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Ash behavior during hydrothermal treatment for solid fuel applications. Part 2: Effects of treatment conditions on industrial waste biomass

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ABSTRACT

This second half of our work on ash behavior concentrates on the effects of hydrothermal treatment conditions on paper sludge. Ash composition and solubility were determined based on treatment temperature, reactor solid load and liquid pH using experimental design and univariate regression methods. In addition, ash properties for combustion were evaluated based on recent developments on ash classification. Based on the results, all experimental variables had a statistically significant effect on ash yields. Only reactor solid load was statistically insignificant for char ash content, which increased based on increasing treatment temperature due to the decomposition of organic components. Ash dissolution and ash yield were governed by liquid pH and the generation of acids mainly due to the solubility of calcium carbonate identified as the main mineral species of paper sludge. Dissolution of calcium carbonate however decreased ash fusion temperatures more likely causing problems during char incineration. This indicated that decreasing the ash content of sludge during hydrothermal treatment can actually weaken ash properties for solid fuel applications.

1. Introduction

A wide variety of biomass and waste can be converted into direct replacements for existing solid fuels. Second generation feedstock, such as agricultural and forest residues or municipal and industrial waste biomass, are attractive alternatives as they are low cost, often readily available and do not compete with land requirements for food production [1]. As opposed to agricultural and forest residues, municipal and industrial waste biomass is generated in large quantities and does not suffer from expensive distributed logistics or seasonal availability. The properties of industrial residues also remain relatively constant over time reflecting control over process conditions and quality of the main products.

The pulp and paper industry generates a variety of sludge residues from paper recycling and wastewater treatment that are currently not utilized to meet their full potential. In Finland the industry produces roughly 550,000 dry tons of sludge each year [2] with an estimated energy potential of 2.5 TW h. In 2014, 37% of generated sludge was recycled as material and 62% was incinerated on-site [2]. However, current means of sludge dewatering can only reach a final solids content of 10–50% reducing energy recovery and creating capacity problems for mill boilers. In addition, current trends in waste regulation are increasingly hindering sludge landfilling and difficulty in acquiring new sites [3]. In Finland landfill deposition of organic material was banned in 2016 coupled with an increase in waste taxation [4,5]. These recent developments will generate additional pressure for finding suitable solutions for efficient sludge management.

Hydrothermal treatment has shown promise for upgrading various sludge residues for solid fuel applications [6–8]. Thermochemical conversion in hot compressed water under relatively low temperature and self-generated pressure enables high energy efficiency, relatively high yields and does not require drying of a feedstock [9]. The drying and combustion properties of sludge are simultaneously enhanced [10,11], which increases the efficiency of mechanical dewatering and eases char incineration. Part of feedstock carbon is inevitably lost due to decomposition of organic components to the liquid phase, which can be biologically treated by wastewater treatment plants [12]. Successful commercial examples can be found from treating hospital waste and sewage sludge [13,14] as several pilot facilities have recently been reported operational [15,16].

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Hydrothermal treatment can also be used for modifying the ash properties of a feedstock. This is beneficial for fuel applications as it can increase energy densification, help to avoid the formation of low temperature eutectics, and decrease potential problems related to char incineration or corrosion of process equipment [17–19]. Ash behavior is an important part of sludge treatment as especially pulp and paper mill residues contain elevated levels of paper pigments and other additives from paper manufacture or wastewater treatment. Although published information on hydrothermal treatment has been steadily increasing during the recent years [20], ash behavior of different biomass and waste feedstock is still not well understood [14].

This work was divided into two separate parts. The first part provided an overview on ash behavior during hydrothermal treatment of different biomass and waste feedstock using multivariate data analysis [21]. Hydrochar produced from virgin biomass and e.g. herbaceous and agricultural residues showed lower ash content and ash yield compared to char from municipal wastes and sludge indicating differences in chemical composition and ash solubility. Further evaluation of available data indicated that industrial sludge had high contents of anthropogenic Al, Fe and P or Ca and Si, as corn stover, miscanthus, switch grass, rice hulls and some agricultural wastes generally contained high K, Mg, S and Si. This second part focuses in detail on paper sludge. The effects of treatment temperature, solid load and liquid pH on the solubility of ash components were determined using experimental design and univariate regression methods. In addition, ash properties for combustion were evaluated based on recent methods for ash classification. The attained results will help in understanding the effect of treatment conditions on ash from paper sludge and controlling ash properties based on treatment conditions.

2. Materials and methods

2.1. Sludge sampling

Recycled paper sludge was sampled from a pulp and paper mill producing unbleached kraft/eurokraft liner for corrugated cardboard. Recycled paper was first pulped and washed at the mill. Fibers unsuitable for papermaking were then separated, thickened and screw pressed to approximately 45% dry solids. A fresh sludge sample of 100 kg was taken from the outlet transport screw under normal operating conditions. The sludge was dried at 105 °C overnight to enable reliably adjusting reactor solid load for the experiments and subsequently stored at room temperature and humidity in a sealed container.

2.2. Hydrothermal treatment

Paper sludge was hydrothermally treated in a glass tube using a 0.5 L MMJ-500 (OM Lab-tech Co., Ltd., Japan) autoclave with a final working volume of approximately 0.4 L. A constant 20 g mass of dried sludge was mixed with 20–180 g of liquid to attain a reactor solid load of 10–50% dry solids. The reactor was closed, purged three times with argon, and heated to 180–260 °C using a PID controlled 0.95 kW electric heater. Reactor pressure was observed from a pressure gauge and was approximately equal to saturated vapor pressure at the respective reactor temperatures. After an isothermal holding time of 30 min the reactor was cooled with the help of a fan and the gases released to a fume hood. The solid and liquid phases were separated by vacuum filtration through a 1.6 µm Whatman filter paper. Reactor heating and cool-down profiles for various treatment temperatures are given in Fig. A.1 (Supplementary material).

A total of 21 individual experiments were carried out. First, 15 experiments were performed according to a Box Behnken design [22] by varying treatment temperature, solid load and liquid pH on three different levels (Table 1). Liquid pH was adjusted by using distilled water or AcOH (99.7%, Wako Chemical Industries, Ltd.) or NaOH (97%, Wako Chemical Industries, Ltd.) diluted to pH values 2.2 (1.78 M) or 11.7 (5.6 mM), respectively. Diluted solutions were manufactured prior to the experiments. Finally, 6 verification experiments were performed with distilled water in locations not included in the original design (Table 1).

2.3. Sample analyses

After solid and liquid separation, the pH values of the liquid samples were determined. The attained hydrochar samples were dried at 105 °C overnight. The ash contents of untreated sludge and char were determined based on loss on ignition in a muffle furnace at 550 °C for 2 h. Respective ash yields were calculated based on char solid yield (db) and ash contents of the char and the feed. The chemical compositions of the ignited samples were determined with an energy dispersive X-ray fluorescence spectrometer (XRF, S2 Ranger, Bruker Corp.). The spectrometer was operated with a 10–50 kV voltage coupled with a current of 0.98–1.35 mA depending on the individual element. Mineral composition of untreated sludge ash was determined with an X-ray diffractometer (XRD, Ultima iV, Rigaku Corp.) equipped with a copper tube. Diffractometer voltage and current were set to 40 kV and 40 mA coupled with a scan rate of 2° min^{-1} within 5–90°. Spectral peaks were identified by using outputs from the ICDD (the International Centre for Diffraction Data) PDF-4+ database. A scanning electron microscope (SEM, JSM-6610LA, JEOL Ltd.) equipped with an energy dispersive X-ray analyzer (EDX, EX-94300S4L1Q, JEOL Ltd.) was also used for evaluating the composition of individual Pt–Pd coated sludge ash particles.

2.4. Data interpretation

Correlations and groupings in attained data were determined through principal components. The data included 21 individual experiments as row objects and 16 variables describing experimental conditions or sample properties as the corresponding

Table 1
Individual experiments.

Experiment	Treatment temperature (°C)	Solid load (–)	Liquid pH
1	180	0.1	7
2	260	0.1	7
3	180	0.5	7
4	260	0.5	7
5	180	0.3	2.2
6	260	0.3	2.2
7	180	0.3	11.7
8	260	0.3	11.7
9	220	0.1	2.2
10	220	0.5	2.2
11	220	0.1	11.7
12	220	0.5	11.7
13	220	0.3	7
14	220	0.3	7
15	220	0.3	7
16[a]	180	0.3	7
17[a]	260	0.3	7
18[a]	220	0.1	7
19[a]	220	0.5	7
20[a]	200	0.4	7
21[a]	240	0.2	7

[a] Verification experiments.