Contents lists available at ScienceDirect





Bioresource Technology

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

# Hydrothermal carbonization of *Opuntia ficus-indica* cladodes: Role of process parameters on hydrochar properties



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## ARTICLE INFO

Keywords: Hydrothermal carbonization HTC Solid biofuel Opuntia ficus-indica Hydrochar

# ABSTRACT

*Opuntia ficus-indica* cladodes are a potential source of solid biofuel from marginal, dry land. Experiments assessed the effects of temperature (180–250 °C), reaction time (0.5–3 h) and biomass to water ratio (B/W; 0.07–0.30) on chars produced via hydrothermal carbonization. Multivariate linear regression demonstrated that the three process parameters are critically important to hydrochar solid yield, while B/W drives energy yield. Heating value increased together with temperature and reaction time and was maximized at intermediate B/W (0.14–0.20). Microscopy shows evidence of secondary char formed at higher temperatures and B/W ratios. X-ray diffraction, thermogravimetric data, microscopy and inductively coupled plasma mass spectrometry suggest that calcium oxalate in the raw biomass remains in the hydrochar; at higher temperatures, the mineral decomposes into  $CO_2$  and may catalyze char/tar decomposition.

# 1. Introduction

Environmental issues surrounding fossil fuels have spurred interest in identifying renewable, carbon-neutral fuel replacements. Lignocellulosic biomass, in particular agricultural and agro-industrial wastes, are potential feedstocks for the production of chemicals and fuels, as their use reduces greenhouse gas emissions without competing with land for food crops (Corneli et al., 2016; Volpe et al., 2014). *Opuntia ficus-indica*, a drought-tolerant plat of the cactacee family, was recently suggested by Yang et al. (2015) as a potential feedstock for biofuel production in semi-arid abandoned marginal lands. *Opuntia ficus-indica* is native to Mexico and was naturalized throughout the Mediterranean basin and in the temperate zones of America, Africa, Asia and Oceania. *Opuntia* species are harvested worldwide for the production of fodder and forage and, over the last decades, for their succulent fruits (prickly pears) and young cladodes for human consumption.

At present, depending on the cultivation procedure (rain-fed or well-irrigated) dry matter productivity of *Opuntia* species ranges between 15 and 50 t ha<sup>-1</sup> year<sup>-1</sup> (Yang et al., 2015). In Italy, the average annual production of prickly pears amounts to about 85,000 tons, 90% of which is produced in Sicily, with 4000 ha of cultivated land (ISTAT, 2016). In Sicily alone, between 60,000 and 200,000 t year<sup>-1</sup> of dry

matter related to *Opuntia* could be available for transformation into biofuels from a relatively limited geographic area. Furthermore, the agro-industrial production of *Opuntia* is expected to increase due to the recent discovery that consumption of prickly pears is potentially linked to reductions in percentage body fat, blood pressure, and total cholesterol (Onakpoya et al., 2015). Thus, the cultivation of *Opuntia* species in semi-arid marginal lands could lead to the simultaneous production of food for human consumption, food supplements, and residual biomass for biofuels.

Santos et al. (2016) recently investigated the chemical composition and use of *Opuntia ficus-indica* cladodes (OC) as a feedstock for the production of bio-ethanol and bio-methane. However, the use of OC for biofuel production must account for its compositional characteristics, especially the high ash and moisture content. *Opuntia* structural ashes range between 8% (Santos et al., 2016) and 23% (Yang et al., 2015) by mass on a dry basis. The high water content (85–94 wt%), low lignin content (8–12 wt%, dry basis) and high fraction of amorphous cellulose (> 80 wt%, dry basis), suggest that OC can be easily decomposed by thermochemical aqueous phase processes with a reduced exogenous water input (as compared to other terrestrial biomasses) (Yang et al., 2015).

During biomass combustion and gasification, a high alkali metals, alkaline earth metals, and silicon content contributes to slagging and

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http://dx.doi.org/10.1016/j.biortech.2017.09.072

Received 30 June 2017; Received in revised form 8 September 2017; Accepted 9 September 2017 Available online 11 September 2017 0960-8524/ © 2017 Elsevier Ltd. All rights reserved.

#### Table 1

Process parameters and resulting properties of solid residues. Compositional analyses performed in duplicate; average values shown ( $Er\% \le 3.3\%$  for proximate and 1.0% for ultimate analyses); HHVs average of three measurements,  $Er\% \le 1.0$ ).

Sample description				Proximate analysis			Elemental analysis				Energy properties	
Sample	T (°C)	Time (h)	B/W	VM	FC	Ash	С	Н	Ν	0*	HHV (MJ kg <sup>-1</sup> )	EY
Raw				70.62	14.23	15.15	39.68	4.70	0.48	39.98	13.87	1
180_0.5_20	180	0.5	0.20	71.36	16.22	12.42	44.82	4.91	0.75	37.11	16.80	0.80
180_1_20	180	1.0	0.20	68.96	16.92	14.12	49.38	4.71	0.72	31.07	17.31	0.81
180_3_20	180	3.0	0.20	67.00	18.39	14.61	50.23	4.63	0.77	27.74	17.93	0.83
220_0.5_20	220	0.5	0.20	67.14	19.69	13.17	46.20	4.59	0.80	35.24	18.82	0.84
220_1_20	220	1.0	0.20	64.57	20.26	15.17	51.29	4.72	0.84	27.98	18.93	0.81
220_3_20	220	3.0	0.20	64.23	20.81	14.96	50.32	4.90	0.77	29.05	19.48	0.83
250_0.5_20	250	0.5	0.20	63.89	22.07	14.04	47.47	4.61	0.77	33.11	20.34	0.78
250_1_20	250	1.0	0.20	60.83	24.98	14.19	52.86	4.81	0.89	27.25	21.03	0.80
250_3_20	250	3.0	0.20	56.88	28.17	14.95	50.48	4.83	0.81	28.94	22.39	0.83
250_0.5_30	250	0.5	0.30	64.04	19.53	16.43	49.02	4.62	0.87	28.29	20.12	0.92
250_1_30	250	1.0	0.30	61.86	21.73	16.41	52.53	4.65	1.03	23.99	20.90	0.92
250_3_30	250	3.0	0.30	63.20	21.53	15.27	50.91	4.70	0.97	26.23	21.07	0.92
250_0.5_14	250	0.5	0.14	65.77	19.91	14.32	50.52	4.83	0.78	29.55	20.76	0.79
250_1_14	250	1.0	0.14	65.94	19.92	14.13	51.08	4.88	0.84	29.07	20.96	0.72
250_3_14	250	3.0	0.14	63.32	22.85	13.84	53.08	4.77	0.95	27.35	22.31	0.73
250_0.5_7	250	0.5	0.07	66.33	20.63	13.04	49.64	4.88	0.75	31.69	19.17	0.64
250_1_7	250	1.0	0.07	65.21	20.66	14.13	53.95	4.74	0.91	26.28	19.53	0.63
250_3_7	250	3.0	0.07	60.61	24.69	14.69	52.77	4.69	1.03	26.81	20.82	0.63
-	(VM = volatile matter, FC = fixed carbon, Ash = ashes; all dry basis), *calculated by difference											

fouling of heat transfer surfaces, decreasing overall thermal efficiency (Reza et al., 2013). However, wet thermochemical treatments are receiving considerable attention for the upgrading of moist biomasses to solid biofuels with reduced inorganic content. For example, hydrothermal carbonization (HTC) was shown to upgrade: pulp mill waste (Mäkelä et al., 2015; Wikberg et al., 2016), wine industry waste (Pala et al., 2014; Basso et al., 2016), olive mill industry residual biomasses (Álvarez-Murillo et al., 2015; Volpe et al. 2016; Volpe and Fiori, 2017), tobacco stalks (Cai et al., 2016), citrus wastes (Erdogan et al., 2015) and wheat straw (Reza et al., 2015b) into solid biofuels with increased energy content. Upgrading via HTC is particularly suited to biomasses with residues high in inorganic elements, i.e. to residues with a high ash mass fraction. HTC, unlike dry thermochemical processes, can reduce the ash content of biomass and produce a solid hydrochar with coal-like properties that can be substituted in combustion systems (Kambo and Dutta, 2015; Reza et al., 2015a; Mäkelä et al., 2016; Mäkelä and Yoshikawa, 2016; Smith et al., 2016; Yang et al. 2016).

Given the need to develop renewable fuels and to valorize marginal land, and the high moisture and ash content of *Opuntia ficus-indica*, application of HTC technology to OC may represent a sustainable bioenergy generation pathway. This investigation analyzes the effects of HTC process variables (temperature, residence time and solid load) on the energy, thermal and chemical properties of the solid bio-fuel produced, including secondary char and mineral content. While the literature is replete with examples of the influence of temperature and residence time on hydrochar yield for a variety of biomasses, few studies probe the effect of solid loading on yield (Álvarez-Murillo et al., 2015; Mäkelä et al., 2015; Sabio et al., 2016; Volpe and Fiori, 2017), a potentially important parameter to address the economical evaluation of the technology at industrial scale (Lucian and Fiori, 2017).

#### 2. Material and methods

#### 2.1. Materials and sample preparation

5 kg of *Opuntia ficus-indica* cladodes (OC) were collected from 2 to 3year old plants in the Palermo province of Sicily (Italy). The moisture content (as received) was 93 wt%. The collected cladodes were cut into 10 mm squares and dried in a ventilated oven at 105 °C for 48 h. This pre-treatment was carried out to prevent degradation and to begin with a dry baseline. The samples were ground and sieved to a particle size between 300 and 850  $\mu$ m. All samples were oven dried overnight at 105 °C before HTC tests, and the water added immediately before each HTC run to the desired dry biomass to water ratio (B/W).

# 2.2. Hydrothermal carbonization of OC

Samples were carbonized in a 50-mL stainless steel (AISI 316) batch reactor, designed and constructed in-house (Fiori et al., 2014; Basso et al., 2015). For each experiment, the reactor was charged with 2.4 to  $6.0 \pm 0.001$  g of dried sample and 20 to  $34 \pm 0.01$  g of deionized water to obtain the desired B/W. The amount of biomass and water was chosen in order to fully submerge the feedstock and leave comparable free volumes in the system. After sealing, air was purged from the reactor by flushing with nitrogen (Airliquide Alphagaz 1<sup>TM</sup>) three times. Nitrogen pressure was lowered to ambient, the valves upstream and downstream of the reactor were closed, the reactor was heated to the desired temperature, and held at this value for a desired residence time. The heating step lasted for 15–20 min, depending on the set point, resulting in a heating rate of approximately 10 °C/min. The pressure reached in the various HTC runs ranged from 13.5 to 60.2 bar and depended predominantly on the set point temperature.

Following this hold time, the reactor was rapidly quenched by placing it on a cold stainless steel disk at -24 °C, while compressed air was blown into the reactor walls (quenching time less than 15 min). As the reactor reached room temperature, the valve at the reactor outlet was opened to let the produced gases flow into a graduated cylinder filled with water. Gas mass yield was calculated from the gas volume by considering CO<sub>2</sub> as the sole gaseous product. While gas composition varies, the typical CO<sub>2</sub> molar fraction in dry HTC gas is between 0.95 and 0.99, with minor amounts of CO and traces of H<sub>2</sub> and CH<sub>4</sub> (Hitzl et al., 2015; Basso et al., 2016). The solid residue was recovered by filtration and dried in a ventilated oven at 105 °C to constant weight.

Reaction temperature was set to either 180, 220 or 250 °C, for dry biomass to water ratios equal to 0.20, and then kept constant at 250 °C for experiments with varying B/W of 0.07, 0.14 and 0.30. Residence time was either 0.5, 1 or 3 h, performed at each temperature and solid load. 18 different hydrochars were produced (Table 1), each of which was made in at least duplicate. Hydrochar yield (MY) was calculated as  $MY = M_{HCdb}/M_{Rdb}$ , where  $M_{HCdb}$  is the mass (dry basis) of the solid after thermal treatment (*i.e.*, hydrochar), and  $M_{Rdb}$  is the mass (dry basis) of the raw sample. Similarly, gas yield was defined as the mass of gas



Fig. 1. HTC mass balance. Mass yield of solid, gas and liquid (by difference); (a) at different temperatures and reaction times (B/W = 0.20); (b) at different biomass loads and reaction times (T = 250 °C). Black closed indicators: 0.5 h; grey closed indicators: 1 h; open indicators: 3 h. Straight lines represent the linear fitting of the data and help in reading the graph.

produced per unit mass of dry raw biomass sample. Liquid yield was calculated by difference.

calcined in a tube furnace at 900  $^{\circ}$ C for 3 h, then the ash was digested in concentrated nitric acid (Fisher Scientific USA) and diluted to 2% nitric acid using Milli-Q water prior to analysis in triplicate.

## 2.3. Hydrochar characterization

Ultimate analyses were performed using a LECO 628 analyser equipped with Sulphur module for CHN (ASTM D-5373 standard method) and S (ASTM D-1552 standard method). Proximate analyses were carried out by a LECO Thermogravimetric Analyser TGA 701 employing ASTM D-3175-89 standard method: 20 °C/min ramp to 105 °C in air, held until constant weight ( $< \pm 0.05\%$ ) (moisture content); 16 °C/min ramp from 105 °C to 900 °C, hold time 7 min in N<sub>2</sub> (loss due to VM); isothermal hold at 800 °C in air (loss attributed to FC). Inorganic matter ("ash") comprised the residual. The parameter "hydrochar volatility" (V<sub>HC</sub>) was here defined as  $V_{HC} = VM/(1-ash)$  to express the quantity of "volatilizable" matter as a function of total "oxidizable" matter (comprising majority C, plus also H, N, and O).

The higher heating value (HHV) of the solid samples was evaluated according to the CEN/TS 14918 standard using an IKA C 200 calorimeter. The energy yield (EY) of hydrochars was calculated as the hydrochar yield times the ratio of the HHV (dry basis) of the hydrochar and raw biomass,  $EY = MY * HHV_{HCdb}/HHV_{Rdb}$ .

To assess surface functional groups, FTIR spectra of raw OC and hydrochars were obtained using a Perkin Elmer Spectrum 400FT-IR/ NIR spectrometer in mid-IR mode, equipped with a Universal ATR (attenuated total reflectance) sampling device containing a diamond/ ZnSe crystal.

SEM/EDS analysis was performed using a JEOL IT 300 scanning electron microscope and an EDS Bruker Quantax equipped with a SDDXFlash 630 M detector. SEM analysis probed the impact of the severity of reaction conditions on morphology.

An analytical TGA (Mettler-Toledo TGA/DSC-1,  $0.1 \mu g/0.1$  °C resolution) was used to understand the impact of mineral matter on the thermal stability of the raw biomass versus increasingly "carbonized" samples, alongside calcium oxalate monohydrate, identified via EDS as the primary mineral present (Fisher Scientific USA, minimum purity 98%). The thermal program consisted of a 5 °C/min ramp up to 950 °C under high purity nitrogen (min 99.99%, Airgas USA). The DSC was calibrated with NIST-traceable indium and gold at 5 °C/min. Samples were analyzed for the presence of crystalline phases by X-ray powder diffraction (XRD, Bruker D8 Discover) using Cu Ka radiation at 40 kV and 40 mA with a step size of 0.05 and dwell time of 0.5 s. Inorganic element concentrations (Ca, Mg, K, Mn, Fe, Cu) in raw OC and three hydrochars were determined using inductively coupled plasma mass spectrometry (Aglient 7800 ICP-MS) in helium mode (tuning and calibration solutions from High Purity Standards, USA). Samples were

# 3. Results and discussion

The present work evaluates the potential to transform *Opuntia ficusindica* cladodes (OC), a draught-tolerant plant that can be grown on marginalized land, into a solid biomass fuel via hydrothermal carbonization. Using a large experimental matrix of 18 samples across mild to severe carbonization conditions, and applying ordinary least squares (OLS) linear regression analyses in both bivariate and multivariate cases (STATA v.13), enabled determination of the key process variables that result in solid fuel quality and yield. While higher order and more complex correlations have been reported in the literature (see: Álvarez-Murillo et al., 2015, Mäkelä et al., 2015; Sabio et al., 2016), such linear relationships were previously demonstrated to accurately represent such data (Mäkelä et al., 2015).

#### 3.1. Effect of process variables on mass yields

The design of HTC processes requires knowledge of the overall solid yield of hydrochar produced as a function of reaction temperature, time, and biomass to water ratio. Fig. 1 reports the yield of solid, liquid and gas of OC HTC residues as a function of residence time, when varying temperature (Fig. 1a) and B/W (Fig. 1b). Data reported in Fig. 1 are the average of at least of two trials with relative percentage errors ( $E_r$ %) lower than 1.7% for solid yields and 2.2% for gas yields.

As shown in Fig. 1a, at constant B/W = 0.20, the hydrochar yield was equal to 0.66 (T = 180 °C, time = 0.5 h) for mild conditions, and at the most severe conditions it decreased to 0.51 (T = 250 °C, time = 3 h). At this constant B/W loading, the relationship between hydrochar yield and temperature was highly linear with similar slopes, suggesting similar rates of biomass conversion. The observation that hydrochar yield decreased with increasing HTC temperature (all other variables constant) is well established in the literature; see for instance Benavente et al. (2015) and Mäkelä et al. (2015). The inverse relationship between reaction time and yield for OC is in agreement with the bulk of prior research; see for example Román et al. (2012), Basso et al. (2016) and Sabio et al. (2016), with contradicting results presented by Knežević et al. (2010).

As shown in Fig. 1b, at a constant temperature of 250 °C, hydrochar yield varied between 0.42 (B/W = 0.07, 3 h) and 0.63 (B/W = 0.30, 0.5 h), overall increasing as B/W increased. These general trends are in agreement with previous results on HTC of olive waste (Volpe and Fiori, 2017) and woody biomass (Sermyagina et al. 2015). As noted by

Álvarez-Murillo et al. (2015) and Sabio et al. (2016) for HTC of olive stone and tomato-peel waste, in general an increase in B/W results in a slight increase in hydrochar yield, but such correlations between hydrochar yield and B/W did not hold across the range of operational conditions investigated. Likewise, Mäkelä et al. (2015) found no statistically significant effect of solid loading on multiple process outputs (including hydrochar yield) for HTC of lignocellulosic sludge. To date, the effect of solid loading on yield is not well established in the literature, and the available data are too scarce from which to generalize. For OC, moving from B/W = 0.07 to B/W = 0.30 resulted in an increase in hydrochar yield between 36 and 46%, depending on reaction time.

Gas yield increased both with temperature, residence time and solid load (Fig. 1a and b). At B/W = 0.20, gas yield varied between 0.03 (T = 180 °C, time = 0.5 h) and 0.14 (T = 250 °C, time = 3 h). At 250 °C, gas yield varied between 0.07 (B/W = 0.07, time = 0.5 h) and 0.14 (B/W = 0.20 and 0.30, time = 3 h).

Liquid yield increased when increasing the temperature (Fig. 1a) and decreased when increasing solid load (Fig. 1b), while the effect of reaction time was almost negligible.

Data reported in Fig. 1a testify that at higher reaction temperatures and longer times, greater mass transfers from the solid to the liquid and gas phases. Gaseous molecules such as  $CO_2$  and CO are generated directly from raw solid biomass via decarboxylation and decarbonylation reactions, and in the liquid phase where the organic molecules released from the biomass further decompose to  $CO_2$  (Funke and Ziegler, 2010). Thus, the gas phase "receives" molecules from both the solid and liquid phases; in turn, its mass yield increased from 0.03 (at the lowest reaction temperature and time) to 0.14 (at the highest reaction temperature and time). Conversely, the liquid phase receives mass from the solid phase and releases mass to the gas phase (and eventually back to the solid phase): liquid mass yield varied to a limited extent (0.30–0.37, Fig. 1a), due to such partial counterbalancing of mass fluxes at varying HTC operating conditions.

Fig. 1b highlights how different solid loads translate into different amounts of liquid water available as extracting medium: it is expected that increasing the amount of water increases the transfer of matter from solid to liquid phase. Going from B/W = 0.30 to B/W = 0.07 (a fourfold increase in the amount of water per unit mass of feedstock) the liquid yield almost doubled (from 0.25 to 0.47) and, correspondingly, the concentration of dissolved organics in the liquid phase at B/W = 0.07 was about half of that at B/W = 0.30. At low B/W the liquid phase is more diluted in organics and, consequently, less reactive. This translates into a lower capacity to produce gaseous species: at low B/W, the gas yield was lower than at high B/W; this could also affect the tendency of organics to polymerize into the liquid phase and precipitate back as a solid phase.

To capture the extent to which one process variable is more critical in determining yield (and other product parameters) than others, statistical analyses were performed. Table 2 shows the results of bivariate and multivariate OLS linear regression analyses on the solid yield across all 18 samples. The bivariate (e.g. solid yield vs. temperature) regression suggests that temperature is indeed a highly statistically significant variable (p < 0.01) in determining yield, as noted above. As temperature increases, the solid yield decreases (according to the regression) at a rate of 0.196  $\pm$  0.054% per °C. However, this linear model explains only 45% of the variation in the dependent variable ( $R^2 = 0.456$ ). In the bivariate cases, time is not statistically significant. B/W is statistically significant, but with an  $R^2$  of 0.609, this correlation explains only a slight majority of the variance in the data. This inability of a bivariate linear correlation using a single process variable to predict resulting solid yield is highlighted in Fig. 2a.

Therefore, we turn to multivariate linear analysis to consider the combined impacts of these process variables on yield. From Table 2, it is clear that the three input variables are all statistically significant in

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#### Table 2

Results of OLS linear regression (bivariate and multivariate) to determine impact of process variables on solid yield and energy content of hydrochars.

	Bivariate OLS	Multivariate					
Impact of process variables on hydrochar yield							
Temperature (°C)	-0.196**				-0.168**		
	(0.054)				(0.014)		
Time (h)		-1.184			$-1.184^{**}$		
		(1.739)			(0.346)		
B/W			85.304**		76.651**		
	**	**	(17.089)		(5.409)		
Constant	101.040	57.090	39.533		82.144		
	(12.572)	(3.214)	(3.378)		(3.683)		
R-squared	0.456	0.028	0.609		0.966		
Impact of process variables on energy yield (EY)							
Temperature (°C)	-0.062				-0.017		
	(0.083)				(0.021)		
Time (h)		0.195			0.195		
		(2.062)			(0.495)		
B/W			$124.397^{**}$		$123.521^{**}$		
			(7.387)		(7.743)		
Solid Yield (%)				0.947**			
				(0.172)			
Constant	93.420	78.696	55.975	26.604	59.816		
	(19.598)	(3.812)	(1.460)	(9.582)	(5.271)		
R-squared	0.033	0.001	0.947	0.656	0.950		
Impact of process variables on higher heating value (HHV)							
Temperature (°C)	0.050**	0			0.051**		
	(0.007)				(0.005)		
Time (h)		0.508			0.508**		
		(0.329)			(0.129)		
B/W			0.110		2.726		
			(5.462)		(2.016)		
Solid Yield (%)				$-0.117^{*}$			
				(0.040)			
Constant	8.295**	$19.165^{**}$	19.906**	$26.420^{**}$	6.798 <sup>**</sup>		
	(1.743)	(0.608)	(1.080)	(2.258)	(1.373)		
R-squared	0.738	0.130	0.000	0.345	0.883		
Observations	18	18	18	18	18		
Standard errors in parentheses $p < 0.01, p < 0.05$							

determining the solid yield from HTC of OC, with the regression equation (Eq. (1)) explaining over 96% of the variance of the data.

(1)

 $MY_{Char} (\%) = -0.168*Temp(^{\circ}C) - 1.184*time(h) + 76.651*B/W(g/g) + 82.144$ 

As a note, MY is expressed in Eq. (1) as a percentage to avoid a number of unnecessary digits after the commas. The same applies to EY in Eq. (2) and is reflected in Fig. 2. Indeed, as shown in Fig. 2a, this correlation provides an excellent fit for the 18 samples produced at varying process conditions; hydrochar yield shows a statistically significant linear dependence on all process variables: T, t, and B/W.

# 3.2. Hydrochar composition as a function of process variables

Ultimate analysis (Table 1) shows that HTC had little effect on the hydrogen content, which ranged between 4.6 and 4.9%. Hydrochars showed a small increase in nitrogen compared to the raw material; the nitrogen content does not show any clear dependence on HTC process variables. A negligible amount of sulphur (0.01–0.15%, data not reported) was detected for both raw biomass and hydrochars.

Carbon content increased with the increase in temperature and when the reaction time increased from 0.5 to 1 h. Carbon contents at residence times of 1 and 3 h were quite similar. Oxygen content had an opposite trend compared to that of carbon. The multivariate OLS regression, shown in Table 3, confirms that reaction temperature is



yield as a function of temperature (closed circle) or B/W (open circle); and Predicted (multivariate OLS regression, Eq. (1)) (half filled square) versus actual solid yield, with v=x line



(2)) versus measured energy yield, with y=x line



Fig. 2. Predicted versus measured hydrochar yield (a), energy yield (b), higher heating value (c).

#### Table 3

Results of OLS multivariate linear regression to determine impact of process variables on hydrochar composition.

Multivariate regressions to determine impact of process parameters on						
	Elemental C	Elemental O				
Temperature (°C)	0.043*	$-0.060^{*}$				
	(-0.018)	(0.024)				
Time (h)	0.88	$-1.363^{*}$				
	(-0.424)	(0.588)				
B/W	-6.507	-7.954				
	(-6.631)	(9.201)				
Constant	40.172**	46.689**				
	(-4.514)	(6.264)				
R-squared	0.463	0.453				
	Volatile Matter (VM)	Fixed Carbon (FC)				
Temperature (°C)	$-0.087^{**}$	0.071**				
-	(0.017)	(0.017)				
Time (h)	$-1.398^{**}$	1.161*				
	(0.416)	(0.404)				
B/W	-8.518	-0.620				
	(6.508)	(6.316)				
Constant	88.439**	2.806				
	(4.431)	(4.300)				
R-squared	0.725	0.657				
Observations	18	18				
Standard errors in parent	${}^{**}p < 0.01, {}^{*}p < 0.05$					

statistically significant (p < 0.05) in increasing C content, while decreasing both time and temperature lead to increases in O content. However, this linear regression explains only 46 and 45% of the variance of the data, respectively.

Overall, as HTC temperature and residence time increased, the fixed carbon content (FC) increased, and the volatile matter (VM) content decreased, as shown in Table 1. And in fact, a multivariate linear regression considering temperature, time and B/W confirms that temperature and time are statistically significant in describing the VM and FC contents resulting from carbonization, though only with correlation coefficients of 0.725 and 0.657, respectively (Table 3). Thus, nonlinear models that enable interactions between the process variables may better represent such compositional data (Álvarez-Murillo et al., 2015; Sabio et al., 2016).

When compared to the raw biomass, the inorganic (ash) content decreased by  $\sim 2.0-2.5\%$  in absolute terms for low-temperature (180 and 220 °C) and short residence time (0.5 h) hydrochars, while it

remained approximately constant (  $\pm$  1%) for samples carbonized at 250 °C with a reaction time of 1-3 h. During hydrothermal treatments inorganic elements (in particular Na<sup>+</sup> and K<sup>+</sup>) are removed from the solid phase, even under mild processing conditions (Reza et al., 2015a). At longer residence times and higher temperatures, the organic mass depletion compensates for the inorganic element loss, resulting in an approximately constant "ash" mass fraction.

# 3.3. Impact of processing on hydrochar energy properties and char formation

Table 1 shows the HHV and the EY of the hydrochars obtained at the different operating conditions. As expected, at fixed B/W = 0.20, the hydrochars' HHVs increase with increasing HTC temperature and residence time (Fig. 3a). The highest HHV is seen for the hydrochar obtained at 250 °C and 3 h of residence time: 22.4 MJ kg<sup>-1</sup>, 1.6 times greater than the HHV of the raw feedstock.

As shown in Table 1, for samples carbonized at B/W = 0.20 the energy yield is rather uniform and ranges from 0.78 to 0.84, without any obvious trends between EY and process variables. This behavior results from the counterbalancing effects of the process variables reaction temperature and time on hydrochar yield and HHV. Notably, EY varies significantly with B/W; it is at a maximum for the highest B/W (EY = 0.92) and minimum for the lowest B/W (EY = 0.63). These observations are underscored in Table 2; in a multivariate regression, only B/W is statistically significant; Eq. (2) was able to explain 95% of the variance within the energy yield as a function of process parameters (see Fig. 2b for measured vs predicted plot).

$$EY (\%) = -0.017 * Temp(^{\circ}C) + 0.195 * time(h) + 123.521 * B/W(g/g) + 59.816$$

(2)

If the HTC process goal is to maximize EY, this suggests working at higher values of B/W, which would also maximize the profitability of an industrial HTC plant by enabling higher throughput (Lucian and Fiori, 2017).

Fig. 3 shows the behaviour of HHV and "hydrochar volatility" V<sub>HC</sub> obtained at fixed B/W (Fig. 3a and b) and fixed temperature (Fig. 3c and d) when varying the other operating conditions. The HHVs increase with temperature follows a linear trend (Fig. 3a). V<sub>HC</sub> increases together with hydrochar yield (Fig. 3b); at less severe operating conditions, higher mass yields and more volatile hydrochars are obtained.

The comparison of the behaviour of HHV vs. hydrochar yield outlined by Fig. 3b and c is of particular interest. The inverse proportionality of HHV to hydrochar yield, well documented in the HTC



Fig. 3. Dependence of the hydrochar higher heating value and volatility on process variables. (a) HHV vs. temperature at B/W = 0.20 and different reaction times, linear trendlines with  $R^2$  are reported; (b) HHV and  $V_{HC}$  vs. hydrochar yield at B/W = 0.20 and different reaction temperatures and times, linear trendlines with  $R^2$  are reported; (c) HHV vs. hydrochar yield at T = 250 °C and different B/W and times, linear trendlines with  $R^2$  are reported; (d) HHV and  $V_{HC}$  vs. B/W at T = 250 °C and different reaction times, the curves connecting the indicators are intended to help the reader in the comprehension of the figure.

literature (Basso et al., 2015; Sermyagina et al., 2015), applies only when working at variable reaction temperature and time, but at fixed B/W. If B/W also varies, such a correlation is no longer valid: correlating linearly all the HHV and yield data of Fig. 3c returns a  $R^2 = 0.0005$ . Conversely, the linear relationship between HHV and yield holds when considering the subgroups of data obtained at fixed B/ W: this strictly applies for B/W equal to 0.07, 0.20 and 0.30  $(0.97 \le R^2 \le 1)$ , while is less evident for B/W = 0.14 (R<sup>2</sup> = 0.61). Such behaviour is emphasized by the bivariate analysis used to predict HHV as a function of solid yield, which describes less than 35% of the variance in the data, as shown in Table 2 (and graphically in Fig. 2c). Temperature is the only single process variable that can describe a majority of the variance of the data ( $R^2 = 0.738$ ) in a bivariate analysis (HHV vs temperature). In the multivariable linear analysis (regression including time, temperature, and B/W; inclusion of solid yield, given its dependence on these variables, would introduce collinearity issues) only temperature and time are statistically significant. This results in a regression equation of:

HHV (MJ/kg) = 
$$0.051*Temp(^{\circ}C) + 0.508*time(h) + 2.726*B/W(g/g) + 6.798$$
(3)

whose outputs are shown graphically in Fig. 2c.

While the coefficient for B/W is large (2.726), its error is of equal magnitude (2.016). However, this does not mean that B/W is not a critically important factor in HTC of biomass, rather, it is not *linearly* correlated with HHV. Fig. 3d highlights that the HHV behaviour vs. B/W yields a maximum. Starting from B/W = 0.07, HHV first increases, is maximized at B/W equal to 0.14 or 0.20 (depending on residence time), then decreases at B/W = 0.30. This trend appears to be inversely correlated to the hydrochar volatility.  $V_{HC}$  appears relatively stable for B/W = 0.07 and B/W = 0.14, then it drops down at B/W = 0.20, and increases again at B/W = 0.30.  $V_{HC}$  values obtained at reaction times of 0.5 and 1 h are quite similar, while increasing the duration of HTC

decreases the volatile matter present. While linear models are quite effective for some hydrochar descriptors, this is a case where using a more complex multivariate approach could substantially improve the model.

SEM images analysis sheds light on the morphological changes due to HTC. SEM images show how at 180 °C (3 h, B/W = 0.20) the HTC conditions were not sufficient to destroy the fibrous nature of the biomass; intact OC fibers abound in the low temperature samples. Given the low HHV, high solid yield and VM of these samples, the lack of complete fiber decomposition is not surprising. The impact of reaction time on surface morphology becomes evident at more severe HTC conditions, as can be seen in the chars obtained at 250 °C, 0.5 h, B/W = 0.20 and 250 °C, 3 h, B/W = 0.20. As the carbonization time increases, there is a distinct transition from a char with a residual fibrous nature to a more amorphous solid with spherical carbon deposits, which are likely linked to secondary char formation.

The solid residue resulting from HTC processes can be either primary char or secondary char (Knežević et al., 2010). The former results from solid-solid conversion: the primary char maintains the original shape of the raw biomass, representing the non-liquefied remainder of the biomass. The latter, sometimes referred to as coke (Karayildirim et al., 2008), results from hydrolysis, dissolution, polymerization, aromatization, and condensation to produce spherical carbonized particles (Karayildirim et al., 2008; Knežević et al., 2010; Titirici et al., 2008; Titirici et al., 2012; Castello et al., 2014). Recent results from this laboratory on the HTC of olive waste demonstrated that secondary char is richer in carbon than primary char, and higher amounts of secondary char are often seen for chars with high HHV and FC content (Volpe and Fiori, 2017).

To probe the characteristics of the primary char, the 250 °C, 3 h, B/W = 0.20 sample was washed repeatedly with a 50:50 methanol:acetone mixture (until the solution ran clear), which allowed to dissolve the secondary char (future work will probe the nature of this char). SEM

images of the solid residue after washing showed a crater-filled landscape, dotted with "pockets" that were originally covered by the spherical secondary char particles. The dimensions of these "craters" are similar to those of the spherical particles.

The data of Fig. 3 and the SEM images testify to the importance (very often neglected in the HTC literature) of B/W on HTC reactions, in terms of degree of carbonization and, perhaps more importantly, secondary char formation. The 250 °C, 3 h, B/W = 0.07 sample shows some evidence of secondary char formation with amorphous carbon regions, but the spherical nature of the secondary char is not nearly as developed as in the samples with B/W of 0.20 and 0.30. At low B/W (0.07), the aqueous phase is diluted in organics (Section 3.1), which limits their polymerization and back precipitation to the solid phase. At higher B/W there is a higher concentration of species like HMF and furfural, which can later polymerize, producing secondary char. The differences in HHV and V<sub>HC</sub> between the samples obtained at B/W of 0.20 and 0.30 (Fig. 3d) could be because biomass hydrolysed to a lesser extent due to the limited availability of water at higher B/W.

It appears that the trends on Fig. 3d result from opposing effects. On the one hand, the higher the B/W, the higher the formation of energydense secondary char; this is in agreement with results previously observed (Volpe and Fiori, 2017). This also explains the increase in HHV at increasing B/W in the range 0.07-0.20. On the other hand, a further increase in B/W modifies the reaction environment. That is, when the water is reduced to the minimum necessary to "wet" the biomass, the char produced shows a lower HHV; similar results were obtained by Funke et al. (2013) for carbonized wheat straw. Interestingly, Funke et al. (2013) found the minimum amount of water to soak the straw corresponding to a B/W = 0.33, a value very close to the highest B/Wvalue here used of 0.30. At such water-lean conditions, the water-biomass environment is likely less reactive, as should be expected considering the key role of water in enhancing reactivity and, thus, biomass carbonization. Future work will probe the aqueous and solid phase composition (especially concentrations of HMF and furfural) in conjunction with qualitative observations of the hydrochar samples.

#### 3.4. Inorganic content of hydrochars

In addition to the two carbonaceous phases brought to light via SEM imaging, the nature of the inorganic ("ash") content was also revealed. SEM images showed crystalline structures separate from the char particles. EDS analysis suggested a composition of 1 atom of calcium per ~2 carbon and ~4 oxygen, suggesting that the crystalline material may be calcium oxalate,  $CaC_2O_4$ . XRD analysis also suggested the presence of  $CaC_2O_4$  in the HTC char (signal too weak to detect in raw biomass). Notably, primary peaks for  $CaC_2O_4$ ·H<sub>2</sub>O at  $2\theta = 28$  (0 2 0); 30.5 (2 0 2); 31.0 (1 2 1); 31.2 (3 1 0); 36.5 (3 0 1); 37.2 (1 3 0) and 40.8 (2 0 2) were detected (Girija et al. 1998).

TGA analysis of the raw OC, pure  $CaC_2O_4H_2O$  and four hydrochars suggests that calcium oxalate may indeed be a primary constituent of the hydrochar's inorganic components, which is supported by XRD, SEM-EDS and ICP-MS analysis, as described below. Calcium oxalate (monohydrate) undergoes three thermal decomposition reactions in an inert atmosphere (Fig. 4a):

Loss of hydrated water:  $CaC_2O_4 \cdot H_2 O \rightarrow CaC_2O_4 + H_2O$ 

Decomposition to calcium carbonate: $CaC_2O_4 \rightarrow CaCO_3 + CO$ 

Decomposition to calcium oxide:  $CaCO_3 \rightarrow CaO + CO_2$ 

Derivative thermogravimetric (DTG) curves of  $CaC_2O_4H_2O$  show three peaks, corresponding to each decomposition phase. Theoretically, 12.3% of the mass will be lost during the first decomposition reaction, 19.2% during the second, and 30.1% during the third. This was indeed observed for pure  $CaC_2O_4H_2O$  (Fig. 4b).

Furthermore, in Fig. 4, the raw and carbonized biomasses showed



 b. Derivative thermogravimetric curves (rate of total mass fraction converted, X=(m<sub>i</sub>, m<sub>t</sub>)/m<sub>i</sub> used to determine relative decomposition of CaOx)



normalized to sample mass)

Fig. 4. Thermal analysis of raw OC, 4 HTC samples, and CaC\_2O\_4H\_2O (CaOx) at 5  $^\circ\text{C/min}$  in  $N_2$  atmosphere.

evidence of calcium oxalate present, with peak mass loss rates occurring at similar temperatures to the decomposition reactions (Fig. 4b). It also appears that the hydrochars have a higher concentration of Ca-C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O, which increases as the degree of carbonization increases (expected given above discussion concerning removal of inorganics and depletion of organics during HTC). This increase in Ca (and corresponding decrease in K) was confirmed via ICP-MS analysis of the raw OC and hydrochars produced at 180, 220, 250 °C (3 h, B/W = 0.20), in both the ash and solid fuel samples (Fig. 5).

The thermogravimetric (Fig. 4a) curves show that the raw biomass pyrolyzes fairly continuously across the temperature range, but with DTG peaks (Fig. 4b) occurring at the same temperatures as for Ca- $C_2O_4$ ·H<sub>2</sub>O. However, the hydrochars' TG and DTG curves more closely mimic those of the calcium oxalate, especially as the degree of carbonization increases.

DSC curves (Fig. 4c) show that the CaC<sub>2</sub>O<sub>4</sub>H<sub>2</sub>O curve is entirely endothermic, as expected for this thermal decomposition reaction where the calcium carbonate decomposition to CaO and CO<sub>2</sub> is endothermic with a peak around 700 °C, depending on heating rate (Archarya et al., 2009), as seen in Fig. 4c, CaOx. Conversely, all the raw



b. Concentration in Raw or Hydrochar (Ca, Mg, K on right axis, Mn, Fe, Cu on left axis)

Fig. 5. Inorganic composition of raw *Opuntia*, 180, 220 and 250  $^{\circ}$ C hydrochars (carbonized for 3 h, B/W = 0.20) and corresponding ashes (error bars indicate 95% confidence interval).

and hydrochar samples display exothermic behavior at temperatures greater than ~500 °C, and peak at the same temperature of the calcium carbonate decomposition reaction. The release of  $CO_2$  from the calcium carbonate may gasify the chars through the Boudouard reaction  $C + CO_2 \rightarrow 2CO$ ; however, this reaction is endothermic and usually does not occur below 1000 °C (Mathieu and Dubuisson, 2002). However, CaO has been shown to be an *in situ* CO<sub>2</sub> adsorbent and an active catalyst for tar destruction and water-gas shift reactions, the former being endothermic in an inert atmosphere, the latter exothermic (Delgado et al., 1996; Grabow et al., 2008). Others have hypothesized that the energy released from the exothermic CaO carbonation reaction may compensate for endothermic gasification and cracking reactions (Wei et al., 2008). As such, further research is needed to understand this exothermic behavior.

#### 3.5. Surface characteristics of hydrochars

ATR-FTIR spectroscopy was used to assess the surface functional group changes in *Opuntia Indica cladodes* resulting from carbonization with FTIR peak assignments according to Xu et al. (2013). While strong single bond vibrations typical of lignocellulosic biomass, such as C–O, C–H and O–H, are still present in carbonized samples, significant decreases were observed at increasing HTC temperature and, although with less intensity, at increasing residence time.

A broad peak between 3600 and 3000 cm<sup>-1</sup> is attributed to the stretching vibration of aliphatic O–H (hydroxyl, phenols and carboxyl); the peaks between 1100 and 1000 cm<sup>-1</sup> correspond to C–O stretching vibration from esters, phenols and aliphatic alcohols while the peak at 1200 cm<sup>-1</sup> is assigned to the O–H bending mode. The lower intensity of these peaks in the hydrochars suggests that dehydration (weakening of bands at 3600–3000 cm<sup>-1</sup> due to O–H stretching and at 1200 cm<sup>-1</sup> due to O–H bending) and decarboxylation reactions (disappearing of bands at 1100–1000 cm<sup>-1</sup>) occurred during HTC (Parshetti et al.,

## 2013).

The peak between 1700 and 1650  $\text{cm}^{-1}$  corresponds to the C–O stretching vibration of esters, carboxylic acids or aldehydes from cellulose or lignin, while the peak between 1650 and  $1450 \text{ cm}^{-1}$  represents the C=C vibrations of the aromatic rings in lignin. These peaks demonstrate considerable changes in the hydrochars due to the breakdown of cellulose and aromatic rings (lignin partial fragmentation) during HTC (Liu et al., 2013). The peaks between 2940 and  $2840 \text{ cm}^{-1}$  and  $1450 \text{ and } 1200 \text{ cm}^{-1}$  are due to the stretching and bending vibration of aliphatic C–H bonds, respectively. The presence of such typical bands in hydrochar FTIR spectra indicates that aliphatic structures are maintained in hydrochars. The appearance, with increasing HTC temperature, of a shoulder around 2950-2970 cm<sup>-1</sup>, and the peaks at 825 and 660 (C-H aromatic vibrations) suggest an increase in aromatic character during carbonization. The progressive decrease in intensity, with increasing HTC temperature, of the bands between 930 and 875 cm<sup>-1</sup>, assigned to the glycosidic linkage of hemicellulose and cellulose, clearly attests the breakage of such bonds during carbonization. Similar chemical transformations, with hemicellulose and cellulose destruction and increasing aromatization, were observed using FTIR when corncob and miscanthus were converted into carbonaceous products by means of HTC (Calucci et al., 2013).

# 4. Conclusions

Hydrothermal carbonization was demonstrated as a potential technology to convert high-moisture *Opuntia ficus-indica* cladodes, a biomass cultivable on arid and marginal lands, into a sustainable solid biofuel. Using multivariate statistical analysis, it was shown that hydrochar yield, energy content, composition, surface chemistry and morphology, depend, to varying degrees, on carbonization temperature, reaction time, and solid loading. Electron microscopy showed evidence of secondary char formation at higher temperatures and residence times. Crystallographic and thermal analyses suggest calcium oxalate, present in biomass, concentrates in char, and may promote gasification at high temperature.

## Acknowledgements

The authors thank L. Gao for assistance with running TGA. This work was partially supported by the U.S.-Italy Fulbright Commission.

# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.09.072.

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