Hydrothermal carbonization of industrial mixed sludge from a pulp and paper mill

Mikko Mäkelä, Verónica Benavente, Andrés Fullana

PII: S0960-8524(15)01465-0
DOI: http://dx.doi.org/10.1016/j.biortech.2015.10.062
Reference: BITE 15687

To appear in: *Bioresource Technology*

Received Date: 17 September 2015
Revised Date: 16 October 2015
Accepted Date: 17 October 2015

Please cite this article as: Mäkelä, M., Benavente, V., Fullana, A., Hydrothermal carbonization of industrial mixed sludge from a pulp and paper mill, *Bioresource Technology* (2015), doi: http://dx.doi.org/10.1016/j.biortech.2015.10.062

Hydrothermal carbonization of industrial mixed sludge from a pulp and paper mill

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

[a] Swedish University of Agricultural Sciences, Department of Forest Biomaterials and Technology, Skogsmarksgränd, 90183 Umeå, Sweden

Current address: Tokyo Institute of Technology, Department of Environmental Science and Technology, G5-8, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

[b] University of Alicante, Department of Chemical Engineering, P.O. Box 99, 03080 Alicante, Spain (V. Benavente: veronica.benavente@ua.es, A. Fullana: andres.fullana@ua.es)

*corresponding author, tel.: +81 (0)45 924 5507, fax: +81 (0)45 924 5507, email: makela.m.aa@m.titech.ac.jp, mikko.makela@slu.se

Abstract

Mixed sludge from a pulp and paper mill was hydrothermally carbonized at 180-260 °C for 0.5-5 h with the use of HCl or NaOH for determining the effect of acid and base additions during sludge carbonization. Based on the results carbonization was mainly governed by dehydration, depolymerization and decarboxylation of sludge components. Additive type had a statistically significant effect on hydrochar carbon content and carbon and energy yield, of which especially energy yield increased through the use of HCl. The theoretical energy efficiencies of carbonization increased with decreasing reaction temperature, retention time and the use of HCl and suggested that the energy requirement could be covered by the energy content of attained hydrochar. The BOD_5/COD –ratios of analyzed liquid samples indicated that the dissolved organic components could be treated by conventional biological methods.

Keywords: Biosolids; Hydrothermal treatment; Sludge treatment; Wet torrefaction; Waste biomass

1. Introduction

Hydrothermal carbonization has received considerable attention during the last 5 years (ScienceDirect, 2015) as a prominent alternative for upgrading renewable biomass. In addition to virgin wood and algae resources, a wide variety of work has been published on pretreating agricultural and forest residues and industrial or municipal waste biomass for material and solid fuel applications. These second generation feedstocks are promising feed materials for hydrothermal processes as, in addition to low energy densities and heterogeneous properties, they are hydrophilic in nature and possess relative high moisture contents. In addition, they are often found readily available, low-cost and do not compete with land requirements for food production (Ho et al., 2014).

One of the main advantages of hydrothermal carbonization is the use of aqueous solutions under high temperature and autogenously generated pressure. Under these conditions water acts as a solvent, a reactant or even a catalyst or catalyst precursor and hence no prior drying of a feedstock is required (Jin et al., 2014). During carbonization the increasing ion product of water favors reactions which are typically catalyzed by acids and bases and are generally understood to proceed via a network of hydrolysis, dehydration, decarboxylation, polymerization and aromatization of biomass components (Falco et al., 2011; Sevilla & Fuertes, 2009). As the former reaction path is largely governed by dehydration and decarboxylation it is essentially exothermic (Funke & Ziegler, 2010; Zhao et al., 2014). Part of feedstock carbon is inevitably lost due to dissolution of organics into the aqueous phase as minor quantities of gas are also generated. However, as hydrothermal carbonization ideally operates under saturated steam pressures, the latent heat requirement of evaporation can be avoided which

significantly decreases the respective energy requirement compared to active drying required for other thermochemical treatment alternatives.

Hydrothermal treatment of industrial and municipal sludge materials is especially appealing due to current difficulties in removing water from the polymeric matrix of sludge suspensions (Mowla et al., 2013) and the potential presence of biologically active organisms or compounds. Within the pulp and paper industry sludge is mainly generated during primary and secondary wastewater treatment processes by mechanical, chemical or biological methods. Traditionally these residues have been disposed of by landfilling or incineration which however suffer from weak economics due to the need for sludge dewatering or energy-intensive evaporation in the recovery boilers of pulp mills (Xu & Lancaster, 2008). Overall, sludge management can form a major part of the total operating costs of wastewater treatment plants and is currently the most significant solid waste issue at most pulp and paper mills.

Hydrothermal carbonization of municipal sludge has previously been investigated for respective solid fuel properties and gas yield of the liquid fraction (Danso-Boateng et al., 2015; He et al., 2013). In addition, carbonization of faecal biomass with or without primary municipal sludge has been reported (Danso-Boateng et al., 2013; Fakkaew et al., 2015). Carbonization of various sludge residues from the pulp and paper industry have also been studied for fuel properties and process energetics (Areeprasert et al., 2014a; Mäkelä et al., 2015), combustion characteristics (Areeprasert et al., 2014b) and potential use as adsorbents for environmental applications (Alatalo et al., 2013). The objective of this work was to determine the effect of acid and base additions to the properties of hydrochar produced through hydrothermal carbonization of mixed sludge

from the pulp and paper industry. Effects of acids and bases have previously been determined for model compounds such as cellulose (Lu et al., 2014), virgin wood (Lynam et al., 2011) and agricultural residues (Reza et al., 2015; Yang et al., 2015). However, no information exists on whether these trends apply to industrial sludge materials. The attained information on pulp and paper mill sludge will be used for evaluating possibilities for integrating hydrothermal carbonization and wastewater treatment processes within the mills, a potentially efficient way to ease future handling and management of generated sludge residues.

2. Materials and methods

2.1 Sludge sampling

Sludge samples were attained from a Swedish pulp and paper mill using virgin sulphate and recycled fiber pulp for the production of unbleached kraft/euroliner for corrugated cardboard. Gravitational settling followed by a biological activated sludge process was used for treating mill effluents. Approximately 300 kg of sludge containing 60% primary sludge and 40% biosludge was sampled after primary and surplus biosludge from secondary sedimentation had been mixed and dewatered using a belt filter and a centrifuge. The attained sample was coned and quartered to a representative 10 kg subsample which was stored in +4 °C during the experiments. The representative sludge sample was analyzed as described in Section 2.3 and the results are provided in Table 1.

Please insert Table 1 here

2.2 Hydrothermal carbonization

The carbonization experiments were performed with a constant 300 g mass of mixed sludge and 75 mL of additive in a 1 L non-stirred pressure reactor (Amar Equipments PVT Ltd., Mumbai, India). After closure the reactor was heated to reaction temperature with 1.5 kW electric heating resistance and an additional heating plate placed under the reactor. The 1.5 kW heating resistance was steered with a PID controller as the additional heating plate was set to reaction temperature. Reactor pressure was monitored from a pressure gauge, which indicated that the pressure was approximately equivalent to saturated vapor pressure under the respective temperature range (1-5 MPa). After the set retention time was complete, the reactor was cooled with pressurized air and the gases were released to a fume hood. The solid and liquid phases were subsequently separated by vacuum filtration through a grade 413 VWR® filter paper (VWR International LLC, Radnor, PA, USA).

The individual experiments were organized according to an experimental design including reaction temperature (180-260 °C) and log-transformed retention time (0.5-5 h) as continuous variables. In addition, additive type was included as a discrete variable by using reagent grade HCl (0.01 N, pH 2.5) or NaOH (0.01 N, pH 12.1). Deionized H_2O (conductivity <6 mS cm^{-1}) was used as a control. As the design included a discrete variable it was constructed to allow the use of dummy variables in regression modeling (Myers et al., 2009). The final design was composed of 15 individual experiments (Table 2).

Please insert Table 2 here

2.3 Analyses

Dry solids contents of all solid samples were determined in a drying oven at 105 °C (overnight) according to the guidelines of international standard EN 14774-1:2009. Respective heating values of dried samples were measured according to EN 14918:2009 by combustion under pure oxygen at 25 °C using a Leco AC-350 oxygen bomb calorimeter calibrated with benzoic acid. The CHNS contents were determined with a Thermo Finnigan Flash 1112 Series elemental microanalyzer as respective oxygen contents were calculated by subtraction. Sample ash contents were determined according to EN 14775:2009 under atmospheric conditions at 550 °C with a Heron muffle furnace (serie-74, model 12-R/300). All solid analyses were performed in duplicate and the mean value used for further calculations. In addition, the extractive, hemicellulose, cellulose and lignin contents of dry, ash-free sludge were determined through extractive, holocellulose and lignin extractions respectively described by Di Blasi et al. (1999) and Yang et al. (2006).

Solid-state ^{13}C cross polarization nuclear magnetic resonance (NMR) was performed on ground mixed sludge and selected hydrochar samples (no. 7, 10 and 15, Table 2) with a Bruker Avance DRX500 spectrometer at a frequency of 125 MHz. For each spectrum 8000 scans were accumulated with a contact time of 1 ms, an acquisition time of 14 ms, and a recycled decay delay of 1.5 s. All spectra were processed with a 50 Hz Lorentzian line broadening and a 0.01 s Gaussian broadening. The shift values were calibrated using a glycine carbonyl signal set at 176.04 ppm relative to tetramethylsilane. The pH values of separated liquid samples were also recorded and respective chemical oxygen demands (COD) determined using LCK014 digestion vials (Hach Co., Loveland, CO, USA) and measuring the chromate flux with a DR 3800 SC spectrophotometer. In

addition, the 5-day biological oxygen demand (BOD_5) of selected samples were measured according to international standard ISO 5815-1:2003.

2.4 Calculations

After the analyses of solid and liquid fractions a 15x18 data matrix (see Supplementary information) including 4 variables on carbonization conditions and 14 measured or calculated responses describing hydrochar and liquid properties was constructed. In addition to reaction temperature and retention time the effects of HCl and NaOH were included through the use of dummy variables c_1 and c_2, where:

$$c_1 = \begin{matrix} 1 \text{ if NaOH is the discrete value} \\ 0 \text{ elsewhere} \end{matrix} \quad (1)$$

$$c_2 = \begin{matrix} 1 \text{ if HCl is the discrete value} \\ 0 \text{ elsewhere} \end{matrix} \quad (2)$$

Hydrochar solid yield (%), carbon content (%), oxygen/carbon (O/C) ratio, higher heating value (MJ kg^{-1}) and energy densification were expressed on a dry, ash-free (daf) basis as previously described (Mäkelä et al., 2015). In addition, respective ash, carbon and energy yields (%) were calculated and expressed on a dry basis (Mäkelä et al., 2015). Total organic carbon (TOC) contents of the liquid samples were estimated from the respective COD measurements according to:

$$TOC = m_{O2} \cdot \frac{C_{mw}}{O_{2,mw}} \quad (3)$$

where m_{O2} denotes the mass of O_2 equivalent (mg) and C_{mw} and $O_{2,mw}$ the molecular weights of carbon and O_2 (g mol^{-1}), respectively. TOC was expressed as mg g^{-1} (daf) feed and was also used for calculating the carbon yield (%) in liquid samples.

The energy efficiency (%) of sludge carbonization was estimated based on the energy content of hydrochar and the theoretical energy requirement of carbonization. The energy requirement was determined based on the enthalpy difference of saturated liquid at room temperature and saturated water vapour at reaction temperature including the heating of sludge solids (Areeprasert et al., 2014). The specific heat capacity of dry sludge was estimated as 1.7 kJ kg^{-1}. The exact enthalpies of water vapour under reaction temperatures were calculated by fitting a fourth-order polynomial to the respective enthalpy values for 1, 2, 3, 4 and 5 MPa reported by Wanger and Pruß (2002). The coefficients of the attained polynomial were then used for determining these enthalpies at 180, 220 and 260 °C with corresponding saturated vapour pressures of 1.0, 2.3 and 4.7 MPa reported by Lide (2005).

Principal component scores and loadings of the resulting 15x18 data matrix were determined through singular value decomposition:

$$\mathbf{X_{ms}} = \mathbf{U\,S\,V^T} = \mathbf{t_1 p_1^T} + \mathbf{t_2 p_2^T} + \cdots + \mathbf{t_n p_n^T} + \mathbf{E} \quad (4)$$

where $\mathbf{X_{ms}}$ is the mean-centered and z-scaled data matrix, **U** an orthogonal matrix of row scores, **V** is orthogonal matrix of column loadings and **S** a diagonal matrix containing respective singular values of $\mathbf{X_{ms}}$. Vectors **t** and **p** denote the principal component scores and loadings, and **E** the residual matrix after n components. The scores **t** were calculated by multiplying with respective singular values ($\mathbf{t_n} = \mathbf{u_n s_n}$) and both scores and loadings ($\mathbf{p_n} = \mathbf{v_n}$) were scaled for plotting purposes with c=1/4 as described by Smilde et al. (2004).

Individual multiple regression models describing the response columns of the data matrix were determined based on carbonization conditions. The general model equation:

$$\mathbf{y} = \mathbf{Zb} + \mathbf{e} \quad (5)$$

was solved by minimizing the sum of squares of model residuals **e** through:

$$\mathbf{b} = (\mathbf{Z^T Z})^{-1}\mathbf{Z^T y} \quad (6)$$

where **y** is a vector of hydrochar or liquid properties, **Z** a coded and mean-centered matrix including the experimental conditions and respective interaction terms, **b** the model vector and **e** a vector of model residuals. The variance explained by a model coefficient was F-tested against the variance of model residuals and the insignificant coefficients excluded from the final models. The explanatory capability of a model was calculated through the R^2 value:

$$R^2 = 1 - \frac{SSres}{SStot} \quad (7)$$

where SS_{res} denotes the sum of squares of model residuals **e** and SS_{tot} the total sum of squares of **y** corrected for the mean. Calculations and data plotting were performed with Matlab® (The Mathworks, Inc.), DesignExpert® (Stat-Ease, Inc.) and OriginLab® (OriginLab Corporation) software packages.

3. Results and Discussion

Combined hydrochar and liquid recoveries were within 91-94% during the experiments. The solid content of hydrochar increased to a maximum of 53% depending on reaction temperature and retention time ($p < 0.01$). However, the ash content of hydrochar also increased within a range of 35-48% due to the decomposition of sludge components

during carbonization. Respective ash yields varied in the range 81-99% and were found inversely correlated with reaction temperature ($p < 0.05$).

Three possible outlier values were found within the carbon contents of attained hydrochar during the interpretation of principal components, which also affected char carbon yields and O/C –ratios. To verify the outliers, individual linear regression models were respectively calculated based on only 12 observations, which increased the R^2 values of the models from 0.55-0.72 to 0.93-0.96. The reduced regression models were then used for predicting and replacing the outliers after which the regression models were refitted with 15 observations. The following results are based on the corrected data.

3.1 Principal components

Correlations between experimental conditions and attained hydrochar or liquid properties are conveniently illustrated through the use of principal component loadings. As illustrated in Fig. 1, the first principal component included the effects of reaction temperature and retention time, which generally determine reaction severity. Reaction temperature and retention time correlated with the carbon content of the solid and thus increased hydrochar heating value and energy densification (Fig. 1a). However, respective solid and carbon yields were simultaneously decreased coupled with a decrease in the energy yield and energy efficiency of carbonization. In addition, sludge decomposition during carbonization increased the TOC content and carbon yield of the liquid samples.

Please insert Fig. 1 here

Based on the second principal component, no correlation was found between the use of HCl or NaOH and the post-treatment pH values of the liquid samples (Fig. 1a). This indicated that the hydronium and hydroxide ion concentrations provided by the additives were neutralized during carbonization, most likely due to the well-known production of carboxylic acids during hydrothermal carbonization of biomass (Danso-Boateng et al., 2015; Hoekman et al., 2011; Weiner et al., 2014). However, the second principal component suggested that the addition of HCl increased the carbon contents and respective carbon yields in the solid and thus seemed to enhance the energy yield and energy efficiency of carbonization (Fig. 1a). The third principal component explained mainly correlations between reaction temperature, retention time and post-treatment liquid pH. As illustrated in Fig. 1b, increasing reaction temperature lowered post-treatment liquid pH. However, retention time correlated with increasing liquid pH, which could be an indication of further transformation of produced acids under prolonged retention times. The first three principal components explained approximately 89% of variation in the corrected results.

3.2 Chemical structure of sludge and hydrochar

The NMR results suggested that untreated sludge was mainly composed of cellulose and hemicellulose sugars. The spectral region at 0-120 ppm characteristic for sp3 carbon atoms indicated a wide distribution of CH_x sites. Chemical shifts within 0-40 ppm are generally related to acetyl methyl groups of hemicellulose carbon, an up-field shoulder at approximately 60 ppm to C-6 carbon and peaks at 70-80 ppm to C-2, C-3 and C-5 carbons (Bardet et al., 1986; Wikberg and Maunu, 2004). In addition, a minor signal at approximately 85 ppm indicated the presence of C-4 carbons and a well-resolved peak at 105 ppm the anomeric C-1 carbon of sugars (Bardet et al., 1986;

Wikberg and Maunu, 2004). No noticeable peaks were found with untreated sludge within 120-160 ppm which are generally characteristic for sp2 carbon atoms in the C=C double and O-C=C oxygen bonds (Holtman et al., 2006). Nor did the spectra support the presence of C=O groups in either carboxylic acids (170-200 ppm) or ketones and aldehydes (200-220 ppm) of hemicellulose.

Based on the spectra of hydrochar samples, hydrothermal carbonization did not lead to considerable changes in the chemical structure of sludge until higher reaction temperature and retention time. The spectra after carbonization at 180 °C for 0.5 h and at 220 °C for 1.6 h were almost identical to that of untreated sludge. However, the aliphatic carbon signals within 40-120 ppm disappeared almost completely after carbonization at 260 °C for 5 h indicating a high decomposition of carbohydrates. The remaining wide peak associated with the acetyl methyl group of cellulose at 0-40 ppm suggested that alkyl carbon was still present. The small peaks associated with lignin and the methoxyl groups of lignin at approximately 140 and 56 ppm (Holtman et al., 2006; Park et al., 2013), respectively, were also more distinguishable after carbonization at 260 °C for 5 h most likely due to the decomposition of carbohydrates. The relatively low increase in the intensity of aromatic peaks indicated that sludge carbonization was mainly governed by dehydration, depolymerization and decarboxylation rather than polymerization and aromatization of sludge components.

3.3 Individual response models

The effect of acid and base additions to hydrochar and liquid properties were further evaluated through the determination of individual response models. As illustrated in Table 3, the effect of additive type was statistically significant ($p < 0.05$) for the carbon

content, carbon yield and O/C-ratio attained hydrochar. However these differences were more pronounced with the use of NaOH, which decreased carbon content, carbon yield and increased O/C-ratio, than with HCl compared to the control. Significance of additive type for hydrochar energy yield and energy efficiency ($p < 0.10$) supported the information attained by principal components and indicated that acidic additives can enhance the energy yield and overall energy efficiency of sludge carbonization. Previously the effect of HCl and NaOH during hydrothermal carbonization of cellulose has been reported by Lu et al. (2014). The authors found that both additives had a significant effect on solid yield, carbon content and oxygen content of hydrochar carbonized at 250 °C for 1-1.5 h likely due to reaction kinetics. In addition, Lynam et al. (2011) found that acetic acid additions affected cellulose dissolution and respectively decreased solid yield and increased energy densification of loblolly pine. Reza et al. (2015) also reported lower mass yields and higher carbon contents in hydrochar produced from wheat straw through the use of acetic acid. It should be noted that if the additives become partly or entirely neutralized during carbonization their use can be unattractive in industrial scale as they require large inputs of acid or base or expensive recovery and regeneration cycles (Kumar et al., 2015). Potential positive effects of NaOH or sodium salts would have practical relevance for pulp and paper mills as they are continuously used, recovered and regenerated during the chemical recovery cycles of kraft pulp mills.

Please insert Table 3 here

As illustrated by our results in Fig. 2, hydrochar solid yield was not considerable affected by the use of HCl or NaOH during sludge carbonization. Althought the NMR

spectra of hydrochar suggested no considerable changes in the chemical structure of sludge a part of the sludge matrix was decomposed during carbonization at 180 °C for 0.5 h. It is likely that the polymeric matrix of bacterial biomass from secondary sludge became soluble at temperatures lower than 180 °C thus affecting respective solid yields. The effect of additive type on hydrochar carbon yield is clearly illustrated in Fig. 2. However, although the use of NaOH decreased char carbon yields, no clear difference could be seen between HCl and the control. Minor differences could be seen in the carbon yields of the liquid samples between HCl and the control although additive type was found statistically insignificant for the response model (Table 3). Hydrochar energy yield was increased with the addition of HCl as also suggested by the principal components (Fig. 1).

Please insert Fig. 2 here

Theoretical energy efficiencies were determined to estimate the feasibility of sludge carbonization. Based on the results the energy content of attained hydrochar ranged from 97 to 147% compared with the energy requirement of carbonization. Higher efficiencies were attained at lower reaction temperature and retention time due to increasing solid and energy yields (Fig. 2). In addition, the use of HCl increased respective efficiencies compared to the use NaOH. As an example, carbonizing sludge at a reaction temperature of 220 °C with a retention time of 1 h without additives would provide respective hydrochar solid, carbon and energy yields of 69 ± 4%, 85 ± 2% and 78 ± 4% with 95% certainty. At these conditions, the produced hydrochar would contain 117 ± 6% of the energy theoretically required for sludge carbonization. Based on our previous work (Mäkelä et al., 2015) reactor solid load plays an important role in enhancing the theoretical energy efficiency of hydrothermal carbonization. Hence in

future efforts, sludge should be carbonized at high reactor solid loads coupled with the treatment of separated liquid at the wastewater treatment plants of pulp and paper mills. The determined BOD_5/COD –ratios of 4 liquid samples attained at 180-260 °C for 0.5-5 h were in the range 0.4-0.6 suggesting that the dissolved organics of analysed samples were sufficiently biodegradable to be treated by conventional biological methods (Berge et al., 2011).

Conclusions

Hydrothermal carbonization shows promise for mixed sludge treatment. Sludge carbonization was governed by dehydration, depolymerization and decarboxylation rather than polymerization and aromatization of sludge components. Although used additives were neutralized during carbonization, additive type had a statistically significant effect on hydrochar carbon content and respective carbon and energy yield. Especially energy yield was enhanced through the use of HCl. The theoretical energy efficiencies suggested that 97-147% of the energy required for carbonization could be attained from the produced hydrochar. The BOD_5/COD -ratios of liquid samples indicated that the dissolved organic components could be treated by conventional biological methods.

Acknowledgements

The contributions of Markus Segerström and Gunnar Kalén from the Swedish University of Agricultural Sciences in sample processing, and Maria Esperanza Iñiguez and Ana Belén Martínez from the University of Alicante in material analyses are deeply

appreciated. This work was performed in cooperation with SCA Obbola AB with partial funding from SP Processum AB.

References

Alatalo, S.-M., Repo, E., Mäkilä, E., Salonen, J., Vakkilainen, E., Sillanpää, M., 2013. Adsorption behavior of hydrothermally treated municipal sludge & pulp and paper industry sludge. Bioresour. Technol. 147, 71-76.

Areeprasert, C., Zhao, P., Ma, D., Shen, Y., Yoshikawa, K., 2014a. Alternative solid fuel production from paper sludge employing hydrothermal treatment. Energ. Fuel. 28, 1198-1206.

Areeprasert, C., Chanyavanich, P., Ma, D., Shen, Y., Prabowo, B., Yoshikawa, K., 2014b. Combustion characteristics and kinetics study of hydrothermally treated paper sludge by thermogravimetric analysis. Biofuels 5, 673-685.

Bardet, M., Gagnaire, D., Nardin, R., Robert, D., Vincendom, M., 1986. Use of C-13 enriched wood for structural investion of wood and wood components, cellulose and lignins, in solid and liquid. Holzforschung 40, 17-24.

Berge, N.D., Ro, K.S., Mao, J., Flora, J.R.V., Chappell, M.A., Bae, S., 2011. Hydrothermal carbonization of municipal waste streams. Environ. Sci. Technol. 45, 5696-5703.

Danso-Boateng, E., Holdich, R.G., Shama, G., Wheatley, A.D., Sohail, M., Martin, S.J., 2013. Kinetics of faecal biomass hydrothermal carbonization for hydrochar production. Appl. Energ. 111, 351-357.

Danso-Boateng, E., Shama, G., Wheatley, A.D., Martin, S.J., Holdich, R.G., 2015. Hydrothermal carbonisation of sewage sludge: effect of process conditions on product characteristics and methane production. Bioresour. Technol. 177, 318-327.

Di Blasi, C., Signorelli, G., Di Russo, C., Rea, G., 1999. Product distribution from pyrolysis of wood and agricultural residues. Ind. Eng. Chem. Res. 38, 2216-2224.

Fakkaew, F., Koottatep, T., Polprasert, C., 2015. Effects of hydrolysis and carbonization reactions on hydrochar production. Bioresour. Technol. 192, 328-334.

Falco, C., Baccile, N., Titirici, M.-M., 2011. Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons. Green Chem.13, 3273-3281.

Funke, A., Ziegler, F., 2010. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. Biofuels Bioprod. Biorefin. 4, 160-177.

He, C., Giannis, A., Wang, J.-Y., 2013. Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: hydrochar fuel characteristics and combustion behavior. Appl. Energ. 111, 257-266.

Ho, D.P., Ngo, H.H., Guo, W., 2014. A mini review on renewable sources for biofuel. Bioresour. Technol. 169, 742-749.

Hoekman, S.K., Broch, A., Robbins, C., 2011. Hydrothermal carbonization (HTC) of lignocellulosic biomass. Energ. Fuel. 25, 1802-18210.

Holtman, K.M., Chang, H.M., Jameel, H., Kadla, J.F.J., 2006. Quantitative 13C NMR characterization of milled wood lignins isolated by different milling techniques. J. Wood Chem. Technol. 26, 21-34.

Jin, F., Wang, Y., Zeng, X., Shen, Z., Yao, G., 2014. Water Under High Temperature and Pressure Conditions and Its Applications to Develop Green Technologies for Biomass Conversion. in: Jin, F. (Eds.), Application of Hydrothermal Reactions to Biomass Conversion, Springer. Heidelberg, pp. 3-28.

Kumar, S., Lange, J.-P., Van Rossum, G., Kersten, S.R.A., 2015. Liquefaction of lignocellulose: do basic and acidic additives help out? Chem. Eng. J. 278, 99-104.

Lide, R., 2005. Vapor pressure of water from 0 to 370 °C. in: Lide, R. (Eds.), Handbook of Chemistry and Physics, CRC Press. Boca Raton, pp. 6-8.

Lu, X., Flora, J.R.V., Berge, N.D., 2014. Influence of process water quality on hydrothermal carbonization of cellulose. Bioresour. Technol. 154, 229-239.

Lynam, J.G., Coronella, C.J., Yan, W., Reza, M.T., Vasquez, V.R., 2011. Acetic acid and lithium chloride effects on hydrothermal carbonization of lignocellulosic biomass. Bioresour. Technol. 102, 6192-6199.

Mäkelä, M., Benavente, V., Fullana, A., 2015. Hydrothermal carbonization of lignocellulosic biomass: effect of process conditions on hydrochar properties. Appl. Energ. 155, 576-584.

Mowla, D., Tran, H.N., Grant Allen, D., 2013. A review of the properties of biosludge and its relevance to enhanced dewatering processes. Biomass Bioenerg. 58, 365-378.

Myers, R.H., Montgomery, D.C., Anderson-Cook, C.M., 2009. Experimental Designs for Fitting Response Surfaces - II. in: Myers, R.H., Montgomery, D.C., Anderson-Cook, C.M. (Eds.), Response Surface Methodology: Process and Product Optimization Using Designed Experiments (3rd ed.), John Wiley & Sons, Inc., Hoboken, pp. 349-416.

Park, J., Meng, J., Lim, K.H., Rojas, O.J., Park, S., 2013. Transformation of lignocellulosic biomass during torrefaction. J. Anal. Appl. Pyrolysis 100, 199-206.

Reza, M.T., Rottler, E., Herklotz, L., Wirth, B., 2015. Hydrothermal carbonization (HTC) of wheat straw: influence of feedwater pH prepared by acetic acid and potassium hydroxide. Bioresour. Technol. 182, 336-344.

ScienceDirect, http://www.sciencedirect.com, accessed: October 13th, 2015.

Sevilla, M., Fuertes, A.B., 2009. The production of carbon materials by hydrothermal carbonization of cellulose. Carbon 47, 2281-2289.

Smilde, A., Bro, R., Geladi, P., 2004. Visualization. in: Smilde, A., Bro, R., Geladi, P. (Eds.), Multi-way Analysis with Applications in the Chemical Sciences, John Wiley & Sons Ltd., Sussex, England, pp. 175-220.

Wanger, W., Pruß, A., 2002. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data 31, 387-535.

Weiner, B., Poerschmann, J., Wedwitschka, H., Koehler, R., Kopinke, F.-D., 2014. Influence of process water reuse on the hydrothermal carbonization of paper. ACS Sustain. Chem. Eng. 2, 2165-2171.

Wikberg, H., Maunu, S.L., 2004. Characterization of thermally modified hard- and softwoods by 13C CPMAS NMR. Carbohydr. Polym. 58, 461-466.

Xu, C., Lancaster, J., 2008. Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water. Water Res. 42, 1571-1582.

Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D.H., Liang, D.T., 2006. In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. Energ. Fuel. 2006, 288-393.

Yang, W., Shimanouchi, T., Kimura, Y., 2015. Characterization of the residue and liquid products produced from husks of nuts from Carya cathayensis sarg by hydrothermal carbonization. ACS Sustain. Chem. Eng. 3, 591-598.

Zhao, P., Shen, G., Ge, S., Chen, Z., Yoshikawa, K., 2014. Clean solid biofuel production from high moisture content waste biomass employing hydrothermal treatment. Appl. Energ. 131, 345-367.

Figure captions

Fig. 1: Biplots of experimental scores and variable loadings on the (a) first and second and (b) first and third principal components (PCs). Solids: char solids content (%), Ash: ash content (%, db), SY: solid yield (%, daf), AY: ash yield (%, db), C: char carbon content (%, daf), CY: char carbon yield (%), O/C: char O/C –ratio, HHV: char heating value (MJ kg^{-1}, daf), ED: energy densification, EY: energy yield (%), EE: energy efficiency (%), pH: liquid pH, TOC: liquid TOC and CYL: liquid carbon yield (%).

Fig. 2: Response contours of (a) hydrochar solid yield (%, daf), (b) carbon yield (%), (c) liquid carbon yield (%) and (d) hydrochar energy yield (%) as functions of reaction temperature and retention time using HCl, H_2O (control) or NaOH as an additive.

Tables

Table 1: Characterization of mixed sludge

Parameter	Unit	Mixed sludge
Dry solids (105 °C)	%	25.6
Ash content (550 °C)	% (db)	35.4
Higher heating value	MJ kg^{-1} (db)	16.3
Lower heating value	MJ kg^{-1} (db)	15.1
C	% (db)	39.2
H	% (db)	5.6
N	% (db)	2.1
S	% (db)	0.0
Extractive content	% (daf)	16.6
Hemicellulose content	% (daf)	19.5
Cellulose content	% (daf)	8.0
Lignin content[b]	% (daf)	32.5

db = dry basis

daf = dry ash-free

Table 2: The experimental design

Experiment n:o	Reaction temperature (°C)	Retention time (h)	Additive
1	180	0.5	NaOH
2	260	0.5	NaOH
3	180	5.0	NaOH
4	260	5.0	NaOH
5	180	1.6	NaOH
6	220	5.0	NaOH
7	180	0.5	H_2O
8	260	0.5	H_2O
9	180	5.0	H_2O
10	260	5.0	H_2O
11	180	0.5	HCl
12	260	0.5	HCl
13	180	5.0	HCl
14	260	5.0	HCl
15	220	1.6	HCl

Table 3: The statistical significance of process variables for individual response models.

Model	Solid yield	C content, char	C yield, char	C yield, liquid	O/C – ratio, char	Energy densification	Energy yield	Energy efficiency
Unit	% (daf)	%, daf	%	%	-	-	%	%
Temperature p-value	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Retention time p-value	< 0.01	< 0.01	0.08	0.07	< 0.01	0.06	0.05	0.04
Additive p-value	> 0.10	< 0.01	< 0.01	> 0.10	< 0.01	> 0.10	0.06	0.07
Model R^2	0.96	0.97	0.96	0.94	0.94	0.87	0.86	0.88

Figures

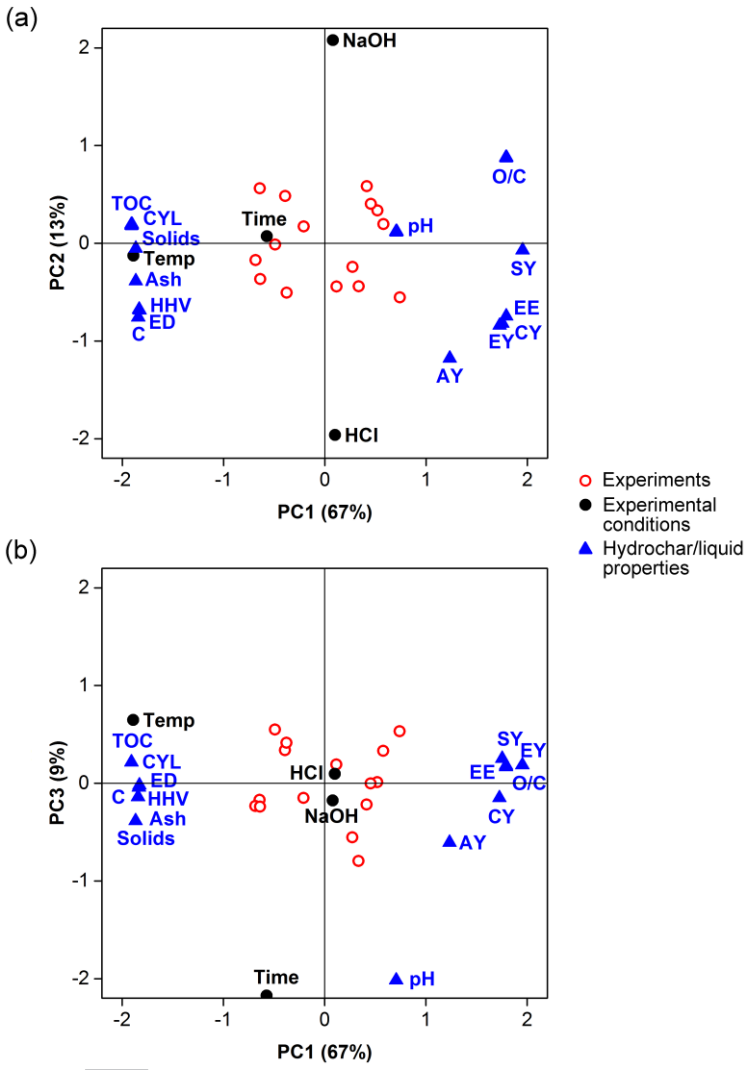
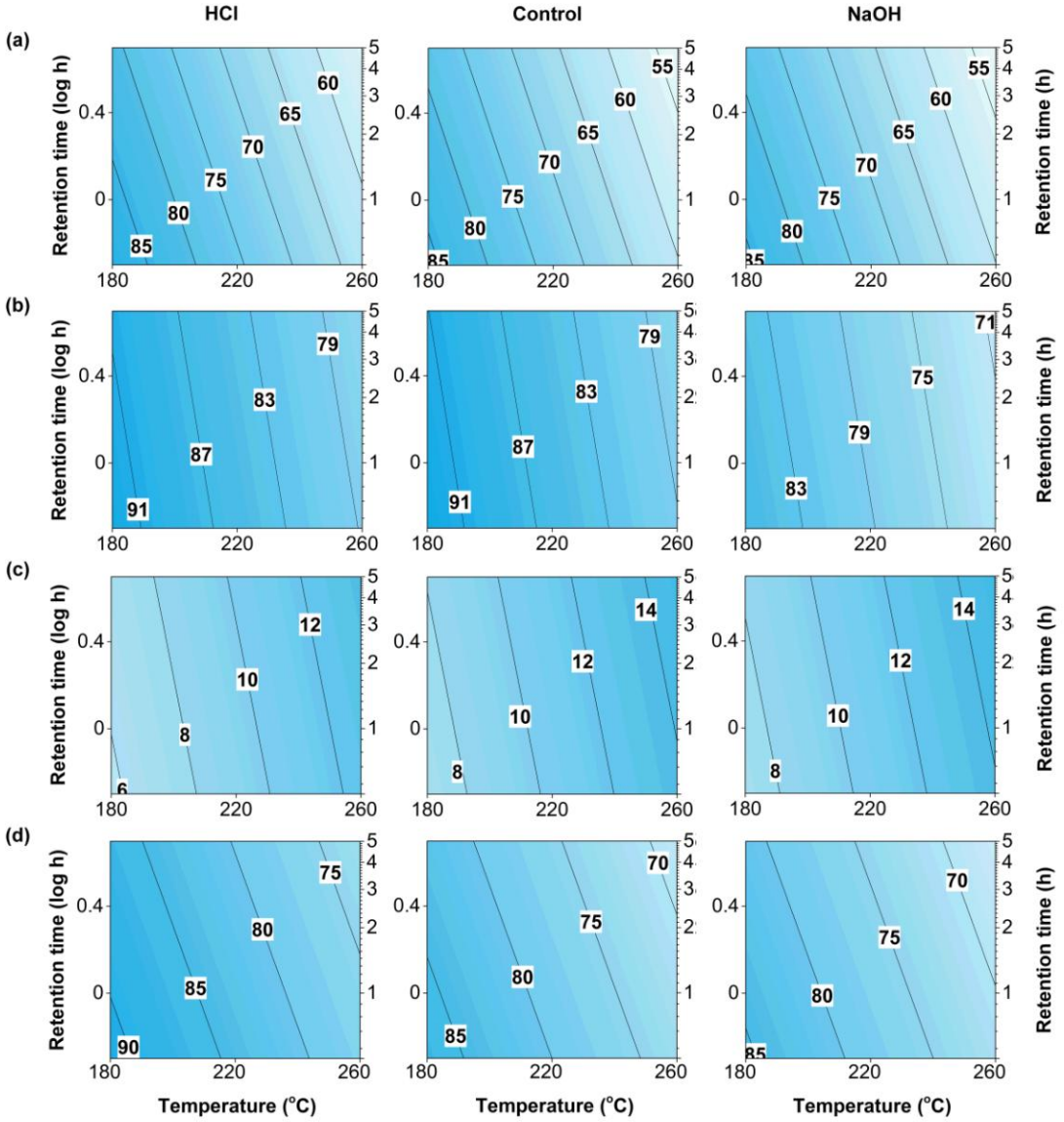


Fig. 1: Biplots of experimental scores and variable loadings on the (a) first and second and (b) first and third principal components (PCs). Solids: char solids content (%), Ash: ash content (%, db), SY: solid yield (%, daf), AY: ash yield (%, db), C: char carbon content (%, daf), CY: char carbon yield (%), O/C: char O/C –ratio, HHV: char heating value (MJ kg^{-1}, daf), ED: energy densification, EY: energy yield (%), EE: energy efficiency (%), pH: liquid pH, TOC: liquid TOC and CYL: liquid carbon yield (%).



457

458 Fig. 2: Response contours of (a) hydrochar solid yield (%, daf), (b) carbon yield (%), (c)

459 liquid carbon yield (%) and (d) hydrochar energy yield (%) as functions of reaction

460 temperature and retention time using HCl, H_2O (control) or NaOH as an additive.

Highlights

- Sludge carbonization governed by dehydration, depolymerization and decarboxylation
- Additive type significant for hydrochar carbon content and carbon and energy yield
- 97-147% of the theoretical energy requirement potentially attainable from hydrochar
- Dissolved organic components can be treated by conventional biological methods