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Integrated supercritical fluid extraction and subcritical water hydrolysis for the recovery of bioactive compounds from pressed palm fiber

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ABSTRACT

Pressed palm fiber (PPF), a residue obtained from palm oil industry, is a source of bioactive compounds, such as carotenoids, which are used as food additives. It also has cellulose and hemicellulose that can be used to yield fermentable sugars for the production of second generation ethanol. Supercritical fluid extraction (SFE) of pressed palm fiber provides an oil rich in carotenoids while subcritical water hydrolysis (SubWH) produces hydrolysates with high amounts of fermentable sugars. In this work, the effects of pressure (15–30 MPa) and temperature (318 and 328 K) on SFE of carotenoids were investigated. The SFE extract with highest carotenoid content was obtained at 318 K and 15 MPa (2.3% d.b., 0.81 mg β-carotene/g extract). After the extraction, the influence of process temperature (423–633 K), pressure (15 and 25 MPa), solvent:feed ratio (120 and 240), and residence time (1.25–5 min) on SubWH of the extraction residue was studied. At the temperature of 523 K, the highest total reducing sugar yield (11–23 g glucose/100 g carbohydrate) and the highest biomass conversion (40–97%) were obtained for any pressure and solvent:feed ratio. The highest selectivity for saccharide formation was found at 423 K (20–59 mol glucose/mol furfural equivalent). Optimal conditions for high saccharide formation and low sugar degradation product in subcritical hydrolysis were obtained at 523 K, 15 MPa, solvent:feed ratio of 120, residence time of 2.5 min with a total reducing sugar yield of 22.9 g glucose/100 g carbohydrate and a conversion of 84.9%.

1. Introduction

In recent years, there is an increasing public interest in sustainable development as a response to environmental problems generated by industrial and economic activities. An interesting alternative is the sustainable conversion of biomass because they are widely available in nature and they are source of important components such as cellulose, hemicellulose, starch, lignin, and in some cases antioxidants and vitamins, among others. These components can be transformed into high added-value products, such as bioactives for food; additives for the cosmetic and pharmaceutical industries, intermediates for the chemical industry, and saccharides as fermentation substrates for the production of second generation ethanol [1–5].

Supercritical fluid technology offers an interesting option for sustainable utilization of biomass as an alternative to conventional solvents. Supercritical fluids present unique physicochemical properties because of their duality between liquid and pure gas. More importantly, these properties can be adjusted with operating conditions allowing to achieve high diffusion coefficient, high solvation power, high degree of selectivity and easy solvent separation [6–9].

Supercritical carbon dioxide (SC-CO_2) is a common solvent in an extraction process because of its mild critical temperature and pressure (304.2 K and 7.4 MPa). Due to its hydrophobic character, SC-CO_2 is used for the extraction of hydrophobic to slightly hydrophilic compounds. Another advantage of SC-CO_2 is that it is highly selective and can be easily separated from the extracted compounds without leaving toxic residues in extracts while reducing the risk of thermal degradation. Furthermore, several studies have demonstrated that supercritical fluid extraction

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(SFE) is more effective than conventional techniques for the extraction of compounds with antioxidant action (phenolics, terpenoids, carotenoids, and tocopherols) [2,10].

Another "green" substance that can be explored as a sub or supercritical fluid is water. Subcritical water refers to water with temperature between 423 K and 647 K (critical temperature), and with a pressure higher than its vapor saturation pressure. As temperature increases, the ion product increases and dielectric constant decreases, drastically changing the physical–chemical properties of water causing it to readily ionize into hydrogen and hydroxide ions thus promoting hydrolysis reactions and solubilizing non-polar compounds and polar gases. These modifications of the characteristics of water influence the kinetics and selectivity of chemical reactions within a network, acting as a catalyst in many cases [11]. Studies on sub- and supercritical hydrolysis (SubWH and SupWH, respectively) of model solutions of cellulose and hemicellulose allowed a better understanding of the reaction pathway involved. These studies demonstrated that cellulose and hemicellulose are readily converted into oligosaccharides, monosaccharides and, degradation products. In fact, there is a competition between hydrolysis and product degradation rates. In contrast, in lignocellulosic materials such as corn stover and sugar cane bagasse, lignin is present in a complex structure with cellulose and hemicellulose, increasing the resistance of the material to hydrolysis processes and requiring that more aggressive conditions are used. Thus the composition of the raw material is of fundamental importance in SubWH and SupWH processes, since it will determine the operational conditions to allow a rapid conversion of polysaccharides with high saccharide production and low degradation products [4,12,13].

In Brazil, the major agro industrial residues are soy, wheat, corn stalks, sugarcane bagasse, corn cob, pressed palm fiber and coconut. The palm oil industry produces an estimated amount of 123,000 ton of residues per year, which are burned as fuel for energy production. One of these residues, the pressed palm fiber (PPF), contains oil rich in α- and β-carotene, precursors of vitamin A, and large amounts of carbohydrates. The separation of this oil can be done by SFE and the conversion of carbohydrates, cellulose and hemicellulose into value-added products can be attained by SubWH and SupWH on an integrated process platform [2,14]. Thus, PPF has a great potential to be explored within the context of a "green" biorefinery using supercritical fluid technology.

In this context, the objective of the present work is to propose an integrated process of SFE followed by a sequential SubWH process of pressed palm fiber as a model of effective utilization of agro industrial residues through optimization of the overall process. The influence of operational parameters on SC-CO_2 extraction and SubWH were investigated. SFE was evaluated as a function of extract and carotenoid yields. Using a similar approach, the conditions of SubWH of the residue of the SFE process were evaluated to achieve the highest recovery of saccharides while minimizing the formation of sugar degradation products.

2. Materials and methods

2.1. Chemicals and reagents

The standard reagents used for UV and HPLC analysis, namely β-carotene (Type I, ≥93%), L(+)arabinose (≥98%), D(−)fructose (≥99%), D(+)galactose (≥99%), D(+)glucose (≥99.5%), D(+)mannose (≥99%), D(+)xylose (≥99%), D(+)cellobiose (≥98%), 5-(hydroxymethyl)furfural (≥99%), furfural (≥98%), were obtained from Sigma Aldrich (Saint Louis, USA). Carbon dioxide (99% of purity) was provided by White Martins (São Paulo, Brazil). All other reagents used were of analytical grade.

2.2. Raw material preparation and characterization

The PPF was provided by Agropalma Company (Tailândia, Brazil). It consisted of a palm fiber and palm husk mixture obtained after the palm oil extraction by expelling. Approximately 5 kg of this PPF was selected considering its physical integrity. This raw material was dried at 313 K for 24 h in a forced air circulation drying oven (Marconi, model MA-35, São Paulo, Brazil). Then, it was comminuted using a knife mill (Marconi, model A340/0204244, São Paulo, Brazil) to homogenize the sample. Particles smaller than 80 mesh were separated using sieves (Series Tyler, W.S. Tyler, Wheeling, USA) in a vertical vibratory shaker (Bertel Metallurgic Ind. Ltda., São Paulo, Brazil) to prevent clogging problems during the extraction process. The milled PPF was protected from light and stored in a freezer (Metalfrio, DA420, São Paulo, Brazil) at 268 K until used as raw material in the SFE experiments.

The average geometric particle diameter (d_{gw}) of PPF was determined according to American Society of Agricultural Engineer [15]. The bed apparent density (ρ_a) was calculated as an occupied mass in the extraction cell vessel volume. The porosity (ε) was calculated as $1 - \rho_a/\rho_t$, where ρ_t is the real density [2]. The moisture, extractives in water and alcohol, ash and lignin content were determined according to the Standard Biomass Analytical Methods provided by the National Renewable Energy Laboratory (NREL) [16]. Protein was determined according to official methods published by the Association of Official Analytical Chemists (AOAC) [17]. The carbohydrate content was determined as a mass balance.

2.3. Extraction experiments

2.3.1. Conventional extraction

A conventional extraction technique (Soxhlet) was used as reference for comparison with performance of supercritical fluid extraction process. A 500 cm^3 Soxhlet apparatus was employed in which 5 g of the milled PPF was placed inside the extraction cartridge with 275 cm^3 of hexane (P.A., Synth, Brazil). Duplicate extractions were carried out at 342 K for 6 h [17].

2.3.2. Supercritical fluid extraction (SFE)

The extraction experiments were performed in a commercial SFE unit (Spe-ed 7071, Applied Separations, Allentown, USA) equipped with a cooling bath (Marconi, model MA184, São Paulo, Brazil), a pneumatic pump, an electric oven, two extraction vessels, one of 4.6 cm^3 and another of 290 cm^3 (Thar Designs, Pittsburgh, PA), a compressor (Shulz S/A, Model MS 3, Santa Catarina, Brazil), and a flow totalizer (LAO G0, São Paulo, Brazil). SC-CO_2 was used as the extracting solvent. The extraction procedure was similar to that described by Albuquerque and Meireles [18]. An apparent density of 294 ± 1 kg/m^3 was considered for all experiments. The extraction vessel was assembled and placed inside the oven at the preselected temperature and CO_2 was pumped into the system until reaching the experimental pressure. A static period of 10 min was used before the dynamic extraction step. The total CO_2 mass was measured by means of the flow totalizer and it was not recirculated. The extract was collected inside a sealed 100 cm^3 amber glass flask immersed on an ice bath. The extract mass was measured gravimetrically on an analytical balance (model A200S, Sartorius Analytic GmbH, Göttingen, Germany).

Total global yield (X_0) represents the maximum amount of extract that can be recovered from a raw material over time or S/F ratio (solvent mass/feed mass d.b.) at a given pressure and temperature [19]. A preliminary extraction of pressed palm fiber with SC-CO_2 was performed to find a suitable S/F ratio to evaluate the influence of pressure and temperature on global yield isotherm (GYI). For this purpose, the preliminary SFE was performed at 328 K and 25 MPa using an extraction vessel of 290 cm^3