Hydrothermal Process of Chicken Manure for Production of Hydrogen Fuel and Hydroxylapatite

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Hydrothermal Process of Chicken Manure for Production of Hydrogen Fuel and Hydroxylapatite

(水素燃料およびハイドロキシアパタイト生成のための鶏糞の水熱処理)

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Chapter 1 Introduction

1.1 Background

Energy consumption is increasing regularly with increasing human population (Figure 1.1) [1]. The bell-shaped curve (Figure 1.2) is used for making accurate predictions of global oil decline [2]. Finite resources of fossil fuels which were also shown on Figure 1.2, security of other energy sources (especially nuclear energy), and concerns over greenhouse gases produced by combustion of fossil fuels (Figure 1.3) 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 advantage of disposing of wastes [6]. Therefore, biomass has been selected for generation of energy by using hydrothermal gasification.

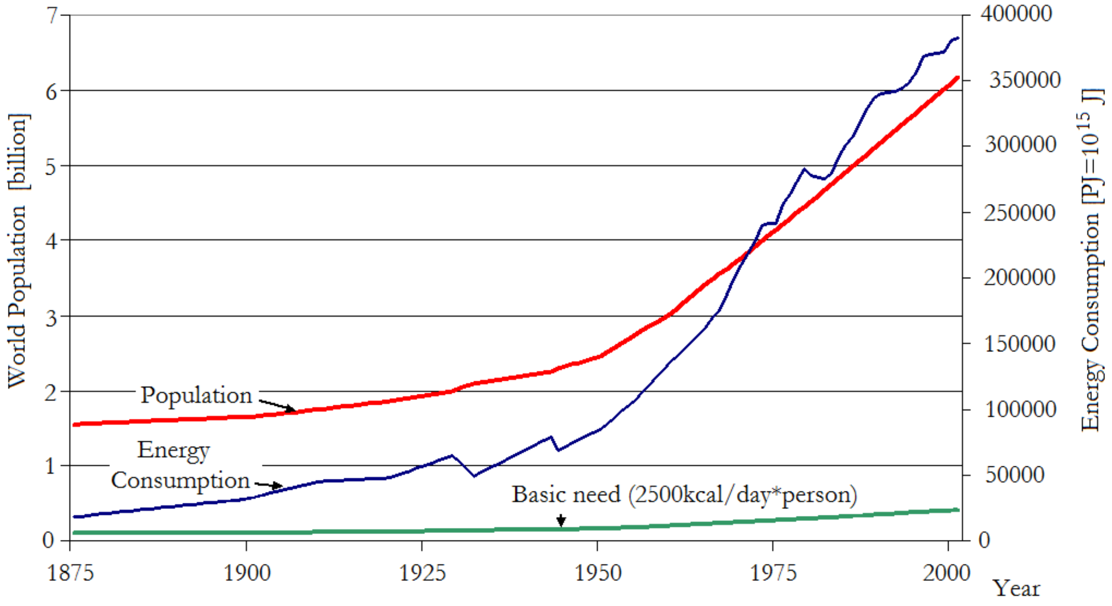

Figure 1.1 World population and energy consumption [1]

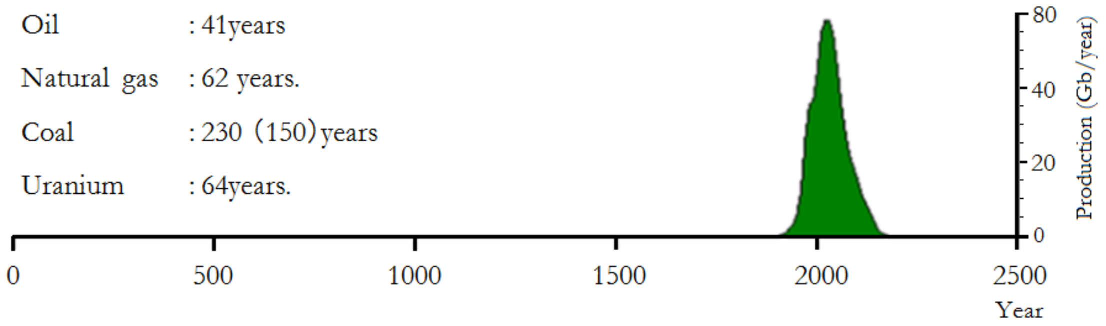

Figure 1.2 Exhaustion of resources in the 2500 years [2]

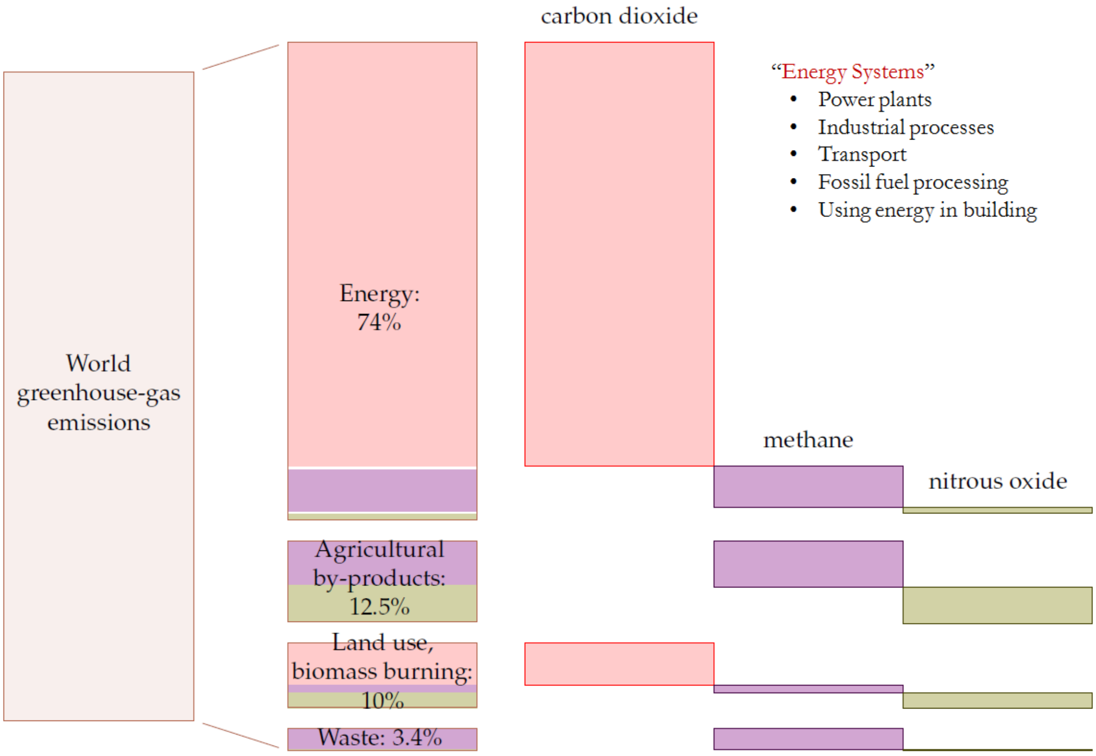

Figure 1.3 Breakdown of world greenhouse-gas emissions (2000) by cause and by gas [3]

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 super-critical 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 to produce the various gases [4, 9, 12]. This process is therefore more suitable to biowastes with high water content, such as food wastes and animal dungs, than the conventional thermal gasification process that requires additional energy due to the latent heat of water.

There were numerous studies related to the hydrothermal gasification process, which were used 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 corn starch and wood dust. Yoshida *et al.* [15] studied supercritical water gasification of cellulose, hemi-cellulose and lignin. However, this process has not been applied to animal waste, because, environmental pollutions are caused potentially by animal wastes [16, 17, 18].

This method would not be a good solution. However, hydrogen production by hydrothermal gasification of biomass appears to be a promising source for the predicted hydrogen fuel production [19].

1.2 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].

As illustrated in Figure 1.4, processing pressure must be increased as 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 hydrocarbon-rich liquid known as biocrude. At 600-650 °C and 30.4 MPa the primary reaction product is gas, including a significant fraction of methane [20].

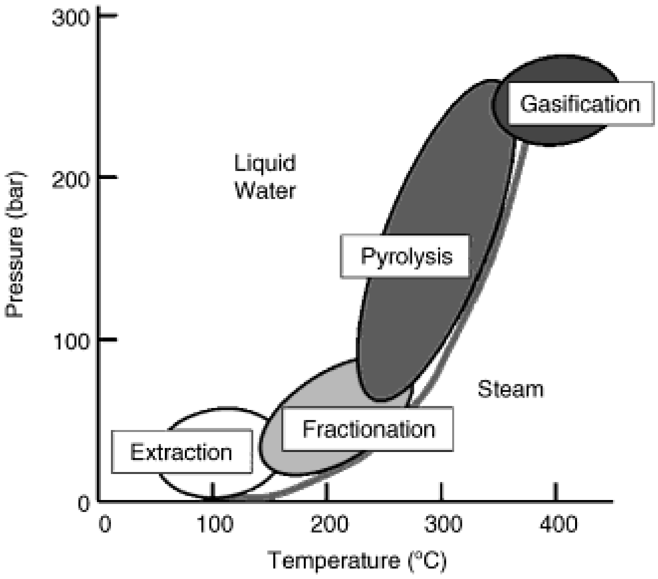

Figure 1.4 Temperature/pressure regimes of hydrothermal processing [20]

Hydrothermal pyrolysis is also called 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 reactant, so this process is significantly different from pyrolysis [22].

Biomass can be thermally processed through 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 super critical water as solvent and its presence as reaction partner. Relatively fast hydrolysis of biomass in sub- and super critical water leads to a rapid degradation of the polymeric structure of biomass. [9]

1.3 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.

A comparison of typical values for density, viscosity and diffusivity of gases, liquids, and SCFs for water is presented in Table 1.1 [24]. Diffusivity increases as the temperature of the fluid rises, while the viscosity and density both decrease.

Table 1.1 Properties of gas, supercritical fluid, and liquid.

Property	Density (kg/m^3)	Viscosity (μPa·s)	Diffusivity (mm^2/s)
Gas	1	10	1-10
SCF	100-800	50-100	0.01-0.1
Liquid	1000	500-1000	0.001

At conditions around the critical point (Figure 1.5), water has several great properties. Among them are low viscosity and high solubility of organic substances, which make subcritical water an excellent medium for fast, homogeneous and efficient reactions. Table 1.2 lists some properties of sub- and supercritical water [22]. Supercritical water gasification is a promising technology for gasifying biomass with high moisture content [25]. Use of water as a reaction medium obviates the need to dry the feedstock and allows a fast reaction rate [26]. However corrosion in the subcritical water is a critical issue [22].

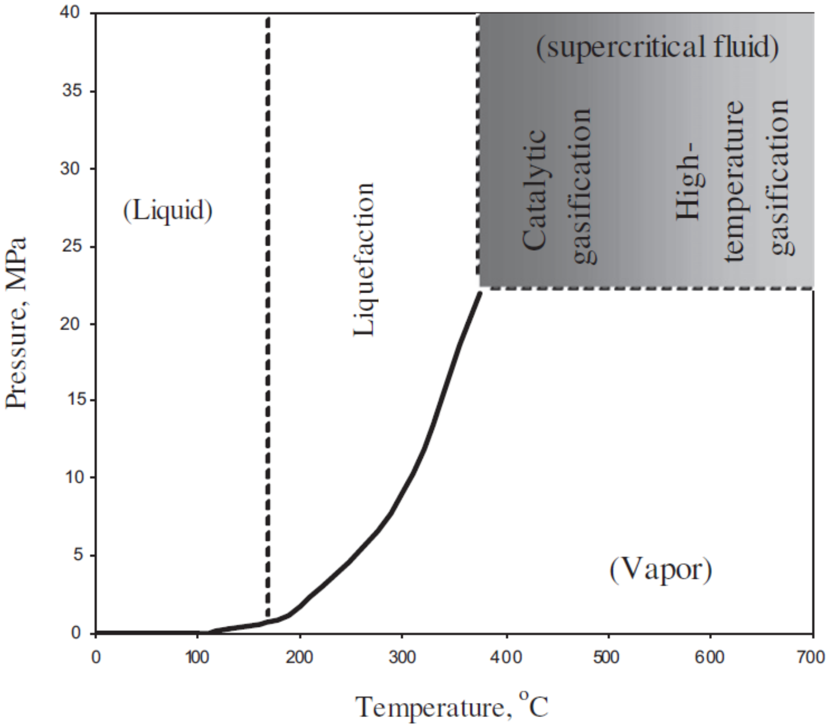

Figure 1.5 The phase diagram of water [22]

Table 1.2 Properties of water, sub and supercritical water.

	Normal water	Subcritical water		Supercritical water	
Temperature (°C)	25	250	350	400	400
Pressure (MPa)	0.1	5	25	25	50
Density, ρ (g cm^{-3})	1	0.80	0.6	0.17	0.58
Dielectric constant, ε (Fm^{-1})	78.5	27.1	14.07	5.9	10.5
Ionic product, pK_w $pK_w=-\log K_w$ [K_w (mol^2 dm^{-6})]	14.0	11.2	12	19.4	11.9
Heat capacity C_p (kJ kg^{-1} K^{-1})	4.22	4.86	10.1	13.0	6.8
Dynamic viscosity, η(mPa s)	0.89	0.11	0.064	0.03	0.07

There are two approaches to biomass gasification in supercritical water. The first: low-temperature catalytic gasification employs reaction temperature ranging from 350 to 600 °C and gasifies the feedstock with the aid of metal catalysts. The second: high-temperature supercritical water gasification employs reaction temperatures ranging from 500 to 750 °C, without catalyst or with non-metallic catalysts [10].

Compared to other usage methods of chicken manure, some disadvantages of the other methods and advantages of hydrothermal gasification method could be find on the diagram below (Figure 1.6)

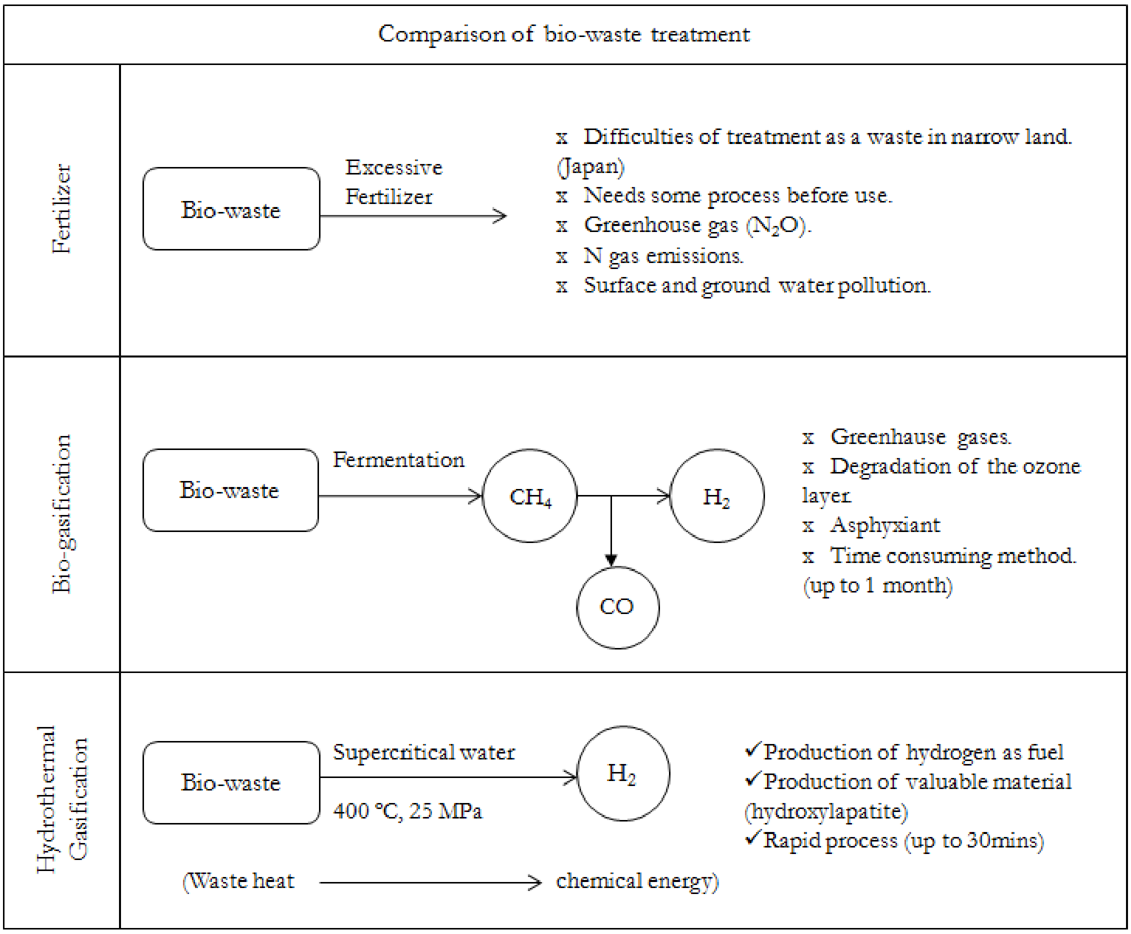

Figure 1.6 Comparison of bio-waste treatment diagram

1.4 Objective of this thesis

The rapid expansion of poultry production has caused an increased production of poultry biowaste, i.e. chicken manure [27]. Chicken manure productions were 13 - 26 million tons annually on U.S [28], 29 million tons on Turkey in 2009 [29], 13 million tons on Japan in 2008 [30]. Utilization of chicken manure could make improper use effect in narrow land (Japan). Improper use of chicken manure can result in pollution of air, soil and groundwater [31]. Using chicken manure in the hydrothermal gasification provides disposal of chicken manure while at the same time providing an energy production method [32].

Experimental methodology of this thesis was explained in Chapter 2. Experimental equipments and procedures of hydrothermal gasification, reagents, and analytical equipments were mentioned in detail.

O-phospho-DL-serine was employed as a pure test sample to predict results for chicken manure, since O-phospho-DL-serine contains P atom in the molecule. For identification of the generated species and for reduction of the formation of pollutants, the hydrothermal gasification was examined under various experimental conditions by using O-phospho-DL-serine, which was shown in Chapter 3. And also in Chapter 3, chicken manure was tested as a real biomass waste sample for the production of hydrogen gas through the hydrothermal gasification and for the suppression of the pollutants, which was also mentioned in papers [32, 33].

Additives were used to enhance the reaction rate of the hydrothermal gasification in sub or supercritical water at low reaction temperatures [10]. The addition of catalysts could also enhance the hydrogen yield [34]. The effects of the Na_2CO_3 and Ni catalysts as additives on the hydrothermal gasification of cellulose at 400 °C were reported [35]. The addition of the optimum amount of Na_2CO_3 increased hydrogen yield and suppressed CO_2 emission in the gas phase. Yanik *et al.* [36] reported that trona, red mud, K_2CO_3 and Raney-Ni were useful for lignocellulosic and proteinous materials. Watanabe *et al.* [37] studied the effect of ZrO_2 as a catalyst, and reported that for glucose and cellulose, the hydrogen yield with ZrO_2 was almost twice as much as without the catalyst.

Various additives used for hydrothermal gasification were studied and a reasonable alkaline element compound, $Ca(OH)_2$ was found to be a suitable additive because it could suppress the production of heteroatom pollutants in the liquid phase (Figure 1.7). The cost of additives was an important factor for treatment of a large amount of biowaste [32]. The mechanisms of the hydrothermal gasification have been reported [38]. It was important to identify the pollutants generated from the hydrothermal gasification and to find out the optimum conditions for reducing the formation of these pollutants. These results were shown in Chapter 3.

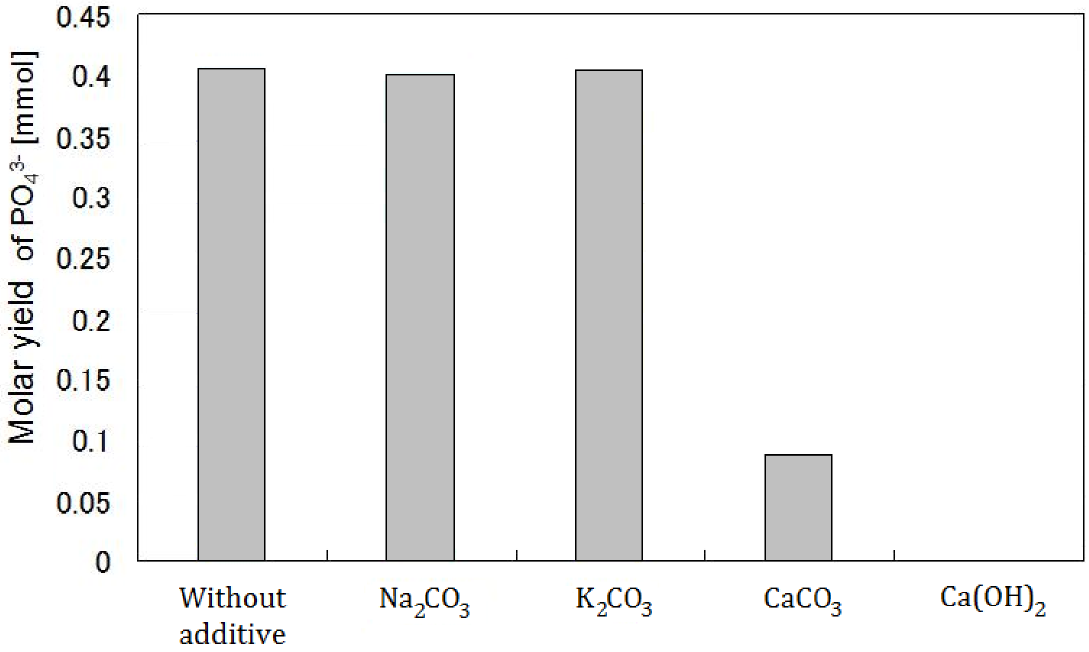

Figure 1.7 The effect of additives on formation of PO_4^{3-} in liquid phase through the hydrothermal gasification.

No study has been reported on pollutants generated by the hydrothermal gasification in detail. However, toxic compounds would be produced through the hydrothermal gasification of real biomass. This thesis focused on the determination of dioxins which are among the most toxic substances.

The compounds produced under the various experimental conditions were separated by filtration. The solid and liquid samples were analyzed by gas chromatography /mass spectrometry (GC/MS) for determination of dioxins in Chapter 4.

PCDDs (polychlorinated dibenzo para dioxins), PCDFs (polychlorinated dibenzofurans) and PCBs (certain dioxin-like polychlorinated biphenyls) are included under the term "dioxins" [39]. The formation mechanisms for them are not yet completely understood because of their complex reaction mechanisms [40]. Dioxins do have a damaging effect on human health and the environment [39, 41], and 30 dioxins are known to have significant toxicity [39]. The toxic dioxins detected in this study have been included the calculations.

One of the valuable material, that can be obtained from hydrothermal gasification process of wet biomass is hydroxylapatite which is a calcium orthophosphate containing water with chemical composition of $Ca_{10}(PO_4)_6(OH)_2$ [26]. There are chemical similarities between hydroxyapatite and the mineral part of human bone. Therefore it is highly useful for biomedical applications [42, 43, 44]. Production of valuable byproduct through the hydrothermal gasification [33] was not studied before this study. Production of hydroxylapatite was studied and results were shown in Chapter 5.

For obtaining more pure hydroxylapatite three purification methods were applied. Their results have taken place in Chapter 5.

In Chapter 6, new approach of using biowaste as an additive instead of $Ca(OH)_2$ was described. This approach was also investigated first time with this study.

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Chapter 2 Experimental Methodology

2.1 Experimental equipments

Figure 2.1 shows a schematic diagram of the experimental setup which is 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 (a). One side of the reactor is sealed with a connector (Swagelok Co.) and the other side is connected with a 1/2 to 1/8 inch reducing union to which the Tee (b) is connected. The strain amplifier for pressure measurement (Kyowa-Dengyo, Co., Japan) (c) is connected to the one side of the Tee, and the stop valve (d) is to the other side. The gas chromatograph oven (Hewlett Packard, 5890 GC) is used for heating the reactor at a programmed temperature.

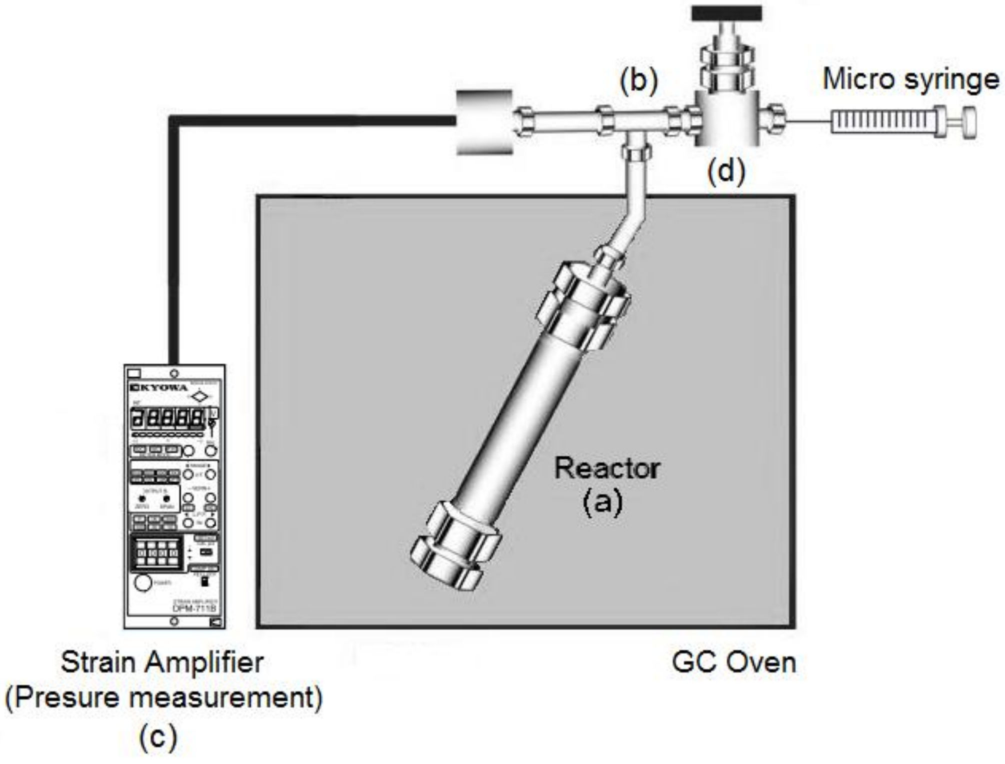

Figure 2.1 Schematic diagram of experimental setup for hydrothermal gasification

2.2 Reagents

Chicken manure

Chicken manure (G.I. Ltd., Japan) containing phosphorus of 9% was selected as a real biomass waste. The elemental analysis is listed in Table 2.1.

Table 2.1 Elemental composition of chicken manure

Components	Chicken manure %
C	30.3
H	4.7
N	2.6
S	0.8
K	4.4
P	9.0
Ca	5.4
Cl	0.7
O	42.1 (a)

(a) Calculated as the difference between C, H, N, S, K, P, Ca, and Cl

O-Phospho-DL-serine

As a model sample containing phosphorus element, O-Phospho-DL-serine (Figure 2.2) (Wako Chemical Co. Ltd, Japan) was used. O-Phospho-DL-serine 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 most abundant amino acids in chicken manure [1]. Some of the constituent amino acids were found in range from 24.7 percent (for valine) to 76.4 percent (for serine) in poultry manure [2]. O-phospho-DL-serine also contains P atom in the molecule. Therefore it was chosen as the test sample.

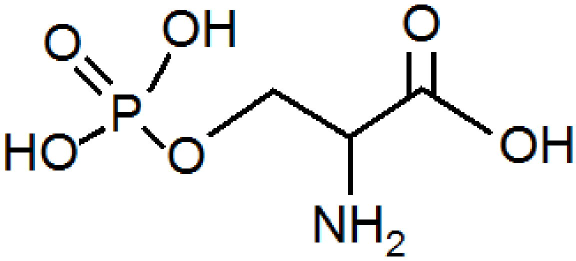

Figure 2.2 Structural formula of O-Phospho-DL-serine

Activated oyster shell

Activated oyster shell sample was received from Prof. Chan Won Lee of Department of Environmental Engineering, Kyungnam University.

Others

Hydroxylapatite of analytical grade was purchased from Wako Chemical Co. Ltd (Japan).

As additives, alkaline reagents, such as $Ca(OH)_2$, $CaCO_3$ and CaO etc. were purchased from Wako Chemical Co. Ltd, Japan.

2.3 Procedure for hydrothermal gasification

The sample was weighed (about 100 mg) and put into the reactor. Additionally, the alkaline additive such as $Ca(OH)_2$, $CaCO_3$ etc. was weighed and added into the reactor. Then 5 ml water was poured. 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 into the oven. Then the oven was heated up to 400°C at 0.025°C s^{-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 generated components were analyzed. Figure 2.3 shows temperature-time program graph of hydrothermal gasification.

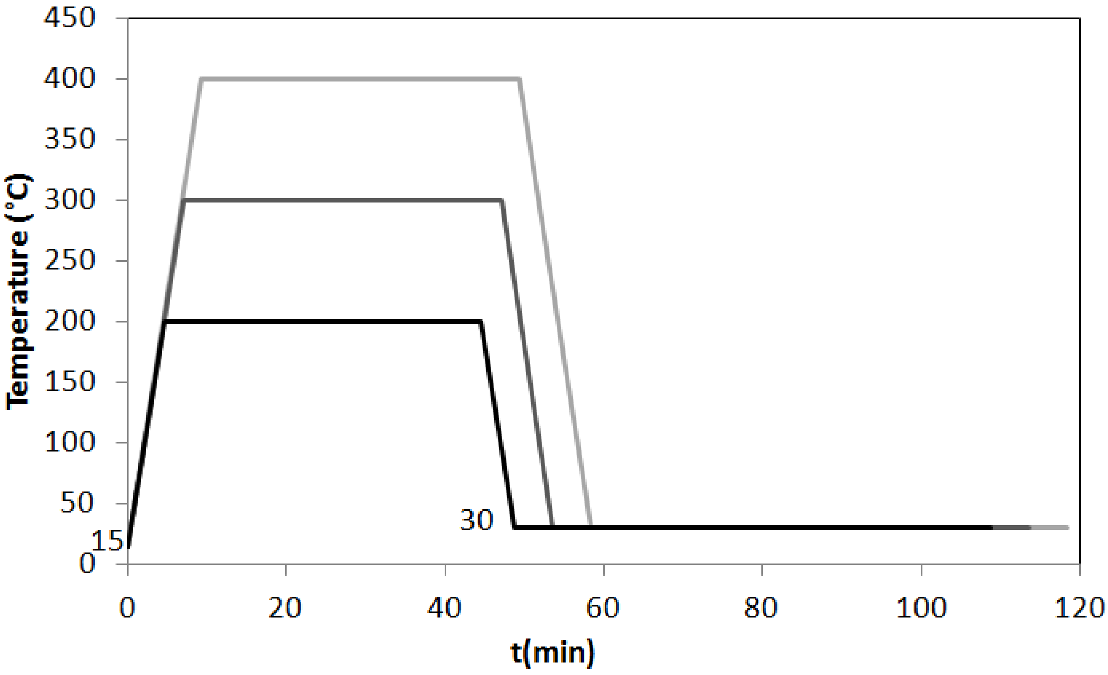

Figure 2.3 Temperature–time program graph of hydrothermal gasification

The experimental procedures are illustrated in Fig. 2.4 and comprised of three main stages; sample preparation, hydrothermal gasification, and analysis of the compounds produced.

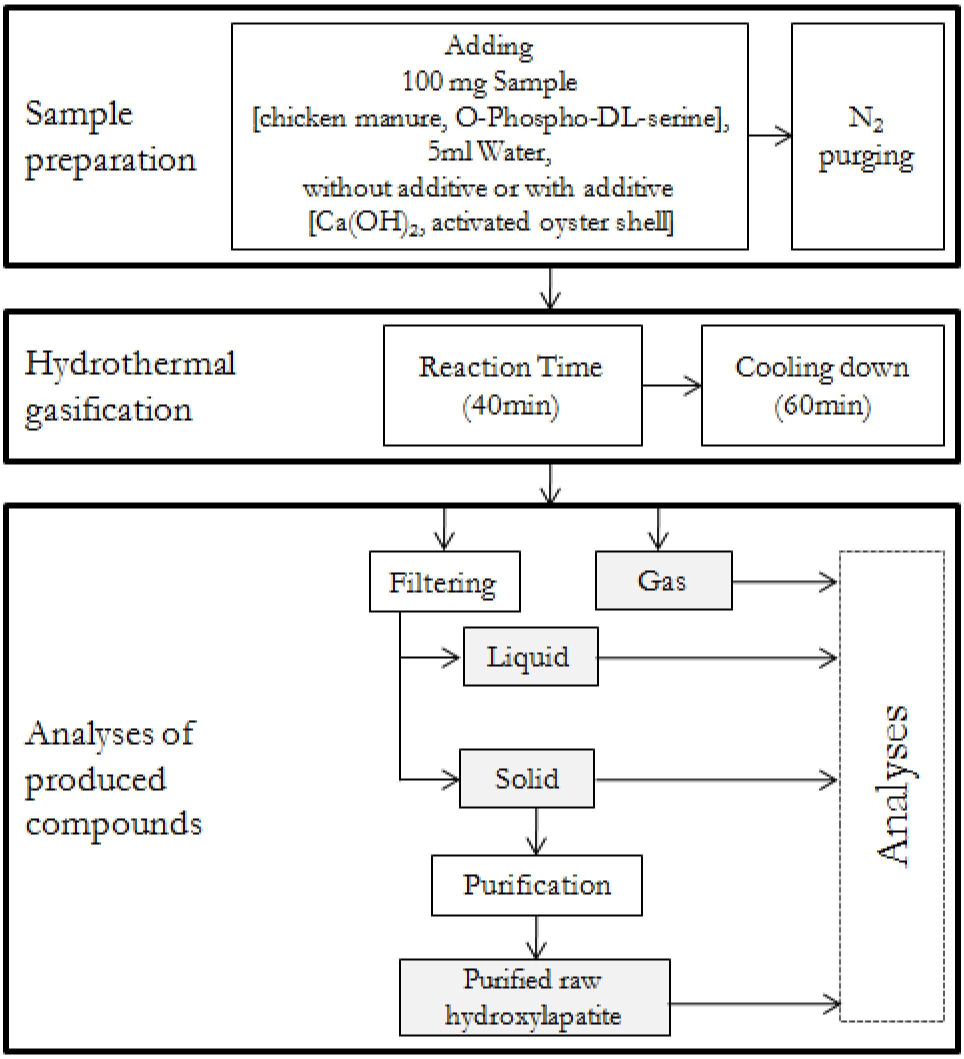

Figure 2.4 The experimental procedures of hydrothermal gasification

2.4 Analytical equipments

GC-TCD (Gas Chromatography - Thermal Conductivity Detector)

A GC of Shimadzu 5A equipped with a thermal conductivity detector (TCD) was used for the analysis of chemical species in the gas phase. The parameters for GC analysis are given in Table 2.2.

Table 2.2 Operational conditions for Gas Chromatograph analysis

	H_2 Analysis	CH_4、CO, etc. Analysis
Column	Porapak Q (length: 2m, diameter 3mm)	Porapak Q (length: 2m, diameter 3mm)
Carrier gas	Argon	Helium
Inlet pressure	98 kPa	170 kPa
Inlet temperature	80°C	80°C
Column temperature	50°C	50°C

IC (Ion Cromotography)

An IC of Shimadzu (HIC-SP) was used for the analysis of ionic species in the liquid phase. The negative and positive ionic species were determined with the conditions listed in Table 2.3.

Table 2.3 Operational conditions of Ion Chromatograph Analysis

Shimadzu HIC-SP Suppressor Ion Chromatograph

	Cation	Anion
Column	Shimadzu IC-SC-1	Shodex IC SI-50
Mobile Phase	Oxalic acid 3.0 mM	Na_2CO_3 3.2 mM $NaHCO_3$ 1.0 mM
Flow	1.5 mL/min	1.5 mL/min
Column temperature	40°C	25°C

GC/MS (Gas Chromatography/Mass Spectrometry)

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

Dioxin analysis was performed on the resulting liquid and solid samples using a gas chromatograph combined with a mass spectrometer. This process was shown Fig. 2.5. 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 (60 m×0.32 mm i.d.) for Cl4-6 PCDDs/Fs and a HT8-PCB capillary column (60 m×0.25 mm i.d.) for Cl7,8 PCDDs/Fs and PCBs. The mass spectrometer was operated in the EI mode at a resolution of RN10,000 (10% valley). 13 C12-Labeled standards were added to the extracts (clean-up spike). These solutions were treated with concentrated sulfuric acid, multi-layered silica gel column chromatography and activated carbon impregnated silica gel column chromatography. These treated solutions were carefully concentrated and spiked with 13 C12-labeled standards (13 C-1,2,7,8-T4CDF, 13 C-1,2,3,4,6,8,9-H7CDF and 13 C-2,3',4',5-T4CB(#70)) as syringe spike compounds. Then, the volume was adjusted to 20 μL under a nitrogen flow prior to GC/MS analysis.

XRD (X-Ray Diffraction)

An XRD system (RINT 2500/PC by Rigaku Co., Japan) was used for qualitative and quantitative analyses of residual solid samples formed by hydrothermal processes. The diffraction data were collected from 10° to 90°, 2θ values with step size of 0.02°. An elemental analyzer (Perkin Elmer 2400 Series II CHNS/O System) was used for determinations of C, H, and N in solid residues.

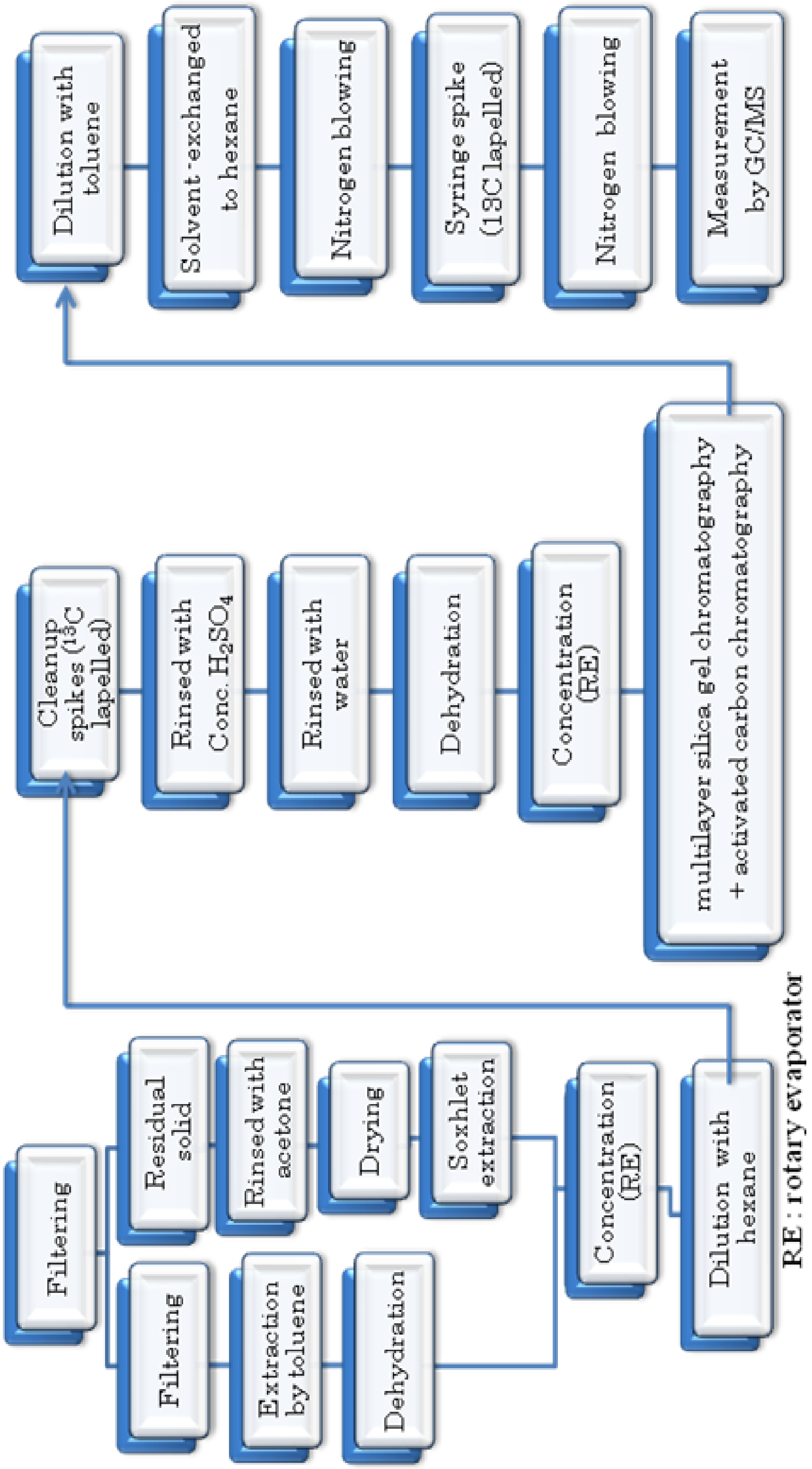

Figure 2.5 Sample treatments for GC/MS analysis.

2.5 References

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Chapter 3 Generation of Hydrogen Gas

3.1 Introduction

O-phospho-DL-serine was used as a test sample to obtain optimum conditions for production of hydrogen gas. For reduction of the formation of pollutants and for effective production of hydrogen, the hydrothermal gasification was examined under various experimental conditions by using O-phospho-DL-serine (Table 3.1).

Table 3.1 Experimental conditions.

Run No	Reaction Sample	Temperature [°C]	Amount of additive [mmol]
1	O-phospho-DL-serine	200°C	3 mmol $Ca(OH)_2$
2	O-phospho-DL-serine	300°C	3 mmol $Ca(OH)_2$
3	O-phospho-DL-serine	400°C	0
4	O-phospho-DL-serine	400°C	2 mmol $Ca(OH)_2$
5	O-phospho-DL-serine	400°C	3 mmol $Ca(OH)_2$
6	Chicken manure	200°C	0
7	Chicken manure	200°C	3 mmol $Ca(OH)_2$
8	Chicken manure	300°C	0
9	Chicken manure	300°C	3 mmol $Ca(OH)_2$
10	Chicken manure	400°C	0
11	Chicken manure	400°C	3 mmol $Ca(OH)_2$

Chicken manure was used as a real biomass waste sample for the production of hydrogen gas through 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 [1]. The addition of catalysts could also enhance the hydrogen yield [2].

Several additives were used on previous studies in our laboratory. Figure 3.1 shows the dependence of the amount of generated gases on the various alkaline metals [3]. Hydrogen gas was produced with K_2CO_3 as the main product gas. However, the significant amount of CO_2 gas was also produced. On the other hand, when $Ca(OH)_2$ was used, only hydrogen gases produced without production of other gases. This should be the result of Equation (3.1).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3.1)$$

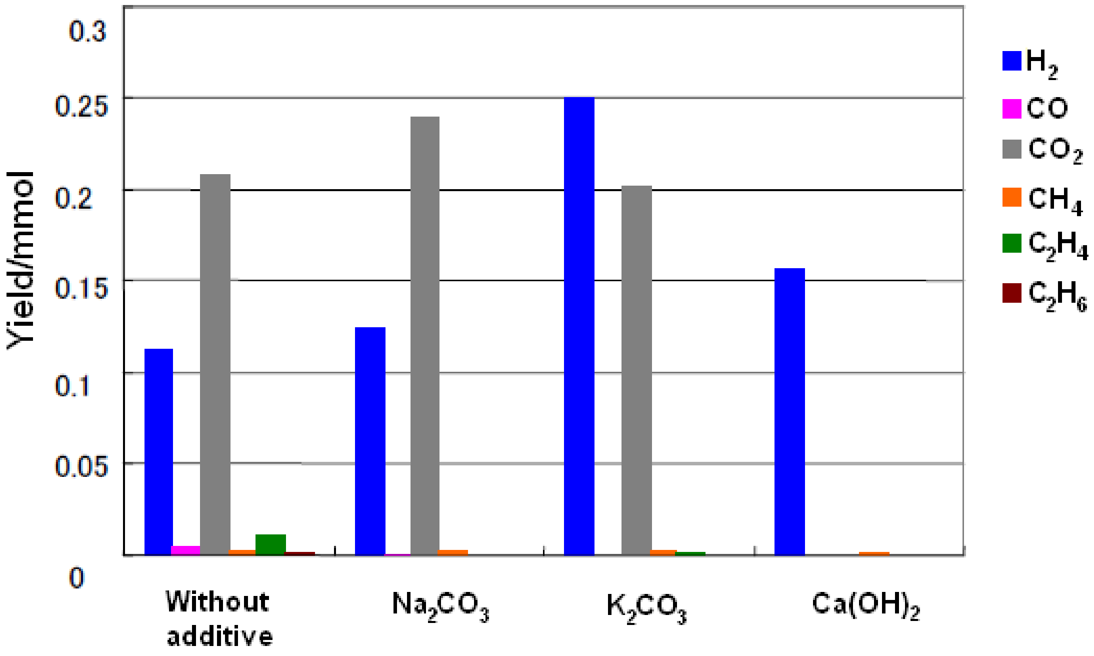

Figure 3.1 Effects of various alkaline metals on generated gas yield

Figure 3.2 [3] shows the effects of the addition of various kinds of alkaline metals on the amounts of phosphate ion. The addition of Na_2CO_3 and K_2CO_3 has no suppression effect on the production of phosphate ion in the liquid phase. However, when $Ca(OH)_2$ was added, phosphate ion was not detected.

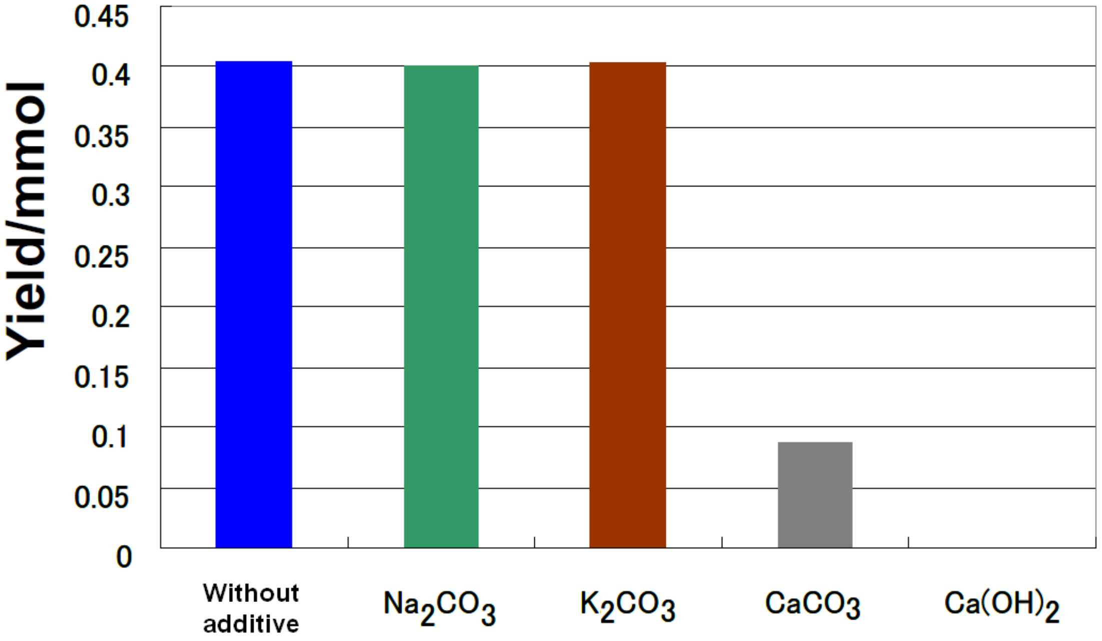

Figure 3.2 Effects of various alkaline metals on concentration of phosphate ion in liquid phase

From these experimental results (Fig. 3.2) [3], we obtained the following conclusion that a reasonable alkaline element compound, $Ca(OH)_2$ was found to be a suitable additive because it could suppress the production of heteroatom pollutants in the gas phase and enhance the hydrogen yield [4].

3.2 Terms and definitions

Hydrogen gasification ratio was calculated from Equation (3.2) [5].

Hydrogen amount in the product gas was 0.35 mmol, hydrogen amount in the material was 4.7 mmol. The amount of hydrogen in a loaded starting material was 10.7 mmol.

$$\text{Hydrogen gasification ratio} = \frac{\text{Hydrogen amount in the product gas}}{\text{Hydrogen amount in the material (chicken manure)}} \quad (3.2)$$

Hydrogen yield (H_2 yield, mol%) was calculated from Equation (3.3) [6].

$$H_2 \text{ yield [mol\%]} = \frac{\text{Hydrogen amount in the product gas}}{\begin{array}{c}\text{Hydrogen amount in a loaded starting material}\\ \text{(chicken manure, additive)}\end{array}} \text{x100} \quad (3.3)$$

Energy balance was calculated from Equation (3.4), Equation (3.5), and Equation (3.6). E_{output} is the energy which is produced by the system. E_{input} is the energy which is used by the system. E_{H2} is the total enthalpy of produced hydrogen which can calculate by multiplying the enthalpy of combustion for hydrogen (286 kJ/mol) [7] with hydrogen amount. E_{heat} is the heat value that is needed for providing the hydrothermal gasification. η indicates the efficiency of the system.

$$E_{output} = E_{H2} \quad (3.4)$$

$$E_{input} = E_{heat} \quad (3.5)$$

$$\eta = E_{output}/E_{input} \quad (3.6)$$

3.3 Results and discussion

3.3.1 Hydrothermal gasification of O-phospho-DL-serine

Gas phase

Figure 3.3 shows the effects of the amounts of the additive on the yield of gases generated. Without the additive, the main produced gas is CO while hydrogen gas is also generated. With the addition of 2 mmol $Ca(OH)_2$, the yield of CO, CO_2 and C_2H_4 gases were suppressed. However, the generation of hydrogen gas was not decreased in yield. With addition of 3 mmol $Ca(OH)_2$, the main gas is hydrogen gas, while other gases were hardly detected.

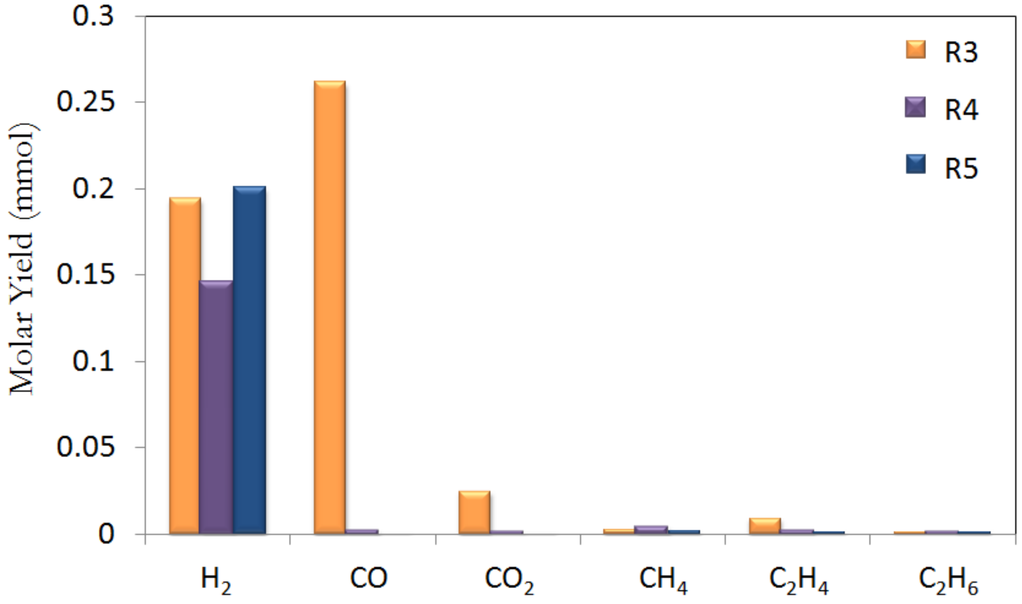

Figure 3.3 Effects of $Ca(OH)_2$ amount on gas yield at 400 °C (R3; without additive, R4; 2 mmol $Ca(OH)_2$, R5; 3 mmol $Ca(OH)_2$)

Figure 3.4 shows the effects of the temperature on the yield of gases generated. 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.

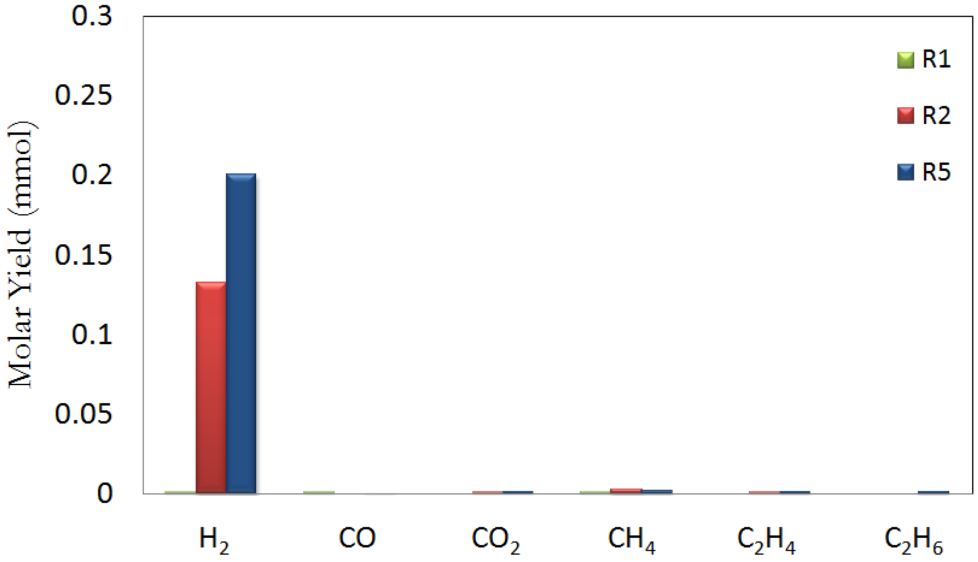

Figure 3.4 Effects of temperature on gas yield with 3 mmol $Ca(OH)_2$ (R1; 200 °C, R2; 300 °C, R5; 400 °C)

The enhancement of H_2 yield by adding alkali was due to the 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: the amount of the addition of 3 mmol $Ca(OH)_2$, the reaction temperature at 400°C, and the pressure of 22 MPa (super critical state).

Liquid phase

Figure 3.5 shows the effect 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. Without the additive, the yield of phosphate ion ratio was 93.3% on the basis of P contained in the sample. However, the addition of 2mmol $Ca(OH)_2$ suppressed the formation of phosphate ion yield. When 3mmol of $Ca(OH)_2$ was added, the generation of phosphate ion was decreased to 5.6%. Phosphorus containing compounds were hardly found in the gaseous phase and the liquid phase. Phosphorus was converted from the sample and precipitated as solid compounds (Figure 3.6).

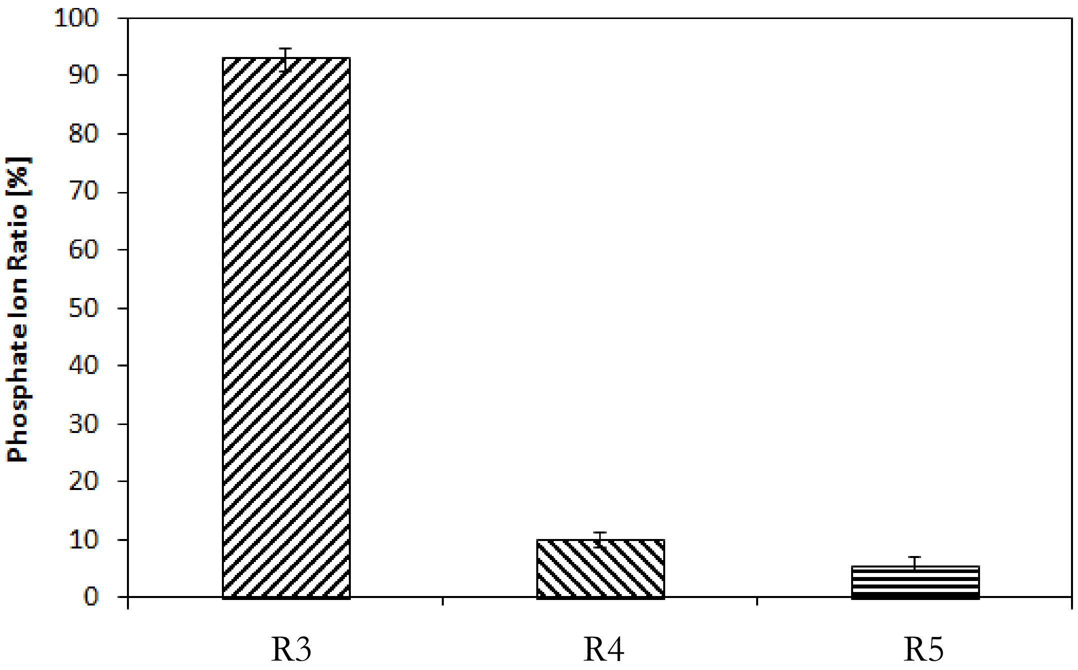

Figure 3.5 Effects of $Ca(OH)_2$ amount on phosphate ion ratio of liquid phase at 400°C(R3; without additive, R4; 2 mmol $Ca(OH)_2$, R5; 3 mmol $Ca(OH)_2$)

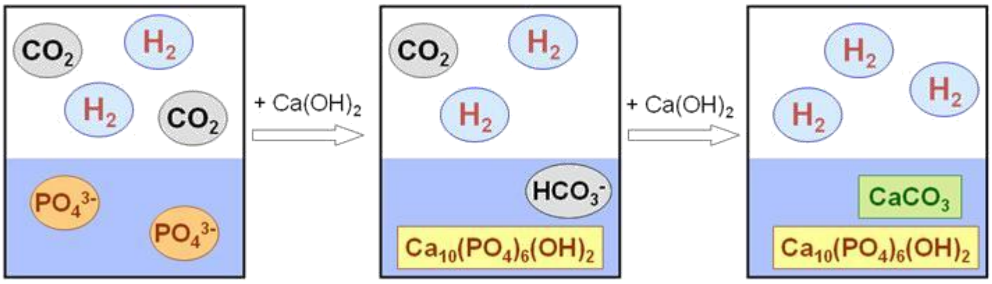

Figure 3.6 Estimation of phosphorus conversion

3.3.2 Hydrothermal gasification of chicken manure

Chicken manure, which contains phosphorus, was selected as a real bio-waste for obtaining 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 that 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 and 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 are likely to yield precipitations in the solid phase by the hydrothermal reaction.

According to these results we obtained the following equations. When the sample includes hetero atom such as P, this element would be transformed into PO_4^{3-} by the hydrothermal reaction [4].

$$\text{Sample} \qquad P \quad \text{-----}H_2O\text{----}\longrightarrow \quad PO_4^{3-} \tag{3.7}$$

Figure 3.7 shows the effect of additive on the yields of various gases generated through a hydrothermal gasification by using chicken manure at 400°C.

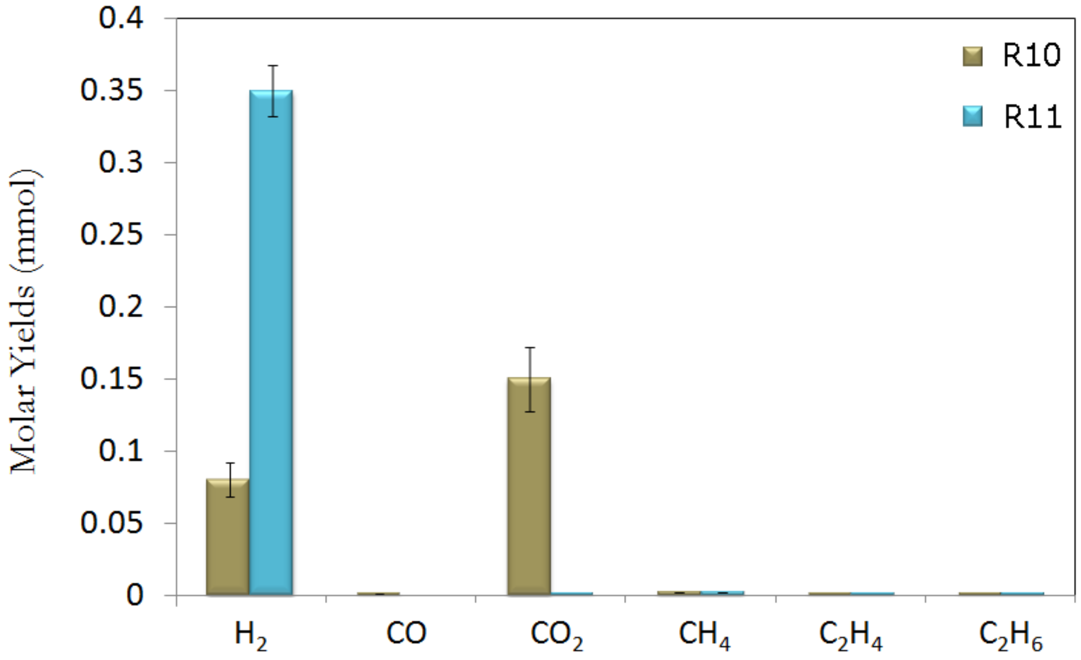

Figure 3.7 Effects of $Ca(OH)_2$ amount on gas yield at 400 °C (R10; without additive, R11; 3 mmol $Ca(OH)_2$)

Alkaline additive provides significant changes in yields. Hydrogen gas was found to be produced mainly in the gas phase. H_2 yields were increased and other gasses were suppressed by using additive, especially for CO_2, which was suppressed very effectively. It was considered that the enhancement of H_2 yield by adding alkali was due to the water gas shift reactions (Equation (3.8) and Equation (3.9). Equation (3.10) shows production of $CaCO_3$ after hydrothermal gasification by adding $Ca(OH)_2$.

$$\text{Org. C} + H_2O \rightarrow CO + H_2 \tag{3.8}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{3.9}$$

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \tag{3.10}$$

In addition, these results proved that the optimum condition (400°C and 3mmol $Ca(OH)_2$) was the same as that of O-Phospho-DL-serine.

According to Equation (3.2), hydrogen gasification ratio was found 7.4%.

According to Equation (3.3), H_2 yield [mol%] was found 3.3%.

These hydrogen yield levels are higher than without additive conditions, but they are still low. For increasing these levels, a new additive could be found. According to Equation (3.4), Equation (3.5), and Equation (3.6), energy efficiency was found 24% for this experimental scale. Industrial scale system which uses waste heat for providing the hydrothermal gasification could have high efficiency than this value.

3.4 Conclusions

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 hetero-atoms, 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. We decided to use $Ca(OH)_2$ as the additive for understanding the reaction mechanisms for 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 (3.9) and Equation (3.10).

For confirming the equations, X-ray diffraction of the residual solid sample after the reaction with the additive of $Ca(OH)_2$ was measured. The formation of $CaCO_3$ was confirmed. These results will be mentioned in Chapter 5.

3.5 References

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Chapter 4 Dioxins Analysis

4.1 Introduction

Pollutants generated by the hydrothermal reaction were not clarified in detail. 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 human body even with exposures to trace amounts. This study focused on the determination of dioxins which were among the most toxic substances.

Dioxins

The name "dioxins" is often used for the family of structurally and chemically related polychlorinated dibenzo para dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Figure 4.1). 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, with TCDD (2,3,7,8- tetrachlorodibenzo para dioxin) being the most toxic [1]. The formation mechanisms for them are not yet completely understood because of their complex production mechanisms [2]. Dioxins do have a damaging effect on human health and the environment [1, 3], and 30 dioxins are known to have significant toxicity [1]. 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 phased produced through the hydrothermal reaction of chicken manure were determined.

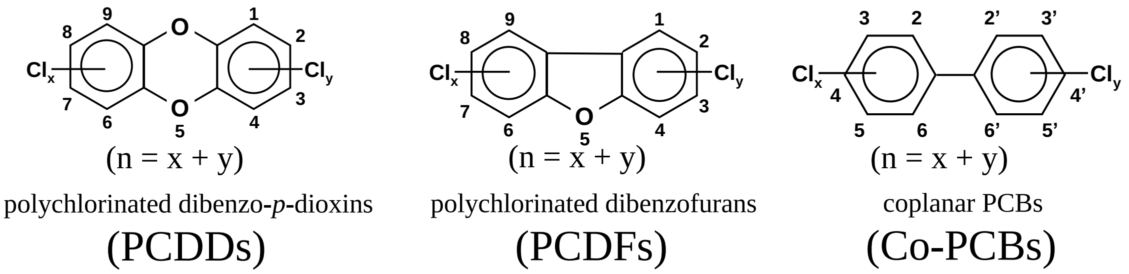

Figure 4.1 Chemical structures of dioxins

TEF and TEQ

TEQ (toxic equivalent quantity) is total toxicity of dioxins contained in sample, calculated by the Equation (4.1),

$$\mathrm{TEQ} = \sum f_i g_i \tag{4.1}$$

f_i : toxic equivalency factor for i_{th} dioxin (TEF)

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

The typical values of TEF were listed in Table 4.1 which was decelerated by WHO in 2006 [4].

Table 4.1 List of TEF (WHO 2006)

Compound	Isomer	TEF(WHO2006)
T4CDD	1368	-
T4CDD	1379	-
T4CDD	2378	1
P5CDD	12378	1
H6CDD	123478	0.1
H6CDD	123678	0.1
H6CDD	123789	0.1
H7CDD	1234678	0.01
O8CDD	12346789	0.0003
T4CDF	1278	-
T4CDF	2378	0.1
P5CDF	12378	0.03
P5CDF	23478	0.3
H6CDF	123478	0.1
H6CDF	123678	0.1
H6CDF	123789	0.1
H6CDF	234678	0.1
H7CDF	1234678	0.01
H7CDF	1234789	0.01
O8CDF	12346789	0.0003
T4CB	#81	0.0003
T4CB	#77	0.0001
P5CB	#126	0.1
H6CB	#169	0.03
P5CB	#123	0.00003
P5CB	#118	0.00003
P5CB	#105	0.00003
P5CB	#114	0.00003
H6CB	#167	0.00003
H6CB	#156	0.00003
H6CB	#157	0.00003
H7CB	#189	0.00003

4.2 Experimental procedure

The procedures for the sample preparation and hydrothermal gasification were described in detail in a Chapter 2.

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 4.2 and Table 3.1).

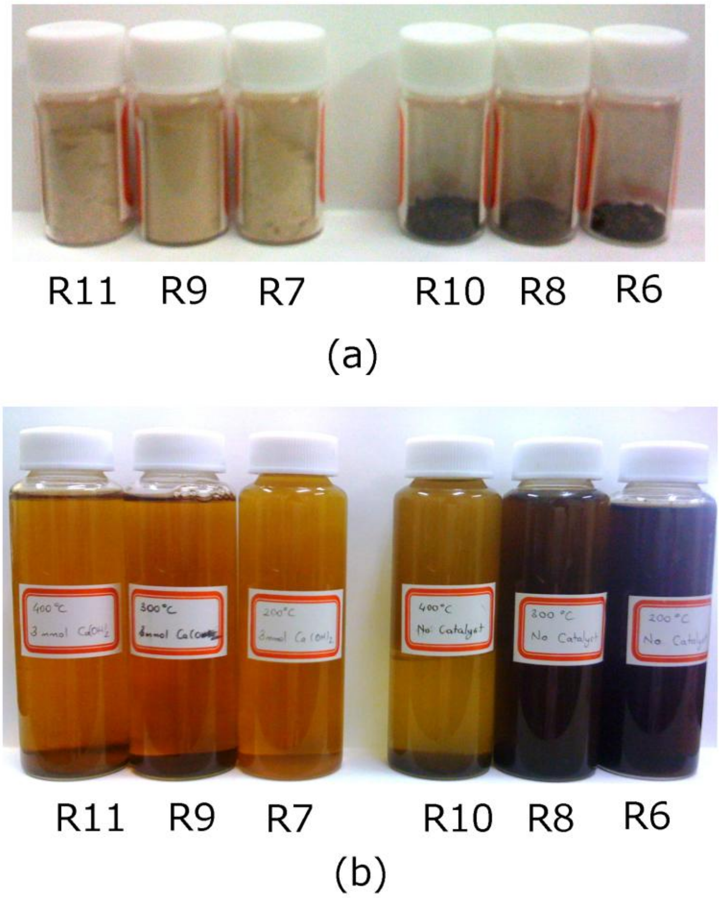

Figure 4.2 Solid (a) and liquid (b) samples of six different condition of chicken manure (R6; without additive, 200 °C, R7; 3 mmol $Ca(OH)_2$, 200 °C, R8; without additive, 300 °C, R9; 3 mmol $Ca(OH)_2$, 300 °C, R10; without additive, 400 °C, R11; 3 mmol $Ca(OH)_2$, 400 °C)

The samples produced under the various experimental conditions were separated into liquid and solid phases by filtration. The liquid and solid residues obtained were analyzed by gas chromatography / mass spectrometry (GC/MS) to determine the dioxins.

4.3 Results and discussion

The generated liquid and solid residues were analyzed using gas chromatography/ mass spectrometry (GC/MS).

Solid samples

Fig. 4.3 shows the toxic equivalent quantity (TEQ) of each dioxin for the solid phase under the various conditions for the different runs of the hydrothermal gasification experiment in the chicken manure case. PCDDs and PCDFs were not detected. Three kinds of PCBs were detected. These were T4CB#77 (Fig. 4.4) (TEF=0.0001), P5CB#118 (Fig. 4.5) (TEF=0.00003) and P5CB#105 (Fig. 4.6) (TEF=0.00003).

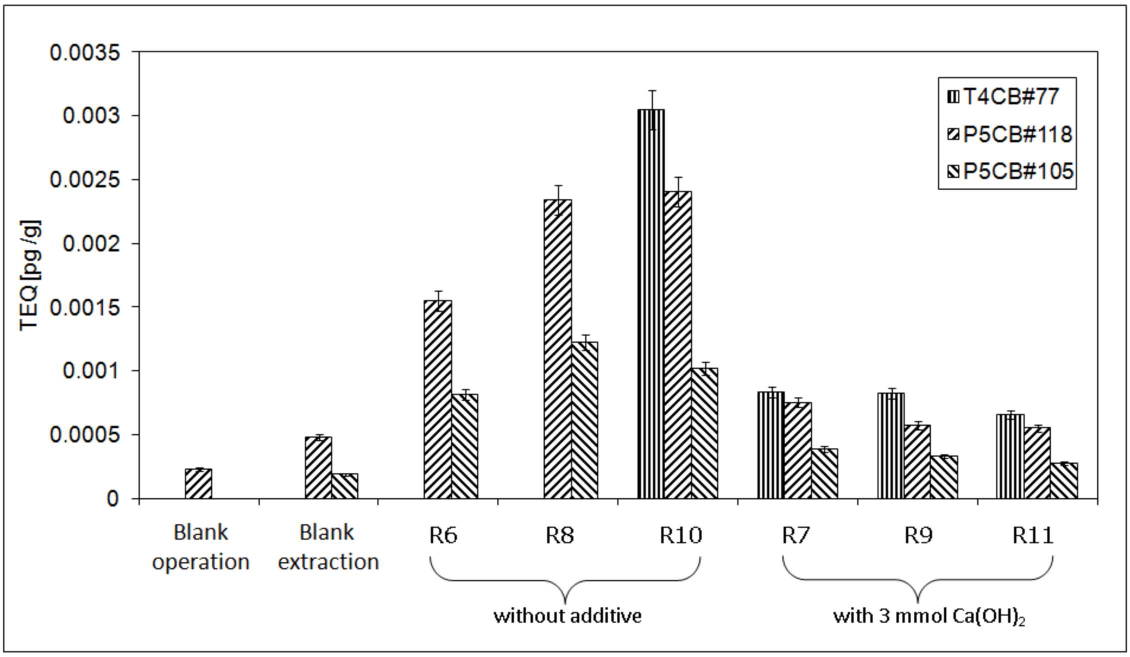

Figure 4.3 TEQ [pgTEQg^{-1}] of solid phases (chicken manure)

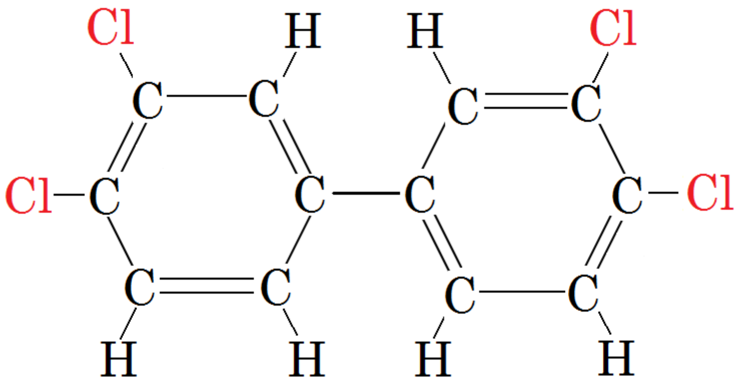

Figure 4.4 Chemical structures of T4CB#77

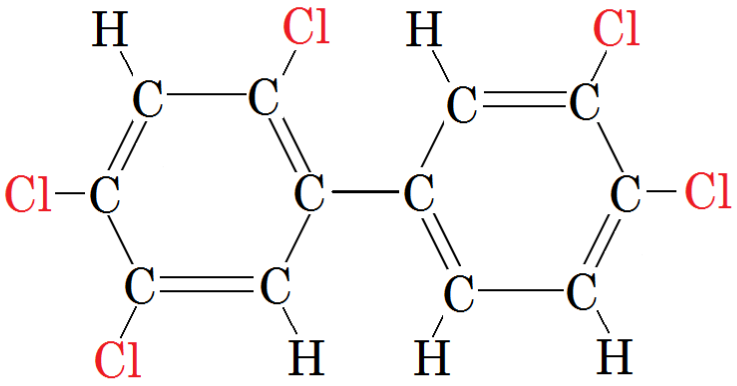

Figure 4.5 Chemical structures of P5CB#118

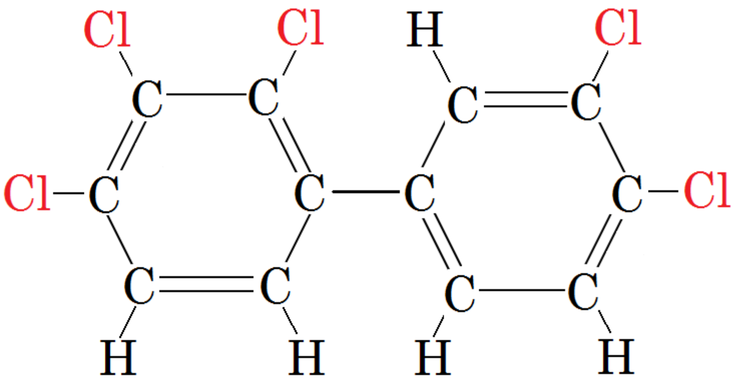

Figure 4.6 Chemical structures of P5CB#105

The total TEQ values were 0.00237 pgTEQg^{-1} for Run 6, 0.00357 pgTEQg^{-1} for Run 8, 0.00647pgTEQg^{-1} for Run 10, 0.00196 pgTEQg^{-1} for Run 7, 0.00172 pgTEQg^{-1} for Run 9 and 0.00148 pgTEQg^{-1} for Run 11.

The highest total TEQ of 0.00647 pgTEQg^{-1} was observed for the reaction temperature of 400°C without additive (Run 10). This level is well below the permitted Japanese level for solid residue (3000 pgTEQg^{-1}) [5].

Liquid samples

Fig. 4.7 shows the TEQs for the liquid phase products obtained under the various amounts of the additive at the different reaction temperatures. 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 pgTEQL^{-1} for Run 6, 0.00054 pgTEQL^{-1} for Run 8, 0.00029 pgTEQL^{-1} for Run 10, 0.00023 pgTEQL^{-1} for Run 7, 0.00028 pgTEQL^{-1} for Run 9 and 0.00042 pgTEQL^{-1} for Run 11.

With and without the additive, the total TEQs are nearly equal to the level of plain 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 6). This total TEQ was well below the permitted Japanese limit for liquid residue (10 pgTEQL^{-1}) [5].

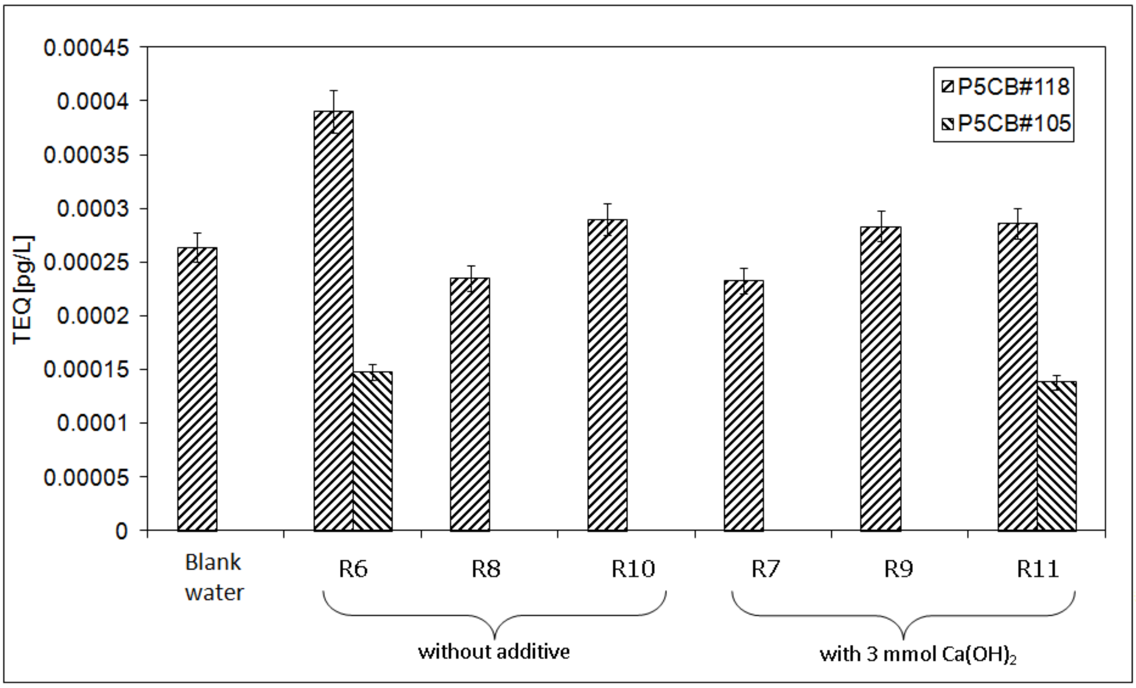

Figure 4.7 TEQ [pgTEQL^{-1}] of liquid phases (chicken manure)

4.4 Conclusions

Dioxins were determined in the liquid and solid samples produced by the hydrothermal gasification of chicken manure under various experimental conditions.

PCDDs and PCDFs were not detected in either the solid or the liquid residues resulting from hydrothermal gasification of chicken manure. The highest dioxin level found for the solid residues was 0.00647 pgTEQg^{-1}, and the highest dioxin level found for the liquid residues was 0.00054 pgTEQL^{-1}.

The total TEQ of dioxins was found to be less than 3000 pgTEQg^{-1} for the solid and 10 pgTEQL^{-1} for the liquid phase residue, both within the allowable limits in Japan. It is therefore analytically demonstrated that the hydrothermal process for animal manure is safe in terms of production of dioxins.

Using chicken manure in the hydrothermal gasification provides a means of disposing of biowastes and producing hydrogen. The generation of hydrogen gas through the hydrothermal gasification can be conducted without considering the toxicity of dioxins.

4.5 References

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Chapter 5 Production of Hydroxylapatite

5.1 Introduction

Hydroxylapatite is a naturally occurring mineral form of calcium apatite with the formula $Ca_5(PO_4)_3(OH)$. Physical properties of hydroxylapatite were listed in Table 5.1. And also Fig. 5.1 shows typical photographs of natural hydroxylapatite (a), and commercially available hydroxylapatite (b).

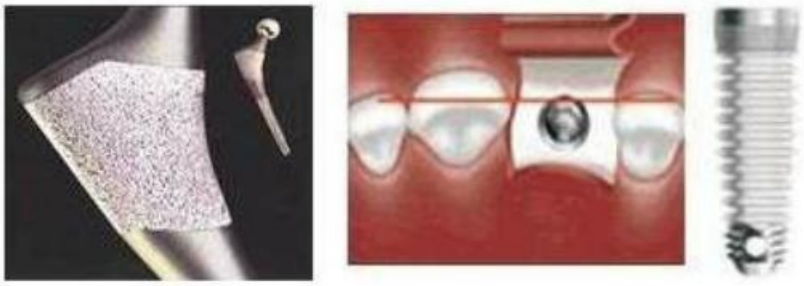
Table 5.1 Physical properties of hydroxylapatite

Appearance	White
Molar ratio (Ca/P)	1.667
Melting point (^{o}C)	1670
Bulk density (g cm^{-3})	3156
Young's modulus (GPa)	80-110
Fracture Toughness (MPa. m$^{1/2}$)	0.8-1.2
Vickers hardness (GPa)	5.0

(a) **(b)**

Figure 5.1 Natural hydroxylapatite (a) and commercial hydroxylapatite (b).

The valuable material, Hydroxylapatite, can be produced during hydrothermal gasification process of wet biomass. Hydroxylapatite is a calcium orthophosphate with chemical composition of $Ca_{10}(PO_4)_6(OH)_2$. There are chemical similarities between hydroxyapatite and the mineral part of human bones and teeth. Therefore it is widely used for biomedical applications [1, 2, 3, 4]. Figure 5.2 shows two examples of hydroxylapatite application; hip implant (a), and dental implant (b).



(a) **(b)**

Figure 5.2 Hydroxylapatite application; hip implant (a) and dental implant (b)

5.2 Results and discussion

Production of hydroxylapatite

The optimum hydrothermal gasification condition (400°C and 3mmol $Ca(OH)_2$) found for the model sample was applied to the chicken manure sample (Figure 5.3 (a)).

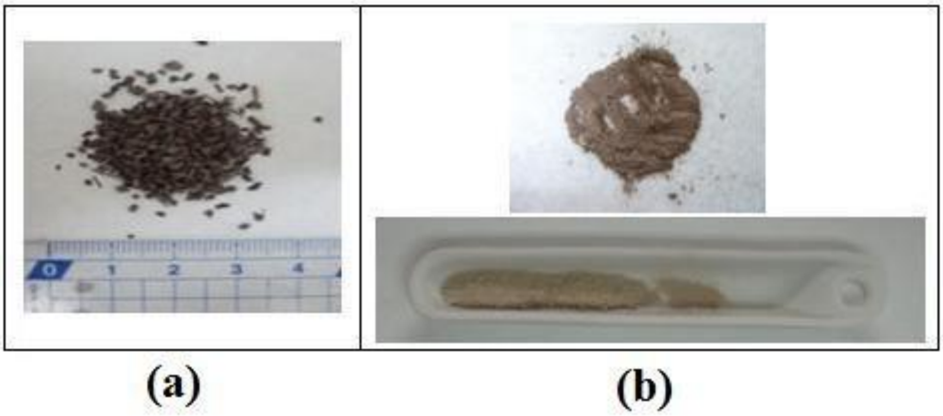


Figure 5.3 Photographs of (a) chicken manure, (b) crude sample

Hydroxylapatite was confirmed in the solid residue by XRD (Fig. 5.4).

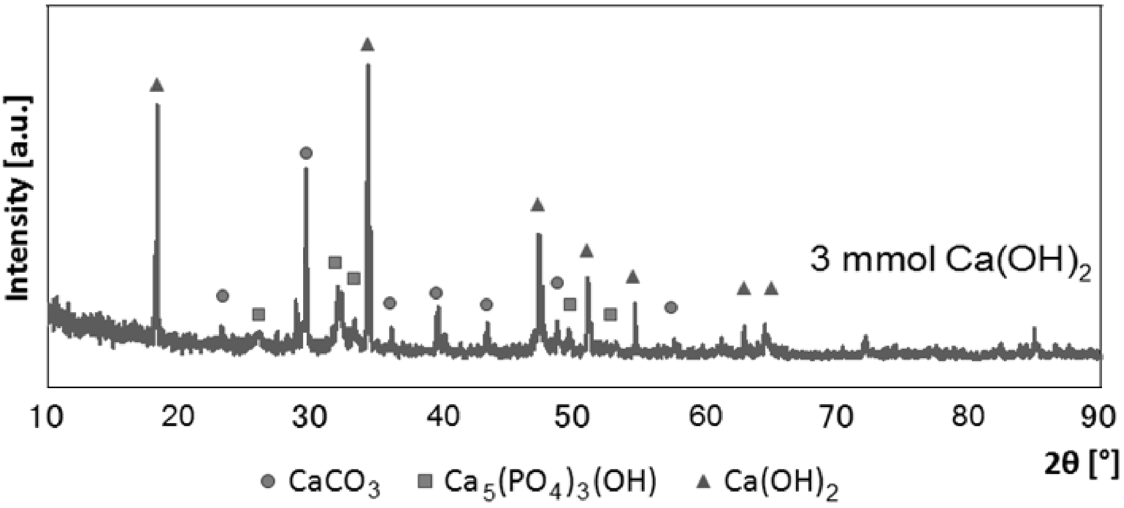


Figure 5.4 XRD patern of chicken manure sample.

However, the color of the solid residue was not white but gray (Figure. 5.3 (b)), while the commercially available pure hydroxyl apatite was white. To obtain the pure hydroxyl apatite, purification process should be carried out.

Purification by heating

The main contaminant was likely char. To remove the char, the crude product was heated in an IR image furnace (Ulvac-Rico, Inc.) at various temperatures (600°C - 1000°C) and reaction times (5 – 20 min) (Fig. 5.5) under airflow of 1.5 dm^3min^{-1}. Figure 5.6 shows the infrared image furnace equipment with the ceramic sample boat and thermocouple.

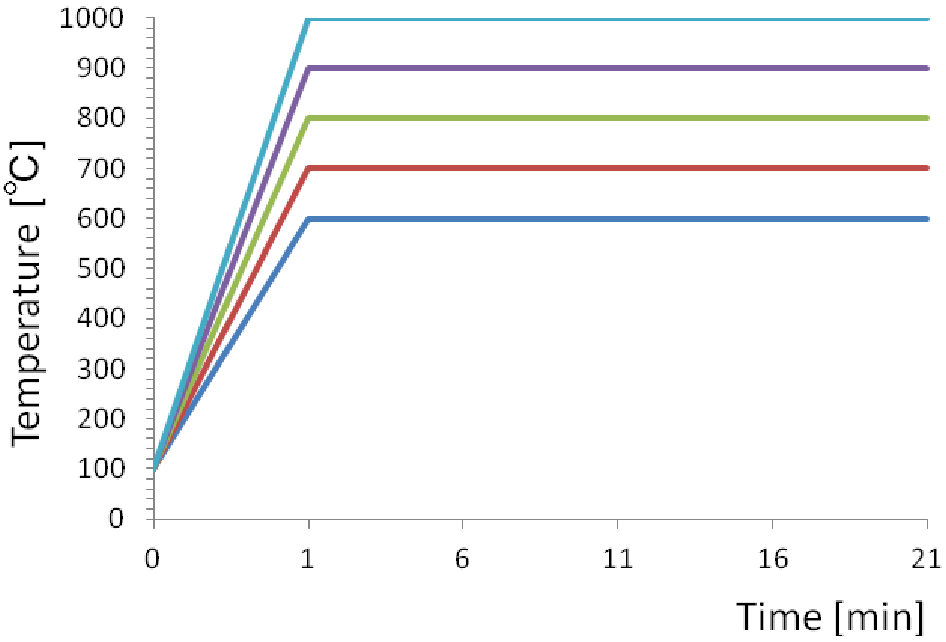


Figure 5.5 Temperature–time program graph of purification by heating

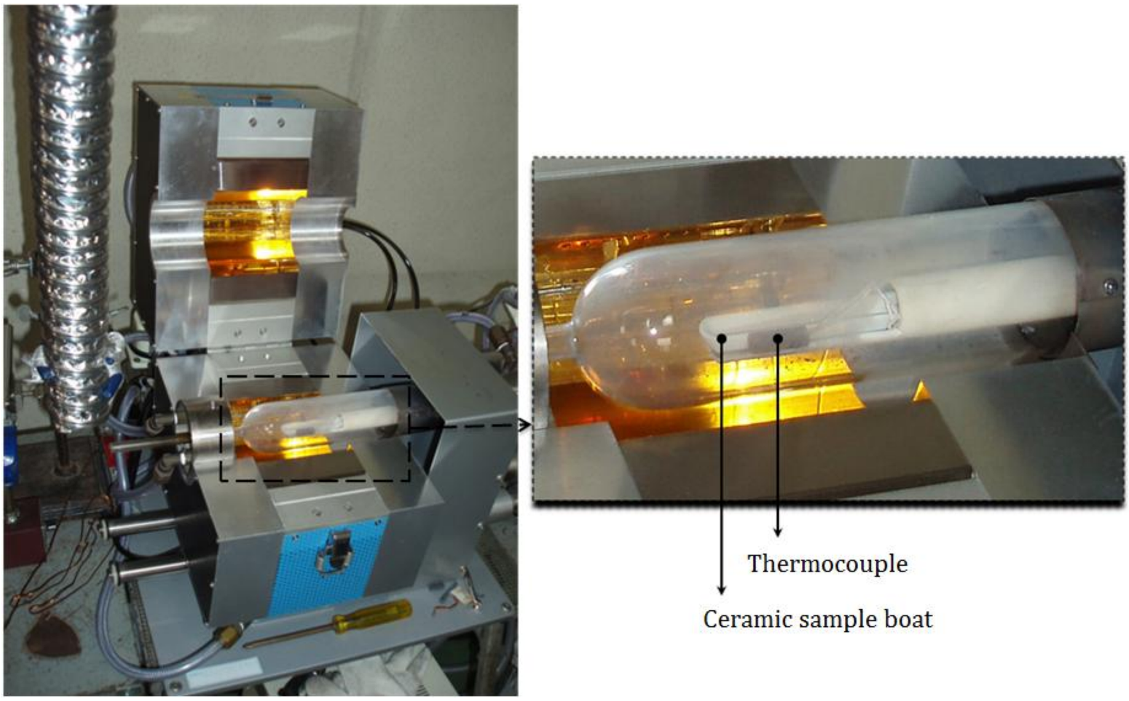


Figure 5.6 Photograph of infrared image furnace used for HA purification.

Table 5.2 lists the purification conditions for the crude residue which was produced under the optimum hydrothermal conditions mentioned previous chapters (3 mmol $Ca(OH)_2$, 400°C, 22 MPa).

Table 5.2 The purification conditions

Purification Run No	Purification Temperature [°C]	Purification Time [min]
1	600°C	5 min
2	600°C	10 min
3	600°C	15 min
4	600°C	20 min
5	700°C	5 min
6	700°C	10 min
7	700°C	15 min
8	700°C	20 min
9	800°C	5 min
10	800°C	10 min
11	800°C	15 min
12	800°C	20 min
13	900°C	5 min
14	900°C	10 min
15	900°C	15 min
16	900°C	20 min
17	1000°C	5 min
18	1000°C	10 min
19	1000°C	15 min
20	1000°C	20 min

Figure 5.7 shows the photographs of samples treated under the various purification conditions. Above the purification conditions at 700°C for 20 min (R8), the color of the purified residue turned into white.

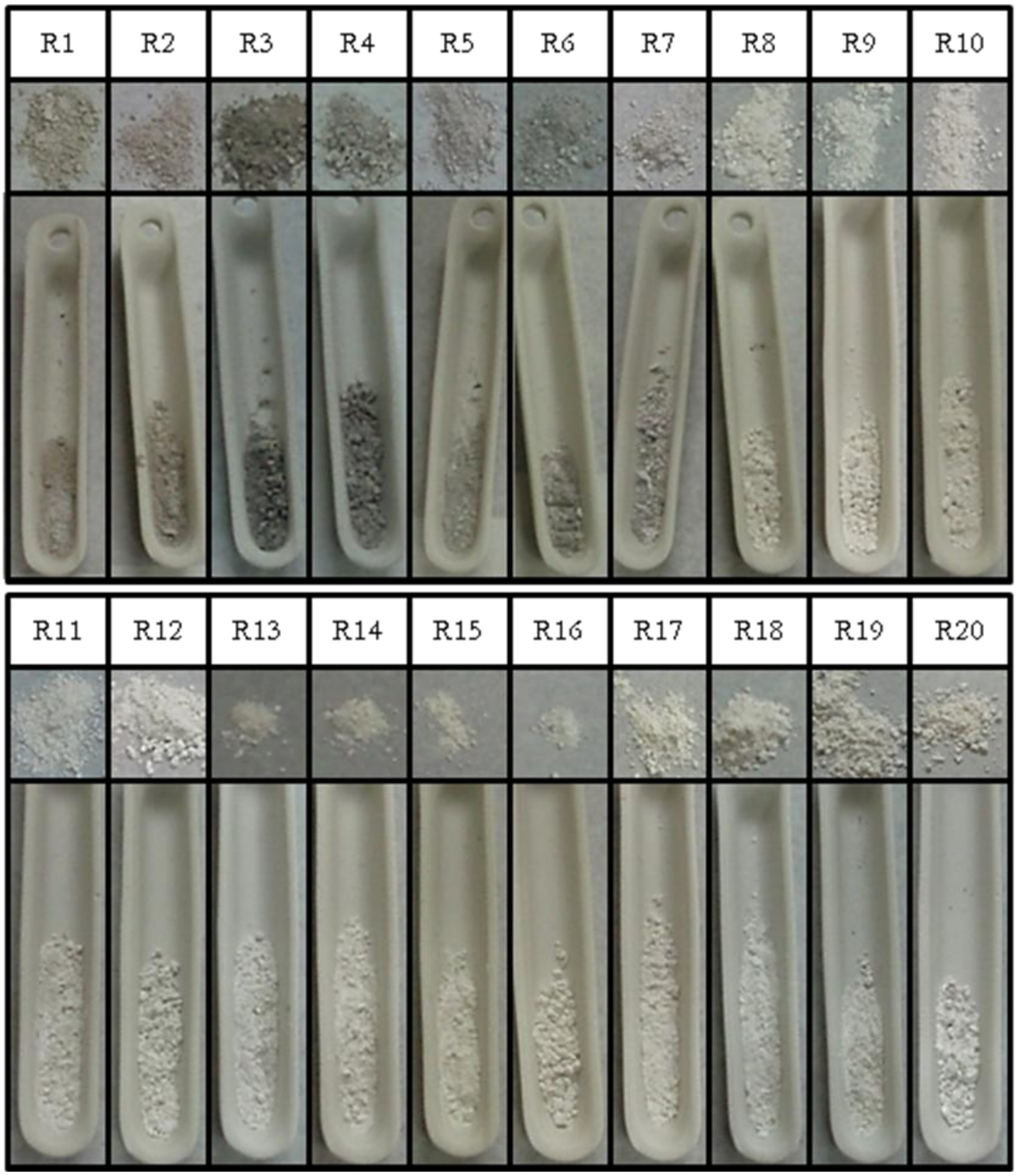


Figure 5.7 The photographs of purified samples obtained with the purification process

Fig. 5.8 shows the XRD patterns for the solid residues which were purified under the various conditions. The XRD peak at 31.80° (2θ) indicates hydroxylapatite [5] and the two satellite peaks at 32.22° and 32.92° were also detected. It was confirmed that the phosphorous atom in the sample was converted into the valuable compound, hydroxylapatite, through the hydrothermal gasification.

Additionally, $CaCO_3$ was identified for the purification conditions between (R1-R7) while CaO for (R8-R20). The following thermal decomposition takes place (Equation 5.1).

$$CaCO_3 \rightarrow CaO + CO_2 \tag{5.1}$$

The elemental analysis was carried out for the purified samples (Fig. 5.9). Above the purification conditions at R8, the values of C, H, and N were 1.5, 1.5, and 0% respectively. The carbon content in the crude sample of 7% was reduced to 1.5%. The purified sample includes some material such as hydroxylapatite, which have melting point higher than 1000 ^{0}C. Because of this reason, reduced carbon ratio did not become zero.

Using the higher temperatures of 800-1000 ^{0}C with reaction times of 20 min, the results were almost the same and the organic compounds contained in the crude hydroxylapatite can be successfully removed.

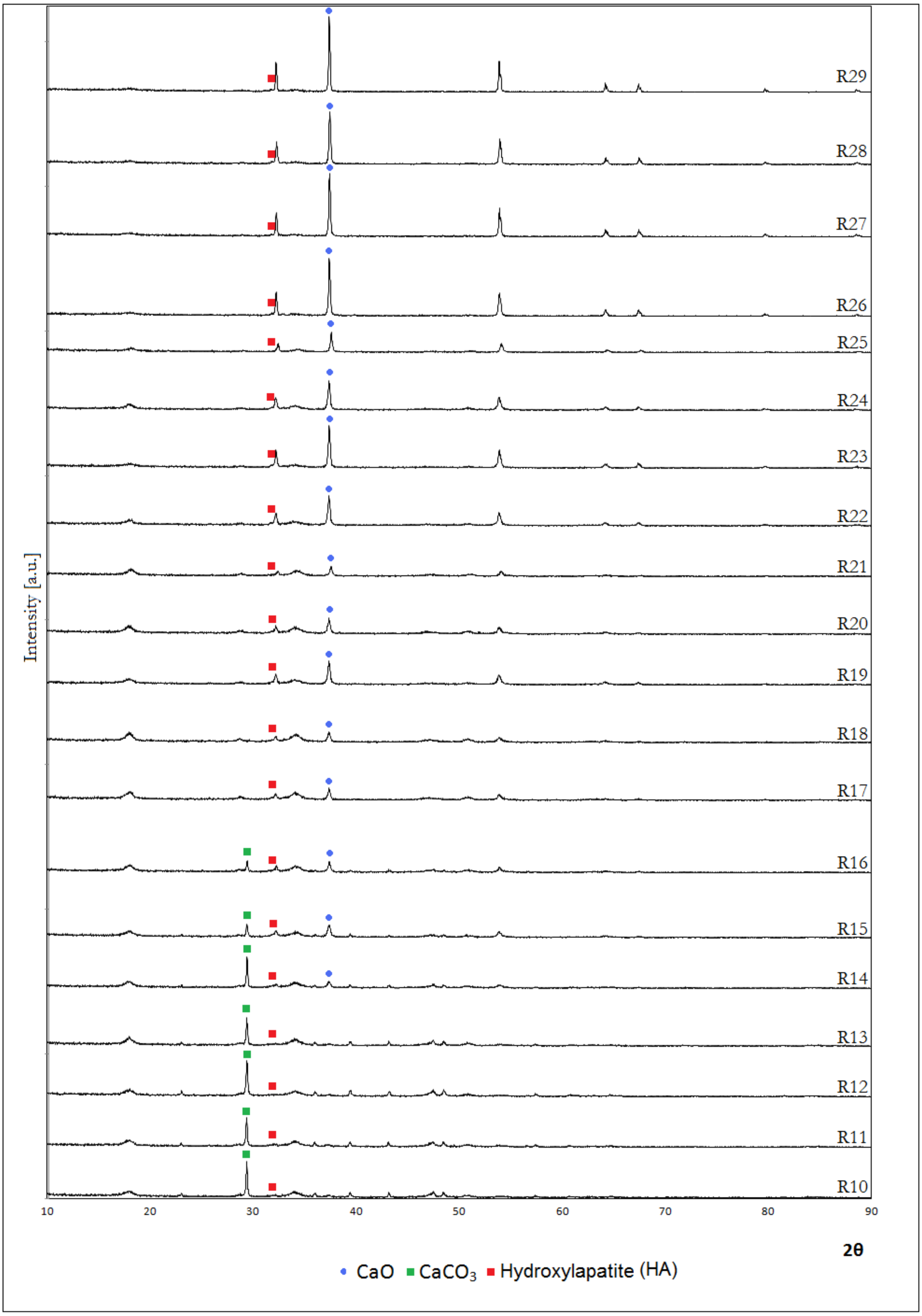


Figure 5.8 XRD patterns of purification process conditions.

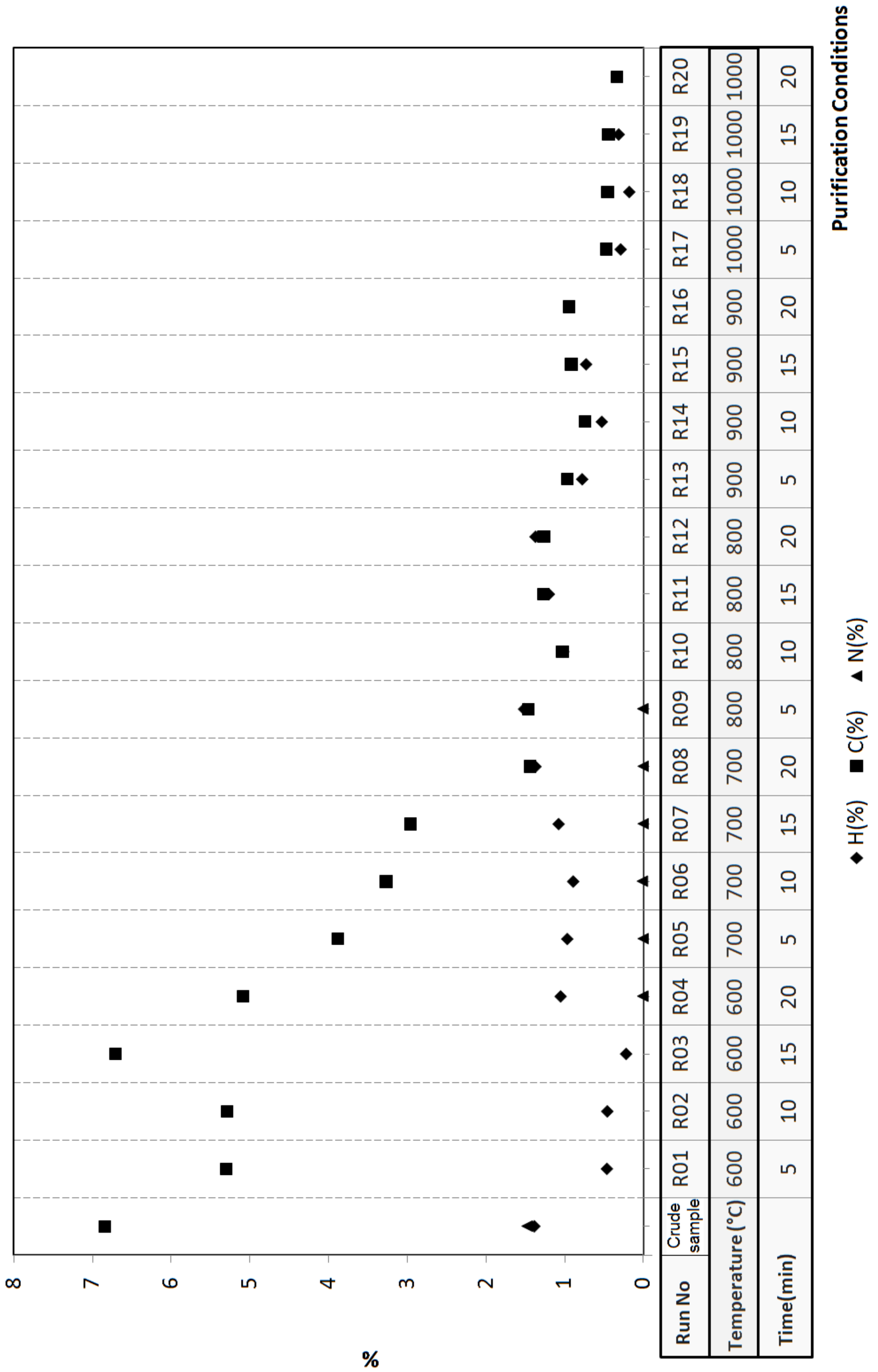


Figure 5.9 Elements analysis of purified samples (chicken manure).

Quantitative analysis

To make a quantitative determination of the yield of hydroxylapatite from the chicken manure, the relationship between the concentration of pure hydroxylapatite (HA) and the height of the peak on the XRD patterns (31.68°~31.96° (2θ)) was measured. Figure 5.10 shows the calibration curves of "Intenisty of HA" and "Intensity of HA / Intensity of $CaCO_3$" from mixture of HA+$CaCO_3$ as a diluter. Almost the same "Intenisty of HA" calibration curve was obtained with mixture of HA+CaO as a diluter (Fig 5.11). With the use of "Intenisty of HA" calibration curves and the peak height for the resulting hydroxylapatite (Fig.5.12), it was concluded that about 68.3% of the P in the chicken manure could be converted to hydroxylapatite. This ratio was validated with the use of "Intensity of HA / Intensity of $CaCO_3$" and "Intensity of HA /Intensity of CaO" calibration curves, without effect of intensity scale.

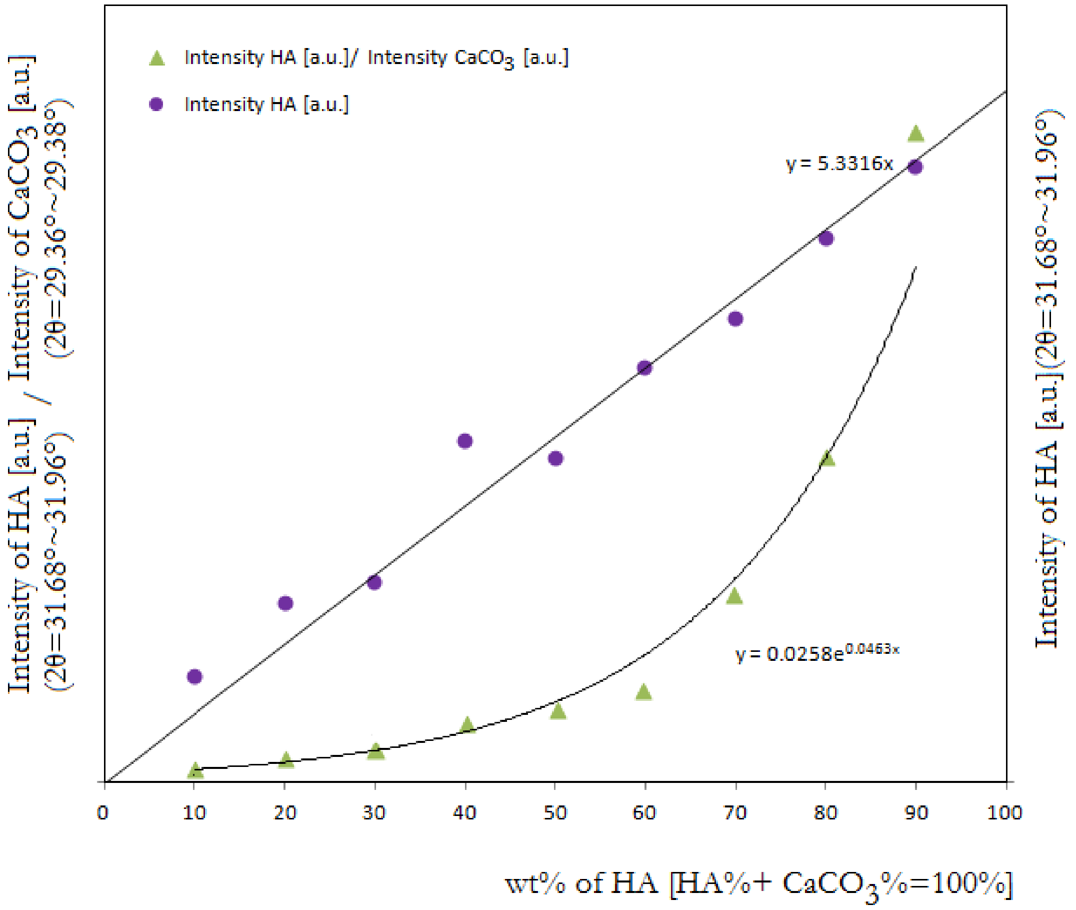


Figure 5.10 Calibration curve HA+$CaCO_3$

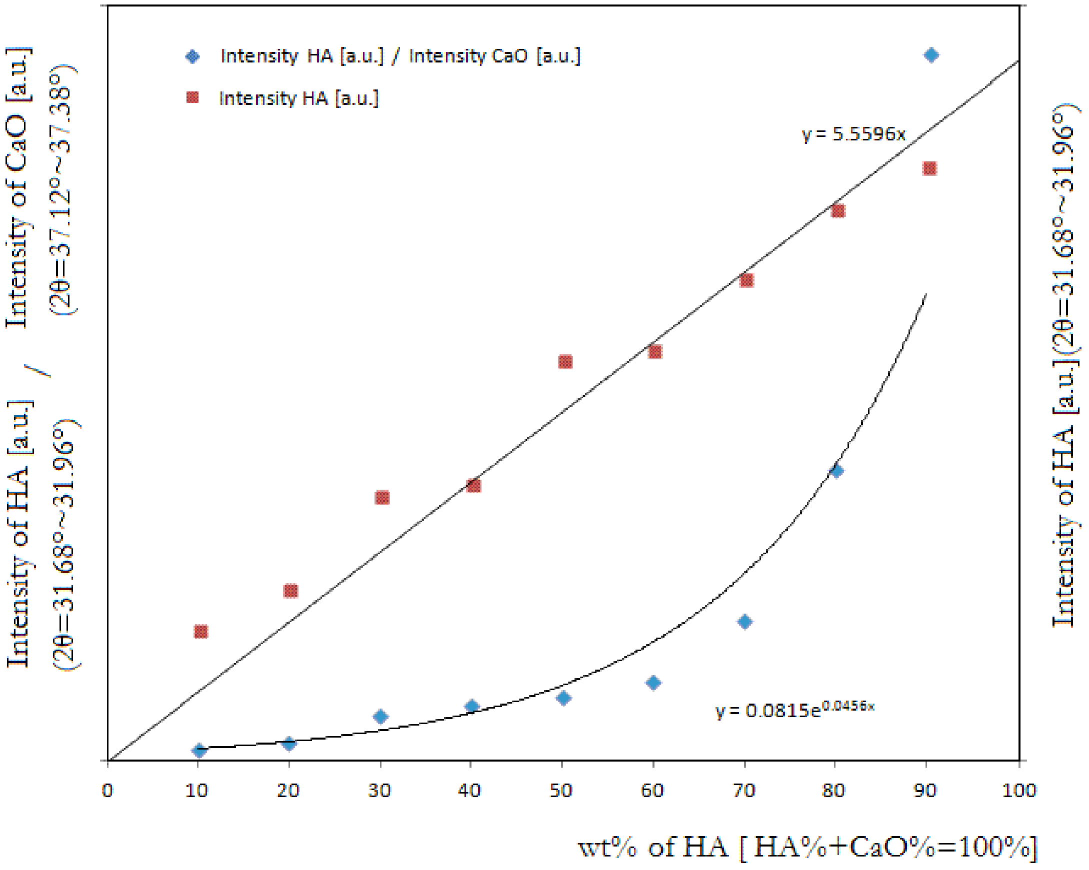


Figure 5.11 Calibration curve HA+CaO

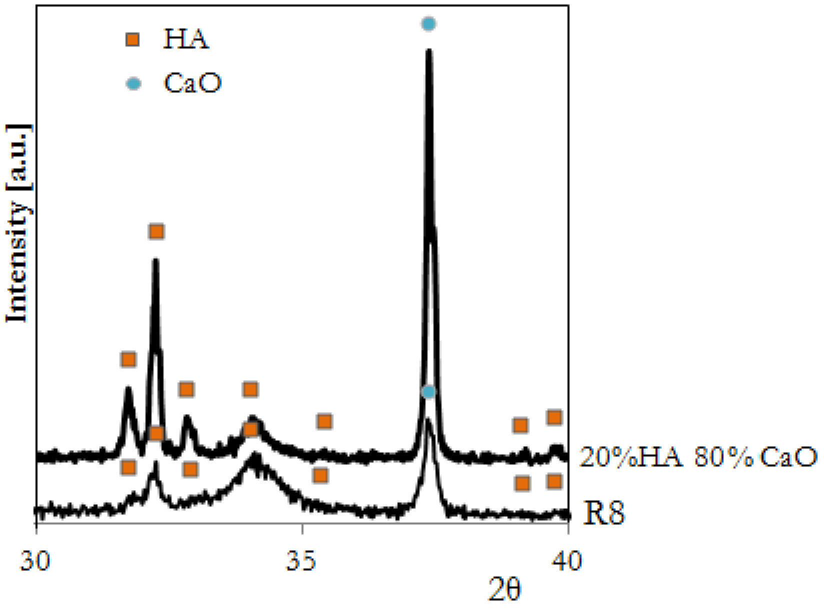


Figure 5.12 XRD patterns of mixture sample (20%HA + 80%$CaCO_3$) and R8.

5.3 Purification by CH_3COOH

Introduction

The sample has 20% hydroxylapatite which was purified by heating. However further purification was needed for obtaining purer hydroxylapatite by additional process.

Purification process was not succeeded with solution of hydrochloric acid. Then, acetic acid solution was tested for purification of hydroxylapatite. Acetic acid is an organic acid with the chemical formula CH_3COOH and classified as a weak acid although concentrated acetic acid is corrosive and attacks the skin [6].

Under the purification conditions of R1-R7, $CaCO_3$ was remained after neutralization of CO_2 produced in the hydrothermal process. CaO was yielded from $CaCO_3$ decomposition under the conditions of R8-R20.

There are two different scenarios as for the acetic acid treatments. The first scenario was for $CaCO_3$. It was shown on Equation (5.2) and also Fig. 5.13 (a) schematically.

The first scenario;

$Ca_5(PO_4)_3(OH) + CaCO_3 + 2CH_3COOH \rightarrow Ca_5(PO_4)_3(OH) + \ldots$

$\ldots + Ca(CH_3COO)_2 + H_2O + CO_2$ (5.2)

Acetic acid will react with calcium carbonate to give calcium acetate, water and carbon dioxide and not with hydroxylapatite. Carbon dioxide will evolve as a gas. The solid hydroxylapatite can be separated from the $Ca(CH_3COO)_2$ solution by filtration.

The second scenario;

Second scenario was for CaO. It was shown on Equation (5.3), Equation (5.4) and also Figure 5.13 (b) schematically.

$Ca_5(PO_4)_3(OH) + CaO + H_2O \rightarrow Ca_5(PO_4)_3(OH) + Ca(OH)_2$ (5.3)

$$Ca_5(PO_4)_3(OH) + Ca(OH)_2 + 2CH_3COOH \rightarrow Ca_5(PO_4)_3(OH) + \ldots$$

$$\ldots + Ca(CH_3COO)_2 + 2H_2O \qquad (5.4)$$

The second scenario has the two steps. Calcium oxide will react with water to yield calcium hydroxide. On the second step, acetic acid reacts with calcium hydroxide to give calcium acetate and water and does react with hydroxylapatite. Then, hydoxylapatite, water and calcium acetate will be remained. The pure hydroxylapatite could be obtained.

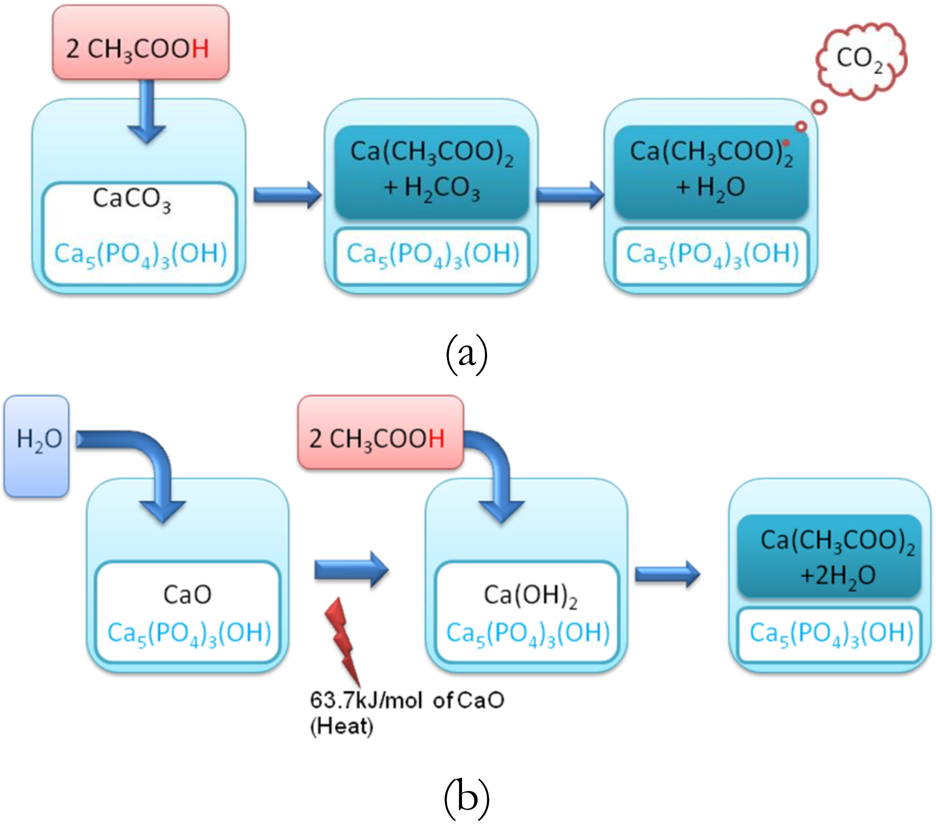
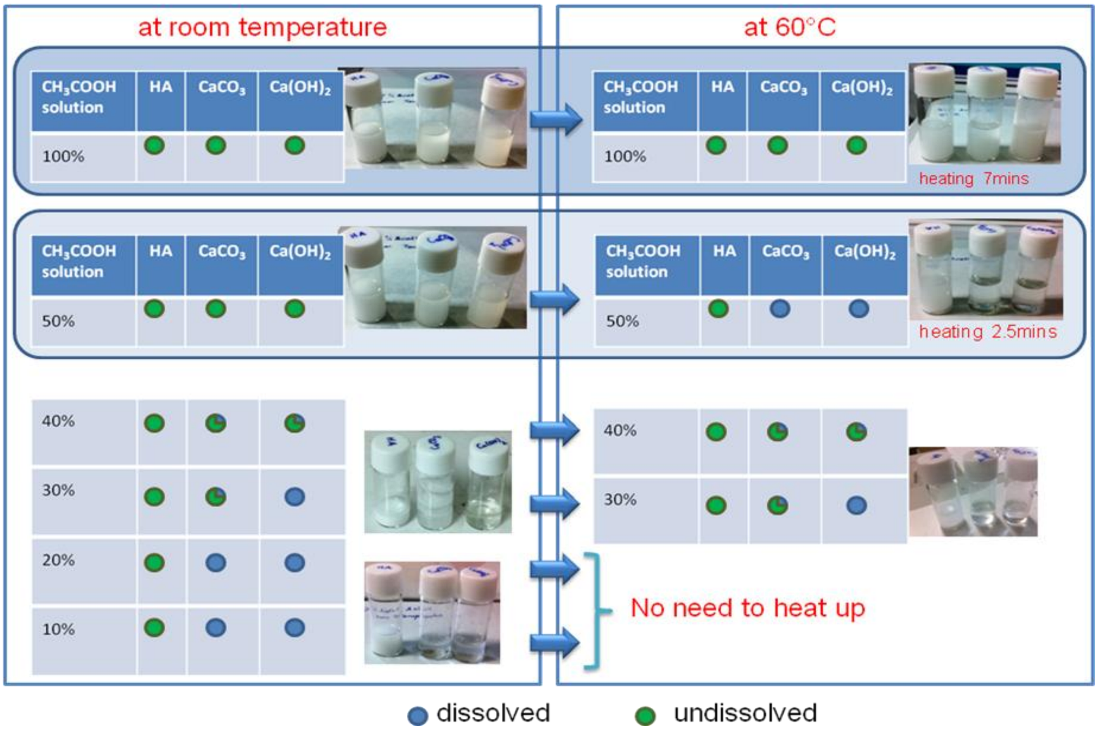


Figure 5.13 (a) First scenario (b) second scenario of purification process by CH_3COOH

Results and discussion

To obtain the purified hydroxylapatie, following the above interpolations, acetic acid solutions were prepared. Figure 5.14 shows a diagram of solubility – dissolubility process for HA, $CaCO_3$, and $Ca(OH)_2$ in the acetic acid solutions.



at room temperature

CH_3COOH solution	HA	$CaCO_3$	$Ca(OH)_2$
100%	🟢	🟢	🟢
50%	🟢	🟢	🟢
40%	🟢	◔	◔
30%	🟢	◔	🔵
20%	🟢	🔵	🔵
10%	🟢	🔵	🔵

at 60°C

CH_3COOH solution	HA	$CaCO_3$	$Ca(OH)_2$
100%	🟢	🟢	🟢
50%	🟢	🔵	🔵
40%	🟢	◔	◔
30%	🟢	◔	🔵

Figure 5.14 Schematic diagrams of 100%, 50%, 40%, 30%, 20% and 10% hydrochloric acid solution results at room temperature and 60°C.

Figure 5.14 shows the results of solubility of the compounds in the hydrochloric acid solutions of 100%, 50%, 40%, 30%, 20%, and 10% at the reaction conditions of room temperature and 60°C. The solubility of $CaCO_3$ and $Ca(OH)_2$ was increased by decreasing the percent of acetic acid in solution. With high concentration of acetic acid in water, thermal energy was needed to dissolve the compounds, $CaCO_3$ and $Ca(OH)_2$. However, with the concentrations of 20% and 10%, the two compounds could be dissolved at room temperature. The result indicated that $CaCO_3$ and $Ca(OH)_2$ could be removed from the crude sample, by use of the 10% acetic acid solution at room temperature. It was confirmed that pure hydroxilapatite could be obtained from the hydrothermal reaction of chicken manure.

Fig 5.15 shows XRD patterns of 20%HA, 100%HA before and after acetic acid. It shows that after 10%acetic acid solution for 5 min, 20%HA becomes pure HA.

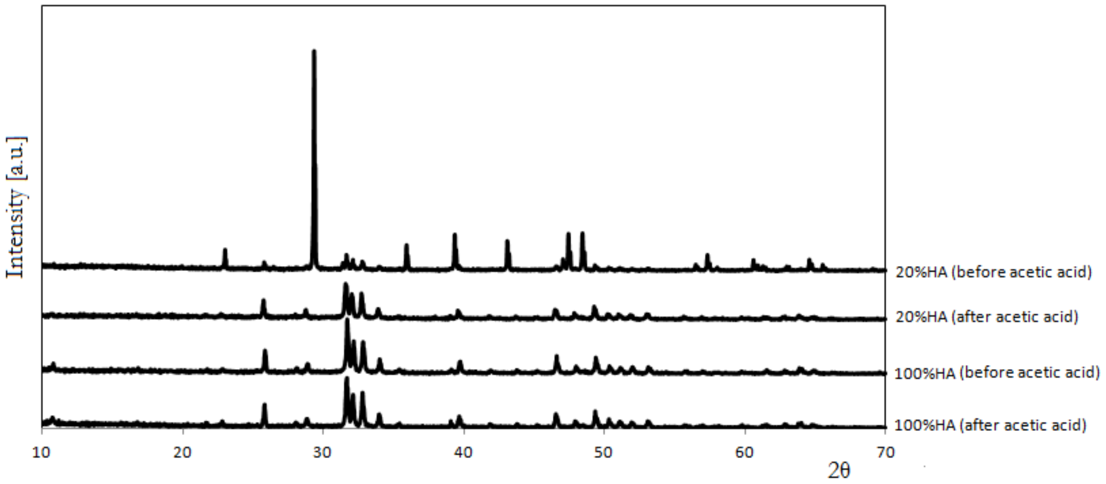


Figure 5.15 XRD patterns of 20%HA, 100%HA before and after acetic acid.

5.4 Conclusions

O-phospho-DL-serine was used as a model test sample to determine the optimum conditions of the hydrothermal gasification to produce hydrogen. Under these same optimum conditions (i.e. the reaction temperature of 400°C, use of 3mmol $Ca(OH)_2$ additive, and a reaction time of 40 min.), with sample of biowaste, chicken manure containing 9% (wt/wt) phosphorus, the hydrogen was obtained in the gas phase and hydroxylapatite in the purified solid phase.

Phosphorus recycle occurs by hydrothermal gasification of chicken manure. About 68% of the phosphorus in the chicken manure was converted into hydroxylapatite through the hydrothermal gasification.

Valuable material, hydroxylapatite production was provided through the hydrothermal gasification by using biowaste chicken manure. Disposing of chicken manure has a cost. When the chicken manure is used in this method, it doesn’t need disposing. Because of this reason this method is more environmental friendly. And also without disposing cost of chicken manure and worth of hydroxylapatite make this method more reasonable.

It was found that in the solid residue produced by the hydrothermal reaction of chicken manure with the additive of $Ca(OH)_2$, hydroxylapatite was identified by XRD. The crude sample contained impurity such as $Ca(OH)_2$ and $CaCO_3$. However, by use of chemical purification method, the impurities could be removed. A new method was proposed for synthesizing of pure hydroxylapatite by hydrothermal reaction of chicken manure.

5.5 References

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Chapter 6

New Approach

Chicken Manure + Biowaste = Energy

6.1 Introduction

The various additives have been used to promote the hydrothermal gasification reactions [1]. The cost of $Ca(OH)_2$ is less expensive than other additives. To treat a large amount of bio-wastes, more reasonable reagents are more preferable. Therefore $Ca(OH)_2$ was chosen as an additive in this study. The mainly produced gas was hydrogen gas and the generation of CO_2 gas was suppressed efficiently when alkaline $Ca(OH)_2$ was used as the additive.

When the biowastes are used as additives in place of the alkaline to treat a large amount of biowastes and then, the same results are obtained, the method can provide concurrent treatments of both biowastes.

Oyster shell is a kind of biowastes, which is a waste product from mariculture that a major disposal problem in coastal regions.

Activated oyster shell sample was received from Prof. Chan Won Lee of Department of Environmental Engineering, Kyungnam University. They used activated oyster shell for recovering phosphate from waste water.

In this study, the activated oyster shell was used. Crude oyster shell could be more reasonable. And also it could be giving more efficient results. But in this case, activated oyster shell was chosen for clarifying hydrogen and also hydroxylapatite production by hydrothermal gasification.

Activated oyster shell (Fig. 6.1) was adopted as an alkaline additive for hydrothermal process. And also it shows characteristics of calcium oxide on XRD pattern [2, 3]. Calcium oxide reacts with water to yield calcium hydroxide (Equation (6.1)).

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{6.1}$$

The procedures for the sample preparation and hydrothermal gasification were described in detail in a Chapter 2. The experimental conditions were listed in Table 6.1.

Figure 6.1 Activated oyster shell

Table 6.1 Experimental conditions.

Run No	Reaction Sample	Temperature [°C]	Amount of additive
12	-	400°C	200mg oyster shell
13	100mg chicken manure	400°C	50mg oyster shell
14	100mg chicken manure	400°C	100mg oyster shell
15	100mg chicken manure	400°C	200mg oyster shell

6.2 Results and discussion

Figure 6.2 shows the XRD patterns of the product of 200mg activated oyster shell (R12), activated oyster shell before hydrothermal gasification, and $Ca(OH)_2$. The XRD pattern for the product generated from 200mg activated oyster shell without chicken manure (R12) are similar to that for $Ca(OH)_2$. This result supported the usability of oyster shell as the additive instead of $Ca(OH)_2$ in hydrothermal gasification.

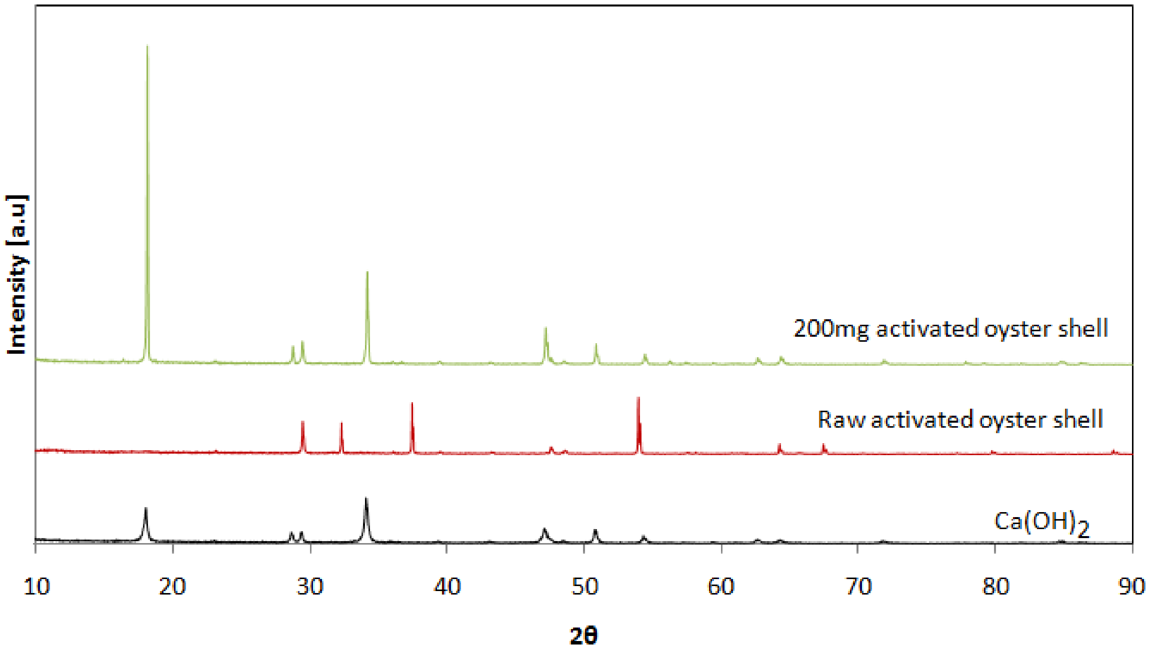

Figure 6.2 XRD patterns of R12, activated oyster shell before hydrothermal gasification, and $Ca(OH)_2$

Figure 6.3 shows the effects of oyster shell amount on the gas yield for R14 (100mg oyster shell, 100mg chicken manure) and R15 (200mg oyster shell, 100mg chicken manure). Hydrogen generation was increased around 63% by adding additional 100mg oyster shell. However, generation of CO_2 was also increased and CH_4 was decreased.

Figure 6.4 shows hydrogen yields of R11 (3 mmol $Ca(OH)_2$, 100mg chicken manure), R14 (100mg oyster shell, 100mg chicken manure) and R15 (200mg oyster shell, 100mg chicken manure). The highest hydrogen yield was attained in R-15. Under the hydrothermal gasification of chicken manure, the addition of 200mg oyster shell as the additive promoted the hydrogen yield more efficiently than that of 3 mmol $Ca(OH)_2$. This result implied that the use of real biowaste as the additive would develop a new field of hydrothermal gasification for production of hydrogen gas and deposition of the biowaste.

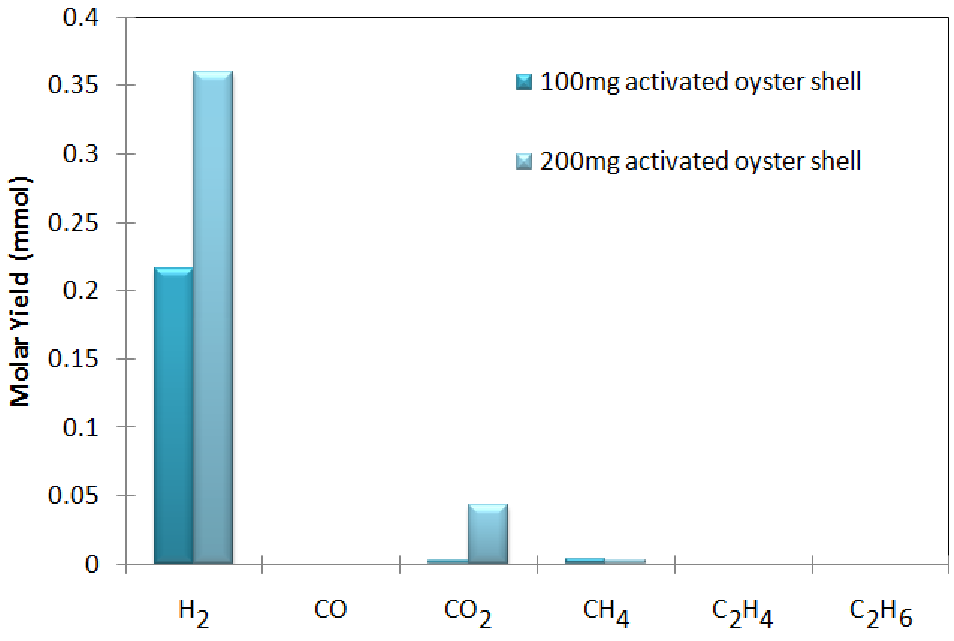

Figure 6.3 Effects of oyster shell amount on gas yield at 400°C

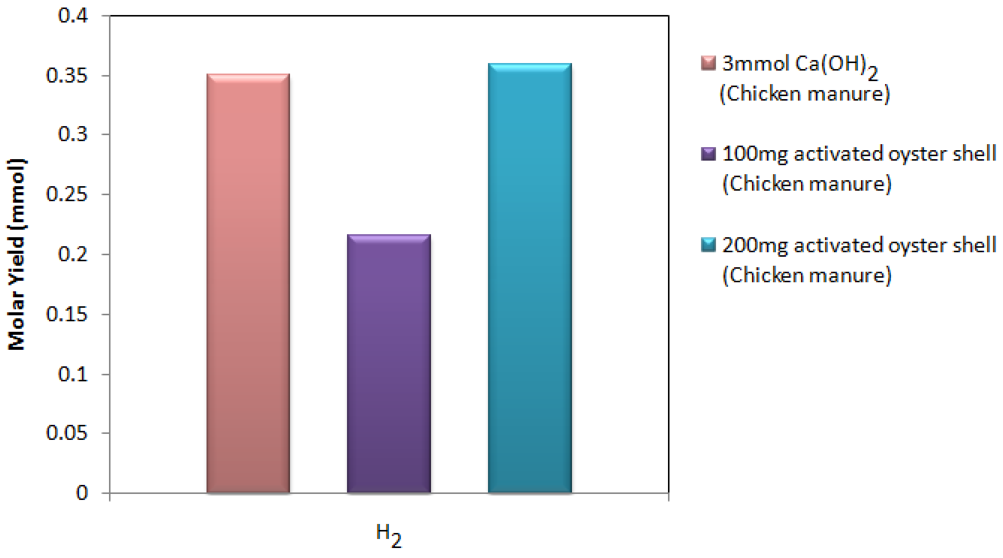

Figure 6.4 Effects of additives on hydrogen yield at 400°C

The XRD patterns of R13, R14, R15, $CaCO_3$, $Ca(OH)_2$ and hydroxylapatite are shown in Fig. 6.5. With R13 and R14, characteristic peaks of $CaCO_3$ are recognized. In R15, characteristic peaks of $Ca(OH)_2$ are observed. In R13, R14 and R15, no peak of hydroxylapatite was observed.

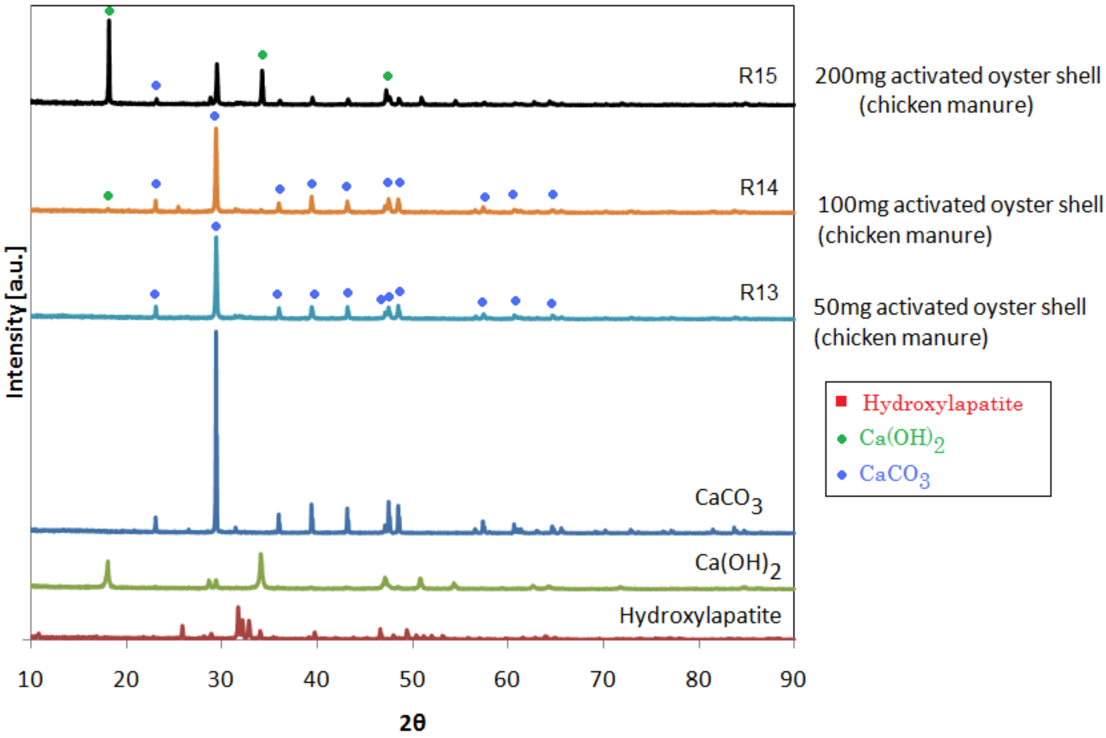

Figure 6.5 XRD patterns of R15, R14, R13, $CaCO_3$, $Ca(OH)_2$ and hydroxylapatite.

6.3 Conclusions

For the biowaste disposal, the activated oyster shell (one of the real biowastes) was used as the additive in place of $Ca(OH)_2$ for the hydrothermal gasification of chicken manure. The hydrogen was produced more efficiently by this method than by the early method with $Ca(OH)_2$. However, the valuable material, hydoxiapatite could not be synthesized by this method.

6.4 References

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Chapter 7 Conclusions

Increase in energy consumption, limited availability and environmental concerns of fossil fuels, security concerns of some energy sources, have all motivated the search for renewable energy sources.

A real biowaste, chicken manure was used in hydrothermal gasification process for producing hydrogen as an energy source in this study. Chicken manure was not a food competitor for human and also for animals. Also by this process, treatment problem of chicken manure was solved and at the same time production of hydroxylapatite was provided as another benefit.

In Chapter 3, the optimum conditions for producing more hydrogen gas were investigated by using O-Phospho-DL-serine and chicken manure samples. Different additives were tested and when $Ca(OH)_2$ was used as an additive in the process, the main produced gas became hydrogen and the generation of CO_2 was suppressed efficiently. Also for the amount of $Ca(OH)_2$ additive, optimum condition was found as 400 °C and 3 mmol for both of the samples .

In chapter 4, possible environmental side effects of this process were investigated by measuring the dioxin levels. Dioxins were determined in the liquid and solid phases of the residues produced by the hydrothermal gasification of chicken manure under various experimental conditions. The highest dioxin levels were found to be less than 3000 $pgTEQg^{-1}$ for the solid and 10 $pgTEQL^{-1}$ for the liquid phase residue, both within the allowable limits in Japan. Using chicken manure in the hydrothermal gasification provides a means of disposing of these biowastes and producing hydrogen as well as the valuable material, hydroxylapatite. The generation of hydrogen gas through the hydrothermal gasification can be conducted without considering the toxicity of dioxins.

In chapter 5, production of hydroxylapatite was clarified. Acetic acid was provided for the purification process of the crude hydroxylapatite. The purified solid residue (700°C for 20 min (R8)) showed XRD peaks that indicated the existence of hydroxylapatite. The pattern confirmed that the phosphorous atom in the sample was converted into the valuable compound, hydroxylapatite, through the hydrothermal gasification. With the use of the calibration curve and the peak height for the resulting hydroxylapatite, about 68.3% of the P in the chicken manure was converted to hydroxylapatite. After the thermal treatment of the crude samples, the pure hydroxylapatite could be obtained by use of 10% acetic acid solution.

In chapter 6, oyster shell was used as the additive instead of $Ca(OH)_2$. Hydrogen gas could be produced also by this method. This approach indicated possibility of producing energy by using chicken manure with biowaste as an additive (chicken manure + biowaste = energy). However, production of hydroxylapatite was not observed for this mixture. For obtaining hydrogen and hydroxylapatie by hydrothermal reaction of biowaste together with other biowaste as the additive, more efficient condition should be found by further study. Other valuable material would be produced by this method.

In this study chicken manure was used as an energy source. Other kinds of biowastes could be used for producing hydrogen through the hydrothermal gasification. Varieties of studies were going on about this subject by using several kinds of biowastes such as, sewage, cattle manure, etc. Some of them were already studied by our laboratory members.

A small size batch reactor was used in this study. For commercial plant, a continuous reactor with high loading capacity should be developed to dispose a huge of chicken manure. Additionally, the system should be operated for a long time with safety. The supercritical water is corrosive to the equipment. Many researchers have studied on solving the corrosion problem by developing new material and trying to reduce the corrosion by changing conditions of hydrothermal gasification. In the near future, the suitable equipment would be produced.

This newly developed method of hydrothermal gasification of chicken manure is a promising method for producing hydrogen as energy and valuable material and for disposing the biowaste. Additionally, this method is one of the answers for solving energy issues in the future.

APPENDIX A

List of Journals

1. Behavior of heteroatom compounds in hydrothermal gasification of biowaste for hydrogen production, S. Yildiz Bircan, H. Kamoshita, R.Kanamori, Y. Ishida, K. Matsumoto,Y. Hasegawa, K. Kitagawa, Applied Energy (2011) Volume 88, Issue 12, December 2011, Pages 4874-4878

2. GC-MS ultra trace analysis of dioxins produced through hydrothermal gasification of biowastes, S. Yildiz Bircan, R. Kanamori, Y. Hasegawa, K. Ohba, K. Matsumoto, K. Kitagawa, Microchemical Journal (2011) Volume 99, Issue 2, November 2011, Pages 556-560

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APPENDIX B

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1. International Symposium on EcoTopia Science 2011, ISETS '11, Nagoya, Japan, Solution of Environmental Issues Originated by Chicken Manure, S. Yildiz Bircan, N. Ichiro, K. Ohba, K. Matsumoto, and K. Kitagawa, (2011.12).
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