Environmental Impacts of Hydrogen Production by Hydrothermal Gasification of a Real Biowaste

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Additional information is available at the end of the chapter

1. Introduction

Energy consumption is increasing regularly with increasing human population [1]. Finite resources of fossil fuels [2], security of other energy sources (especially nuclear energy), and concerns over greenhouse gases produced by combustion of fossil fuels have all motivated the search for renewable energy sources [3]. Energy from biomass could reduce the increase of carbon dioxide in the atmosphere and provide 14% of the world's energy needs [4, 5]. Also biomass gasification through the hydrothermal process has the added advantage of disposing of wastes [6]. Therefore, biomass has been selected for generation of energy by using hydrothermal gasification.

Hydrogen gas is anticipated as a fuel for clean power systems such as fuel cells. Many techniques have been reported for producing hydrogen gas [7, 8]. Hydrothermal gasification in sub or supercritical water has also been studied as a promising process for hydrogen production. The fluid can dissolve and decompose organic compounds [9]. Hydrothermal gasification is carried out at a relatively low temperature (about 400 °C) and occurs rapidly, compared with fermentation processes [10, 11]. Furthermore, hydrothermal gasification is carried out in supercritical fluid water, so this method is applicable to wet biomass samples without the necessity for a drying process, while the conventional thermal gasification needs excessive energy to dry wet biomass before it is gasified [4, 9, 12]. This process is therefore more suitable for biowastes with high water content, such as food wastes and animal dungs, than the conventional thermal gasification process that requires additional energy to overcome the latent heat of water.

There have been numerous studies related to the hydrothermal gasification process, and conducted for wide range of materials. Morimoto *et al.* [13] of Kyoto University studied hydrothermal gasification process of brown coal. Antal *et al.* [14] reported the gasification of cornstarch and wood dust. Yoshida *et al.* [15] studied supercritical water gasification of

cellulose, hemi-cellulose, and lignin. However, this process has not been studied for animal waste, because animal wastes were thought to have the potential for environmental pollution [16, 17, 18].

Toxic compounds might be produced through the hydrothermal gasification of real biomass. Some chlorinated organic compounds are very toxic and can cause serious damage to the human body even with exposures of trace amounts. This study has also made a determination of resulting dioxins as these are among the most toxic substances.

This method would not be an optimum solution for disposing biowaste. However, hydrogen production by hydrothermal gasification of biowaste appears to be a promising source for the predicted hydrogen fuel production needs [19].

1.1. Hydrothermal gasification

Hydrothermal processing describes the thermal treatment of wet biomass at elevated pressures to produce carbohydrate, liquid hydrocarbons, or gaseous products depending upon the reaction conditions [20].

The processing pressure must be increased as the reaction temperature increases to prevent boiling of water in the wet biomass. At temperatures around 100 °C, extraction of high-value plant chemicals such as reins, fats, phenolics, and phytosterols is possible. At 200 °C and 2 MPa, fibrous biomass undergoes a fractionation process to yield cellulose, lignin, and hemicellulose degradation products such as furfural. Further hydrothermal processing can hydrolyze the cellulose to glucose. At 300-350 °C and 12.2-18.2 MPa, biomass undergoes more extensive chemical reactions, yielding a hydrocarbon-rich liquid known as biocrude. At 600-650 °C and 30.4 MPa the main products are gases, including a significant fraction of methane [20].

Hydrothermal pyrolysis is also known as hydrothermal liquefaction. Hydrothermal pyrolysis is a feasible method for waste treatment and conversion of wastes into liquid bio-products such as bio-oil. Hydrothermal liquefaction of biomass is a depolymerization process to break the solid organic compounds into smaller fragments [21].

In hydrothermal liquefaction, water simultaneously acts as a reactant and so this process is significantly different from pyrolysis [22].

Biomass can be thermally processed through either gasification or pyrolysis to produce hydrogen and other fuels. In general, the main gaseous products from the pyrolysis of biomass are H_2, CO_2, CO, and hydrocarbon gases, whereas the main gaseous products from the gasification of biomass are H_2, CO_2, CO, and N_2 [23].

Hydrothermal biomass gasification benefits from the special properties of near- and supercritical water as the solvent and its presence as the reaction partner. Relatively fast hydrolysis of biomass in sub and supercritical water leads to a rapid degradation of the polymeric structure of biomass [9].

1.2. Super critical water

A supercritical fluid (SCF) is any substances at a temperature and pressure above the critical point. Above the critical temperature of a substance, the pure, gaseous component cannot be liquefied regardless of the pressure applied. The critical pressure is the vapor pressure of the gas at the critical temperature. In the supercritical environment only one phase exists. The fluid, as it is termed, is neither a gas nor a liquid and is best described as intermediate to the two extremes. This phase retains solvent power approximating liquids as well as the transport properties common to gases.

At conditions around the critical point water has several valuable properties. Among them are low viscosity and high solubility of organic substances, making subcritical water an excellent medium for fast, homogeneous and efficient reactions. Supercritical water gasification is a promising technology for gasifying biomass with high moisture content [24]. Use of water as a reaction medium obviates the need to dry the feedstock and allows a fast reaction rate [25]. However corrosion in the subcritical water is a key issue [22].

There are two approaches to biomass gasification in supercritical water. The first: low-temperature catalytic gasification employs a reaction temperature ranging from 350 to 600 ºC (above 22.05 MPa) and gasifies the reaction material with the aid of metal catalysts. The second: high-temperature supercritical water gasification employs reaction temperatures ranging from 500 to 750 ºC (above 25 MPa), either without a catalyst or with non-metallic catalysts [10].

For the disposal of chicken manure, the advantages of hydrothermal gasification method are summarized in the Figure 1 below, which also shows some disadvantages of other methods.

1.3. Experimental equipment

The experimental setup was developed in this work for hydrothermal gasification. A stainless steel tube of SUS 316 of 1/2 inch in O.D., 12 cm in length is used as the reactor. One side of the reactor was sealed with a connector (Swagelok Co.) and the other side was connected with a 1/2 to 1/8 inch reducing union to which the Tee was connected. The strain amplifier for pressure measurement (Kyowa-Dengyo, Co., Japan) was connected to the one side of the Tee, and the stop valve was to the other side. A gas chromatograph oven (Hewlett Packard, 5890 GC) was used for heating the reactor at a programmed temperature [26, 27].

1.4. Reagents

Chicken manure (G.I. Ltd., Japan) containing 9% phosphorus was selected as a real biomass waste.

As a model sample containing phosphorus element, O-Phospho-DL-serine (Wako Chemical Co. Ltd, Japan) was used. O-Phospho-DL-serine, as the name implies, has a serine, which is an amino acid with the formula $HO_2CCH(NH_2)CH_2OH$. It is one of the proteinogenic amino

acids. By virtue of the hydroxyl group, serine is classified as a polar amino acid. O-Phospho-DL-serine consists with phosphorylation of serine. Aspartate, glutamate, proline and serine are abundant amino acids in chicken manure [28]. Some of the constituent amino acids were found in a range from 24.7% (for valine) to 76.4% (for serine) in poultry manure [29]. O-phospho-DL-serine also contains the P atom in the molecule. Therefore it was chosen as the test sample.

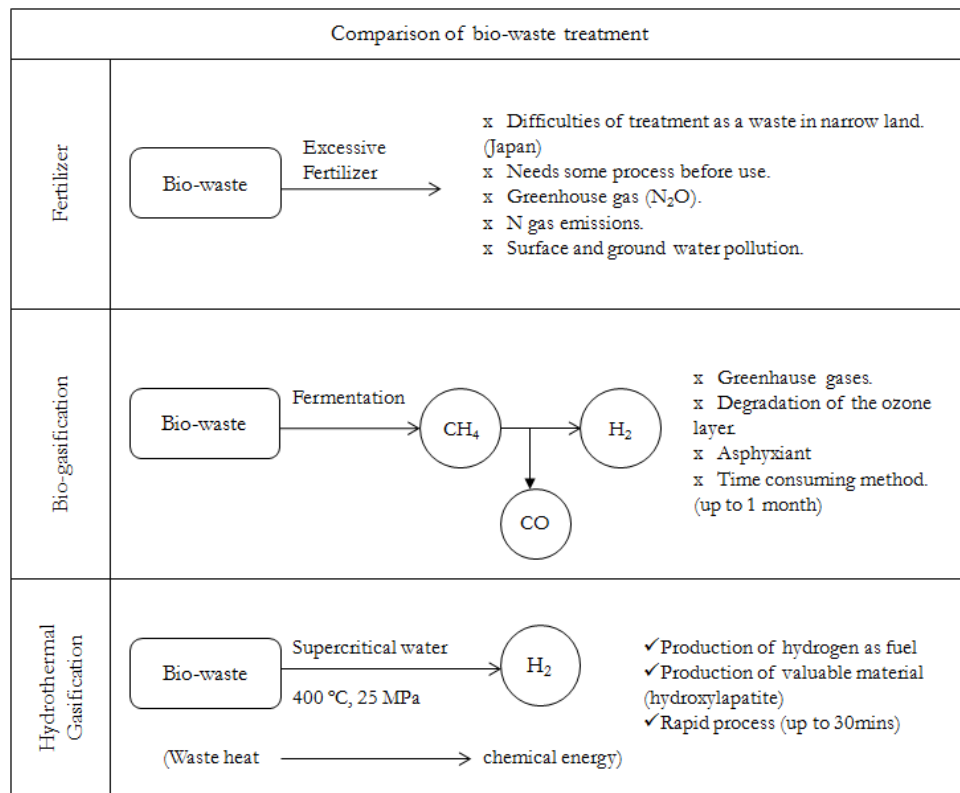$Ca(OH)_2$ used as an additive was purchased from Wako Chemical Co. Ltd, Japan.

Figure 1. Diagram of comparison for bio-waste treatment.

1.5. Procedure for hydrothermal gasification

The biomass sample (chicken manure or O-Phospho-DL-serine) was weighed (about 100 mg) and put into the reactor. Additionally, the alkaline additive $Ca(OH)_2$ was weighed and added into the reactor (without $Ca(OH)_2$, with 2 mmol and 3 mmol $Ca(OH)_2$). Then 5 ml water was added. N_2 gas was introduced to purge the residual O_2 gas in the reactor. After the reactor was connected to the reducing unit with the pressure gauge and the stop valve, the reactor was placed in the oven. Then the oven was heated to 400°C at 0.025°C min^{-1}. The

reactor was kept at 400°C for 40 minutes to complete the hydrothermal reaction under a pressure of 26~27 MPa. Subsequently, the oven was cooled down to room temperature and the components generated were analyzed [26, 27].

The experimental procedures are illustrated in Fig. 2 and comprised three main stages; sample preparation, hydrothermal gasification, and analysis of the compounds produced.
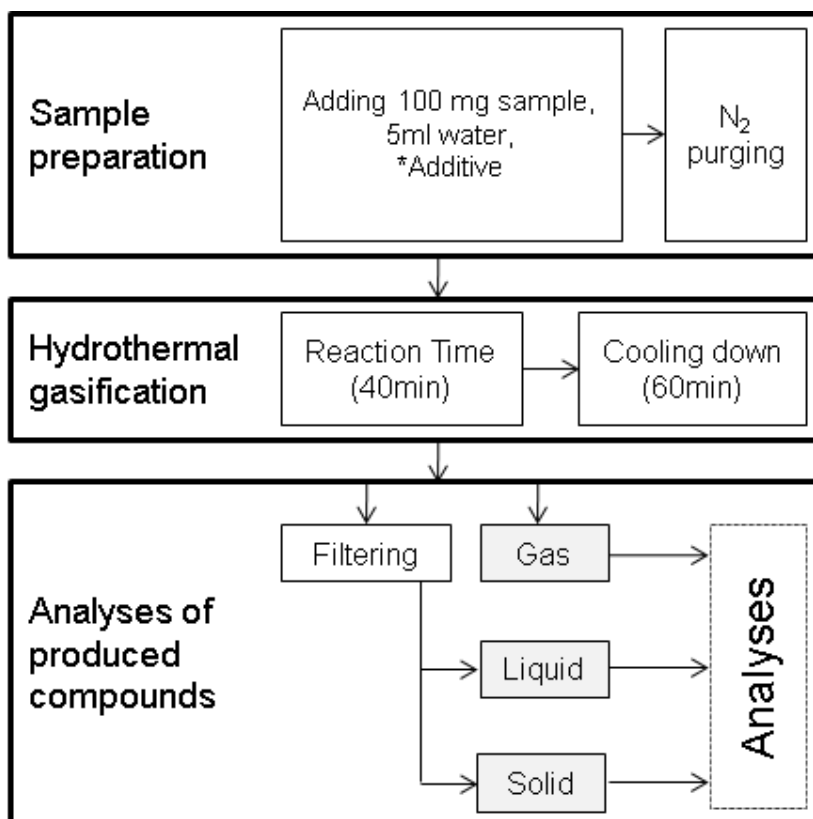

Figure 2. Experimental procedures of hydrothermal gasification

1.6. Analytical equipment

GC-TCD (Gas Chromatography - Thermal Conductivity Detector)

A 5A Shimadzu Gas Chromatograph (GC) of equipped with a thermal conductivity detector (TCD) was used for the analysis of chemical species in the gas phase.

IC (Ion Chromatography)

A Shimadzu (HIC-SP) Ion Chromatograph (IC) was used for the analysis of ionic species in the liquid phase.

GC/MS (Gas Chromatography/Mass Spectrometry)

More than 100 ml of the liquid sample was required for the determination of dioxins by GC/MS. The reaction procedure was repeated 27 to 30 times for each sample.

Dioxin analysis was performed on the resulting liquid and solid samples using a gas chromatograph combined with a mass spectrometer. An Agilent model 6890-GC interfaced with a JMS-700D double focus MS (JEOL, Japan) was used for the analysis [27].

2. Generation of hydrogen gas

For effective production of hydrogen gas and reduction of the formation of pollutants, optimum conditions for hydrothermal gasification of biowaste were examined under various experimental conditions by using O-phospho-DL-serine as a test sample. Next, chicken manure was used as a real biomass waste sample for the production of hydrogen gas by the hydrothermal gasification and for the suppression of the pollutants.

Additives were used to enhance the reaction rate of the hydrothermal gasification in sub or supercritical water at low reaction temperature [10]. The study also looked at whether the addition of catalysts could also enhance the hydrogen yield [30].

Several additives were used in earlier studies. The effects of the various alkaline metals on the amounts of generated gases have been reported [31]. When $Ca(OH)_2$ was used, only hydrogen gas was produced without production of other gases. This would be explained by the following Equations 1 and 2.

$$H_2O + CO \text{ -------}\rightarrow CO_2 + H_2 \tag{1}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{2}$$
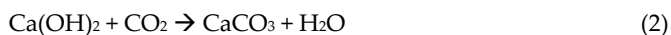
The effects of the addition of various kinds of alkaline metals on the amounts of phosphate ion were also studied. The addition of Na_2CO_3 or K_2CO_3 was found to have no suppression effect on the production of phosphate ions in the liquid phase. However, when $Ca(OH)_2$ was added, no phosphate ions were detected. From these experimental results [31], it can be concluded that reasonable alkaline element compound, $Ca(OH)_2$ was a suitable additive because it could suppress the production of heteroatom pollutants in the gas phase and enhance the hydrogen yield [26].

2.1. Gas phase

The effects of the amounts of additive and temperature on the yield of gases generated were studied.

Without the additive, the main produced gas is CO, while hydrogen gas is also generated. 0.1943 mmol H_2, 0.2617 mmol CO, 0.0244 mmol CO_2, 0.0024 mmol CH_4, and 0.0088 mmol C_2H_4, 0.0010 C_2H_6 were detected [26].

With the addition of 2 mmol Ca(OH)$_2$, the yield of CO, CO$_2$ and C$_2$H$_4$ gases were suppressed. However, the generation of hydrogen gas was decreased in yield. 0.1459 mmol H$_2$, 0.0019 mmol CO, 0.0009 mmol CO$_2$, 0.0039 mmol CH$_4$, and 0.0019 mmol C$_2$H$_4$, 0.0003 C$_2$H$_6$ were detected [26].

With the addition of 3 mmol Ca(OH)$_2$, the main gas is hydrogen gas, while other gases were hardly detected. With addition of 3 mmol Ca(OH)$_2$, the main gas is hydrogen gas. Generation of hydrogen gas increases with an increase of gasification temperature. 0.2007 mmol H$_2$, 0.0002 mmol CO, 0.0009 mmol CO$_2$, 0.0017 mmol CH$_4$, and 0.0012 mmol C$_2$H$_4$, 0.0016 C$_2$H$_6$ were detected [26].

The enhancement of H$_2$ yield by adding alkali was due to water-gas shift reactions. These results indicate that the most suitable conditions for obtaining pure hydrogen gas from the hydrothermal reaction of the model sample, O-Phospho-DL-serine, are as follows: 3 mmol of additive Ca(OH)$_2$, reaction temperature at 400°C, and pressure of 22 MPa (super critical state).

2.2. Liquid phase

The effects of the added amount of Ca(OH)$_2$ on the yield of phosphate ion dissolved in the liquid phase through the hydrothermal reaction under the supercritical conditions at 400°C were also studied. When no additive was used, the yield of phosphate ion in the liquid phase found was 93.3% of the P in the original sample. However, the addition of 2mmol Ca(OH)$_2$ resulted in the suppression of the formation of phosphate ion in the liquid phase. When 3mmol of Ca(OH)$_2$ was added, the generation of phosphate ion was further decreased to 5.6%. Phosphorus containing compounds were barely detectable in the liquid phase. Phosphorus in the sample would be converted and precipitated as solid compounds (Figure 3).
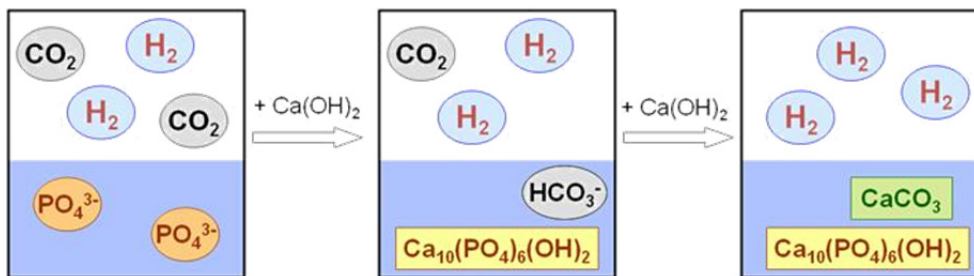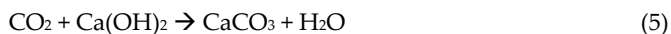

**Figure 3.** Estimation of phosphorus conversion.

2.3. Hydrothermal gasification of chicken manure

Chicken manure, which contains phosphorus, was selected as a real biowaste for the production of hydrogen gas and suppressing formation of pollutants by the hydrothermal reaction. Various reaction conditions were investigated for suitable conditions. The same optimum conditions were obtained as those of the hydrothermal reaction of the model test compound, O-Phospho-DL-serine. With the same conditions of 3mmol Ca(OH)$_2$ and 400°C,

hydrogen gas was mainly produced in the gas phase. 0.1122 mmol H_2, 0.0044 mmol CO, 0.2088 mmol CO_2, 0.0025 mmol CH_4, and 0.0114 mmol C_2H_4, 0.0014 C_2H_6 were detected. H_2 yields were increased and other gasses were suppressed by using the additive, especially in the case of CO_2, which was suppressed very effectively. It was concluded that the enhancement of H_2 yield by adding the alkali was due to the water-gas shift reactions (Equations 3 and 4). Equation (5) shows the production of $CaCO_3$ after hydrothermal gasification by adding $Ca(OH)_2$ [26].

$$Org.\ C + H_2O \rightarrow CO + H_2 \tag{3}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{4}$$

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \tag{5}$$

Additionally, phosphate ion was hardly detected in the liquid phase as in case of the model sample. The phosphorus compounds in the real sample are decomposed and new compounds would be produced and precipitated in the solid phase by the hydrothermal reaction. From these results the following equation is obtained (Equation 6). When the sample includes phosphorus, the P element would be converted into PO_4^{3-} by the hydrothermal reaction [26]. The ion, PO_4^{3-}, would react with Ca^{2-} ion and some insoluble compound would be produced.

$$P\ (\ in\ a\ Sample) + H_2O \rightarrow PO_4^{3-} \tag{6}$$
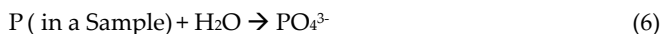
When $Ca(OH)_2$ was used as the additive, the main produced gas was hydrogen gas, and the generation of CO_2 gas was suppressed efficiently. Additionally, calcium ion easily reacts with heteroatoms, and would form insoluble solid material in water. The cost of $Ca(OH)_2$ is less expensive than other additives. To treat a large amount of bio-wastes, reasonable reagents are more preferable. $Ca(OH)_2$ was decided to use as the additive for understanding the reaction mechanisms for disposal of hetero-atom containing compounds under the hydrothermal process.

In the hydrothermal reactions with the use of $Ca(OH)_2$ as the additive, the suppression of CO_2 and the promotion of H_2 generation are expected from the reactions which are expressed on Equation 3 and 4.

3. Dioxins analysis

3.1. Dioxins

The name "dioxins" is often used for the family of structurally and chemically related polychlorinated dibenzo para dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Certain dioxin-like polychlorinated biphenyls (PCBs) with similar toxic properties are also included under the term "dioxins". Some 419 types of dioxin-related compounds have been identified but only about 30 of these are considered to have significant toxicity, in which TCDD (2,3,7,8- tetrachlorodibenzo para dioxin) is the most toxic [32]. The formation

mechanisms for them are not yet completely understood because of their complex production mechanisms [33]. Dioxins do have a damaging effect on human health and the environment [32, 34], and 30 dioxins are known to have significant toxicity [32]. When biomass-containing chlorine is gasified in supercritical water, PCDDs, PCDFs and PCBs might be formed. In this study, dioxins in the liquid and solid phases produced through the hydrothermal reaction of chicken manure were determined.

TEF and TEQ

TEQ (toxic equivalent quantity) is total toxicity of dioxins contained in a sample and calculated by the Equation (7),

$$TEQ = \sum f_i g_i \tag{7}$$

f_i : toxic equivalency factor for i_{th} dioxin (TEF, WHO 2006 [35])

g_i : the abundance of i_{th} dioxin in the sample.

3.2. Experimental procedure

In order to examine the effect of the additive and the effect of temperature on dioxin formation in the chicken manure, the experiments were performed under six different conditions (Figure 4).
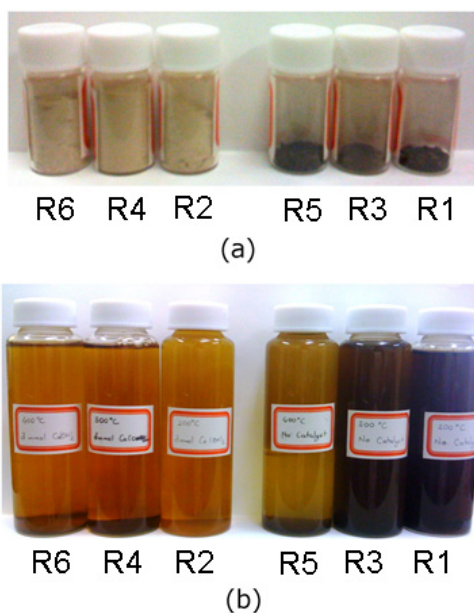

Figure 4. Photographs of solid (a) and liquid (b) samples from six different conditions. R1; without additive, 200 ºC, R2; 3 mmol Ca(OH)$_2$, 200 ºC,R3; without additive, 300 ºC, R4; 3 mmol Ca(OH)$_2$, 300 ºC, R5; without additive, 400 ºC, R6; 3 mmol Ca(OH)$_2$, 400 ºC.

The samples produced under the various experimental conditions were separated into liquid and solid phases by filtration.

Solid samples

For determination of toxic equivalent quantity (TEQ) of each dioxin for the solid phase, the hydrothermal gasification experiment was carried out under the various conditions for the chicken manure. PCDDs and PCDFs were not detected. Three kinds of PCBs were only detected. These were T4CB#77 (Fig. 5) (TEF=0.0001), P5CB#118 (Fig. 6) (TEF=0.00003), and P5CB#105 (Fig. 7) (TEF=0.00003).

The total TEQ values for solid samples were 0.00237, 0.00357, 0.00647, 0.00196, 0.00172, and 0.00148 pgTEQg^{-1} for Run 1, 3, 5, 2, 4, and 6, respectively.

The highest total TEQ of 0.00647 pgTEQg^{-1} was observed for the reaction temperature of 400°C without additive (Run 5). This level is well below the permitted Japanese level for solid residue (3000 pgTEQg^{-1}) [36].
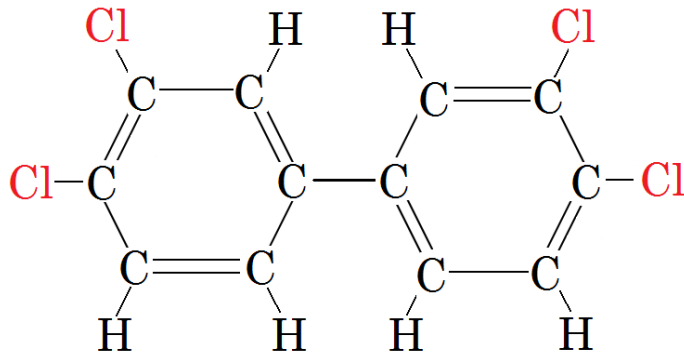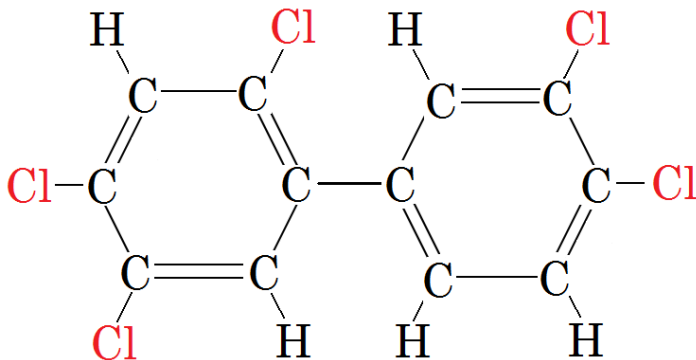

Figure 5. Chemical structure of T4CB#77.

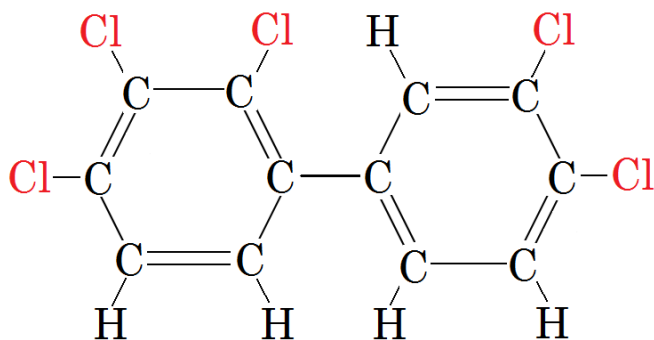**Figure 6.** Chemical structure of P5CB#118.

Figure 7. Chemical structure of P5CB#105.

Liquid samples

In the case of the liquid phase products, PCDDs and PCDFs were not detected as they were in the case of the solid phase products. Two kinds of PCBs were detected (vs. three in the solid phase material). These were P5CB#118 (TEF=0.00003) and P5CB#105 (TEF=0.00003).

The total TEQ values were 0.00026, 0.00054, 0.00029, 0.00023, 0.00028 and 0.00042 pgTEQL^{-1} for Run 1, 3, 5, 2, 4, and 6, respectively.

With and without the additive, the total TEQs are nearly equal to the level of tap water. The results show that reaction temperature has little effect on the formation of dioxins. However, the addition of Ca(OH)$_2$ increases the value of the TEQ at reaction temperatures of 300 °C and 400 °C. The highest total TEQ measured was 0.00054 pgTEQL^{-1}, observed at the reaction temperature of 200 °C without the additive (Run 1). This total TEQ was well below the permitted Japanese limit for liquid residue (10 pgTEQL^{-1}) [36].

4. Conclusions

Increase in energy consumption, limited energy capacity, environmental concerns related to fossil fuels, and security/safety concerns of some energy sources have all motivated the search for renewable energy sources.

A real biowaste, chicken manure, was used as an energy source and Ca(OH)$_2$ was the most effective additive among the tested additive candidates for producing hydrogen in this study by the hydrothermal gasification process. Almost pure hydrogen gas could be obtained by adding Ca(OH)$_2$ under supercritical conditions. It was found that the generation of hydrogen gas through hydrothermal gasification could be conducted without considering the toxicity of dioxins. Dioxins were detected, but they were far below the environmental regulation values. An added benefit found was that this process solves the problem of treatment of chicken manure while producing hydrogen.

This newly developed method of hydrothermal gasification of chicken manure is a promising method for producing hydrogen as a fuel and for disposing of the biowaste.

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