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Valorization of coffee industry residues by subcritical water hydrolysis: Recovery of sugars and phenolic compounds

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ABSTRACT

Two abundant coffee waste residues (powder and defatted cake) were treated using subcritical water (SubCW) for hydrolysis and extraction of reducing sugars (RS), total reducing sugars (TRS), and total phenolic compounds (TPC) under semi-continuous flow conditions. The flow-through process was carried out at 150, 175, 200 and 250 °C, with a water flow of 10 mL/min and reaction pressures of either 22.5 or 30 MPa. For treated coffee powder, the maximum observed sugar recovery was 6.3% for RS (150 °C and 30 MPa) and 9.0% for TRS (150 °C and 30 MPa). The maximum TPC recovery was 26.64 mg GAE (Gallic Acid Equivalent)/g powder coffee, observed at 200 °C and 22.5 MPa. For the defatted coffee cake, the maximum sugar yields were 8.79% and 17.23% for RS and TRS; both observed at a treatment temperature of 175 °C. The highest TPC yield was 55.31 mg TPC GAE/g defatted coffee cake, also at 175 °C. HPLC was used to quantify specific carbohydrates (arabinose, cellobiose, glucose, and xylose), 5-hydroxy-methyl-furfural (5-HMF) and furfural in both coffee waste hydrolyzates, providing evidence of thermal degradation of the coffee carbohydrates. Scanning electron microscopy of the treated samples revealed particles deposited on the surface and other signs of physical degradation of the biomass structure. Fourier Transform Infrared Spectroscopy of the residues revealed that the density of surface bound acid groups increased with increasing treatment temperature. The results presented here provide a basis for the use of subcritical water to obtain reducing sugars and phenolic compounds from coffee residue.

1. Introduction

Biomass is renewable, abundant, inexpensive, and does not compete with food production. Industrial food processing residues are a source of biomass that can be transformed into energy, biofuels, and chemicals. Biomass from food waste typically consists of 50–75% carbohydrates (cellulose and hemicellulose, the main biodegradable polymers), 5–25% lignin [1,2], and modest amounts of other substances, including phenolic compounds, lipids, and acidic compounds, which may be processed into higher value-added products [3–7]. For this reason, biomass is an ideal source for obtaining simple sugars (short-chain monomers), which are used as fermentation substrates for the production of ethanol [8], and phenolic compounds that possess antioxidant properties of value in pharmaceutical, food, and health applications [9,10].

Subcritical water (SubCW), also called "hot compressed water", is defined as liquid water held at temperatures between 100 °C and 374 °C [11,12]. Under these conditions, water can act as both a solvent less toxic than organic solvents and as an acid that has a lower corrosion risk than mineral acids [13,14]. For these reasons, SubCW can be used as an environmentally benign and sustainable solvent for converting wet biomass into smaller molecules by depolymerization and hydrolysis reactions [13]. As a pre-treatment process prior to fermentation, water at subcritical conditions provides rapid reaction rates that increase the hydrolysis and subsequent solubilization of organic matter [15–17]. Hydrothermal liquefaction is a medium-temperature, high-pressure thermochemical process, which produces a liquid product, because the macromolecules of the biomass are first hydrolyzed and/or degraded into smaller molecules. Therefore, at higher temperatures, or with addition of a

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co-catalyst, it is possible to convert a large portion of the carbohydrate and lignin content of biomass into soluble products [18].

Currently, Brazil is the leading worldwide coffee producer and exporter, representing 34.0% of global production [10,19]. The coffee industry produces considerable amounts of residues at all stages of production, from harvest to the final product [20]. Two main types of coffee bean residues are produced, powder and defatted cake. Powder is produced by mechanical transport and friction between the grains. The defatted cake is a residue obtained after extraction of oil from green coffee beans. Both residues have a high content of lipids, carbohydrates, proteins, and phenolic compounds; likewise, both waste products are currently disposed of in landfills [21]. Instead, using these wastes as raw materials for bioenergy or chemicals production would be a more sustainable solution that would divert them from landfills and provide additional revenue to the coffee producers and/or manufacturers.

The biomass hydrolysis and pretreatment literature focuses primarily on processing under batch conditions [22–24]; however, batch conditions typically result in uncontrolled sugar degradation stemming in part from long reactor heat-up and cool down times, transient conditions which can be on the order of ten minutes [23,25]. On the other hand, excellent sugar recovery has been reported for subCW and supercritical water hydrolysis of cellulose in slurry-fed flow reactors operating at very short contact times (less than 1 s) [26,27]. Unfortunately, the slurry-fed reactor approach necessarily requires delivering a high-pressure concentrated slurry to the subCW reactor, which is a difficult technical challenge [28,29]. An intermediate solution between batch and continuous conditions is to operate the biomass as a fixed bed with a semi-continuous flow of the water phase. The advantage of flow-through conditions is that sugars produced by biopolymer hydrolysis are continuously removed from the reactor, reducing their chances of degradation [30,31]. Despite concerns about excessive dilution of the hydrolyzate produced by the continuous process, a recent study suggests that heat integration to recover energy from the hot liquid water product combined with steam venting to re-concentrate the product sugars can lead to an overall biofuel production process with high energy efficiency [31].

The objective of the present work was to evaluate the performance of flow-through subCW for recovering sugars and valuable phenolic compounds from two coffee wastes: green coffee powder and defatted cake. Hydrolyzate composition was monitored periodically as a function of reaction time to quantify yields of reducing sugars, total reducing sugars and phenols, and to correlate evidence of sugar degradation products with measurements of hydrolyzate pH. The effects of subCW temperature were studied systematically over the range from 150 to 250 °C and at both 22.5 and 30 MPa. The subCW-treated solids were analyzed using scanning electron microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy to investigate structural and chemical changes in the solid materials that occurred during treatment. The results provided here establish a quantitative basis for future work on flow-through hydrolysis of food waste streams.

2. Materials and methods

2.1. Raw material and reagents

Green coffee powder and defatted cake (obtained from green coffee beans, *Coffea arabica*) were donated by Brazil Cooxupé (Regional Cooperative of Coffee Growers, Guaxupé Ltda). Mechanical abrasion, either by friction during transportation or during sieving processes used during quality control, generates green coffee powder. Defatted coffee cake is produced by cold-pressing extraction of low-quality beans rejected during the quality control process. Both types of coffee waste were stored at −18 °C before testing. Prior to subCW treatment, the samples size was reduced using a knife mill (Marconi, model MA 340, Piracicaba, Brazil) equipped with a 1 mm sieve. Distilled water was used in all experiments.

Table 1
Initial characterization of coffee residues.

Composition	Defatted cake [%] Wet basis	Powder [%]
Moisture	5.2 ± 0.1	8.6 ± 0.1
	Dry basis	
Ashes	4.4 ± 0.3	4.6 ± 0.3
Extractives in water	3.5 ± 0.1	2.5 ± 0.1
Extractives in ethanol	9 ± 1	6.2 ± 1.4
Total lignin	23 ± 2	36 ± 3
Holocellulose (cellulose and hemicellulose)	49.5 ± 0.6	62 ± 6
Protein	7.4 ± 0.4	11.2 ± 0.3
Elemental analysis		
Carbon	44.5 ± 0.2	45.2 ± 0.2
Hydrogen	6.9 ± 0.1	6.2 ± 0.4
Nitrogen	2.7 ± 0.1	1.62 ± 0.02
Oxygen (by difference)	46.98	45.92

Values presented as mean ± standard deviation.

Acetic acid, ethanol, sodium chlorite, and sodium hydroxide (Wako Pure Chem. Ind., Ltd., Osaka, Japan) were used without purification for determining the composition of raw materials. For the evaluation of total phenolic content, the Folin–Ciocalteu reagent and gallic acid (used as a standard) were purchased from Sigma-Aldrich (SP, Brazil). High performance liquid chromatography (HPLC) standards were obtained from Sigma-Aldrich (St. Louis, MO, USA) to confirm retention times and calibrate detector response for compounds present in the hydrolyzate: D-(+)-arabinose, D-(+)-glucose, D-(+)-xylose D(+)-Cellobiose with purity (>96%), 5-(hydroxymethyl)furfural (≥99%), furfural (≥98%).

2.2. Raw material characterization

Both raw materials were analyzed for moisture content, ash, extractives, protein, holocellulose, and lignin, using the National Renewable Energy Laboratory (NREL) methodology described in technical reports: NREL/TP-510-42618-42619-42621-42622-42625 [32–36]. Table 1 provides the composition of the coffee residues prior to SubCW treatment.

2.3. Subcritical water hydrolysis

Hydrolysis was performed in SubCW using a semi-continuous flow reactor constructed entirely of SS316. Fig. 1 is a schematic diagram of the semi-continuous reactor system. The reactor itself has an internal volume of 110 mL (maximum working conditions of 400 °C and 40 MPa). A high-pressure liquid pump (Dual piston pump, model Prep 36 Pump, Apple Valley, MN, USA) was used to deliver pressurized water to the reactor. The pressure in the reactor was controlled by a back-pressure regulator (High-Pressure Piston-Sensing Back-Pressure Regulators, KHB Series, Lafayette, LA) and measured by two pressure transducers. The reaction temperature was monitored by a thermocouples (type K) positioned at the outlet of the reactor. The hot effluent exiting the hydrolysis reactor is cooled to less than 27 °C in a stainless steel shell-and-tube heat exchanger coupled to a temperature-controlled recirculating bath (Marconi, model MA-184, Piracicaba, SP, Brazil) maintained at −10 °C (using aqueous ethylene glycol 50% as the heat transfer fluid), and equipped with a temperature controller, as described previously [11].

Prior to each experiment, 5.0 g of the desired coffee residue were placed inside the hydrolysis reactor before it was sealed. The liquid

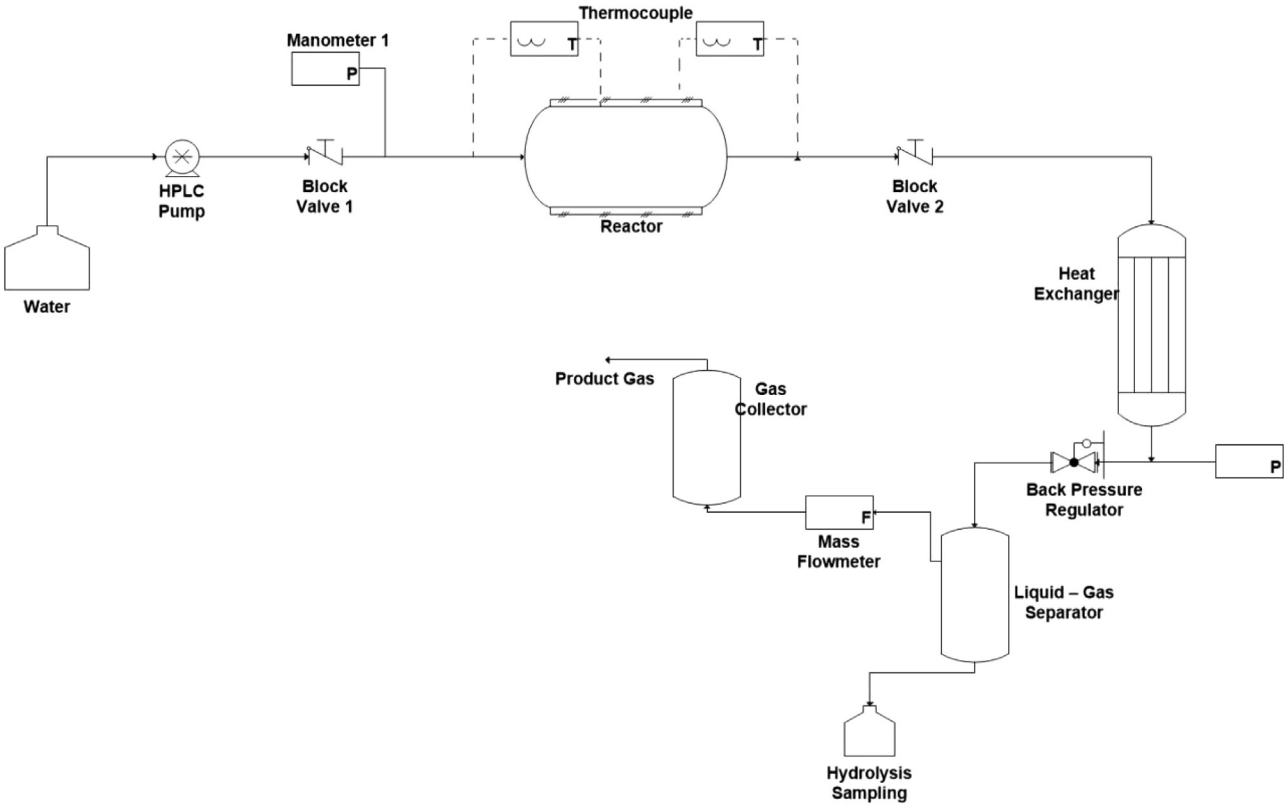

Fig. 1. Schematic diagram of experimental apparatus.

pump was used to fill the reactor with water, remove residual air, and to pressurize the reactor. Once all system components were filled with water and fully pressurized, the pump was switched off. Pressurization required approximately 10 min. Following pressurization, the heating system was switched on and adjusted to reach the process temperature. Once the set point temperature was reached the process was initiated by pumping water through the system. The temperature recorded at the reactor outlet increased when flow was initiated; temperature stabilization, both inside the reactor and at the outlet, required about 12–15 min of steady water flow. Samples of the liquid hydrolyzate were collected every 2 min for 36 min and stored in glass vials prior to analysis.

Table 2 provides operating parameters used for subcritical water hydrolysis of coffee residues. All experiments were performed in duplicate. The parameters studied in this work were: hydrolysis temperature (150, 175, 200 and 250 °C) and pressure (22.5–30 MPa). Water flow rate was held constant throughout at 10 mL/min for stablish a dynamic period of the process was started by press-surizing the system and pumping water at the set-point at this flow rate according [11]. Lower flow rate increases the residence time of the hydrolysate in the reactor, and, therefore, increases monomers degradation. Uncertainties are reported based on the range of the two duplicate measurements. The fluid residence time (τ) was estimated by:

$$\tau = \frac{V_R \rho_R(T,P)}{v_0 \rho_0} \quad (1)$$

where V_R is the reactor volume (m^3), v_o is the volumetric water flow rate (m^3/s), ρ_0 is the density of the liquid feed (1080 kg/m^3), and ρ_R is the density of the fluid under reactor temperature and pressure, which was estimated using steam tables [37]. Eq. (1) assumes the fluid stream is uniform throughout the reactor at the set-point temperature and pressure and does not account for density changes associated with non-isothermal conditions inside the reactor. In all cases, the uncertainties in estimated residence times introduced by the assumption of temperature/pressure uniformity should be no more than 5%.

2.4. Hydrolyzate analysis

2.4.1. Determination of reducing sugars and total reducing

The RS and TRS content of the hydrolyzate were determined by the Somogyi-Nelson colorimetric method [38,39]. For TRS measurements, the hydrolyzate was subjected to acid hydrolysis to convert sugar oligomers into monomeric form before further analysis. After the coloring reaction, the absorbance of the sample was measured at a wavelength of 540 nm using a spectrophotometer (Hach, model DR/4000U, Colorado, USA). The RS and TRS concentrations were calculated using a calibration curve based on standard glucose solutions (50, 150, 250, 350, 450, 500 mg/L) and expressed as glucose equivalents [11]. In some cases, hydrolyzate samples were diluted with deionized water before photometric analysis to ensure that the measured absorbance fell within the calibration range.

2.4.2. Total phenolic compounds (TPC)

The yield of total phenolic compounds (TPC) was determined according to the Folin–Ciocalteu method [40]. Each extract was first diluted in deionized water. Aliquots containing 0.5 mL of sample and 0.5 mL of Folin-Ciocalteu reagent were mixed for 15 s and incubated at room temperature for 3 min. Then, 0.5 mL of saturated sodium carbonate and 3.5 mL of distilled water were added to the analysis mixture. After 2 h of storage in the dark at room temperature, the absorbance at 760 nm of the mixture was measured using a spectrophotometer (Hach, model DR/4000U, Colorado, USA). Standard solutions containing known concentrations of gallic acid (i.e., trihydroxybenzoic acid) were used to determine a calibration curve (0.015 to 0.05 mg/mL), and the results were expressed in terms of

Table 2
Operating Parameters hydrolysis of coffee residues.

Experiment	Feedstock	Mass [g]	Pressure [MPa]	Temperature [°C]	Density [kg ∅ m^3]	Residence time [min]
1	Powder	5	22.5	150	928.82	9.46
2		5	22.5	175	905.50	9.22
3		10	22.5	200	879.78	8.96
4		10	22.5	250	818.44	8.34
5		5	30	150	932.75	9.50
6		5	30	175	909.88	9.26
7		10	30	200	884.80	9.01
8		10	30	250	825.66	8.40
1	Cake defatted	5	22.5	150	928.82	9.46
2		5	22.5	175	905.50	9.22
3		10	22.5	200	879.78	8.96
4		5	30	150	932.75	9.50
5		5	30	175	909.88	9.26
6		10	30	200	884.80	9.01

mg gallic acid equivalent (GAE) per g of powder and defatted cake coffee. Each analysis was performed in triplicate and average values are reported here.

2.4.3. Determination of pH

The pH of the hydrolyzates was determined using a digital pH meter (Digimed, model DM-22, Brazil).

2.4.4. Quantification of carbohydrates, 5-HMF, and furfural by high-performance liquid chromatography (HPLC)

The carbohydrate content in the hydrolyzates was measured using HPLC (Thermo Scientific Dionex Ultimate system 3000). The analysis conditions were: column type HPX-87H Aminex, sulfuric acid phase 5 mmol^{-1}, flow of 0.6 mL/min, volume 20 μL injection, oven temperature 35 °C and detector RI-101 (Shodex). Before analysis, the hydrolyzates were filtered using syringe filters (0.45 μm pore diameter). Solutions containing known concentrations of arabinose, cellobiose, glucose, and xylose were used to calibrate the detector response.

5-HMF and furfural content of the hydrolyzate samples were measured on the same HPLC. The analysis conditions were: column packed with core-shell particles (Kinetex C18, Phenomenex), the mobile phase consisting of milliQ water containing 1% phosphoric acid (solvent A) and acetonitrile containing 1% phosphoric acid (solvent B). The mobile phase flow rate was 1.3 mL/min; the total run time was 15 min per sample and absorbance was measured at 280 nm UV. Detector response was calibrated using standard solutions of 5-HMF and furfural with known concentrations. Hydrolyzates were membrane filtered (0.22 μm pore diameter) before analysis.

2.5. Solid residue after hydrolysis

2.5.1. Field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscopy (FESEM) was used to analyze the microstructure of the coffee samples surfaces before and after hydrolysis in SubCW. Before analysis, the samples were coated with a nanometer-thick gold film using an SCD 050 sputter coater to improve their conductivity (Oerlikon-Balzers, Balzers, Liechtenstein). The FESEM was equipped with a field emission gun (Quanta 650, FEI, Hillsboro, Oregon, USA). FESEM analysis was performed under vacuum, using a 5 kV acceleration voltage. Both the FESEM itself and the sputter coater were located at the National Laboratory of Nanotechnology (LNNano, Campinas-SP, Brazil). A general scan was first performed on each sample to confirm morphological uniformity. Next, a total of four representative locations areas imaged for each sample, and at least 16 images were obtained at different magnifications to assure the representativeness of the FESEM imaging results.

2.5.2. FTIR spectroscopy

FTIR spectra were obtained using a Bruker Vertex 70 FTIR spectrometer equipped with a La-DTGS detector operated at room temperature. A diamond attenuated total reflectance (ATR) cell, manufactured by Specac, was used for all measurements. For all samples, the resolution was 4 cm^{-1}, and 512 scans were acquired and then averaged over the 600–4000 cm^{-1} spectral range. Data only in the range from 1500 to 1900 cm^{-1} are provided here.

3. Results and discussion

3.1. Reducing sugars (RS) and total reducing sugars (TRS) in hydrolyzates

Fig. 2 (green coffee powder) and Fig. 3 (defatted cake) show concentrations of RS and TRS concentrations measured over time under low-through hydrolysis conditions. In all cases, RS and TRS are expressed as grams of sugar obtained (in glucose equivalents) per 100 g of residue. For green coffee powder treated at 22.5 MPa, Fig. 2 shows that the highest RS and TRS yield were obtained at 150 °C: 6.3 ± 0.6 g RS and 8.3 g ± 0.4 TRS, respectively. With increasing treatment temperature, the RS and TRS yields both decreased. For hydrolysis conducted at 30 MPa, the highest yields were again obtained at 150 °C: 5.8 ± 0.2 g RS and 9.1 ± 0.4 g TRS. The effect of increasing the pressure from 22.5 to 30 MPa was only slightly greater than measurement uncertainty, suggesting that the operating pressure needs only to be high enough to maintain water in a liquid, subcritical state.

Fig. 3 shows yields of RS and TRS observed for SubCW hydrolysis of defatted cake. In comparison with Fig. 2, Fig. 3 shows sugar yields for the defatted cake were higher than those obtained for SubCW treatment of green coffee powder. In contrast with powder, maximum RS and TRS yields obtained from treatment of coffee powder were observed at 175 °C. Similar to coffee powder, RS and TRS yields decreased as the temperature was increased from 175 °C to 200 °C; experiments at 250 °C were not possible because the defatted coffee residue clogged the tubing at this temperature.

The low RS and TRS yields obtained here may indicate that temperatures above at least 250 °C are required for cellulose degradation in coffee wastes, as has been observed for other wastes [13,41]. In fact, some literature reports increasing RS yields with increasing temperature [8,30]; contradictory behavior was observed in this study, possibly due to sugar degradation resulting in the formation of organic acids at higher temperatures [30]. Supporting this explanation, Narita and Inouye [42] treated coffee wastes using SubCW, reporting maximum RS and TRS yields at

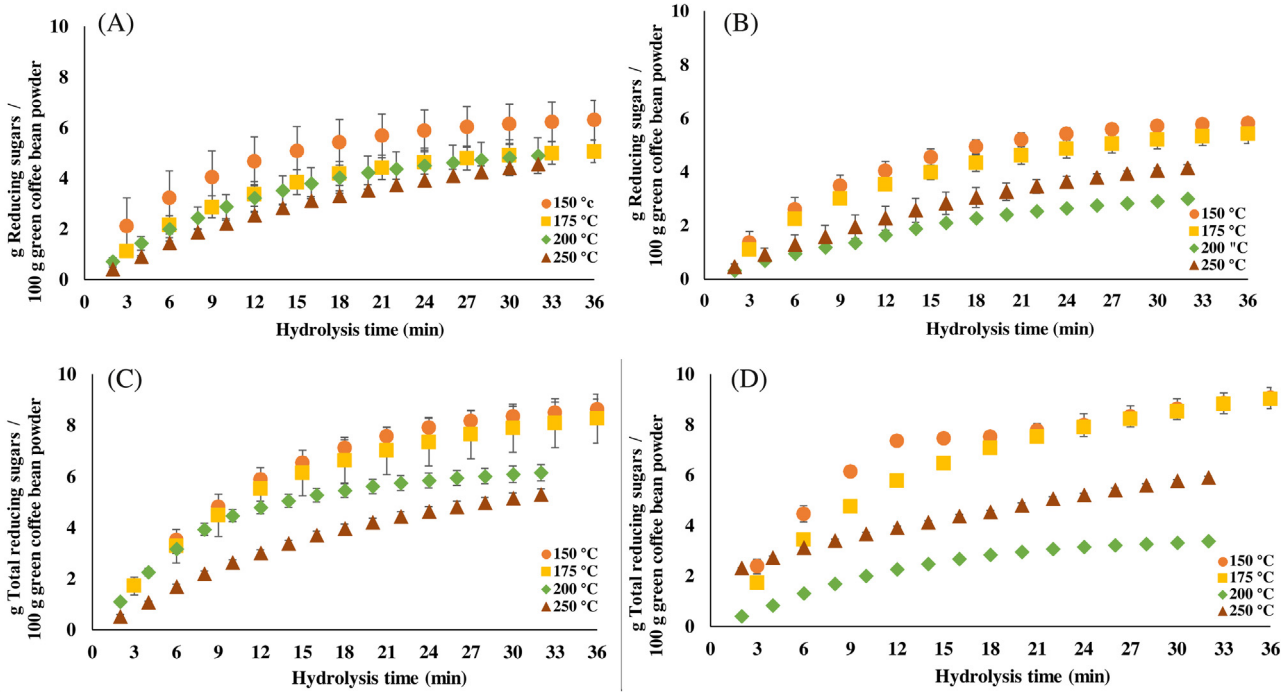

Fig. 2. Yield of reducing sugars (RS) and total reducing sugars (TRS), in glucose equivalents, of green coffee bean powder at different temperatures as a function of time: (A) RS at 22.5 MPa; (B) RS at 30.0 MPa; (C) TRS at 22.5 MPa; (D) TRS at 30.0 MPa.

180 °C and diminished yields when the process was carried out at 270 °C. Hata et al., [43] studied subCW hydrolysis of defatted rice bran (which may behave similarly to defatted coffee), reporting that sugar yield increased with increasing treatment temperatures up to 200 °C, but decreased above this temperature.

Controlling residence time is key to maximizing RS and TRS yields; sufficient contact time is required to break down the holocellulose components, while longer residence times result in sugar degradation. The current study examined residence times on the order of 9 min (Table 2). For hydrolysis of purified cellulose in con-

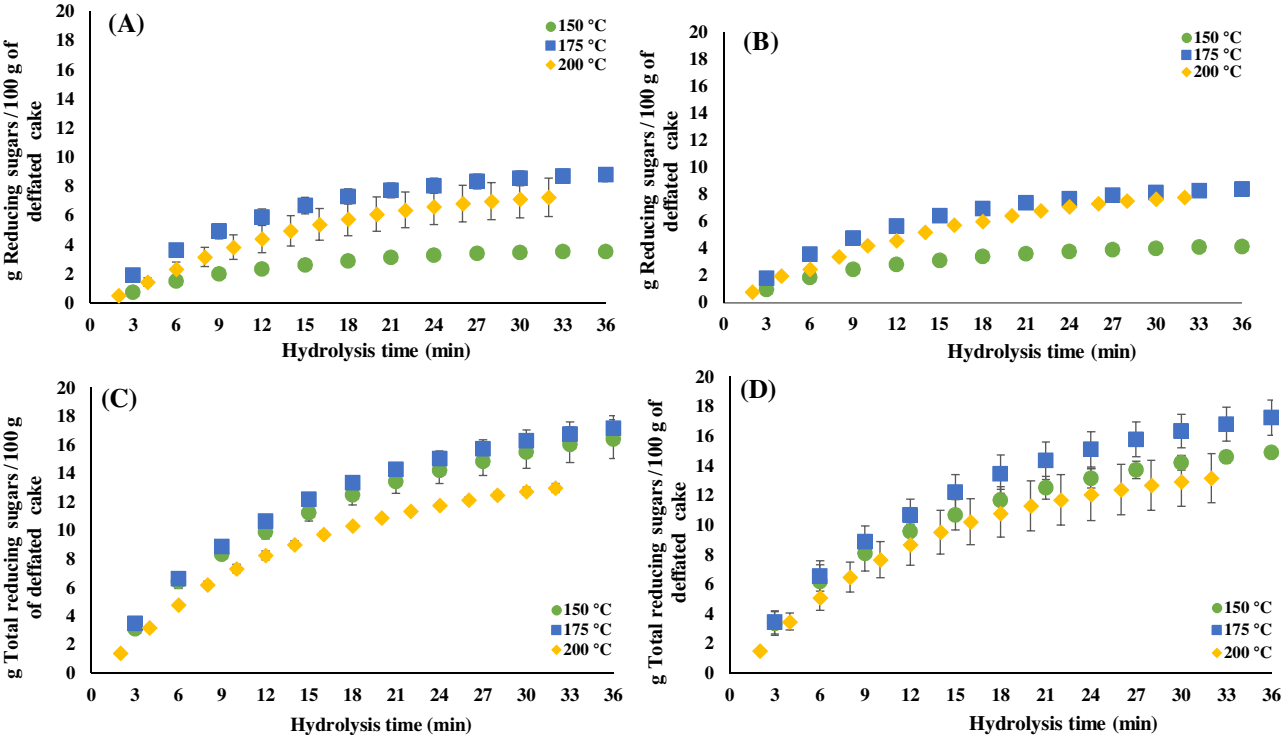

Fig. 3. Yield of reducing sugars (RS) and total reducing sugars (TRS), in glucose equivalents, of defatted cake at different temperatures as a function of time: (A) RS at 22.5 MPa; (B) RS at 30.0 MPa; (C) TRS at 22.5 MPa; (D) TRS at 30.0 MPa.

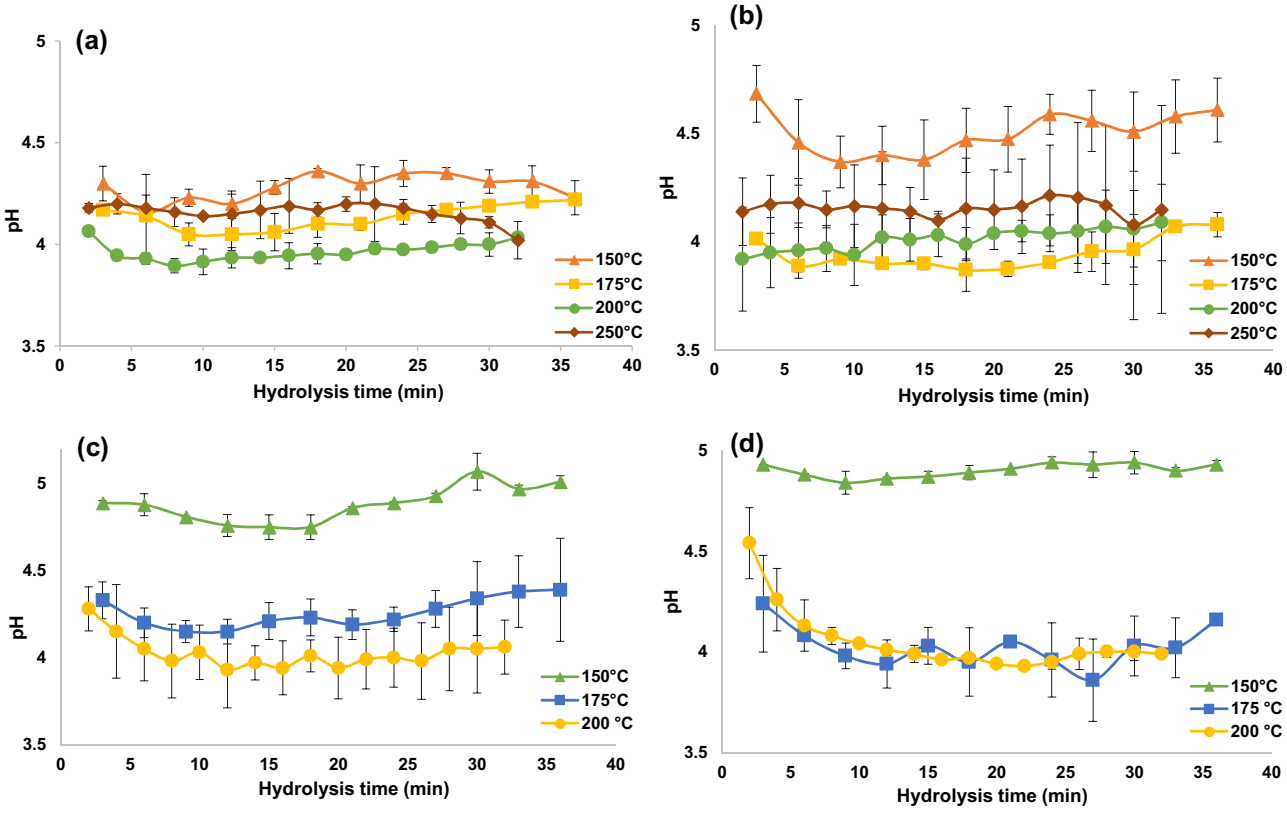

Fig. 4. pH of the hydrolysates obtained by subcritical water hydrolysis at different temperatures as a function of time: of green coffee bean powder (A) at 22.5 MPa; (B) at 30.0 MPa; and of defatted cake (C) at 22.5 MPa; (D) at 30.0 MPa.

tinuous flow, Cantero et al. [27] reported optimal yields at residence times of about 1 s; longer residence times resulted in conversion of the sugars into secondary decomposition products. Residence times less than about 60 s are not economically feasible in a packed-bed flow-through SubCW reactor as designed here, largely due to the dilution of the hydrolyzate. Instead, Cantero et al. [26] fed a cellulose slurry to the reactor, a strategy which afforded rapid heat up and cool down while minimizing hydrolyzate dilution. Feeding biomass slurry to a high-pressure reactor brings significant technical challenges and may not be practical in all cases. In comparison, the packed-bed flow-through reactor is easy to load, although with decreased maximum sugar yields compared to those that can be obtained using a slurry reactor [30].

The sugar yields observed at temperatures greater than 175 °C can be explained by a combination of thermal and ionic effects. Similar behavior has been observed previously for TRS yields obtained from subCW treatment and are attributed to the decomposition of the lignocellulose complex to form monomers (sugars) and subsequent degradation of sugars to form acids and other compounds [30,44,45]. When the temperature is increased from 150 °C to 200 °C, the ionic product of water increases, thereby increasing the concentration of both H_3O^+ and OH^- ions in solution. H_3O^+ catalyzes carbohydrates dehydration reactions that form organic acids and other break down products; therefore, increasing the temperature from 150 to 200 °C is expected to increase sugar decomposition rates due to both the expected thermal Arrhenius effect as well as an ionic effect. Furthermore, sugar decomposition releases organic acids, which further catalyzes sugar degradation, in an autocatalytic process.

3.2. Temperature effect on the pH

Hydrolyzate pH was measured to further investigate the possibility of auto-catalytic sugar degradation. Fig. 4 shows the hydrolyzate pH measured at different experimental conditions and as a function of reaction time. At a given hydrolysis temperature, hydrolyzate pH was acidic and stable over the treatment time. Hydrolyzate pH became increasingly acidic with increasing treatment temperature. Similar to the observations for coffee waste hydrolyzate, Prado et al. [8] studied SubCW hydrolysis of sugar cane bagasse and observed that hydrolyzate pH decreased with increasing reaction temperature. The pH measurements are consistent with the degradation of sugars to form organic acids, as inferred from the RS and TRS yield data and reported previously [30,46]. Moreover, the measured hydrolyzate pH is consistent with the presence of carboxylic acids. Supporting this conclusion, Pourali et al. [46] identified four carboxylic acids (acetic, formic, glycolic and levulinic acids) in the hydrolyzate obtained by SubCW hydrolysis of rice bran. In conclusion, the measured hydrolyzate pH is consistent with thermal and acid-catalyzed breakdown of sugars into carboxylic acids via an auto-catalytic process that apparently occurs even under flow conditions.

3.3. TPC in hydrolyzates

Despite the low RS and TRS yields obtained under flow conditions, coffee contains other components, including phenolic compounds, with potential value as high added-value extracts. Naturally occurring phenolic compounds are valuable due to their

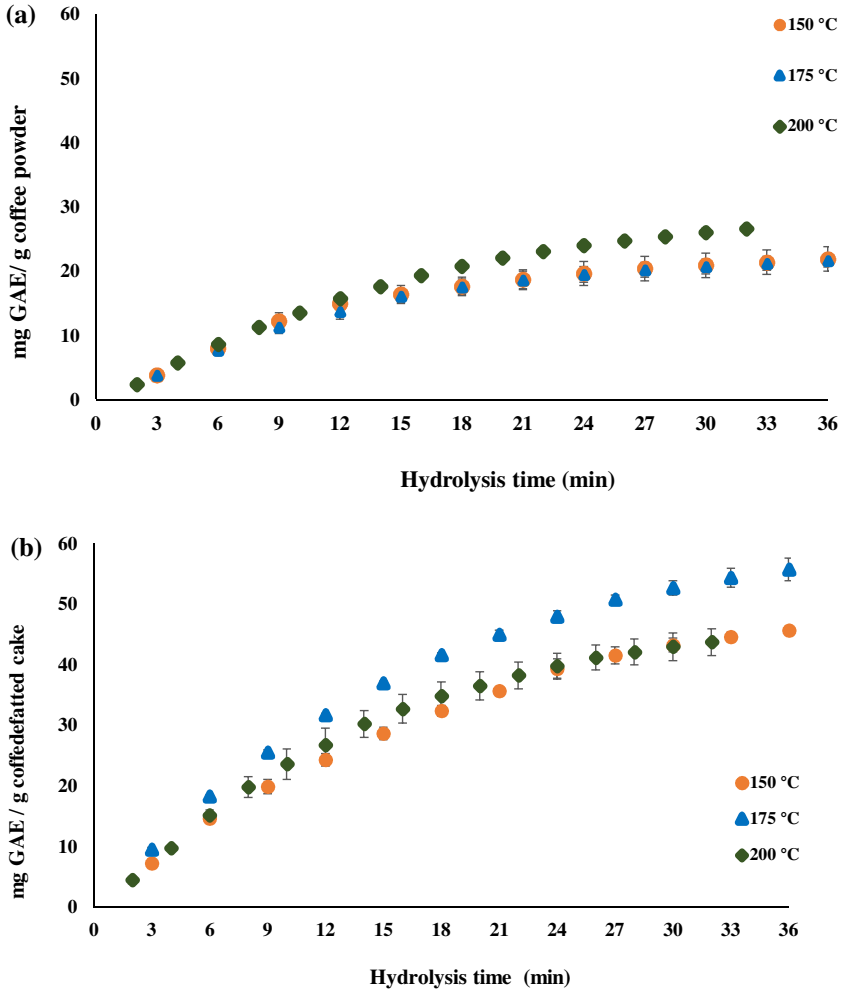

Fig. 5. Effect of subcritical water temperature on TPC (mg GAE ⁄ g residue coffee): (a) green coffee bean powder; (b) defatted cake.

potential antioxidant properties [47,48], and simultaneous recovery of sugars for bioenergy applications and phenols for food and nutraceutical applications, has potential to maximize the value of food wastes. Fig. 5 shows TPC yields obtained from SubCW processing of green coffee bean powder and defatted cake treated at 150, 175 and 200 °C, all at 22.5 MPa. The highest TPC yields were obtained at 200 °C for coffee powder (26.6 ± 0.6 mg GAE/g powder) and at 175 °C for the defatted cake (55.7 ± 1.9 mg GAE/g defatted cake). Increasing the temperature from 150 to 175 °C improved TPC yield for defatted cake but had no effect on coffee powder yield. For coffee powder, increasing the temperature from 175 to 200 °C led to a modest improvement in TPC yield, whereas TPC yield obtained from the defatted cake decreased when the temperature was increased from 175 to 200 °C.

Singh and Saldaña [49] studied the extraction of total phenolic compounds from potato peel at temperatures ranging from 100 to 240 °C, achieving the highest TPC yields at temperatures ranging from 140 to 180 °C, and a reduced yield when the temperature was increased to 240 °C. Similarly, Xu et al. [21] noted that the optimal temperatures for TPC extraction were in the range 160–180 °C; again, TPC yield decreased when treatment temperature was increased beyond 180 °C.

The observed TPC extraction performance is consistent with the properties of SubCW. For temperatures greater than 25 °C, the dielectric constant of water monotonously decreases from its familiar value of 78–1 at the critical point [50]. As a result of reduced dielectric constant, water's solvation capability approximates that of organic solvents, increasing the water solubility of organic compounds such as phenols [51,52]. Simultaneously, water becomes more aggressive chemically with increasing temperature, as already discussed. On the one hand the aggressive conditions have the effect of opening the biomass structure to improve phenol extraction performance. On the other hand, the increasingly aggressive chemical properties of water, possibly combined with organic acids formed by carbohydrate degradation, appears to result in decreasing TPC yield with increasing treatment temperature as phenolic compound degradation becomes increasingly rapid at high temperatures [53].

3.4. Hydrolyzate sugar content

Hydrolyzate sugar content was quantified by HPLC for several specific carbohydrates. Fig. 6 provides data on the hydrolyzate sugar content observed after treatment at 22.5 MPa for green coffee bean powder and defatted cake. Fig. 6a shows that SubCW hydrolysis of coffee powder produced hydrolyzates with lower sugar content compared to the defatted cake (Fig. 6b). Interestingly, glucose is the main sugar present in the coffee powder hydrolyzate whereas cellobiose is for the defatted cake hydrolyzate. In both cases, increasing temperature led to a decrease in the dominant sugar product, again consistent with sugar degradation occurring at increasing temperature. Bobleter [54] obtained similar results, finding that hemicellulose degrades at temperatures in the range from 150 to 200 °C and that cellulose does not degrade until tem-

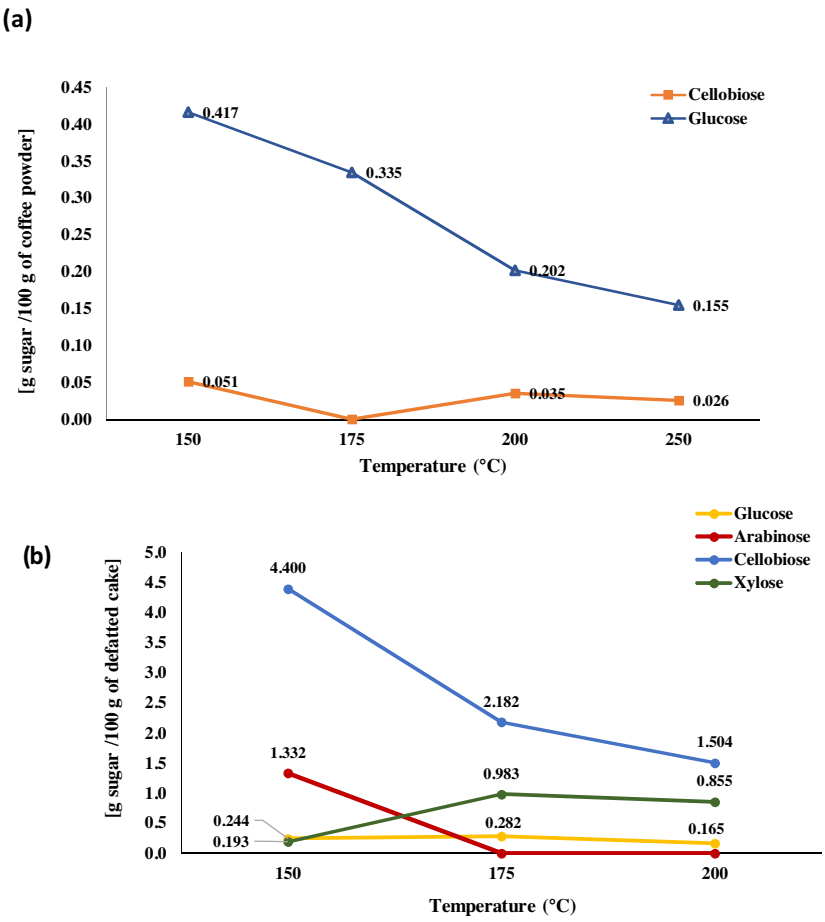

Fig. 6. Sugars obtained by hydrolysis with subcritical water at different temperatures and 22.5 MPa as a function of time: (a) green coffee bean powder; (b) defatted cake.

perature is increased to at least about 240 °C. Therefore, the main effect of increasing temperature from 150 to 250 °C may be to accelerate degradation of simple sugars obtained from hemicellulose hydrolysis; temperatures greater than 250 °C may be required to benefit from cellulose hydrolysis.

Comparing the results in Fig. 6 with data obtained from the RS and TRS measurements of green coffee powder (Fig. 2a and c) is instructive. Both RS and TRS yields decrease monotonically with increasing temperature at 22.5 MPa; in comparison, at 30.0 MPa both RS and TRS increase from 200 to 250 °C (Figs. 2b and 2d). It follows that hemicellulose hydrolysis occurs from 150 to 200 °C and that hemicellulose sugar decomposition rates become increasingly rapid when the temperature is increased from 175 to 200 °C. At 200 °C, cellulose begins to hydrolyze to form glucose, cellobiose, and especially longer chain glucose oligomers. Differences in RS and TRS yields are therefore likely attributable to the relative production rates of sugars and oligosaccharides at 250 °C compared to those obtained at 200 °C.

For the defatted cake residue, in contrast, cellulose hydrolysis may begin at a lower temperature (175 versus compared to 200 °C for the powder) to produce cellobiose in relatively high concentrations (4.4 g of cellobiose/100 g of defatted cake) (Fig. 6). Fig. 3 showed that TRS yield was higher than RS yield for defatted cake hydrolysis, an observation that is attributable to a higher yield of oligosaccharides from defatted cake than of powder coffee and consistent with the HPLC results in Fig. 6b showing greater cellobiose content obtained by hydrolysis of the defatted cake.

Measurements of C_5-sugars provide further insight into sugars degradation. Arabinose and xylose were monitored as representative C_5-sugars. Xylose and arabinose are products from hemicellulose hydrolysis [55,56]. Hemicellulose is hydrolyzed and degraded over the range from 150 to 200 °C [54]. Arabinose and xylose were absent in hydrolyzates of coffee powder at all temperatures. This is likely attributable to rapid degradation of the C_5-sugars obtained from hemicellulose hydrolysis present in coffee powder. For the defatted cake, the hydrolyzate obtained at 150 °C contained only arabinose. Xylose content in the hydrolyzate obtained from treatment of defatted cake increased at 175 °C but decreased slightly at 200 °C, consistent with its degradation.

Table 3 provides hydrolyzate concentrations of 5-HMF and furfural. The maximum concentration of 5-HMF was obtained at 175 °C for both wastes. HMF and furfural compounds are products of the dehydration of glucose, arabinose, fructose and xylose [23,55]; in general the furanic compounds are not desirable products as they are fermentation inhibitors [30]. The observation of maximum furanic compound yield at 175 °C may suggest their breakdown into smaller compounds and/or polymerization to form insoluble humins as temperature is increased to 200 and especially 250 °C [57].

3.5. FESEM

Fig. 7 shows FESEM images of defatted cake: (a), (e), and (i) prior to hydrolysis in SubCW treatment; (b), (f) and (j) after treatment at 150 °C; (c), (g), and (k) after treatment at 175 °C; and (d), (h), and (l) after treatment at 200 °C, all at a treatment pressure of 22.5 MPa. Figs. 7 (a), (e) and (i) show that the surface of the raw defatted cake is brighter than those of the samples that underwent SubCW treatment, consistent with decreased oleoresin content in the treated samples [58]. The presence of oleoresin in a sample

Table 3
Inhibitors obtained by subcritical water hydrolysis of residues coffee during 36 min.

Residue	Temperature (°C)	5 –HMF (μg/g residue)	Furfural (μg/g residue)
powder	150	9.7 ± 0.9	15 ± 5
	175	49 ± 2	31 ± 8
	200	19 ± 1	17.02 ± 0.74
	250	16 ± 3	18 ± 7
Cake defatted	150	4.8 ± 0.6	([a])
	175	156 ± 10	([a])
	200	74.2 ± 3.2	3.7 ± 0.3

[a] below the limit of quantification. Values presented as mean ± standard deviation.

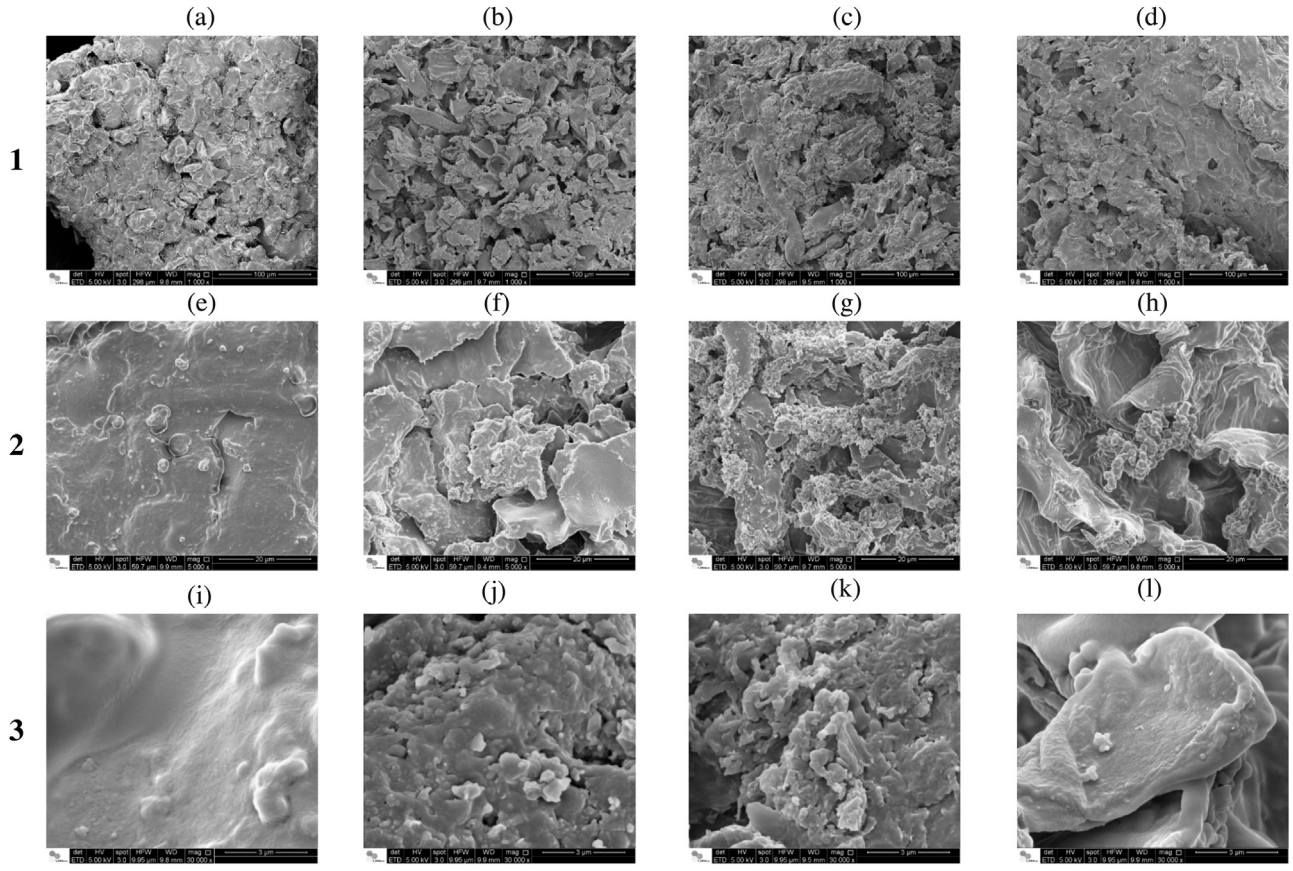

Fig. 7. Images obtained by FESEM on the surface of cake defatted green coffee beans analyzed before (column a) and after the subcritical water hydrolysis at 150 °C and 22.5 MPa (column b), 175 °C and 22.5 MPa (column c) and at 200 °C and 22.5 MPa (column d) at different magnifications. Scale bar: 100 μm (row 1); 20 μm (row 2); 3 μm (row 3).

hinders the flow of primary electrons to the focal point of the electron beam, thus artificially brightening the image due to charging. SubCW treatment decreases the sample oil content, thereby reducing the appearance of artificial brightness due to charging. Here, FESEM images indicate extraction of oleoresin content at even the mildest subCW conditions.

The SubCW treated samples in Fig. 7(b)–(d) show important differences compared to the raw sample. While granules are present on the entire surface of the raw sample (a), the sample treated at 150 °C presents a fractured surface that is covered with particulate material (b). Likewise, the sample treated at 175 °C (c) has particulate material visibly deposited on the surface. The sample treated at 200 °C (d) has a smooth surface with fewer beads and less deposited particulate matter when compared to samples treated at lower temperatures. At higher magnifications, the raw samples exhibit very smooth surfaces, as shown in Fig. 7(e) and (i). However, the samples treated at 150 °C have irregularly shaped and rough surfaces (f); more deposited material can be seen in the enlarged image (j). The sample treated at 175 °C shows still greater amounts of deposited particles, as is apparent in (g) and in the magnified image (k). The images obtained from samples treated at 175 °C show a distinct morphology, which coincidentally corresponds to the maximum RS, TRS, and TPC yields. Finally, treatment at 200 °C results in a surface with reduced amounts of surface particulate, for example as can be seen when comparing (k) to (l).

3.6. FTIR

Fig. 8 provides representative FTIR spectra obtained for raw coffee powder and its treated residues. Data in the range 1500–1800 cm^{-1} are shown in Fig. 8, as this spectral region allows specific, clearly identifiable bands to be highlighted. The band at 1590 cm^{-1} can be attributed to lignin [59]. Consistent with this assignment, the band at 1590 cm^{-1} is present at all treatment temperatures and increases in prominence at the highest treatment temperature of 250 °C. A second prominent peak present in the

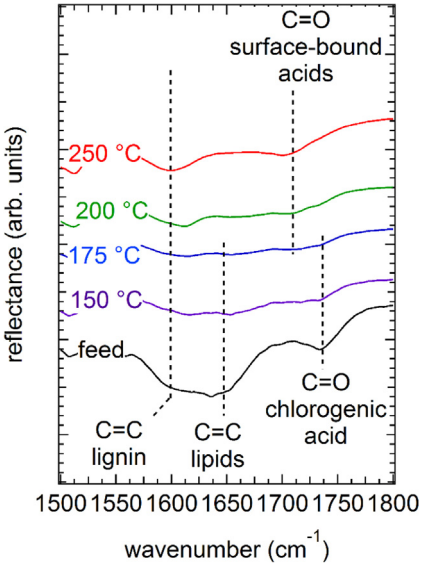

Fig. 8. FTIR spectra of the raw and subCW treated green coffee powder.

raw powder at approximately 1650 cm^{-1} may be associated with lipid content, an assignment which is based both on band location [60,61] and its disappearance after treatment at 150 °C.

Bands present from 1700 to 1740 cm^{-1} require specific attention, as bands in this range are associated with carbonyl content [62]. In the raw powder, a clear carbonyl band is present at 1740 cm^{-1} and then disappears with mild treatment at 150 °C. The presence of the band at 1740 cm^{-1} in the raw powder is attributable to carboxylic acids that are naturally occurring in coffee, likely the carboxylic acid associated with chlorogenic acid [63]. Disappearance of the band after mild treatment is consistent with behavior expected for components that are not covalently linked to the lignocellulosic structure [63].

When the treatment temperature is increased to 175 °C, a new band in the carbonyl range appears at approximately 1710 cm^{-1} and increases in relative intensity with increasing treatment temperature. The 1710 cm^{-1} band can be attributed to surface bound carboxylic acids which are covalently linked to (or otherwise trapped within) the residual lignocellulosic complex and which remain after SubCW treatment. Surface-bound carboxylic acids, which would have pKa's on the order of 4–5, are consistent with the observation of acidic hydrolyzate and indicate that the degradation reactions responsible for formation of water soluble organic acids may occur in the solid phase. Alternatively, surface-bound carboxylic acids may be an indication of solution phase polymerization to form insoluble complexes that re-deposit on the biomass surface. In either event, flow-through treatment may need to be combined with shorter residence times or an alkali buffered feed to limit sugar degradation [64,65].

4. Conclusions

Coffee powder and defatted cake were treated under flow-through subCW conditions to investigate valorization of coffee factory residues for the production of chemicals and biofuels. The flow-through operation was investigated as a means to reduce degradation of sugars and thereby improve sugar and phenolic compound yield. The maximum yields of reducing sugars and phenolic compounds were observed for SubCW hydrolysis at 175 °C. Quantitatively, the maximum yields were 8.8 g RS/100 g and TCP of 55.7 mg GAE/g of defatted cake (175 °C, 22.5 MPa). The sugar yield decreased at temperatures above 175 °C, an observation attributed to break down of sugars to produce 5-HMF, furfural, and organic acids. Flow conditions (with residence times of approximately 9 min) were insufficient to prevent sugar degradation.

FESEM was used to examine biomass surface morphology before and after treatment SubCW. FESEM images revelaed physical degradation of the material by hydrolysis, including deposition of particulate material and surface fracturing. FTIR spectroscopy indicated that mild conditions resulted in removal of non-covalently bonded carboxylic acids For samples treated at temperatures greater than 150 °C, FTIR identified carboxylic acid groups associated with the biomass surface and not present in the original sample. The carboxylic acid groups observed in samples treated at temperatures greater than 150 °C suggest the possibility of solid phase conversion of carbohydrates to acids or the formation of water-insoluble complexes bearing acid groups during hydrolysis.

In summary, flow-through SubCW hydrolysis of coffee wastes shows promise for recovering sugars and chemicals; additional work is required to identify optimal conditions which simultaneously maximize holocellulose hydrolysis and minimize both sugar degradation and dilution.

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