Applied Energy 155 (2015) 576–584

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Hydrothermal carbonization of lignocellulosic biomass: Effect of process conditions on hydrochar properties

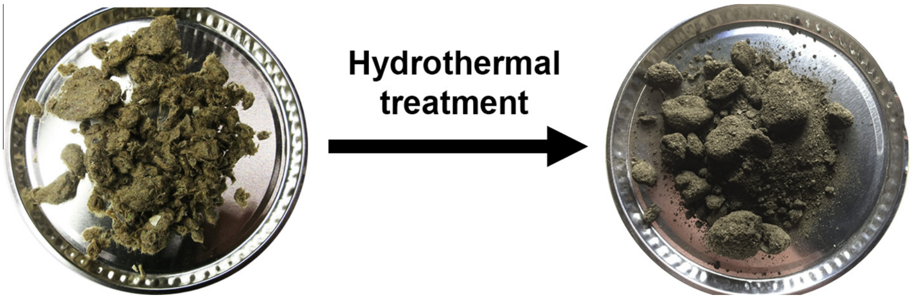
Mikko Mäkelä [a,*], Verónica Benavente [b], Andrés Fullana [b]

[a] Swedish University of Agricultural Sciences, Department of Forest Biomaterials and Technology, Division of Biomass Technology and Chemistry, Skogsmarksgränd, SE-90183 Umeå, Sweden
[b] University of Alicante, Department of Chemical Engineering, P.O. Box 99, E-03080 Alicante, Spain

HIGHLIGHTS

- Effect and statistical significance of process conditions on hydrochar properties.
- Reaction temperature had 3–7 times the effect of retention time.
- Predicted solid yields decreased to approx. 40% at higher temperatures.
- Predicted energy densification and energy yields within 1–1.5 and 60–100%.
- Attained results enable future prediction of hydrochar properties.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form 2 June 2015
Accepted 14 June 2015

Keywords:
Biosolids
Experimental design
Hydrothermal treatment
Response surface methodology
Sludge

ABSTRACT

Although hydrothermal carbonization of biomass components is known to be mainly governed by reaction temperature, consistent reports on the effect and statistical significance of process conditions on hydrochar properties are still lacking. The objective of this research was to determine the importance and significance of reaction temperature, retention time and solid load on the properties of hydrochar produced from an industrial lignocellulosic sludge residue. According to the results, reaction temperature and retention time had a statistically significant effect on hydrochar ash content, solid yield, carbon content, O/C-ratio, energy densification and energy yield as reactor solid load was statistically insignificant for all acquired models within the design range. Although statistically significant, the effect of retention time was 3–7 times lower than that of reaction temperature. Predicted dry ash-free solid yields of attained hydrochar decreased to approximately 40% due to the dissolution of biomass components at higher reaction temperatures, as respective oxygen contents were comparable to subbituminous coal. Significant increases in the carbon contents of hydrochar led to predicted energy densification ratios of 1–1.5 with respective energy yields of 60–100%. Estimated theoretical energy requirements of carbonization were dependent on the literature method used and mainly controlled by reaction temperature and reactor solid load. The attained results enable future prediction of hydrochar properties from this feedstock and help to understand the effect of process conditions on hydrothermal treatment of lignocellulosic biomass.

1. Introduction

Lignocellulosic biomass is an attractive feedstock for solid fuel production as it is widely considered carbon neutral and can be used as a direct replacement for existing fossil fuels. As opposed

---

* Corresponding author. Tel.: +46 (0)72 223 4035; fax: +46 (0)90 786 8125.
E-mail addresses: mikko.makela@slu.se, mmaekelae@gmail.com (M. Mäkelä), veronica.benavente@ua.es (V. Benavente), andres.fullana@ua.es (A. Fullana).

http://dx.doi.org/10.1016/j.apenergy.2015.06.022
0306-2619/© 2015 Elsevier Ltd. All rights reserved.

to primary virgin wood materials and energy crops, second generation feedstocks such as agricultural and forest residues and industrial waste biomass are low-cost, often readily available, and do not compete with land requirements for food production [1]. However, these heterogeneous residue streams require pretreatment to enhance respective handling, storage and transport properties and to increase subsequent efficiency of energy conversion.

The pulp and paper industry generates a variety of biomass residues that do not suffer from seasonal availability or expensive, distributed logistics. In Sweden the industry is a significant energy consumer currently covering approximately 46% of the total energy consumed within the Swedish mining and manufacturing sector [2]. Although 65% of the energy used by the industry is already produced from renewable energy sources, roughly 5% per year is still covered by fossil fuels and 30% per year by electricity [2]. Besides efficiently utilized wood wastes, residual sludge streams from fiber recycling and wastewater treatment offer further possibilities to increase the share of renewable energy and simultaneously decrease external sludge management costs. The energy potential of generated sludge residues within the Swedish pulp and paper industry has been estimated as 2 TW h per year, only a half of which is currently utilized in mill boilers [3].

As sludge is an inherently moist material, enhanced energy recovery through thermochemical conversion requires active drying for upgrading the feedstock [4]. However, current means of mechanical dewatering can only reach dry solids contents of 18–50% depending of the sludge type and applied dewatering technique [5]. Hydrothermal treatment, combining elevated temperature and pressure, is generally performed with water acting as a solvent, a reactant and even a catalyst or catalyst precursor and hence does not require active drying of a feedstock [6]. Biomass can be hydrothermally treated in a range of conditions, sub- and supercritical conditions separated by the critical temperature (374 °C) and pressure (22 MPa) of water [7]. The reaction temperature can be further limited to approximately 180–260 °C to minimize hydrothermal liquefaction and gasification thus maximizing solid recovery through a process known as hydrothermal carbonization, HTC. Under these conditions the dielectric constant of water is significantly reduced enabling properties comparable to organic solvents at room temperature while the increased ionization constant favors reactions which are generally catalyzed by acids or bases [7,8]. Hydrothermal carbonization of biomass was first reported already in the early 20th century as a method for simulating natural coalification [9], but has not received significant attention for upgrading various biomass and waste feedstocks until the recent 5–10 years.

Hydrothermal carbonization seems feasible for upgrading wet, low-value fuels by increasing respective energy density, decreasing oxygen and volatile contents and enhancing hydrophobic properties [10,11]. Especially for sludge, a low-cost waste feedstock, HTC could be used to convert biomass to a solid product (i.e., hydrochar) approaching the characteristics of low-rank natural coals thereby increasing potential use in energy production and providing significant ease in handling, storage and transport [4,10,12]. As HTC is ideally operated under saturated steam pressure, the energy required for evaporation can be avoided making the theoretical energy requirement for heating the reaction medium significantly lower compared to active drying [7,13]. Energy is still required for post-treatment separation of the solid and liquid phases, but can be significantly lower compared to conventional sludge drying due to potential sludge cell breakage and enhanced drying characteristics [14].

Thus far the majority of published academic literature on HTC of biomass for solid fuel production has concentrated on the carbonization of model compounds such as cellulose [15,16] along with virgin wood materials [17,18], herbaceous [19,20] and mixed feedstock [20–22] for clarifying carbonization mechanisms and hydrochar properties. Although dehydration, decarboxylation, polymerization and aromatization of biomass components during HTC are known to be mainly governed by reaction temperature, consistent reports on the effect and statistical significance of process conditions on hydrochar properties are still lacking. Such information would allow reliable estimations on the behavior of hydrochar properties and prediction of optimum conditions according to a given set of boundary conditions. Based on this background, our objective was to determine the effect and significance of reaction temperature, retention time and solid load on the properties of hydrochar produced from an industrial lignocellulosic sludge residue thereby enabling future prediction of hydrochar properties.

2. Material and methods

2.1. Feed material

A recycled paper mill sludge residue from a Swedish pulp and paper mill was used as the carbonization feed. Recycled paper is pulped and washed at the mill for the production of unbleached kraft/eurokraft liner for corrugated cardboard. After pulp washing reject fibers unsuitable for papermaking are separated by pressure sieves and screw pressed producing approximately 9000 t per year of recycled paper mill sludge. A fresh 300 kg sample taken under normal operating conditions was coned and quartered [23] to approximately 10 kg and stored in a refrigerator (+4 °C) during the experiments. The feed was characterized according to methods described in Section 2.3 and the results are provided Table 1.

2.2. Laboratory experiments

The carbonization experiments were performed according to a spherical, three-factor experimental design first introduced by Box and Behnken [24]. Reaction temperature, retention time and liquid to solid-ratio were selected as controlled design factors varying on three respective levels within 180–260 °C, 1–6.25 h and 1–2 (equivalent dry solids 13.4–20.0%). Reaction temperature and liquid to solid-ratio levels were evenly spaced within the design space with respective mid-point levels of 220 °C and 1.5. The retention time parameter was log10 transformed providing a range of 0–0.796 with a respective mid-point level of 0.398 (2.5 h). The final design (see Fig. A.1, Appendix A) was thus composed of 15 individual experiments including three replicated center-points.

Table 1
Characterization of the sludge feed.

Parameter	Unit	Sludge
Dry solids content (105 °C)	%	40.2
Loss on ignition (LOI, 550 °C)	% (db)	53.2
Ash content (550 °C)	% (db)	46.8
Higher heating value	MJ kg^{-1} (db)	10.6
Lower heating value	MJ kg^{-1} (db)	10.2
C	% (db)	20.9
H	% (db)	1.7
N	% (db)	0.2
S	% (db)	0.0
Extractive content	% (daf)	10.0
Hemicellulose content	% (daf)	11.6
Cellulose content	% (daf)	39.2
Lignin content	% (daf)	33.0

db = dry basis.
daf = dry ash-free.