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Hydrothermal Carbonization of Lemon Peel Waste: Preliminary Results on the Effects of Temperature during Process Water Recirculation

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Abstract: Hydrothermal carbonization (HTC) is a promising thermochemical pre-treatment to convert waste biomass into solid biofuels. However, the process yields large amounts of organic process water (PW), which must be properly disposed of or reused. In this study, the PW produced from the hydrothermal carbonization of lemon peel waste (LP) was recycled into HTC process of LP with the aim of maximize energy recovery from the aqueous phase while saving water resources and mitigating the overall environmental impact of the process. The effects of HTC temperature on the properties of solid and liquid products were investigated during PW recirculation. Experiments were carried out at three different operating temperatures (180, 220, 250 °C), fixed residence times of 60 min, and solid to liquid load of 20 wt%, on a dry basis. Hydrochars were characterized in terms of proximate analysis and higher heating values while liquid phases were analyzed in terms of pH and total organic carbon content (TOC). PW recirculation led to a solid mass yield increase and the effect was more pronounced at lower HTC temperature. The increase of solid mass yield, after recirculation steps (maximum increase of about 6% at 180 °C), also led to a significant energy yield enhancement. Results showed that PW recirculation is a viable strategy for a reduction of water consumption and further carbon recovery; moreover preliminary results encourage for an in-depth analysis of the effects of the PW recirculation for different biomasses and at various operating conditions.

Keywords: lemon peel waste; hydrothermal carbonization; hydrochar; process water recirculation; biofuel

1. Introduction

The rising world energy demand together with the decrease in the fossil fuels reservoirs threaten environmental sustainability and push the research for reliable and renewable resources.

Biomass exploitation represents one of the most common form producing renewable energy. Waste biomass in particular is widely available in large amounts at low cost and represents a carbon-neutral and programmable resource for the production of energy dense biofuels and valuable carbonaceous materials for several other applications [1]. Waste biomass direct conversion into energy suffers of several drawbacks, mainly due to its high moisture content low energy density and low chemical stability [2]. In the last decades thermochemical upgrading of waste biomass has been largely investigated to yield high energy dense biofuels. In particular, dry thermochemical treatments like torrefaction [3–5], pyrolysis [6,7], and gasification [8–10] have been used to produce solid, liquid, and gaseous bio-fuels, respectively. The high moisture content (typically higher than 50%), commonly found in waste biomass, deeply affects energy efficiency of dry thermochemical technologies conversion. Wet thermochemical treatments like Hydrothermal Carbonization (HTC) have been more recently taking in consideration by the scientists

of the sector due to the possibility of direct treatment of wet biomass without the need of a drying pre-treatment [11]. HTC also known as wet torrefaction is a process where wet biomass is processed in a batch mode in presence of water at subcritical condition, temperature range typically between 180–250 °C and corresponding autogenous water pressure of 10–40 bar, for a residence time varying between few minutes and several hours (0.5–12 h) [12–14]. When compared to dry torrefaction, HTC revealed enhanced biomass degradation at same reaction temperature and residence time due to the catalytic role of water on biomass constituent degradation [5,15]. Heterogeneous lignocellulosic structure of biomass is degraded by reaction routes mechanism such as hydrolysis, dehydration, decarboxylation, polymerization, poly-condensation, and aromatization [16–19]. Some reactions are known to be exothermic, while others are endothermic. It has been recently reported that HTC process overall shows an exothermic behavior also depending on the nature of the starting material, reaction temperature, and solid load [13]. The exothermal character of HTC and of all hydrothermal processes of biomass is of high technological importance for the correct energy analysis and the design of the reaction system.

The main advantage of HTC over other thermochemical conversion technologies (such as pyrolysis, gasification, and incineration) is its ability to convert the wet feedstock to a solid carbonaceous product (hydrochar) at relatively high yields without prior de-watering and drying [20]. Moreover HTC process has been efficiently applied to very low-value residues as the organic fraction of municipal waste [21,22], sewage, and agro-industrial sludge to enhance sludge dewaterability and/or for the production of soil amendments [23–26]. HTC has been also successfully used as a pre-treatment for the production activated carbons to be used as water remediation agents [27,28].

Together with HTC, two other wet thermochemical technologies are nowadays being investigated to waste biomass upgrading. Hydrothermal liquefaction (HTL) and supercritical water gasification (SCWG) are distinguished from HTC by the process temperature and thus by the main products obtainable. During HTL, biomass is processed at 300–350 °C and 15–20 MPa for the production of a liquid 'biocrude' [29], while during SCWG biomass is treated at temperature reaching 600–700 °C in supercritical water condition, with the main aim to obtain gas products (mainly hydrogen and carbon dioxide). [29,30]. The present study focused on the upgrading of waste biomass to yield a solid bio-fuel, and thus HTL and SCWG, higher energy demanding technologies, were not taken in consideration.

Since HTC occurs in aqueous medium, large amounts of carbon in feedstock distributes to the by-product aqueous phase known as process water (PW) [31].

PW consists mainly of organic acids (formic, acetic, lactic, and propionic), sugars (glucose, fructose, and xylose), furans (furfural and 5-HMF), and phenols [32–37].

In order to make the process more economically viable and environmentally friendly, a feasible way to treat or utilize the PW needs to be figured out.

The recirculation of PW as reaction medium of the hydrothermal process is a promising approach, which could not only minimize the hydrothermal wastewater discharge but also increase the yield of biofuel and thus carbon recovery.

On an industrial scale, reuse of PW could be also an efficient method of heat recovery; moreover, it could significantly reduce the water demand for the process.

Recirculation of process water is a potential method for increasing the overall efficiency of the HTC system. However, it should not be the only alternative and methodologies such as biological degradation [38], oxidation treatment [39], and other possible utilization paths [40] should be considered.

Recent investigations on the recirculation of PW show promising results for a cleaner production of hydrochar. Catalkopru et al. [41] determined the yield and fuel properties of hydrochars from HTC of three different biomass types (grape pomace, orange pomace and poultry litter) for three recirculation steps. HTC test were performed at 225 °C with a residence time of 10–30 min.

By recirculation, mass and energy yields of the hydrochar increased. The elemental composition and heating value of hydrochars did not change but their combustion

characteristics did: The ignition temperature and combustion reactivity decreased. The authors [41] suggested that PW might lead to a resistance to diffusion of the degraded soluble fragments from surface of biomass to the aqueous solution, leading to an increase in hydrochar yield.

Stemann et al. [42] studied the effects of the recirculation of process water during HTC of poplar wood chips (temperature of 220 °C and residence time of 4 h).

Organic acids in the liquid phase catalyzed dehydration reactions and provoked a rise of the carbon content and higher heating value (HHV) of hydrochars. In contrast to what reported by Catalkopru et al. [41] hydrochar yield increase was not observed. Recirculation of PW during HTC of chlorella and soybean straw was investigated by Leng et al. [43] for four cycles. The yield of hydrochar was increased from 20.5% to 26.7% for chlorella and from 47.7% to 54.7% for soybean straw; the energy yield was increased by about 10%.

Other studies [44–47] confirmed that for the majority of the studied biomasses, the biofuel yield and properties could be improved by PW recirculation.

There are few studies describing the effects of temperature during water recycling on HTC.

Köchermann et al. [48] examined effect of PW recycling at 180 and 220 °C. Results showed that hydrochar mass yield increases with progressing PW recirculation and higher temperatures strengthen this effect. Arauzo et al. [49] analyzed the effects of PW recirculation in the range of 200–220 °C. At 200 °C the hydrochar yield decreased using only one PW recirculation and then increased after the second recycle; at 220 °C the opposite effect was observed. The influence of residual water recirculation on hydrochar properties is described in a contradictory way probably due to the different feedstock nature and differences in the experimental procedure.

In this work, the conversion of lemon peel waste by HTC process with DI and recirculated PW was studied for the first time. The aim was to contribute overcome a large gap in literature regarding the use of residual fractions obtained from HTC, such as process water, for a cleaner production of solid biofuels. More specifically, the objectives of this study were: (i) To evaluate temperature influence during PW recirculation in the range of 180–250 °C for two recycling steps; (ii) to detect effects of PW recirculation on hydrochar and aqueous phase properties; (iii) to identify pathways, which could lead to improve properties of hydrochars by analyzing HTC products and comparing results with available literature.

2. Materials and Methods

2.1. Materials and Sample Preparation

In this study, peel waste from lemon (LP) of the Verdello variety (cultivated in the province of Palermo) were used as feedstock.

Raw material was dried in a ventilated oven at 105 °C for 48 h to prevent any degradation between its collection and its actual usage in HTC tests and to start with a dry baseline. The samples were then ground and sieved to a particle size lower than 850 μm and again oven dried for 2 h. The moisture content of raw material was 78 wt% while density value of dried LP feedstock was 0.64 g mL^{-1}.

All samples were preserved in plastic containers before the HTC tests, and the solvent (deionized water or recirculated PW) added just before each HTC run to the desired dry biomass to water ratio (B/W). Elemental analysis of a similar lemon peel waste feedstock has been reported in the literature, where LP showed a CHNS content of 50.2, 5.6, 1.3, and 0.1 wt%, respectively [50].

2.2. HTC Experimental Procedure

The HTC experimental apparatus used in this study, including a 50 mL internal volume stainless-steel (AISI 316) batch reactor, consisted of an adaptation of reaction system configuration already reported in the literature [51]. A schematic diagram of the experimental system and few pictures of the apparatus are shown in the Supplementary Materials (Figures S1 and S2, respectively).

Figure 1 shows the temperature trend during HTC trials at the different operating conditions. The apparatus took between 21 and 34 min to reach the set temperature and 33 to 37 min to cool down from set temperature to room temperature, once the HTC run was stopped.
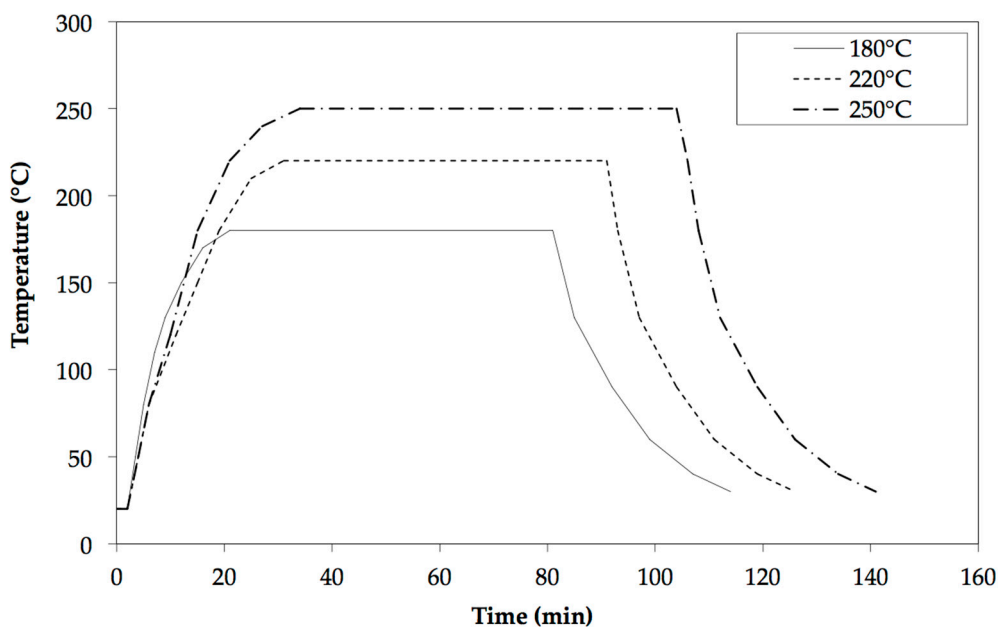

Figure 1. Typical trends of temperature during hydrothermal carbonization (HTC) runs performed at 180, 220, and 250 °C.

It can be observed that the temperature of the reactor rose after about two minutes after the beginning of the heating phase. This can be explained by the time delay due to heat transfer between the thermal input of the band heater and the temperature measured by the thermocouple.

Experimental trials were carried out at three different temperatures (180, 220, and 250 °C) keeping a fixed residence time of 1 h. In the first step (HTC_R0), a mixture of 5.0 ± 0.1 g of dried biomass and 25.0 ± 0.1 g of deionized water (DI) was loaded into the reactor, in order to obtain a biomass to water ratio on a dry basis (B/W) of 0.2. The reactor was then sealed and N_2 was fluxed through the system to purge the reactor from the air. After purging, excess nitrogen pressure was released and all the needle valves were closed, before starting the heating phase. The residence time was measured starting from the instant the controller indicated the desired value of the temperature set point.

At the end of the residence time, the reactor was cooled down by a two-step procedure. Firstly, a massive stainless-steel disc at -10 °C was positioned at the bottom of the reactor; secondly, once the reactor reached the temperature of about 130 °C, quenching to room temperature was achieved by using a stainless-steel radiator with flowing tap water. The radiator was specifically designed for the scope, to be easily inserted into the reactor body. To evaluate the gas yield, the excess of pressure was released by opening the reactor valve and the gas left flowing inside the graduated cylinder.

Once the volume was measured, the reactor was opened and the reaction mixture (slurry) was filtered to separate solid phase from aqueous phase by vacuum filtration.

The solid phase was washed with 30 mL of DI and dried in a ventilated oven at 105 °C for 24 h. The filtrate was referred as process water (PW) and stored at -10 °C.

For the recirculating steps 1–2 (HTC_R1 and HTC_R2), PW of the previous step was used as solvent and mixed with biomass at BW of 0.2. Each run was repeated at least three times, to evaluate the deviation of the data and ensure reproducibility.

After drying the solid yield was then computed as mass of dry hydrochar collected to the mass of initial dry feedstock ($g_{hydrochar}/g_{dry\ feedstock}$). The gas yield was computed

with the ideal gas law, assuming atmospheric pressure, temperature of 30 °C and CO_2 as the sole gaseous product [51]. The liquid yield was computed by difference.

Hydrochar (HC) and PW obtained from the HTC process with DI were designated as R0. The products obtained from the two recirculating steps were defined as R1 and R2, as it can also be seen in Figure 2.
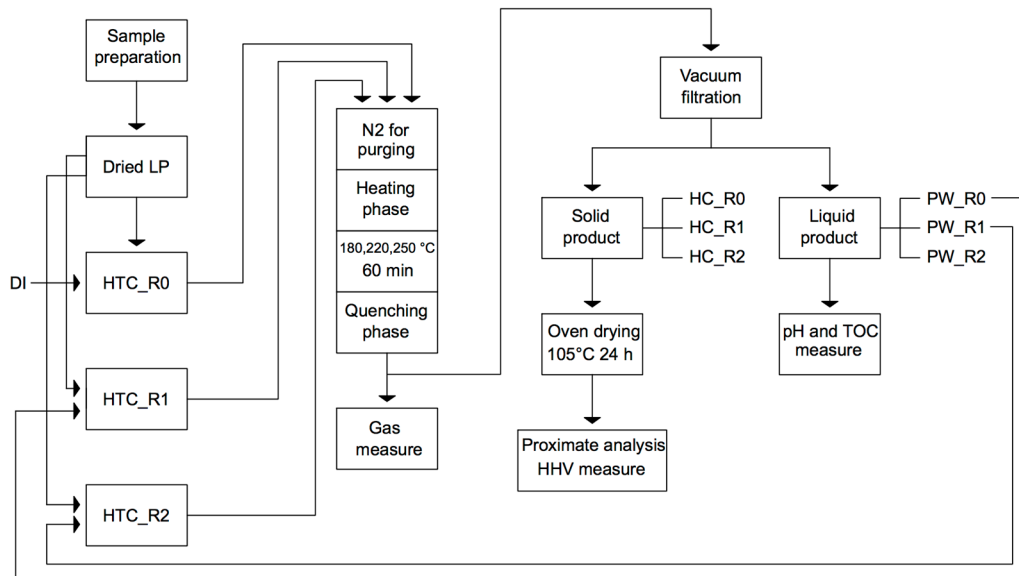

Figure 2. Flow diagram of HTC experimental procedure and HTC products characterization.

2.3. Characterization of Solid and Liquid Products

Raw materials and hydrochars obtained from HTC runs were characterized in terms of proximate analysis and higher heating value (HHV).

Proximate analysis were carried out by a LECO Thermogravimetric Analyser TGA 701. Approximately, 400–500 mg of solid samples were used to evaluate moisture content (MC), volatile matter (VM), ashes (Ash), and fixed carbon (FC) according to the following a thermal program: (1) 5 °C/min ramp to 105 °C in air until constant weight (<±0.05%) for MC calculation; (2) 16 °C/min ramp to 900 °C, hold time 7 min in N_2, to determine the VM; (3) natural cooling down to 500 °C in N_2; (4) 30 °C/min ramp in air to 800 °C and isothermal until constant weight to determine ash content. Fixed carbon was evaluated by difference.

Higher heating values of raw and treated feedstock were evaluated according to the CEN/TS 14918 standard by means of a LECO AC500 calorimeter.

The energy densification ratio (EDR) and the energy yield (EY) of hydrochars were determined via Equations (1) and (2), respectively:

$$EDR(\%) = (HHV_{HCdb}/HHV_{Rdb}) \times 100 \tag{1}$$

$$EY(\%) = MY{\cdot}EDR \tag{2}$$

where HHV_{HCdb} and HHV_{Rdb} are the higher heating values of hydrochar and raw LP (on dry basis), respectively; MY is the hydrochar yield computed as mass of dry hydrochar collected to the mass of initial dry feedstock.

Process water collected after each HTC test was characterized in terms of pH and TOC. The pH of liquid samples was measured using a XS instruments Bench pH-meter. TOC content was measured by a Shimadzu Total Organic Carbon Analyser (liquid samples were previously filtered through 0.45 μm syringe filters).

3. Results and Discussion

3.1. The Influence of Temperature on Mass Yields during PW Recirculation

Table 1 shows mass yields obtained after HTC tests performed with deionized water or recirculated PW as a solvent (deviations of data measured through Er% are shown in Table S1 in Supplementary Materials) As documented in the literature [16,17], at step R0 (HTC runs carried out with deionized water), as temperature rises, a solid yield decrease and a gas yield increase were observed. More specifically, at 220 °C, the gas yield increased at the expense of the liquid one. Indeed, as reported in literature, only a small amount of cellulose has been degraded at 220 °C [52], therefore the increase in gas yield was due to decarboxylation of organic acids derived from hemicellulose hydrolysis and dehydration. At 250 °C, the enhanced carbonization of biomass led to a noticeable decrease of hydrochar mass yield and gaseous phase increase.

Table 1. Mass yields (dry basis) and process water characterization. Solid and gas fractions were measured after each HTC test performed in triplicate; average values showed (Er% $\leq$ 1.5% for solid yield and 2.3% for gas yield). Average values of three pH and TOC measurements showed (Er% $\leq$ 0.4% for pH and 0.5% for TOC).

Sample	Mass Yields wt% d.b.			Process Water	
	Solid	Liquid [1]	Gas	pH	TOC (g/L)
180_R0	50.1%	43.7%	6.2%	3.87	16.06
220_R0	49.2%	40.7%	10.1%	4.40	13.30
250_R0	40.9%	44.4%	14.7%	4.66	9.70
180_R1	55.9%	37.6%	6.5%	3.95	18.82
220_R1	51.2%	37.6%	11.2%	4.49	16.92
250_R1	41.9%	43.4%	14.8%	4.69	14.25
180_R2	55.0%	38.1%	6.9%	3.97	20.08
220_R2	49.9%	38.7%	11.3%	4.50	17.79
250_R2	42.5%	42.8%	14.7%	4.70	18.06

[1] Computed by difference.

The liquid fraction resulting from HTC process contains water soluble substances like carboxylic acids, sugars, and reactive intermediates such as furfural and HMF [31]. During recirculation steps (R1 and R2), these organic compounds reacted and influenced properties of the HTC products in a different way according to the process temperature.

Dissolved organic matter in recirculated PW was involved in multiphase reactions.

At HTC temperatures of 180 and 220 °C, a fraction of organic acids like acetic, lactic, propionic, levulinic, and formic [17] was degraded to result in the formation of further gaseous compounds. At 250 °C, recirculation of process water did not lead to an increase of gas mass yield, probably due to the relatively low concentration of these acids in the aqueous solution.

An increase of hydrochar mass yield was observed at all three temperatures investigated; this effect was more pronounced at 180 °C (solid yield increase of about 6% after step R1). During second recirculation step, at temperatures of 180 and 220 °C, the solid yield increase was less pronounced while a modestly reverse trend was found at 250 °C.

Effects of PW recirculation on mass yields could be explained by an interaction of different chemical reaction pathways. During HTC process, water in subcritical conditions catalyzes hydrolysis of hemicellulose, cellulose, and lignin to produce small-chain polymers and monomers [20]. These compounds are subsequently dehydrated to form reactive intermediates (e.g., furans and furfurals) and organic acids [18,53]. Organic acids, accumulated in the recirculated PW, could promote further hydrolysis and decomposition of biomass polymers leading to a growing concentration of soluble intermediates. The intermediates could be involved in condensation and polymerization reactions to form solid phase aromatic clusters [44]. When their concentration reaches a certain value, the

new aromatic structures aggregate on the surface of hydrochar matrix and could being responsible for the solid yield increase [45].

Hence, during first recirculation step, the solid yield increase resulted in being less pronounced at higher temperatures probably due to the lower concentration of acids and soluble intermediates, which could promote hydrolysis and re-polymerization reactions, respectively.

During step R2, at 180 and 220 °C, the concentration of reactive intermediates could be decreased due to their solid precipitation that occurred in the previous recirculation cycle [42,44]; this might be the reason for the lower solid yield increase found. At 250 °C, the lower initial concentration of dissolved organic matter in the liquid phase, when compared to the process water obtained at 180 and 220 °C, probably led to a delayed accumulation of compounds with high reactivity. This could be the explanation for the greater solid yield increase obtained at 250 °C in the second recirculation step.

3.2. Effect of Temperature and PW Recycling on Hydrochars Properties

Raw biomass and hydrochars' volatile matter (VM), ashes (Ash), and fixed carbon (FC) content determined are reported in Table 2 (deviations of data measured through Er% are shown in Table S2 in Supplementary Materials).

Table 2. Proximate analysis and energy properties of raw LP and hydrochars. Proximate analysis performed in duplicate; average values showed (Er% $\leq$ 2.9%). Higher heating values (HHVs) average of two measurements, Er% $\leq$ 0.9.

Sample	Proximate Analysis wt% d.b.			Energy Properties		
	VM	Ash	FC [1]	HHV (MJ kg^{-1})	EDR (%)	EY (%)
Raw LP	75.0%	3.8%	21.2%	17.1	100.0	100.0
180_R0	65.3%	2.3%	32.4%	22.4	130.8	65.5
220_R0	58.1%	3.1%	38.8%	24.4	143.0	70.4
250_R0	50.5%	3.2%	46.3%	26.7	156.0	63.7
180_R1	63.6%	3.0%	33.4%	22.0	128.9	72.1
220_R1	59.1%	3.7%	37.1%	23.9	139.9	71.7
250_R1	51.6%	3.2%	45.2%	26.8	156.9	65.7
180_R2	62.6%	3.0%	34.4%	22.2	129.9	71.4
220_R2	58.1%	3.2%	38.7%	24.7	144.6	72.2
250_R2	51.7%	3.3%	45.1%	27.2	159.3	67.7

[1] Computed by difference.

As expected the highest VM content was found in the raw LP (VM = 75.0%). After step R0, proximate analysis shows a decrease in VM with increasing temperature while FC content follows an opposite trend. This is, as well documented in literature, due the enhanced carbonization of biomass at increasing temperature [54]. In recirculation steps, at 180 °C, the fixed carbon of hydrochars increased while volatile matter decreased. These could be related to the increased extent of condensation reaction (polymerization) of organic intermediates in liquid phase and to the increased decomposition of the staring material possibly promoted by increased acids activity, respectively as recently reported by Chen and co-workers [46].

At higher temperatures, VM and FC contents were only slightly influenced by PW recirculation.

With PW recirculation an increase of ash content was observed. This may be as a result of an increased concentration of inorganics into PW resulting on a lower leaching activity from the starting raw biomass [41,46].

In order to evaluate the increased ash content contribute in solid yield, obtained after recirculation steps, solid yield dry ash free (d.a.f.) was computed.

The results showed that the increased ash content slightly affected the solid yield increase at 180 °C and 220 °C while at 250 °C hydrochars yield remained almost unchanged (Figure 3).
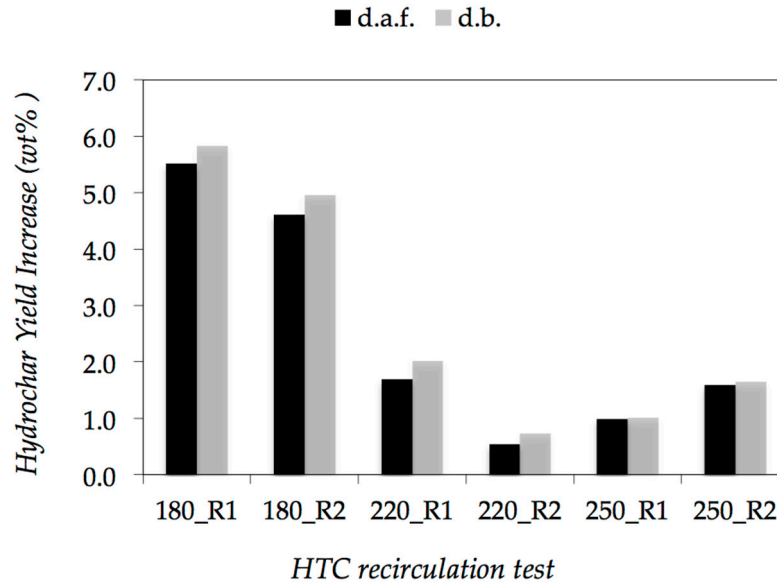

Figure 3. Contribute of ash content in hydrochar yield increase after recirculation steps.

All hydrochars exhibited higher HHV than the raw feedstock and the increased carbon content of the hydrochars obtained at higher temperatures underlines this result (Table 2). By recirculation, HHV of hydrochars remained nearly constant [41]. Due to the increase in hydrochars yield, energy yield significantly increased after recirculation steps (Figure 4).
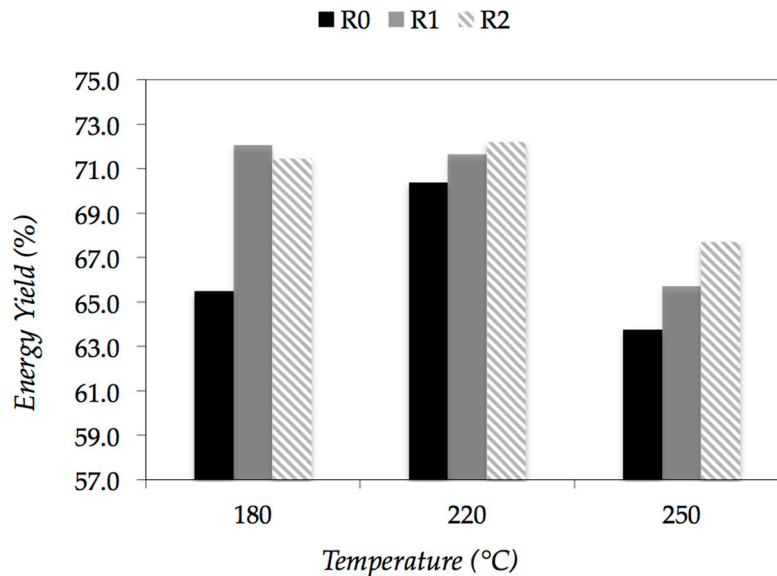

Figure 4. Effect of process water (PW) recirculation on hydrochars energy yield at the three temperatures investigated.

3.3. Process water pH and TOC

Process water obtained from HTC runs was characterized in terms of pH and TOC (Table 1). For all HTC tests, the pH of PW was in the acidic pH range and slightly increased after recirculation steps. This is in good agreement with observations done by previous researchers [41,45].

Particularly, the recirculation of PW led to an increase of pH from 3.87 to 3.97 at 180 °C, from 4.40 to 4.50 at 220 °C and from 4.66 to 4.70 at 250 °C.

It can be seen that the higher the temperature, the higher the pH, while it also appears that the pH became more or less stable after step R1.

As expected, TOC results showed a considerable increase in values after PW recirculation due to the increase of organic soluble compounds at each step, in addition to those produced in the previous cycle. Not surprisingly, this trend was more pronounced at higher HTC temperatures.

Trends of pH and TOC are consistent with the interpretation reported in the Section 3.1. At higher temperature, pH increased while TOC decreased, thus the concentration of organic acids and reactive compounds also reduced, leading to lower hydrochar yield increase during step R1. This explanation seems to be supported by the fact that, at a higher acid concentration, the degradation of biomass macro-components is promoted and newly formed compounds are added to the surface of hydrochar [44]. During step R2, the increment in TOC decreased probably because some of the dissolved organic matter took part in polymerization reactions (condensation). Organic acids were subjected to decarboxylation to form further gaseous products at temperatures of 180 and 220 °C. At 250 °C, TOC increased almost constantly during recirculation steps, probably due the lower initial concentration of soluble compounds, which led to a delay in reaching a dynamic equilibrium of organic species concentration in aqueous phase [42]. Thus, an increment of the concentration of reactive substances in the liquid phase at step R2 for HTC at 250 °C may have accelerated the rate of polymerization and led to a greater solid mass yield increase.

Recent literature [42,46,49] has reported that organic acids concentration in PW initially increases to reach a nearly constant value of a dynamic equilibrium thus the pH slight increase during recirculation can be also attributed to an inorganic ions (i.e., alkali metals) up-take [44,45].

4. Conclusions

Hydrothermal carbonization of agro-waste has been shown to be a viable technology to convert lignocellulosic waste biomass into energy dense solid biofuels. To mitigate the environmental effect and increase the economic appeal of HTC, the produced liquid fraction, which is highly concentrated in organic by-products such as carboxylic acids, sugars, and other water-soluble substances, must be properly valorized. This work described the effects of process water recirculation on solid and liquid products obtained after HTC tests carried out at temperatures of 180, 220, and 250 °C using dried lemon peel waste as starting material. The aim was to detect temperature influence, during the use of recirculated PW as a solvent, on hydrochar yield and properties and to suggest chemical pathways that could be involved during recirculation. Results have shown that PW recirculation can influence hydrochars properties positively. Hydrochar yield increased slightly with PW recycling and this effect was more pronounced at lower temperatures. Moreover, PW reuse has resulted in an increase of the energy yield. Hydrolysis of biomass macro-components could be promoted by organic acids dissolved in the recirculated PW leading to an increase of such compounds in the liquid phase promoting their reactivity. These compounds could undergo condensation reactions to yield more complex solid aromatic structures causing a solid mass yield increase. In the first recirculation step, as HTC temperature increased, the hydrochar yield increase was less pronounced. Indeed, an increase of about 6% was observed at 180 °C while solid yield increase decreased to 2% and 1% at 220 and 250 °C, respectively. In the second recycle step, at temperatures of 180 and 220 °C, a lower solid yield increase, when compared to the first recycle step (solid yield increase of 5% and 1% respectively), while at 250 °C, the delayed accumulation of reactive organic matter probably led to a greater increase in hydrochar production (hydrochar yield increase of 2%).

Volatile matter, fixed carbon, and HHV of hydrochars were only slightly influenced. Further experiments are required to assess how HTC operating conditions and number of

recirculation steps could improve hydrochars physicochemical properties and optimize the process for different biomasses as well as supporting the suggested reaction pathways. Moreover, an energy balance is required in view of an actual use of this strategy for large-scale applications. In conclusion, PW recirculation appears to be a suitable method to utilize the liquid by-product of HTC process, recovering energy and mitigating the possible environmental impact of the process itself. This strategy is aimed at both further carbon and energy recovery and reduction of water consumption for a cleaner production system of renewable solid biofuels.

Supplementary Materials: The following are available online at https://www.mdpi.com/2571-5577/4/1/19/s1, Figure S1: Piping and Instrumentation diagram (P&Id) of the HTC experimental system (TC = thermocouple; PI = pressure gauge; PID = temperature controller), Figure S2: HTC apparatus: (a) HTC system during heating phase; (b) HTC reactor cooled down through a massive stainless steel disc at $-10\ ^\circ$C; (c) HTC reactor cooled down through a stainless steel radiator with flowing tap water, Table S1: Mass yields (dry basis) and process water characterization (Er% with three replications), Table S2. Proximate analysis and energy properties of raw LP and hydrochars (Er% with two replications).

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Data Availability Statement: Data available on request from the authors.

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