Analysis of Hydrothermal Solid Fuel Characteristics Using Waste Wood and Verification of Scalability through a Pilot Plant

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Abstract: Increases in energy demand and waste are a major cause of natural resource depletion and environmental pollution, and technology capable of processing waste to convert it into energy is required to mitigate this issue. Hydrothermal carbonization (HTC) is an example of this technology that can convert waste into energy, and various studies have been conducted using it for fuel conversion. This study focused on the production of a solid fuel equivalent to coal for power generation through HTC processes using waste wood. Unlike previous work, which consists only of laboratory-scale HTC experiments, we confirmed scalability through pilot-scale HTC experiments. Overall, it was possible to convert waste wood into HTC solid fuel with a calorific value of over 27,000 kJ/kg through the pilot plant HTC process. Additionally, heavy metal and hazardous substance analyses proved that it can be used as a biosolid fuel.

Keywords: hydrothermal carbonization; waste wood; solid fuel; biosolid fuel; laboratory-scale; pilot-scale

1. Introduction

Increases in energy demand and waste are causing natural resource depletion and environmental pollution, making technologies capable of solving these problems crucial worldwide [1]. Many Asian, North American, and European governments are focusing on developing technologies that convert various organic wastes into energy as a solution to the zero organic waste policy. Among organic waste-to-energy technologies, hydrothermal carbonization (HTC) is used in various fields, such as energy conversion, environmental improvement, and nutrient recovery, and can convert waste into high-energy-density carbon materials [2].

HTC is a reaction that combines dehydration and decarboxylation processes, and its solid fuels have high calorific values with increasing carbon contents [3]. To convert organic waste into solid fuel using HTC, a temperature of approximately 180–250 °C is required to be maintained for 1–12 h [4,5]. It is relatively low compared with other energization technologies, such as pyrolysis requiring 400 °C and gasification requiring 800 °C. Thus, there is an advantage in that less input energy is required. Additionally, HTC has the advantage of producing solid fuel without dehydration and drying in the pretreatment process [6].

Recently, many studies have been conducted to confirm the possibility of biofuel conversion from various wastes using HTC technology. In these studies, various organic wastes have been used including waste wood, paper, MSW, food waste, and animal waste [7–10]. Additionally, the calorific value of hydrochar after HTC is relatively high in
lignocellulosic biomass, such as wood or wood chips, which contain a substantial amount of carbon [11]. However, considering commercial facility design, if the HTC reaction time has to be increased from 4 to 72 h when producing biofuels, it is not an efficient fuel production per hour [7,8,12,13].

Research on HTC biofuel generation using catalysts is also being conducted. The catalysts are made by dissolving in distilled water by mixing with one or more chloride-based metal salts and acids. The catalyst concentration in the aqueous solution is in the range of 2–20 g/L. Hence, the catalyst is used to lower the pH concentration, thereby lowering the activation energy and reducing the hydrothermal carbonization reaction time. When lignocellulosic biomass feedstock HTC was compared according to the presence or absence of catalysts, the reaction time was reduced from 4 to 1 h when catalysts were absent and present, respectively [14,15]. The reaction temperature can be lowered from 10 to 40 °C, and the reaction pressure can be lowered by 1–2 MPa, which reduces the cost when manufacturing the reactor. Additionally, after HTC, the lignin component in the organic material decomposes in the hydrochar, but catalytic HTC showed less lignin degradation by FTIR spectroscopy [15]. Furthermore, when the lignin components are maintained, they have an adsorption effect on each other, making it possible to produce advantageous pellets without the additional attachment of materials during fuel transport. It was confirmed that there was no breakdown through the electrochemical water ingress (EWI) test [16].

Some researchers have expanded their facility capacity for commercialization. For example, Hoekman et al. [17] fabricated an expanded hydrothermal carbonization reactor (40 L) to process 3 kg of lignocellulosic biomass and showed that the experimental results were similar to those of a laboratory-scale 2 L reactor. They compared the experimental results when the HTC reaction temperature was 235 and 275 °C. At 275 °C, the calorific value increased by 40% compared to the supplied raw material. However, considering the effect of increasing the calorific value, when the reaction temperature condition is 275 °C, energy cost and cooling time increase. Furthermore, Ismail et al. [18] numerically analyzed the expected energy and production volume when converting municipal solid waste (MSW) into solid fuel in a pilot-scale facility. They proposed a numerical model for a pilot plant facility that converts MSW to coal through numerical analysis. These studies are meaningful from the perspective of commercial design, but verification has not been conducted through commercialization facilities. Mackintosh et al. [19] designed a pilot plant-scale binary reactor, performed proximate analyses, and determined the calorific value of hydrochar according to the HTC reaction of the catalyst [15] they applied to their lab-scale HTC experiments. They further analyzed the fuel characteristics by expanding the pilot scale, but a comparative study with and without a catalyst is required to verify the effect of the catalyst.

In this study, biofuel with a calorific value equivalent to that of coal for power generation was produced in a pilot plant through waste wood HTC. To verify the scalability, HTC reaction experiments were conducted using lab-scale (0.2 L—3 sphere) and pilot-scale (500 L) reactors, and the pilot-scale reactor was composed of the equipment for the entire process. First, the calorific values and mass yields of solid fuels generated through laboratory-scale HTC experiments were compared according to the presence or absence of catalysts and catalyst concentration. The added catalyst is a mixture of a chloride-based metal salt and an acid, which is a different combination from the catalysts of previous studies. Next, heavy metal and hazardous substance analyses were used to confirm whether the solid fuel that satisfied the desired calorific value and yield condition met the fuel use standard. Based on the determined catalyst conditions, a pilot-scale HTC experiment was performed according to the catalytic concentrations. The effect of catalyst addition was confirmed via comparative analyses of the generated solid fuel according to the presence or absence of catalysts. Overall, the trends of the pilot- and laboratory-scale experimental results were consistent, and their scalability was verified. The biosolid fuel produced through HTC with catalyst additions in the pilot plant proved that it can be used as fuel through heavy metal and hazardous substance analyses.
2. Experimental Setup and Procedure

2.1. Fuel Characteristics of the Waste Wood Raw Material

The waste wood used in the experiment was selected as a product that can be supplied in large quantities because it is required for both laboratory- and pilot-scale HTC experiments. The waste wood is acquired through a company that specializes in recycling. In the test site, only waste wood that has not been stained with adhesives, paints, oil, or preservatives was permitted to be brought in. The same waste wood was used for both the laboratory- and pilot-scale HTC experiments. To compare the fuel properties of the hydrochar after HTC, we analyzed the fuel properties of the raw materials (Table 1). Table 1 shows the results of the fuel characteristic analyses of the waste wood. Detailed fuel characteristic analyses can be divided into proximate, elemental, and calorific value analyses. The collected samples were subjected to proximate analysis before drying, while elemental and calorific value analyses were performed after drying. The analysis method used followed the American Society for Testing and Materials (ASTM), and different equipment were used according to each analysis method. Proximate analysis was performed using the TGA-701 Proximate analyzer, and the ratio of volatile substances, ash, water, and fixed carbon can be known. Elemental analysis was performed using TruSpec Elemental Analyzer. To measure carbon and hydrogen, the sample was burned in a tube furnace and the water and CO₂ produced were absorbed and analyzed. The nitrogen concentration was measured by the Kjeldahl–Gunning method [20]. Sulfur was analyzed using an SC-832DR Sulfur Analyzer. Sulfur was measured by conversion to sulfur dioxide, followed by absorption in hydrogen peroxide solution, and titration with barium acetate solution. The calorific value is divided into a Higher Heating Value (HHV) and a Lower Heating Value (LHV). In this study, the calorific value was confirmed to be measurable HHV. The calorific value was analyzed using an AC600 Semi-Auto Calorimeter. The calorific value is confirmed by analyzing the temperature change after the combustion of the sample based on the initial temperature.

Table 1. Waste wood chip fuel characteristics.

| Element Analysis (wt%) | Proximate Analysis (wt%) | Calorific Value (kJ/kg) |
|------------------------|--------------------------|------------------------|
| C          | H          | O          | N          | S          | M          | VM   | Ash   | F.C   | HHV     | LHV     |
| 43.97      | 6.05       | 30.19      | 0.1        | 0.016      | 7.98       | 73.56 | 0.77  | 17.69 | 19,929   | 18,338   |

2.2. Specification of a Laboratory-Scale Reactor for HTC Experiments

Three 200 mL reactors were installed in the laboratory-scale HTC experiment equipment (Figure 1), and a heating jacket was used as the heat source of the reactor. The maximum allowable temperature was 250 °C, and the reactor temperature was capable of reaching the reaction temperature using the heating jacket and temperature sensor. The time to reach the reaction temperature is about 50 min. Therefore, the average heating rate of the reactor is 4.5 °C/min. The electric capacity supplied to one unit of the heating jacket was 1.5 kW, and the maximum electric power of the HTC test equipment for the experiment was 5 kW. A temperature sensor that could measure the temperature and a control device that could maintain the reaction temperature were installed. Additionally, a pressure sensor was installed to check the pressure according to the temperature inside the reactor, which was measured to be approximately 2.32 MPa when the temperature inside the reactor was 220 °C. SUS316L, which has strong corrosion resistance, was used as the reactor material in consideration of corrosion and the catalyst, and the maximum allowable pressure of the reactor was designed to be 5.39 MPa considering safety.
2.3. Laboratory-Scale Reactor HTC Experimental Conditions and Process

The HTC process can be divided into pretreatment, reaction, and post-treatment steps. In the pretreatment step, the raw material was pulverized into particles of 2 mm or less to produce uniform particles. The moisture content of the pulverized raw material was then measured and placed into an aqueous solution inside the reactor to obtain a moisture content of 80%. The total volume of the raw material and the aqueous solution was 60–70% of the total volume of the reactor. The amount of catalyst added to the input aqueous solution varied depending on the catalyst concentration, including the case with or without the catalyst. The added catalyst contains a chloride-based metal salt and acid. At this time, the case where a catalyst is added to HTC is called Catalytic HTC. Additionally, the amount of catalyst added is determined by catalyst concentration conditions. In this study, the initial catalyst concentration was 2 g/L, and the catalytic HTC experiment was conducted while gradually increasing the concentration. If the catalyst concentration is 2 g/L, the number of moles of the catalyst is calculated considering the molecular weight of the catalyst. As a result, 2 g of the catalyst is dissolved in 1 L of distilled water. Then, adding the catalyst, the catalyst was diluted in 40% of the total aqueous solution, mixed with the remaining aqueous solution, stirred for 20 min, then added into the reactor. In the reaction step, a heat source was supplied such that the temperature inside the reactor reached the reaction temperature, and the reaction temperature was maintained for the reaction time. In the post-treatment step, it was cooled after the reaction holding time while discharging the vapor inside the reactor. When the temperature reached 80 °C, the HTC product inside the reactor was recovered, and the liquid and solid wastes were separated. Finally, the calorific values and mass yields were measured by drying the solid.

2.4. Pilot Plant Reactor Configuration and Process

The pilot plant facility for the pilot-scale HTC experiment was connected from raw material storage to the pellet production process, as shown in Figure 2. The capacity of the HTC reactor was 500 L, and the heat source was waste heat steam generated at the installation site and electrical energy through the heating jacket. First, waste heat steam with a pressure and temperature of 1.96 MPa and 200 °C raises the reactor temperature to 200 °C. After that, the reactor’s internal temperature is increased through the heating jacket. The temperature could be maintained constant after reaching the target reaction temperature because the PID controller was connected to the heating jacket.
Figure 2. HTC biofuel production pilot plant.

For each process of the pilot plant, the conversion of waste wood to HTC solid fuel through the process is shown in Figure 3. The raw material of waste wood was homogenized into particles within 2 mm using a shredder. Pulverized waste wood produced HTC solid fuel through HTC, and its shape changed depending on its moisture content and molding. The process consisted of the following steps: raw material storage and pretreatment, HTC, solid–liquid separation, drying, and pellet production.
Figure 3. HTC solid fuel according to the pilot plant process.

Step 1. Raw Material Storage and Pretreatment Process

Waste wood, which is a raw material, is transported to a waste wood storage tank where it could be stored and transported. To pulverize into uniform particles, metal materials that are mixed in the waste wood are first removed using a magnetic separator. The inclusion of non-ferrous metals is minimized in sorting waste wood before transport. However, the reason for installing the magnetic separator is that the residual metal mixed in the waste wood may cause a malfunction of the conveying machine. The waste wood is then pulverized into uniform particles within 2 mm using a grinder. The pulverized waste wood is transported to the pulverized wood storage tank through a screw conveyor and stored for use in the next process.

Step 2. HTC Process

The pulverized waste wood is moved to the reactor inlet via a bucket conveyor. The feeding speed of the bucket conveyor can be adjusted through the control panel. At this time, the input amount can be known through the mass sensor in the pulverized waste wood storage tank. The reactor is a batch type, and the inlet and outlet can also be opened and closed through the control panel. The water for processing is placed in the reactor, and the stirrer is operated simultaneously so that the pulverized waste wood and water content are 70–80%. At this time, approximately 60–70% of the total volume of the HTC reactor is filled. When the input is completed, the input valve of the HTC reactor is shut off, and a heat source is supplied to the HTC tank to increase the target reaction temperature. The reaction temperature is raised by introducing steam up to 200 °C, at which point the waste heat steam is cut off. At 200 °C or higher, the heat source of the heating jacket is used to increase the temperature to the target reaction temperature. After maintaining the reaction temperature for the target reaction time, the HTC reactor is cooled through steam discharge. When the internal temperature of the HTC reactor is 120 °C, it is discharged into the carbide storage tank using the internal pressure of the HTC reactor.

Step 3. Solid–Liquid Separation Process

The water contained in the hydrothermally carbonized solid is removed by transporting it to a high-pressure filter press using a pump. The solid–liquid separation liquid removed from the solid–liquid separation process is stored in a separate wastewater storage tank. Furthermore, the water content of the hydrothermally carbonized solid is approximately 50%. Subsequently, it is moved to a solid storage tank.

Step 4. Drying Process and Pellet Production Process

The hydrothermally carbonized solid is dried to a moisture content of 20% after being transferred to a dryer. The moisture that evaporated during the drying process is
condensed using a condenser, and the condensed water is moved to the wastewater storage tank. It is transported to the condensed gas treatment facility to remove pollutants and then discharged to the outside. After the drying process, the HTC solid fuel is moved to a pellet-forming machine. The pellet-forming machine produces HTC solid fuel in the form of pellets with a length of 2–3 mm.

3. Results

3.1. Setting of HTC Reaction Conditions of the Pilot Plant through Lab-Scale HTC Effect Analyses

The HTC experiment was conducted (Table 2) using a laboratory-scale reactor. The change in calorific value and mass yield of the HTC solid fuel was confirmed according to the reaction temperature and time. Sawdust has properties similar to those of waste wood, and because the particles are uniform, uniform results can be confirmed when analyzing carbides after HTC. The experimental conditions were the same as 80% moisture content according to the waste wood raw material in a 0.2 L laboratory-scale reactor, and the HTC reaction was performed by changing the reaction temperature and time.

Table 2. Comparison of calorific value and mass yield after HTC of sawdust.

| Reaction Condition | Temperature (°C) | Lab-Scale Results |
|--------------------|------------------|-------------------|
|                    | Time (h)         | HHV (kJ/kg)       | Mass Yield (%) |
|                    | 180              | 19,762            | 73.8           |
|                    | 190              | 20,100            | 71.7           |
|                    | 200              | 20,372            | 70.6           |
|                    | 210              | 22,839            | 70.3           |
|                    | 220              | 23,777            | 65.4           |
|                    | 230              | 25,158            | 59.7           |
|                    | 180              | 20,750            | 72.3           |
|                    | 190              | 21,060            | 70.2           |
|                    | 200              | 22,052            | 66.5           |
|                    | 210              | 22,948            | 65.3           |
|                    | 220              | 24,095            | 63.4           |
|                    | 230              | 27,001            | 50.1           |
|                    | 180              | 20,804            | 71.6           |
|                    | 190              | 21,034            | 69.9           |
|                    | 200              | 22,491            | 65.5           |
|                    | 210              | 23,777            | 65.1           |
|                    | 220              | 25,309            | 57.3           |
|                    | 230              | 29,898            | 35.1           |

Overall, as the reaction temperature and time increased, the calorific value of the hydrothermal carbides increased, and the mass yield decreased. The reaction temperature did not show a sharp change at 180–200 °C but a rapid change at 200–230 °C. The experimental results confirmed that the effective reaction temperature for converting waste wood to hydrochar should be at least 200 °C. In this experiment, as the reaction temperature and time increased, the mass yield of the reactants decreased to 35.1% when the calorific value increased to a maximum of 29,898 kJ/kg. The conditions for producing 23,027 kJ/kg or more, equivalent to coal for power generation with a mass yield of 60% or more, were analyzed. As a result, when the reaction time was 1–2 h, the reaction temperature was 220 °C. Furthermore, when the reaction time is 3 h, the condition is satisfied if the reaction temperature is 210 °C. However, in terms of production per hour, the reaction time is preferably within 1 h. Since the pilot plant may require more reaction time, the reaction time was set in the range of 1–1.5 h.

Under the HTC test conditions using waste wood, the moisture content was 80%, and the reaction temperature was in the range of 200–220 °C. The reaction time was tested in the range of 1–1.5 h to be applied to the pilot plant. As with sawdust, as the reaction
temperature and time increased, the calorific value increased and the mass yield decreased. It was confirmed that the change in the reaction temperature had a greater effect on the HTC reaction than the change in the reaction time. Unlike sawdust, in waste wood, the calorific value was low at reaction temperatures of 210 °C or higher. In this experiment (Table 3), a calorific value of 23,000 kJ/kg or more and the conditions for production with a mass yield of 60% or more was when the reaction temperature was 220 °C. Therefore, in the pilot-scale HTC experiment, the equipment were configured such that the heat source of the heating jacket could be raised to at least 220 °C.

Table 3. Comparison of calorific value and mass yield after HTC of waste wood.

| Input Ratio |
|Solid (%)| Moisture (%)|
| 20 | 80 |
| 1.5 |
| 200 | 21,373 | 78.0 |
| 210 | 21,629 | 74.9 |
| 220 | 23,082 | 67.5 |

3.2. Laboratory-Scale Catalytic HTC Effect Analysis

A HTC experiment was conducted (Table 4) with reference to the results of a previous study [14,15] for catalyst types and concentrations. When the catalyst concentration was 4 g/L, the calorific value and mass yield after HTC were compared. If the calorific value increases after catalytic HTC, it is a combination of hydrochloric acid and iron chloride (HCl + FeCl3). The higher the hydrochloric acid and iron chloride concentration, the better the catalytic HTC reaction occurred. Additionally, as in the previous experiment, the yield tends to decrease as the reaction progresses well. The catalyst concentrations of hydrochloric acid and iron chloride were determined to have a calorific value of ≥25,120 kJ/kg at a minimum of 3.0 g/L. When the catalyst concentration was reduced to 2 g/L, the calorific value decreased to 25,120 kJ/kg or less, which did not reach the target calorific value. Therefore, in the pilot plant HTC experiment, we decided to add a catalyst concentration of 4 g/L or more.

Table 4. Comparison of calorific value and mass yield after catalytic HTC of waste wood according to catalytic density.

| Input Condition | Reaction Condition | Lab-Scale Results |
| Catalyst | Catalytic Density (g/L) | Moisture (%) | Time (h) | Temperature (°C) | HHV (kJ/kg) | Mass Yield (%) |
| Non | 0 | 80 | 1 | 220 | 23,082 | 67.5 |
| HCl + FeCl3 | 2 | 80 | 1 | 220 | 23,890 | 62.8 |
| HCl + FeCl3 | 3 | 80 | 1 | 220 | 25,602 | 62.1 |
| HCl + FeCl3 | 4 | 80 | 1 | 220 | 26,687 | 61.3 |
| H3PO4 + FeCl3 | 4 | 80 | 1 | 220 | 25,263 | 67.4 |

Furthermore, a HTC experiment was conducted with a catalyst with a reaction time of 1.5 h, and as a result, the calorific value increased slightly, as shown in Table 5. This was consistent with the tendency of HTC to occur more easily as the reaction time increased under the same reaction temperature conditions. Although the catalyst concentrations were the same, hydrochloric acid was added in a larger amount than phosphoric acid, considering the purity of the catalyst. When hydrochloric acid and iron chloride were added, the calorific value was high, but the yield was lowered and the amount of catalyst
added was increased. When phosphoric acid and iron chloride were added, the calorific value was lower than when hydrochloric acid was used, but a stable yield was obtained.

Table 5. Comparison of calorific value and mass yield after catalytic HTC of waste wood according to reaction time.

| Input Condition | Reaction Condition | Lab-Scale Results |
|-----------------|---------------------|-------------------|
| catalyst        | catalytic density (g/L) | moisture (%) | time (h) | temperature (°C) | HHV (kJ/kg) | mass yield (%) |
| Non             | 0                   | 80             | 1       | 220             | 23,082     | 67.5          |
| HCl + FeCl₃     | 4                   | 80             | 1       | 220             | 26,687     | 61.3          |
| HCl + FeCl₃     | 4                   | 80             | 1.5     | 220             | 27,369     | 61.0          |
| H₃PO₄ + FeCl₃   | 4                   | 80             | 1       | 220             | 25,263     | 67.4          |
| H₃PO₄ + FeCl₃   | 4                   | 80             | 1.5     | 220             | 26,038     | 65.3          |

3.3. Analysis of Heavy Metals and Hazardous Substances on Laboratory-Scale HTC Solid Fuel

Prior to the production of HTC solid fuel in the pilot plant, heavy metals and hazardous substances were analyzed using specific samples in laboratory-scale HTC experiments. Table 6 is the quality standard applied when producing biosolid fuel at the test site where the pilot plant is installed. Therefore, it was a rule that had to be followed when conducting this study. The analysis method was carried out according to ISO 17022-1 biosolid fuel. Chlorine and sulfur were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), and metals were analyzed by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). When the HTC reaction proceeded, the mass yield decreased, but heavy metals and harmful substances did not decrease; therefore, the content per unit mass or volume increased. The heavy metals and toxic substances contained in the non-catalyst HTC solid fuel slightly increased from the raw material waste wood standard; however, in the catalyst HTC solid fuel, among the heavy metals, chromium increased by more than 7 fold and lead increased by more than 2 fold. Among the harmful substances, sulfur has a synergistic effect because the amount of raw material is small, but chlorine increased by 8–37 fold. It was confirmed that the catalyst combination of hydrochloric acid and iron chloride had the highest calorific value, but it was not a catalyst combination that could be used in the pilot plant because the chlorine content exceeded the standard for hazardous substances. Therefore, we decided to use a catalyst in which phosphoric acid and iron chloride were mixed as the catalyst combination to be used in the pilot plant-scale experiment.

Table 6. Laboratory-scale HTC solid fuel analysis according to heavy metal and hazardous substance standards of biosolid fuel.

| biosolid fuel production condition | lab-scale results |
|----------------------------------|-------------------|
| List Unit On-Site Standard Waste Wood (Raw Material) HTC (Non) Catalytic HTC (HCl + FeCl₃) Catalytic HTC (H₃PO₄ + FeCl₃) |
| Cl wt% 0.5 0.02 0.06 0.75 (excess) 0.17 |
| S wt% 0.6 0.0161 0.04 0.06 0.03 |
| Hg ppm 0.6 0.00289 ≤0.001 0.002 ≤0.001 |
| Cd ppm 5 ≤0.1 ≤0.1 ≤0.1 ≤0.1 |
| Pb ppm 100 0.52 0.96 1.15 1.45 |
| As ppm 5 ≤0.1 ≤0.1 0.15 0.11 |
| Cr ppm 70 3.6 4.34 30 28.1 |

3.4. Pilot-Scale HTC Effect Analysis and Scalability Verification

In the pilot-scale HTC experiment, the analysis was performed based on the HTC solid fuel discharged from the filler press during the process. The analyzed results were
compared with the laboratory-scale experimental results, as shown in Table 7. The reaction temperature was fixed at 220 °C, and the reaction times were 1 and 1.5 h, and it was confirmed that there was no significant difference with the laboratory-scale test result. The calorific value was 23,027 kJ/kg and the mass yield was 60% or more.

Table 7. Comparison of calorific value and mass yield after HTC of waste wood at the laboratory and pilot scales.

| Reaction Condition | Laboratory-Scale Results | Pilot-Scale Results |
|--------------------|--------------------------|---------------------|
|                    | Time (h) | Temperature (°C) | HHV (kJ/kg) | Mass Yield (%) | HHV (kJ/kg) | Mass Yield (%) |
|                    | 1        | 220               | 23,082      | 67.5           | 22,960      | 67             |
|                    | 1.5      | 220               | 23,266      | 66.4           | 23,236      | 65             |

The catalytic HTC experiment was performed according to the reaction conditions listed in Table 8. Unlike the laboratory-scale HTC experiment, the calorific value did not exceed 25,120 kJ/kg at a catalyst concentration of 4 g/L. The reduction in calorific value and mass yield is an effect of catalyst addition, thus additional experiments were conducted by increasing the catalyst concentration. It was increased by 2 g/L, and the calorific value was measured to be higher than 25,120 kJ/kg at 6 g/L, and it was confirmed that the mass yield was more than 60% up to 8 g/L.

Table 8. Comparison of calorific value and mass yield after catalytic HTC of waste wood according to catalytic density at pilot scales.

| Reaction Condition | Pilot-Scale Results |
|--------------------|---------------------|
| Catalyst Density (g/L) | Time (h) | Temperature (°C) | HHV (kJ/kg) | Mass Yield (%) |
| Non                | 0        | 1.5              | 220         | 23,027        | 65           |
| H₃PO₄ + FeCl₃     | 4        | 1.5              | 220         | 23,697        | 64           |
| H₃PO₄ + FeCl₃     | 6        | 1.5              | 220         | 25,787        | 61.2         |
| H₃PO₄ + FeCl₃     | 8        | 1.5              | 220         | 27,189        | 60           |

In the next step, heavy metals and hazardous substances were analyzed to determine whether the HTC solid fuel produced by the pilot plant satisfied the biosolid fuel standard. As shown in Table 9, it was confirmed that the HTC solid fuel produced in the laboratory satisfied the prescribed conditions. As a result, it did not exceed the standard for hazardous substances in the test site, and it was analyzed with a result similar to that of the laboratory-scale HTC solid fuel.

Table 9. Laboratory- and pilot-scale hydrothermal carbonization solid fuel comparison according to heavy metal and hazardous substance standards of biosolid fuel.

| Biosolid Fuel Production Condition | Laboratory-Scale Results | Pilot-Scale Results |
|-----------------------------------|--------------------------|---------------------|
| List                             | Unit | On-Site Standard | Catalytic HTC (H₃PO₄ + FeCl₃) | Catalytic HTC (H₃PO₄ + FeCl₃) |
| Cl                                | wt%  | 0.5            | 0.17            | 0.2                |
| S                                 | wt%  | 0.6            | 0.03            | 0.02               |
| Hg                                | ppm  | 0.6            | ≤0.001          | 0.0022             |
| Cd                                | ppm  | 5              | ≤0.1            | ≤0.1               |
| Pb                                | ppm  | 100            | 1.45            | 1.44               |
| As                                | ppm  | 5              | 0.11            | ≤0.1               |
| Cr                                | ppm  | 70             | 28.1            | 29.8               |
4. Conclusions

The purpose of this study was to convert waste wood into solid fuel with a calorific value equivalent to coal for power generation using HTC. First, a laboratory-scale HTC experiment confirmed that the mass yield was lowered with a higher calorific value than when no catalyst was added under the same reaction conditions. Then, to verify the scalability of the HTC effect, pilot-scale HTC test conditions were determined based on laboratory-scale HTC test results. The pilot-scale HTC experiment confirmed that the reaction temperature was 220 °C, and the reaction time was increased to 1.5 h, similar to the laboratory-scale HTC experiment result. However, in the catalytic HTC experiment, the laboratory-scale experimental results were similar when the catalyst concentration was increased by 1.5 fold or more. Therefore, it was confirmed that optimization of the catalyst concentration is necessary for a commercial HTC plant to which a catalyst is added. In conclusion, the optimal catalyst combination and concentration through the pilot plant produced solid fuel with a calorific value 18% higher than coal for power generation. In addition, it was verified through scalability that it could be used as a biosolid fuel.

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