J. of Supercritical Fluids 89 (2014) 89–98

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Obtaining sugars from coconut husk, defatted grape seed, and pressed palm fiber by hydrolysis with subcritical water

Juliana M. Prado*,[1], Tânia Forster-Carneiro, Mauricio A. Rostagno, Luis A. Follegatti-Romero, Francisco Maugeri Filho, M. Angela A. Meireles

DEA/FEA (School of Food Engineering), UNICAMP (University of Campinas), R. Monteiro Lobato, 80, 13083-862 Campinas, SP, Brazil

ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form 20 February 2014
Accepted 21 February 2014
Available online 3 March 2014

Keywords:
Coconut husk
Defatted grape seed
Pressed palm fiber
Subcritical water hydrolysis
Sugars

ABSTRACT

In this work, three residues from the food industry (coconut husk, defatted grape seed and pressed palm fiber) were subjected to subcritical water hydrolysis with the aim of producing fermentable sugars. Hydrolysis kinetics were determined using a semi-batch unit equipped with a 50 mL reactor. The process was conducted at 208 °C and 257 °C for 30 min, with water flow rate of 33 mL/min and under 20 MPa. The liquefaction degree of the raw materials increased with temperature. The total reducing sugars recovered also increased with temperature. Maximum total reducing sugars recovered for coconut husk, defatted grape seed and pressed palm fiber using SWH were 11.7%, 6.4% and 11.9% from total raw material, respectively. Coconut husk presented the highest amount of monosaccharides (3.4%), followed by pressed palm fiber (2.4%) and defatted grape seeds (0.7%). On the other hand, the degradation products that are also fermentation inhibitors increased with temperature as well. Each raw material presented a different monosaccharides and inhibitors profile, which indicates that SWH should be evaluated and optimized individually for each case.

1. Introduction

In principle, using the renewable energy obtained from agri-food industry wastes improves the carbon balance, because in their production cycle there is one step that consists on the removal of carbon dioxide, a greenhouse gas, from the atmosphere, in contrast with fossil fuels [1]. Agricultural wastes contain a high amount of cellulose, hemicellulose and lignin, which have high energy content. Therefore, they are recognized as potential sources of renewable energy based on the benefits of both the generation of energy and the environmental protection.

The biomass conversion into 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. This last category includes high-pressure liquefaction using sub/supercritical fluids. Each technology has its own advantages, depending on the type of biomass and the form of energy needed [2]. 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 [3]. Due to these features, the sub/supercritical water hydrolysis (SWH) process has gained attention during the past years.

Subcritical water is defined as liquid water in the temperature range of boiling point to critical point or near critical point (100–374 °C). In order to keep the water in the liquid state, pressure is applied. It is a very promising reaction medium for the conversion of lignocellulosic biomass, 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 [4–6]. One of the main products of SWH of lignocellulosic biomass is sugars that can be fermented to produce second-generation bioethanol [7].

The hydrolysis of lignocellulosic raw materials for the production of fermentable sugars is not yet economically feasible at industrial scale, but as the knowledge of the mechanisms taking place during the hydrolysis processes is increasing, new techniques are being exploited to overcome the drawbacks of the conventional methods. The SWH of biomass presents several advantages when compared to traditional technologies (acid, alkali and enzymatic

* Corresponding author. Tel.: +55 15 98151 3940.
E-mail address: tuska.ju@gmail.com (J.M. Prado).
[1] Present address: Centro de Ciências da Natureza/Campus Lagoa do Sino UFSCar (Federal University of São Carlos), Rod. Lauri Simões de Barros, km 12, SP-189, 18290-000 Buri, SP, Brazil.

http://dx.doi.org/10.1016/j.supflu.2014.02.017
0896-8446/

hydrolysis). 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 non-aggressive waste to the environment [8]. Moreover, it does not require biomass pre-treatment, it is fast, presents less corrosion, lower residue generation and lower sugars degradation when compared to conventional hydrolysis methods [9–11].

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 [8,12–17].

There are relatively few applications of SWH for the hydrolysis of agricultural and food industry residues in literature. Most relevant examples include corn stalks and stover, sugarcane bagasse and rice bran. Besides these important residues there are other potential raw materials that could be used to produce fermentable sugars by SWH. Some of them are grape seeds, pressed palm fiber and coconut husk. Grape seeds are a residue of wineries that present a high content of oil, which can be extracted and used in several applications, such as cosmetics and foods [18]. After the oil fraction is extracted, the residue, composed mainly by lignin and hemicellulose, has no other immediate use. Pressed palm fiber is a residue from the pressing of palm fruits to produce palm oil. The residue still has residual oil (around 5%), which is around 20 times richer in β-carotene than the pressed oil. This residual oil can be extracted by a more efficient technique, before the pressed palm fiber, rich in cellulose and hemicellulose, is ultimately disposed [19,20]. Coconut husk is another lignocellulosic material resulting from processing coconuts to produce beverages and coconut powder. It is categorized as hard wood and it is characterized by high toughness due to its high lignin content. Since these three 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.

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. A new semi-batch equipment was assembled for this purpose.

2. Material and methods

2.1. Raw material

The dry palm pressed fiber was donated by Agropalma (Tailândia, PA, Brazil) after the palm had been used to manufacture palm oil. The coconut husk resulting from coconut processing to produce coconut water and milk 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 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, yielding around 13% oil [18]. The residue from the supercritical extraction process was stored at −18 °C and subsequently it was used for SWH.

Distilled water was used in all experiments.

Table 1
Raw materials characterization (%, wet basis).

	Coconut husk	Defatted grape seed	Pressed palm fiber
Moisture	10.66 ± 0.05	6.5 ± 0.2	10.1 ± 0.2
Ashes	0.92 ± 0.01	5.7 ± 0.4	5.7 ± 0.3
Extractives in water	3.8 ± 0.2	8.1 ± 0.5	5.03 ± 0.03
Extractives in ethanol	1.5 ± 0.3	5.3 ± 0.6	5.39 ± 0.05
Protein	0.9 ± 0.2	11 ± 2	5.1 ± 0.2
Acid soluble lignin	1.61 ± 0.07	1.4 ± 0.7	1.6 ± 0.6
Acid insoluble lignin	33 ± 3	46 ± 5	30 ± 3
Sugars			
Glucan	15 ± 2	7 ± 1	19 ± 1
Xylan	19 ± 2	7.7 ± 0.9	19 ± 4
Galactan	0.09 ± 0.02	0.29 ± 0.02	0.16 ± 0.04
Arabinan	0.27 ± 0.02	0.58 ± 0.09	0.68 ± 0.07
Mannan	0.020 ± 0.003	0.5 ± 0.1	1.1 ± 0.4

2.2. Raw material characterization

The three raw materials were characterized according to the methodologies of the NREL, in triplicate [21–25]. Table 1 presents their composition.

2.3. Hydrolysis equipment

The semi-batch unit shown in Fig. 1 was built to hydrolyze lignocellulosic biomasses using sub/supercritical water. The equipment can operate up to 400 °C 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, 2.34 cm i.d. × 11.7 cm, Campinas, Brazil) with metal-to-metal fit to allow using temperatures up to 400 °C, heated by an electric jacket, a micrometric needle valve (Autoclave Engineers, Erie, PA, USA) for pressure control, 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. The thermocouples for reading temperature in the extractor inlet and outlet were placed right before and right after it, respectively. The thermocouple that was connected to the temperature controller of the reactor was placed in its wall, at half thickness and half length.

2.4. Hydrolysis of biomasses

The experiments were carried out using 10–35 g of raw material. The sample was inserted inside 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 about 20 min, the dynamic period of the process was started by pumping water at 33 mL/min through the system for 30 min. The flow rate was measured at the pump, at ambient conditions, and it was determined in a previous study [26]. When the dynamic period was started, the reactor temperature was set to process temperature (200 °C or 250 °C),