



# Ash behavior during hydrothermal treatment for solid fuel applications. Part 1: Overview of different feedstock



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## ABSTRACT

Differences in ash behavior during hydrothermal treatment were identified based on multivariate data analysis of literature information on 29 different feedstock. In addition, the solubility of individual elements was evaluated based on a smaller data set. As a result two different groups were distinguished based on char ash content and ash yield. Virgin terrestrial and aquatic biomass, such as different types of wood and algae, in addition to herbaceous and agricultural biomass, bark, brewer's spent grain, compost and faecal waste showed lower char ash content than municipal solid wastes, anaerobic digestion residues and municipal and industrial sludge. Lower char ash content also correlated with lower ash yield indicating differences in chemical composition and ash solubility. Further evaluation of available data showed that ash in industrial sludge mainly contained anthropogenic Al, Fe and P or Ca and Si with low solubility during hydrothermal treatment. Char from corn stover, miscanthus, switch grass, rice hulls, olive, artichoke and orange wastes and empty fruit bunch had generally higher contents of K, Mg, S and Si than industrial sludge although differences existed within the group. In the future information on ash behavior should be used for enhancing the fuel properties of char based on feedstock type and hydrothermal treatment conditions.

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## 1. Introduction

Hydrothermal treatment can be used for upgrading a wide variety of biomass and waste feedstock for solid fuel applications. Thermochemical conversion in hot compressed water under relatively low temperature and self-generated pressure can offer several advantages over other processing routes. Hydrothermal treatment enables robust operation, high energy efficiency, relatively high yields and the production of direct replacements for existing solid fuels [1,2]. In addition, no prior drying of a feedstock is required making hydrothermal processes ideal for wet materials such as agricultural and forest residues or municipal and industrial waste biomass [3,4]. Material handling and drying properties are simultaneously enhanced [5,6] generating significant cost savings during handling, storage and transport of attained hydrochar.

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Although hydrothermal treatment has been reported already in the early 20th century as a method for simulating natural coalification [7], the wealth of published information has increased considerably during the last 5 years [8]. It is currently considered well known that reaction temperature governs char properties mainly through hydrolysis, dehydration, decarboxylation and aromatization of organic components [9–11]. The characteristics of subcritical water resemble those of organic solvents at room temperature and favor reactions normally catalyzed by acids and bases [1,12]. Oxygen and volatile contents of the solid are decreased followed by an increase in energy densification and hydrophobicity [2,9]. Depending on the feedstock and prevailing process conditions, hydrothermal treatment can be used for producing solid fuels that approach the characteristics of low rank natural coals.

Hydrothermal treatment leads to partial dissolution of inorganic components and has been reported to enable nitrogen and chlorine removal from municipal solid waste (MSW) [4]. Properties of subcritical water and production of organic acids during hydrothermal treatment increase the solubility of alkali and alkaline earth metals [13,14]. Manipulation of ash content and composition of a solid is a major benefit for fuel production as it can increase energy densification, improve slagging and fouling

behavior during combustion, and decrease corrosion of process equipment [15,16]. Previously, equal or improved slagging, fouling or alkali indices have been reported for hydrothermally treated energy crops and agricultural residues [17,18]. In addition, removal of alkali metals was recently reported to improve combustion properties of a variety of treated biomass and waste feedstock [19].

Behavior of ash components varies based on feedstock and hydrothermal treatment conditions. Even though the number of published information in the field has been expanding, no comprehensive reports exist on ash behavior from different biomass and waste feedstock under a wide range of treatment conditions. This work was divided into two separate parts. The objective of this first part was to identify differences in ash behavior based on feedstock type. Literature data on individual experiments on various feed materials were compiled, reviewed and interpreted using multivariate data analysis. In addition, the solubility of individual elements was evaluated based on a smaller data set. The second part of this work focuses on determining the effect of treatment conditions on ash properties of industrial waste biomass using univariate regression techniques. Overall the attained results will help in understanding ash behavior during hydrothermal treatment of different biomass and waste feedstock for solid fuel applications.

## 2. Materials and methods

### 2.1. Data compilation and review

Experimental data on the effects of hydrothermal treatment temperature, retention time and reactor solid load on char ash con-

tent, mass yield, energy densification and energy yield were compiled from relevant literature reports. Papers that did not report the ash contents of the feed and attained char samples were excluded. Papers that failed to include mass yield, energy densification or energy yield, but allowed respective estimation based on given information were however included. In addition, previously unpublished data on char ash from ref. [10] was taken into account. The final data set included 206 individual experiments on 29 different feedstock (Table 1). The data set was not exhaustive, but provided an overview of different feedstock used in the hydrothermal treatment field.

Compiled data were revised to enable comparison between different experiments. Retention time was expressed in hours (h) and was log10 transformed. Reactor solid load was expressed as a weight percentage (%) of the combined mass of added liquid and the feed on a dry basis (db). If no liquid was added solid load was taken as the dry solids content (%) of the feed. Ash yield was calculated as:

$$\text{Ash yield (\%, db)} = \left( \frac{ac_{hc}}{ac_f} \cdot MY \right) \cdot 100\% \quad (1)$$

where  $ac_{hc}$  and  $ac_f$  denoted the ash contents (db) of char and the feed, respectively, and MY char mass yield (db). To separate between the dissolution of organic and ash components, final mass yield was expressed on a dry, ash-free (daf) basis:

$$\text{Mass yield (\%, daf)} = \left( MY \cdot \frac{1 - ac_f}{1 - ac_{hc}} \right) \cdot 100\% \quad (2)$$

**Table 1**

Information on different feedstock and treatment conditions included in the overview.

Index	Feedstock	Refs.	Treatment temperature (°C)	Retention time (h)	Solid load (%) <sup>a</sup>	Additive	Reactor size (L)	No. of compiled data points
1	Oak wood	[19]	200–250	1.0	10		0.6	2
2	Loblolly pine	[20–22]	200–280	0.1–0.5	9.1–17		0.1	14
3	Coniferous wood	[23]	180–250	3.0–6.0	11–14		1.0	15
4	Eucalyptus bark	[24]	220–300	2.0–10	9.1		0.1	8
5	Willow	[19]	200–250	1.0	10		0.6	2
6	Miscanthus	[17,19,25]	190–260	0.1–1.0	10–17		0.1–0.6	8
7	Switch grass	[17]	200–260	0.1	17		0.1	3
8	Corn stover	[17]	200–260	0.1	17		0.1	3
9	Rice hulls	[17]	200–260	0.1	17		0.1	3
10	Maize silage	[26]	200–260	0.3–10	6.7		1.0	9
11	Wheat straw	[27]	200–260	6.0	4.8	Acetic acid and potassium hydroxide	1.0	22
12	Macroalgae	[19,28]	180–250	1.0–16	4.8–17	Citric acid [28]	0.1–0.6	18
13	Microalgae	[19]	200–250	1.0	10		0.6	2
14	Olive waste	[18]	200–250	2.0–24	29		1.0	6
15	Artichoke waste	[18]	200–250	2.0	14		1.0	3
16	Orange waste	[18]	200–250	2.0	21		1.0	3
17	Empty fruit bunch	[29]	100–260	0.5	9.1		0.5	4
18	Brewer's spent grain	[30]	200–240	14	12	Citric acid	0.2	2
19	Greenhouse waste	[19]	200–250	1.0	10		0.6	2
20	Food waste	[19,31]	200–250	1–16	10–20		0.2–0.6	3
21	Paper	[31]	250	16	20		0.2	1
22	MSW fiber	[19]	200–250	1.0	10		0.6	2
23	MSW	[31,32]	225–250	1.5–16	20–67		0.2 and 3.0 m <sup>3</sup>	2
24	Compost	[33]	180–250	1.0–8.0	7.0		0.1	9
25	Faecal waste	[34]	180–200	0.5–2.0	4.5		N/A	6
26	Sewage sludge	[19,34,35]	160–200	0.5–1.0	3.4		N/A	21
27	Anaerobic digestion residue	[19,31]	200–250	1.0–16	10–20		0.2–0.6	3
28	Mixed sludge <sup>b</sup>	[36]	180–260	0.5–5	21	Hydrogen chloride and sodium hydroxide	1.0	15
29	Paper sludge <sup>b</sup>	[10]	180–260	1.0–6.3	13–20		1.0	15

N/A = not available.

<sup>a</sup> Weight percentage of the combined mass of liquid and the feed on a dry basis.

<sup>b</sup> From pulp and paper mills.

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