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

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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^{-1} $year^{-1}$ (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 $year^{-1}$ 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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Table 1
Process parameters and resulting properties of solid residues. Compositional analyses performed in duplicate; average values shown (Er% ≤ 3.3% for proximate and 1.0% for ultimate analyses); HHVs average of three measurements, Er% ≤ 1.0).

Sample description				Proximate analysis			Elemental analysis				Energy properties	
Sample	T (°C)	Time (h)	B/W	VM	FC	Ash	C	H	N	O*	HHV (MJ kg^{-1})	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 3-year 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 μm. 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 ± 0.001 g of dried sample and 20 to 34 ± 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™) 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_2 as the sole gaseous product. While gas composition varies, the typical CO_2 molar fraction in dry HTC gas is between 0.95 and 0.99, with minor amounts of CO and traces of H_2 and CH_4 (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