



Full Length Article

Impact of hydrothermal carbonization conditions on the formation of hydrochars and secondary chars from the organic fraction of municipal solid waste

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ABSTRACT

Hydrothermal carbonization of the organic fraction of municipal solid waste (OFMSW) could mitigate landfill issues while providing a sustainable solid fuel source. This paper demonstrates the impact of processing conditions on the formation and composition of hydrochars and secondary char of OFMSW. Harsher conditions (higher temperatures, longer residence times) decrease generally the solid yield while increasing the higher heating value (HHV), fixed carbon, and elemental carbon. Energy yields upwards of 80% can be obtained at both intermediate and high temperatures (220 and 260–280 °C), but the thermal stability and reactivity of the intermediate hydrochars suggest the formation of a reactive secondary char that condenses on the surface of the primary hydrochar. This secondary char is extractable with organic solvents and is comprised predominantly of organic acids, furfurals and phenols, which peak at 220 and 240 °C and decrease at higher carbonization conditions. The HHVs of secondary char are significantly higher than those of primary char.

1. Introduction

Global production of municipal solid waste is approximately 1300 million tons per year [1]; by 2025 annual production will reach 2200 million tons [2]. In Italy, municipal solid waste production is about 29 million tons annually [3]. A considerable amount of the organic fraction (OF), which accounts for 30–40% [4] of the total waste, is incinerated or landfilled, low-cost but polluting processes [1]. The remainder undergoes biological treatments such as composting or anaerobic digestion, which are considered more environmentally friendly technologies, but are often not economically viable because of long holding times (20–30 days). In addition, composting has a high energy consumption and CO₂ footprint, with a relatively low product sale price [5]. Anaerobic digestion suffers from complexity of reactor start-up, toxic and inhibiting compounds in the OF, and process instability due to feedstock heterogeneity [1].

To address these issues, technologies such as hydrothermal carbonization (HTC) are attracting considerable attention to treat the organic

fraction of municipal solid waste (OFMSW). During HTC, wet biomass is reacted in subcritical water up to 300 °C [6], over a few minutes to several hours [7]. HTC converts organic wastes into a carbon-rich solid fuel known as hydrochar, with a high energy density and heating value, high carbon content, homogeneity and grindability [8,9]. One of the main advantages of HTC is that the heterogeneous wet biomass can be processed without preliminary pre-treatment such as the separating and drying required for pyrolysis and other thermochemical techniques [10]. For these reasons, HTC is applied to various wet residues, including: grape marc [11], off-specification compost [12], olive wastes [7], food wastes [13], digestate [14], sewage sludge [15–17] and banana stalk [18]. Our group recently demonstrated the feasibility of this technology for large-scale development through a comprehensive economic and process analysis [19]. However, despite its potential, there is no systematic study on the HTC of wet, as-received OFMSW that investigates the influence of process variables on resulting hydrochar formation. Reza et al. [6] carried out HTC tests on OFMSW pulp mixed with paper, pre-treated by steam autoclaving sterilization. Berge et al.

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[20] demonstrated the feasibility of HTC for mixed MSW, including paper, food, plastics, glass and metals. Lin et al. [21] tested hydrochar from MSW as solid fuel. Ingelia S.L. [22], a small enterprise commercializing HTC plants, lists data related to the energy properties and composition of hydrochar from OFMSW acquired at one operating condition.

Hydrochar forms via two pathways: (1) *solid-solid conversion*, in which the hydrochar maintains the original structural elements and morphology of the parent biomass; (2) *aqueous phase degradation* of biomass followed by polymerization of organic molecules into a solid phase [7,23,24]. Throughout the literature “primary char” or “char” is often used to describe the hydrochar formed following pathway (1) and “secondary char” or “coke” to refer to the amorphous solid formed following pathway (2)¹. This secondary char is thought to result from sequential hydrolysis, dehydration, and isomerization during HTC that produces furfurals, as well as from cleavage reactions yielding intermediate organic acids. These dissolved intermediates can lead to precipitation of the furfurals as a secondary organic phase, which polymerize as microspheres [10,24–28]. The spheres can be further carbonized by dehydration reactions, resulting in an amorphous solid that is soluble in organic solvents such as acetone and methanol [29].

It is thought that secondary char formation is promoted at high carbonization temperatures, solid loadings, and residence times. It is characterized by spherical-like structures that deposit on the carbonaceous primary char. The high carbon content and high heating value of secondary char is of interest for its potential use as a biofuel [7,29]. As reported by Sevilla et al. [30] and Funke et al. [14], the morphology and structure make secondary char suitable for advanced carbonaceous material applications, including lithium ion batteries [31]. To date, most studies focus on the application of secondary char obtained from model compounds such as glucose and fructose. However, no one has yet systematically investigated how HTC reaction conditions affect the formation and characteristics of primary versus secondary char obtained from HTC of a heterogeneous organic residual feedstock. The present paper addresses the gaps identified in the literature by studying the influence of temperature, time and solid load on the mass yields and energy properties of the hydrochar produced. It probes the nature of primary versus secondary char formation resulting from the HTC of OFMSW in terms of composition, heating value and thermal stability. The results of this work suggest the potential for using secondary char as a source of biorefinery platform chemicals (phenols, furfurals, organic acids).

2. Materials and methods

2.1. Feedstock

Approximately 30 kg of OFMSW was provided by AMNU, a municipal waste management company in Trento, Italy in November 2016. After elimination of some residual packaging and inert material, the biomass was shredded and homogenized using a knife mill. The average moisture content, evaluated by drying overnight in a ventilated oven at 105 °C, was 78% ± 0.4 wt%. To preserve the biomass, milled samples of ~16 g each were stored individually in sealed plastic bags in a freezer at -34 °C. OFMSW samples were thawed to room temperature prior to carbonization.

The modified van Soest method was used to determine the extractives, holocellulosic and lignin fractions in the feedstock. Samples were dried at 105 °C, and milled and sieved to > 300 µm. The composition was determined using neutral detergent fiber (NDF) to remove extractives, acid detergent fiber (ADF) to extract hemicellulose, and

¹ As coke is often used to refer to the formation of non-desorbed products on a secondary substrate (i.e. catalyst surface), in this paper we refer to the products of pathway (2), which condense on the original carbonaceous substrate, as “secondary char” [58].

acid detergent lignin (ADL) for cellulose removal. Klason lignin [32] content was taken as the remaining fraction. This analysis was repeated thrice and the average composition is reported.

2.2. Hydrothermal carbonization

The hydrothermal reactions were carried out in a 50 mL stainless steel (AISI 316) batch reactor as described previously [12,33]. A series of experiments were run with reaction time ranging from 0 to 6 h, temperatures between 120 and 280 °C, and dry biomass to water ratios (B/W) from 0.05 to 0.25. B/W is the ratio between the dry feedstock and the total water (moisture + additional deionized water). For each experiment, the reactor was loaded with 8 to 16 g ± 0.01 g of wet (as-received) OFMSW and 1 to 28 g ± 0.01 g of deionized water. The choice to use the wet feedstock without any pre-drying may modestly affect the control of B/W, however, this is in agreement with an industrial-scale approach. The amount of feedstock and water at each condition was chosen in order to completely cover the biomass with water and to leave comparable free volumes (about 40%) in the system during the different runs.

Prior to commencing the carbonization, the reactor was purged by flushing with N₂ gas. The system was then heated to the desired reaction temperature, and the HTC residence time started when the system reached the set temperature. After the set reaction time, the reactor was quenched by positioning a stainless steel disc at -34 °C at the bottom of the reactor and blowing compressed air into the outer reactor walls. When the system reached ambient temperature, the volume of gas produced was measured by flowing it into a graduated cylinder [12]. The gas yield was calculated assuming that the gas produced is entirely CO₂; literature shows that CO₂ is always greater than 90 vol% [11,12]. The condensed phases were filtered using 45 µm cellulose filters. The pH of both the aqueous biomass mixture before carbonization and the liquid after HTC were measured using a Profi-Line pH 3310 portable pH-meter. The hydrochar was dried in a ventilated oven at 105 °C for at least 8 h. Hydrochar yield was calculated as the mass ratio between hydrochar and raw biomass (dry basis). Gas yield is the mass of gas produced per unit of dry raw biomass; liquid yield was determined by difference. Seventeen individual runs were performed at least twice to insure reproducibility. Hydrochars were named as T_tB/W, where T denotes temperature in °C, t the residence time in hours, and B/W the dry biomass to water ratio, respectively.

2.3. Hydrochar characterization

Elemental compositions of the raw OFMSW and hydrochars were determined using a LECO 628 analyzer equipped with sulphur module for CHN (ASTM D-5373 standard method) and S (ASTM D-1552 standard method) determination. The oxygen content was determined by difference. Two runs were performed for each sample, and the average values are presented. Proximate analyses were carried out on a LECO Thermogravimetric Analyser TGA 701 using a modified ASTM D-3175-89 standard method: samples were dried at 20 °C/min to 105 °C in air and held until constant weight (< ± 0.05%), heated at 16 °C/min from 105 °C to 900 °C in nitrogen with a hold time of 7 min (loss attributed to volatile matter, VM). Finally, the sample was held at 800 °C in air (mass loss due to fixed carbon, FC), with the remaining matter attributed to ash content. Higher heating values (HHV) of the raw OFMSW and hydrochars were evaluated according to the CEN/TS 14918 standard by means of a LECO AC500 calorimeter. The energy yield, EY, was calculated as:

$$EY = SY * HHV_{HCdb} / HHV_{Rdb} \quad (1)$$

where SY is the solid yield (i.e. the hydrochar yield), which is multiplied by the ratio of the HHVs of the hydrochar (HC) to raw (R) sample (both on a dry basis, db).

The thermal stability and reactivity of a subset of hydrochars were

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