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Combustion of solid biofuels from hydrothermal carbonization of food waste

Matteo Pecchi^{1,2,*}, Parvaneh Motiei³, James L. Adair², Jacqueline O'Connor³,
Jillian L. Goldfarb^{1,2}

¹ Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY USA

² Biological and Environmental Engineering, Cornell University, Ithaca, NY USA

³ Mechanical Engineering, Pennsylvania State University, University Park, PA USA

*Corresponding Author Email: mp933@cornell.edu

Abstract: Hydrothermal Carbonization (HTC) is a promising method to convert food waste into hydrochar (HC), a low-rank solid fuel with an amorphous secondary char (comprised of liquid biofuel precursor molecules) embedded in a carbon-condensed primary char (PC) that resembles a lignite coal. The two char phases can be separated via solvent extraction to facilitate energy recovery. Despite numerous fuel science studies on the topic reporting oxidative reactivity, little is known about the true combustion properties of primary char produced from HTC. Thermogravimetric analysis is paired with combustion measurements performed in a Hencken burner to assess the potential of food waste-derived hydrochar as a solid biofuel. While unextracted HC is likely unsuitable for direct combustion due to its tarry nature, the PCs exhibit coal-like combustion properties, highlighting the feasibility of HTC to produce solid biofuels from waste resources.

Keywords: Combustion; Secondary Char; Food Waste; Ignition Time

1. Introduction

In the US, food waste (FW) is the largest component of landfilled municipal solid waste and the third largest human methane emission source. Hydrothermal carbonization (HTC) represents a sustainable strategy to valorize this FW management [1]. HTC upconverts FW into biofuels [2,3] by heating the biomass in compressed water up to ~250°C. The primary product of HTC is hydrochar (HC), a low-rank coal-like material, suggested, across the literature, to be a renewable coal substitute [4]. Biomass hydrothermally carbonizes through a series of deoxygenation, dehydration, and decarboxylation reactions that intensify as the severity (time and temperature) of the carbonization process increases [5]. Increasing severity increases the gas yield and decreases the solid char yield [6]. HC forms via two pathways: (1) *solid-solid conversion*, in which the hydrochar maintains some structure and morphology of the parent biomass – this phase is referred to as primary char (PC), and (2) *aqueous phase degradation* of the biomass followed by partial polymerization of organic molecules back into the solid phase [7] – this phase is called secondary char (SC). SC is often identified as microspheres on the surface of the PC, comprising mainly of volatile and semi-volatile organic compounds [8]. HC’s “combustion” behavior is routinely investigated in the fuel science literature via thermogravimetric analysis (TGA) [4], which provides information about oxidation and not true combustion behavior given the TGA’s low (<100°C/min) heating rate. Such TGA studies suggest that potential problems could arise when combusting HC because of the SC’s high reactivity. These issues may be mitigated by SC

extraction as shown via TGA [2,3], from radiation heating studies of FW hydrochars [9], and from cone calorimetry studies of HC [10]. In this work, we convert a simulated retail-level FW into HC, which we then separate into PC and SC by means of solvent extraction with two different solvents: ethanol (ETH) and dichloromethane (DCM). Oxidation analysis via TGA of HCs and PCs is coupled with combustion studies using a Hencken Burner to assess the suitability of FW-based HCs and PCs as solid fuels.

2. Methods / Experimental

The FW mixture resembled a typical retail-level FW in the US. It was created by blending together selected ingredients as detailed in our prior work [2]. HCs were produced via HTC at 250 °C for 1 hour at a biomass to water ratio of 0.15; tests were repeated 5 times to produce sufficient material for extraction of SC [2]. For SC extraction, 15 g of HC were placed in 0.5 dm³ of solvent (ACS grade ethanol, ETH, or dichloromethane, DCM) and shaken for 3 hours. Then the PC was separated from the solvent using vacuum filtration using an additional 0.5 dm³ of solvent to rinse the PC. The HC and PC yields were obtained as the dry mass of HC or PC and divided by the dry feedstock mass. For the liquid yield, the initial water and the feedstock moisture were subtracted from the final mass of liquid and divided by the dry feedstock mass. The gas yield was calculated using measured pressure and reactor headspace volume and applying the ideal gas law, considering it to be 100 % CO₂ [2,3]. Proximate analysis and slow-oxidation kinetic analysis of HC and PC using TGA followed our prior works [11]. Oxidation curves at different heating rates were used to compute apparent activation energy values using the KAS isoconversional method [12], which relies on DTG curves (derivative of mass loss) to compute the extent of reaction and the apparent activation energy. HHV was assessed using a Parr 6200 Isoperibol Calorimeter [2].

HC and PC samples were dry sieved to yield particles of 25-37 μm in diameter, and then burned in a Hencken burner, equipped with a fluidized bed and a flow measurement system. Combustion diagnostics utilized CH* chemiluminescence imaging and high-speed particle image velocimetry (PIV) to measure particle ignition and burnout times. Data analysis involved time-averaged intensity and velocity profiles, while uncertainty was quantified through a multivariate approach considering variations in particle ignition and burnout locations and velocities [11].

3. Results and Discussion

FW contains ~30 % lipids and ~60 % carbohydrates, which explain the relatively high HHV (for a waste) and volatile matter fraction [2] (Table 1). Compared to the raw FW, HC shows increased HHV and reduced ash fraction (35.9 vs 25.0 MJ/kg and 0.8 vs 1.3 %), which are both desirable properties for a solid fuel; volatile matter (and fixed carbon) only decreases (increases) by ~5 % in HC compared to FW (Table 1). However, the DTG curves in air for HC (Figure 1a) see major devolatilization around 500 K, a potential source of inefficiencies in real combustion scenarios [2].

HC solvent extraction with ETH or DCM produces 30 % PC and 70 % SC on a HC basis. While most of our results align with our previous findings [2,3], our prior work found SC yield on a HC basis (not feedstock) of 80 and 50 % for ETH and DCM, respectively [2]. The use of vacuum filtration instead of simple gravity filtration, the intrinsic variability of the feedstock, and the larger batches that minimize the importance of small losses can explain the difference. Compared to HC, PCs show significantly lower HHV (-20 %) and 4-fold more ash, but an increased fixed carbon fraction (Table 1) that matches that of bituminous coals [13]. DTG curves for PCs (Figure 1b, c)

lose the peak at 500 K, behaving like a bituminous coal, with maximum mass loss around 800 K [13,14]. ETH and DCM show comparable behaviors.

Table 1: Feedstock, HC, PC, and SC properties and yields. Yields are on a feedstock basis. HHV, VM, FC, and Ash are on dry basis.

	Yield [wt%]	HHV [MJ/kg]	Volatile Matter [wt%]	Fixed Carbon [wt%]	Ash [wt%]
FW	n.a.	25.0 ± 0.7	86.8 ± 0.2	12 ± 0.2	1.3 ± 0
HC	54.9 ± 0.5	35.9 ± 0.1	81.2 ± 1.3	18 ± 1.3	0.8 ± 0.1
liquid	41.4 ± 0.5	n.a.	n.a.	n.a.	n.a.
gas	3.6 ± 0.2	n.a.	n.a.	n.a.	n.a.
PC-ETH	16.8 ± 0.5	29.2 ± 0.5	46.7 ± 0.4	50.6 ± 0.2	2.7 ± 0.3
PC-DCM	17.6 ± 0.3	29.5 ± 0.2	48.4 ± 0.3	49.1 ± 0.2	2.4 ± 0.1
SC-ETH	38.2 ± 0.5	38.8 ± 0.3	n.a.	n.a.	n.a.
SC-DCM	37.3 ± 0.3	38.9 ± 0.2	n.a.	n.a.	n.a.

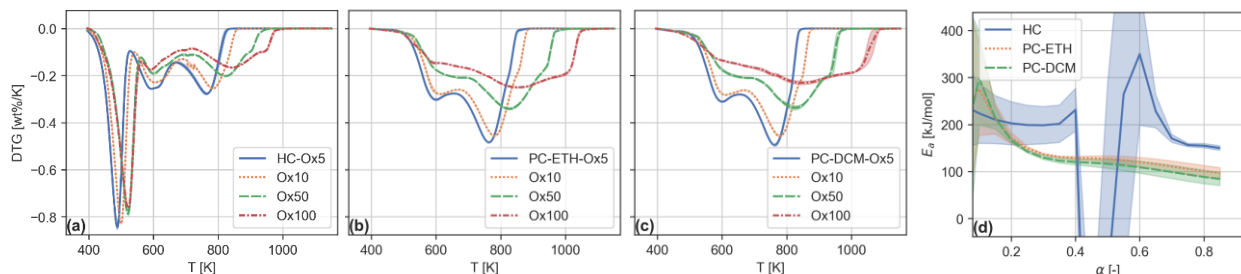


Figure 1. DTG curves under oxidative atmosphere at different heating rates for (a) HC, (b) PC-ETH, (c) PC-DCM. (d) apparent activation energy vs extent of reaction α obtained using the KAS method for HC and PCs.

SC is mostly comprised of long chain fatty acids, valuable liquid fuel precursors; We estimated $> 50\%$ of the energy in the FW can be recovered in the SC [2,3]. Demonstrating the suitability of HC or PC as a solid fuel is more complicated. In the biofuel literature, conclusions upon the suitability, of lack thereof, of solid materials as solid fuels come from the oxidation DTG curves, which can be used to compute the apparent activation energy of the oxidation process (Figure 1d). In the present work, while HC shows unpredictable behavior due to the presence of the SC peak at low temperature (Figure 1a), PCs both show apparent activation energy values between 100 and 200 kJ/mol that are comparable to results obtained with coals [15] and from HCs with lower SC content obtained from different feedstocks (based on the lack of a devolatilization peak at ~ 500 K in the HC's DTG curves) [12].

Since TGA operates at much lower heating rates than standard combustion apparatuses [11], we coupled oxidation studies using TGA with combustion experiments in a Hencken burner to investigate conditions that are more relevant to real combustion scenarios [11]. CH* intensity profiles of burning PC particles and corresponding ignition times are shown in Figure 3. We could not achieve HC fluidization due to its tarry and sticky nature, and so HC is missing from Figure 3. At these conditions, ETH and DCM do not produce appreciable differences. PCs results are very close to those obtained using PC produced from cellulose at 250°C and extracted using ETH (data not shown); HTC at 250°C followed by solvent extraction tends to produce PCs—regardless of the

material– with comparable ignition times and similar CH*emission profiles. This similarity suggests that, while HC suitability for combustion depends strongly on the feedstock composition, for PC, the production temperature plays the main role.

Generally, ignition location and resultant ignition delay time are inversely proportional to surrounding gas temperature and O₂ concentration. Here, ignition locations are shortened by increasing the ambient temperature and oxygen concentration resulting in a faster ignition for higher temperature and O₂ environments.

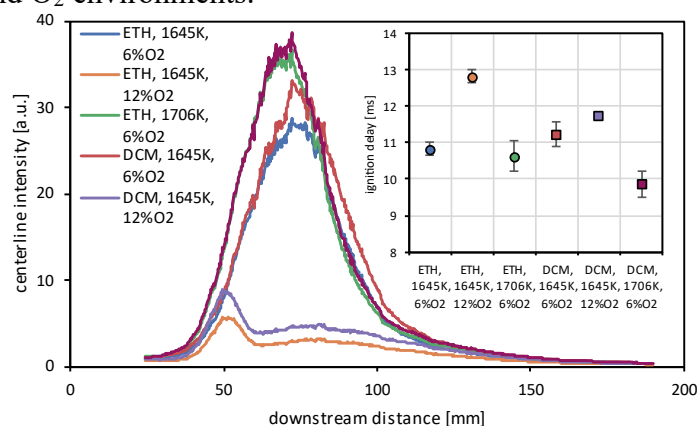


Figure 2. centerline CH* chemiluminescence intensity profiles versus downstream distance. Resulting ignition time (inset plot) for PC-ETH and PC-DCM at different flame temperatures and O₂ mole fraction%.

4. Conclusions

FW was converted into HC using HTC; HC was separated into PC and SC using solvent extraction using ETH and DCM. While HC is likely unsuitable for combustion, PC and SC show more promising characteristics, regardless of the solvent used. SC is an oily phase rich in long chain fatty acids that can contain more than 50 % of the original feedstock energy and represents a liquid fuel precursor. PC is a solid carbonaceous material that shows promise as a solid fuel. Thermogravimetry and CH* chemiluminescence analysis of PC obtained from FW show combustion properties that are similar to those of bituminous coal.

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6. References

- [1] N. Kassem, M. Pecchi, A.R. Maag, M. Baratieri, J.W. Tester, J.L. Goldfarb, Developing Decision-Making Tools for Food Waste Management via Spatially Explicit Integration of Experimental Hydrothermal Carbonization Data and Computational Models Using New York as a Case Study, *ACS Sustainable Chem. Eng.* 10 (2022) 16578–16587. <https://doi.org/10.1021/acssuschemeng.2c04188>.
- [2] M. Pecchi, M. Baratieri, J.L. Goldfarb, A.R. Maag, Effect of solvent and feedstock selection on primary and secondary chars produced via hydrothermal carbonization of food wastes,

- Bioresource Technology 348 (2022) 126799. <https://doi.org/10.1016/j.biortech.2022.126799>.
- [3] M. Pecchi, M. Baratieri, A.R. Maag, J.L. Goldfarb, Uncovering the transition between hydrothermal carbonization and liquefaction via secondary char extraction: A case study using food waste, *Waste Management* 168 (2023) 281–289. <https://doi.org/10.1016/j.wasman.2023.06.009>.
- [4] Y. Li, H. Liu, K. Xiao, M. Jin, H. Xiao, H. Yao, Combustion and Pyrolysis Characteristics of Hydrochar Prepared by Hydrothermal Carbonization of Typical Food Waste: Influence of Carbohydrates, Proteins, and Lipids, *Energy Fuels* 34 (2020) 430–439. <https://doi.org/10.1021/acs.energyfuels.9b02940>.
- [5] M. Mäkelä, V. Benavente, A. Fullana, Hydrothermal carbonization of lignocellulosic biomass: Effect of process conditions on hydrochar properties, *Applied Energy* 155 (2015) 576–584. <https://doi.org/10.1016/j.apenergy.2015.06.022>.
- [6] M. Volpe, J.L. Goldfarb, L. Fiori, Hydrothermal carbonization of *Opuntia ficus-indica* cladodes: Role of process parameters on hydrochar properties, *Bioresource Technology* 247 (2018) 310–318. <https://doi.org/10.1016/j.biortech.2017.09.072>.
- [7] A. Kruse, F. Koch, K. Stelzl, D. Wüst, M. Zeller, Fate of Nitrogen during Hydrothermal Carbonization, *Energy and Fuels* 30 (2016) 8037–8042. <https://doi.org/10.1021/acs.energyfuels.6b01312>.
- [8] A. Kruse, A. Funke, M.M. Titirici, Hydrothermal conversion of biomass to fuels and energetic materials, *Current Opinion in Chemical Biology* 17 (2013) 515–521. <https://doi.org/10.1016/j.cbpa.2013.05.004>.
- [9] D. Nguyen, W. Zhao, M. Mäkelä, Z.T. Alwahabi, C.W. Kwong, Effect of hydrothermal carbonisation temperature on the ignition properties of grape marc hydrochar fuels, *Fuel* 313 (2022) 122668. <https://doi.org/10.1016/j.fuel.2021.122668>.
- [10] M. Tahmid Islam, J.L. Klinger, M. Toufiq Reza, Evaluating combustion characteristics and combustion kinetics of corn stover-derived hydrochars by cone calorimeter, *Chemical Engineering Journal* 452 (2023) 139419. <https://doi.org/10.1016/j.cej.2022.139419>.
- [11] P. Motiei, M. Pecchi, J.L. Adair, J.L. Goldfarb, J. O’Connor, Pairing combustion experiments and thermogravimetric analysis to uncover timescales controlling cellulose ignition and burnout in a Hencken burner, *Combustion and Flame* 258 (2023) 113092. <https://doi.org/10.1016/j.combustflame.2023.113092>.
- [12] V. Benedetti, M. Pecchi, M. Baratieri, Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, *Bioresource Technology* 353 (2022) 127142. <https://doi.org/10.1016/j.biortech.2022.127142>.
- [13] A. Coppola, R. Solimene, P. Bareschino, P. Salatino, Mathematical modeling of a two-stage fuel reactor for chemical looping combustion with oxygen uncoupling of solid fuels, *Applied Energy* 157 (2015) 449–461. <https://doi.org/10.1016/j.apenergy.2015.04.052>.
- [14] K. Baek, C.-S. Kim, H.-H. Lee, H.-J. Shin, J.-W. Yang, Microbial desulfurization of solubilized coal, *Biotechnology Letters* 24 (2002) 401–405. <https://doi.org/10.1023/A:1014546104553>.
- [15] L. Tang, J. Xiao, Q. Mao, Z. Zhang, Z. Yao, X. Zhu, S. Ye, Q. Zhong, Thermogravimetric Analysis of the Combustion Characteristics and Combustion Kinetics of Coals Subjected to Different Chemical Demineralization Processes, *ACS Omega* 7 (2022) 13998–14008. <https://doi.org/10.1021/acsomega.2c00522>.