OBTAINING SUGARS FROM PALM FIBER, COCONUT HUSK AND GRAPE SEED BY HYDROLYSIS WITH SUBCRITICAL WATER

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Abstract. The need to substitute fossil sources of energy by others renewable and non-pollutant stimulates researches on conversion of lignocellulosic biomass into fermentable sugars for production of bioethanol. The clean and rapid method of sub/supercritical hydrolysis (SWH) has been proven technically feasible in face of acid and enzymatic hydrolysis, with the advantages of no need of pre-treatment, shorter reaction time, lower corrosivity, lower residue generation and no use of toxic solvents. In this work, a semi-batch unit equipped with a 50 mL reaction vessel was used to perform SWH of three residues from the food industry: pressed palm fiber, coconut husk and grape seed previously defatted by supercritical fluid extraction. The process was conducted at 208 and 257 °C for 30 min, with water flow rate of 33 mL/min and under 20 MPa. The hydrolysates were analyzed by HPLC as for their contents of 5-hydroxymethylfurfural (5-HMF), arabinose, fructose, galactose, glucose, mannose, xylose, cellobiose and raffinose. For pressed palm fiber, as temperature increased, the yield of raffinose decreased (1.4 % vs. 1.0 %), while the yield of glucose (0.1 % vs. 0.7 %) and 5-HMF (0.1 % vs. 0.8 %) increased; total saccharides analyzed accounted for 3.9 % at 257 °C. The yield of sugars from coconut husk did not vary with the temperature (4.5-4.8 %), but 5-HMF yield increased with it (0.4 % vs. 1.3 %). Grape seed presented the lowest sugars yield (around 1 %). The results indicate that SHW should be evaluated and optimized individually for each raw material.

Keywords: Coconut husk; Defatted grape seeds; Pressed palm fiber; Subcritical water hydrolysis, Sugars

1. Introduction

The energy obtained from agricultural wastes or agricultural by-products is a form of renewable energy. In principle, using this energy does not add carbon dioxide, a greenhouse gas, to the atmosphere, in contrast to fossil fuels [1]. Agricultural wastes contain a high amount of organic constituents as cellulose, hemicellulose and lignin, having a high-energy content [2, 3]. Therefore, they can be recognized as potential sources of renewable energy based on benefits of both the generation of energy and environmental protection.

The biomass conversion to energy can be divided into three main approaches: direct combustion processes, biochemical processes and thermochemical processes. Thermochemical processes may be further subdivided into pyrolysis, gasification and liquefaction, which includes high-pressure liquefaction using sub/supercritical fluids. These processes convert waste biomass into energy-rich products. Each technology has its own advantages, depending on the type of biomass and the form of energy needed [4]. For instance, pyrolysis and gasification have the advantage of not requiring high pressure, but the biomass has to be pretreated by drying to reduce the water content. On the other hand, the liquefaction technology using subcritical water can be used to process wet biomass and is able to achieve high liquefaction efficiency as in conventional pyrolysis [5]. Due to these features, the sub/supercritical water hydrolysis (SWH) process has gained wide.

Subcritical water is defined as liquid water in the temperature range of boiling point to critical point (100-374 °C) or near critical point. In order to keep the water in the liquid state, pressure is applied. It is a very promising reaction medium for the conversion of biomasses, such as lignocellulosic materials, since

it has the ability to break the rigid structure of the lignocellulosic complex and to decompose it into smaller components by hydrolysis and further reactions [6-8].

The hydrolysis of lignocellulosic biomasses with subcritical water presents several advantages when compared to traditional technologies. Its main advantage is that it does not use organic solvents, which is a factor of major importance in any process, since organic solvents must be recycled, incinerated or submitted to an appropriate unitary operation that results in a waste non-aggressive to the environment [9].

However, the application of SWH to agricultural residues is a challenging task because hydrolysis rates and yields depend on the characteristics of the residue, including cell wall composition and structure as well as the monosaccharides present and the type of bonds between them. Moreover, lignin is an especially problematic component of agricultural residues. Therefore, each raw material represents a technological challenge that needs to be studied individually, since the optimal process conditions for a given raw material may not be the most efficient for other types of residues [10].

There are relatively few examples of applications of SWH for the hydrolysis of agricultural and food industry residues. Most relevant examples include corn stalks and stover, sugarcane bagasse and rice bran. Besides these important residues there are other potential raw materials that can be used to produce simple sugars using SWH, including grape seeds, pressed palm fiber and coconut husk. Grape seeds are a residue of wineries, composed mainly by lignin and hemicellulose. They also present a high content of oil, which can be extracted and used in several applications, such as cosmetics, foods, etc. After the oil fraction is extracted, grape seeds have no other immediate use. Pressed palm fiber is a residue from the pressing of palm fruits to produce oil. It is rich in cellulose and hemicellulose. Coconut husk is another lignocellulosic material produced from processing of coconuts for beverages and coconut powder, categorized as hard wood and characterized by high toughness due to its high lignin content. Since these residues are produced in relatively high amounts in Brazil, they represent an opportunity to make better use of cheap and abundant waste to produce high added value sub products.

Therefore, the objective of this work was to evaluate the use of SWH under different temperatures to produce sugars from three residues from agricultural industry: coconut husk, defatted grape seeds and pressed palm fiber.

2. Material and methods

2.1 Raw Material

The dry palm pressed fiber was supplied by Agropalma (Tailândia, PA, Brazil) after the palm had been used to manufacture palm oil. The coconut husk was donated by Ducoco Alimentos (Linhares, ES, Brazil). The raw materials were stored at -18 °C and then they were comminuted in a knife mill (Marconi, model MA 340, Piracicaba, Brazil) equipped with a 1 mm sieve before they were used as samples in the experiments.

The grape seeds were provided by the Villa Francioni winery (São Joaquim, SC, Brazil). The seeds were collected after wine fermentation, and were separated from stalks and peels by sieving and air blowing. The resulting sample was dried under the sun for 7 days. The seeds were ground frozen to preserve their vegetable oil and then they were extracted by supercritical CO_2 [11]. The residue from the supercritical extraction process was stored at -18 °C and subsequently it was used for SWH.

2.2 Hydrolysis equipment

The semi-batch unit shown in Figure 1 was built to hydrolyze lignocellulosic biomasses using sub/supercritical water. The equipment can operate up to 400 ºC and 40 MPa. The system is composed by a liquid high pressure pump (Thar, model P-50, Pittsburgh, PA, USA) for water pumping, a stainless steel heating coil (Autic, 6 m × 1/8" i.d., Campinas, Brazil) for water heating, a 50 mL stainless steel reactor (Autic, Campinas, Brazil) with metal-to-metal fit to allow using temperatures up to 400 °C, a micrometric needle valve (Autoclave Engineers, Erie, PA, USA) and a stainless steel refrigeration coil coupled to a thermostatic bath (Marconi, model MA-184, Piracicaba, SP, Brazil) operating at 40 °C to assure that the reaction is quickly quenched after the hydrolysate exits the reactor. The equipment also contains block valves, thermocouples and manometers.
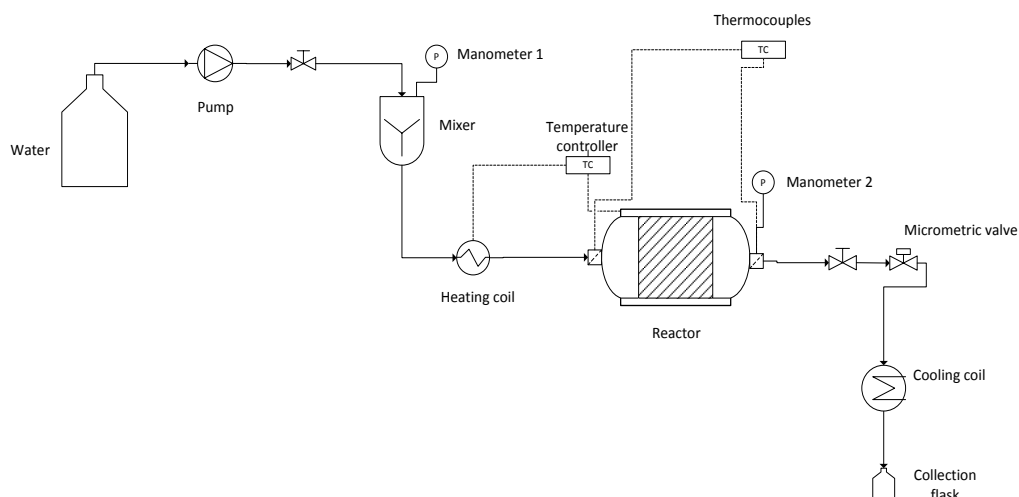
Figure 1. Scheme of the equipment used for subcritical water hydrolysis.

2.3 Hydrolysis of raw materials

The experiments were carried out using 10-35 g of raw material. The sample was inserted in the reactor, which was connected to the equipment. Distilled water was pumped through the system to remove the air from it. Once the system was filled with water, the pump was stopped, the micrometric valve was closed and the heating of the coil and of the reactor was started. The heating coil temperature was set at process temperature (200 °C or 250 °C) while the reactor was pre-heated to 120 °C to assure that there was no hydrolysis of hemicellulose during the pre-heating time. After the temperature stabilized, which took around 20 min, the dynamic period of the process was started by pumping water at 33 mL/min through the system for 30 min. When the dynamic period was started, the reactor temperature was set to process temperature (200 °C or 250 °C), causing a temperature profile with time until its stabilization. Pressure was kept constant at 20 MPa. Hydrolysate samples were collected each 2 min. All the experiments were performed in duplicate.

2.4 Analysis of the hydrolysate

Determination of pH. The pH of the hydrolysates was determined using a digital pHmeter (Digimed, model DM-22, Santo Amaro, Brazil).

Determination of 5-HMF and saccharides. The saccharides and 5-HMF were determined by ion exchange chromatography (HPLC-PAD). Prior to the analysis the samples were diluted in distilled water (when necessary) and filtered through a 0.45 μm filter. Samples were identified and quantified using a Dionex DX-500 system (Sunnyvale, CA) consisting of a GP50 gradient pump and an ED-40 electrochemical detector operating in the amperometric pulse mode (gold electrode and AgCl reference electrode). A Carbopac PA-1 (4 × 250 mm) column and a PA-1 (4 × 50mm) guard column were used. Elution was performed at 1 mL/min with NaOH solution following the gradient program: 1 mM for 12 min, linear gradient 1-20 mM, and 150 mM for 15 min. The standard calibration curve was built with pure standards of 5-HMF, arabinose, fructose, galactose, glucose, mannose, xylose, cellobiose and raffinose (Sigma-Aldrich, Milwaukee, WI, USA). The identification and quantification of sugars were performed, respectively, using the retention time (t_R) and external standardization with injection of at least seven points of different concentrations of the chromatographic grade standards.

3. Results and discussion

In all experiments the heating coil was adjusted to the process temperature (200 °C or 250 °C) and the reactor temperature was adjusted to 120 °C during the static period. After this period, both the heating coil (inlet) and the reactor jacket (outlet) temperatures were adjusted to the process temperature, which generated a temperature profile in the reactor (Figure 2). As there was a difference between inlet and outlet temperatures, the results are expressed throughout the text in terms of the outlet temperatures: 204-212 °C and 256-259 °C for process temperatures of 200 °C and 250 °C, respectively.
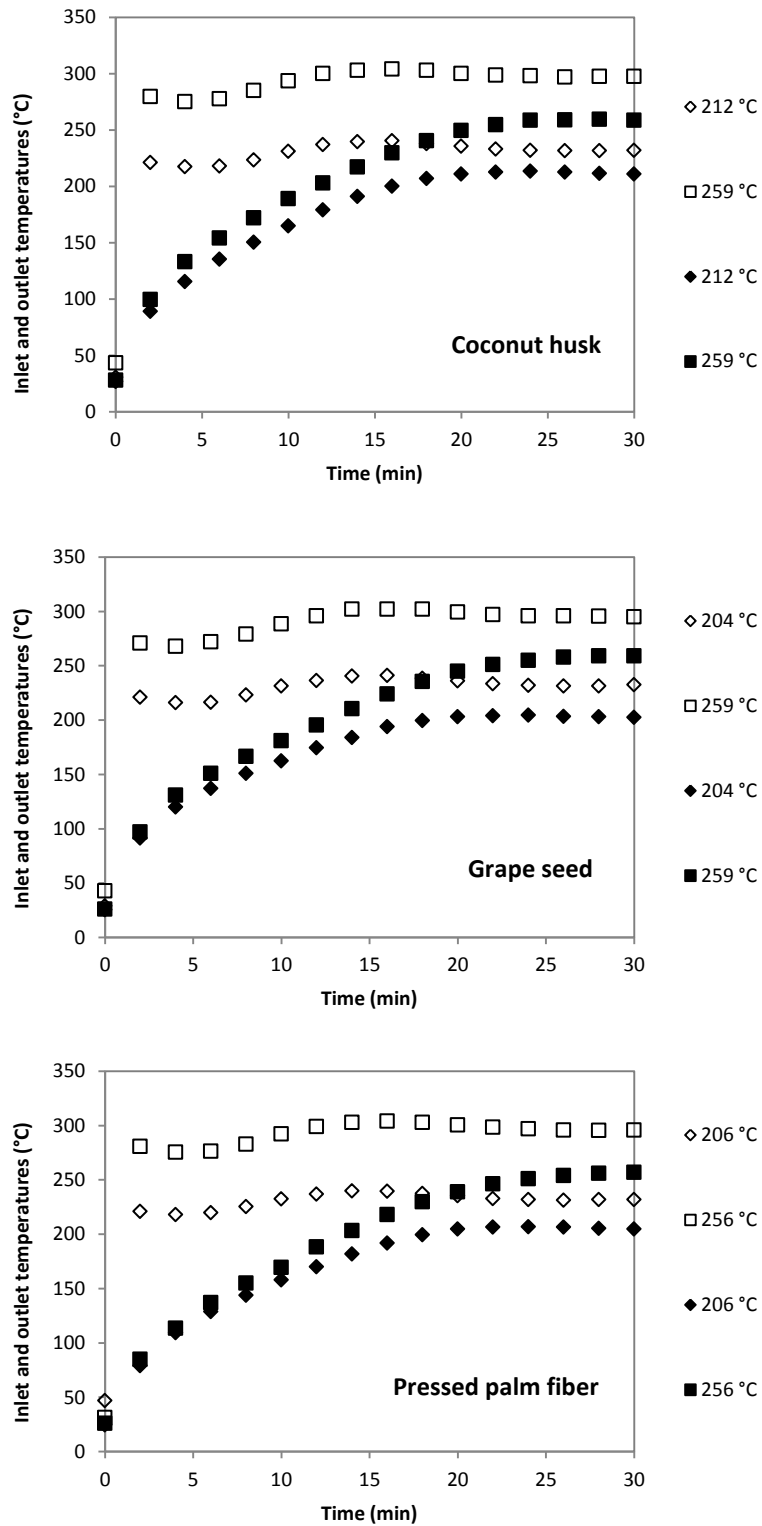
Figure 2. Reactor inlet (open symbols) and outlet (filled symbols) temperatures in the subcritical water hydrolysis at different temperatures.

The solid residue at the end of the experiments is shown in Figure 3. It decreased with temperature for all the raw materials, which indicates that the lignocellulosic complex was degraded at 250 °C. On the other hand, 200 °C was not enough to break it down; therefore, only hemicellulose sugars could be recovered at lower temperature.
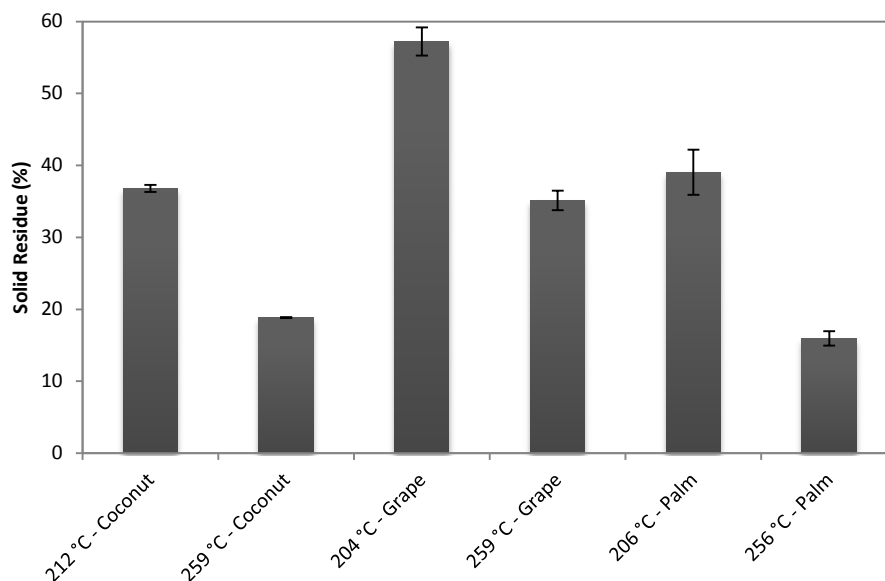
Figure 3. Solid residue in the reactor after the subcritical water hydrolysis for 30 min.

The pH of the hydrolysate fractions obtained at different temperatures is presented in Figure 4. The lower pH was obtained when working at lower temperature indicates a higher degradation of sugars under this condition; the sugars degrade to organic acids among other compounds. Liu and Wyman [12, 13] reported pH of 3.5-5.5 for corn stover SWH in semi-batch mode.

The hydrolysates were also analyzed for their contents of 5-HMF, arabinose, fructose, galactose, glucose, mannose, xylose, cellobiose and raffinose (Table 1). For coconut husk and grape seed there was a slight decrease on saccharides recovered with temperature increase. As for pressed palm fiber, the saccharides recovered increased with temperature. On the other hand, the total reducing sugars recovered increased with temperature for all raw materials [14]. This behavior can be explained by the hydrolysis mechanisms taking place at different temperatures. According to the literature all the hemicellulose is hydrolyzed at 190-230 °C during 2-15 min [15, 16]. On the other hand, little cellulose hydrolysis occurs below 230 °C, either in its pure form or when in lignocellulosic complexes [17-19], so that when hemicellulosic sugars recovery is intended, the process is usually carried out at 150-230 °C [20-22]. Therefore, as the reactor temperature gradually increased from the pre-heating temperature of 120 °C up to the process temperature, the hemicellulose was increasingly solubilized during the period of the stabilization of the temperature (Figure 2). The treatment at 250 °C, on the other hand, collapses the lignocellulosic structure [23], and above this temperature the hydrolysis rates increase by up to one order of magnitude.

In the SWH process the sugars can be degraded to organic acids, erythrose, glycolaldehyde, glyceraldehyde, dihydroxyacetone, furfural and 5-HMF, among others [24, 25].

The degradation also increased with temperature, which can be demonstrated by the higher 5-HMF yield, despite the higher yield of sugars. The production and degradation rates of the monomers vary with the type of sugar, but the degradation of the sugars always increases with time and temperature. In the subcritical process, the glucose or oligomers degradation rates are higher than the hydrolysis rate of cellulose; therefore, high yields of monosaccharides cannot be obtained. As the temperature increases, the hydrolysis rate of the cellulose and oligosaccharides increase faster than the decomposition rates of the monosaccharides. The cellulose hydrolysis rate increases tenfold when the temperature is increased from 240 °C to 310 °C. On the other hand, the glucose decomposition rate also increases rapidly with temperature and becomes higher than the glucose release rate between 250 °C and 270 °C [9, 24, 27-29]. As the different raw materials may present different bonds in the lignocellulosic complex, each one should be individually studied and optimized.

The total saccharides yield determined by HPLC (Table 1) was lower than the total reducing sugars determined by the Somogyi-Nelson method [14], which indicates that around 20 % to 80 % of the sugars recovered in the process are in the oligomeric form as cellotriose, cellotetraose, cellopentaose, etc. The degree of polymerization of the solubilized oligosaccharides tends to decrease with temperature [21-23, 30-32]. This indicates that the glycosidic bond may be easier to destroy and oligosaccharides may exist for extremely short times before breaking down into monomers [19]. In Table 1 this behavior can be confirmed, where it can be noticed that the yield of cellobiose and raffinose decreased with temperature.
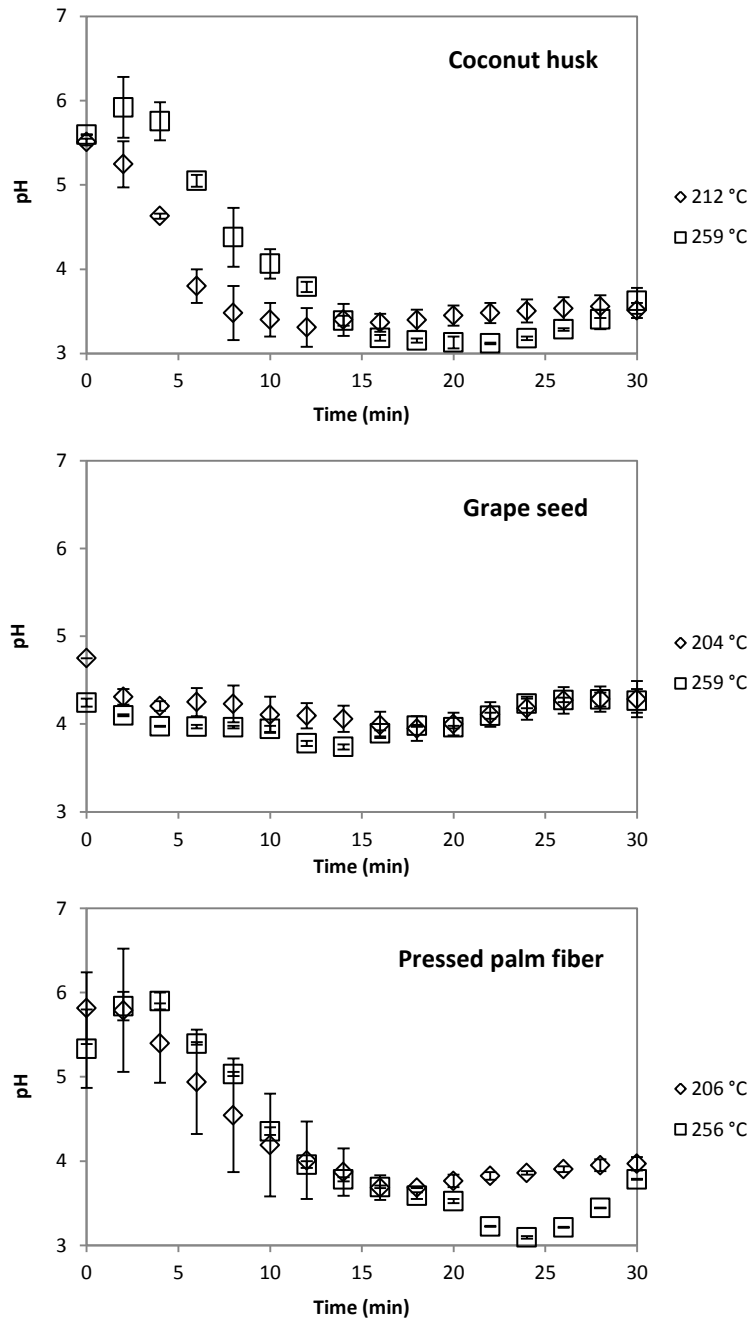
Figure 4. pH of the hydrolysates obtained by subcritical water hydrolysis at different temperatures.

Table 1. Saccharides and 5-HMF obtained by subcritical water hydrolysis of coconut husk, grape seeds and pressed palm fiber during 30 min (w, %)

	Coconut husk		Grape seeds		Pressed palm fiber	
	212 °C	**251 °C**	**204 °C**	**259 °C**	**206 °C**	**256 °C**
5-HMF	0.43	1.27	0.03	0.08	0.10	0.81
Arabinose	0.23	0.26	0.05	0.12	0.42	0.34
Fructose	3.16	0.25	0.08	0.11	0.30	0.24
Galactose	0.12	0.15	0.19	0.09	0.12	0.10
Glucose	1.17	1.22	0.23	0.14	0.14	0.76
Mannose	0.02	0.19	0.05	0.07	0.06	0.12
Xylose	1.58	1.31	0.23	0.16	0.77	0.87
Cellobiose	0.14	0.12	0.05	0.04	0.19	0.41
Raffinose	1.20	0.97	0.58	0.23	1.44	1.05
Monosaccharides	3.43	3.39	0.65	0.69	1.54	2.42
Total saccharides	4.77	4.48	1.29	0.96	3.18	3.88

Figures 5-7 show the yield of sugars and 5-HMF in the hydrolysates obtained at different temperatures during the SWH process for each raw material. For coconut husk (Figure 5) at 212 °C mainly hemicellulose sugars were recovered up to 15 min, while glucose was recovered after this period. For 259 °C the fractions recovered at 10-20 min had higher concentration of both cellulosic and hemicellulosic sugars, and the hydrolysis process finished earlier; after 22 min only degradation products were recovered. The cellulose degradation at higher temperature leads to lower residue at the end of the process in the reactor (Figure 3).
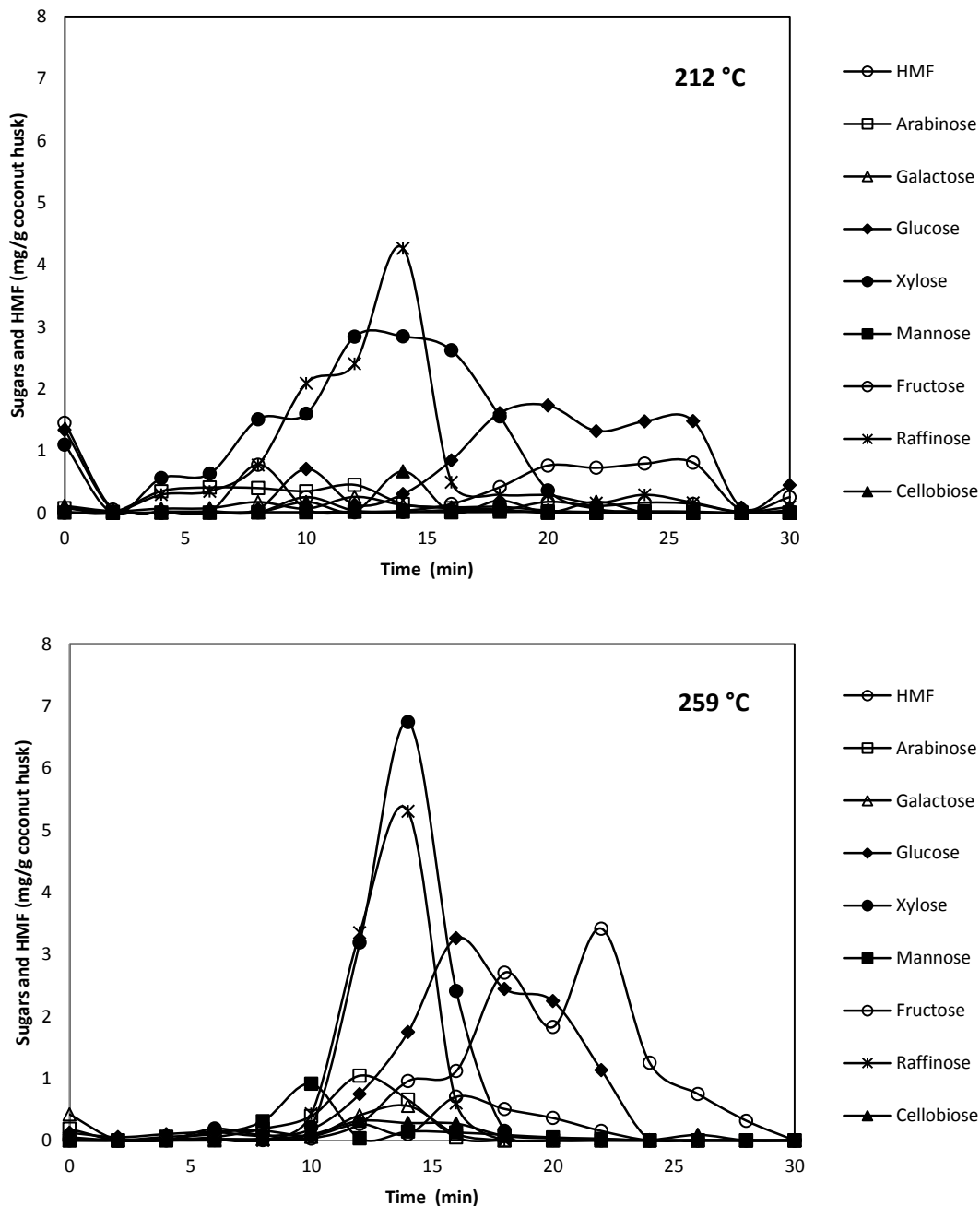

Figure 5. Yield of sugars and 5-HMF obtained by SWH of coconut husk at different temperatures.
For grape seed (Figure 6) the raffinose yield was higher at 204 °C than at 259 °C, which indicates oligomers decomposition with temperature increase. The process at 204 °C was able to hydrolyze only hemicellulose, while the process at 259 °C hydrolyzed part of the cellulose after 20 min of process, time at which the reactor outlet temperature reached 245 °C (Figure 2).
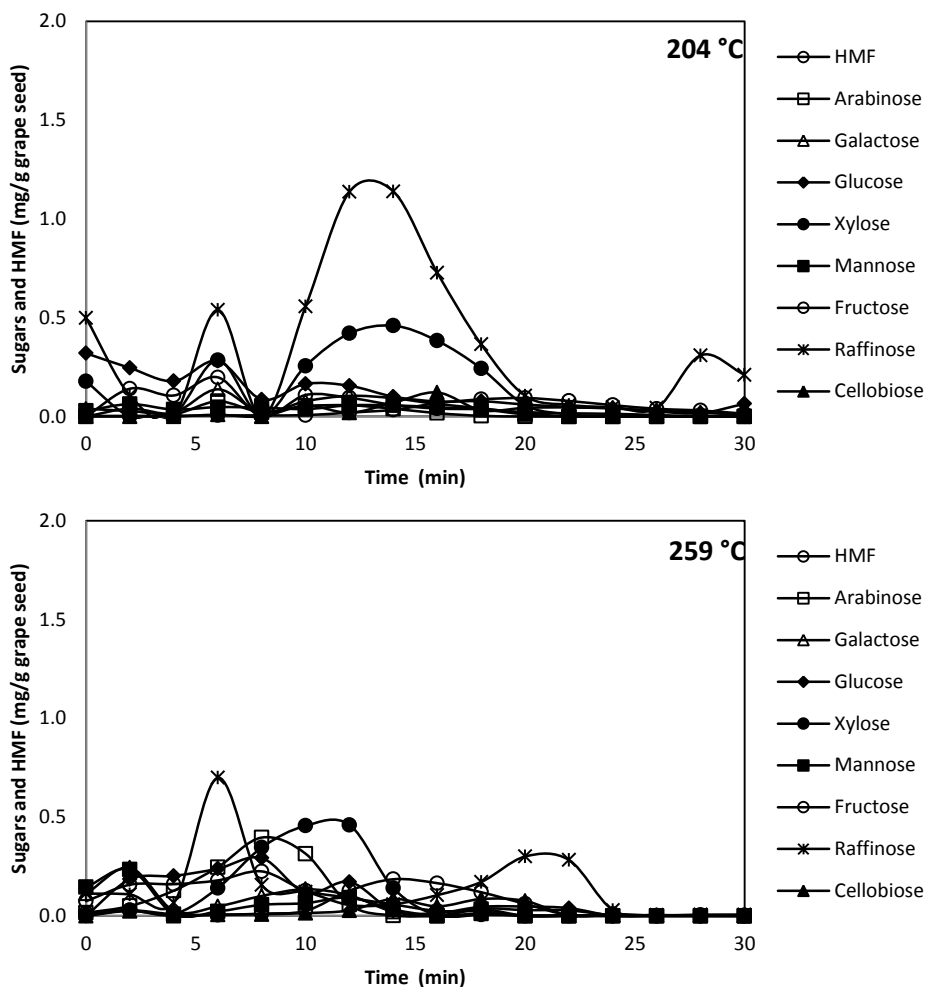
Figure 6. Yield of sugars and 5-HMF obtained by SWH of defatted grape seed at different temperatures.

For pressed palm fiber (Figure 7) at 206 °C there was recovery only of hemicellulosic sugars. At 256 °C, on the other hand, it can be noticed that a first fraction rich in pentoses is hydrolyzed up to 18 min, followed by a fraction rich in glucose, which indicates hydrolysis of the cellulosic fraction of the biomass after that time. The degradation of the cellulosic portion is also accompanied by high degradation of sugars, leading to the formation of degradation products, as 5-HMF.

4. Conclusions

The hemicellulose is degraded since the beginning of the process, while cellulosic sugars start being recovered when the temperature reaches around 230-240 °C. The degree of polymerization of the solubilized oligosaccharides decreased with temperature. The yield of sugars recovered from coconut husk was approximately constant with temperature (4.5-4.8 %), but 5-HMF yield increased with it (0.4 % vs. 1.3 %). Grape seed presented the lowest sugars yield (around 1 %). For pressed palm fiber, as temperature increased, the yield of raffinose decreased, while the yield of glucose and 5-HMF increased; total saccharides analyzed accounted for 3.9 % at 256 °C. The results indicate that SHW should be evaluated and optimized individually for each raw material.
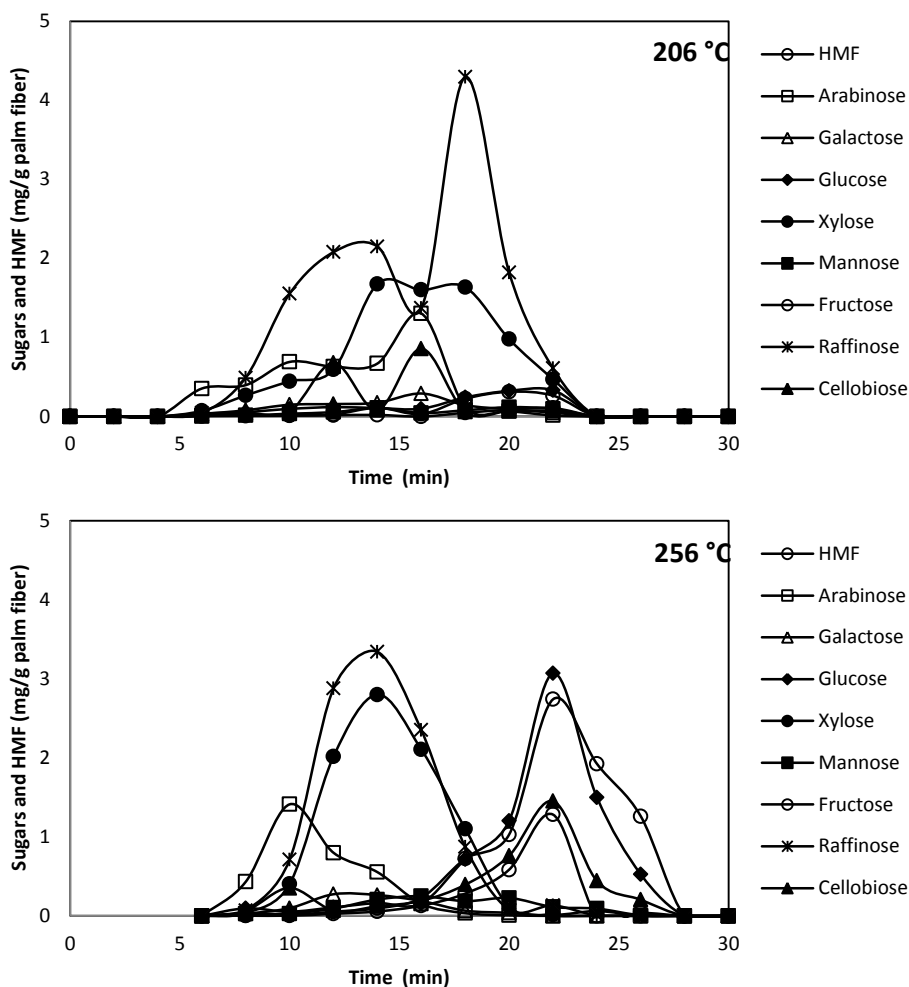
Figure 7. Yield of sugars and 5-HMF obtained by SWH of pressed palm fiber at different temperatures.

Acknowledgements

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