Pyrolysis of Sugarcane Bagasse and Polyvinyl Chloride in Superheated Steam Atmosphere

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Chapter 1 General introduction

1.1 Organic waste

The main forms of organic waste are household food waste, agricultural waste, human and animal waste and industrial waste [1-2]. Organic waste is considered as an important source of energy because of the presence of the organic compounds. Organic waste can be converted into energy such as solid and liquid fuels which are renewable and environmentally friendly [3-8]. Dumping and landfilling normally used for the treatment of household and industrial wastes while agricultural and human and animal wastes were treated by biological treatment [9]. The other method for treating these wastes are thermal treatment such as incineration, gasification and pyrolysis [10].

1.2 Pyrolysis process

Pyrolysis, the organic (carbon-based) materials decomposes chemically through the application of heat in the absence of oxygen or low oxygen level. The word is derived from the Greek words “pyro” meaning fire and “lysis” meaning decomposition. There are three types of pyrolysis depending on the operating conditions: slow pyrolysis or carbonization (550-950 K), intermediate pyrolysis (850-1250 K) and fast pyrolysis (1050-1300 K) [11]. The main goal for slow pyrolysis or carbonization is production of charcoal with lower moisture content and higher energy content while the main target products of intermediate and fast pyrolysis are bio-oil [11-16]. Pyrolysis products can be used as substitute charcoal or as industrial fuel [1, 17]. In pyrolysis process, product yield and quality can be influenced by many factors such as: catalysts, contact time, feed pretreatment, feed material, heating rate, particle size, moisture content, pressure, reactor geometry, temperature, residence time, reagents and treatment atmosphere [18].

1.3 Sugarcane bagasse carbonization

Sugarcane is used as a feedstock for ethanol and sugar production. Sugarcane bagasse is the residual material derived from sugarcane after extracting cane juice. Bagasse is discarded as agricultural waste or burned for energy supply in sugar and ethanol mill. Bagasse is a lignocellulosic compound which contains cellulose, hemicellulose and lignin. The decomposition of these components occurs at different temperatures during the pyrolysis [19]. Hemicellulose typically decomposes in the range of 433- 633 K, while cellulose degrades at the higher temperature range of 513-663 K and lignin at 550-770 K. Biochar, bio-oil and gaseous products are the main product that can be obtain during the pyrolysis at different operating conditions. Biochar mainly obtained during carbonization and can be use as adsorbent (activated carbon), catalyst support, fuel feedstock, and soil fertilizer [20]. The bio-oil is the main product of fast pyrolysis, which has a great potential to be used in the equipment such as static engines, turbines, burners, boilers, and diesel engines. Gaseous products are obtained mainly at higher temperatures, and can be consumed to generate heat for pyrolysis reactor, to run a gas turbine for electricity generation, and to produce syngas that can be converted into gasoline and diesel through Fischer-Tropsch process. The hydrogen obtained from pyrolysis can be applied in hydrotreating processes, ammonia production, and in fuel cells [20].

1.4 Polyvinyl Chloride (PVC) dechlorination

Polyvinyl chlorine (PVC) is one the widely used plastic polymer after polyethene (PE) [21-23]. PVC is widely used in use in building, transport, packaging, electrical/electronic components and healthcare applications [11]. PVC is obtain from the polymerization of vinyl chloride monomer (VCM) with general chemical formula: -(CH_2CHCl)n- as shown in Fig. 1-1. The disposal of PVC become a major environmental issue because it is non-biodegradable and contain chlorine compound which could be released during waste treatment and cause the corrosion of the boiler and other environmental problems [3,7, 13-30]. Usually PVC waste was treated using thermal degradations such as pyrolysis, gasification and combustion. The main objective for the PVC treatment is to remove the chlorine because it will cause the corrosion of the treatment plant and other environmental problems. The degradation of PVC under pyrolytic conditions can be divided into two stages [31-33]. In the first stage at temperature around 600 K, the degradation is mostly by dehydrochlorination and followed by the formation of polyene, and others aromatic products. The second stage starts at temperature around 750 K with the degradation of polyene leading to the evolution of aromatic compounds such as benzene, toluene, naphthalene, indene, and various chlorobenzenes. Stepwise pyrolysis, catalytic pyrolysis and pyrolysis with adsorbent were the main pyrolysis method used [34-35]. During stepwise pyrolysis, maximum chlorine released from PVC at 573 K [36-37]. In catalytic pyrolysis, solid acid catalysts and metal oxides can increase the chlorine removal rate and some of metal oxide can act as adsorbent which will suppress the HCl formation [34, 38]. The pyrolysis with adsorbents of catalysts usually carried out with the alkali compound such as KOH, NaOH, $Ca(OH)_2$, CaO, Na_2CO_3 etc. The addition of these adsorbents will trap evolved HCl in the solid sample by physical or chemical adsorption [34].

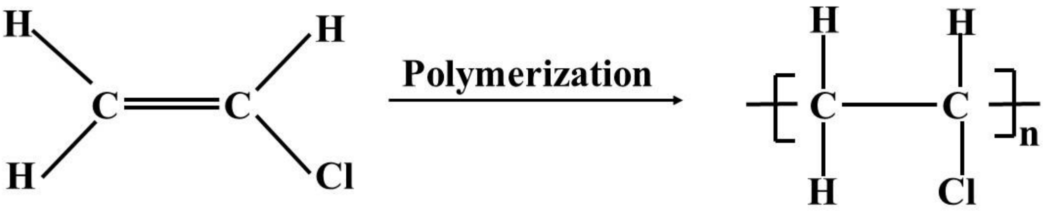

Fig. 1-1 Polymerization of vinyl chloride to PVC.

1.5 Superheated steam

Superheated steam is produced by heating saturated steam to the temperatures higher than the boiling point of water [39-42]. Superheated steam usually used in the food, medical, and other industries where cleaning, disinfection, and drying play a crucial role. During the drying process, superheated steam can be act both as dry hot gas and as steam [43]. Compared with hot air and inert gas at the same temperature, this superheated steam has very unique properties such as, 1) high temperature at normal temperature, 2) Extremely high thermal conductivity, 3) a higher heating rate due to radiative heating in addition to convective heating as illustrated in Fig. 1-2, and 4) in low oxygen conditions [43-49]. The only problem of using superheated steam is that a large amount of energy needed to generate superheated steam compared with hot air or gas at the same temperature. The only way to solve this problem is to make use of the extra energy for superheated steam generation at works such as steelmaking plant etc.

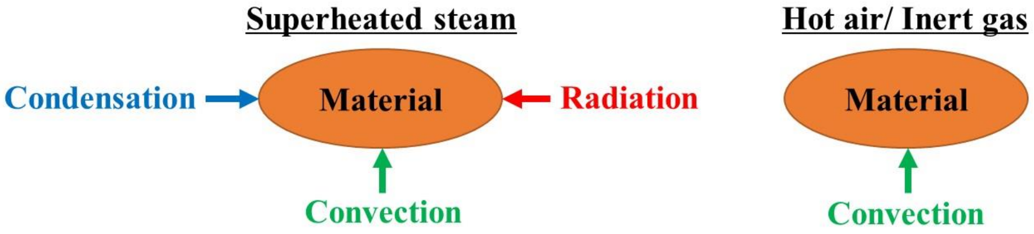

Fig. 1-2 Superheated steam drying properties.

1.6 Research objectives

A considerable amount of research has been conducted in the area of organic waste pyrolysis process using inert gas such as nitrogen. Less attention has been paid to the others pyrolysis atmospheres such as superheated steam and CO_2. Superheated steam is produced by heating saturated steam to the temperature higher than boiling point. Compared with hot air and inert gas at the same temperature, this superheated steam has very unique properties such as, 1) a higher heating rate due to radiative heating in addition to convective heating, 2) higher specific enthalpy 3. Thus, using superheated steam in the pyrolysis atmosphere may lead to substantial energy saving if no oxidation occurs [50-51]. The main purposes of the research are to study the pyrolysis behavior of two types of organic wastes with, sugarcane bagasse and polyvinyl chloride (PVC) under superheated steam atmosphere. In the case of sugarcane bagasse, the effect of superheated steam on the yield of carbonization products and the heat transfer properties steam were investigated. In the case of low temperature pyrolysis of PVC, effect of pyrolysis atmosphere such as superheated steam and nitrogen on the dechlorination of PVC were investigated. Furthermore, the effects of addition of chemicals, adsorbents and catalysts such as solid acid catalysts, alkali adsorbents and metal oxides on the dechlorination of PVC were investigated.

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Chapter 2 Carbonization of sugarcane bagasse and heat transfer property by pyrolysis in superheated steam and nitrogen atmospheres

2.1 Introduction

Recently, the utilization of biomass resources has gained many interests due to the depletion of fossil fuel. Biomass is also one of the organic wastes which are produced in agriculture and forestry [1]. Biomass waste can be converted into biofuels which are renewable and environmentally friendly [1, 2]. Carbon, hydrogen, oxygen and nitrogen are the most common substances in biomass [3]. The main elemental composition of woody biomass is carbon (52.0 wt%), oxygen (40.5 wt%), hydrogen (6.3 wt%), and nitrogen (0.4 wt%) [3]. Meanwhile, proximate analysis of that woody biomass contains volatile matter (80.0 wt%), fixed carbon (19.4 wt%), and ash (0.65 wt%) [4-7].

Physical, biological and thermochemical processes are normally being used to convert biomass to energy [4]. Grinding, drying, filtration, pressing, extraction, and briquetting are the example of physical process pretreatment before being used in another process. Biological process includes anaerobic digestion and fermentation. Thermochemical process can be divided into gasification, pyrolysis and combustion [5, 8]. Pyrolysis is a process which converts biomass into liquid (tar and other organics), solid (charcoal) [9, 10], and gaseous products (H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6) by heating biomass in the absence of oxygen or very low oxygen level [4]. There are three types of biomass pyrolysis depending on the operating conditions: slow pyrolysis or carbonization (550-950 K), intermediate pyrolysis (850-1250 K) and fast pyrolysis

(1050-1300 K) [11]. The main goal for slow pyrolysis or carbonization is charcoal with lower moisture content and higher energy content while the main goal for intermediate and fast pyrolysis are bio-oil [4, 11-17]. Pyrolysis products can be used as substitute charcoal or as industrial fuel [1, 18]. In biomass pyrolysis, product yield and quality can be influenced by many factors such as: catalysts, contact time, feed pretreatment, feed material, heating rate, particle size, moisture content, pressure, reactor geometry, temperature, residence time, and reagents [19]. A considerable amount of research has been conducted to the pyrolysis process using inert gas such as nitrogen. Less attention has been paid to the others pyrolysis atmospheres such as superheated steam.

Superheated steam is produced by heating saturated steam to the temperature higher than boiling point [20-23]. Compared with hot air and inert gas at the same temperature, this superheated steam has very unique properties such as, 1) a higher heating rate due to radiative heating in addition to convective heating, 2) higher specific enthalpy [20, 24-29]. Thus, using superheated steam in the pyrolysis atmosphere may lead to substantial energy saving if no biomass oxidation occurs.

The main purpose of this research is to investigate the carbonization of sugarcane bagasse and heating property via superheated steam and nitrogen gas heating. Sugarcane bagasse was used as a material of the organic wastes in this research because of their high thermal value when dried [30]. Sugarcane bagasse is the residual material derived from sugarcane after extracting cane juice. Bagasse is carbon-rich biomass and suitable for biochar production. One of the possible ways to obtain high thermal value sugarcane bagasse is to convert to biochar by carbonization process. Some studies have been devoted to the problems of sugarcane bagasse hydrolysis to obtain sugar and furfural [31, 32], but less attention has been paid to the sugarcane bagasse carbonization using superheated steam. In this research, the temperature increasing behavior and carbonization of the sugarcane bagasse under superheated steam and nitrogen atmosphere has been investigated and the results of both methods were compared.

2.2 Experimental

2.2.1 Method

Carbonization of the bagasse was conducted using the superheated steam device (Dai-ichi High Frequency Co. Ltd., Hi-HEATER 2005S) as shown in Fig. 2-1. The equipment consists of a boiler, a superheated steam generator, and a reaction chamber. Steam was produced from the boiler and then the temperature was risen to the setting temperature using superheated steam generator. Two thermocouples (A, B) were attached to the reaction chamber (A) and sample (B) to measure chamber and sample temperature.

First, superheated steam temperature, T_{shs} [K], in the chamber was set to the experimental temperature (491,541, 579, 617, 650, and 702 K). When the chamber temperature became almost constant, 5 g of the dried pellet as described in 2.3 was inserted in a sample basket, and placed in the chamber. Carbonization was carried out for 5, 10, 15, 20, 25 and 30 minutes at all temperatures. The flow rate of superheated steam in the reaction chamber was fixed to 10 kg/h. After the carbonization finished, sample was cooled down below 343 K. Then, the sample was dried at 383 K for 24 h to remove condensed water trapped in the carbonized residue.

On the other hand, carbonization via nitrogen gas was carried out by using the electric furnace (As One Co. Ltd., TMF-500N) shown in Fig. 2-2. The reaction tube and sample temperatures were measured by two thermocouples (A, B) attached on the outer wall of the reaction tube (A) and sample (B), respectively. The reaction tube temperature, T_{N2} [K], was set to be equal to T_{shs} [K] for superheated steam such as 491, 541, 579, 617, 650 and 702 K. The effect of carbonization time for nitrogen heating was studied at T_{N2} = 617 K (T_m=592 K) for 5-30 min. Nitrogen flow rate in the reaction chamber was fixed to 6.0 kg/h. Sample preparation and experimental setting is the same as superheated steam carbonization.

The relationship between the chamber (superheated steam) or reaction tube (nitrogen gas) and sample temperatures at 30 min is shown in Table 2-1. The sample temperature, T_m [K], in the reaction tube of Fig. 2-2 became finally lower than that of superheated steam in Fig. 2-1.

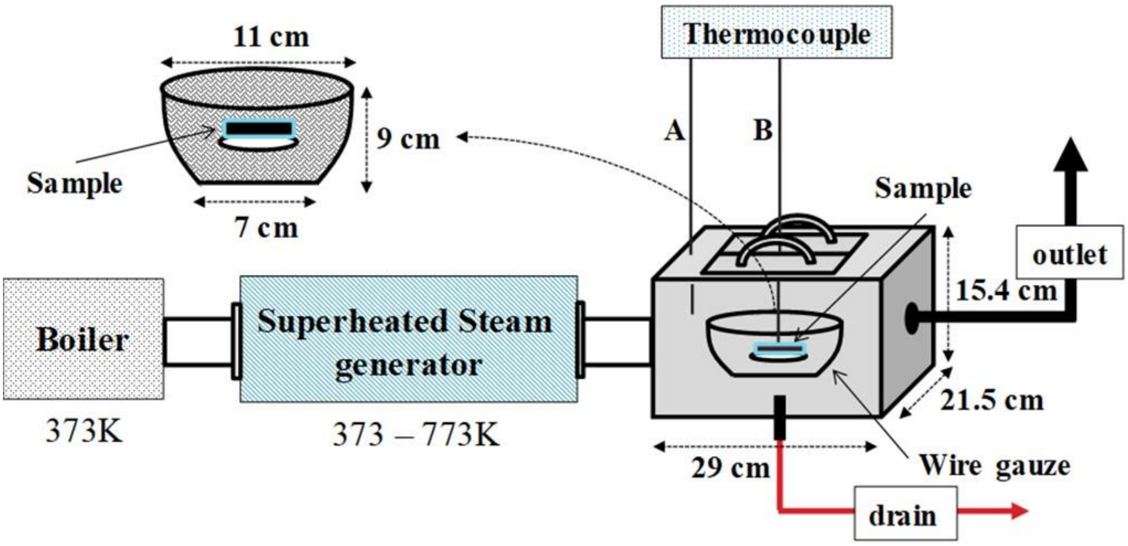

Fig. 2-1 Schematic diagram of superheated steam device.

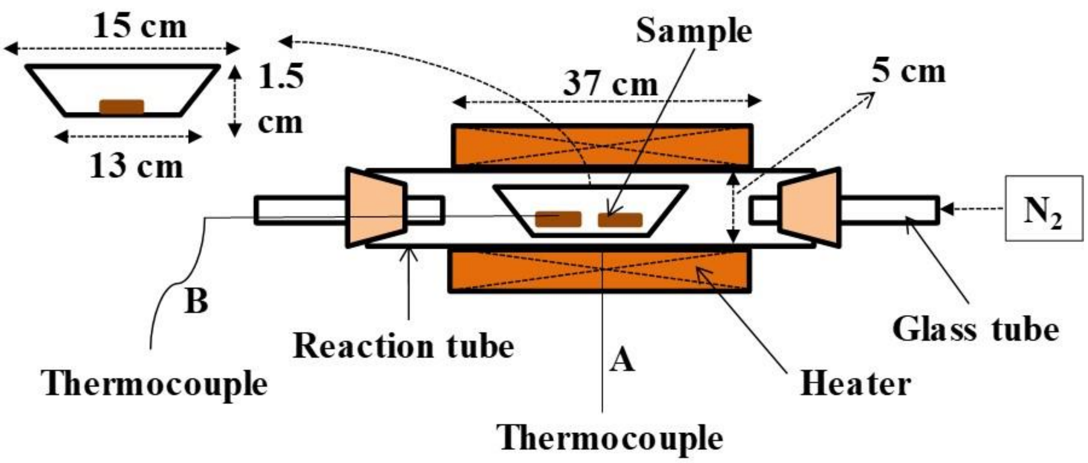

Fig. 2-2 Schematic diagram of electric furnace.

Table 2-1 Temperatures of chamber or reaction tube and sample for superheated steam and nitrogen heating practices at 30 min.

Superheated steam		Nitrogen gas	
Chamber temperature, T_{shs} [K]	Sample temperature, T_m [K]	Reaction tube temperature, T_{N2} [K]	Sample temperature, T_m [K]
491	490	491	471
541	539	541	503
579	576	579	554
617	616	617	592
650	647	650	615
702	701	702	663

2.2.2 Characterization of bagasse

The remaining of the sample after carbonization was measured for the char yield. The char yield was calculated using the following equation:

$$\text{Char yield [wt\%]} = \text{(Sample residue weight after carbonization [g])/ (Solid weight before carbonization [g])} \times 100 \tag{1}$$

Elemental analysis of the sample was done before and after carbonization. Carbon, C [wt%], hydrogen, H [wt%] nitrogen, N [wt%] and sulfur, S [wt%] contents were analyzed by CHNS analyzer (Perkin Elmer series, 2004 II) for the ultimate analysis. While oxygen, O, [wt%] content was calculated from the equation below.

$$O = 100 - (C + H + N + S) \tag{2}$$

Higher heating value, HHV [kJ/kg], of the sample can be calculated with ultimate analysis data and the equations can be obtained as follows [33]:

$$HHV = 343.08C + 424.92\mathrm{H} + 261.98\mathrm{N} + 27.76\mathrm{O} \tag{3}$$

Carbon losing rate was calculated using the following equation:

$$\text{Carbon losing rate [wt\%]} = \{(W_{\mathrm{INIT}}C_{\mathrm{INIT}} - W_{\mathrm{FIN}}C_{\mathrm{FIN}}) / (W_{\mathrm{INIT}}C_{\mathrm{INIT}})\} \times 100 \tag{4}$$

where W_{INIT} and C_{INIT} are the initial weight [g] and carbon content [wt%] of sugarcane bagasse, respectively, while W_{FIN} and C_{FIN} are the weight [g] and carbon content [wt%] of the sample after carbonization, respectively.

2.2.3 Sample preparation

Sugarcane bagasse from Okinawa, Japan, was selected as a raw material in this study. Tables 2-2 and 2-3 show the ultimate and proximate analyses [34], respectively. Carbon, hydrogen, nitrogen and oxygen were recognized from the ultimate analysis. The fixed carbon became 20.4 wt% and HHV was calculated from Eq. (3) as shown in Table 2-3.

In order to make it easy to put it in the sample basket, the sample was pelletized. After grinded in a mixer, the resulting pulverized bagasse was dried in a dryer at temperature of 383 K for 24 h to remove the moisture content from the sample. It was compressed using a hydraulic presser to obtain the pellet form of the bagasse. The pellets were also dried in a dryer at temperature of 383 K for 24 h prior to the experiment. Photographic image of the pellet used for the experiment is shown in Fig. 2-3.

Table 2-2 Ultimate analysis of raw material (dry basis).

C [wt%]	H [wt%]	N [wt%]	S [wt%]	O [wt%]
46.0	6.2	0.4	0.9	46.5

Table 2-3 Proximate analysis of raw material.

Volatile matter [wt%]	Fixed carbon [wt%]	Ash [wt%]	HHV [MJ/kg]
78.7	20.4	0.9	19.8

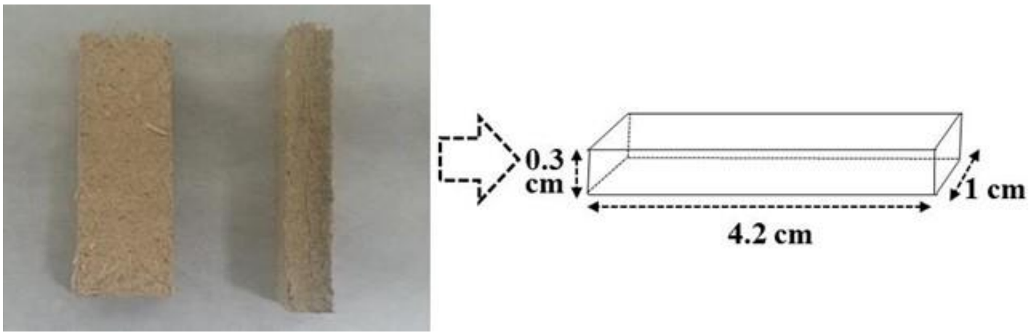

Fig. 2-3 Photographic image of the sample pellet.

2.3 Results and discussion

2.3.1 Char yield

Figure 2-4 shows the effect of carbonization time on the char yield in superheated steam and nitrogen gas. Both char yields in superheated steam and nitrogen gas atmospheres decreased at the first 10 to 15 minutes and became constant within 25-30 minutes of carbonization.

The relationship between the char yield and carbonization temperature at carbonization time of 30 min is shown in Fig. 2-5. The char yield decreased with the increasing temperature and there was no different tendency between superheated steam and nitrogen gas. This suggests that the oxidation rate of carbon by superheated steam is very small and negligible.

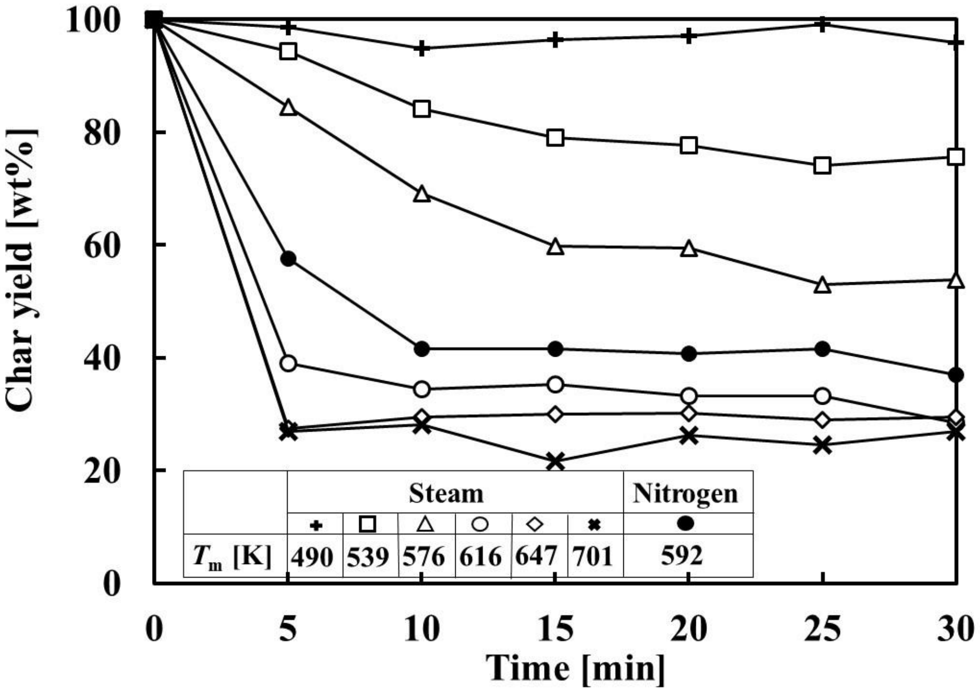

Fig. 2-4 Temporal change in char yield for superheated steam and nitrogen gas.

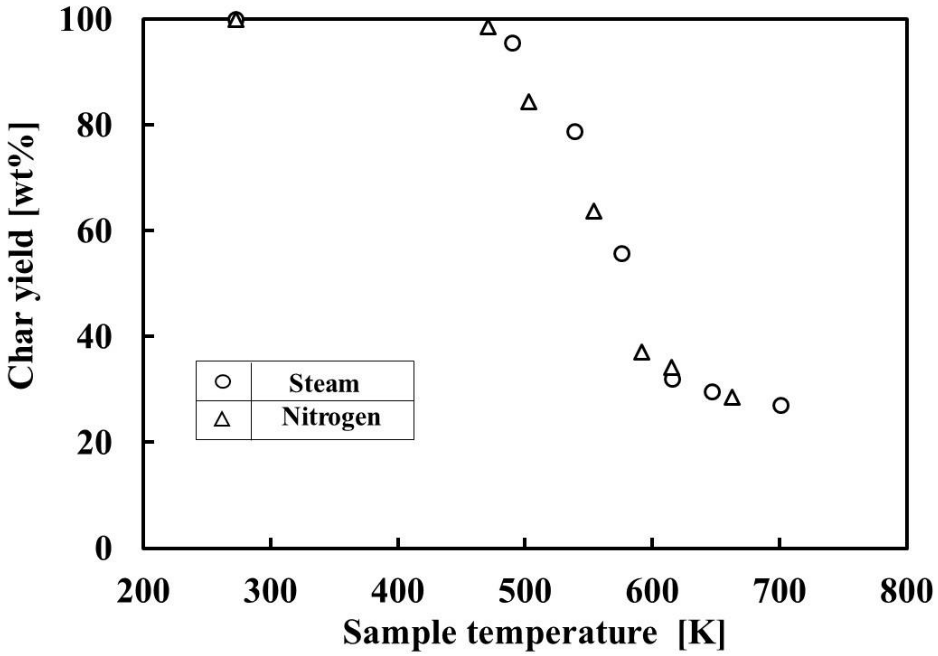

Fig. 2-5 Relationship between char yield and sample temperature at 30 min of carbonization.

A possibility of carbon oxidation by superheated steam was examined by thermodynamic equilibrium [34]. The relationship between Gibbs free energy, ΔG [J/mol], of $C + H_2O \rightarrow CO + H_2$ and $(1/2)\ C + H_2O \rightarrow (1/2)\ CO_2 + H_2$ and temperature with P_{H2}/P_{H2O} as a parameter is shown in Fig. 2-6. It was found that $\Delta G<0$, that is, the oxidation reaction of carbon may occur according to temperature and P_{H2}/P_{H2O}. For example, when the char yield in Fig. 2-4 reduced to 25wt % at T_m=701 K at 5 min and the sample carbon content was 60.8 wt.% as described later in Table 2-5, P_{H2}/P_{H2O} of $C + H_2O \rightarrow CO + H_2$ and $(1/2)\ C + H_2O \rightarrow (1/2)\ CO_2 + H_2$ were calculated as 0.003 and 0.006. Thus, from Fig. 6, these ΔG values became -3×10^4 and -4×10^4 J/mol, respectively, and the oxidation of carbon was possible thermochemically. In conclusion, the oxidation rate of carbon by superheated steam was negligible small in this experiment.

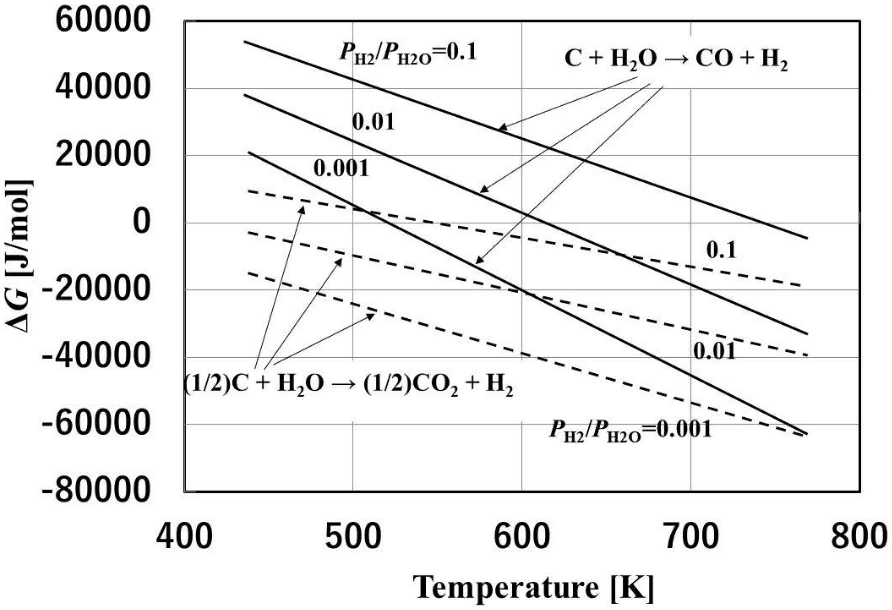

Fig. 2-6 Relationship between Gibbs free energy change of water gas reaction and temperature in superheated steam.

2.3.2 Elemental analysis

Table 2-4 presents an example of temporal change in the sample composition at T_m of 616 K for the treatment in superheated steam and 592 K for nitrogen, respectively. There was only a small difference in the char composition between both carbonization atmospheres at each carbonization time. The temperature rising in superheated steam was unstable at the first 10 minutes of carbonization which resulted in the increasing and decreasing in the carbon content. The effect of sample temperature on the composition at 30 min of carbonization time is shown in Table 2-5. The increasing carbonization temperature resulted in the increase of carbon contents and decrease of oxygen contents [35], however the carbon content decreased and the oxygen content increased at the sample temperature of 701 K in superheated steam and 663 K in nitrogen gas. It might be due to secondary cracking of the char into gaseous products [36, 37].

Table 2-4 An example of temporal change in sample composition for superheated steam and nitrogen heating practices.

Time [min]	Superheated steam at T_m = 616 K [wt%]					Nitrogen gas at T_m = 592 K [wt%]				
	C	*H*	*N*	*S*	*O*	*C*	*H*	*N*	*S*	*O*
0	46.0	6.2	0.4	0.9	46.5	46.0	6.2	0.4	0.9	46.5
5	62.5	4.7	0.6	0.7	31.5	58.1	4.7	0.5	0.7	36.0
10	57.6	4.8	0.6	0.7	36.3	64.6	4.0	0.6	0.6	30.2
15	60.3	4.3	0.6	0.7	34.1	62.4	3.3	0.6	0.5	33.2
20	62.8	4.1	0.7	0.7	31.7	62.3	4.4	0.6	0.6	32.1
25	62.9	4.2	0.6	0.6	31.7	63.0	4.6	0.6	0.7	31.1
30	63.4	4.4	0.6	0.7	30.9	62.2	3.7	0.7	0.4	33.0

Table 2-5 Effect of sample temperature on product composition at 30 min of carbonization time.

	Superheated steam [wt%]						Nitrogen gas [wt%]				
Sample temperature [K]	*C*	*H*	*N*	*S*	*O*	Sample temperature [K]	*C*	*H*	*N*	*S*	*O*
Raw material	46.0	6.2	0.4	0.9	46.5	Raw material	46.0	6.2	0.4	0.9	46.5
490	47.3	6.2	0.4	0.9	45.2	471	47.0	6.0	0.3	0.9	45.8
539	50.1	6.0	0.4	0.9	42.6	503	48.6	5.7	0.4	0.9	44.3
576	54.5	5.7	0.5	0.7	38.6	554	52.8	5.5	0.5	0.8	40.4
616	63.4	4.4	0.6	0.7	30.9	592	62.2	2.7	0.7	0.4	34.0
647	64.1	4.0	0.6	0.6	30.7	615	65.8	4.0	0.6	0.6	29.0
701	60.8	3.2	0.7	0.5	34.8	663	63.7	2.5	1.1	0.4	32.3

Figure 2-7 shows an example of Thermogravimetric analysis (TGA) curve of sugarcane bagasse. The TGA curve was measured under nitrogen atmosphere with flow rate of 200 ml/min and heating rate of 5 K/min. Weight loss of the sample starts with the evaporation of water (350 K) and followed by decomposition of hemicellulose (470-530 K), cellulose (510-620 K) and lignin (550-770 K). The carbonization via superheated steam and nitrogen gas seems to proceed due to the thermal decomposition as shown in Fig. 2-6.

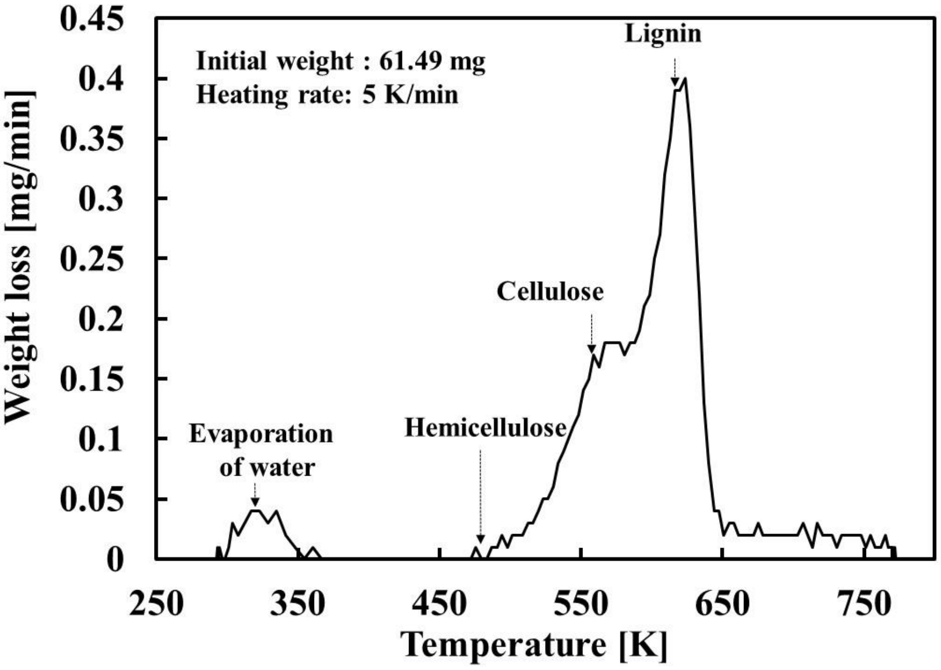

Fig. 2-7 An example of TGA curve of bagasse.

2.3.3 Higher heating value (HHV)

The HHV for both atmospheres of superheated steam and nitrogen gas were calculated by Eq. (3) to evaluate the quality of char as a fuel. Figure 2-8 shows the effect of carbonization temperature on the HHV. Carbon is the element that increases the heating value while oxygen is the element that suppresses the heating value of char. With the increase in carbonization temperature, the HHV remained almost constant until about 500 K, increased until about 650 K and decreased slightly after that as shown in Fig. 2-7. The decrease in the HHV was due to the decreasing carbon content at this temperature as shown in Table 2-5. As described before, the secondary cracking of the char into gaseous products seems to cause the decrease in carbon content above the temperature around 650 K.

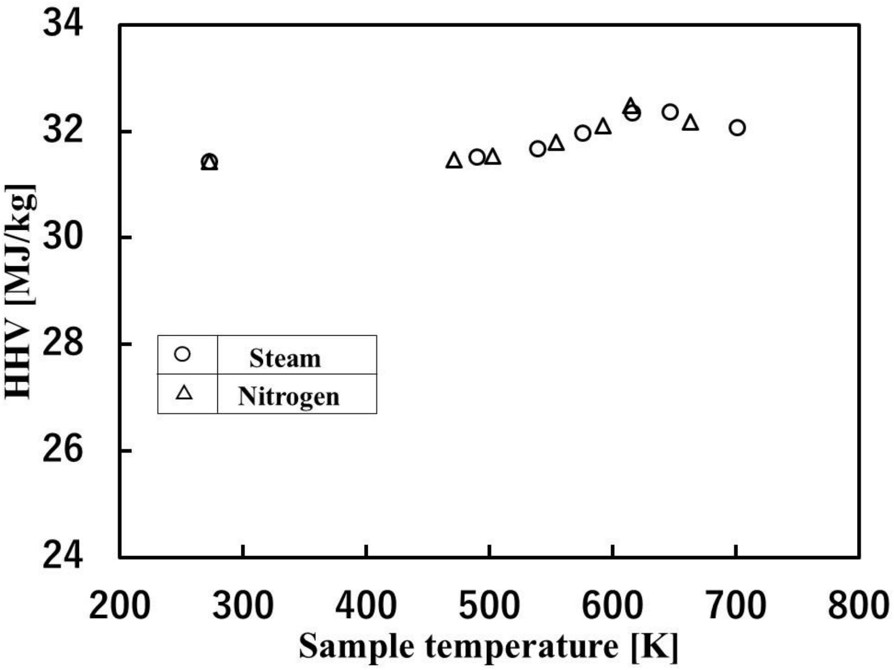

Fig. 2-8 Relationship between higher heating value and sample temperature in superheated steam and nitrogen gas heating practices at 30 min of carbonization.

2.3.4 Carbon losing rate

The effect of carbonization time on the carbon losing rate calculated by Eq. (4) is shown in Fig. 2-9. The results indicated that the carbon losing rate for both superheated steam and nitrogen have the same trend, that is, the carbon losing rate increased until 10 min and after that it was almost kept constant. Due to the difference of sample temperature between superheated steam and nitrogen, superheated steam practice had a higher carbon losing rate compared with nitrogen.

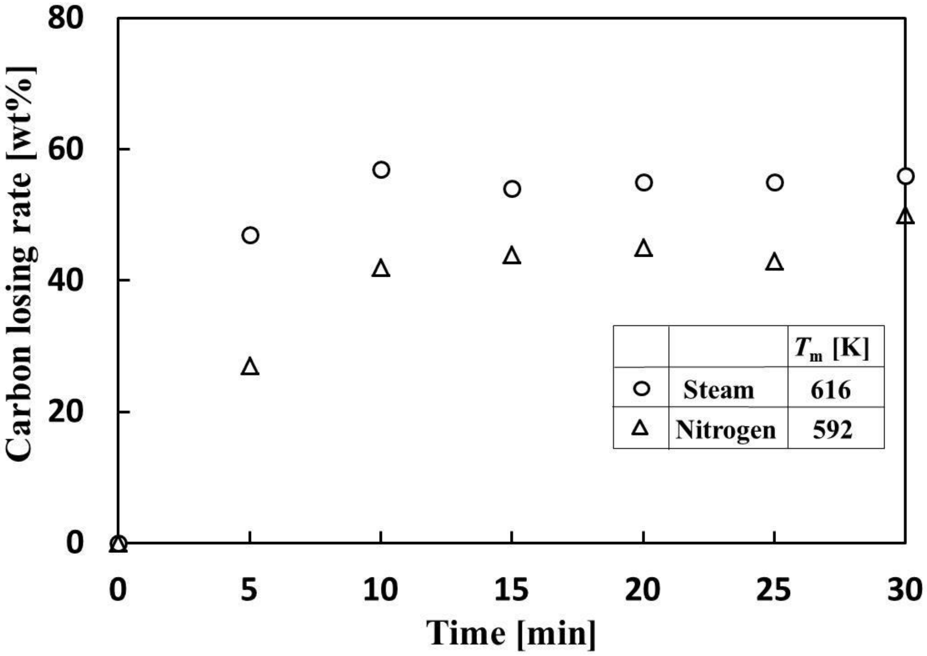

Fig. 2-9 Change in carbon losing rate with time.

Figure 2-10 shows the effect of carbonization temperature on the carbon losing rate for superheated steam and nitrogen practices at 30 min of carbonization time. Carbon losing rate increased with the increase in carbonization temperature for both methods. There was no different trend between superheated steam and nitrogen heating practices. It suggests that the pyrolysis by superheated steam occurs without oxidation and hence the char yield in both cases were almost the same in Fig. 2-5.

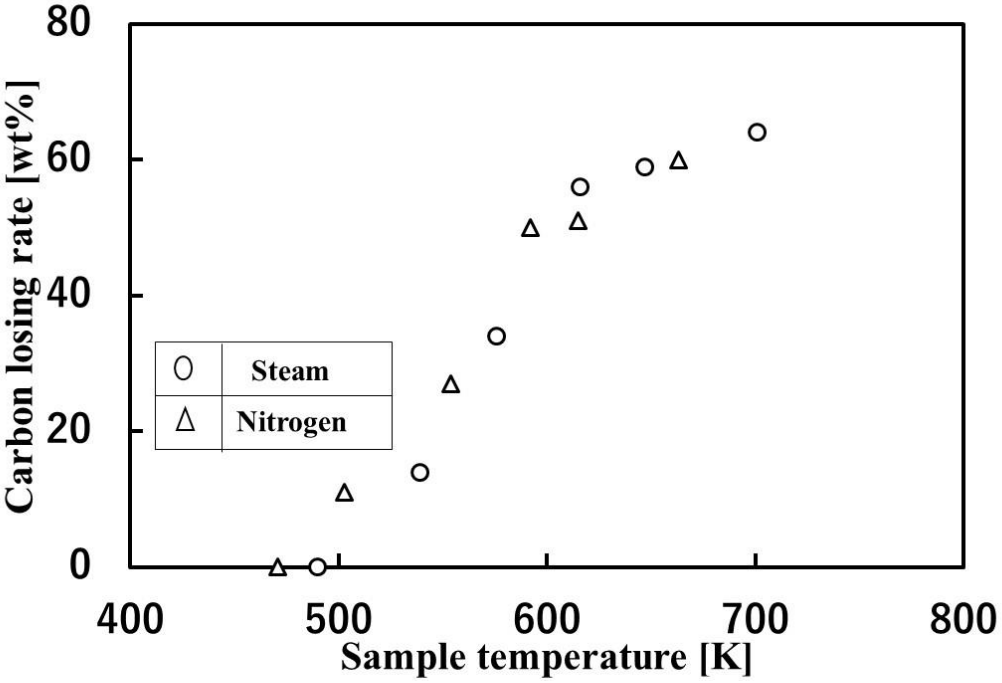

Fig. 2-10 Relationship between carbon losing rate and sample temperature at 30 min of carbonization.

2.3.5 Calculation model for heat transfer behavior of superheated steam and nitrogen in bagasse pyrolysis

Heat transfer of superheated steam and nitrogen heating practices has been studied in this research. Superheated steam dries the material by convection, radiation and condensation heat transfers compared with hot air or nitrogen gas which only dries through convective heat transfer [20, 24, 28, 29, 38]. Heat transfer properties of superheated steam can be calculated by using a heat balance equation as follows [39]:

$$hA(T_{shs} - T_m) + \varepsilon_{12}\sigma A(T_{shs}^4 - T_m^4) + m_0(dW/dt)r_s = \{m_0(C_0 + WC_w)\}(dT_m/dt) \qquad (5)$$

where, h: heat transfer coefficient [W/m^2·K], A: surface area of sample [m^2], T_{shs} : steam temperature [K], T_m : sample temperature [K], ε_{12} : emissivity of superheated steam and sample [-], σ: Stefan–Boltzmann constant [W/m^2·K^4] , m_0 : sample weight [kg], r_s : latent heat of condensation [J/kg], C_0 : specific heat of sample (= 2000 [J/kg·K]) [39], W : water content in sample [kg-water/kg-sample] , C_w : specific heat of water [J/kg·K].

The left side of Eq. (5) is convection, radiation and condensation heat transfers, respectively, and at the right side is the sensible heat of the sample. The following assumptions should be given to obtain the proper calculation.

1) There is no steam condensation during the carbonization because the experimental temperature is sufficiently high.
2) Each heat transfer coefficient of superheated steam and nitrogen heating is constant in the temperature range of this experiment.

According to the above assumption 1) and the initial water content, W_i = 0 [kg-water/kg-sample], in this experimental condition, terms of the water condensation and the heat of evaporation can be neglected in Eq. (5), that is, $dW/dt = W = 0$.

The h value in Eq. (5) was changed until the calculated sample temperature matched with the experimental temperature. Using ε_{12} described in 2.3.6, heat balance equation of Eq. (5) was solved by Runge-Kutta Fehlberg method.

2.3.6 Setting of emissivity, ε_{12}

Emissivity between superheated steam and the sample were calculated by using the following equation:

$$1/\varepsilon_{12} = 1/\varepsilon_1 + A_1/A_2\{(1/\varepsilon_2)-1\} \tag{6}$$

where ε_1 is biomass sample emissivity [-], ε_2 is superheated steam emissivity [-], A_1 is surface area of the sample [m^2], and A_2 is the surface area of superheated steam [m^2]. Emissivity of the sample used in this research was 0.90 which is the emissivity value of woody biomass. Effective gas thickness, L_G [m], of the superheated steam is required for the calculation of the emissivity, ε_2, of the superheated steam and can be calculated using the equation below [39].

$$L_G = 4 \times (\text{Volume of superheated steam /surface area of superheated steam}) \times 0.85 \tag{7}$$

Volume and surface area of superheated steam were calculated from the size of the reaction chamber used in this experiment (Fig. 2-1) and the effective gas thickness became 0.17 m. From the superheated steam radiation diagram and L_G =0.17 m, the value of superheated steam emissivity, ε_2, was 0.29 at 491 K, 0.28 at 541 K, 0.27 at 579 K, 0.26 at 617 K, 0.26 at 650 K and 0.24 at 663 K, respectively [40]. Finally, the emissivity between superheated steam and the sample was calculated and the result was 0.88 at all temperatures.

2.3.7 Comparison of sample temperature change between experimental and calculated values

Figure 2-11 shows the temporal change in sample temperature of the experiment and calculation for superheated steam practice. The sample temperature increased rapidly and became constant until 5 min. Most of the results showed a good agreement between the calculated and experimental temperature when $h = 7\ \mathrm{W/m^2 \cdot K}$ was used. The temporal change in sample temperature of the experiment and calculation with no radiation, that is, $\varepsilon_{12}\sigma A(T_{\mathrm{shs}}^4 - T_{\mathrm{m}}^4) = 0$ in Eq. (5) is shown in Fig. 2-12. The calculated curve increased more slowly than the experimental one. Thus, the radiation heat transfer by superheated steam played an important role in the pyrolysis of sugarcane bagasse [40].

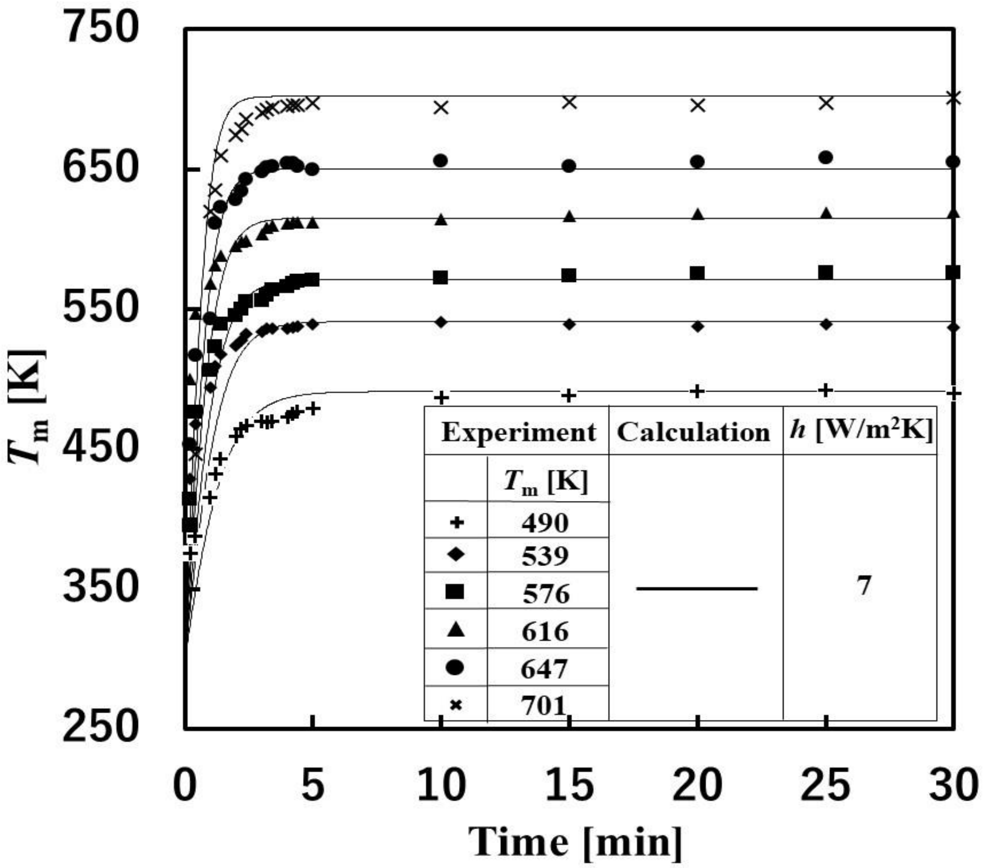

Fig. 2-11 Experimental and calculated sample temperature change with time for superheated steam heating.

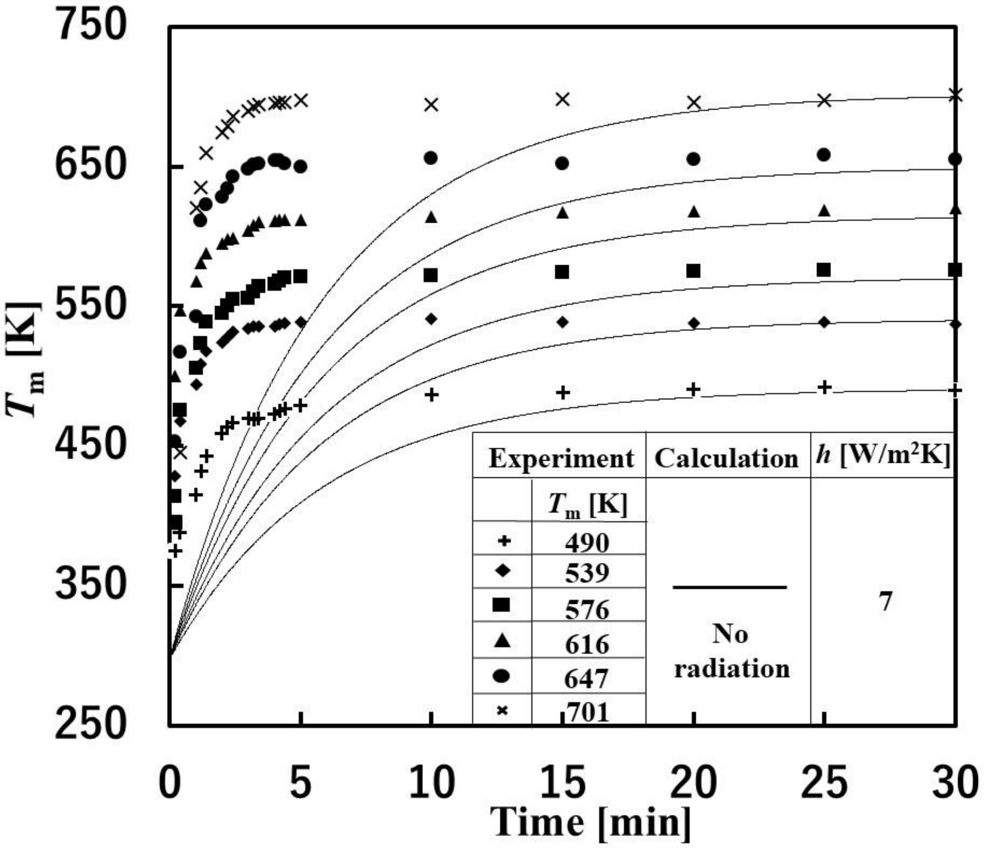

Fig. 2-12 Experimental and calculated sample temperature change with time for superheated steam heating (calculation of no radiation).

Two kinds of the temporal change in sample temperature of the experiment and calculation for nitrogen gas using electric furnace is shown in Fig. 2-13. Here, the calculation model of nitrogen only consists of convective heat transfer because neither condensation nor radiation occurs during the carbonization with nitrogen gas. The experimental sample temperature was moderately increased and held constant between 10 and 15 min. A good agreement was achieved between the experiment and calculation when the value of h=9 W/m$^2 \cdot$K in Eq. (5) was used.

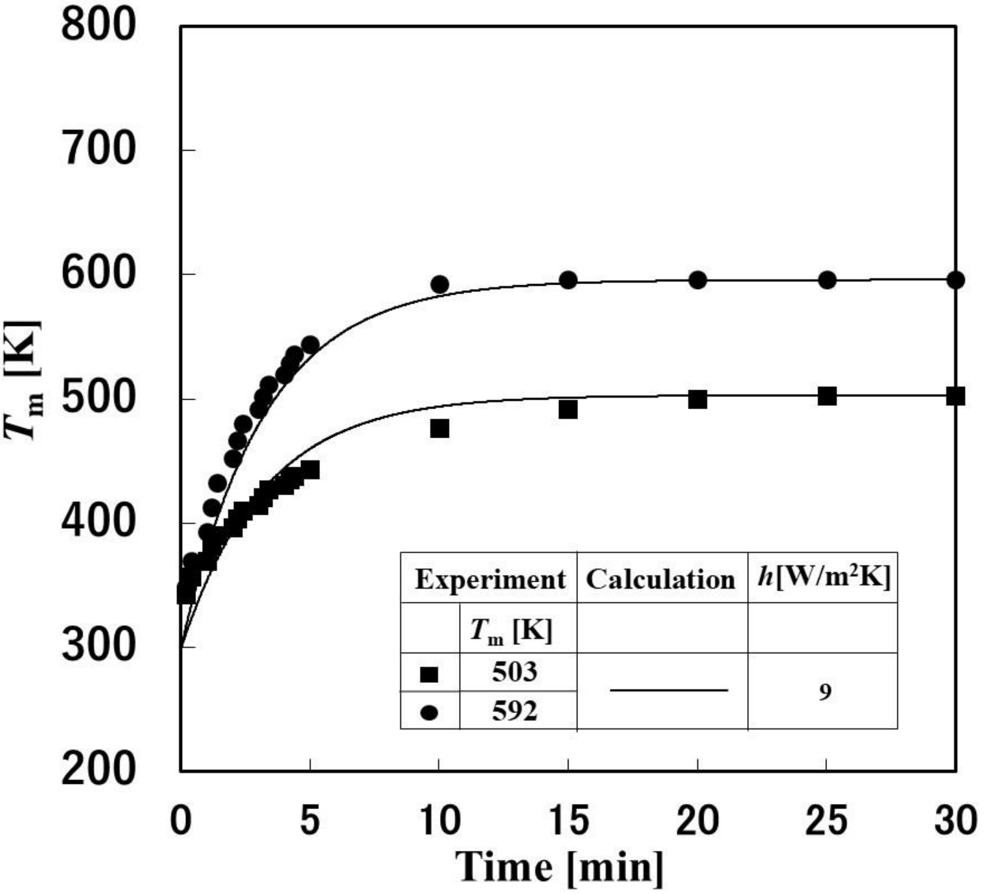

Fig. 2-13 Experimental and calculated sample temperature change with time for nitrogen gas heating.

The difference of the h value between superheated steam and nitrogen is estimated to be due to the physical properties and the experimental conditions.

The correlation for heat convection of fluid parallel to flat plate is given by Eq. (8). [41].

$$Nu \propto Re^{1/2}\, Pr^{1/3} \tag{8}$$

$$Nu \equiv hL/\lambda \tag{9}$$

$$Re \equiv \rho ud/\mu \tag{10}$$

$$Pr \equiv C_p\mu/\lambda \tag{11}$$

Here, Nu: Nusselt number [-], Re: Reynolds number [-], Pr: Prandtl number [-], L: plate length [m], λ: thermal conductivity [W/m·K], ρ: fluid density [kg/m^3], u: fluid velocity [m/s], d: equivalent cross-sectional area diameter [m], μ: viscosity [Pa·s], C_p: heat capacity at constant pressure [J/K·kg]. Substituting the average physical properties between 490 and 702 K and the experimental conditions into Eq. (8), the following equation is given.

$$\begin{aligned} Nu_{steam}/Nu_{nitrogen} &= (Re_{steam}/Re_{nitrogen})^{1/2}\,(Pr_{steam}/Pr_{nitrogen})^{1/3} \\ &= [(0.37/0.57)(0.23/1.48)(0.21/0.05)/(3.1\text{x}10^{-5}/3.6\text{x}10^{-5})]^{1/2}\text{x} \\ &\quad [(2.0\text{x}10^{3}/1.1\text{x}10^{3})(3.1\text{x}10^{-5}/3.6\text{x}10^{-5})/(4.6\text{x}10^{-2}/4.4\text{x}10^{-2})]^{1/3} \\ &= 0.80 \end{aligned} \tag{12}$$

Here, the suffixes of steam and nitrogen mean superheated steam and nitrogen heating, respectively. Thus,

$$\begin{aligned} h_{steam}/h_{nitrogen} &= (\lambda_{steam}/\lambda_{nitrogen})\,(Nu_{steam}/Nu_{nitrogen}) \\ &= (4.6\text{x}10^{-2}/4.4\text{x}10^{-2})(0.80) = 0.84 \end{aligned} \tag{13}$$

On the other hand, $h_{\mathrm{steam}}/h_{\mathrm{nitrogen}}$ value of this experimental study is obtained from Figs. 10 and 12 as follows.

$$h_{\mathrm{steam}}/h_{\mathrm{nitrogen}} = 7/9 = 0.78 \tag{14}$$

Considering that the average values of the physical properties and the experimental conditions were used for the calculation of Eq. (12), the experimental heat transfer coefficient was roughly explained by the correlation equation of heat transfer coefficient in Eq. (8).

Next, we compare the heat transfer coefficients of superheated steam and nitrogen at the same experimental conditions, that is, the same u and d values in Eq. (10). Thus,

$$\begin{aligned} h_{\mathrm{steam}}/h_{\mathrm{nitrogen}} &= (\lambda_{\mathrm{steam}}/\lambda_{\mathrm{nitrogen}})\,(Nu_{\mathrm{steam}}/Nu_{\mathrm{nitrogen}}) \\ &= (\lambda_{\mathrm{steam}}/\lambda_{\mathrm{nitrogen}})\,(Re_{\mathrm{steam}}/Re_{\mathrm{nitrogen}})^{1/2}\,(Pr_{\mathrm{steam}}/Pr_{\mathrm{nitrogen}})^{1/3} \\ &=(4.6\mathrm{x}10^{-2}/4.4\mathrm{x}10^{-2})\mathrm{x}[(0.37/0.57)/(3.1\mathrm{x}10^{-5}/3.6\mathrm{x}10^{-5})]^{1/2}\mathrm{x} \\ &\quad [(2.0\mathrm{x}10^{3}/1.1\mathrm{x}10^{3})(3.1\mathrm{x}10^{-5}/3.6\mathrm{x}10^{-5})/(4.6\mathrm{x}10^{-2}/4.4\mathrm{x}10^{-2})]^{1/3} \\ &=1.04 \end{aligned} \tag{15}$$

The almost same heat transfer coefficient was obtained for superheated steam and nitrogen in the above temperature range.

Figure 2-14 shows the predicted sample temperature change of superheated steam and nitrogen gas when the final sample temperatures are 616 and 539 K, and the same h value of 5 $\mathrm{W/m^2 \cdot K}$. The temperature of superheated steam approached to the set temperature faster than that of nitrogen gas due to the addition of radiation heat transfer. In this situation, carbonization of biomass via superheated steam is preferable to heated nitrogen.

As large amount of heat is necessary to produce superheated steam compared to the same temperature of nitrogen, it is desirable to make use of the extra energy for superheated steam generation at works such as steelmaking plant etc.

In this study, the dry sugarcane bagasse was used to investigate the carbonization and heat transfer behavior. As the next step, the raw sugarcane bagasse with water content will be used to make clear the effect of water condensation and evaporation on the temperature change during pyrolysis in superheated steam.

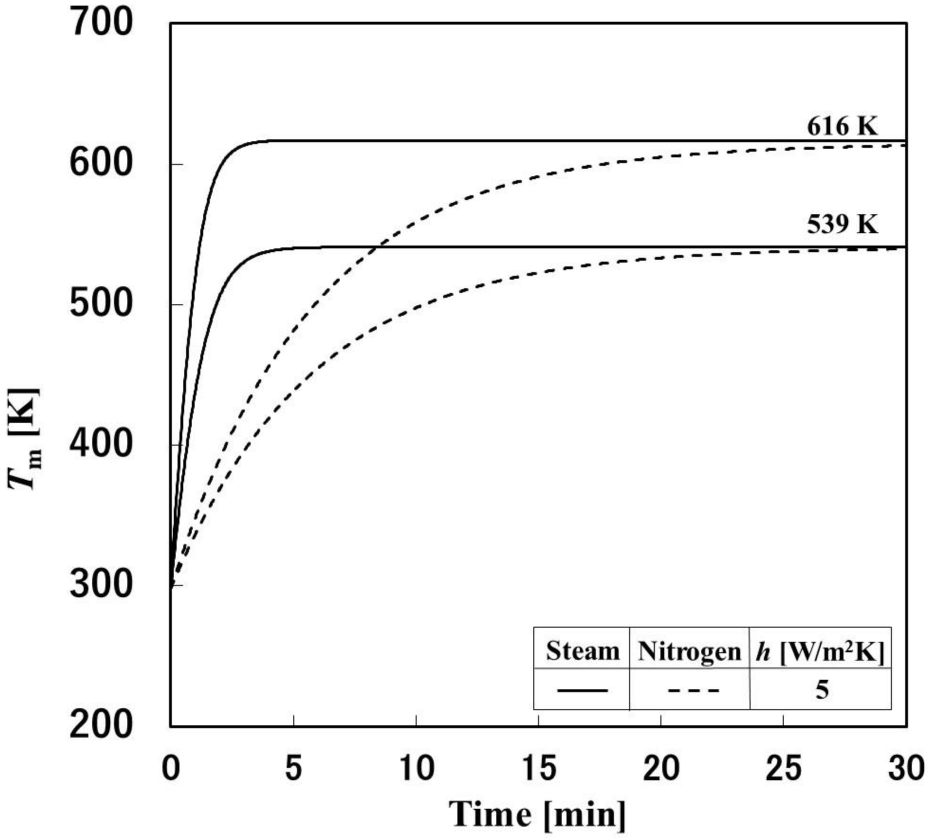

Fig. 2-14 Comparison of temporal change in calculated temperature change between superheated steam and nitrogen gas at the same carbonization temperature.

2.4 Conclusions

The carbonization of the sugarcane bagasse and its heat transfer behavior during the pyrolysis in superheated steam and nitrogen atmospheres.

1) The char yield, elemental analysis, higher heat value, and carbon losing rate of superheated steam showed the same tendency as that of nitrogen heating at the treatment temperature between 491 and 702 K.
2) The same carbonization behavior of sugarcane bagasse during the pyrolysis between superheated steam and nitrogen gas suggests no additional oxidation by superheated steam occured.
3) The differences in the char yield, elemental analysis, higher heat value, and carbon losing rate between superheated steam and nitrogen in this experiment were due to the difference in the sample temperature.
4) A good agreement was achieved between the temporal change in sample temperature of the experiment and calculation for superheated steam and nitrogen gas heating practices.
5) The heat transfer of superheated steam was faster than that of nitrogen gas due to additional radiative heating.

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Chapter 3 Dechlorination of polyvinyl chloride under superheated steam

3.1 Introduction

In recent year, the use of plastics materials in daily life have been increased because of their low price and good durability, which resulted in the huge amount of plastic waste released in the world. This plastic waste is considered as an important source of energy due to the presence of the organic compounds which can be served as hydrocarbon raw material or fuel if treated correctly [1-6]. However, the disposal of plastic wastes become a major environmental issue because plastic waste is normally non-biodegradable and contain polyvinyl chloride (PVC) [1, 6-8]. Generally, 7 to 10% of total plastic waste contains PVC [9-10].

Thermal degradation (pyrolysis, gasification, hydrogenation, etc.) and incineration was the main technology used for PVC recycle [3, 11]. Because of their high chlorine content, PVC is resistant to incineration. Incineration of PVC also emit greenhouse gas such as CO_2 and other toxic pollutants [3, 5, 11-16]. However, thermal degradation of PVC generates a lot of HCl and other toxic substances which cause corrosion of the equipment and other environmental problems [9, 13, 15, 17-26]. For the reasons described above, dechlorination of PVC is an essential step before being used in another chemical process for the conversion into energy, fuel, and other useful chemicals [16, 27]. Numerous studies have been conducted on dechlorination of PVC. Pyrolysis is considered the most efficient way for PVC dechlorination [1, 3, 6, 14, 28-30]. It is a thermal process which decomposes organic materials in the absence of air [16, 31-33].

During this process, HCl was eliminated and the formation of conjugated double bonds occurs [13]. HCl product can be used for vinyl chloride production [34].

Recently, superheated steam treatment has gained much attention due to simplicity of the dechlorination equipment and low operating temperature [35-36]. Using superheated steam as dechlorination atmosphere, the dechlorination can be faster [37-39]. Moreover, the addition of catalysts such as solid acid catalysts and adsorbents alkali and metal oxide can increase dechlorination rate and lowered reaction temperature [2, 10-11, 17, 31, 40-42]. If the dechlorination can be carried out at low temperature, it can reduce organic volatile, increase solid product yield and save energy. The purpose of this study is to investigate the process conditions for the removal of chlorinated compounds from PVC using catalysts and adsorbents under superheated steam atmosphere.

3.2 Experimental

Commercial PVC powder (Kishida Chemical Co., Ltd.) (99.0% purity) has been used as feedstock in this experiment. The chlorine content of PVC was 55.9% (analytical data). 5 g of PVC powder was compressed to the pellet using a hydraulic press to make it easy to put it in the sample basket.

Dechlorination experiment was carried out using superheated steam device (Dai-ichi High Frequency Co., Ltd., Hi-Heater 2005S) as shown in Fig. 3-1. The device consists of a boiler, superheated steam generator, and reaction chamber. Steam was produced by the boiler and then the temperature was risen to the setting temperature using a superheated steam generator. Two thermocouples (A, B) were attached to the reaction chamber (A) and sample (B) to measure chamber and sample temperatures. The flow rate of superheated steam was kept to 10 kg/h. The dechlorination reaction was carried out for 60 min. After the reaction was complete, the sample was cooled down to 343 K and the residue was ground with a blender before further analysis.

The sample after the experiment was treated with hot water and then filtered to obtain inorganic chlorine solution. Organic chlorine content from the remaining sample after filtration was analyzed by Eschka method [43-45]. The chlorine content of both inorganic and organic solution was analyzed using Mercury thiocyanate absorption spectrophotometry method [46].

The yield and dechlorination ratio were defined as Eqs. (1) and (2), respectively.

$$\text{Yield [\%]} = (W_f/W_0)\text{x}100 \tag{1}$$

$$\text{Dechlorination ratio [\%]} = \{(W_0Cl_0\text{-}W_fCl_f)/(W_0Cl_0)\}\text{x}100 \tag{2}$$

where, W_f and W_0 are the masses of the initial and final PVC sample [g], respectively, Cl_0 and Cl_f are the total chlorine contents in the initial and final PVC sample [%]. The total chlorine content means the sum of organic and inorganic chlorine contents in the sample.

For the temperature effect, the reaction was carried out at 473, 498, 523 and 573 K for 60 min. 30, 60, and 90 min of residence times were utilized for 498 K to investigate the effect of residence time on the dechlorination of PVC. In the case of dechlorination using catalysts, β-zeolite and TiO_2 were used. NaOH was used as alkali adsorbent and MgO and CoO were used as metal oxide adsorbents in this study. All the reaction with the catalysts and adsorbents were carried out at 473 K for 60 min and PVC weight was fixed to 5 g.

The effect of dechlorination atmosphere was studied under nitrogen gas using electric furnace as shown in Fig. 3-2. The experimental conditions were 473 and 523 K with 60 min of dechlorination time.

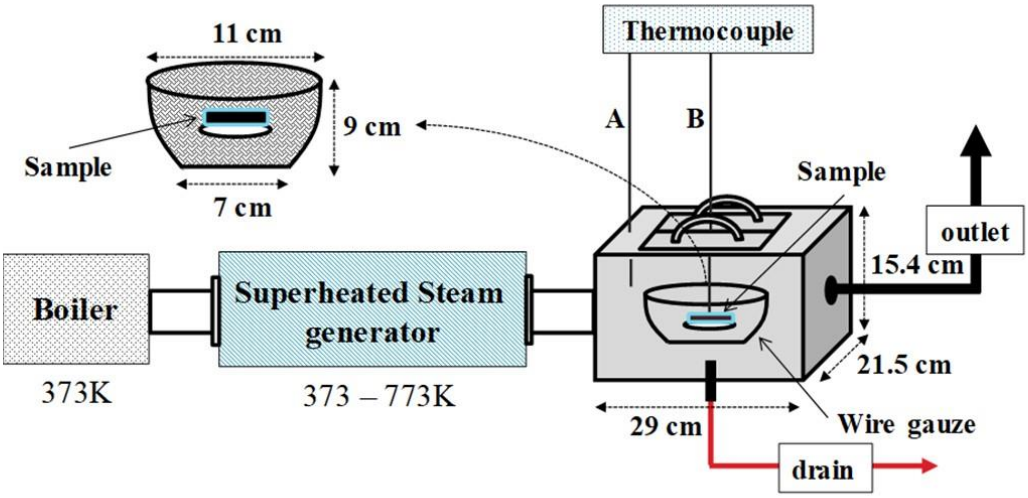

Fig. 3-1 Schematic diagram of superheated steam.

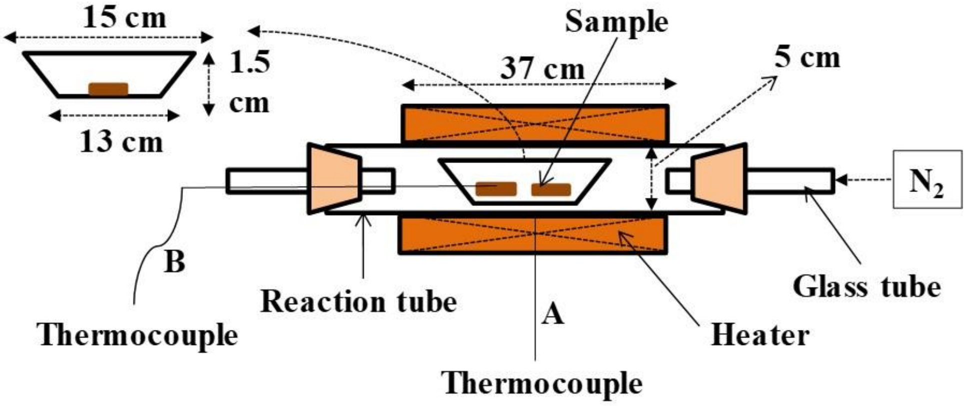

Fig. 3-2 Schematic diagram of electric furnace.

3.3 Results and discussion

3.3.1 Effect of dechlorination temperature and residence time

The effect of the dechlorination temperature on solid product yield and dechlorination ratio are shown in Fig. 3-3. Generally, product yield decreased with the temperature because the reaction rate increased. Product yield decreased to 37.4% at 573 K. The dechlorination ratio of PVC without additive at 473, 298, 523 and 573 K were 12.9, 42.7, 79.8, and 96.5%, respectively. Almost all chlorine was released at 573 K [47]. These results indicated that the temperature is the most important factor that controlled dechlorination process. Remaining of the chlorine compounds in PVC after the experiment without additives is in the state of organic chlorine. The color of PVC also changed from white to brown and became darker at higher temperatures as shown in Fig. 3-4. The color change is influenced by conjugated double bond of polyene [5, 48].

Figure 3-5 shows the effect of residence time on the solid product yield and dechlorination ratio of PVC after the reaction. Solid product yield decreased and become constant after 60 min after 60 min of dechlorination. The same trends were observed in dechlorination rate after 60 min. This indicates that one hour is enough time for the declorination of PVC.

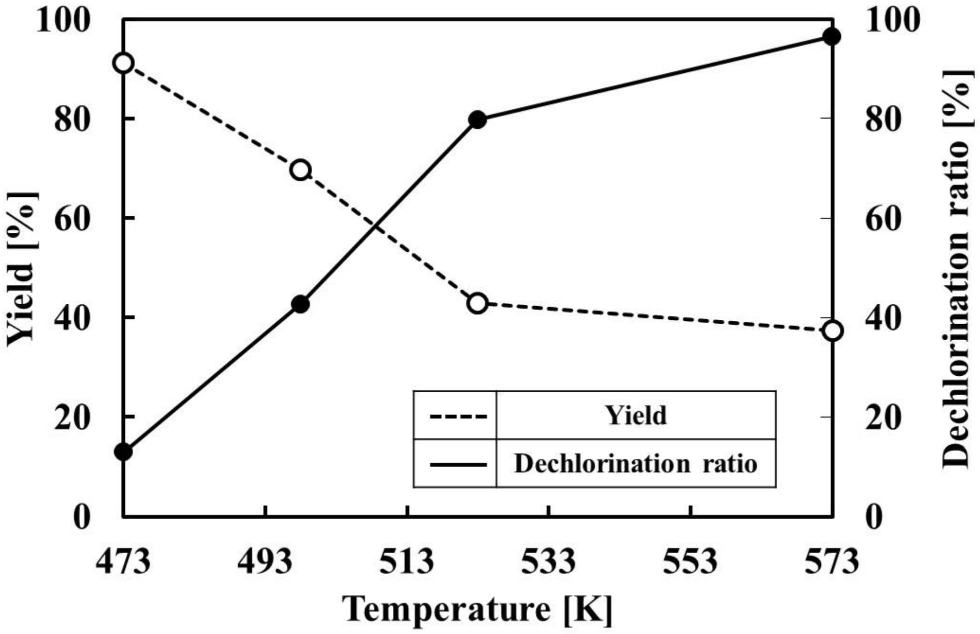

Fig. 3-3 Effect of the dechlorination temperature on solid product yield and dechlorination ratio.

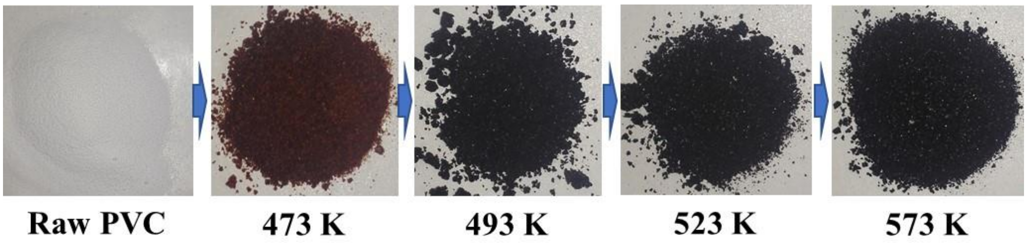

Fig. 3-4 Color change of the sample after dechlorination.

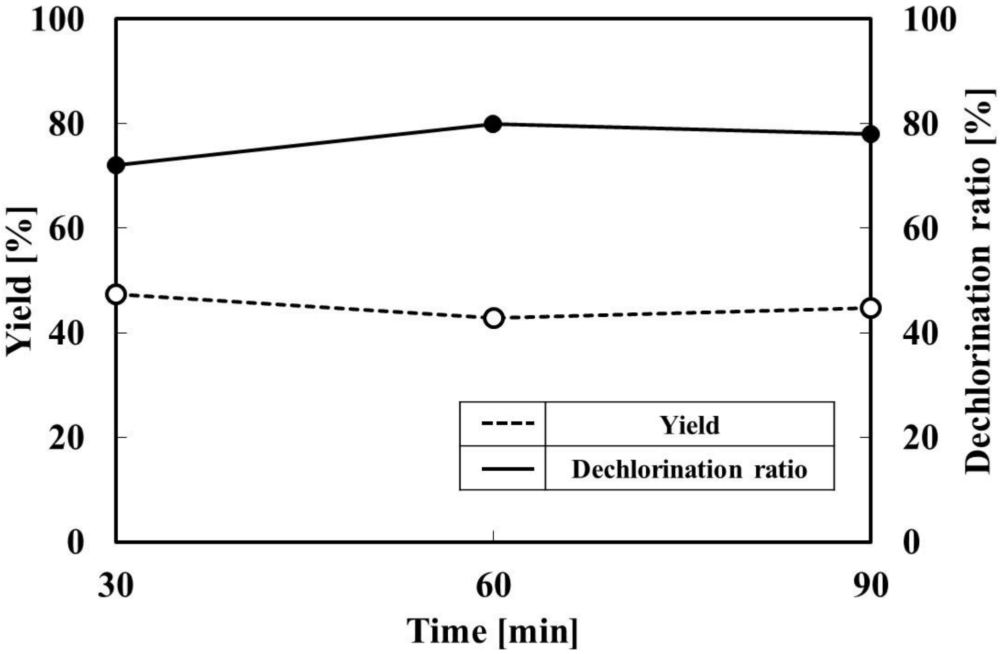

Fig. 3-5 Effect of residence time on the solid product yield and dechlorination ratio.

3.3.2 Effect of solid acid catalysts

Solid acid catalysts, alkali compound and metal oxides are often used in decomposition of the plastic [7,11,27,32]. In this study two types of solid acid catalysts, β-zeolite and TiO_2 were used. 0.5 g of TiO_2 and β-zeolite were added to the PVC powder (5.0 g), respectively, and mixed sufficiently before compression. Only a small change observed in the solid product yield with the addition of solid acid catalyst as shown in Fig. 3-6. TiO_2 showed the highest dechlorination ratio among the catalysts. In the case of β-zeolite addition, there was only a small increased observed probably due to the presence of water which will lower the catalytic activity of zeolite. None of inorganic chlorine observed using these catalysts and these results agree with Lopez et al. which reported that the acid site of the catalyst can improved PVC declorination but lacked chlorine capture ability [49].

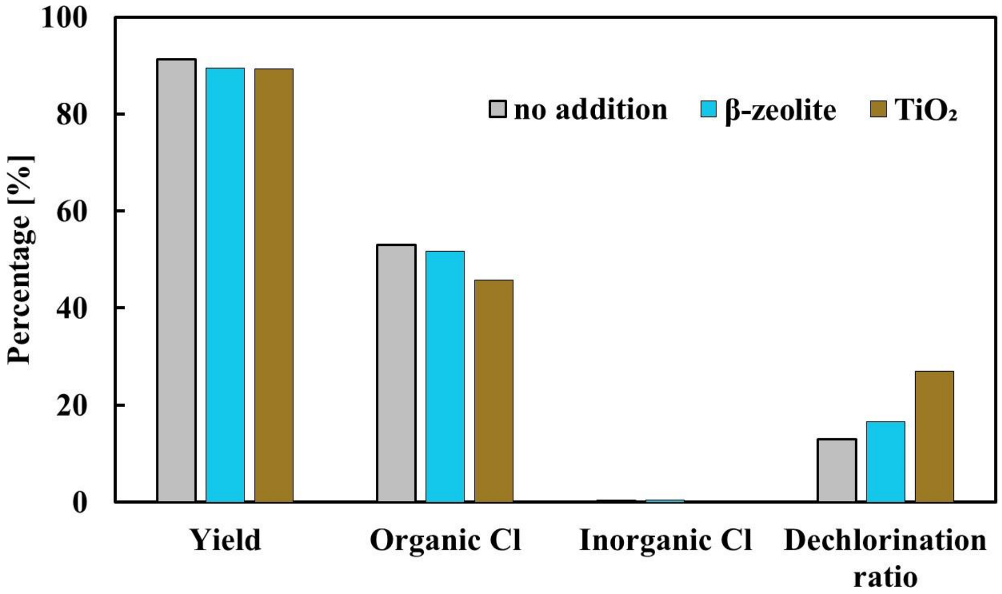

Fig. 3-6 Effect of solid acid catalysts on PVC dechlorination.

3.3.3 Effect of alkali adsorbent

The effect of alkali additive on the dechlorination ratio of PVC was studied using NaOH and the result is shown in Fig. 3-7. The mixture of the NaOH and PVC (5.0 g) was 1:1 mole ratio. The addition of NaOH increased the dechlorination rate from 12.9 to 21.1%. There is some increased observed in the inorganic chlorine with the addition of NaOH, which mean that NaOH reacted with HCl to form an inorganic chlorine [36]. Normally, the addition of alkali adsorbent only increases the chlorine capture ability not the dechlorination ratio as observed in the results. The increased in dechlorination ratio was estimated due to the neutralization reaction between HCl and NaOH which was an exothermic reaction. In this experiment, the reaction temperature increased from 273 to 283 K. It is assumed that PVC degradation started with the breaking of C-Cl bond because of their lower binding energy compared with C-C and C-H bond, the increase in the reaction temperature will enhance the cracking of C-Cl bond and led to higher dechlorination rate [1, 6, 12, 40].

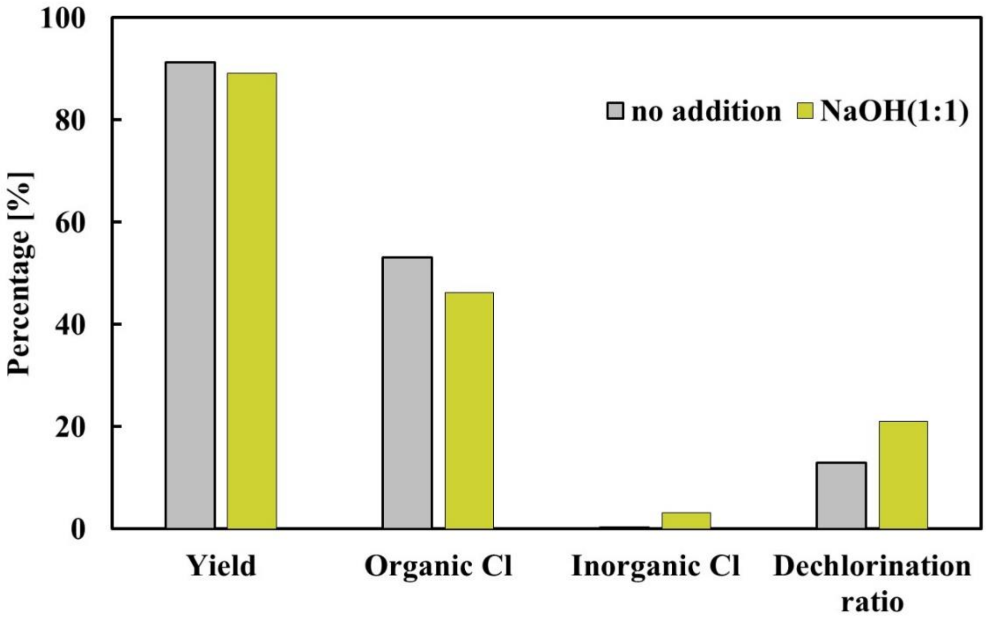

Fig. 3-7 Effect of alkali adsorbent on PVC dechlorination.

3.3.4 Effect of metal oxides loading amount

It is reported that the addition of metal oxide can affect the degradation of PVC [42]. The effect of metal oxide adsorbents was studied with MgO and CoO. The mixture of the catalyst and PVC were 1:0.5 and 1:1 mole ratios. 35.0% of dechlorination rate was obtained with MgO, while CoO was 28.3% with loading amount 1:0.5 mole ratio as shown in Fig. 3-8. MgO showed almost no effect with the loading amount but CoO showed a great result. Solid product decreased from 87.1% to 70.3%, while dechlorination ratio increased from 28.3 to 56.7% with the increasing of catalyst loading amount. CoO loading amount not only promoted the decomposition but also dechlorination ratio of PVC. There was no inorganic chlorine observed as shown in this result. This indicates that there was no reaction between metal oxide and HCl to form inorganic salt.

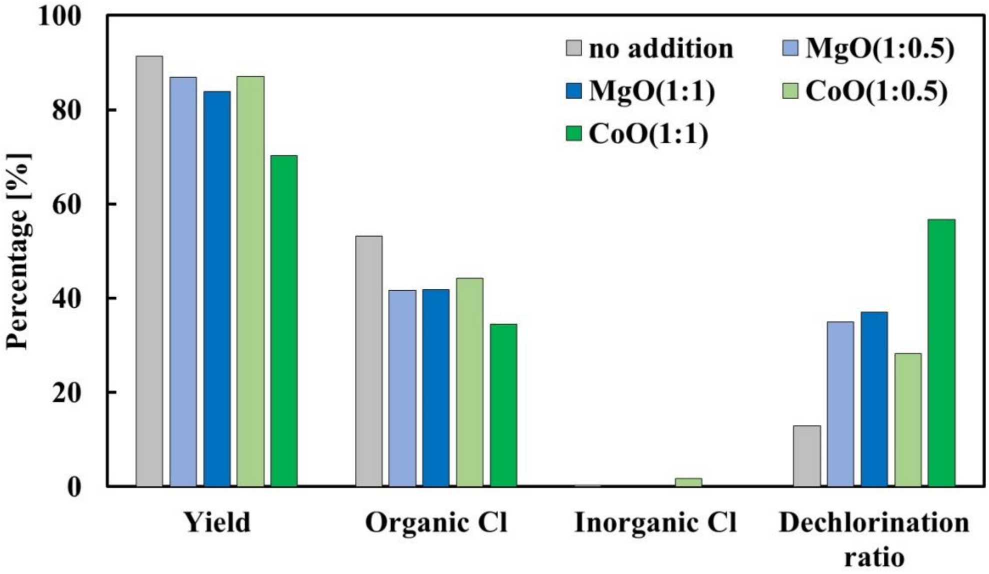

Fig. 3-8 Effect of metal oxide loading amount on PVC dechlorination.

3.3.5 Effect of metal oxides supported adsorbents

To increase the dechlorination and decomposition of the adsorbent, metal oxide supported adsorbent was used. These multicomponent adsorbents can increase the dechlorination and chlorine capture ability compared with single component adsorbent which either has a good dechlorination ability or chlorine capture ability [9]. The adsorbent was prepared using impregnation method as shown in Fig. 3-9. CoO was used as support and MgO, NiO and ZnO were added to this support. The prepared adsorbents were 50MgO/ZnO, 50NiO/ZnO and 50ZnO/CoO.

The effect of metal oxides supported adsorbents on PVC dechlorination are shown in Fig. 3-10. The adsorbent was added to the PVC with the same amount as CoO which was 5.8 g. The addition of ZnO increased the decomposition and dechlorination rate. MgO and NiO addition decreased the decomposition and dechlorination ratio compared with CoO alone. The dechlorination ratio with CoO, 50ZnO/CoO, 50MgO/CoO and 50NiO/CoO were 12.9, 56.7, 69.6, 48.1 and 27.6% respectively. The used of metal oxide mixed adsorbent also show an increased in inorganic chlorine content which mean that this adsorbent has a chlorine capture ability.

XRD results before the dechlorination revealed that Zinc cobaltite peak was observed in the 50ZnO/CoO (Fig. 3-11). As reported by Bazuev et al., this zinc cobaltite compound has a catalytic activity and proved with increased of dechlorination abilty when using this adsorbent [50]. The presence of zinc cobaltite compound in the dechlorination led to the increased of formation inorganic chlorine in the form of cobalt chloride ($CoCl_2$) and cobalt chloride dihydrate ($CoCl_2 \cdot 2H_2O$) as observed in Figure 3-12. The formation of this metal chloride compound also can act as catalyst for PVC decomposition and will accelerate the dehydrochlorination of PVC [42, 51-53].

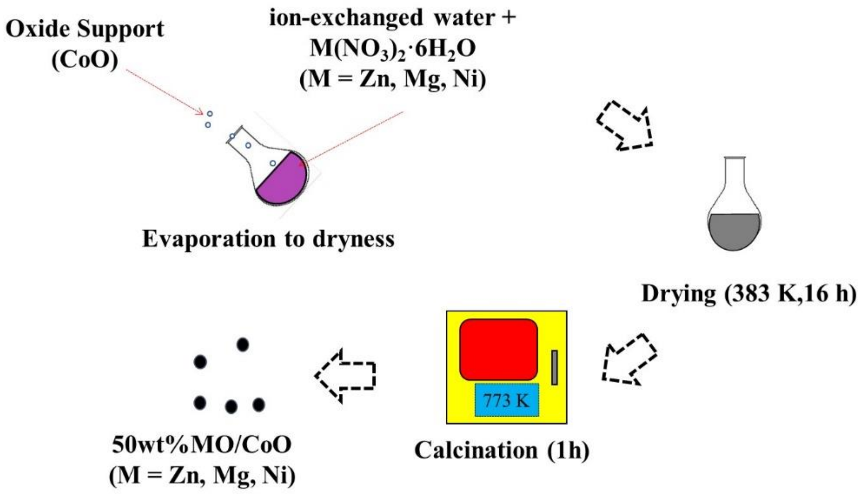

Fig. 3-9 Metal oxides supported adsorbent preparation (impregnation method).

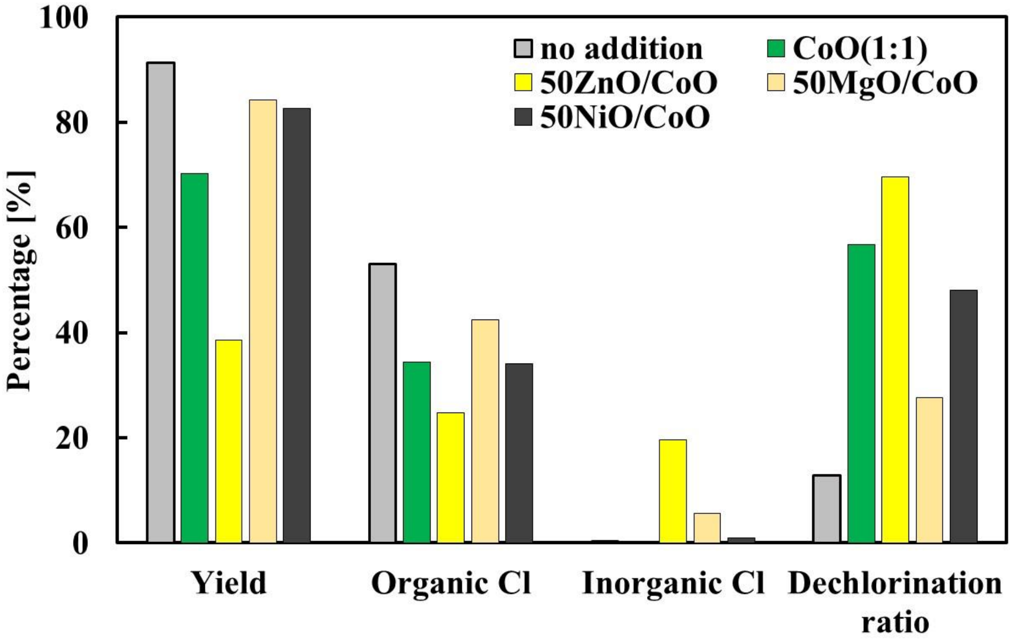

Fig. 3-10 Effect of metal oxide supported adsorbent on PVC dechlorination.

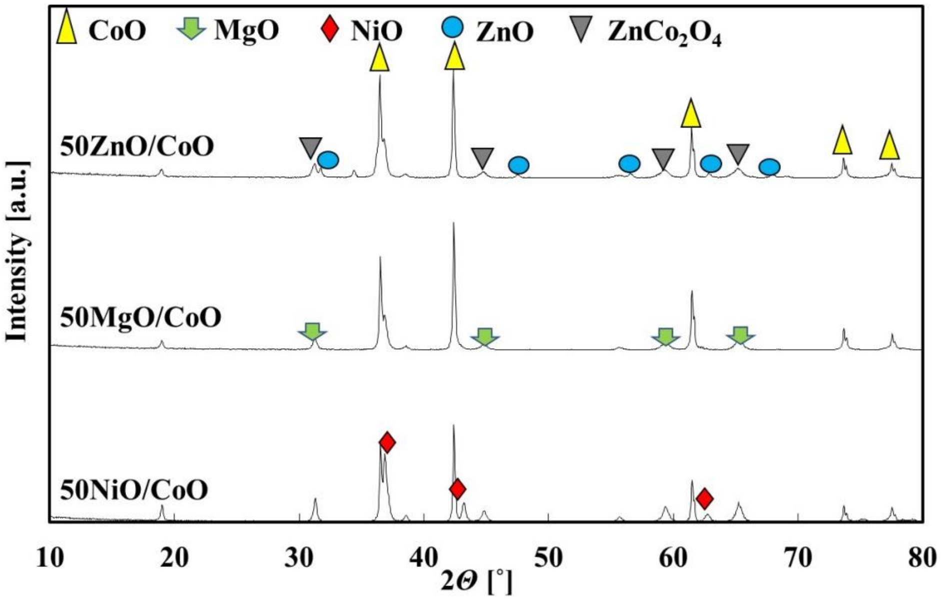

Fig. 3-11 XRD pattern of metal oxides supported adsorbents before dechlorination.

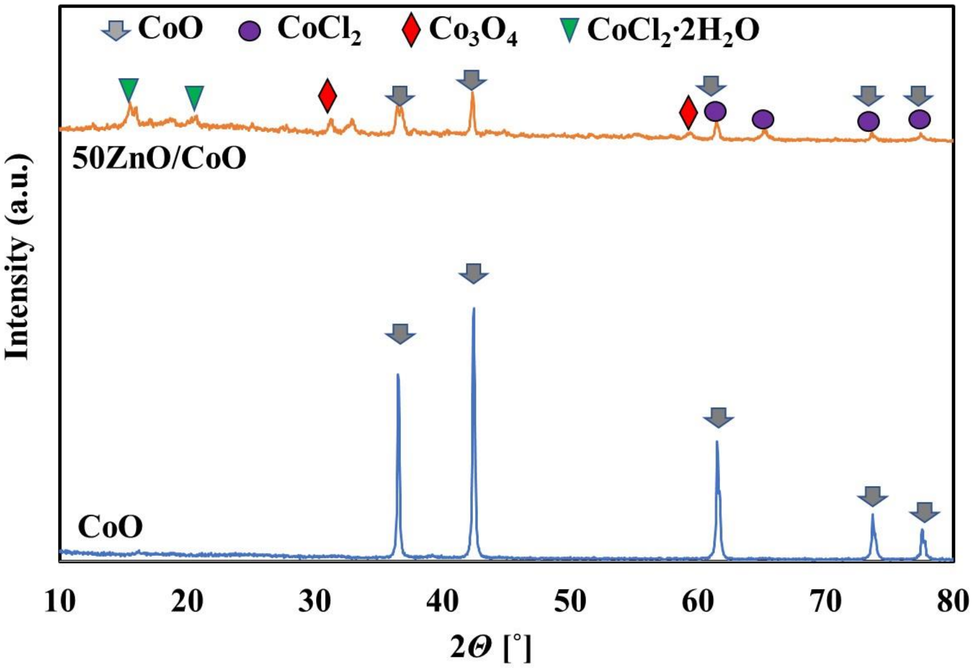

Fig. 3-12 Comparison of XRD patterns of CoO and 50ZnO/CoO supported adsorbent.

3.3.6 Effect of ZnO loading amount

The effect of ZnO loading amount was investigated with ZnO loading 10, 25 and 50 wt%. The result is shown in Fig. 3-13. Solid product and organic chlorine content decreased with the increasing of ZnO loading amount and became almost constant when ZnO loading exceed 25 wt%. Inorganic chlorine content also decreased with the increasing of ZnO loading amount because of the cobalt amount reacted with chlorine to form $CoCl_2$ decreased with the ZnO loading amount.

Chlorine recovery rate was calculated using Eq. (3) to evaluate the chlorine capture properties with ZnO loading amount and the results is shown in Table 3-1.

$$\text{Chlorine recovery rate} = (\text{Chlorine capture rate [\%]}/\text{Chlorine release rate [\%]}) \times 100 \qquad (3)$$

ZnO increased the decomposition of PVC while the formation of zinc cobaltite compound during the reaction increased when the CoO amount was higher than ZnO and will increased the recovery rate of the chlorine in inorganic form even the dechlorination rate was lower. From this results, we can conclude that ZnO has a better decomposition rate compared with others metal oxides, but using ZnO alone PVC will suffer a great weight loss at this experimental temperature because ZnO was the most active catalyst as reported by A. Ballistreri et. al [52]. The formation of zinc cobaltite compoud can inreased the chlorine capture ability of the adsorbent.

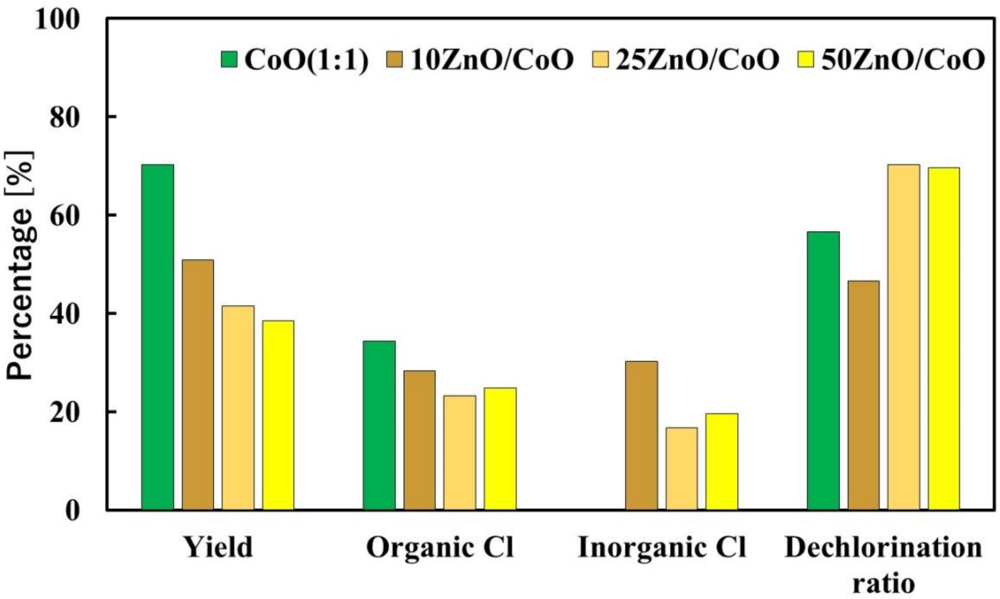

Fig. 3-13 Effect of ZnO loading amount on PVC dechlorination.

Table 3-1 Chlorine recovery ratio with ZnO loading amount.

	Chlorine recovery ratio [%]	Dechlorination ratio [%]
no addition	10.7	12.9
CoO(1:1)	0.0	56.7
10ZnO/CoO	100.0	46.6
25ZnO/CoO	51.1	70.3
50ZnO/CoO	63.0	69.6

3.3.7 Effect of dechlorination atmospheres

To study the effect of dechlorination atmosphere on PVC dechlorination, the experiment was carried out under nitrogen atmosphere and superheated steam atmosphere with at 473 K with the same reaction conditions. Solid product yield and dechlorination ratio were almost the same for both nitrogen and superheated steam atmosphere without addition and CoO adsorbent as shown in Fig. 3-14. However, different results were obtained with 25ZnO/CoO adsorbent, superheated steam had a higher decomposition and dechlorination ratio compared with nitrogen atmosphere. Figure 3-15 shows XRD of the sample after the dechlorination of both superheated steam and nitrogen atmospheres with 25ZnO/CoO adsorbent. Inorganic chlorine obtained with superheated steam atmosphere was in the form of $CoCl_2$ and $CoCl_2 \cdot 2H_2O$ while nitrogen atmosphere was inorganic chlorine was only in the form of $CoCl_2$ which led to the higher dechlorination rate in superheated steam atmosphere [42].

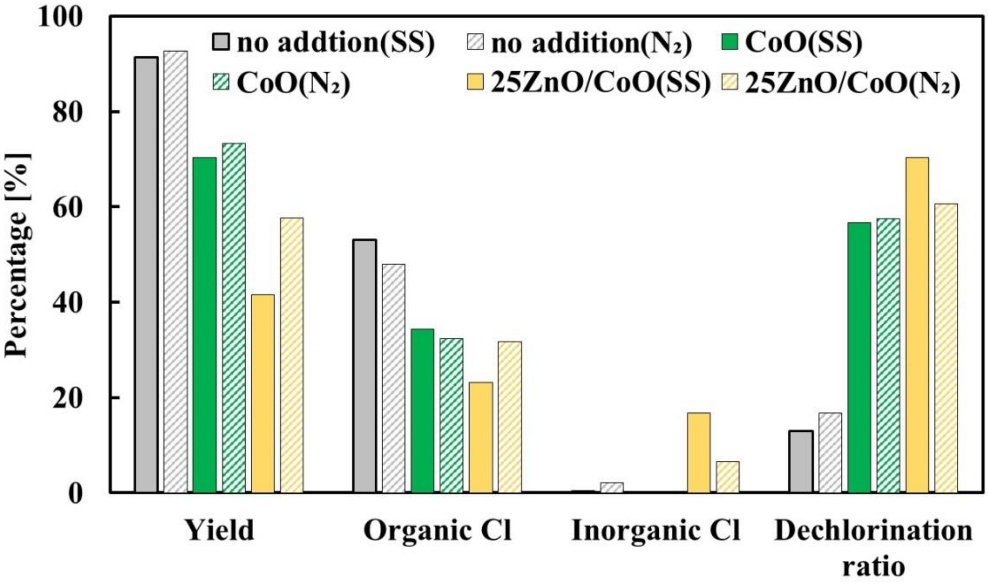

Fig. 3-14 Effect of dechlorination atmosphere on PVC dechlorination.

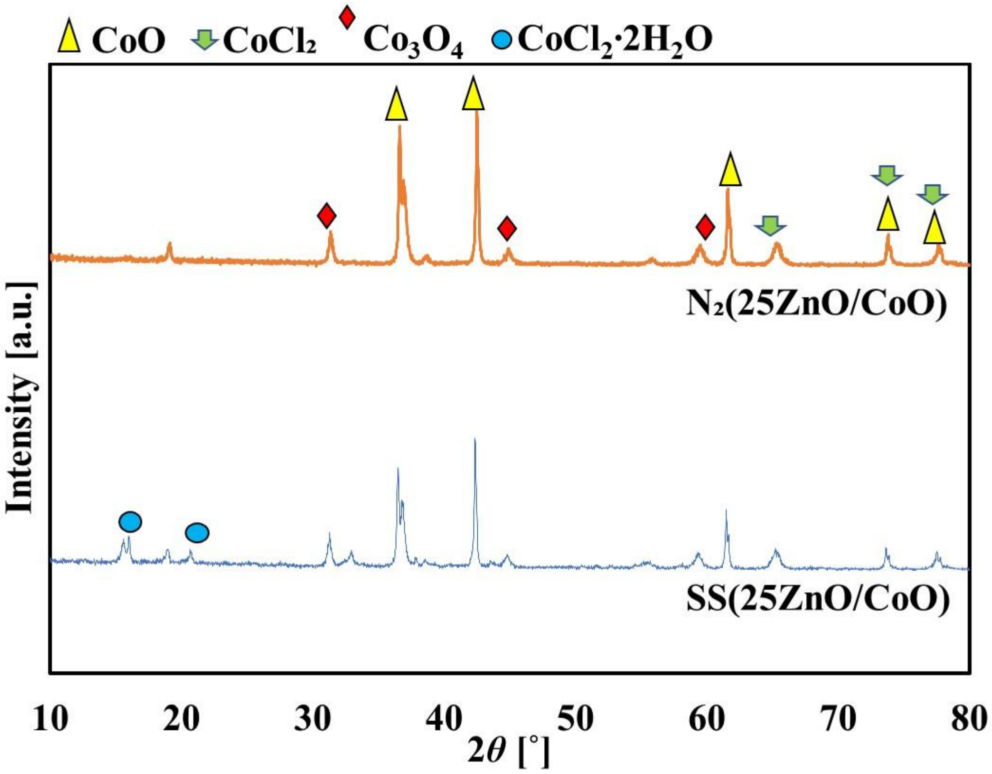

Fig. 3-15 XRD of the sample after the dechlorination of both superheated steam and nitrogen atmospheres with 25ZnO/CoO adsorbent.

Figure 3-16 shows the effect of the dechlorination atmosphere at temperature of 473 and 523 K. Two types of temperature were used because at 473 K, there was almost no dechlorination occurred and led to the similar result both in superheated steam and nitrogen atmospheres. The effect of superheated steam was observed in temperature 523 K. Decomposition and dechlorination ratio in superheated steam were higher than nitrogen atmosphere due to the superior heat transfer ability of superheated steam as state in Chapter 2. The addition of 25ZnO/CoO adsorbent increased the decomposition and dechlorination ratio to the almost the same value as 523 K. From these results, we can conclude that the addition of metal oxide supported adsorbent such as 25ZnO/CoO can lower the reaction temperature.

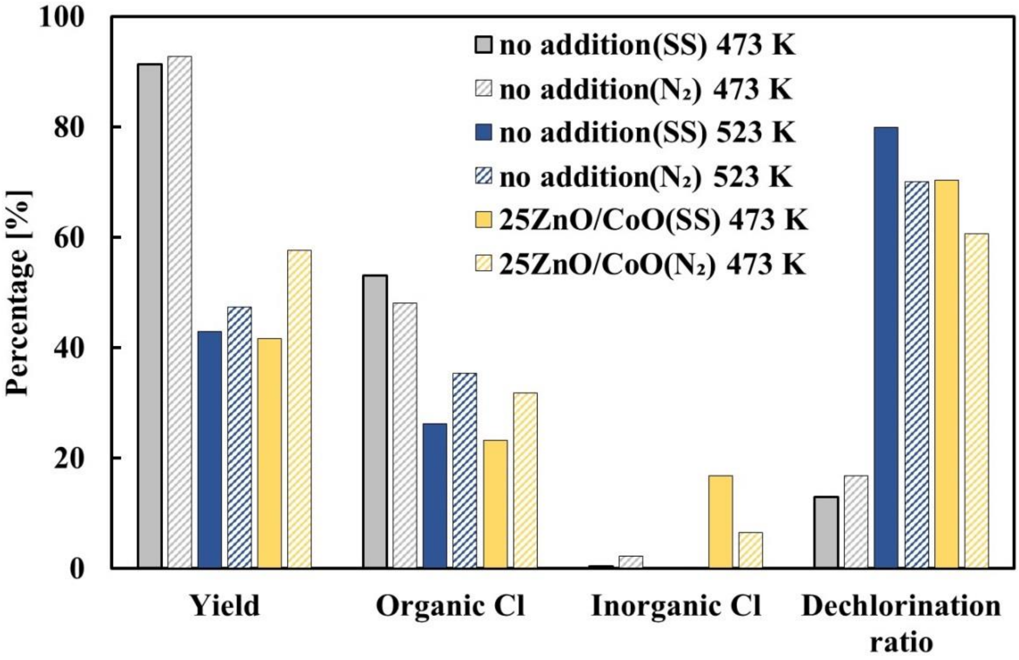

Fig. 3-16 Effect of the dechlorination atmosphere at temperature of 473 and 523 K.

3.3.8 Comparison of dechlorination ability and solid yield

Figure 3-17 shows the comparison of the dechlorination ratio and solid product yield for all reactions conditions. The horizontal axis shows the yield of PVC and the vertical axis shows the dechlorination rate of PVC calculated with the remaining chlorine in the sample after dechlorination. The slope indicates the standard value for PVC dechlorination. If the declorination occur the value should be all over the slope. If the reaction proceeds upper left over the slope, the dechlorination proceed not only with the cracking of C-Cl bond but also the craking of the other bond than C-Cl which led to the poor solid yield. The ideal dechlorination is the reaction proceed to the upper right and with solid yield of 44% and 100% of dechlorination rate. In our results, dechlorination under superheated steam with mixed metal adsorbent of 10, 25 and 50wt% ZnO loading at 473 K and 523 K without addition showed a great result which approaching to the ideal rate. This mean that we can obtained this ideal dechlorination and yield by adding over 50wt% of ZnO to the CoO with the reaction temperature lower than 473 K.

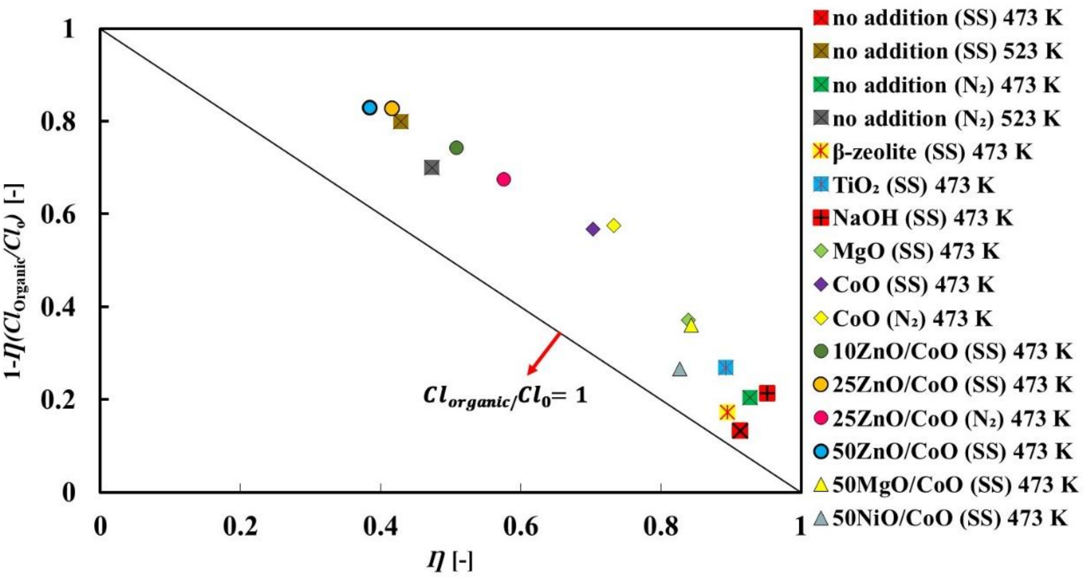

Fig. 3-17 Comparison of the dechlorination rate and solid product yield for all reactions conditions.

3.4 Conclusions

The dechlorination of PVC using superheated steam with catalysts and adsorbent were investigated and it can be concluded that:

1. Temperature was the most important factor that affect PVC decomposition and dechlorination.
2. Metal oxide showed a better declorination ability compared with solid acid catalyst and alkali adsorbent. Among the metal oxides, CoO had the highest dechlorination ability.
3. The addition of ZnO to CoO increased the declorination rate of PVC because of the formation of zinc cobaltite ($ZnCo_2O_4$) and metal chloride ($CoCl_2$) acted as catalyst during the dechlorination.
4. Declorination in nitrogen atmosphere had the same results as superheated steam except during the addition of 25ZnO/CoO adsorbent at temperature 473 K and at temperature 523 K without any addition which had higher declorination ability in superheated steam because of higher decomposition rate in superheated steam.

3.5 References

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Chapter 4 Summary

In this research two types of organic wastes, sugarcane bagasse and polyvinyl chloride (PVC) were used and the pyrolysis properties of sugarcane bagasse and polyvinyl chloride by pyrolysis in superheated steam atmosphere were investigated.

In chapter 1 the background and rationales of this research were explained. The types of organic wastes and the main process used for the treatment of these wastes were described. Among the treatment used, one of the thermochemical process, pyrolysis was focused on this study. By using this process sugarcane bagasse was carbonized to obtain biochar as the main product while in the case of PVC waste, chlorine removal through pyrolysis process have been investigated. Both of carbonization and dechlorination were studied under superheated steam atmosphere and their results were compared with nitrogen atmosphere.

In chapter 2, the carbonization of sugarcane bagasse under superheated steam and nitrogen atmospheres and their heat transfer behavior was investigated. Carbonization was carried out for 5, 10, 15, 20, 25 and 30 minutes at temperature 491,541, 579, 617, 650, and 702 K under superheated steam atmosphere. The char yield increased at the first 10-15 min and became constant within 25-30 min of carbonization. The effect of the temperature was studied at temperature 491,541, 579, 617, 650, and 702 K for 30 minutes. The increasing carbonization temperature led to the decrease in the solid yield and showed almost the same trend in carbon losing rate. The thermogravimetric analysis (TGA) under nitrogen atmosphere showed similar trend with the weight loss in superheated steam atmosphere which mean that the carbonization in superheated steam proceed with the same as nitrogen atmosphere. The heat transfer properties in superheated steam and nitrogen atmospheres were calculated using a simplified heat balance equation model and the results were compared with the experimental value. The results showed a good agreement between the calculated and experimental temperature when $h = 7$ W/m^{2}K was used in case of superheated steam. While for the nitrogen gas pyrolysis, a good agreement was achieved between the experiment and calculation when the value of $h = 9$ W/m^2 K. The increasing rate of sample temperature in superheated steam was faster than that of nitrogen due to the large heat transfer ability of superheated steam based on radiation and convection.

In chapter 3, the chlorine removal from polyvinyl chloride (PVC) with the addition of catalysts such as solid acid catalysts and adsorbents such as alkali and metal oxide adsorbents were described using superheated steam and nitrogen as pyrolysis media. The effect of the dechlorination temperature was studied at 473, 498, 523 and 573 K for 60 min in the case of superheated steam and in the case of nitrogen gas dechlorination was studied at 473 and 523 K for 60 min. The results indicated that the treatment temperature was the important factors to control the carbonization and dechlorination ratio of PVC. The effect of residence time on PVC dechlorination ratio was studied at temperature 523 K for 30, 60 and 90 min. The decomposition and dechlorination became almost constant after 60 min. This indicates that 60 min is enough time for the the declorination of PVC. The effect of solid acid acid catalysts addition on PVC dechlorination was studied with β-zeolite and TiO_2 at 473 K and treatment time of 60 min. The addition of solid acid catalysts increased the dechlorination rate of PVC but lacked chlorine capture ability. The addition of NaOH as alkali adsorbent increased dechlorination ratio from 12.9% to 21.1% and showed a little chlorine capture ability. 56.7% of dechlorination was obtained by CoO addition of 1:1 mole ratio in the case of metal oxide adsorbent. Metal oxide supported adsorbents were prepared in this study by impregnation method in order to increase decomposition and chlorine capture ability of the adsorbent during dechlorination. Prepared metal oxide supported adsorbents were 50ZnO/CoO, 50MgO/ZnO and 50NiO/CoO. These adsorbents showed an increased in dechlorination and chlorine capture ability compared with the results of no addition. The combination of ZnO and CoO adsorbents showed the highest dechlorination and chlorine capture ability. Effect of ZnO loading amount on PVC dechlorination was studied with 10, 25 and 50wt% of ZnO loading. The results indicated that the loading amount increased the decomposition and dechlorination ratio and became almost constant when loading amount over than 25wt%. The comparison between superheated steam and nitrogen atmosphere showed that the effect of superheated steam start at temperature 523 K, with higher decomposition and dechlorination ratio were obtained in superheated steam atmosphere.

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