



# Caffeinating the biofuels market: Effect of the processing conditions during the production of biofuels and high-value chemicals by hydrothermal treatment of residual coffee pulp

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## ABSTRACT

The manufacturing of coffee, one of the most popular beverages globally, renders enormous amounts of by-products and wastes, which may trigger severe environmental issues if not treated appropriately. The coffee pulp, resulting from the wet processing of coffee, is the predominant by-product, with around 10 Mt annually produced worldwide. For the first time, this work addresses the hydrothermal treatment of coffee pulp to produce biofuels and platform molecules, scrutinising the influence of the processing conditions (temperature, pressure, reaction time and solid/water ratio) on the process. This strategy allowed the transformation of coffee pulp into bio-crude and hydrochar in different yields (10–26% and 10–42%, respectively), depending on the conditions. The bio-crude included a pool of alkanes, carboxylic acids, ketones, phenols and nitrogen species, with varying quantities of C (54–71 wt%), H (6–7 wt%), O (18–34 wt%) and N (3–5 wt%) and a calorific value shifting from 23 to 32 MJ/kg. The hydrochar contained different proportions of C (57–72 wt%), H (4–6 wt%), O (20–35 wt%) and N (2–3 wt%) and had a calorific value between 22 and 29 MJ/kg. Process optimisation showed that up to 45% of the coffee pulp could be simultaneously converted into energy-rich (29 MJ/kg), merchantable liquid (20% bio-crude) and solid (24% hydrochar) biofuels during the treatment of a 15 wt% coffee pulp suspension at 320 °C and 162 bar for 1 h. At the same time, a bio-crude with a high proportion of profitable phenolic derivatives (42%) can be attained in high yield (25%) when a 5 wt% suspension is treated at 280 °C and 120 bar for 2 h. These promising results, along with the bespoke nature of this hydrothermal treatment, are a landmark achievement for the economy and sustainability of coffee producer countries, thus representing a pioneering step change towards the sustainable management of early-stage coffee leftovers.

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## 1. Introduction

Coffee, brewed from roasted coffee beans, is one of the most popular beverages in the world (Murthy and Madhava Naidu, 2012; Oktaviani et al., 2020) and the second-largest merchandised commodity after petroleum (Adam, 2020; Mussatto et al., 2011). It is produced in more than 70 different countries, and its production has increased over the past few years, reaching a worldwide production greater than 10 Mt a year (Oktaviani et al., 2020). As a

result, there has also been a substantial spread in the volume of residues generated from this activity, annually accounting for more than 15 Mt disposed of (Adam, 2020). The amount and nature of these leftovers depend on the methodology used for the transformation of the harvested coffee fruits into marketable coffee beans (Mussatto et al., 2011; Oktaviani et al., 2020), with two distinctive technologies being commonly employed, termed as dry and wet processing (Adam, 2020; Murthy and Madhava Naidu, 2012). In the dry method, coffee fruits are dried before being hulled mechanically to remove the husk (skin, pulp, mucilage and parchment) and the silverskin. In the wet process, the skin and the pulp of the sunken fruits are firstly removed mechanically. The pulp remnants and the mucilage layer are then removed by

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fermentation (Bonilla-Hermosa et al., 2014; Esquivel and Jiménez, 2012). As a result of these technical differences, the production of tradable coffee beans renders several by-products (Gurram et al., 2015; Oktaviani et al., 2020). On the one hand, in the dry process, a solid material termed as coffee hulk, containing the skin, pulp, mucilage and parchment, is released. On the other, the wet process discharges a large amount of water (coffee wastewater) along with three different solid fractions: the coffee pulp (including part of the skin), together with the mucilage and the parchment, which are produced in much fewer amounts.

Most of the studies addressing the valorisation of coffee by-products are limited to the spent coffee ground (Massaya et al., 2019), i.e., the end of life product resulted from coffee consumption, whose composition is significantly different to that of the spent coffee pulp produced during cultivation and processing (Murthy and Madhava Naidu, 2012). For example, of significant merit are the works developed by Codignole Luz et al. (2018), addressing an integrating carbonisation process, Dattatraya Saratale et al. (2020), utilising spent coffee for the manufacturing of catalysts and biopolymers and Arauzo et al. (2020), producing phenols via a dual delignification ultrasound extraction process. Nonetheless, the knowledge regarding the valorisation of the by-products produced at the early stages of the coffee production process is scarce (Murthy and Madhava Naidu, 2012; Mussatto et al., 2011). Accordingly, it is paramount to develop responsible management strategies and novel procedures for the treatment and valorisation of these residues. Of particular interest is the valorisation of the coffee pulp produced in the wet process. This technology is preferred over the dry process, as the coffee obtained is commonly attributed with a superior aroma and, therefore, a higher recognition (Adam, 2020; Oktaviani et al., 2020). Besides, the coffee pulp accounts for the vast majority of the solid fraction produced with this methodology (Adam, 2020; Murthy and Madhava Naidu, 2012). It corresponds to around 40 wt% of the original coffee berry, thus converting coffee pulp into the most critical solid residue discharged (Mussatto et al., 2011; Oktaviani et al., 2020).

Despite the increasing pollution awareness and waste minimisation policies, the proper management of coffee production wastes remains a challenge. Traditionally, the coffee pulp has been only used as fertiliser, livestock feed or compost. These applications use only small amounts of the pulp produced and are not technically very efficient. Also, the direct use of these by-products as animal food is not always appropriate, owing to the presence of antiphenological and antinutritional compounds such as tannins and caffeine (Murthy and Madhava Naidu, 2012; Mussatto et al., 2011). Consequently, there is still a need to find other alternative uses for this solid residue. Recent attempts have been directed towards the detoxification of this substrate to be used as animal food, along with the use of different processes to obtain value-added products (including fertilisers and compost, enzymes, and colourants, flavours and aroma for food) (Aristizábal-Marulanda et al., 2017), biomaterials (Esquivel and Jiménez, 2012) and bioenergy (Mussatto et al., 2011; Oktaviani et al., 2020).

These data represent a substantial attempt to manage coffee pulp; however, it is yet crucial to developing new approaches to accomplish a broad and greener valorisation of this by-product. The latter is in good agreement with the emerging circular economy philosophy and intrinsically linked to the United Nations Sustainable Development Goals (UN SDGs), as societies must strive towards a more environmentally friendly and sustainable future. They must also reduce inequalities and ensure decent work and economical and safe growth. Given this, a very appealing alternative that has not yet been considered for managing coffee pulp is manufacturing biofuels and building block platform molecules by

hydrothermal treatment (HTT). This thermochemical process is capable of converting the lignocellulosic biomass into a plethora of biofuels, value-added chemicals and biomaterials (bio-crude and hydrochar), using subcritical water (150–400 °C and 50–250 bar) as the reaction medium (Arcelus-Arrillaga et al., 2020; Dimitriadis and Bezergeanni, 2017; Elliott et al., 2015). Bio-crude is a brownish, viscous liquid with a superior energy density in comparison to the original biomass. It offers several environmental advantages over fossil fuels and has a somewhat elevated Higher Heating Value (HHV = 20–30 MJ/kg) (García-Pérez et al., 2007). Hydrochar is a solid bio-material with improved physicochemical and fuel properties than the original biomass. The chemical composition, surface properties, morphological characteristics and fuel properties of this solid are determined by the source of biomass and the technology and processing parameters used during their production (Cao et al., 2013). Therefore, the valorisation of spent coffee pulp into bio-crude and hydrochar might ensure a much cleaner coffee production worldwide, reduce waste and pollution, and contribute to decreasing environmental pollution and our current dependence on fossil fuels.

One of the main advantages of the HTT is that there is no need to dehydrate the feedstock or remove the water content of the liquid effluent under consideration, both factors substantially contributing to the improvement of the process energy efficiency (Remon et al., 2021). Besides, not only does HTT use much lower temperatures than other thermochemical processes commonly employed for the valorisation of biomass, such as fast pyrolysis and/or gasification, but also the biofuels (bio-crude and hydrochar) produced have superior physicochemical and fuel properties (Kumar et al., 2018; Toor et al., 2011). While most of the biomasses can be processed by HTT due to their hydrophilic nature and reasonable capability to form pumpable slurries, all work reported to date have focused on only a few types of feedstocks. These include lignocellulosic (wood, agricultural wastes, waste paper and spent coffee grounds) and algae biomasses, along with residual wet effluents, such as manures and sewage sludge (Gollakota et al., 2018). This approach can also be used for the valorisation of waste of different nature. For example, Khan et al. (2020) reported a very interesting work using quail beaks to synthesise solid catalysts to produce biodiesel from different oleaginous biomasses. Jamil et al. (2020) produced biodiesel from the transesterification of *Balanites Aegyptiaca* seed oil using a BaO–MoO<sub>2</sub> catalyst, while Inayat et al. (2019) produced biodiesel from waste cooking oil using solid catalysts derived from waste date seeds.

Although HTT has been used for the valorisation of spent coffee grounds (end of life coffee by-product), to the best of our knowledge, this technology has never been considered for the management of any of the most representative coffee by-products produced at the early stages of the process. Also, the fact that water is used as the reaction medium converts this process into an excellent candidate for the simultaneous management of the wet coffee pulp, either alone or in combination with the residual water stream obtained during the wet coffee manufacturing process. Herein, for the first time, this work explores the HTT of the coffee pulp obtained during the wet processing of coffee cherries harvested in Huatusco, Veracruz (Mexico), to manufacture marketable biofuels and value-added building block chemicals. Firstly, the effects of the processing conditions on the overall distribution of the reaction products (bio-crude, gas, hydrochar and liquid fraction yields) and the most essential physicochemical and fuel properties of the bio-crude and hydrochar have been thoroughly investigated. Then, the process has been optimised to find adequate processing conditions for the production of energy-dense liquid (bio-crude) and solid (hydrochar) biofuels and marketable value-added liquid chemicals. The rigorous analysis and process optimisation

conducted, along with the lack of works exploring the HTT of coffee pulp, demonstrate that this work represents a step forward in developing innovative and carbon-neutral methodologies for responsible management and sustainable valorisation of this unavoidable coffee by-product.

## 2. Material and methods

### 2.1. Coffee pulp production and characterisation

The coffee cherries were harvested in Huatusco, Veracruz (Mexico) and processed using the wet methodology. In particular, the coffee cherries were initially washed with water to remove dust and dirt remaining from the harvesting process. Then, 400 g of clean coffee cherry was placed in a 1 L container, along with 280 g of deionised water, and the slurry was left fermenting for 8 h at room temperature. The solid fraction was recovered from the aqueous effluent by filtration. Subsequently, it was thoroughly washed with deionised water to remove microorganisms and organic matter produced during the fermentation. The cherry was then peeled to separate the coffee bean from the pulp and the parchment fraction. These fractions were separated manually and dried individually for 20 h at 60 °C in a Blue M electric oven (model OV-18A) for research purposes and to avoid their decomposition during the experimentation. After drying, these fractions were quantified and stored. The coffee pulp fraction accounted for 29 wt % of the original coffee treated, which is in excellent agreement with the literature (Murthy and Madhava Naidu, 2012). The following techniques were used to analyse the structural composition and physicochemical properties of this solid: proximate and ultimate analyses, fibre composition and calorimetry. Proximate and ultimate analyses were conducted according to ISO-18134:2016, ISO-18122:2016 and ISO-18123:2016. The ash composition was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) on a Spectroblue (AMETEK) apparatus. Fibre composition (cellulose, hemicellulose and lignin contents) was determined by Van Soest titration (Hu et al., 2014), with the protein content being calculated using the N quantity attained by elemental analysis (Meneses et al., 2013). A Carlo Erba EA1108 Elemental Analyser was employed for the elemental analysis, while the HHV was determined in an Ika Werke C2000 calorimeter.

### 2.2. Hydrothermal upgrading procedure

The coffee pulp was hydrothermally treated in a 100 mL, high-pressure, batch reactor made of stainless steel and designed and manufactured by Parker Autoclave Engineers. The reaction vessel was heated employing an electric jacket, with the temperature being monitored and controlled by an internal thermocouple connected to a PID controller, and the pressure observed through a pressure gauge. A magnetic rotor (MagneDrive) was used to mechanically move a stirrer bar to homogenise the reaction mix with a coiled tube and a baffle, which produce turbulence in the reaction fluid. A more detailed description of the reactor is reported in previous publications (Ochoa et al., 2018; Remón et al., 2019a). In each trial, the reactor was loaded with 40 mL of deionised water together with different amounts of coffee pulp, depending on the experimental solid/water ratio used in the experiment. Subsequently, a tailored amount of N<sub>2</sub>, based on an internal calibration to achieve the desired pressure at reaction conditions, was introduced in the reactor. Once the reaction terminated, the reactor was quenched with cold water to drop the temperature to around 50–60 °C as rapidly as possible, conditions at which a gas sample was collected to determine the gas phase chemical composition.

Then, the reactor was depressurised, opened, and its content, consisting of a liquid-solid mix, was transferred to a flask. The stirrer bar and autoclave reactor were rinsed with chloroform and the products recovered were transferred to the same container. Afterwards, the solid fraction (hydrochar) was retrieved from the liquid product (bio-crude and aqueous phase) by vacuum filtration. The hydrochar was dried overnight at 105 °C, gravimetrically quantified and stored for subsequent characterisation. Then, the bio-crude was recouped from the aqueous phase via an optimised liquid-liquid separation, using chloroform (CHCl<sub>3</sub>) and ethyl acetate (EtOAc) as the solvents (Ren et al., 2017). The aqueous product was weighed and stored, while the bio-crude solubilised in the extraction mixture was recovered using a sequential procedure. In the first step, CHCl<sub>3</sub> and EtOAc were substantially removed in a rotary evaporator. Additionally, a stream of N<sub>2</sub> gas was used in a second step to vaporise both solvents and retrieve the bio-crude, which was quantified gravimetrically and stored for additional characterisation.

### 2.3. Response variables and analytical methods

The yields to gas, bio-crude, aqueous fraction and hydrochar together with key fuel and chemical properties of these fractions were used as the response variables to analyse the effects of the processing parameters on the HHT of coffee pulp. The processing conditions include the temperature (200–320 °C), pressure (120–180 bar), reaction time (20–180 min) and solid/water ratio (5–15 wt%). The upper limit for the temperature and pressure were selected based on safety issues, considering the saturation pressure of water and the maximum operating pressure of the reactor. The lower limit for the pressure was chosen to ensure the water was in the liquid phase at the temperature interval considered. The reaction time was varied to study a quick and lengthy treatment, while the solid/water ratio shifted from a diluted to a concentrated suspension. Table 1 lists these variables and the procedures used for their calculation. The composition of the gas phase was determined in a micro gas chromatograph (Varian CP4900) using two packed columns (Molecular sieve and Porapak) and a thermal conductivity detector. The gas yield was determined as the N<sub>2</sub>-free total amount of gaseous products in the mix, assuming an ideal gas behaviour at the collecting conditions. At the same time, the molar calorific value of each gas in the stream was used to determine the LHV of the mixture. The chemical composition of the bio-crude was determined by gas chromatography-mass spectroscopy (GC-MS) in an Agilent 7890 GC-system, using an Agilent HP-FFAP column. In this analysis, an aliquot of the bio-crude was solubilised in a mix comprising CHCl<sub>3</sub>/CH<sub>3</sub>OH (2:1 vol). The elemental compositions of the bio-crude and hydrochar were determined by Elemental Analysis using a Carlo Erba EA1108 Elemental Analyser, while the HHV of these fractions was calculated with the correlation established by Channiwala and Parikh (2002).

### 2.4. Experimental matrix and statistical analyses of the results

The experimental matrix to analyse the effects of the processing conditions (temperature, pressure, time and biomass/H<sub>2</sub>O ratio) on the HTT of coffee pulp was built up following a statistical 2 level 4 factor (2<sup>4</sup>) Box-Wilson Central Composite Face Centred (CCF,  $\alpha$ :  $\pm 1$ ) design. It contains 2<sup>4</sup> (16) experiments to evaluate the influence of linear effects and simple interactions, coupled with 4 centre points (intermediate conditions for all variables) to determine the error variance of the system (reaction, recovery and analysis), and 8 axial runs to evaluate the potential impact of quadratic effects (curvature) together with non-linear interactions. An analysis of variance (ANOVA) was used as the statistical tool to determine the variables

**Table 1**  
Response variables and methods.

Product	Response variable	Method
Gas	Gas yield (%) = $\frac{\text{mass of gas (g)}}{\text{mass of coffee pulp (g)}} \cdot 100$	GC/TCD
	Composition (vol. %) = $\frac{\text{mol of each gas}}{\text{total mol of gas}} \cdot 100$	GC/TCD
	LHV (MJ/m <sup>3</sup> STP) = 0.1079 H <sub>2</sub> (vol%) + 0.1263 CO (vol%) + 0.3581 CH <sub>4</sub> (vol%) (Perry and Green, 2008)	Estimated
Bio-crude	Bio – crude yield (%) = $\frac{\text{bio – crude (g)}}{\text{mass of coffee pulp (g)}} \cdot 100$	Gravimetric
	C, H, O, N, S (wt. %) = $\frac{\text{mass of C, H, O, N (g)}}{\text{mass of bio – crude (g)}} \cdot 100$	Elemental Analysis
	HHV (MJ/kg) = 0.3491 C (wt.%) + 1.1783 H (wt.%) – 0.1034 O (wt.%) – 0.015 N (wt.%) + 0.1005 S (wt.%). (Channiwal and Parikh, 2002)	Estimated
	Composition (Area %) = $\frac{\text{Area of each compound}}{\text{Total area of compounds}} \cdot 100$	GC/MS
Hydrochar	Solid yield (%) = $\frac{\text{mass of solid (g)}}{\text{mass of coffee pulp (g)}} \cdot 100$	Gravimetric
	HHV (MJ/kg) = 0.3491 C (wt.%) + 1.1783 H (wt.%) – 0.1034 O (wt.%) – 0.015 N (wt.%) + 0.1005 S (wt.%). (Channiwal and Parikh, 2002)	Estimated
	C, H, O, N (wt. %) = $\frac{\text{mass of C, H, O, N (g)}}{\text{mass of hydrochar (g)}} \cdot 100$	Elemental Analysis
Aqueous soluble products	Liquid yield (%) = $\frac{\text{liquid compounds (g)}}{\text{mass of coffee pulp (g)}} \cdot 100 = 100 - (\text{Gas yield} + \text{Bio – crude yield} + \text{Solid yield})$	Balance
Energy Efficiency	$E(\%) = \frac{\text{Gas yield} \cdot \text{LHV} + \text{Bio – crude yield} \cdot \text{HHV} + \text{Hydrochar yield} \cdot \text{HHV}}{\text{HHV coffee pulp}} \cdot 100$	Calculated

and interactions exerting a statistically significant effect on the process with 95% confidence ( $p$ -value < 0.05). Besides, the cause-effect Pareto test compared the relative impact of these factors on the experimental results. This allowed the classification of the variables and interactions attending their relevance. In both tests, the operating variables were coded to vary from –1 to 1, which allows a direct comparison to be gathered. Interaction plots were made from the formulae obtained from ANOVA analysis of the 28 runs conducted to visually represents the outcomes of the operating parameters and interactions. At the same time, in these interaction figures, some experimental data points were incorporated if feasible, to illustrate that the lack of fit is not meaningful. The least significant difference (LSD) bars represented in the interaction plots were obtained from the design, model, confidence interval and unexplained variation with 95% ( $p$ -value 0.05) of confidence. This methodology helps analyse the effects of processing variables and interactions in complex reaction systems, as demonstrated in the work of Inayat et al. (2020).

### 3. Results and discussion

#### 3.1. Coffee pulp characterisation results

Table 2 lists the physicochemical properties of the coffee pulp used in this work. Reasonably similar results for the fibre analyses to those reported by Bonilla-Hermosa et al. (2014) and Murthy and Madhava Naidu (2012) are observed.

#### 3.2. HHT of coffee pulp: effects of processing conditions

Table 3 lists the processing conditions and the experimental results obtained during the HTT of the coffee pulp. The influence of the conditions has been evaluated on the global distribution of the reaction products (gas, bio-crude, hydrochar and aqueous phase yields) along with some of the most crucial chemical and fuel properties of these products, such as the chemical and elemental analyses and the calorific values of the gas, bio-crude and hydrochar. After the bio-crude extraction, the aqueous phase mostly contains oligosaccharides and a few organic compounds. In the scope of this publication, the properties of the aqueous phase were

not analysed. The detailed influence of the processing conditions (ANOVA and Pareto analyses) is provided as supplementary material in Table S1. The formulae recapped in Table S1 have been used to develop the interaction plots shown as follows, to visually address, compare and study the impact of the processing parameters and interactions on the experimental results.

##### 3.2.1. Reaction products distribution

The HHT of coffee pulp originates four fractions: gas, bio-crude, hydrochar and aqueous soluble products. The yields to these fractions depend on the processing conditions and vary as follows: 4–14%, 10–26%, 10–42% and 41–57%, respectively. The Pareto test (Table S1) reveals that the gas yield is primarily affected by the temperature and pressure and its interaction with the solid loading. Simultaneously, the temperature, time and solid/water ratio are the operating variables exerting the most significant influence on the bio-crude, hydrochar and aqueous phase yields. These influences correlate well with the parametric analysis conducted by Madsen et al. (2017) for different types of biomass. These influences and interactions are visually represented in Fig. 1. In particular, Fig. 1 a/ e/i/m and b/f/j/n shows the influence on the overall reaction products of the temperature at 120 and 180 bar (pressure interval used in this work) when a low solid loading (5 wt%) is used for a quick (20 min) and extended (180 min) process, respectively. These same outcomes are plot in Fig. 1 c/g/k/o and d/h/l/p for a 15 wt% solid loading.

The effect of the temperature on the gas and aqueous fraction yields is primarily induced by the reaction time. Irrespective of the solid loading, the gas yield is relatively low and practically unaffected by the temperature for a brief reaction time (20 min) and a low pressure (120 bar). In contrast, the aqueous yield increases linearly as the temperature augments from 200 to 320 °C. These developments suggest that at a low temperature and using a short reaction time, gas formation is primarily the result of the decomposition of labile organic matter in the coffee pulp, such as lipids and waxes, via hydrolysis, decarboxylation and thermal cracking. Furthermore, the levelling-off for gas production might also result from the competition between different types of reactions involved in the HTT. These transformations comprise, on the one end cracking and pyrolysis, which promote the gas formation, and on



**Table 2**  
Spent coffee pulp characterisation.

Proximate analysis (wt.%)	
Moisture	7.42 ± 2.43
Volatiles	67.24 ± 1.87
Fixed carbon	16.61 ± 0.47
Ash	8.73 ± 0.13
<b>Fibre analysis (wt.%)</b>	
Cellulose	14.20 ± 0.25
Hemicellulose	24.10 ± 1.28
Lignin	17.20 ± 2.27
Proteins	13.10 ± 0.24
Ash	8.73 ± 0.19
Others (lipids, waxes)	22.60 ± 1.45
<b>Ash Composition (wt.%)</b>	
K	77.99
Ca	12.76
P	3.87
Mg	3.42
Na	0.89
Fe	0.32
Si	0.57
Al	0.18
<b>Elemental analysis (wt.%)</b>	
C	42.40 ± 1.47
H	5.71 ± 0.24
N	2.17 ± 0.07
O <sup>a</sup>	49.57 ± 1.35
HHV (MJ/kg)	15.39 ± 0.53

<sup>a</sup> Oxygen was calculated by difference.

the other, condensation, crystallisation and re-polymerisation, which favours bio-crude and hydrochar productions (Dimitriadis and Bezergianni, 2017; Xu and Lancaster, 2008).

Under these conditions, increasing the pressure results in a slight decrease in the gas yield due to an increase in the aqueous fraction yield, particularly between 220 and 300 °C. Augmenting the pressure promotes the diffusion of water into the core structure of the coffee pulp, thus favouring a more intimate solid-water interaction. At the same time, the auto dissociation of water also spreads with rising the pressure (Schienbein and Marx, 2020), which leads to an increase in the concentration of protons in the liquid phase, which can promote acid-catalysed reactions. As a result of all these developments, hydrolysis reactions happen to a more substantial extent (Dimitriadis and Bezergianni, 2017; Gollakota et al., 2018), which favours the production of water-soluble liquid species (Kumar et al., 2018; Thiruvengadam et al., 2015). As an outcome, at high pressure (180 bar), gas formation takes place in two steps and competes against the formation of liquid products. Increasing the temperature from 200 to 250 °C drops the gas yield and upsurges the aqueous fraction yield. This pressure enlargement favours water penetration into the coffee pulp core structure, aiding in the reaction of the material. This promotes the formation of reactive species which evolve towards the formation of aqueous soluble products (Madsen et al., 2017; Madsen and Glasius, 2019), principally high-molecular-weight oligomers via hydrolysis (Lorente et al., 2019; Remón et al., 2019b), rather than the direct decomposition of the material by pyrolysis or thermal cracking to produce gaseous species. However, an additional upsurge up to 320 °C declines the aqueous fraction yield due to the increase observed in the gas yield, thus suggesting the transformation into gases of the organic compounds initially solubilised in the aqueous phase. This is the result of pyrolysis and thermal cracking reactions being more likely to happen at high temperature (Madsen and Glasius, 2019; Remón et al., 2019b).

Besides, variations in the reaction time modify the effects of the temperature and pressure. Regardless of the solid loading and the pressure, an increase in the reaction time from 20 to 180 min

decreases the gas formation between 220 and 300 °C at the expense of the aqueous fraction yield. For a fast HTT (20 min), the labile biomass content, which readily decomposes to gaseous products, is responsible for the high gas yield. On the contrary, a more prolonged exposure of the biomass to hydrothermal conditions allows a more significant extension of biomass hydrolysis and depolymerisation reactions, thus increasing the production of water-soluble liquids to the detriment of the formation of gas. It is also important to note that these variations are notably more significant for low than for high pressures, as the positive kinetic effect of the pressure can disguise the kinetic influences of the reaction time. More precisely, the use of a high pressure favours not only the initial liquid production but also its subsequent decomposition into gaseous species. As a result, when a reaction time of 180 min is used, between 200 and 250 °C, the gas yield decreases to the detriment of the increase taking place in the aqueous fraction yield. In contrast, a further increase up to 320 °C leads to the opposite outcome, i.e., the gas yield increases and the liquid yield drops due to the gradual conversion into gaseous products of species solubilised in the aqueous phase (Dimitriadis and Bezergianni, 2017; Gollakota et al., 2018).

The impact of the temperature on the yields to bio-crude and hydrochar is substantially influenced by the solid loading used during the HTT. For a 5 wt% solid loading, increasing the temperature promotes the formation of bio-crude at the expense of hydrochar. These variations take place irrespective of the reaction time or system pressure and are particularly marked between 200 and 280 °C. A further increase in the temperature up to 320 °C does not substantially modify the yields to these factions, and a trade-off takes place. These facts suggest that at low temperature, biomass depolymerisation and fragmentation take place to a considerable extent, leading to the formation of oligomers and reactive fragments evolving towards the formation of water soluble-products and hydrochar (Gollakota et al., 2018). Conversely, increasing the temperature enhances the production of bio-crude at the expenses of hydrochar. This might be an outcome of the favourable effect of the temperature, promoting the recombination of the reactive

**Table 3**

Hydrothermal treatment of coffee pulp: processing conditions and experimental results.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17–20	21	22	23	24	25	26	27	28
T (°C)	200	320	200	320	200	320	200	320	200	320	200	320	200	320	200	320	260	200	320	260	260	260	260	260	260
P (bar)	120	120	180	180	120	120	180	180	120	120	180	120	180	120	180	180	150	150	150	120	180	150	150	150	150
t (min)	20	20	20	20	180	180	180	180	20	20	20	20	180	180	180	100	100	100	100	100	100	20	180	100	100
Solid/water (wt.%)	5	5	5	5	5	5	5	5	15	15	15	15	15	15	15	15	10	10	10	10	10	10	10	5	15
<b>Global results</b>																									
Gas yield (%)	6.52	7.07	8.70	7.97	7.71	6.90	9.04	9.48	5.61	6.50	6.00	7.13	4.05	7.78	5.88	8.68	7.92 ± 1.44	5.94	8.43	7.37	5.12	7.71	4.11	7.43	7.29
Aqueous yield (%)	47.17	52.28	44.55	52.09	45.32	57.15	42.02	55.23	41.39	52.98	42.05	51.12	46.68	54.98	42.78	54.51	49.43 ± 0.99	44.28	49.50	48.57	51.99	51.00	56.18	50.34	50.15
Hydrochar yield (%)	30.79	16.16	35.84	13.72	27.99	12.16	31.42	10.57	39.60	20.36	41.71	20.33	37.94	18.98	38.34	17.62	24.24 ± 0.66	36.34	16.23	24.31	24.62	23.91	23.33	18.75	26.96
Bio-crude yield (%)	15.52	24.49	10.90	26.23	18.98	23.79	17.53	24.73	13.40	20.17	10.24	21.42	11.33	18.26	13.00	19.20	18.33 ± 2.07	13.45	25.84	19.75	18.27	17.39	16.38	23.47	15.60
<b>Gas composition and LHV</b>																									
H <sub>2</sub> (vol%)	12.48	3.62	11.10	5.39	4.76	13.13	12.10	10.26	7.40	5.96	6.11	1.21	3.57	4.56	5.85	4.89	4.39 ± 3.32	6.78	6.07	3.64	0.85	4.47	4.03	3.89	4.08
CO <sub>2</sub> (vol%)	61.25	87.67	45.14	90.18	66.55	69.81	53.67	70.07	69.56	89.48	70.00	95.86	76.89	92.13	71.17	84.83	76.76 ± 10.52	65.26	78.11	88.12	93.62	72.41	79.41	74.10	79.92
CO (vol%)	12.84	8.71	17.77	4.43	10.84	8.84	11.19	9.46	10.10	2.04	8.90	2.64	8.07	0.68	9.29	3.51	8.46 ± 2.37	15.60	7.64	5.33	5.53	12.09	4.48	10.61	7.79
CH <sub>4</sub> (vol%)	13.43	0.00	25.98	0.00	17.85	8.22	23.04	10.20	12.93	2.52	14.98	0.30	11.46	2.63	13.70	6.76	9.88 ± 5.05	12.37	8.19	2.91	0.00	11.04	12.09	11.40	8.22
LHV (MJ/m <sup>3</sup> STP)	7.78	1.49	12.75	1.14	8.27	5.48	10.97	5.96	6.71	1.80	7.15	0.57	5.51	1.52	6.71	3.39	5.15 ± 2.43	7.13	4.55	2.11	0.79	5.96	5.33	5.84	4.37
<b>Bio-crude elemental composition and HHV</b>																									
N (wt.%)	4.07	2.90	4.32	2.97	3.97	2.81	3.93	2.71	4.35	3.63	4.74	3.67	4.47	3.74	4.59	3.62	4.19 ± 0.13	4.69	3.52	3.99	4.14	4.13	3.86	3.96	4.59
C (wt.%)	59.20	65.53	59.20	63.47	57.40	69.47	57.07	66.77	57.70	66.23	58.30	67.67	59.70	70.87	56.00	67.83	62.85 ± 9.77	53.97	66.57	61.47	59.47	59.17	64.97	62.13	61.43
H (wt.%)	6.53	6.88	6.33	6.70	6.44	7.27	6.53	6.86	6.57	6.92	6.62	7.24	6.84	7.48	6.44	7.06	6.79 ± 0.07	7.00	7.18	6.77	6.52	6.55	7.06	6.81	6.70
O (wt.%)	30.12	24.67	30.04	26.81	32.06	20.43	32.36	23.66	31.29	23.22	30.25	21.31	28.87	17.87	32.85	21.49	26.03 ± 13.47	34.24	22.68	27.70	29.75	30.12	24.10	27.08	27.25
S (wt.%)	0.08	0.01	0.11	0.05	0.12	0.02	0.11	0.00	0.09	0.00	0.09	0.12	0.11	0.05	0.13	0.00	0.07 ± 0.01	0.10	0.05	0.08	0.12	0.04	0.01	0.02	0.02
HHV (MJ/kg)	25.19	28.39	24.96	27.23	24.26	30.67	24.22	28.90	24.59	28.82	24.96	29.90	25.86	31.65	23.68	29.72	27.28 ± 2.95	23.48	29.31	26.52	25.31	25.20	28.45	26.85	26.46
<b>Hydrochar elemental composition and HHV</b>																									
N (wt.%)	2.27	2.83	2.16	2.93	2.61	2.88	2.38	2.93	2.51	3.21	2.45	3.22	2.52	3.12	2.59	3.19	3.21 ± 0.11	2.39	3.12	3.14	3.22	3.12	3.20	3.13	3.34
C (wt.%)	58.80	66.80	56.70	66.20	60.70	69.80	60.10	69.90	58.80	70.90	57.20	71.50	60.70	71.90	61.20	71.10	68.9 ± 3.91	60.60	71.80	67.10	69.80	67.10	70.10	70.00	70.50
H (wt.%)	5.36	4.68	5.52	4.40	4.86	4.73	5.26	4.67	5.46	4.73	5.21	5.14	5.31	4.93	5.41	4.61	5.03 ± 0.32	5.37	4.94	4.87	5.28	5.14	5.24	5.13	5.35
O (wt.%)	33.49	25.49	35.48	26.31	31.70	22.30	32.17	22.29	33.09	20.97	35.03	19.89	31.34	19.92	30.68	20.95	22.68 ± 6.44	31.51	19.92	24.68	21.54	24.48	21.28	21.58	20.62
S (wt.%)	0.08	0.20	0.14	0.16	0.13	0.29	0.09	0.21	0.14	0.19	0.11	0.25	0.13	0.13	0.12	0.15	0.17 ± 0.01	0.13	0.22	0.21	0.16	0.16	0.18	0.16	0.19
HHV (MJ/kg)	23.35	26.17	22.61	25.55	23.61	27.62	23.82	27.58	23.51	28.13	22.46	28.94	24.18	28.81	24.54	28.05	27.61 ± 2.61	24.20	28.80	26.58	28.33	26.92	28.41	28.22	28.75
<b>Bio-crude chemical composition (% Chromatography area)</b>																									
Alkanes	2.93	10.81	1.59	11.37	3.17	18.28	0.00	4.82	0.00	2.76	0.00	2.85	0.00	4.21	0.00	2.46	2.26 ± 0.18	0.00	4.99	9.20	0.00	2.12	0.42	0.00	0.00
Aldehydes	0.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.87	0.00	0.83	0.10 ± 0.01	0.00	0.67	0.00	0.00	0.00	0.00	0.00	0.00
Carboxylic acids	0.86	11.56	0.00	14.73	0.00	6.83	4.09	9.15	5.16	13.17	8.93	30.63	9.49	15.02	11.02	6.96	8.42 ± 1.02	11.09	15.24	4.02	14.95	4.55	19.44	15.90	10.25
Ketones	8.66	16.90	3.92	15.87	2.61	25.27	8.25	28.49	6.57	21.04	5.48	15.44	1.51	27.16	2.23	27.92	8.56 ± 0.69	2.63	29.68	15.42	8.95	10.51	9.30	10.29	7.22
Phenols	5.71	33.07	4.52	32.14	8.61	27.37	5.19	28.95	6.46	34.49	5.09	22.56	4.40	30.13	4.79	38.35	19.36 ± 0.52	5.00	26.01	37.73	15.04	11.47	19.10	20.55	17.12
Alcohols	0.00	0.00	0.00	0.00	0.00	0.00	1.09	0.00	1.04	0.00	0.00	0.73	1.67	0.00	1.53	0.00	0.55 ± 0.39	1.16	0.00	0.00	0.97	0.00	0.74	0.00	1.45
Furans	4.12	0.00	7.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.27	0.00	2.05	0.00	0.00	0.00	0.51 ± 0.43	0.00	0.00	0.00	0.00	0.00	0.00	1.84	0.00
Cyclic compounds	0.00	3.49	0.00	0.98	0.00	3.86	0.00	1.78	0.00	1.08	0.00	3.22	0.00	4.87	0.00	5.18	0.56 ± 0.67	0.00	1.78	0.00	1.02	0.00	1.01	1.10	1.08
Nitrogen compounds	75.81	18.41	82.48	24.91	79.00	12.18	79.18	19.12	78.63	19.24	77.23	20.67	80.88	16.13	79.64	16.58	57.92 ± 2.49	79.30	13.44	27.41	55.67	70.24	45.94	47.26	60.03
Benzenes	1.26	5.76	0.00	0.00	6.62	6.22	2.20	7.71	2.13	8.22	0.00	3.90	0.00	1.62	0.79	1.73	2.83 ± 0.28	0.81	8.19	6.22	3.42	1.10	4.04	3.06	2.85

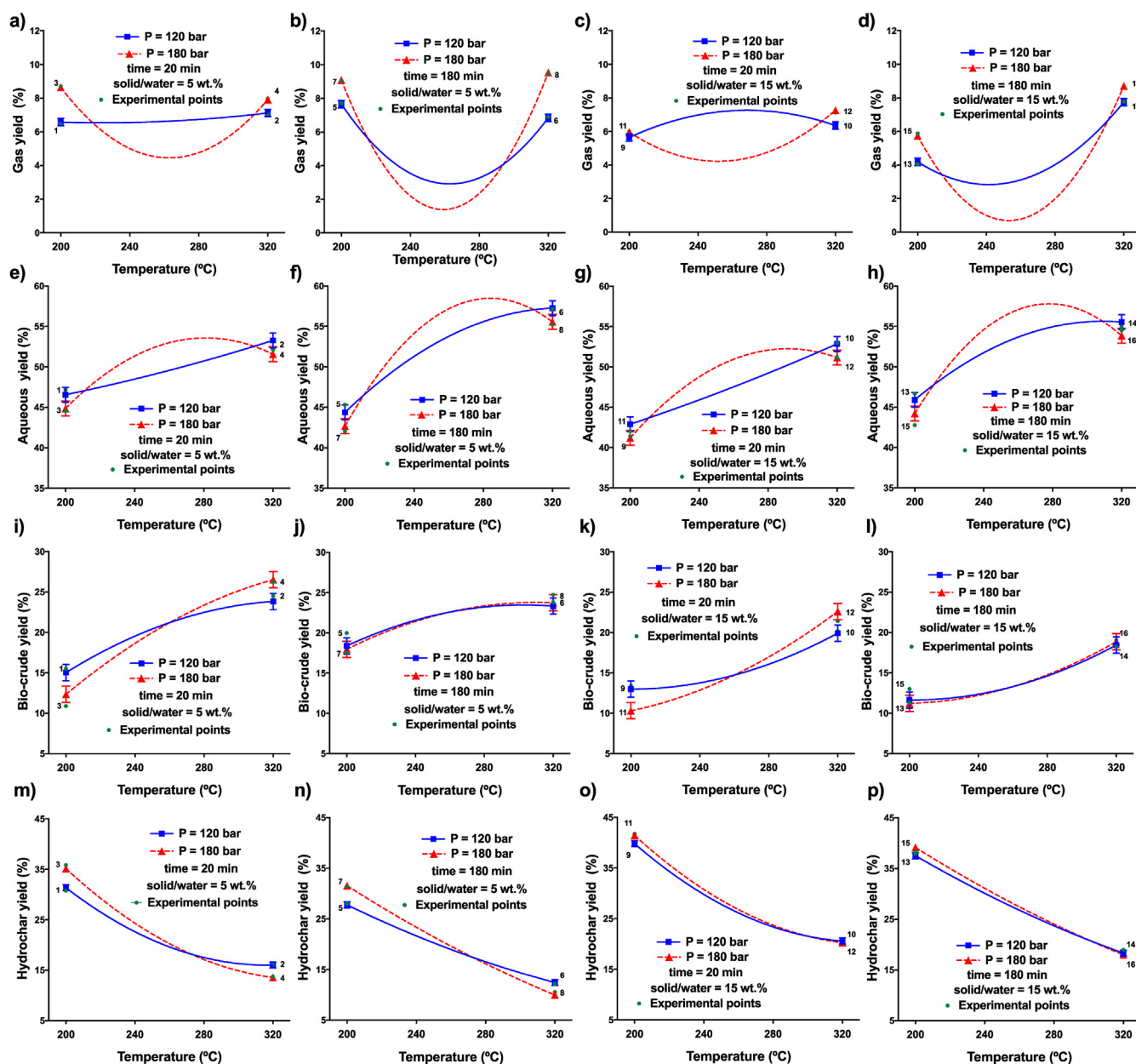


Fig. 1. Impact of the HTT reaction parameters on the distribution of the overall reaction products.

fragments produced in the early steps of the process via depolymerisation, thus leading to the bio-crude formation (Gollakota et al., 2018; Remón et al., 2019b). Several authors addressing the HTT of biomass have reported that bio-crude production increases up to around 300 °C and then, either stabilises or drops, such a phenomenon that has been attributed to the thermodynamics of the process (Madsen et al., 2017; Madsen and Glasius, 2019). In particular, bio-crude production via liquefaction is endothermic at low temperatures and exothermic at high temperatures, promoting bio-crude formation until the temperature reaches a point after which liquefaction is suppressed (Kumar et al., 2018; Muppaneni et al., 2017). Besides, other authors have suggested that this behaviour is a result of the competition between hydrolysis, promoting bio-crude formation, and repolymerisation, enhancing the formation of hydrochar (Dimitriadis and Bezergianni, 2017).

Increasing the solid loading in the water suspension from 5 to 15 wt% alters the impact of the temperature on the bio-crude and

hydrochar yields due to the significant role of the water on the process. At low temperature (200–250 °C), such an increase in the solid loading diminishes the bio-crude formation at the expenses of the formation of hydrochar. The lower amount of water in the reaction medium promotes condensation, cyclisation, crystallisation and/or repolymerisation reactions (Xu and Lancaster, 2008), leading to hydrochar production (Dimitriadis and Bezergianni, 2017; Gollakota et al., 2018). Besides, with the use of high solid loadings, it is necessary to have higher temperatures to promote the formation of bio-crude, due to the lower amount of water available for depolymerisation and hydrolysis reactions. As such, the increase in the bio-crude yield with increasing the temperature displays a concave trend, rather than the convex pattern shown when a low solid loading is used. This indicates that the trade-off commonly observed for the bio-crude yield depends on the solid loading and reaction time. Therefore, higher temperatures and longer reaction times are required to transform coffee pulp into bio-crude and

observe a levelling in this product. This explains the steadiness in the bio-crude yield between 200 and 250 °C and the sharp increment with a further increase in the reaction temperature up to 320 °C. Conversely, the hydrochar yield shows the same pattern with the temperature regardless of the solid loading. However, the higher the solid/water ratio, the greater is the hydrochar produced, which confirms that solid formation is favoured using a concentrated suspension as condensation and cyclisation reactions happen to a more significant extent (Bonilla-Hermosa et al., 2014). The reaction time and total pressure outcomes are also relatively weak, and the same trends described for a diluted suspension are observed during the processing of a concentrated suspension.

The influences of the reaction time and pressure are less critical and are not affected by the solid loading. Increasing the reaction time from 20 to 180 min drops the bio-crude yield and promotes the formation of hydrochar at high temperature. This accounts for hydrothermal carbonisation reactions (condensation, crystallisation and/or repolymerisation) (Xu and Lancaster, 2008) taking place to a more significant extent with the use of lengthy hydrothermal treatments. As a result, for a HTT conducted at 180 min, the bio-crude and the hydrochar yields display a trade-off between 280 and 320 °C, especially at low pressures. Moreover, the effect of the pressure is negligible, and an increase between 120 and 180 bar leads to minor increases in the bio-crude yield and drops the hydrochar yield at elevated temperatures due to the beneficial impact of the pressure during the HTT, as described earlier.

### 3.2.2. Gas phase chemical composition and LHV

The gas stream is made up of H<sub>2</sub> (1–13 vol%), CO<sub>2</sub> (45–96 vol%), CO (1–39 vol%) and CH<sub>4</sub> (1–23 vol%) and has a LHV shifting between 1 and 13 MJ/m<sup>3</sup> STP. The parameters exerting the most important influence on its composition and LHV (Pareto test Table S1) are the temperature, pressure and water/solid ratio; with the relative amount of H<sub>2</sub> also being greatly influenced by the interaction between the pressure and reaction time. Fig. 2 a/e/i/m/q and b/f/j/n/r shows the influence of the temperature for a 5 wt% suspension at 120 and 180 bar, for 20 and 180 min, respectively. Fig. 2 c/g/k/o/s and d/h/l/p/t shows these outcomes for a solid/water ratio of 15 wt%.

The effect of the temperature on the volumetric gas composition largely depends on the pressure and solid loading. When a diluted suspension (5 wt%) is hydrothermally treated, regardless of the pressure, augmenting the temperature from 200 to 250 °C leads to an increase in the relative amount of CO<sub>2</sub>, together with drops in the concentrations of H<sub>2</sub>, CO and CH<sub>4</sub>; with these changes leading to a substantial reduction in the LHV of the gas. Increasing the temperature endorses the development of decarboxylation, pyrolysis, thermal decomposition and cracking reactions (Xu and Lancaster, 2008), with all these transformations resulting in a gas product essentially comprising CO<sub>2</sub>. This is in good agreement with several works addressing the HTT of biomass (Dimitriadis and Bezergianni, 2017; Gollakota et al., 2018). A subsequent increase in the temperature up to 320 °C upsurges the relative content of H<sub>2</sub> and diminishes the concentration of CO<sub>2</sub>, without significantly altering the fractions of CO and CH<sub>4</sub> in the gaseous stream. These variations are accounted for by the exothermic nature of the water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ) (Remón et al., 2016a) and the endothermic character of the methane reforming reaction ( $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$ ) (Remón et al., 2015, 2016b), which overall produce an upturn in the concentration of H<sub>2</sub> in the mix. The effect of the pressure is particularly marked at low temperatures (200–230 °C), the interval at which boosting the pressure from 120 to 180 bar results in a reduction in the relative amounts of H<sub>2</sub> and CO<sub>2</sub> coupled with increments in the proportions of CO and CH<sub>4</sub> and the LHV of the gas product. According to Le Chatelier's Principle, an

increase in the pressure thermodynamically shifts the methane reforming reaction towards CH<sub>4</sub> formation, which accounts for the variations observed in the composition of the gas. An increase in the reaction time does not substantially alter the impacts of the temperature or pressure on the gas properties. However, the increases and decreases observed at high temperature in the concentrations of H<sub>2</sub> and CO<sub>2</sub>, respectively, are accentuated, as so are the increases in the relative amount of CO and LHV of the gas product. This suggests that these transformations might also be kinetically controlled so that an increase in the reaction time allows the gas phase to reach compositions closer to the thermodynamic equilibrium.

The effect of the solid/water ratio is determined by the HTT temperature (Fig. 2 a/b, e/f, i/j, m/n and q/r vs Fig. 2 c/d, g/h, k/l, o/p and s/t). Between 200 and 250 °C, irrespective of the reaction time (20–180 min), increasing the solid loading from 5 to 15 wt% leads to decreases in the concentrations of H<sub>2</sub> and CH<sub>4</sub> at the expense of CO<sub>2</sub> formation, with these alternations dropping the LHV of the gas. Conversely, at high temperature, the effect of the solid/water ratio depends on the reaction time. For a short reaction time (20 min), the solid/water ratio does not affect the gas composition considerably. In comparison, for a lengthy HTT (180 min), such an increase leads to an extensive depletion in the proportions of H<sub>2</sub> and CO, together with an increase in the relative amount of CO<sub>2</sub>. The increases in the relative amount of CO<sub>2</sub>, taking place along with diminishments in the proportions of H<sub>2</sub>, CH<sub>4</sub> or CO, are believed to be the result of a more significant extension of coffee pulp decarboxylation, thermal cracking and pyrolysis (promoting CO<sub>2</sub> formation) occurring when high solid/water loadings are used, in comparison to the hydrolysis or depolymerisation of this biomass (Egües et al., 2010; Piñkowska et al., 2014). Also, increasing the solid/water ratio varies the effect of the temperature and pressure. Although similar trends are observed for the volumetric composition and LHV of the gas, these are less marked due to the lower excess of water. Besides, the pressure exerts a weaker influence on the gas composition and its impact is only significant for a short reaction time at intermediate temperatures. Under such conditions, an upturn in the pressure decreases the proportion of H<sub>2</sub> at the expenses of the relative amount of CO<sub>2</sub> in the gas, probably as the result of the beneficial influence of the pressure on decarboxylation reactions (Xu and Lancaster, 2008).

### 3.2.3. Bio-crude elemental composition and HHV

The amounts of C, H, O, N and the HHV of the bio-crude vary by 54–71 wt%, 6–7 wt%, 18–34 wt%, 3–5 wt% and 23–32 MJ/kg, respectively. The statistical analysis (Pareto principle, Table S1) reveals that the temperature has the strongest influence on the bio-crude elemental composition and HHV, with the relative amount of N being also substantially influenced by the solid/water ratio. These data are in line with the influences reported by other authors studying the impact of the processing variables on some of the characteristics of bio-crudes produced from the HTT of biomass (Madsen et al., 2017; Madsen and Glasius, 2019). Fig. 3 a/e/i/m/q and b/f/j/n/r shows the influence of the temperature for a 5 wt% suspension at 120 and 180 bar for 20 and 180 min, respectively. Fig. 3 c/g/k/o/s and d/h/l/p/t shows these outcomes for a solid/water ratio of 15 wt%.

The effect of the temperature on the elemental composition of the bio-crude primarily depends on the reaction time. For a short reaction time (20 min), regardless of the pressure, the temperature does not meaningfully alter the elemental composition of the bio-crude between 200 and 250 °C. Within this temperature range, small reductions in the proportions of C and H take place, resulting in a slightly higher O content in the bio-crude; which leads to a slight decline in its HHV. The opposite was observed with an



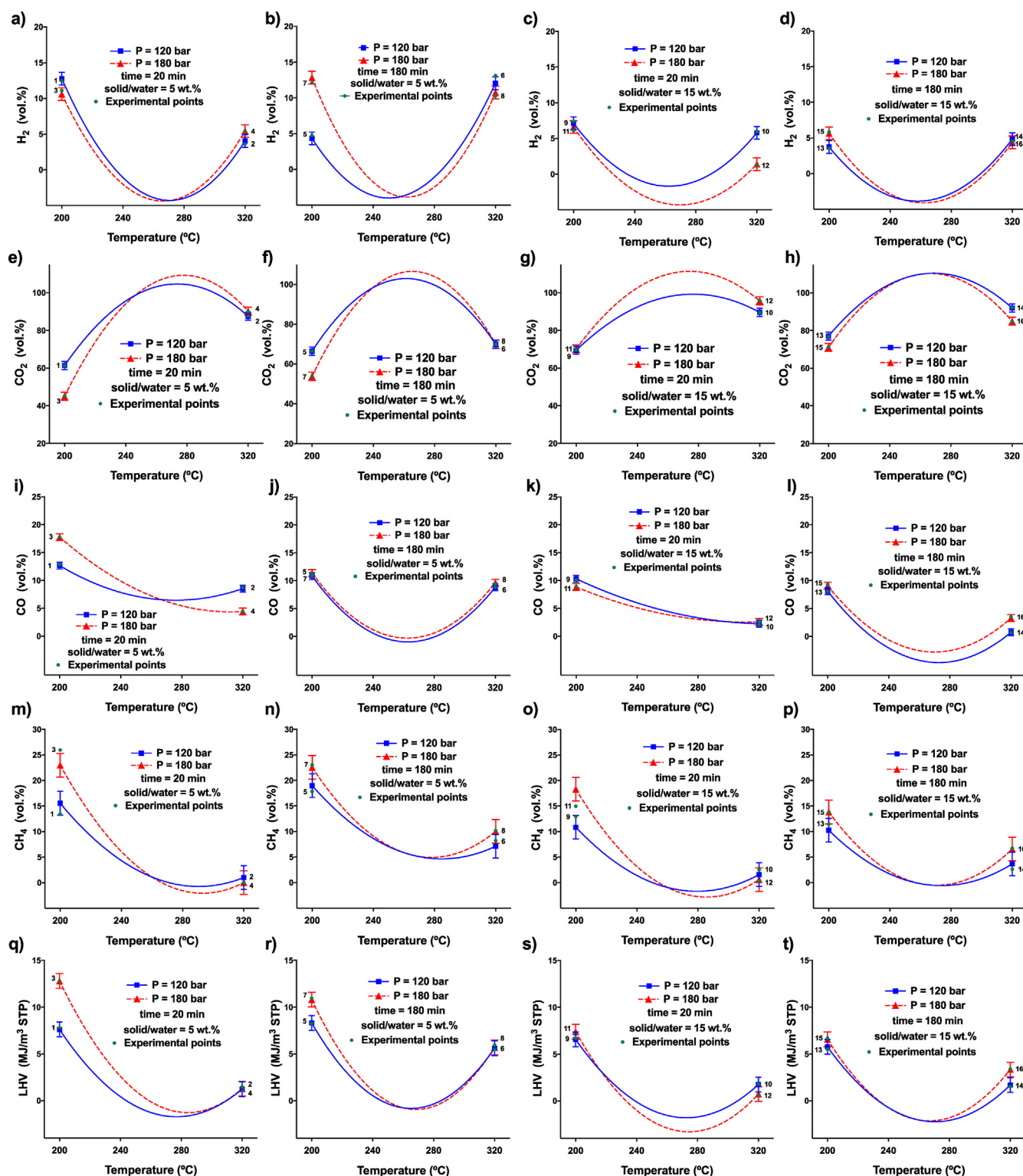


Fig. 2. Impact of the HTT reaction parameters on the chemical composition and LHV of the gas phase.

additional increase in the temperature up to 320 °C, resulting in higher C and H contents at the expenses of the proportion of O, which enhances the HHV of the bio-crude. The relative amount of N is relatively low and decreases between 200 and 320 °C. All these variations are a result of the beneficial kinetic impact of the reaction temperature on the deoxygenation, deamination and thermal

cracking reactions (Duan et al., 2013; Duan and Savage, 2011a, b; Fisk et al., 2009). Enlarging the reaction time from 20 to 180 min improves the bio-crude HHV due to the higher C and H contents in the bio-crude. These developments are accounted for by the influence of reaction time on the kinetics of the process, as a longer reaction time promotes decarboxylation and thermal cracking

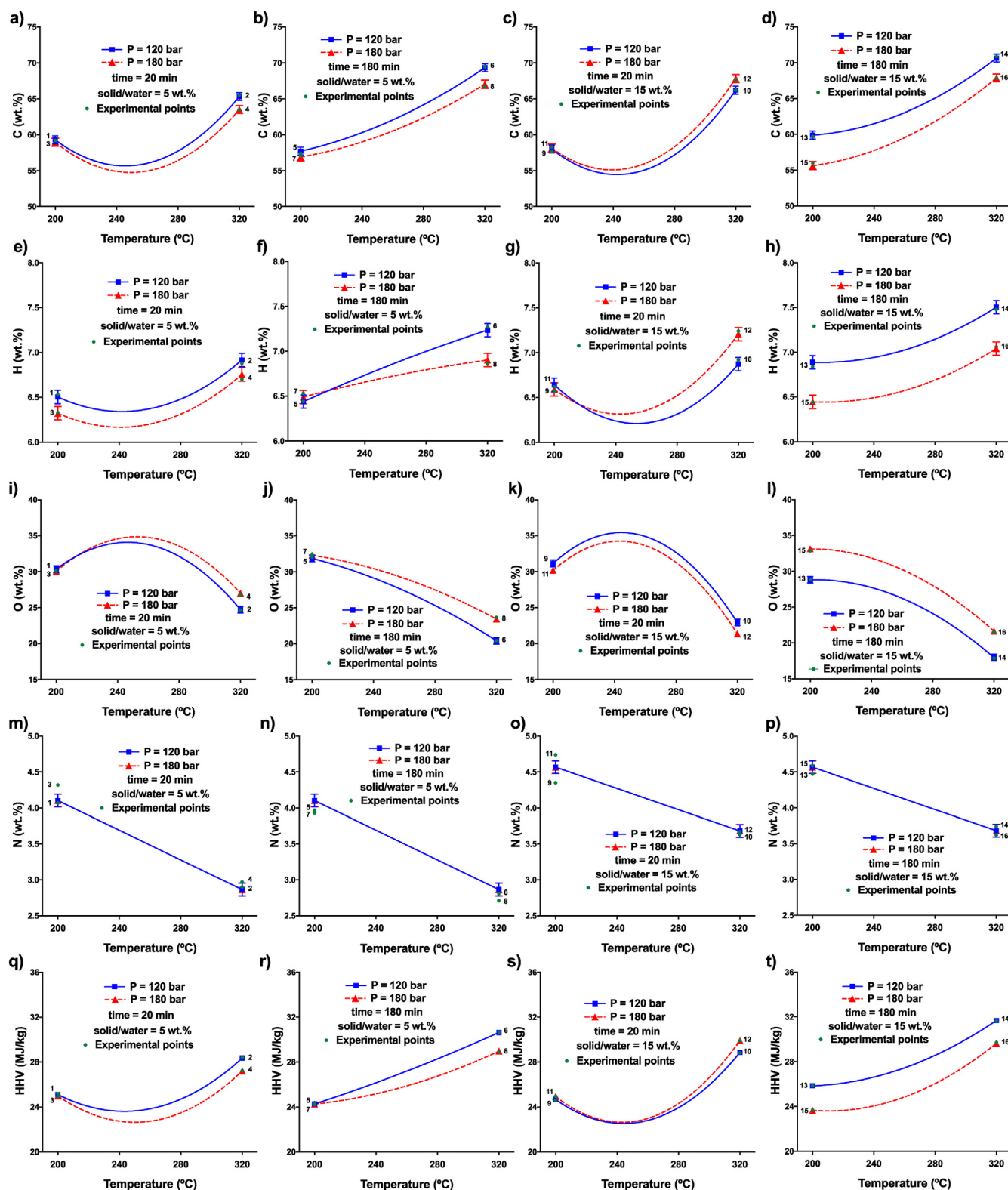


Fig. 3. Impact of the HTT reaction parameters on the elemental composition and HHV of the bio-crude.

reactions, as previously explained. Likewise, these variations are similar to those described for a fast HTT; however, the beneficial impact of the temperature is more meaningful and takes place at lower temperatures. This is believed to be an outcome of the favourable kinetic influence of the HTT duration, which helps

endorse the advance of decarboxylation and thermal cracking transformations (Duan et al., 2013; Fisk et al., 2009).

The pressure and solid loading influences on the elemental composition and HHV of the bio-crude are relatively weak. Irrespective of the reaction conditions, increasing the pressure from

120 to 180 bar decreases the concentrations of C and H and increases the relative amount of O, which leads to a decrease in the HHV of the bio-crude. It is believed that these minor changes might be related to the increases and decreases respectively observed in the yields to the aqueous phase and gas products when the pressure increases from 120 to 180 bar. These variations might help the production of a bio-crude with a higher O content, as there is an equilibrium between the bio-crude and the products in the aqueous phase (Lorente et al., 2019; Remón et al., 2019b), thus allowing the transference of organic species between phases during the treatment (Madsen et al., 2017; Madsen and Glasius, 2019). Besides, increasing the solid loading does not substantially modify the effect of the other processing variables on the bio-crude elemental composition or HHV. Regardless of the conditions, an increase in the solid loading from 5 to 15 wt% decreases the proportions of C and H to the detriment of the relative amount of O, which produces a minimal drop in the HHV. However, all these variations are not significant in a practical matter.

### 3.2.4. Chemical composition of the bio-crude

The bio-crude consists of a pool of alkenes (0–18%), aldehydes (0–1%), acids (0–31%), ketones (2–30%), phenols (4–38%), alcohols (0–2%), furans (0–7%), benzenes (0–8%) and cyclic (0–5%) and nitrogen-containing compounds (12–82%). The chemical composition of this product is enclosed as supplementary data in Table S2. The Pareto analysis (Table S1) reveals that the operating variable exerting the biggest influence on the most abundant compounds of the bio-crude (alkenes, acids, ketones, phenols, furans and nitrogen compounds) is the temperature. Besides, the quantities of alkenes, acids, phenols and furans are also influenced by the interaction between the temperature and other operating parameters, such as the pressure (alkanes, acids, phenols and furans), solid/water ratio (alkanes and acids) and reaction time (acids, ketones and furans). The influences of the processing parameters and interactions on the chemical composition of the most abundant chemical families in the bio-crude are shown in Fig. 4. Specifically, Fig. 4 a/e/i/m/q and b/f/j/n/r shows the influence of the temperature for a 5 wt% suspension at 120 and 180 bar for 20 and 180 min, respectively. Fig. 4 c/g/k/o/s and d/h/l/p/t shows these outcomes for a solid/water ratio of 15 wt%.

Irrespective of the processing conditions, the bio-crude produced at low temperature is primarily made up of high molecular mass oxygenated compounds, which are undetectable by gas chromatography, along with nitrogen derived species, resulting from the hydrolysis and solvolysis of the protein content of coffee pulp (Lorente et al., 2019; Remón et al., 2019b). This is in good agreement with the HTT biomass reaction pathway, as the process begins with the solvolysis of biomass in micellar forms, the disintegration of biomass structural components (i.e., cellulose, hemicellulose, lignin and proteins) and their thermal decomposition into smaller fragments (Kumar et al., 2018). However, significant variations were observed in the chemical composition of the bio-crude depending on the processing conditions. In particular, various trends are observed relying on the solid loading. For a suspension with 5 wt% solid loading, the chemical composition of the bio-crude is directed by the temperature, pressure and reaction time. For a quick process (20 min), irrespective of the pressure, an increase in the temperature enlarges the proportions of alkanes, carboxylic acids, ketones and phenols to the detriment of the amount of bio-crude nitrogen-derived species. Hydrolysis, depolymerisation and recombination reactions are enlarged with the temperature (Duan et al., 2013; Fisk et al., 2009). This enhances the decomposition of the biomass protein content and produces the transformation of bio-polymers (oligosaccharides and lignin oligomers in the biomass) into oligomers with a lower molecular mass.

Proteins firstly decompose into amino acids via hydrolysis, and then, these latter acids undergo either, decarboxylation yielding carbonic acid and amines, or deamination to produce ammonia and organic acids (Kumar et al., 2018). At high temperature, deamination is highly promoted, favouring the transformation of nitrogen derived compounds into carboxylic acids (Madsen et al., 2017; Madsen and Glasius, 2019). This correlates well with the increase described above in the yields to aqueous products with an increase in the temperature. The degradation products of the biomass polysaccharide content comprise phenols, aldehydes, carboxylic acids and cyclic ketones (Kumar et al., 2018). Therefore, the temperature promotes the transformation of lower molecular mass biopolymers into small oxygenated compounds, including alkanes, ketones and phenols, which overall provide evidence for the increases observed in the proportions of these product families and the decreases in the relative amount of nitrogen-containing compounds (Madsen et al., 2017; Madsen and Glasius, 2019).

Additionally, the pressure influences these variations, especially at intermediate temperatures (220–300 °C), the interval at which a boost in the pressure from 120 to 180 bar results in a bio-crude with lower quantities of alkanes, ketones and phenols, along with more significant amounts of carboxylic acids and nitrogen-containing compounds. This pressure influence is particularly important for the relative sums of alkanes, phenols and nitrogen species. This suggests that such pressure spread promotes the deacetylation of carbohydrates and proteins present in the coffee pulp, favouring the formation of carboxylic acids. Besides, the deamination and subsequent reduction of the nitrogen-containing species in bio-crude might occur to a more significant extent in comparison to their decarboxylation to produce gases, which experimentally spreads the amount of these species in the bio-crude (Madsen et al., 2017; Madsen and Glasius, 2019). Likewise, carboxylic acids condensation and lignin depolymerisation might take place to a lesser extent in comparison to deamination and decarboxylation, thus reducing the relative content of phenols in this product. As an outcome, at low pressure (120 bar), the variations (increases or decreases) observed for phenols and nitrogen-containing compounds are significant at low temperature (200–280 °C), with these variations being followed by a trade-off. On the contrary, at elevated pressure (180 bar), a plateau or minimal variations are firstly observed at low temperature (200–250 °C) for the proportions of alkenes, phenols and nitrogen derived species. In contrast, a subsequent increase in the temperature between 250 and 320 °C leads to substantial bio-crude chemical composition variations.

In general, an increase in the reaction time results in a bio-crude with higher proportions of carboxylic acids, phenols and ketones and a lower amount of nitrogen-containing species. These variations are explained by the more substantial spread of hydrolysis, depolymerisation and recombination reactions as the duration of the process increases. Besides, the temperature and pressure have a similar impact on the bio-crude chemical composition. On one end, increasing the temperature results in relatively higher amounts of alkanes and ketones and to a decrease in the relative amount of nitrogen-containing compounds. On the other, a pressure spread upsurges the proportions of carboxylic acids and decreases the relative quantities of alkanes, phenols and nitrogen-containing species, resulting in a higher proportion of carboxylic acids in the bio-crude (Madsen et al., 2017; Madsen and Glasius, 2019). The most critical differences occur for the proportions of alkanes, carboxylic acids and phenols. In particular, for a 180 min reaction, regardless of the pressure, the relative amount of carboxylic acids increases sharply between 200 and 250 °C and decreases with further increments in the temperature up to 320 °C. An initial rise in the temperature promotes depolymerisation, deacetylation and



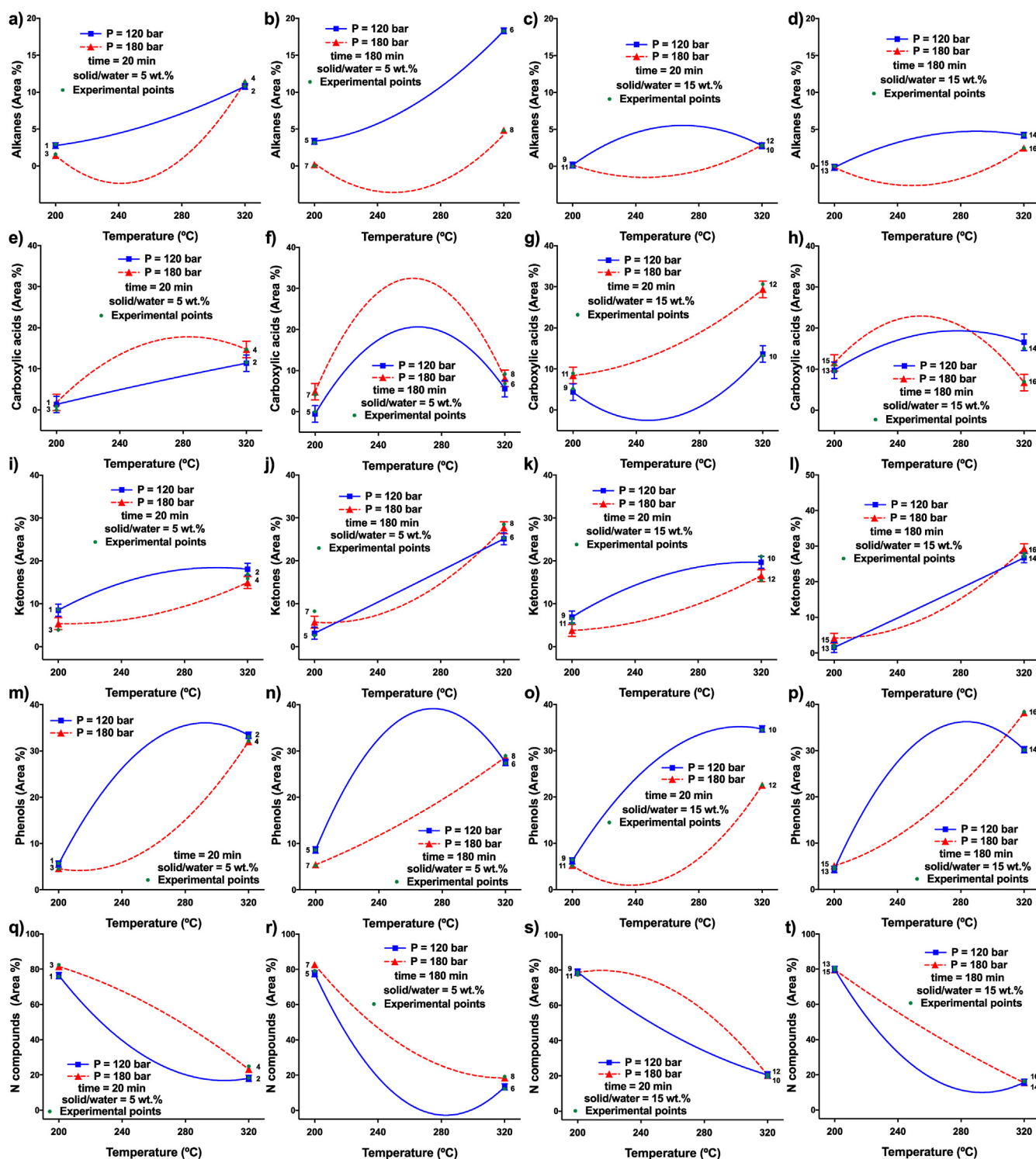


Fig. 4. Impact of the HTT reaction parameters on the chemical composition of the bio-crude.

retro-aldol reactions, which experimentally results in a substantial surge in carboxylic acids. However, carboxylic acids can also undergo thermal cracking, pyrolysis and decarboxylation reactions, with these transformations facilitating their transformation into gases (Lorente et al., 2019; Remón et al., 2019b). The latter correlates well with the increase observed in the gas yield described earlier. Besides, at 120 bar, the relative amount of phenols also decreases substantially at high temperature, with such decrease

being accompanied by a substantial increase in the proportion of alkanes in the bio-crude. These transformations are believed to result from the possible hydrodeoxygenation, via hydrogenations and ring-opening reactions, of phenols to produce alkanes (Remón et al., 2021) due to the increase in the proportion of  $H_2$  in the gas, as described above. Likewise, the acid nature of bio-crude, which can auto-catalyse these transformations (Remón et al., 2019b) and the less important mass transfer limitations occurring when  $H_2$  is



produced in-situ in the reaction medium, can promote these transformations (Remón et al., 2018).

Concentrating the coffee pulp suspension from 5 to 15 wt% alters the chemical composition of the bio-crude, and varies the impact that the temperature and pressure have on its chemical composition. On the one hand, the relative amounts of phenols and nitrogen-containing compounds (i.e., the most abundant species in the bio-crude) display similar behaviours with changes in the temperature and pressure as those described for a low solid loading, regardless of the reaction time. On the other hand, such an increase in the feedstock loading modifies the relative amounts of alkanes and carboxylic acids and produces a minor impact on the proportion of phenolic compounds. In particular, the relative amount of alkanes decreases, which results in a bio-crude with a low concentration of these species irrespective of the process conditions. This might be the consequence of the low  $H_2$  availability to promote hydrodeoxygenation reactions as the gas stream is primarily composed of  $CO_2$  as described earlier, along with the less pronounced decay in the proportion of phenols in the bio-crude. The influence of the solid loading on the proportion of carboxylic acids is only important at high pressure (180 bar), with different outcomes being observed depending on the treatment duration. For a fast HTT (20 min), the proportion of carboxylic acids increases at relatively elevated temperatures (280–320 °C), while for longer reaction times (180 min), the relative amount of carboxylic acids decreases, probably as a result of the more significant amount of phenolic compounds in the liquid. At low pressures and short reaction times, higher amounts of carboxylic acids and alkanes in the bio-crude are observed. This is thought to be due to the hydrolysis and decarboxylation of coffee pulp labile compounds such as lipids and waxes. An increase in the pressure promotes the decomposition of the oligosaccharide and lignin fractions in the coffee pulp, which increases the relative amount of phenols in the bio-crude (Chen et al., 2017). Besides, carboxylic acids can undergo further decarboxylation ending up being converted into gaseous products (Kumar et al., 2018).

### 3.2.5. Hydrochar elemental composition and HHV

The relative amounts of C, H, O and N in the hydrochar vary by 57–72 wt%, 4–6 wt%, 20–35 wt% and 2–3 wt%, respectively; while the HHV of this product shifts between 22 and 29 MJ/kg. The processing parameter with the greatest influence on the elemental composition of the hydrochar (Pareto test, Table S1) is the temperature. Besides, the proportions of C, H and N are also greatly affected by the solid/water ratio, although the influence of this variable is much weaker. These observations are in good agreement with previous publications reporting on the impact that the processing parameters exert on the composition and HHV of hydrochars produced by HTT of biomass (Afolabi et al., 2020; Saqib et al., 2019). Fig. 5 a/e/i/m/q and b/f/j/n/r shows the influence of the temperature for a 5 wt% suspension at 120 and 180 bar for 20 and 180 min, respectively. Fig. 5 c/g/k/o/s and d/h/l/p/t shows these outcomes for a solid/water ratio of 15 wt%.

The elemental analysis and HHV of the hydrochar are highly dependent on the reaction temperature and time, with the effect of the temperature being determined by the pressure. For a low pressure (120 bar), regardless of the reaction time or solid/water ratio, an increase in the temperature increases the hydrochar HHV. It also leads to an increase in the relative amount of C together with decreases in the proportions of H and O, especially between 200 and 280 °C. The favourable impact of the temperature on hydrothermal carbonisation reactions, including deoxygenation, dehydration, condensation, cyclisation, aromatisation and decarboxylation, accounts for these variations (Duan et al., 2013; Fisk et al., 2009). The relative amount of N increases between 200

and 280 °C and decreases with a successive temperature increment up to 320 °C, denoting that the deamination reactions are promoted at high temperature. Thus, at low temperature the proportion of N increases due to O removal, while at high temperature, the hydrochar is enriched in C and H due to the simultaneous removal of O and N via decarboxylation, cracking and deamination reactions (Piñkowska et al., 2014).

An increase in the pressure from 120 to 180 bar primarily results in a hydrochar with higher proportions of C and H, especially at medium temperatures (220–280 °C), and a lower O content; with these developments resulting in an enhancement in the HHV of this product. As described above, the pressure exerts a beneficial influence on the process, facilitating water penetration into the biomass core structure, aiding to polarise water and promoting acid-catalysed reactions. As a result, deoxygenation, decarboxylation, dehydration, condensation, cyclisation, deamination and thermal cracking transformations take place to a more substantial magnitude (Gollakota et al., 2018; Thiruvankadam et al., 2015), which overall results in spreads and diminishments in the proportion of C and O in the hydrochar, respectively (Kumar et al., 2018). Besides, this pressure boost also modifies the effects of the temperature, reaction time and solid/water ration on the product composition. As a result, at 180 bar an increase in the temperature increases the amounts of C and N and drops the O content of the hydrochar, irrespective of the reaction time or solid loading. On the contrary, at high pressure, these changes take place between 200 and 280 °C, while a further increase up to 320 °C leads to decreases in the proportion of C and N to the detriment of the O relative proportion in the hydrochar. Besides, the concentration of H decreases between 200 and 320 °C.; however, these variations are not substantial practically. The spreads observed in the concentrations of C and O in the hydrochar might be the result of the opposing effects caused by cracking and pyrolysis reactions, versus hydrothermal carbonisation (condensation, crystallisation and re-polymerisation) reactions, which promote char formation (Dimitriadis and Bezerianni, 2017; Xu and Lancaster, 2008).

The effects of the HTL reaction time and solid/water ratio are less critical. Concerning the influence of the former, regardless of the solid/water ratio used in the experiments, prolonging the HTT duration results in a solid product with higher proportions of C and N and a depletion in the relative amount of O, thus increasing the HHV of the hydrochar. These developments are the result of a positive influence of the reaction time on the kinetics of deoxygenation, dehydration, decarboxylation and deamination reactions, owing to the more prolonged exposure of the biomass to hydrothermal conditions (Duan and Savage, 2011b; Fisk et al., 2009). Besides, this time increment has a lower impact on the concentration of H, and the variations observed are not essential from a practical perspective. Similarly, the solid/water ratio exerts a comparable influence on the elemental composition and HHV of the hydrochar irrespective of the other process conditions. In general, an increase in the solid loading from 5 to 15 wt% results in higher proportions of C and N in the hydrochar at the expense of the O content in the product, which leads to a higher HHV. Condensation, crystallisation, dehydration and re-polymerisation reactions are promoted using high solid loadings (Dimitriadis and Bezerianni, 2017; Kumar et al., 2018), which experimentally accounts for the changes observed with increasing the solid/water ratio.

### 3.3. Process optimisation and energy evaluation

Four different case scenarios have been considered to find optimum conditions for the hydrothermal conversion of coffee pulp into biofuels and biochemicals, using the empirical formulae

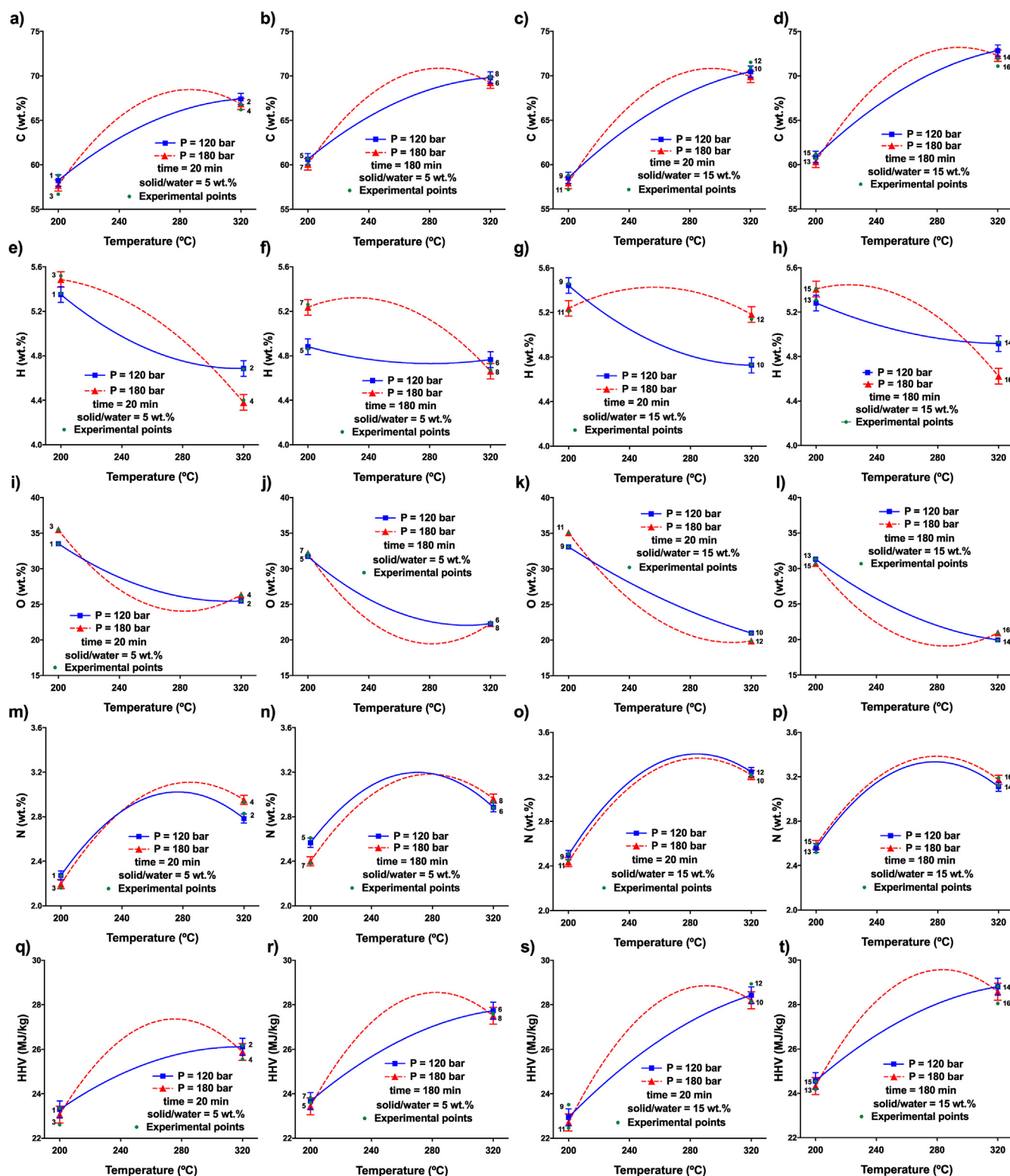


Fig. 5. Impact of the HTT reaction parameters on the elemental composition and HHV of the hydrochar.

produced from the ANOVA of the experimental results. The first and second case studies address the production of liquid and solid biofuels, respectively. Hence, the first optimisation maximises the bio-crude yield, while the second maximises the hydrochar yield, with the HHVs of both products being also maximised in both cases. The third attempts the concurrent conversion of coffee pulp into

solid and liquid biofuels; hence the bio-crude and hydrochar yields, as well as their HHVs, have been maximised. The fourth optimisation is directed towards the production of value-added liquid chemicals. In particular, it explores the possibility of transforming coffee pulp into a bio-crude containing an abundant quantity of phenols by maximising the bio-crude yield and the proportion of

these species in the liquid. In the optimisation process, a relative importance (from 1 to 5) has been given to each constrain to come up with solutions that meet the optimisation criteria. These objectives, along with the relative importance assigned and the optimum results attained, are listed in Table 4.

Considering these restrictions, Opt. 1 shows that it is feasible to convert up to 25% of the coffee pulp into a bio-crude with a high HHV (30 MJ/kg), conducting the HTT at high temperature (320 °C) and low pressure (122 bar) using a low solid loading (5 wt%) for a relatively lengthy (123 min) duration. At the same time, Opt. 2 reveals that if the HTT is conducted at low a temperature (215 °C), and a high pressure (162 bar) for a long reaction time (180 min) with a high solid/water ratio (15 wt%), it is possible to transform around 36% of the original material into a hydrochar with a high HHV (27 MJ/kg). Optimum conditions for the simultaneous production of high-energy dense bio-crude and hydrochar (Opt. 3) are high temperature (320 °C), high pressure (162 bar), short reaction time (57 min) and a high solid/water ratio (15 wt%). At such conditions, both products have a HHV of 29 MJ/kg and are obtained in high yields (24% and 21% for the bio-crude and hydrochar, respectively). The calorific values for the bio-crudes and hydrochar obtained at optimum conditions double the HHV of the spent coffee pulp (15 MJ/kg) and are in excellent agreement with the highest HHVs reported to date for the HTT of distinctive sorts of biomass (26–34 MJ/kg) (Saqib et al., 2019; Yang et al., 2019). Thus, these data confirm that HTT of coffee pulp is an efficient approach for the

conversion of this type of biomass into merchantable biofuels. In particular, the bio-crude elemental composition and HHV are similar to those of diesel (C = 85 wt%, H = 15 wt%, 44 MJ/kg) or biodiesel (C = 75 wt%, H = 12 wt%, O = 11 wt%, 40 MJ/kg) (Prakash et al., 2013), and therefore, this liquid might be compatible for use in current combustion engines, either alone and/or blended (Cataluña et al., 2013). Besides, the hydrochar HHV falls between lignite (29 MJ/kg) and coke (33 MJ/kg) (Li et al., 2017), thus being adequate for energy purposes. Regarding the production of liquid value-added chemicals, Opt. 4 reveals that the production of a bio-crude (25%) containing a high proportion of phenols (42%) is achieved at a relatively high temperature (280 °C) and low pressure (120 bar) for a long reaction time (117 min) with a diluted suspension (5 wt%). This phenolic-rich liquid effluent might serve as a renewable source for aromatic compounds, and, it is also a splendid building block for the manufacturing of renewable antioxidant additives for fuels and/or biofuels, owing to its high aromaticity.

For the optimisations, energy evaluations were conducted comparing the potential calorific values of the products with respect to the HHV of the original coffee pulp (Table 2), and efficiencies between 72 and 83% were achieved for the optima predicted (Table 4). Therefore, given the sustainability, energy implications, along with the bespoke nature of this HTT, these results represent a major contribution towards the production of biofuels and bio-chemicals from the coffee pulp obtained from the wet manufacturing of coffee. As a proof of concept, we have only

**Table 4**  
Optimisations for the conversion of spent coffee pulp into biofuels and chemicals.

Optimisation	1		2		3		4	
	Obj.	Solution	Obj.	Solution	Obj.	Solution	Objective	Solution
Temperature (°C)		320		215		320		280
Pressure (bar)		122		162		162		120
time (min)		123		180		57		117
Solid/water (wt.%)		5.5		15		15		5
<b>Global results</b>								
Gas yield (%)		8.63 ± 0.15		2.31 ± 0.15		7.27 ± 0.15		6.46 ± 0.15
Aqueous yield (%)		52.84 ± 1.06		50.15 ± 1.06		48.35 ± 1.06		51.00 ± 1.06
Hydrochar yield (%)		14.04 ± 0.62	Max. (3)	35.66 ± 0.62	Max. (3)	20.85 ± 0.62		24.19 ± 0.62
Bio-crude yield (%)	Max. (3)	24.81 ± 1.04		10.25 ± 1.04	Max. (3)	23.72 ± 1.04	Max. (3)	16.91 ± 1.04
<b>Gas composition and LHV</b>								
H <sub>2</sub> (vol%)		12.13 ± 0.64		0.00 ± 0.64		0.00 ± 0.64		1.06 ± 0.64
CO <sub>2</sub> (vol%)		68.69 ± 1.13		92.37 ± 1.13		96.10 ± 1.13		95.33 ± 1.13
CO (vol%)		10.51 ± 0.37		6.64 ± 0.37		3.20 ± 0.37		4.66 ± 0.37
CH <sub>4</sub> (vol%)		6.04 ± 2.18		7.93 ± 2.18		8.47 ± 2.18		2.65 ± 2.18
LHV (MJ/m <sup>3</sup> STP)		5.62 ± 0.53		1.71 ± 0.53		0.95 ± 0.53		0.34 ± 0.53
<b>Bio-crude elemental composition and HHV</b>								
N (wt.%)		3.20 ± 0.15		4.46 ± 0.15		3.91 ± 0.15		3.59 ± 0.15
C (wt.%)		68.57 ± 0.43		55.08 ± 0.43		65.97 ± 0.43		62.51 ± 0.43
H (wt.%)		7.14 ± 0.06		6.84 ± 0.06		7.14 ± 0.06		6.80 ± 0.06
O (wt.%)		20.93 ± 0.33		33.67 ± 0.33		23.02 ± 0.33		26.81 ± 0.33
S (wt.%)		0.05 ± 0.02		0.06 ± 0.02		0.03 ± 0.02		0.06 ± 0.02
HHV (MJ/kg)	Max. (5)	30.24 ± 0.10		23.58 ± 0.10	Max. (5)	29.00 ± 0.10		27.38 ± 0.10
<b>Solid elemental composition and HHV</b>								
N (wt.%)		2.88 ± 0.04		2.80 ± 0.04		3.26 ± 0.04		3.12 ± 0.04
C (wt.%)		69.30 ± 0.88		64.85 ± 0.88		71.72 ± 0.88		67.53 ± 0.88
H (wt.%)		4.76 ± 0.05		5.49 ± 0.05		5.09 ± 0.05		4.74 ± 0.05
O (wt.%)		22.06 ± 0.18		26.83 ± 0.18		17.90 ± 0.18		22.88 ± 0.18
S (wt.%)		0.26 ± 0.01		0.13 ± 0.01		0.23 ± 0.01		0.24 ± 0.01
HHV (MJ/kg)		27.35 ± 0.45	Max. (5)	26.46 ± 0.45	Max. (5)	29.00 ± 0.45		26.55 ± 0.45
<b>Bio-crude chemical composition (Area %)</b>								
Alkanes		15.34 ± 0.24		0.00 ± 0.24		0.00 ± 0.24	Min. (5)	10.33 ± 0.24
Carboxylic acids		6.08 ± 1.57		21.07 ± 1.57		28.54 ± 1.57	Min. (5)	12.14 ± 1.57
Ketones		23.85 ± 1.43		1.55 ± 1.43		26.35 ± 1.43	Min. (5)	17.82 ± 1.43
Phenols		32.06 ± 0.48		4.68 ± 0.48		23.54 ± 0.48	Max. (5)	41.51 ± 0.48
Furans		0.03 ± 0.40		0.31 ± 0.40		0.81 ± 0.40	Min. (5)	0.87 ± 0.40
Nitrogen compounds		15.15 ± 1.99		69.99 ± 1.99		13.64 ± 1.99	Min. (5)	6.24 ± 1.99
<b>Energy balance</b>								
E (%)		76.85		77.27		82.55		71.96

considered the spent coffee pulp, as the mucilage and the parchment are produced in fewer amounts. Besides, the coffee pulp was dried before experimentation to facilitate transportation and storage. However, in a real case scenario, the hydrothermal process could be conducted using the entire solid (spent coffee pulp, mucilage and parchment) and liquid (spent wastewater) fractions. Therefore, the production of biofuels by HTT may represent a more profitable option than current alternatives reported for the management of this by-product, such as the manufacturing of fertilisers and compost, enzymes, and colourants, flavours and aroma for food. Besides, it allows the production of bioenergy in early-development countries using their autochthonous resources, ensuring sustainable development. These achievements not only help the development of novel routes for the valorisation of this type of biomass but also constitute a significant step-change to ensure a safer and cleaner coffee production; from cultivation to cup, to disposal. With this in mind, societies must strive towards an efficient waste management and a more environmentally friendly and sustainable energy production. They must also reduce inequalities and ensure decent work and economical and safe growth. These implications align with the circular economy philosophy around fuels and chemicals production and are intrinsically linked to the United Nations Sustainable Development Goals (UN SDGs).

#### 4. Conclusions

The hydrothermal treatment (HTT) of spent coffee pulp resulted in the formation of four main products: a gas stream, an aqueous fraction, a solid bio-fuel (hydrochar) and liquid bio-fuel (bio-crude), whose yields depended on the processing conditions and varied by 4–10%, 41–57%, 10–42% and 10–26%, respectively. Short reaction times and low solid loadings enhanced the production of bio-crude and water-soluble liquid species, with their yields increasing with the temperature due to a more significant extension of hydrothermal liquefaction. On the contrary, low temperatures, long reaction times and high solid loadings promoted the formation of hydrochar. This accounted for a more substantial spread of hydrothermal carbonisation reactions. The gas phase was primarily composed of CO<sub>2</sub>, along with small amounts of H<sub>2</sub>, CO and CH<sub>4</sub> in different proportions. The gas composition depended on the operating conditions, and it is ruled by the thermodynamics and kinetics of the process. The processing conditions significantly impacted liquefaction and carbonisation reactions, which varied the fuel and chemical properties of the hydrochar and bio-crude. The former contained different quantities of C (57–72 wt%), H (4–6 wt%), O (20–35 wt%) and N (2–3 wt%), with a HHV shifting between 22 and 29 MJ/kg. The latter comprised a pool of alkanes, carboxylic acids, ketones, phenols and nitrogen compounds. The amounts of C, H, O and N of this product varied by 54–71 wt%, 6–7 wt%, 18–34 wt%, and 3–5 wt%, respectively, and its HHV shifted from 23 to 32 MJ/kg. Process optimisation showed that up to 25% of the feedstock could be transformed into an energy-dense bio-crude (30 MJ/kg) when a 5.5 wt% suspension is processed at 320 °C and 122 bar for 2 h. Likewise, 36% of this coffee by-product can be transformed into an energetic (27 MJ/kg) hydrochar upgrading a 15 wt% suspension at 215 °C and 162 bar for 3 h. Besides, energy-dense bio-crude and hydrochar (29 MJ/kg) can be produced concurrently in high yields (24 and 20%, respectively) during the treatment of a 15 wt% coffee pulp suspension at 320 °C and 162 bar for 1 h. In contrast, a bio-crude with an elevated quantity of marketable phenolic species (42%) can be attained in high yield (25%) when a 5 wt% suspension is hydrothermally treated at 280 °C and 120 bar for 2 h. These results are a landmark achievement for the economy and sustainability of coffee producer

countries and represent a pioneering strategy for the sustainable management of early-stage coffee leftovers. In particular, this valorisation strategy constitutes a significant step-change to ensure a safer and cleaner coffee production; from cultivation to cup, to disposal. Also, it connects very well with the current circular economy philosophy and is inherently linked to the United Nations Sustainable Development Goals (UN SDGs).

#### CRedit authorship contribution statement

**Javier Remón:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Felipe Ravaglio-Pasquini:** Validation, Formal analysis, Investigation, Data curation. **Lorena Pedraza-Segura:** Methodology, Validation, Formal analysis, Investigation, Data curation. **Pedro Arcelus-Arrillaga:** Validation, Writing – review & editing, Resources, Funding acquisition. **Isabel Suelves:** Conceptualization, Writing – review & editing, Resources, Supervision, Project administration, Funding acquisition. **José Luis Pinilla:** Conceptualization, Writing – review & editing, Resources, Supervision, Project administration, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2021.127008>.

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