Upgrading Hydrothermal Carbonization (HTC) Hydrochar from Sewage Sludge

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Abstract: As a treatment method of sewage sludge, the hydrothermal carbonization (HTC) process was adopted in this work. HTC has a great advantage considering the economic efficiency of its process operation due to its reduced energy consumption and production of solid fuel upgraded through the increased fixed carbon and heating value. The ash of sewage sludge, however, contains up to 52.55% phosphate, which degrades the efficiency of the thermochemical conversion process such as pyrolysis, combustion, and gasification by causing slagging. In this study, three kinds of organic acids, i.e., oxalic, tartaric, and citric acid, were selected to eliminate phosphorus from hydrochars produced through the HTC of sewage sludge. The efficiency of the phosphorus removal and the properties of the corresponding HTC hydrochars were analyzed by adding 20 mmoles of organic acids per 1 g of phosphorus in the HTC sample. In addition, the phosphorus reduction effect and the applicability to an upgrading process were verified. Oxalic acid was selected as the most appropriate organic acid considering the economic efficiency of its process operation. Furthermore, the optimal conditions were selected by analyzing the efficiency of the phosphorus elimination and the characteristic property of the HTC hydrochars with the weight fraction of oxalic acid.

Keywords: sewage sludge; hydrothermal carbonization; hydrochar; phosphate elimination; upgrading of hydrochar

1. Introduction

Sewage sludge is generated after the anaerobic digestion of organic matter in wastewater treatment facilities [1]. The rapidly increasing urbanization and population growth have resulted in a considerable increase in its production in recent years. In South Korea, there are 93 sewage treatment plants, generating 10,527 tons/day of sewage sludge [2]. The reduction and energy conversion projects of sewage sludge have been actively carried out under the government initiative, since 2013, when marine dumping of sewage sludge was banned by the London Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matters. Accordingly, the ever-increasing cost of sewage sludge disposal was a driving force for research efforts towards sustainable sludge treatment [3]. The conventional treatments of sewage sludge are burying, drying, or burning sewage sludge on land. Sewage sludge, however, requires large energy consumption for dewatering and drying because it contains high moisture content above 80 wt.%, causing the problem of low economic value. Hydrothermal carbonization (HTC) has received attention recently as a way to convert organic waste to solid fuel and ultimately to improve the bio-energy production efficiency [4,5].

The HTC process was first introduced by Bergius in early 1913 and has since been researched on to simulate the process of natural coalification [6]. The process could be suitable for upgrading wet low-value feedstocks by increasing energy density, decreasing oxygen, and enhancing hydrophobic properties [7,8]. Furthermore, the process increases the carbon density and calorific value of the raw
materials, and the reaction occurs within the range of 180–250 °C and pressure of approximately 10–50 bar, allowing the treatment of substrates with elevated moisture content, up to 75–90% in a closed system [9]. HTC is characterized by separating the liquid from the raw materials with no water evaporation, by partially decomposing the organic matter using subcritical water under a saturated water vapor pressure or higher at the reaction temperature in a closed system. Hence, based on the raw material with above 70% of moisture content, the amount of the HTC product moisture could be decreased to 30% merely through a mechanical dewatering process [10]. Furthermore, since the HTC process proceeds in a closed system, accordingly, the phase change of the moisture doesn’t occur during the process. The moisture consumes the specific heat, while the evaporation heat is not utilized in the process. Therefore, energy consumption could be reduced by approximately 70% compared to the conventional drying process.

In South Korea wastewater treatment plants (WWTP), there is a variety of ways to remove phosphates from liquid drains. Phosphates can be removed chemically (chemical and physical-chemical methods), biologically (the biological method) by modifying the biological process that incorporates phosphorus in the cellular substance, or by using the biological-chemical method as shown in Figure 1. For total phosphorus, the effluent water quality standard of sewage treatment plants has been strengthened to 0.2–0.5 mg/L in South Korea since 2012. Accordingly, the process of injecting excessive quantities of coagulant to treat phosphorus has been induced. In this process, phosphorus is enriched to high concentrations in the sewage sludge [11]. The high content of phosphate in sewage sludge as solid fuel lowers the ash fusion temperature and causes various problems in the pyrolysis, combustion, and gasification. This leads to slagging and then lowers the efficiency of the thermochemical conversion process [12]. Furthermore, the phosphorous reserves are about 70,000 Mt in the world, while the world mining production is set at 260 Mt/year. Assuming a constant extraction of resource, the raw material of phosphate is predicted to be depleted in just under 270 years. Accordingly, the recovery of phosphorus from sewage sludge, urban waste, and other zootchnical wastes has been implemented in Europe, including Germany and the Netherlands [13]. Therefore, research for the recovery of phosphorus is required from different organic wastes. A number of studies on phosphorous recovery have been published with different approaches including ion exchange [14], wet-chemical leaching [15], wet-oxidation [16], metallurgic melt-gassing [17], thermo-electrical [18], and acidic wet chemical leaching and extraction. A recovery method with organic acids was selected in this study because it could be applied to the HTC process without additional reactors or devices, utilize excess heat of the HTC process, and there was no need to change the conditions for the process. In this study, characteristics of phosphate elimination for HTC products using sewage sludge were analyzed using different organic acids and the upgrading characteristics of the hydrochars produced in this process were analyzed.

Figure 1. Flow charts of phosphate removal methods in Korea WWTP.
2. Materials and Methods

2.1. Materials

The sewage sludge used as the carbonization feed was obtained from the Gongchon branch of the WWTP of South Korea, and its properties were analyzed monthly by sampling over the course of the year. The monthly sludge sample was dried overnight in an oven at about 105 °C, and the components of ash in the sample were analyzed using an X-ray fluorescence analyzer (XRF).

2.2. Hydrothermal Carbonization

The hydrothermal carbonization experiments were conducted with a lab-scale 3 L reactor. The reactants of the process were 1 kg of sewage sludge and 100 g of distilled water. The samples were stirred using a magnetic drive with constant torque at the rate of 250 rpm throughout the entire reaction process so that the heat would be supplied to the external heater jacket of the reactor during the HTC process. The reaction temperature was set to 200 °C under a fully closed system condition, and over 20 bar pressure was achieved by generating steam and volatile matters with no injection of additional gas. The total reaction time was 2 h including the temperature-rising step of 1 h and the retention of major reaction sections of 1 h. After the termination of the reaction, sufficient time was allowed until the atmospheric pressure, and room temperature were reached. Characteristics of the HTC products including the hydrochar, liquid, and gas products were identified, which were in good agreement with previously reported literature [19,20]. Accordingly, after the HTC reaction was finished completely, the gas products were released to reduce the pressure in the reactor. Therefore, the changes in the weight occurred. The changes in the weight and other properties of the reaction product were analyzed. Each test was repeated three times.

2.3. Organic Acids

Organic acids like tartaric acid, citric acid, and lactic acid are used as food additives and raw materials for medicines [21]. They are also widely used for cleaning various manufacturing facilities, as well as in industrial chemicals. Particularly in the metal field, organic acids are used in the precipitation separation process, which forms chelates through the reaction of inorganic mineral ions and organic acids [22]. Furthermore, previously reported studies have presented on the extraction of phosphates from raw materials using various organic acids (e.g., citric, tartaric, and oxalic acids) from phosphate rock or clay loam ultisol [23,24]. Meanwhile, acidic species other than organic acids include H$_2$SO$_4$, HNO$_3$, HCl, HF, and HPO$_4$. The solid fuels produced with those acidic chemical species, however, would be inappropriate for the thermal conversion process, because it causes problems including reactor corrosion, in the process operation, as well as environmental problems, including the production of SO$_x$, NO$_x$, and dioxin precursors. In this study, the characteristics of phosphate elimination via the chelate reaction was observed with different organic acids including oxalic, citric, and tartaric acids by stirring them for 1 hour at 80 °C after the HTC reaction. These conditions were designed to reutilize the heat of the HTC process in the 50 tons per day pilot plant process, which is in operation in the authors’ research center. Three kinds of different organic acids, i.e., oxalic, tartaric, and citric acids were selected, and their phosphorus elimination characteristics in the HTC products were compared. For this removal test, 20 mmoles of each organic acid was added per 1 g of phosphorus [25]. The organic acids were used to produce a 1 M solution and were added in fixed quantities.

3. Results and Discussion

3.1. Characteristics of Phosphorus Elimination in HTC Hydrochars Using Different Organic Acids

The monthly weight fractions of phosphate among the inorganic materials in the sewage sludge are shown in Figure 2. The phosphate content of the sewage sludge ash ranged from 33.01 to 52.55%,
with an average of 40.91%. The phosphate content was higher in spring and summer than in autumn and winter. In addition, the moisture contents of the sewage sludge were analyzed in the range of 81.98–86.23%.

Figure 2. Monthly fraction of phosphate in the sewage sludge ash.

Figure 3 shows the $P_2O_5$ contents of the sewage sludge ash, the HTC hydrochar produced from the raw material, and the HTC hydrochars treated with three organic acids on a dry basis. Three kinds of different organic acids, i.e., oxalic, tartaric, and citric acids were selected as mentioned earlier, and their phosphorus elimination characteristics in HTC products were compared. The results confirmed that the fraction of phosphorus pentoxide in the sludge ash increased from 43.65 to 48.13% via the HTC process. It seemed that the weight of the HTC hydrochar was relatively increased compared to the sludge ash by nitrogen, where sulfur solubilized to a liquid product, and $H_2O$ and $CO_2$ were produced through a series of reactions during the HTC process. The effect of three organic acids treatments in the HTC products show that the fraction of phosphorous pentoxide decreased from 48.13 to 3.10–21.39%. The phosphorus species reduction efficiency can be described as follow:

$$\text{Phosphorous species reduction efficiency} = \frac{P_{HC} - P_{HC,O}}{P_{HC}} \times 100$$

where $P_{HC}$ and $P_{HC,O}$ represent the fraction of the phosphorus in the HTC hydrochar, and the HTC hydrochar-treated organic acids, respectively. The experimental values of oxalic, tartaric, and citric acid relative to the initial HTC hydrochar were 93.55, 86.73, and 55.55%, respectively. The organic acids chelate phosphorus, as mentioned earlier, and convert insoluble phosphate to solubilized forms [26]. Accordingly, phosphorous pentoxide in the HTC hydrochar ash declined significantly with the organic acid treatment. Oxalic acid showed the highest phosphorus elimination effect among the three kinds of organic acids considered in this study.
3.2. Comparison of HTC Hydrochar Properties with Different Organic Acids

Table 1 shows the physical and chemical properties of the raw material, HTC product, and HTC hydrochar treated with three organic acids. As mentioned above, the properties of the samples were analyzed on a dry basis, and the moisture content in the proximate analysis could be used as an indirect indicator of the moisture re-adsorption degree. The moisture content of the raw material was approximately 1% higher than that of the HTC product. The experimental result suggested that the degree of moisture re-adsorption decrease resulted from the enhancement of the hydrophobicity as the temperature of the HTC process increased [7,9]. The volatile matters of sewage sludge decreased from 69.95% to 59.81% after the HTC process but increased from 67.94–72.06% after treatment with the organic acids. The fixed carbon content of the raw materials increased from 10.78 to 12.48% via the HTC reaction. The analysis results indicated that the carbon density was increased by the HTC process.

With the treatment of organic acids, the fraction of volatile matter, and carbon increased from 12.63–14.19%. Such results may be explained by the elimination of a large amount of phosphorus from the HTC chars through the chelating effect of the organic acid [25]. The carbon content of the sewage sludge increased from 42 to 45.34% after the HTC process, and the hydrogen and oxygen contents decreased from 6.2 and 6.09% to 24.60 and 16.91%, respectively. This was due to the release of CO$_2$ and H$_2$O chemical species by dehydration and decarboxylation, which are the major reaction mechanisms of HTC [27]. Furthermore, the nitrogen and sulfur contents of the raw material decreased from 7.8 to 4.73% and from 0.99 to 0.6% due to the solubilization via the HTC, which are in good agreement with previously reported literature [28,29]. The change of properties could lead to the reduction of the potential risk of generating harmful pollutants such as NO$_x$ and SO$_x$ in the thermochemical process. Furthermore, the HTC hydrochar produced by pretreatment with organic acid showed an increase in carbon content from 45.34% to 48.32–55.55%. In addition, the hydrogen and oxygen contents increased from 6.09% to 6.24–6.82%, and from 16.91% to 21.56–25.21%, respectively, and it could be considered that these changes were caused by the addition of organic acid. The nitrogen and sulfur in the HTC product decreased slightly from 4.73 to 3.91–4.65 and from 0.6% to and 0.5–0.54%, respectively, suggesting that the organic acids used in this study may be effective in solubilizing those chemical species. The heating value analysis showed that the heating value of the HTC product increased from 4503 to 4960 kcal/kg on the basis of the raw material. Such a tendency is coincident with other findings [30]. For solid yield (i.e., percentage of HTC hydrochar compared to sewage sludge on dry solid weight) decreased from 65.75% to 51.07–55.28%.

**Table 1.** Characteristic properties of the sludge, HTC, and HTC including organic acids.

| Descriptions | Sludge | HTC (Oxalic) | HTC (Citric) | HTC (Tartaric) |
|--------------|--------|-------------|-------------|---------------|
| **Proximate analysis (wt.%, db a)** | | | | |
| Moisture | 1.10 | 0.11 | 0.12 | 0.14 | 0.13 |
| Volatile | 69.95 | 59.81 | 70.31 | 72.06 | 67.94 |
| Fixed carbon | 10.78 | 12.48 | 12.83 | 14.19 | 12.63 |
| Ash | 18.17 | 27.60 | 17.34 | 13.61 | 19.30 |
| **Ultimate analysis (wt.%, db a)** | | | | |
| C | 42.00 | 45.34 | 50.60 | 53.55 | 48.32 |
| H | 6.20 | 6.09 | 6.40 | 6.78 | 6.82 |
| O | 24.60 | 16.91 | 24.99 | 21.56 | 25.21 |
| N | 7.80 | 4.73 | 3.91 | 4.65 | 4.17 |
| S | 0.99 | 0.60 | 0.50 | 0.54 | 0.51 |
| **Calorific analysis (kcal/kg, db a)** | | | | |
| Higher heating value | 4503 | 4960 | 5350 | 5690 | 5020 |
| **Ash analysis (wt.%, db a)** | | | | |
| Phosphorous content in ash | 43.65 | 48.13 | 3.10 | 6.39 | 21.39 |
| Solid yield (%) | - | 65.76 | 54.71 | 51.07 | 55.28 |

*a On a dry basis.
3.3. Phosphorus Removal Characteristics According to the Amount of Oxalic Acid Added in the HTC Product

The effect of varying the weight fraction of organic acid in the HTC process was analyzed to examine the economic efficiency of the process operation. The weight fractions of the organic acids relative to the HTC product were calculated as the molecular weight of the organic acids to the total weight of the HTC product, and the estimated values used in the present study were 5, 12, and 9 wt.% for oxalic acid, citric acid, and tartaric acid, respectively. The unit costs of oxalic acid, citric acid, and tartaric acid were 480, 600, and 1500 US$/ton-organic acid, respectively [31], and the disposal costs of a ton of sewage sludge were 24, 72, and 135 US$/ton-sludge, respectively. In consideration of the economic feasibility and efficiency of organic acid treatment such as carbon density, heating values, and input weight fractions, oxalic acid was most appropriate for the application of the commercial plant operation. The experimental runs were conducted by varying the different weight fraction of oxalic acid; 0.1, 0.5, 1.0, and 5.0 wt.% relative to the HTC product. The weight fraction of the phosphorous pentoxide with different inputs of oxalic acid in the HTC product is shown in Figure 4.

As the weight fraction of oxalic acid increased, the phosphorus pentoxide content of the hydrochar decreased from 48.13 to 3.10–31.08% linearly, and the removal efficiency was represented within a range of 38.96–93.56%. The linear correlation between the inputs of oxalic acid and the fraction of phosphorous pentoxide is presented in Equation (2) with the linear regression coefficient ($R^2$) higher than 0.98 as follows:

$$y = 28.44 - 5.11x$$

(2)

Figure 4. The fraction of phosphorous pentoxide for the HTC product ash with the weight fraction of oxalic acid.

3.4. Comparison of Solid Fuel Properties According to the Amount of Oxalic Acid Treated in the HTC Product

The characteristic properties of the HTC hydrochar with different fractions of oxalic acid are summarized in Table 2. The volatile matters and fixed carbons increased from 60.10 to 70.31% and from 10.78 to 12.83%, respectively. With a subsequent increase of oxalic acid inputs, those values increased. In contrast, the ash tended to decrease to 17.34–29.01%. Furthermore, the percentages of carbon, hydrogen, and oxygen increased with the elevated amount of oxalic acid, and the fractions of nitrogen and sulfur decreased as the oxalic acid inputs increased. The properties of the HTC hydrochars enhanced at different degrees with an increase in the inputs of oxalic acids. The heating value also increased up to 5130–5350 kcal/kg as the fraction of oxalic acid increased from 0.5–5.0%, which corresponded to the trend of volatile matter, fixed carbon, and carbon contents. Solid yields decreased from 65.75% to 54.71–64.18%. In case of the added 0.1% oxalic acid, however, the properties
of the HTC char that could assess the grade of solid fuel were declined. Accordingly, the appropriate amount of organic acid could be considered to be more than 0.5%. As mentioned earlier, the unit prices on the different inputs of oxalic acid are listed in Table 3 based on 1 ton sludge for disposal. Considering the sludge treatment fee of US$140/ton-sludge, however, the plant operation cost of US$70/ton-sludge, and the selling price of US$25/ton-hydrochar on the basis of the plant capacity of 50 ton-sludge/day, it seemed reasonable to apply inputs of oxalic acid in the 0.5–1.0% range.

### Table 2. Characteristic properties of HTC products including different weight fractions of oxalic acid.

| Descriptions | HTC (Oxalic, 0.1) | HTC (Oxalic, 0.5) | HTC (Oxalic, 1.0) | HTC (Oxalic, 5.0) |
|--------------|------------------|------------------|------------------|------------------|
| Moisture     | 0.11             | 0.11             | 0.11             | 0.12             |
| Volatile     | 60.10            | 63.01            | 64.25            | 70.31            |
| Fixed carbon | 10.78            | 11.01            | 11.05            | 12.83            |
| Ash          | 29.01            | 25.87            | 24.59            | 17.34            |

| Proximate analysis (wt.%, db) |
|--------------------------------|
| C                             | 45.08 | 46.90 | 47.99 | 50.60 |
| H                             | 6.00  | 6.07  | 6.12  | 6.40  |
| O                             | 17.62 | 19.13 | 20.07 | 24.99 |
| N                             | 4.66  | 4.59  | 3.97  | 3.91  |
| S                             | 0.53  | 0.54  | 0.52  | 0.50  |

| Ultimate analysis (wt.%, db) |
|------------------------------|
| C                             | 4870  |
| H                             | 5130  |
| O                             | 5190  |
| N                             | 5350  |

| Calorific analysis (kcal/kg, db) |
|----------------------------------|
| Higher heating value             | 4870  | 5130  | 5190  | 5350  |

| Ash analysis (wt.%, db) |
|-------------------------|
| Phosphorous content in ash| 31.08 | 24.93 | 22.63 | 3.10  |
| Solid yield (%)          | 64.18 | 63.95 | 62.28 | 54.71 |

* On a dry basis.

### Table 3. The unit cost of oxalic acid with input in the HTC products.

| Oxalic Acid Fraction (w/w, %) | 0.1 | 0.5 | 1.0 | 5.0 |
|------------------------------|-----|-----|-----|-----|
| Unit Cost of Oxalic Acid     | 0.48| 2.4 | 4.8 | 24  |

### 4. Conclusions

In order to upgrade the properties of sewage sludge as solid fuel, the hydrothermal carbonization process was adopted, and the large number of phosphorus species contained in the raw material was eliminated with different organic acids. Solid fuel properties were analyzed using different organic acids. The HTC process changed the properties of the sewage sludge by increasing the energy density, decreasing oxygen, and enhancing the hydrophobic properties. The three kinds of organic acids, i.e., oxalic, citric, and tartaric acids were used at the same amount of 20 mmoles in the HTC samples, and the efficiency of the phosphorus pentoxide removal was 93.55, 86.73, and 55.55%, respectively. Thus, oxalic acid showed the highest phosphorus elimination efficiency among the three organic acids. In terms of the solid fuel production, however, such as the fixed carbon content and heating value, citric acid showed the best solid fuel upgrading effect, followed by oxalic acid and tartaric acid. The economic efficiency of each organic acid was indirectly determined by converting the amounts of organic acid added to the weight fractions and considering the efficiency of the phosphorus elimination, solid fuel upgrade, and HTC product. As a result, oxalic acid was selected as the best organic acid applicable to the demonstration plant. Furthermore, the effect of phosphorus removal of the HTC hydrochar with the inputs of organic acid was analyzed by varying the weight fraction of oxalic acid in the range of 0.1, 0.5, 1.0, and 5.0 wt.%. As the fraction of oxalic acid increased, the phosphorus content decreased linearly. Furthermore, when the weight fraction of oxalic acid was increased from 0.5 to 5.0 wt.%, excluding 0.1 wt.%, the properties of the HTC hydrochars was improved such as the
phosphorus removal efficiency and the increase of the volatile matter, fixed carbon content, carbon content, and heating value. Considering the economic feasibility of oxalic acid application to the demonstration plant, 0.5–1.0% was considered a valid amount of oxalic acid.

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