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# Energy Recovery Efficiency of Poultry Slaughterhouse Sludge Cake by Hydrothermal Carbonization

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**Abstract:** Hydrothermal carbonization (HTC) is a promising technology used for bioenergy conversion from bio-wastes such as sewage sludge, livestock manure, and food waste. To determine the optimum HTC reaction temperature in maximizing the gross energy recovery efficiency of poultry slaughterhouse sludge cake, a pilot-scale HTC reactor was designed and operated under reaction temperatures of 170, 180, 190, 200 and 22 °C. During the HTC reaction, the gross energy recovery efficiency was determined based on the calorific value of the HTC-biochar and ultimate methane potential of the HTC-hydrolysate. The poultry slaughterhouse sludge cake was assessed as a useful source for the bioenergy conversion with a high calorific value of approximately 27.7 MJ/kg. The calorific values of the HTC-biochar increased from 29.6 MJ/kg to 31.3 MJ/kg in accordance with the change in the reaction temperature from 170 °C to 220 °C. The ultimate methane potential of the HTC-hydrolysate was 0.222, 0.242, 0.237, 0.228 and 0.197 $Nm^3/kg\text{-}COD_{added}$ for the reaction temperatures of 170, 180, 190, 200 and 220 °C, respectively. The potential energy of feedstock was 4.541 MJ/kg. The total gross energy recovery ($GER_{total}$) was 4318 MJ/kg, of which the maximum value in the HTC reaction temperature was attained at 180 °C. Thus, the optimum temperature of the HTC reaction was 180 °C with a maximum $GER_{total}$ efficiency of 95.1%.

**Keywords:** hydrothermal carbonization; anaerobic digestion; poultry slaughterhouse; sludge cake; energy recovery efficiency

## 1. Introduction

In Korea, meat consumption (e.g., beef, pork, and poultry) has steeply increased, with food consumption patterns changing with economic growth. In particular, the poultry industry has been growing about 5% each year since 2000, and 993 million poultry heads were slaughtered in 2016. Due to the growth of the poultry industry, several environmental problems have occurred relating to the disposal of wastewater treatment sludge and various poultry processing residues (e.g., blood, feathers, bones) generated from the poultry slaughterhouse [1]. In general, poultry processing residues can be utilized as feedstock for animal feed or compost. However, sludge cake containing moisture above 80% is disposed of after incineration due to the prohibition of direct landfill and ocean disposal, although a high amount of drying energy is needed for the incineration of sludge cake [2]. Nowadays, the interest in energy conversion of sludge waste is increasing due to high sludge disposal costs and limited alternative disposal methods. Poultry slaughterhouses sludge cake is characterized by a high solid content that is composed of protein and fat [3–5]. Hence, sludge cake is considered an effective substrate for anaerobic digestion. However, it is difficult to be fed into conventional anaerobic digesters due to its high solid content [5]. Also, high ammonium nitrogen produced from protein degradation and long chain fatty acids from fat degradation can cause inhibition during the anaerobic digestion process [6].

For these reasons, hydrothermal carbonization (HTC) has recently emerged as an alternative technology for the energy conversion of the slaughterhouse sludge cake. HTC technology is a thermo-chemical process converting biomass to a coal-like material with higher carbon content [7,8]. The energy conversion of biomass by HTC technology has several advantages compared to common biological technology, such as anaerobic digestion. The HTC process requires a short operational time within hours, unlike that of biological processes that require 10 days or more [9]. In addition, waste biomass containing toxic substances cannot be biologically converted to bioenergy, and problems related to hygiene can be of concern when the byproducts generated from biological processing are further utilized. However, the high operational temperatures of the HTC process can decompose potentially toxic organic contaminants and sterilize pathogens. Because of these advantages, HTC technology could be a promising technology for the treatment of waste biomass such as sewage sludge, livestock manure, and food waste [10–12].

The HTC process is mainly composed of a relatively simple closed vessel reactor, containing the wet biomass. The HTC reactor is heated to 170–250 °C and maintained at the saturated vapor pressure that is formed in accordance with the given reaction temperature. During the HTC reaction of wet biomass, the oxygen and hydrogen content of feeding material is reduced, and the solid phase (biochar), the liquid phase (hydrothermal hydrolysate) and a small amount of gas (mainly carbon dioxide) are produced [13,14]. These products are attained by mechanisms including hydrolysis, dehydration, decarboxylation, polymerization and aromatization [8,15]. The solid phase, referred as biochar, can be easily separated due its dewatering property, and utilized as a solid fuel of high calorific value. The hydrothermal hydrolysate generated after the HTC processing requires further treatment since it contains a high amount of soluble organic material and ammonium nitrogen. Recently, anaerobic digestion is preferred for the treatment of hydrothermal hydrolysate in terms of energy recovery efficiency from biomass. In particular, for the HTC reaction, organic matter is solubilized by the hydrolysis reaction and the efficiency of anaerobic digestion can be improved [16,17]. The HTC technology has been studied for a wide range of biomass feedstocks, mainly focusing on herbal and woody biomasses with high contents of lignin, cellulose and hemicellulose, generated from the agricultural sector [13,18,19]. In the case of poultry slaughterhouse sludge cake mainly composed of protein and fat, the HTC process was not so widely investigated, but several studies focused on the properties of solid product, energy recovery rate, biochar yields and its combustion characteristic for slaughterhouse sludge cake. In particular, these studies have only focused on the determination of HTC reaction conditions for the energy recovery and their impacts on the quality of final product (HTC-biochar) without considering the appropriate treatment methods on the HTC-hydrolysate generated as the byproduct during the HTC reaction of sludge cake.

This research was focused on the assessment of total energy recovery from the HTC-biochar and HTC-hydrolysate generated from the HTC reaction with slaughterhouse sludge cake. The goal of this study was to determine the optimum HTC reaction temperature in maximizing the gross energy recovery efficiency from poultry slaughterhouse sludge cake in order to improve the operational efficiency of the HTC process. For this purpose, the energy conversion processes of HTC and anaerobic digestion were proposed. The gross energy recovery efficiency was determined based on the calorific value of the HTC-biochar and ultimate methane potential of the HTC-hydrolysate during the HTC reaction of poultry slaughterhouse sludge cake.

## 2. Materials and Methods

### 2.1. Materials

A sludge cake was collected from the wastewater treatment plant at the poultry slaughterhouse facility (Jincheon, South Korea), which has a slaughtering capacity of 300,000 heads per day. A total of 1500 $m^3$/day wastewater is generated and treated by the activated sludge process, and approximately 30 ton of sludge cake is generated daily.

### *2.2. Proposed Energy Conversion System*

The energy conversion system proposed in this study is shown in Figure 1. The activated sludge generated from the wastewater treatment plant of the poultry slaughterhouse is dewatered using solid/liquid separation equipment (a filter press) and sludge cake is fed into the HTC reactor. During the HTC reaction, the organic solid of the sludge cake is fixed as the carbonized solid of high carbon content and solubilized as a lower molecular compound at the same time. Thereafter, the effluent of the HTC reactor is separated into liquid and solid fractions using filter pressing. The solid fraction (HTC-biochar) is utilized as solid fuel for the incineration boiler, and the liquid fraction (HTC-hydrolysate), with its high soluble organic and nitrogen contents, is used for the high performance anaerobic digester. Lastly, digestate discharged from the anaerobic digester is treated at the wastewater treatment plant. This system is able to simultaneously produce solid fuel and biogas through the stepwise process of thermochemical decomposition and biological degradation of organic solid waste.

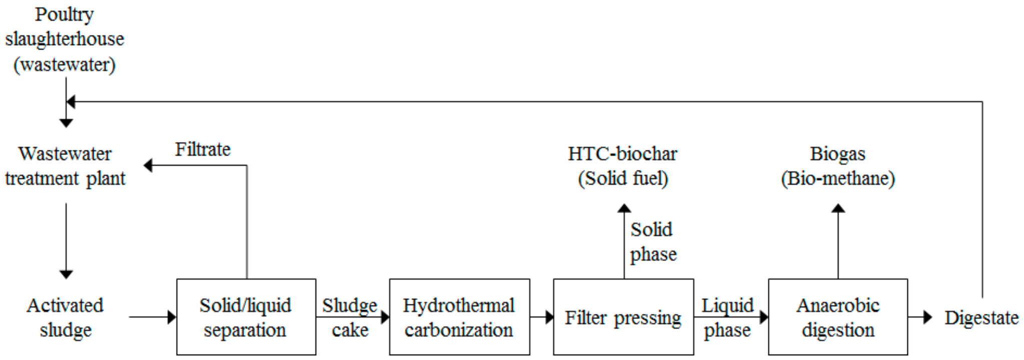

**Figure 1.** Scheme of the HTC (Hydrothermal carbonization) system for the energy conversion of sludge cake generated at the poultry slaughterhouse wastewater treatment plant.

### *2.3. Hydrothermal Carbonization*

In order to assess the energy yield from the production of the HTC-biochar for several HTC reaction temperatures, a batch-type HTC reactor was designed for the thermochemical treatment of sludge cake (Figure 2). The HTC reactor is a closed system with no potential heat loss via vaporization and condensation loss. The designed HTC reactor has a working volume of 1.5 kg and is equipped with electric heater, temperature sensor, and pressure gauge. The reactor was equipped with a heating coil. A temperature sensor and pressure gauge were inserted into the reactor to monitor inner temperature and a saturated vapor pressure during the HTC reaction. For the HTC reaction test, 1.5 kg of sludge cake was directly placed without additional processing water and covered with an airtight sealant. Setting temperatures were 170, 180, 190, 200 and 220 °C. When each temperature was reached to the set point, each HTC reactor was maintained at the isothermic condition for 60 min. The inner vapor pressures were then maintained at 1.05 MPa at 170 °C, 1.18 MPa at 180 °C, 1.42 MPa at 190 °C, 1.78 MPa at 200 °C, and 2.51 MPa at 220 °C. At the end of the HTC reaction, the reactor was cooled to room temperature using a chiller. The effluent of the HTC reactor was separated into HTC-biochar and HTC-hydrolysate using a filter press. A weight loss of 5–10% occurred due to moisture absorption into the filtering cloth. However, for the theoretical valuation, moisture loss was included in the HTC-hydrolysate.

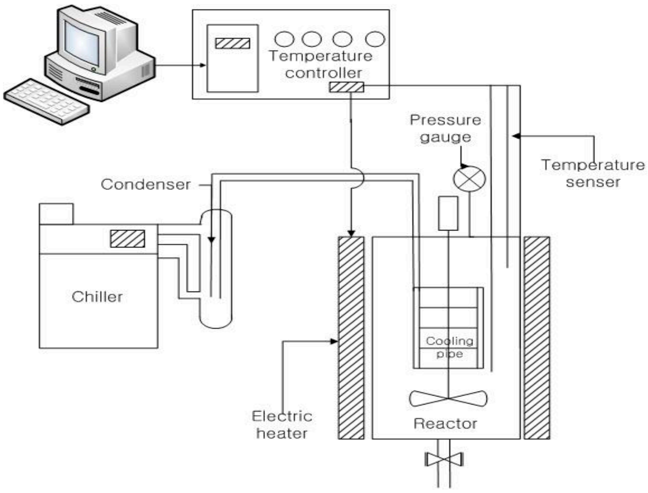

**Figure 2.** Schematic diagram of the lab-scale HTC batch reactor.

### *2.4. Methane Production Potential of HTC-Hydrolysate*

To assess methane production of the HTC-hydrolysate, a batch type anaerobic reactor was operated under mesophilic conditions (38 °C). Anaerobic inoculum in pig slurry was collected from a farm-scale anaerobic digester located in Anseong city, South Korea. The chemical properties of the inoculum are shown in Table 1.

**Table 1.** Chemical characteristics of inoculum used in the methane potential assay of HTC-hydrolysate.

| **Sample** | **pH** | **TS** [1] | **VS** [2] | **$COD_{Cr}$** [3] | **TN** [4] | **$NH_4^+$-N** | **Alkalinity** |
|---|---|---|---|---|---|---|---|
| | **(-)** | **(wt. %, w.b.** [5]**)** | **(wt. %, w.b.)** | **(g/L)** | **(wt. %, w.b.)** | **(wt. %, w.b.)** | **(g/L as $CaCO_3$)** |
| Inoculum | 8.2 (0.0) [6] | 2.6 (0.0) | 1.4 (0.0) | 25.2 (0.1) | 0.4 (0.0) | 0.3 (0.0) | 19.2 (0.3) |

[1] Total solid, [2] Volatile solid, [3] Total chemical oxygen demand, [4] Total nitrogen, [5] Wet basis, [6] Standard deviation (n = 3).

In order to remove any remaining biodegradable fraction, the inoculum for methane production potential analysis of the HTC-hydrolysate was kept under the mesophilic condition at 38 °C for one week. The ratio of substrate to inoculum in all anaerobic batch reactors was equal to 0.3 ($\text{g-VS}_{\text{substrate}}/\text{g-VS}_{\text{inoculum}}$). A working volume for anaerobic batch fermentation was 80 mL of a 160 mL serum bottle. The head space of the serum bottle was filled with $N_2$ gas and sealed with a butyl rubber stopper. The anaerobic batch reactors for each sample and blank were incubated for up to 96 days in the convection incubator and manually mixed each day during the fermentation period. Methane production potential was calculated as the chemical oxygen demand (COD) content. Methane production potentials of the samples were corrected from the blank value and calibration was done under standard temperature and pressure (STP) conditions. To interpret the progress of cumulative methane production, the parallel first-order kinetic model Equation (1) was employed to fit the cumulative methane production data as in the following equation [20,21].

$$B_t = B_u\left\{1 - f_e e^{-k_1 t} - (1 - f_e) e^{-k_2 t}\right\} \quad (1)$$

where $B_t$ (mL) is the amount of methane production at time t, $B_u$ (mL) is the amount of ultimate methane production, $f_e$ (%, g/g) is the organic distribution constant for two first-order kinetics, and $k_1$ and $k_2$ are the kinetic constants in the parallel first-order kinetics. This model considers that the degradation of organic matter is carried out in two stages. In addition, $f_e$ distributes the characteristics of the two types of substrates with different reaction rates under anaerobic conditions, and $k_1$ and $k_2$ indicate the first-order kinetics constants for the first and the second organic degradation stages.

The degree of COD degradation ($COD_{deg}$) of the HTC-hydrolysate was defined as the amount of methane produced during the anaerobic fermentation of the HTC-hydrolysate for the theoretical methane potential, as shown in Equation (2) [22].

$$COD_{deg} = \frac{V_{biogas} \times C_{methane}}{320 \times m_{substrate} \times COD_{substrate}} \times 100 \quad (2)$$

where $V_{biogas}$ is the volume of biogas (mL/day in STP), $C_{methane}$ is the concentration of methane (%), $m_{substrate}$ is the amount of substrate added to the anaerobic reactor (mL), $COD_{substrate}$ is the COD of the substrate (g/mL), and 320 (mL/g-$COD_{added}$ in STP) is the theoretical biochemical methane potential under practical conditions assuming that about 10% of COD added to the anaerobic reactor is consumed in the reformation of biomass.

### 2.5. Analysis

Total solids (TS), volatile solids (VS), pH, chemical oxygen demand ($COD_{Cr}$), total nitrogen (TN), ammonium nitrogen ($NH_4^+$-N) and alkalinity were determined based on standard methods [23]. Volatile fatty acid (VFA) concentrations were measured using a gas chromatograph (GC2010, Shimazhu Scientific Instrument, Inc., Columbia, MD, USA) equipped with a flame ionization detector with an automatic sampler. This chemical analysis was performed in three replicates. Element composition (C, H, N, O, S) was determined using an element analyzer (EA1108, Thermo Finnigan LLC, San Jose, CA, USA). The higher heating value (HHV) was measured by the Bomb calorimeter (AC-350, LECO Corporation, St. Joseph, MI, USA) for a dry sample. In the anaerobic batch reactor experiment, total gas production was measured daily for the first five days and then every two or three days, followed by the displacement of acidified brine solution in a burette and recording the volume of displaced solution after correcting for atmospheric pressure [24]. To investigate the gas composition, the $CH_4$ and $CO_2$ concentrations in the gas samples were determined using a gas chromatograph (Clarus 680, PerkinElmer, Inc., Waltham, MA, USA) equipped with a thermal conductivity detector and a HayeSepQ packed column (CRS, Inc., Louisville, KY, USA). The column was operated with helium carrier gas at a constant flow rate of 5 mL/min. The set temperatures of the injector, the oven, and the detector were 150 °C, 90 °C and 150 °C, respectively.

### 2.6. Efficiency Parameters

The energy recovery by the HTC was assessed using gross energy recovery GER, Equation (3), that was presented as the calorific value of the product (biochar and methane) by HHV. Net energy recovery NER, Equation (4), was calculated by subtracting the thermal energy consumed during the HTC reaction and the drying energy of HTC-biochar. The GER efficiency, Equation (6), of the product was estimated as the ratio of the $GER_{product}$ of the product and the gross energy potential $GEP_{feedstock}$, Equation (5), estimated from the HHV of the dried sludge cake. NER efficiency, Equation (7), was calculated using the ratio between the $NER_{product}$ and $GEP_{feedstock}$.

$$GER_{product} = \text{HHV of product} \quad (3)$$

$$NER_{product} = GER_{product} - \text{Thermal energy}_{HTC} - \text{Drying energy}_{biochar} \quad (4)$$

$$GEP_{feedstock} = \text{HHV of feedstock} \quad (5)$$

$$GER_{product}\ \text{efficiency}(\%) = \frac{GER_{product}\ (\text{MJ})}{GEP_{feedstock}\ (\text{MJ})} \times 100 \quad (6)$$

$$NER_{product}\ \text{efficiency}(\%) = \frac{NER_{product}\ (\text{MJ})}{GEP_{feedstock}\ (\text{MJ})} \times 100 \quad (7)$$

## 3. Results and Discussion

### 3.1. Physicochemical Properties of Sludge Cake

The physicochemical characteristics of the sludge cake generated from the slaughterhouse wastewater treatment plant are shown in Table 2. The physicochemical properties of the sludge cake used in this study were typically different from those of the reported agricultural biomass, such as corn silage, dry straw, cabbage residue, poultry manure, and bedding material. These types of agricultural biomass have a carbon content of 40.7–46.9% and oxygen content of 30.1–44.4%, and calorific values lie between the ranges of 17.8–19.6 MJ/kg [25]. The sludge cake used in this study showed a higher carbon content and lower oxygen content compared to the reported agricultural biomass. In addition, the calorific value was much higher than the reported agricultural biomass.

**Table 2.** Physicochemical properties of raw sludge cake.

| Parameters | Sludge Cake | |
|---|---|---|
| Elemental composition (wt. %, d.b. [1]) | C | 61.9 |
| | H | 7.2 |
| | O | 5.3 |
| | N | 6.5 |
| | S | 0.0 |
| | Ash | 19.1 |
| pH (-) | 7.1 (0.0) [8] | |
| TS [2] (wt. %, w.b. [3]) | 16.4 (0.4) | |
| VS [4] (wt. %, w.b.) | 13.9 (0.1) | |
| VS/TS (%) | 84.8 (0.1) | |
| $COD_{Cr}$ [5] (g/L) | 208.2 (30.4) | |
| TN [6] (wt. %, w.b.) | 11.0 (0.3) | |
| $NH_4^+$-N (wt. %, w.b.) | 2.6 (0.2) | |
| Calorific value [7] (MJ/kg, d.b.) | 27.7 (1.1) | |

[1] Dry basis, [2] Total solid, [3] Wet basis, [4] Volatile solid, [5] Total chemical oxygen demand, [6] Total nitrogen, [7] Calorific value by higher heating value, [8] Standard deviation (n = 3).

### 3.2. Physicochemical Properties of HTC-Biochar and HTC-Hydrolysate

Table 3 shows the physicochemical properties of the products (HTC-biochar) from the HTC reaction. Output yields on a wet basis ranged from 23.8% to 37.7%, showing a decreasing trend as the reaction temperature increased. Solid yields on a dry basis showed a similar trend and the yields were 75.9%, 73.5%, 72.4%, 69.6% and 66.8% at 170, 180, 190, 200 and 220 °C, respectively. TS contents increased from 33.0% to 46.1%, and the ratios of VS to TS decreased from 88.2% to 85.7% with increase in the reaction temperature. These results imply that the rise of the reaction temperature caused an increase in the dewater ability of the product. The O/C atomic ratios of the HTC-biochar did not show any significant changes between 170–200 °C, and fell to 0.06 for the reaction temperature of 220 °C. The H/C atomic ratios decreased from 1.87 to 1.70 with the increase of reaction temperature. The HTC process has similar reaction characteristics as the slow pyrolysis, which is characterized by gradual heating over a wide range of temperatures to produce biochar [26]. The yield and characteristics of pyrolysis products are influenced by different factors, including biomass feedstock and pyrolysis operating parameters (solid residence time, vapor residence time, temperature, heating rate, and carrier gas flow rate). Biochars, which are produced at a slow pyrolysis rate of forest residues, switchgrass, and the solid fraction of pig manure, have elemental characteristics with an O/C ratio between 0.1 and 0.3 and H/C ratio between 0.5 and 0.9 [27]. The calorific values obtained were 29.6, 30.1, 30.2, 30.8 and 31.3 MJ/kg for the reaction temperatures of 170, 180, 190, 200 and 220 °C, respectively, and the energy densification increased from 1.07 for 170 °C to 1.13 for 220 °C. These increased calorific values improve the quality of the HTC-biochar as biofuel. Generally, this effect can be attributed to reaction mechanisms, including hydrolysis, dehydration, decarboxylation [8,15]. The hydrolysis reaction can convert macro-molecules, such as proteins and lipids, to smaller molecules, and the decarboxylation and dehydration reactions that release $H_2O$ and $CO_2$ improve the fuel properties of the HTC-biochar [28–30]. According to Qian et al. [31], those colorific values of HTC-biochar are comparable to high quality coal, which typically has a calorific value of 25–35 MJ/kg. Anderson et al. [32] also reported that biochars derived from woody plants had higher calorific values. In a recent study, bamboo sawdust biochar pyrolysis at 500 °C had a high colorific value of 32.4 MJ/kg [33], which was comparable to the calorific value (31.2 MJ/kg for 220 °C) of HTC-biochar in this study. Therefore, the HTC technique is effective in creating a high quality biochar from sludge cake at lower temperatures as compared to lignocellulosic feedstocks. The physicochemical properties of HTC-hydrolysate are shown in Table 4. The output yields of the HTC-hydrolysate were 62.3%, 69.5%, 69.0%, 74.6% and 76.2% for the reaction temperatures of 170, 180, 190, 200 and 220 °C, respectively. The COD content of the HTC-hydrolysate was in the range of 97.9–103.4 g/L. The alkalinity decreased from 9.5 g/L to 8.6 g/L for the reaction temperatures between 170–180 °C and increased to 12.1 g/L for the reaction temperature of 220 °C. Essentially, the HTC reaction is a simultaneous reaction of hydrolysis and carbonization [34]. Therefore, the COD contained in the HTC-hydrolysate may be composed of a soluble substance caused by the hydrolysis reaction during the HTC reaction. In addition, alkalinity appeared to be caused by the decarboxylation reaction during the HTC reaction [35]. The physicochemical properties of HTC-hydrolysate obtained from sludge cake are typically characterized by a high moisture content over 90% compared to the bio oil produced by pyrolysis of lignocellulosic feedstocks with less than 10% moisture content [36]. The high moisture content of HTC-hydrolysate is primarily affected by the moisture content of feedstock, which attenuates the severity of thermo-chemical reaction.

**Table 3.** Physicochemical properties of HTC-biochar produced at different HTC reaction temperatures.

| Parameters | | HTC Reaction Temperatures | | | | |
|---|---|---|---|---|---|---|
| | | **170 °C** | **180 °C** | **190 °C** | **200 °C** | **220 °C** |
| Output yield [1] (wt. %, w.b. [2]) | | 37.7 (0.1) [10] | 30.5 (0.1) | 31.0 (0.1) | 25.4 (0.1) | 23.8 (0.1) |
| Solid yield [3] (wt. %, d.b. [4]) | | 75.9 (0.2) | 73.5 (0.2) | 72.4 (0.2) | 69.6 (0.2) | 66.8 (0.3) |
| Elemental composition (wt. %, d.b.) | C | 59.9 | 58.9 | 57.9 | 59.2 | 60.8 |
| | H | 9.4 | 8.9 | 8.4 | 8.6 | 8.7 |
| | O | 7.0 | 6.2 | 6.9 | 6.7 | 5.0 |
| | N | 4.1 | 3.9 | 4.4 | 3.7 | 3.8 |
| | S | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Ash | 19.6 | 22.1 | 22.4 | 21.8 | 21.7 |
| Atomic ratio (-) | O/C | 0.09 | 0.08 | 0.09 | 0.09 | 0.06 |
| | H/C | 1.87 | 1.81 | 1.73 | 1.73 | 1.70 |
| pH (-) | | 6.2 (0.0) | 5.9 (0.0) | 5.6 (0.0) | 6.0 (0.0) | 6.1 (0.0) |
| TS [5] (wt. %, w.b.) | | 33.0 (0.7) | 39.5 (0.1) | 38.3 (0.1) | 44.8 (0.7) | 46.1 (0.4) |
| VS [6] (wt. %, w.b.) | | 29.1 (0.8) | 34.5 (0.0) | 33.5 (0.0) | 39.0 (0.5) | 39.5 (0.1) |
| VS/TS (%) | | 88.2 (0.5) | 87.4 (0.3) | 87.4 (0.2) | 87.0 (0.1) | 85.7 (0.3) |
| TN [7] (g/kg) | | 14.0 (0.7) | 11.5 (0.7) | 10.5 (0.5) | 12.0 (1.6) | 12.5 (1.5) |
| $NH_4^+$-N (g/kg) | | 3.2 (0.1) | 3.2 (0.3) | 3.8 (0.2) | 3.6 (0.1) | 3.8 (0.0) |
| Calorific value [8] (MJ/kg, d.b.) | | 29.6 (0.4) | 30.1 (0.1) | 30.2 (0.2) | 30.8 (0.1) | 31.3 (0.4) |
| Energy densification [9] | | 1.07 (0.02) | 1.09 (0.01) | 1.09 (0.01) | 1.11 (0.00) | 1.13 (0.01) |

[1] Mass of output/mass of feedstock, [2] Wet basis, [3] Mass of solid in product/mass of solid in feedstock, [4] Dry basis, [5] Total solid, [6] Volatile solid, [7] Total nitrogen, [8] Calorific value by higher heating value, [9] Calorific value of product/calorific value of feedstock, [10] Standard deviation (n = 3).

**Table 4.** Physicochemical properties of HTC-hydrolysate produced at different HTC reaction temperature.

| Parameters | HTC Reaction Temperatures | | | | |
|---|---|---|---|---|---|
| | **170 °C** | **180 °C** | **190 °C** | **200 °C** | **220 °C** |
| Product yield [1] (wt. %, w.b. [2]) | 62.3 (0.1) [8] | 69.5 (0.2) | 69.0 (0.2) | 74.6 (0.2) | 76.2 (0.4) |
| pH | 6.2 (0.0) | 5.9 (0.0) | 5.6 (0.0) | 6.0 (0.0) | 6.1 (0.0) |
| TS [3] (wt. %, w.b.) | 6.1 (0.1) | 6.6 (0.1) | 6.2 (0.01) | 6.9 (0.1) | 7.2 (0.2) |

**Table 4.** *Cont.*

| **Parameters** | **HTC Reaction Temperatures** | | | | |
|---|---|---|---|---|---|
| | **170 °C** | **180 °C** | **190 °C** | **200 °C** | **220 °C** |
| VS [4] (wt. %, w.b.) | 5.9 (0.1) | 6.3 (0.1) | 6.0 (0.0) | 6.7 (0.1) | 6.9 (0.1) |
| VS/TS (%) | 96.7 (0.1) | 95.5 (0.2) | 96.8 (0.2) | 97.1 (0.0) | 95.8 (0.9) |
| TN [5] (g/L) | 9.7 (0.5) | 10.5 (0.8) | 9.8 (0.3) | 10.9 (0.5) | 11.5 (0.5) |
| $NH_4^+$-N (g/L) | 3.2 (0.5) | 2.9 (0.0) | 3.3 (0.0) | 3.5 (0.3) | 5.3 (0.1) |
| $COD_{Cr}$ [6] (g/L) | 99.3 (1.6) | 103.4 (1.3) | 101.1 (3.7) | 103.0 (1.6) | 97.9 (1.9) |
| VFAs [7] (mg/L) | 188.2 (3.3) | 195.7 (2.2) | 204.3 (1.5) | 191.4 (5.1) | 251.6 (2.7) |
| Alkalinity (g/L) | 9.5 (0.0) | 9.1 (0.0) | 8.6 (0.0) | 9.6 (0.4) | 12.1 (0.3) |

[1] Mass of output/mass of feedstock, [2] Wet basis, [3] Total solid, [4] Volatile solid, [5] Total nitrogen, [6] Chemical oxygen demand, [7] Volatile fatty acids, [8] Standard deviation (n = 3).

### *3.3. Methane Production Potential of HTC-Hydrolysate*

The cumulative methane production of HTC-hydrolysate in each batch anaerobic reactor and the optimization curves fitted by the parallel first order kinetics model are presented in Figure 3. The model parameters and ultimate methane yield are shown in Table 5. In the anaerobic digestion of the HTC-hydrolysate, the degradation of substrate began immediately with the start of anaerobic digestion, with no inhibitory effects observed. Methane production increased steeply for 15 days, and thereafter, showed a slow increase. The cumulative methane production curves were well explained by the parallel first-order kinetics model. The ultimate methane potentials ($B_u$) of the HTC-hydrolysate were 0.222, 0.242, 0.237, 0.228 and 0.197 $Nm^3/kg\text{-}COD_{added}$ for the reaction temperatures of 170, 180, 190, 200 and 220 °C, respectively. The $COD_{deg}$ were 70.6%, 75.6%, 74.7%, 72.8% and 62.8% for the reaction temperatures of 170, 180, 190, 200 and 220 °C, respectively. In the anaerobic digestion of the HTC-hydrolysate, there was significant relationship between the $COD_{deg}$ and ultimate methane yields. The highest $B_u$ and $COD_{deg}$ were obtained at the reaction temperature of 180 °C, while the highest reaction temperature (220 °C) caused the lowest $B_u$ and $COD_{deg}$. In addition, the organic distribution constants ($f_e$) decreased from 0.927 to 0.717 as the reaction temperature increased. These results indicated that the degraded fractions of organic matter decreased according to the increase of the reaction temperature during the first anaerobic degradation stage. These results are in agreement with Mottet et al. [37]. They reported that the methane yield increased to 0.215 $Nm^3/kg\text{-}COD_{added}$ with a COD degradability of 56% in the thermal hydrolysis of 165 °C, while the methane yield decreased to 0.142 $Nm^3/kg\text{-}COD_{added}$ with a COD degradability of 41% in the thermal hydrolysis of 220 °C. These results, along with the reduced methane yield and COD degradability at high thermal reaction temperatures, can be attributed to the Maillard reactions, in which carbohydrates react with amino acids to form melanoidines with a low biodegradability [38,39]. Such a recalcitrant compound is not always generated under conditions of high-temperatures and pressure, while a rapid increase in temperatures within the HTC reactor can more strongly affect the degree of generation of the recalcitrant compound [2].

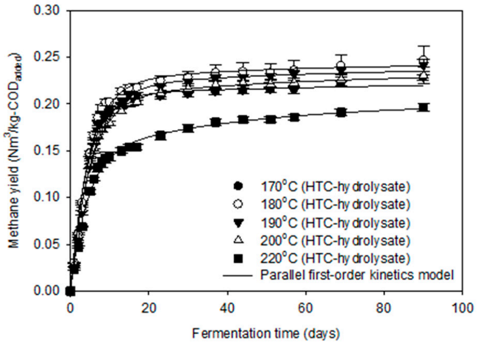

**Figure 3.** Cumulative methane production and optimization curves based on the parallel first-order kinetics model in the anaerobic digestion of HTC-hydrolysate (vertical bars denote standard deviations).

**Table 5.** Ultimate methane potential and model parameters based on the parallel first-order kinetics model.

| Parameters | HTC Reaction Temperatures | | | | |
|---|---|---|---|---|---|
| | **170 °C** | **180 °C** | **190 °C** | **200 °C** | **220 °C** |
| $B_u$ [1] ($Nm^3$/kg-$COD_{added}$) | 0.222 | 0.242 | 0.237 | 0.228 | 0.197 |
| $f_e$ [2] (-) | 0.927 | 0.903 | 0.903 | 0.873 | 0.717 |
| $k_1$ [3] (1/day) | 0.228 | 0.215 | 0.190 | 0.203 | 0.230 |
| $k_2$ [3] (1/day) | 0.011 | 0.028 | 0.019 | 0.020 | 0.024 |
| $COD_{Deg}$ [4] (%) | 70.6 | 75.6 | 74.7 | 72.8 | 62.8 |

[1] Ultimate methane yield, [2] Organic distribution constant in the parallel first-order kinetics, [3] Kinetic constants in the parallel first order kinetics, [4] Degree of COD degradation.

### 3.4. Energy Recovery Efficiency

The gross energy recovery (GER) efficiency is shown in Table 6. The potential energy ($GEP_{feedstock}$) of 1 kg feedstock was 4.541 MJ/kg as HHV. The solid products (i.e., HTC-biochar) produced from 1 kg feedstock were 0.125, 0.121, 0.119, 0.114 and 0.110 kg, and the recovered energy values ($GER_{biochar}$) from each solid products were 3.689, 3.627, 3.583, 3.516 and 3.432 MJ/$kg_{input}$ for the reaction temperatures of 170, 180, 190, 200 and 220 °C, respectively. The $GER_{biochar}$ efficiencies of the HTC-biochar lie in the range of 75.6–81.2% and decreased with the increase in reaction temperature. Meanwhile, the methane yields produced by the HTC-hydrolysate were 12.0, 15.2, 14.5, 15.3 and 12.9 NL (Volume in STP condition), and the recovered energy values ($GER_{methane}$) were 0.546, 0.691, 0.657, 0.696 and 0.584 MJ/$kg_{input}$ for the reaction temperatures of 170, 180, 190, 200 and 220 °C, respectively. The $GER_{methane}$ efficiencies ranged from 12.0% to 15.3%. Therefore, the highest $GER_{total}$ was 4.318 MJ/kg at 180 °C, the lowest value was 4.016 MJ/kg at 220 °C and the optimum HTC reaction temperature for maximizing $GER_{total}$ efficiency was 180 °C, which maximized $GER_{total}$ efficiency by 95.1%. The optimum HTC reaction conditions appear to be the net result of two competing mechanisms from the solubilizing transformation of the refractory particulate organics to degradable particulate organic and the stabilizing transformation of soluble organics to undefined refractory compounds [34]. Therefore, further studies concerned with the structural characteristics of the HTC-biochar and the relative biodegradability of the HTC-hydrolysate inherent in structural characteristics are needed to elucidate the optimum conditions of the HTC reaction. Rodríguez-Abalde et al. [3] and Salminen et al. [4] reported methane potentials of 0.46–0.58 $Nm^3$/kg-$VS_{added}$ and 0.60 $Nm^3$/kg-$VS_{added}$ in the anaerobic digestion of poultry slaughterhouse sludge waste, respectively. These values were estimated to be equivalent to 2.776–3.503 MJ/$kg_{input}$ and 3.625 MJ/$kg_{input}$. Comparing the results of this study, the GER efficiency of the HTC system was much higher than the anaerobic digestion efficiency, suggesting that the GER efficiency of the sludge cake can be improved by adopting HTC technology. However, the results of this study did not take into account the energy consumed during the operation of the HTC reactor and anaerobic digester and only assessed the GER efficiency from the input biomass. Therefore, in order to evaluate the energy conversion efficiency of the sludge cake in terms of commercialization, further work on the net energy balance of the HTC system, considering consumed energy (such as electric power etc.) in the HTC process operation, is needed.

Table 7 shows NER efficiency for the case of direct utilization (e.g., solid fuel) of the sludge cake by simple drying and for the other case of energy conversion by the HTC process. In the case of direct utilization as solid fuel, the drying energy of 1.885 MJ/kg-sludge cake for the solid fuel production was estimated to be physically consumed, considering moisture vaporizing energy (2.255 MJ/kg-moisture). Therefore, the NER and NER efficiency by the simple drying of sludge were assessed as 2.656 MJ/$kg_{input}$ and 58.5%, respectively. In the case of the HTC process, thermal energy for the HTC reaction was estimated to be 0.183 MJ/kg/$kg_{input}$ on the basis of the reported thermal energy of 0.31 kWh/kg-feedstock [40] consumed in the HTC operation, and the drying energy of the HTC-biochar was calculated as 0.416 MJ/$kg_{input}$. The NER and NER efficiency were calculated as

3.628 MJ and 79.9%, respectively, during energy conversion from the HTC process. Therefore, the HTC technique was assessed to be more efficient than solid fuel production by simple drying of the sludge cake. These results were physically reasonable as a high amount of energy was consumed for the drying of moist sludge cakes with the moisture content above 80%.

**Table 6.** Gross energy recovery efficiency of sludge cakes in the poultry slaughterhouse with the HTC system.

| Parameters | | Sludge Cake | HTC Reaction Temperature (°C) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 170 | 180 | 190 | 200 | 220 |
| Feedstock | Solid product (kg/kg$_{input}$) | 0.164 | - | - | - | - | - |
| | GEP$_{feedstock}$ $^1$ (MJ/kg$_{input}$) | 4.541 | - | - | - | - | - |
| HTC-biochar | Solid product (kg/kg$_{input}$) | - | 0.125 | 0.121 | 0.119 | 0.114 | 0.11 |
| | GER$_{biochar}$ $^2$ (MJ/kg$_{input}$) | - | 3.689 | 3.627 | 3.583 | 3.516 | 3.432 |
| | GER$_{biochar}$ efficiency $^3$ (%) | - | 81.2 | 79.9 | 78.9 | 77.4 | 75.6 |
| HTC-hydrolysate | Methane yield (NL/kg$_{input}$) | - | 12.0 | 15.2 | 14.5 | 15.3 | 12.9 |
| | GER$_{methane}$ $^4$ (MJ/kg$_{input}$) | - | 0.546 | 0.691 | 0.657 | 0.696 | 0.584 |
| | GER$_{methane}$ efficiency $^5$ (%) | - | 12.0 | 15.2 | 14.5 | 15.3 | 12.9 |
| GER$_{total}$ $^6$ (MJ/kg$_{input}$) | | - | 4.234 | 4.318 | 4.240 | 4.212 | 4.016 |
| GER$_{total}$ efficiency $^7$ (%) | | - | 93.2 | 95.1 | 93.4 | 92.7 | 88.5 |

[1] Gross energy potential: calorific value as the HHV of sludge cake, [2] Gross energy recovery: calorific value as HHV × solid product of HTC-biochar, [3] GER$_{biochar}$/GEP$_{feedstock}$ × 100, [4] Gross energy recovery: methane yield × HHV of methane, [5] GER$_{methane}$/GEP$_{feedstock}$ × 100, [6] Total GER: GER$_{biochar}$ + GER$_{methane}$, [7] GER$_{total}$/GEP$_{feedstock}$ × 100.

**Table 7.** Net energy recovery efficiency of sludge cakes in the poultry slaughterhouse with the HTC system.

| Parameters | Sludge Cake (Simple Drying) | HTC (180 °C) | |
|---|---|---|---|
| | | Biochar | Hydrolysate |
| Input and output (kg) | 1.000 | 0.305 | 0.695 |
| Moisture content (kg) | 0.836 | 0.185 | - |
| HTC thermal energy $^1$ (MJ/kg$_{input}$) | - | 0.183 | |
| Drying energy $^2$ (MJ/kg$_{input}$) | 1.885 | 0.416 | - |
| GER $^3$ (MJ/kg$_{input}$) | 4.541 | 3.627 | 0.691 |
| NER $^4$ (MJ/kg$_{input}$) | 2.656 | 3.628 | |
| NER efficiency $^5$ (%) | 58.5 | 79.9 | |

[1] Thermal energy consumed in the HTC reaction (specific thermal energy consumption = 0.31 kWh/kg$_{feedstock}$ [40]), [2] Drying energy consumed for the solid fuel production (2.255 MJ/kg-moisture), [3] Gross energy recovery as HHV, [4] Net energy recovery: GER-HTC thermal energy-Drying energy, [5] NER/GER of sludge cake × 100.

## 4. Conclusions

The sludge cake generated from the wastewater treatment plant of the poultry slaughterhouse was a useful source for bioenergy conversion due its high calorific value of approximately 27.7 MJ/kg. The solid yield of the HTC-biochar decreased from 75.9% to 66.8% with the increase of reaction temperature from 170 °C to 220 °C, while the calorific values increased from 29.6 MJ/kg to 31.3 MJ/kg, and the energy densification increased from 1.07 to 1.13. The output yields of the HTC-hydrolysate increased from 62.3% to 76.2% with the rise of the reaction temperature from 170 °C to 220 °C, and the COD contents of the HTC-hydrolysate were in the range of 97.9 and 103.4 g/L. The $B_u$ of the HTC-hydrolysate increased from 0.222 Nm$^3$/kg-COD$_{added}$ to 0.242 Nm$^3$/kg-COD$_{added}$ with the increase of reaction temperature from 170 °C to 180 °C, and decreased to 0.197 Nm$^3$/kg-COD$_{added}$ until 220 °C, in analysis based on the parallel first-order kinetics model. The potential energy of feedstock (1 kg) was 4.541 MJ/kg. The GER$_{biochar}$ efficiencies of the HTC-biochar from the sludge decreased from 81.2% to 75.6% with the increase of reaction temperature. The $GER_{methane}$ efficiencies were calculated as 12.0, 15.2, 14.5, 15.3 and 12.9 for the reaction temperatures of 170, 180, 090, 200 and 220 °C, respectively. Consequently, the $GER_{total}$ peaked at 4318 MJ/kg for the reaction temperature of 180 °C, and exhibited its lowest value (4016 MJ/kg) for the reaction temperature of 220 °C. Therefore, the optimum HTC reaction temperature for maximizing GER efficiency was 180 °C, and the maximum gross energy recovery efficiency was 95.1%. Also, NER efficiency at the production of solid fuel by simple drying was 58.5% (NER-solid fuel = 2656 $MJ/kg_{input}$) and NER efficiency at the energy conversion by the HTC process was 79.9% (NER-HTC = 3628 $MJ/kg_{input}$). These results suggested that the GER and NER efficiencies from the HTC system are much higher than those of the direct utilization of the sludge cake by simple drying and the GER and NER efficiencies of the sludge cake can be improved by adopting HTC technology.

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