Hydrothermal Treatment of Antibiotic Mycelial Dreg: More Understanding from Fuel Characteristics

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ABSTRACT

Antibiotic mycelial dreg is a hazardous pollutant that is difficult to deal with because of its high contents of moisture and biomass pectin. Our previous work has demonstrated that the hydrothermal treatment (HTT) provides a feasible way to produce safe solid biofuel by reducing its moisture and nitrogen contents and decomposing its residual antibiotics. This study is devoted to further investigating the HTT through characterizing the HTT produced solid biofuels using oxygen bomb calorimeter, XPS, FTIR, XRF, TGA, DTA and so on. The results showed that the higher heating value (HHV) of the solid biofuel can reach about 24.4 kJ/g, which was much higher than

the HHV of dried raw antibiotic mycelial dreg made by conventional drying (only 16.7 kJ/g). Moreover, the N content was lowered from 7.7 wt.% in the dried raw antibiotic mycelial dreg to 5.6 wt.% in the 200 °C HTT produced solid biofuel, while most alkaline metals and chlorine in ash of antibiotic mycelial dreg were leached out with centrifugation after HTT. The atomic ratios of H/C and O/C in the solid biofuels both decreased with increasing the temperature of HTT, indicating the occurrence of dehydration, decarboxylation and hydrolysis of solid matters in the dreg. The HTT also greatly improved the combustion reactivity of the solid matters in the antibiotic mycelial dreg. All of these show that HTT provides indeed an effective way to convert the antibiotic mycelial dreg into high-quality solid biofuel.

Keywords: Hydrothermal treatment (HTT); Antibiotic mycelial dreg; Industrial biomass waste; High-moisture waste; Solid biofuel.

1. INTRODUCTION

The exploration and usage of antibiotics were started centuries ago, and now its production has already become a big industry. For instance, the production of primary antibiotics was 0.3 million tons in China and 0.4 million tons worldwide in 2012 [1]. However, the production of antibiotics generates more than ten times of mycelial dreg as residue which reached 4 million tons in China in 2012. Moreover, the residue amount keeps increasing at a rate of about 10% per year.

Antibiotic mycelial dreg has not only high moisture content above 80 wt.% [2] but also high fraction of organic substances. The residual antibiotics in the dreg further make it hazardous and difficult to be tackled with. In fact, antibiotic mycelial dreg is on the list of the most dangerous industrial wastes in many countries [2]. The pharmaceutical companies are forced to treat, even recycle this waste in an environmental friendly way. The conventional treatment via landfill or open disposal has to cause serious secondary pollution by its moisture and residual antibiotics.

Considering the high protein content in the waste, many efforts have been made to recycle antibiotic mycelial dreg into animal feedstuff or organic fertilizer [1]. Apart from the high energy consumption by drying the dreg into solid feedstuff or fertilizer, the potential impact of its residual antibiotics on the security of the food chain is definitely an issue or a risk. Thus, this kind of direct uses of antibiotic mycelial dreg is being forbidden in many countries [2]. We then have to consider the incineration of it after high-efficiency moisture removal, which is expected to provide the feasible way for safe treatment as well as utilization of the waste [3].

For incineration of antibiotic mycelial dreg, the big obstacle is its high contents of moisture (80~90 wt.% in wet basis), oxygen (42.1 wt.% in dry basis) and nitrogen (7.7 wt.% in dry basis), which would cause low efficiency, low energy density and high NO_x emission, respectively. In the raw antibiotic mycelial dreg, the colloid, which is basically protein (30~40 wt.%) [2], leads to the tight bond of water with organic substances. Consequently, the water is hard to be deeply removed

through various traditional mechanical dewatering technologies such as compressing, centrifugation and so on. Furthermore, the full vaporization of its water requires too much energy to make this technical way impractical. We have proposed hydrothermal treatment (HTT) as a feasible pretreatment technology to overcome the problems mentioned above [3].

Basically, hydrothermal treatment (HTT) of a biomass waste involves dehydration and decarboxylation of the waste to raise its carbon (C) content and heating value. HTT has been widely used to simulate the natural coalification processes for a century, and from last decade the application has been further extended to the pretreatment of biomass feedstock for making high-quality biofuel or biomaterial [4]. Many previous studies have demonstrated the effectiveness of HTT for producing clean solid biofuel from high-moisture wastes such as sewage sludge, municipal solid waste (MSW), low-rank coal and so on [5-12]. Namioka et al. [5, 6] conducted studies to develop a two-step system consisting of HTT and mechanical dewatering to replace the traditional thermal drying for producing solid biofuel from sewage sludge. Further verification was made by Zhao et al. [7, 8] and Meng et al. [9] on improvement of the dewaterability for several kinds of sludges by HTT. Upgraded fuel was made also by Mursito et al. [10] through HTT of tropical peat, while Areeprasert et al. [11] made an effort to produce an alternative solid biofuel from paper sludge via HTT.

As for antibiotic mycelial dreg, there was limited study on HTT of the waste and HTT

produced solid product except for our recent work [3] on how HTT improves the dewaterability of the antibiotic mycelial dreg and how it decomposes its residual antibiotics. In succession to that previous work, this study is devoted to fully understanding the HTT produced solid biofuels and thereby to further investigating the mechanism of HTT of antibiotic mycelial dreg for solid biofuel. Detailed characterization of the fuel was performed through fuel analyses, for example, oxygen bomb calorimeter, X-ray photoelectron spectrometer (XPS), Fourier transform infrared spectrophotometer (FTIR), X-ray fluorescence (XRF), thermo gravimetric analyzer (TGA) and differential thermal analyzer (DTA). Understanding fuel properties and their correlations with the HTT conditions are expected to further clarify the mechanism of HTT for upgrading the antibiotic mycelial dreg. The examined solid biofuels were made by, in succession, HTT of raw antibiotic mycelial dreg in a bench-scale autoclave, centrifugation of the resulting HTT suspension in a centrifugal machine and finally drying of the solid matters in an air-drying oven.

2. EXPERIMENTAL SECTION

2.1 HTT Experiment and Materials

The HTT test in this study was conducted in a 1.5-L bench-scale autoclave reactor shown in Fig. 1. The reactor was electronically heated, and a condenser was attached to the outlet of the reactor to cool down the exhaust gas. A rotator was set to enhance the mixing of sample and the heat transfer inside the reactor. Two impingers in series were used in the downstream of the

condenser to absorb the exhausted gas.

HTT in real practice uses saturated steam to heat the mixture of waste and water [12], meaning that additional water is added. Thus, in this study the HTT test was performed by premixing the raw antibiotic mycelial dreg with distilled water in mass ratio of 5:2, which means 80 g water was added into 200 g the raw antibiotic mycelial dreg. Before experiment, argon was introduced to purge out air from the closed autoclave reactor. Then, the reactor was heated up to the targeted temperature (160-220 °C) and held there for 30 min. The rotator inside the reactor was kept stirring at a speed of 100 rpm during the heating and holding period. In turn, the heating was stopped and the autoclave reactor was carefully opened through a valve to reduce its pressure. The vaporized water in this process was discharged into the condenser to recover the condensable liquid. When the temperature in the autoclave was lower than 100 °C, the cover of the autoclave was opened to take out the hydrothermally treated suspension. The released ammonium with the exhausted gas from the reactor was determined by measuring the liquids recovered in the condenser and downstream impingers.

After the HTT was completed, the solid biofuels for analysis were made by centrifugation of the suspension from the autoclave reactor at 3000 rpm for 5 min and drying the centrifuged solid samples in an air-drying oven at 105 °C for 48 h. Besides, the raw dried antibiotic mycelial dreg was prepared via the same procedure but without HTT. All dry solid biofuels were ground into

powders and sieved into sizes below 200 meshes for characterization.

The antibiotic mycelial dreg used in this work was from a cephalosporin production process in a pharmaceutical factory in Hebei Province, China. The basic properties of it were shown in [Table 1](#), indicating that its original moisture content is high as 83 wt.% and the dried solid matter has not fixed carbon (FC) content so that the volatile matter content is over 90 wt.% (in dry basis). Of the element composition, its N is extremely high (7.7 wt.% in dry-ash-free basis), while C and O contents are equivalent in 41-44 wt.%. These properties indicate that the antibiotic mycelial dreg is a high-volatile biomass fuel without FC content but having extremely high contents of N and O.

2.2 Analysis and Characterization

The moisture content for both the original antibiotic mycelial dreg and HTT produced solid biofuels was determined by the mass difference between the original sample and its solid residue after drying in the oven discussed above (for 48 h at 105 °C). Characterization of all solid biofuels was conducted through the following analyses or measurements: proximate and ultimate analyses for fuel properties (including element composition), oxygen bomb calorimeter (SCLR-5000) for the higher heating value (HHV), XPS (ESCALAB250Xi) for carbon and nitrogen electronic states in the fuel, FTIR (Bruker TENSOR 27) for functional groups of the solid fuels, XRF (AXIOS) for inorganic chemical composition in combustion ash, and TGA and DTA (SHIMADZU D 50) for combustion characteristics.

In XRF analysis, the sieved powder was first pressed into tablet form under 2.0 MPa and it was then placed into the multi-channels of the analyzer. All the samples were detected in a vacuum chamber filled with helium. For FTIR, 1 mg powder sample was mixed with 100 mg KBr and the mixture was then pressed into a thin film under 10.0 MPa for measurement of its absorption spectrogram. In XPS analysis, each sample was, in succession, dried in a vacuum dryer, degased at 10^{-7} Pa for 3 h and neutralized by Ar ion sputtering. Monochromatic Al K Alpha (350W, $h\nu = 1486.8\text{ eV}$) X-ray was used to excite the sample. All spectra were obtained at 20 eV of pass energy in the fixed transmission mode. The resolution and analysis area were 0.05 eV and 0.8 mm^2 , respectively. The analysis was automatically performed for 3~5 different positions on the surface to obtain the high-quality C 1s and N 1s spectra. The spectra were shown with the measured electron intensity versus the binding energy (BE). For the TGA test the used air flow rate was 150 ml/min, and the temperature program was first from room temperature to 105 °C at 5 °C/min, then staying at 105 °C for 15 min for complete removal of moisture, finally raising the temperature to 600 °C at a rate of 10 °C/min for the burnout of the tested fuel sample.

3. RESULTS AND DISCUSSIONS

3.1. Solid Biofuel Characterization

Table 2 shows the properties of the HTT produced solid biofuels from different temperatures and the raw antibiotic mycelial dreg. The moisture content of the centrifuged samples after HTT

was lower than that of the centrifuged raw antibiotic mycelial dreg, and it gradually decreased with raising the HTT temperature. As similarly observed in many previous studies [5, 7-9, 12], the result shows that the HTT greatly facilitated the water removing from the treated suspension, and the higher HTT temperature led to the better dewatering for the solid biofuel. The equilibrium moisture shown in Table 2 represents the moisture content of a fuel first dried in oven and then keeping it in at atmospheric conditions for 48 h. It was 5.8 wt.%, 3.6 wt.% and 2.3 wt.% for the dried raw antibiotic mycelial dreg and HTT produced solid biofuels at 160 °C and 220 °C, respectively. Thus, raising the HTT temperature can also decrease the moisture adsorption ability of antibiotic mycelial dreg. From the aspect of solid fuel storage after drying, this is a highly desirable fuel property.

The higher heating value (HHV) of the dried biofuel was increased from 19.3 kJ/g for the dried raw antibiotic mycelial dreg to 26.5 kJ/g for the biofuel from HTT at 220 °C. As the HTT temperature increased, the HHV of the resulting fuel (after drying) gradually elevated, revealing that HTT improved the energy density of the biofuels from antibiotic mycelial dreg. The increase in the fuel heating value with raising the HTT temperature would be due to the gradually increasing removal of oxygen and nitrogen from the solid matters of antibiotic mycelial dreg during HTT. Table 2 shows also the lower heating values (LHVs), corresponding to HHVs, to indicate the net heating values of all the solid biofuels from different HTT temperatures [13].

The biofuels from raw antibiotic mycelial dreg and HTT mostly had high content of volatile

matters (VM) but zero fixed carbon (FC) except for the 220 °C HTT produced solid biofuel . HTT at the higher temperature tended to decrease the VM content (from 93.2 wt.% to 79.1 wt%) and raise the ash content (from 6.8 wt.% to 19.8 wt.%) in the HTT produced solid biofuels. For the fuel from 220 °C HTT, an FC content of 1.1 wt.% appeared, indicating a light degree of carbonization to the carbonaceous matters [4]. Thus, degradation reactions such as hydrolysis, dehydration and decarboxylation definitely occurred during HTT to result in devolatilization. The higher the HTT temperature, the more severe the degradation reactions, resulted in lower volatile but higher ash contents in the fuels.

Table 2 shows that the oxygen (O) content in the HTT produced solid biofuels gradually decreased from 40.1 wt.% to 32.6 wt.%, whereas the carbon (C) content gradually increased from 47.1 wt.% to 55.1 wt.% with raising the HTT temperature from 160 °C to 220 °C. These variations in the element composition corresponded actually to the gradually increased HHV and LHV. Thus, we can view HTT as a process to upgrade the antibiotic mycelial dreg for solid biofuel. HTT also reduced the nitrogen (N) content in the solid biofuels from 7.7 wt.% in the raw antibiotic mycelial dreg to 5.6 wt.% in the 220 °C HTT produced solid biofuel, and the higher HTT temperature led to the lower N content.

Fig. 2 shows the energy recovery ratio in the HTT produced solid biofuel under different temperatures. The recovery ratio was assigned to be 100% for the case of raw antibiotic mycelial

dreg, and the recovered energy for each HTT temperature was obtained multiplying the mass and LHV of the HTT produced solid biofuels. The figure shows that via HTT, above 55% of the energy antibiotic mycelial dreg can be recovered in the solid biofuels. Increasing the HTT temperature from 160 °C to 200 °C did not much vary the energy recovery ratio. With hydrolysis during HTT, a small part of organic matters are converted into gases (mainly CO₂ and vapor), while some others are dissolved into liquid phase [4]. Although the increasing of HTT temperature did not much change the energy recovery ratio in Fig. 2, it considerably elevated the HHVs of the resulting solid biofuels, as shown Table 2. This means that raising HTT temperature decreased the recovered amount of solid biofuels but increased the HHV at the same time. Thus, at the optimal HTT temperature about 200 °C [3], the relatively HHV of the HTT produced solid biofuel can be ensured.

3.2. HTT Fundamental Understanding

Fig. 3 shows the atomic H/C and O/C ratios of the HTT produced solid biofuels in comparison with several types of coals [14] to demonstrate the coalification feature of the biofuels by HTT. It is obvious that both such element ratios decreased with increasing the HTT temperature, but all were above the atomic H/C and O/C ratios for the displayed coals. The fuel from HTT at 220 °C is quite close to the peat coal in terms of such two ratios. In the high-pressure and high-temperature water of HTT, the pectin substances rich in oxygen and hydrogen would dissolve into liquid from the

solid matters in raw antibiotic mycelial dreg. Dehydration and decarboxylation reactions can also occur at high HTT temperatures to release CO₂ and water [4]. Obviously, all of these reactions for raising C content and lowering O content in the resulting fuel are very similar to those occurring in the coalification process for converting biomass into peat. Also, the removal of oxygen and hydrogen was most efficient at the tested highest HTT temperature of 220 °C.

Fig. 4 shows the behavior of nitrogen (N) transfer during HTT, where the percentages for all types of N are against the total N, say, 100% in the plot. The solid-N means the N in the HTT produced solid biofuels, whose actual content is shown in Table 2. The N in the centrifuged liquid included mainly the organic Kjeldahl nitrogen (K-N) and ammonium ion (N-NH₄⁺), and there were almost not obviously detectable nitrate and nitrite ions. The plotted gas-N in Fig. 4 refers to the exhausted NH₃ adsorbed by impingers. A Thermos 9512 Ammonia Analyzer was used to measure the N content of centrifugate (liquid) in the form of N-NH₄⁺ and that of impingers representing the gaseous NH₃. The K-N content in the centrifugate was determined as the difference between its total K-N given by the Kjeldahl nitrogen measurement [15] and the content of N-NH₄⁺.

HTT greatly decreased the solid-N content in the produced biofuel, as shown by the allocation percents in Fig. 4 and the actual contents in Table 2 for all the biofuels. Increasing the HTT temperature further lowered the solid-N amount (Fig. 4) and also the N content in the fuel (Table 2), but the biggest decrease was between the raw mycelial dreg (7.7 wt.% in Table 2 and 67% in Fig. 4)

and the biofuel from HTT at 160 °C (6.3 wt.% in Table 2 and 30% in Fig. 4). The HTT at 220 °C led to a N content of 5.6 wt.% in the solid biofuel, and it took only 19% of the total N, showing the considerable reduction of solid-N through HTT. Corresponding to this decrease, in Fig. 4 the percent of K-N in the HTT liquid (centrifugate) became much higher (around 60%) than in raw mycelial dreg (around 25%). Elevating the HTT temperature did not much vary the percent of liquid K-N. The produced gas in HTT was very little so that the gas-NH₃ was essentially negligible.

In raw mycelial dreg the solid-N refers mainly to organic amide. With degradation of organic matters by, for example, hydrolysis of big molecules in HTT, certain N in solid matters has to be released and further dissolved in liquid to form the Kjeldahl nitrogen (K-N). The proportions of N-NH₄⁺ in liquid phase and gas-NH₃ both tended to increase with raising the HTT temperature, showing actually the enhanced hydrolysis of amino acid in high-temperature HTT to form NH₄⁺ ion and release NH₃. This can also be explained by the gradual increase in the pH value (right ordinate of Fig. 4) of the centrifuged liquid with raising the HTT temperature.

The analysis by XPS has been used to determine the functional groups of carbon and nitrogen in coal and biomass chars in many literature studies [16, 17]. Figs. 5(a) and 5(b) show respectively the XPS spectra of carbon [C 1s in 5(a)] and nitrogen [N 1s in 5(b)] for the dried raw mycelial dreg and 220 °C HTT produced solid biofuel. The detailed information of the C 1s and N 1s curves was obtained by curve fitting function. Every deconvoluted peak (blue curve) typifies a specific bond of

the element. The two inset tables in Fig. 5 summarize the detailed characteristics of the deconvoluted peaks for the displayed C 1s and N 1s spectra, respectively. There, each area percentage was estimated as the area of the cited peak divided by the sum of the areas for all deconvoluted peaks.

In Fig. 5 (a), the deconvoluted peaks centering at the binding energies (BEs) of 284.8 eV, 285.5 eV, 286.3 eV and 288.0 eV are respectively attributed to the C-C or C-H bonds, carbon in connection with amide or amine (C-N), carbon linking to hydroxyl or ether groups (C-OH/C-OR) and carbon in carbonyl or quinonyl groups (C=O) [16]. By HTT, the percentage of the areas for all peaks representing C-OH/C-OR related to carbon and oxygen was greatly lowered from 21.7% to 8.4% due to the occurrence of dehydroxylation and decarboxylation reactions. On the other hand, the area percentage of C-C and C-H increased from 64.9% to 80.3%. This result is also consistent with the results of ultimate analysis shown in Table 2.

When the nitrogen functional groups are taken into account in the N 1s spectra of Fig. 5 (b), two fitting peaks at BEs of 399.8 eV and 401.5 eV can be observed. They might represent amide or amine (399.8 eV) and ammonia or protonated amine (401.5 eV), respectively [16, 17]. Theoretically, hydrolysis reactions occurring in HTT would degrade protein and amino acid into solvable smaller chain molecules. Some kinds of these molecules could even easily be protonated in the presence of hydronium and hydroxide ions. All of these matters are likely to enter the aqueous

phase, as was observed in the previous study [3]. In Fig. 5 (b), the area percentage of the deconvoluted peak at BE of 401.5 eV decreased from 59.6% for raw antibiotic mycelial dreg to 3.7% for the HTT produced solid biofuel, indicating actually the dissolution of amine protonation and ammonia. This correspondingly increased the relative ratio of amide or amine in the solid biofuels from 40.4% in the raw antibiotic mycelial dreg to 96.3% in the HTT produced solid biofuel. The result agrees well with the reports of Liao [15] and Zhao [16] obtained in characterizing the sewage sludge after HTT, and also verifies the N content variation shown in Table 2 for different solid biofuels.

Fig. 6 presents the FTIR spectra of dried raw antibiotic mycelial dreg and HTT produced solid biofuels at different temperatures. There are many irregular and complex absorption peaks, indicating the complicated composition of the raw antibiotic mycelial dreg. Performing HTT incurred some changes in the FTIR adsorption peaks, although the changes were not tremendous. The shoulder around 3200 cm^{-1} to 3700 cm^{-1} , which is supposed to be the overlapping peaks of hydroxyl and amino groups, was overall weakened after HTT especially at $200\text{ }^{\circ}\text{C}$ and $220\text{ }^{\circ}\text{C}$, indicating the decrease of hydroxyl groups in the solid biofuels due to dehydration [4]. The peak intensity at about 1650 cm^{-1} tended to be weaker with raising the HTT temperature from $180\text{ }^{\circ}\text{C}$ to higher values, revealing the removal of carboxyl groups through hydrolysis. The IR adsorption spectra in $1270\text{-}980\text{ cm}^{-1}$ typify the C-O-R groups to indicate especially the presence of pectin

consisting of monosaccharides, polysaccharides or celluloses in raw antibiotic mycelial dreg [2].

HTT tended to simplify the FTIR spectra in this region, showing the removal of carbohydrate components through dehydration and hydrolysis reactions.

3.3 Ash Behavior in Fuel Preparation

Ash in the antibiotic mycelial residue would partially dissolve into water in HTT and be leached out in centrifugation. The mass of ash remaining in the HTT produced solid biofuels was calculated as the ash content of the fuels in Table 2 and the total mass of the biofuels. Its mass in 200 g raw antibiotic mycelial dreg without centrifugation was used to determine the original ash content in the antibiotic mycelial dreg. Fig. 7 shows the percents of ash in the HTT produced solid biofuels from different temperatures, where the pink bar indicates the ash lost during fuel preparation process, which includes dissolution in HTT and leaching via centrifugation. About 17% ash in raw antibiotic mycelial dreg was lost via leaching in centrifugation (denoted as "No HTT" in Fig. 7). Comparing to antibiotic mycelial dreg (100% ash), the ash loss for the 160 °C HTT produced solid biofuel was the highest which reached 55%. Increasing the HTT temperature decreased the ash loss. For example, ash decreased to 40% for the HTT at 220 °C. The results means that at higher HTT temperatures more ash components tended to precipitate and retain in the solid biofuels, whereas at lower HTT temperatures there were more ash species dissolving into the

liquid phase and in turn leached out by centrifugation after HTT.

Table 3 shows the contents of ash components in oxide form determined using XRF for the fuels without ("No HTT") and with HTT at different temperatures. The major ash components are CaO, phosphate (phosphorus pentoxide) and sulfate, with CaO being dominant to take 60-80 wt.% of the XRF-based composition. There was not hazardous heavy metal obviously detected except for a trace amount of strontium (its oxide content ≤ 0.1 wt.%). Comparing the fuels directly dried (No HTT) and with HTT at 160 °C, one can see that most ash components exhibited a decrease in their contents, whereas the contents of CaO and Fe₂O₃ had an increase. The biggest decrease over 50% was shown for the alkali metal oxides K₂O and Na₂O, P₂O₅ and sulfate, while the highest content increase was for CaO from 63 wt.% to 81 wt.%. These results in fact agree with that the former are water-dissolving and the latter is not during HTT. With further increasing the temperature of HTT, obvious increases in content occurred to phosphorus pentoxide (slightly to MgO), whereas evident decrease happened to almost all the other components especially for CaO and sulfate. The ash of the 220 °C HTT produced solid biofuel contained 66 wt.% CaO, 22 wt.% P₂O₅ and 6.6 wt.% sulfate, comparing their contents of 81 wt.%, 6.3 wt.% and 7.8 wt.% for the case of HTT at 160 °C, respectively. The contents K₂O and Na₂O were low (< 2.0 wt.% for HTT produced solid biofuels), and decreased with increasing the HTT temperature. Therefore, there should be low possibility to occur fouling in the downstream combustion of the HTT produced solid biofuel [18]. Furthermore,

HTT decreased the chlorine content in ash, although its original value was only 0.3 wt.% for the case of "No HTT".

Fig. 8 shows further the absolute masses of major ash components remaining in the HTT produced solid biofuels from HTT of 200 g raw antibiotic mycelial dreg. The mass of each kind of ash component or species was calculated with the total ash amount (Table 2 and Fig. 7) and the XRF-measured content (Table 3). The basis for this comparison was the absolute ash mass in the dried antibiotic mycelial dreg, which was about 3300 mg and denoted as "No HTT" in Fig. 8. Then this total mass of ash was decreased to 1700 mg through HTT at 160 °C and its consequent centrifugation, and all the plotted ash species contributed an obvious decrease. For example, the oxides of alkali earth metals (CaO and MgO in violet bar) and phosphorus pentoxide (red bar) decreased from about 2800 mg in "No HTT" case to 1500 mg for HTT at 160 °C. The amounts of sulfate and alkali metal oxides in the fuel ash correspondingly decreased from about 600 mg and 210 mg to about 150 mg and 40 mg, respectively. With increasing the temperature of HTT from 160 °C to 220 °C, all the ash components except for alkali metal oxides (pink bar) showed slight increase in their absolute amounts. The most obvious increase was shown for the phosphate (from 110 mg to 540 mg corresponding to the HTT temperature rise from 160 °C to 220 °C). The mass increase for alkali earth metal oxides (violet bar) was from about 1420 mg to about 1640 mg, while that for sulfate (blue bar) was very slight because its amount was only about 150 mg. The absolute

amount of alkali metal oxides decreased with increasing the HTT temperature, and it was about 40 mg and 20 mg for the cases of HTT at 160 °C and 220 °C, respectively.

As a summary, [Fig. 8](#) shows that increasing the HTT temperature promoted precipitation of all ash components or species except for alkali metal oxides, and this made the ash amount in the HTT produced solid biofuels become more at higher temperature. The major reason is that HTT operation would increase the pH value of its liquid phase [\[3\]](#), thus lowering the solvability of metal oxides to retain more salts or oxide as fuel ash and to cause the gradually increased ash amount with the higher HTT temperature. The phosphorus pentoxide (phosphate possibly) in the biofuel from HTT at 220 °C was even higher than that in the dried mycelial dreg (with centrifugation only). It means that some of phosphate originally transferred to the liquid phase in centrifugation (No HTT) tended to precipitate at high-temperature HTT as ash in the HTT produced solid biofuels.

Noetheless, in comparison with the dried antibiotic mycelial dreg ("No HTT" in [Figs. 7 and 8](#)), the HTT produced solid biofuels at all the tested temperature had lower absolute ash amount. Especially, HTT lowered the absolute amounts of sulfur, chlorine, alkaline metals and also CaO, showing again the upgrading effect of HTT on the solid biofuel from the antibiotic mycelial dreg.

3.4 Fuel Combustion Characteristic in TGA

The combustion characteristic of solid biofuels from HTT was investigated through combustion of 200 °C HTT produced solid biofuel. [Fig. 9 \(a\)](#) shows the resulting profiles of the

measured weight loss (TGA), weight loss rate (DTG) and differential thermal analysis (DTA) as a function of the combustion processing (operating) time. The same profiles for burning the dried raw antibiotic mycelial dreg were shown in Fig. 9 (b) for comparison. The reaction temperature for arbitrary time can also be identified from the temperature curve plotted in the figure. Overall, one can be seen from Fig. 9 that the entire combustion process of the biofuels could be divided into several characteristic stages. Nonetheless, as shown in Table 2, the fuel had almost no fixed carbon. Thus there should not be a clear combustion stage for char.

The free water evaporation occurred at ambient temperature to 105 °C, leading to the weight losses of 5.8 wt.% and 2.4 wt.% for the 200 °C HTT produced solid biofuel and the dried raw antibiotic mycelial dreg, respectively. After 105 °C, the rapid weight loss is usually treated as the period of volatile release and combustion. The DTG curves in Fig. 9 show two obvious peaks at about 150 °C (around 35 min) and 190 °C (around 30 min) in Fig. 9 (a) and Fig. 9 (b), respectively. Their DTG peak values are respectively 0.23 mg/min and 0.56 mg/min. On the other hand, the DTA value slightly increased until reaching about 240 °C in both figures. Considering the ignition of fuel matters should be hard at temperatures about 200 °C [19], such small DTG peaks at low temperatures should be mainly due to the release of bound water. Then, the bigger peak (0.56 mg/min) at the higher temperature of 190 °C in Fig. 9 (b) clarifies that the raw antibiotic mycelial dreg has more bound water. HTT greatly reduced both the amount and binding energy of bound

water in the antibiotic mycelial dreg, convincing further that HTT released bound water into free water to improve the dewaterability of the treated material.

Increasing temperature further from 240 °C resulted in two major DTG and DTA peaks (around 40 and 60 min) for both the solid biofuels, and both DTG and DTA are in good correspondence. In Fig. 9 (b), there was a third small DTG peak between those two major peaks as well as its well-corresponded DTA peak (called in-between peaks, near 55 min). Comparing with the combustion of MSW and sewage sludge [20, 21], the tested fuels here exhibited more DTG peaks, indicating their complicated combustion processes. For both the fuels the temperatures at the second major peak centers were below 550 °C, but the combustion was quick so that the peaks were sharp. Noting further that the fuels had almost no fixed carbon, we supposed that the two major combustion peaks are for two stages of volatile combustion. Before the first major peak, both DTA and DTG had relatively slow increase, even stagnated, comparing to the period of removing bound water. This verifies again that for the tested fuels their substantial release and combustion of volatile matters did not start until initiating the first major DTA and DTG peaks at about 290 °C.

The center of the first DTA peak for volatile combustion is at about 335 °C, and both the fuels shared little difference for this temperature. Carefully examination shows that the peak center for the DTG curve appeared a little bit earlier than the DTA peak center did, complying with the fact that the volatile should first release and then be combusted to lead to a time delay in DTA. The

values of the first major peak centers for DTG and DTA were 0.5 mg/min and 163 uV in Fig. 9 (a) but 0.3 mg/min and 70.7 uV in Fig. 9 (b), respectively. It is also obvious that the first DTA peak is larger in Fig. 9 (a). Table 2 shows conversely a higher volatile content for the raw mycelial dreg. Consequently, HTT greatly improved the reactivity of the antibiotic mycelial dreg to make it easier to release volatile matters at the low temperatures of about 335 °C.

The great difference for the second major volatile-burning peak between the two solid biofuels is the obviously lower temperature in Fig. 9 (a) (centered at 465 °C) than in Fig. 9 (b) (centered at 515 °C). Comparing to the first major DTG and DTA peaks at about 330 °C, the second peaks are rather shaper, indicating the more extensive combustion. The TGA values showed also sudden weight losses for the second peak. The intensive combustion, thus heat release caused a small increase in the recorded temperature as shown in the temperature curves for the two fuels. The lower temperature at the peak center for the HTT produced solid biofuel clarifies that this fuel was easier to be combusted. Also, the values of DTG and DTA at their second-peak centers were 2.0 mg/min and 443.6 uV in Fig. 9 (a), which are much higher than 1.4 mg/min and 320 uV for the dried raw antibiotic mycelial dreg in Fig. 9 (b). All of these demonstrate that in HTT the accompanied hydrolysis and hydrocracking of macromolecule components increased the light and easily-combusting matters in the fuel.

The dried raw antibiotic mycelial dreg had further a third in-between burning peak centered at

460 °C, whose DTG and DTA values at their centers were 0.9 mg/min and 55 uV, respectively. This temperature indicates that the in-between peak roughly corresponded to the second major peak in burning the HTT produced fuel. The existence of this third peak in burning the dried raw antibiotic mycelial dreg reveals essentially that by HTT it converted most of the heavy volatiles into light volatiles so that the volatile burning temperature shifted from about 515 °C to 465 °C.

Overall, the above tests show that the combustion of the solid biofuels derived from antibiotic mycelial dreg basically consists of two major stages, moisture removal and volatile combustion. Each of these stages includes further two to three sub-stages. While the removals of free and bound water are well distinguished, the volatile combustion was identified to be for the volatiles releasing at about 330 °C and 500 °C, respectively. HTT caused the volatile matters in antibiotic mycelial dreg to be easily releasing and combusting at low temperatures. The combustion tests via TGA well proved the conversion of heavy volatiles into light volatiles via HTT.

4. CONCLUSIONS

Hydrothermal treatment (HTT) can dramatically facilitate water removal and restrict water adsorption of solid matters in antibiotic mycelial dreg. Although HTT is accompanied with some loss in volatile matters and certain increase in ash content, the HHV of the resulting solid biofuel was increased by 37% (19.3 kJ/g to 26.5 kJ/g) and the LHV was elevated by 46% (16.7 kJ/g to 24.4 kJ/g) through the HTT at 220 °C in comparison with the directly dried raw antibiotic mycelial dreg.

Both XPS and FTIR analyses of the HTT produced solid biofuels revealed that the increase in the heating value was mainly due to the HTT-accompanied reactions including dehydration, dehydroxylation, decarbonylation and decarboxylation occurring to the organic matters which lowered the oxygen content of the solid biofuel. Nitrogen content in the solid matters of the dreg was found to be reduced by 27 % (7.7 wt% to 5.6 wt.%) through HTT at 200 °C, as a result of hydrolyzing protein or amino acid. Corresponding to this, more than half of the N in the dried raw antibiotic mycelial dreg (solid-N) was transferred into the HTT centrifugate to become Kjeldahl nitrogen (K-N). HTT has great leaching effect on ash components to reduce some harmful elements like alkali metals, sulfur and chlorine from the mycelial dreg. The total ash mass remaining in the biofuel from HTT was much reduced in comparison with the directly dried fuel without HTT, although the ash content in mass percent in the fuel became higher (because of the reduction of fuel amount). Meanwhile, the preferable elements for eliminating slagging and fouling such as calcium and magnesium basically remained in the HTT produced solid biofuels because of their low water solubility and the gradually higher pH value of the HTT liquid (suspension) with the higher temperature. Against the energy in the dried raw antibiotic mycelial dreg, the energy recovery in the HTT produced solid biofuels was shown to be about 55%. All of these indicate that HHT can convert the harmful antibiotic mycelial dreg into clean solid biofuel. Air-combustion tests in TGA revealed further that the HTT produced solid biofuel has much improved combustion activity, and

the fuel burnout can be easily achieved at temperatures below 500 °C. This is because the fuel has not obvious fixed carbon content and through HTT the difficult-burning heavy volatiles were further converted into easy-burning volatiles.

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Table 1. Properties of raw antibiotic mycelial dreg.

Physical properties		Proximate analysis (wt.%) ^b			Ultimate analysis (wt.%) ^c			
Moisture ^a	HHV ^b	Volatile	Ash	Fixed	C	H	N	O ^d
83.0 wt. %	19.3 kJ/g	91.6	8.4	0	43.5	6.7	7.7	42.1

a. As received; b. Dry basis; c. Dry-ash-free; d. By difference, O=100-C-H-N.

Table 2 Properties of solid biofuels from antibiotic mycelial dreg at different HTT temperatures.[†]

Property parameters	Raw	160 °C	180 °C	200 °C	220 °C
Moisture (wt.%) (after centrifugation)	73.6	65.0	58.3	48.7	39.5
Moisture (wt.%) [‡] (equilibrium)	5.8	3.6	2.8	2.4	2.3
Volatile mater (wt.%)	93.2	90.0	87.5	85.2	79.1
Ash (wt.%)	6.8	10.1	12.5	14.8	19.8
Fixed carbon (wt.%)	--	--	--	--	1.1
HHV (kJ/kg)	19.3	20.8	23.1	24.6	26.5
LHV (kJ/g)	16.7	18.6	21.0	22.6	24.4
C (wt.%)	43.5	47.1	51.2	53.3	55.1
H (wt.%)	6.7	6.5	6.4	6.6	6.7
N (wt.%)	7.7	6.3	6.2	5.8	5.6
O (wt.%)	42.1	40.1	36.2	34.3	32.6

[†] Element contents are based on dry-ash-free basis and the others on dry basis.

[‡] It is the moisture after keeping the oven-dried biofuel in air for 48 h.

Table 3. XRF analysis of ashes for biofuels from antibiotic mycelial dreg at different HTT temperatures.

M (wt.%)	raw	160 °C	180 °C	200 °C	220 °C
Na ₂ O	1.6	0.8	0.6	0.4	0.3
MgO	1.2	0.8	1.0	1.8	2.2
Al ₂ O ₃	0.3	0.1	0.1	0.1	0.1
SiO ₂	0.8	0.4	0.3	0.2	0.2
K ₂ O	4.8	1.8	1.2	0.8	0.6
CaO	60.3	81.0	79.3	70.5	66.0
MnO ₂	--	--	0.1	0.1	0.1
Fe ₂ O ₃	0.6	0.7	0.7	1.0	1.2
ZnO	0.1	0.1	0.1	0.1	0.2
SrO	--	--	0.1	0.1	0.1
P ₂ O ₅	12.0	6.3	8.2	17.9	22.4
SO ₄	18.0	7.8	8.2	6.9	6.6
Cl	0.3	0.2	0.1	0.1	0.1

Figure 1. A schematic diagram of the autoclave system for performing HTT test.

Figure 2. Variation with HTT temperature of energy recovery ratio by solid biofuel produced.

Figure 3. Atomic O/C and H/C ratios for solid biofuels of antibiotic mycelial dreg from direct drying or HTT at different temperatures in comparison with those for coals [14].

Figure 4. Nitrogen transfer during HTT and pH value of centrifuged liquid varying temperature.

Figure 5. Spectra of XPS analysis for (a) C 1s and (b) N 1s of solid biofuels from HTT at 200 °C and directly drying raw antibiotic mycelial dreg.

Figure 6. FTIR spectra of solid biofuels from directly drying raw antibiotic mycelial dreg and HTT at different temperatures.

Figure 7. Percent of ash remaining in HTT produced solid biofuels excluding the leached ash during fuel preparation.

Figure 8. Absolute masses of major ash components remaining in solid biofuels from HTT of 200 g antibiotic mycelial dreg at different temperatures and the corresponding pH values of HTT liquid.

Figure 9. Thermogravimetric analysis profiles for burning solid biofuels from (a) HTT at 200 °C and (b) directly drying raw antibiotic mycelial dreg.