is calculated by the following summation equation (1), which shows total toxicity of dioxins contained in the sample.

$$TEQ = \Sigma\ f_1 g_i \quad (1)$$

Where $f_1$ is a toxic equivalency factor (TEF) and $g_i$ the abundance of $i^{th}$ dioxin in the sample.

# III. RESULTS AND DISCUSSION OF DIOXINS ANALYSIS

## A. *Determination of Dioxins in the products by the hydrothermal reaction of chicken manure*

### 1) *Solid phase*

Figure 3 shows the total Toxic Equivalence Quality (TEQ) with the TEQ of each Dioxin for the solid phase resulting under the various conditions of hydrothermal reactions of the chicken manure. With the additive, the total TEQs are nearly equal to those of blank at the high temperatures. The highest total TEQ of 0.0065 $pgg^{-1}$ by the summation of that of P5CB#105 (f=9.32), P5CB #118 (f=21.95) , and T4CB#77 (f=8.35) was observed at the reaction temperature of 400 °C without additive. Even at this temperature, the addition of 3 mmol $Ca(OH)_2$ effectively decreased the total TEQ down to 0.0015 (pg/g).

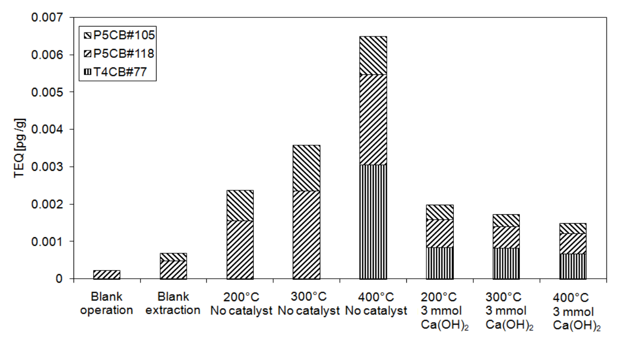


Figure 3 Total TEQ [pg TEQ/g] after treatment in the solid phase

*2) Liquid phase*

Figure 4 shows the TEQs for the liquid phase obtained under the various amounts of the additive at the different reaction temperature. The reaction temperature has little effect on the formation of dioxins. However, addition of $Ca(OH)_2$ increases the value of TEQ. The highest total TEQ was 0.0054 $pgdm^{-3}$ which was however much lower than the permitted level of Japanese Law (0.1 pg $m^{-3}$)[7].

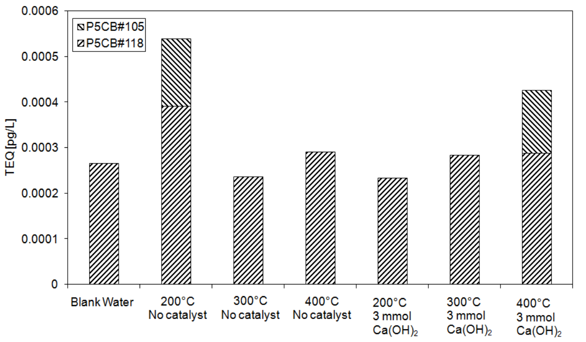


Figure 4 Total TEQ [pg TEQ/L] after treatment in residual liquid phase

## IV. CONCLUSIONS

Dioxins in liquid and solid phases produces by the hydrothermal reaction of the chicken manure under the optimum conditions for hydrogen production (i.e. the reaction temperature of 400°C, and the $Ca(OH)_2$ additive of 3 mmol with the reaction time of 40 min.) were quantitatively analyzed. The total TEQ of dioxins was found to be 0.0015 $pgg^{-1}$ for the residue, and 0.0042 pg $dm^{-3}$ for the liquid. The allowable levels in Japan are 0.1 $pgdm^{-3}$ for liquid samples, and 3$ngg^{-1}$ TEQ for solid sample [7]. These experimental results indicate that the formation of dioxins in hydrothermal reactions of the biowaste, chicken manure is at much lower levels that of the regulation and that the supercritical water is very reactive to cause complete decomposition of resulting dioxins.

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