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Hydrothermal fractionation of grape seeds in subcritical water to produce oil extract, sugars and lignin

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ABSTRACT

In this work, the fractionation of grape seeds as a model biomass was studied using a combination of two processes: solvothermal extraction and hydrothermal fractionation-hydrolysis process in a semicontinuous reactor. First, grape seeds were subjected to an extraction process with ethanol/water (70/30 wt.%) at 90 °C during 60 min obtaining ca. 13.0 wt.% of oil and extractable components with 4.46 wt.% of polyphenols (66% of the maximum). Afterwards, the solvent was water and the biomass was treated in steps at different temperatures (150 °C to 340 °C). During the hydrolysis the pH decreased from 5.5 down to 3.0 due to acetyl group liberation. The total quantity of recovered sugars varied around 20.0 to 23.1 wt.%. The best experimental condition for obtaining the maximum amount of pentoses + hexoses + oligosaccharides was 180 °C (45 min) + 250 to 265 °C (45 min) + 330 to 340 °C (45 min).

1. Introduction

The most abundant source of carbon in the world is biomass. Nowadays, the global primary production of biomass rounds 100 PgC/y (P = Peta = 10^{15}) [1], being the global carbon emissions nearly 10 PgC/y [2]. The production of fuels and value added products from biomass has been widely investigated in the last years. Like any other lignocellulosic residue, grape seeds primarily comprise three major fractions: hemicellulose, cellulose and lignin. In addition, low amounts of minerals (ash) and other compounds, such as extractives, can be found in grape seeds (i.e. grape seed oil and polyphenols).

There are several solvents available for performing the biomass fractionation, such as organic solvents [3], ionic liquids [4] or simply water [5–7]. Fractionation is often considered a pre-treatment process, prior to produce sugars and lignin by conversion. After this process, there are many alternatives for conversion to produce value added components by catalytic or non-catalytic transformations [8]. In 2004 the U.S. Department of Energy and Renewable Energy prepared a comprehensive report including series of compounds and building blocks chosen as candidates to be produced from cellulose, hemicellulose [9,10] and lignin [11].

Hydrothermal treatment is the processing of biomass in water at high pressures and temperatures in liquid phase. This technology is a promising alternative to perform the fractionation of biomass because the reaction medium allows the transformation of the different fractions of biomass by choosing the appropriate conditions [12,13]. Furthermore, water is a clean, safe and environmentally benign solvent [14]. Hydrothermal fractionation can be carried out at soft conditions (<100 °C) to remove the water-soluble extractives and hydrolyze hemicelluloses (<180 °C), yielding a solid phase enriched in lignin and cellulose. The autohydrolysis process (reactions catalyzed by H^+ and OH^- produced by H_2O dissociation [13–15] due to the acetyl group liberation and organic acids produced) can produce oligosaccharides that maintain the polymeric structure. A subsequent hydrolysis at more severe conditions or with enzymes will yield monomeric sugars [16]. On the other hand, hydrothermal carbonization can be an option when the production of a carbon-based nanomaterial is pursued.

The hydrothermal treatment can be used for a double fold, to produce bio-oils or to produce bio-based streams (C5's, C6's and lignin) [17]. Analyzing the production of bio-based streams, Requejo et al. demonstrated that the use of olive tree biomass to produce soluble hemicellulose-derived saccharides can be carried out in a hydrothermal medium obtaining near 26% of the

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original biomass as soluble sugars. In addition, the degree of enzymatic hydrolysis of that product was about 80%, obtaining in this way, a highly fermentable stream (70% conversion in ethanol) [18]. Grenman et al. obtained a rich hemicellulose fraction from spruce in an intensified reactor, determining the kinetics of fractionation. They found that the activation energy was 135 kJ/mol at 150–170 °C [19]. Recently, a comprehensive study in the hydrothermal treatment of sugar cane bagasse has been carried out by Prado et al. [20,21]. The sugar cane bagasse (between 2 g and 11 g) was hydrolyzed in a batch reactor (50 mL) at flow-rates between 11 mL/min and 55 mL/min and temperatures from 213 °C to 290 °C in liquid phase (at 20 MPa). The main products analyzed from sugar cane bagasse were arabinose, fructose, galactose, glucose, mannose, xylose and cellobiose as well as some inhibitors such as 5-hydroxymethylfurfural, 4-hydroxybenzoic acid, vanillin, etc. They found that the all hemicelluloses were hydrolyzed at 190–230 °C during the first 2 to 15 min of process time.

Recently, one of the first processes for sugar production from second generation biomass using supercritical water has been started-up by the company RENMATIX [22,23]. They base the fractionation process in the hydrolytic process itself. The process has been studied thoroughly by Cantero et al. [24] using a reactor operating at supercritical conditions and extremely low residence times, below 1 s.

The wine industry produces ca. 28% of lignocellulosic residues in weight basis of the used biomass (5% stalks and 23% grape seeds). The grape seeds contain one of the highest composition of lignin in nature, ca. 43 wt.% [25,26], being lignin a component of interest due to its direct applications in the chemical industry. Also, the seeds and the skin contain a great quantity of high value polyphenols that can be extracted using ethanol-water or methanol-water mixtures at low temperatures (from 20 to 60 °C), avoiding in this way the degradation of the polyphenols [27,28].

The grape marc (mixture of grape seeds, skin and pulp) contains phenolic acids, colored anthocyanins (important antioxidant activity), simple flavonoids and complex flavonoids, non-flavonoid compounds, flavonols and polyphenolic tannins. At the present time, these components are important in different industries such as food, cosmetic and pharmaceutical, mainly extracted from residual sources [27]. Thus, according to a recent market survey the global polyphenols market was ca. 12,200 t in 2011 (USD 580 million) and is expected to grow up to 21,000 t by 2018 (USD 873.7 million) [29].

The main compounds that can be found in grape seeds are: gallic acid, flavan-3-ols catechin, epicatechin, gallocatechin, epigallocatechin, epicatechin 3-*O*-gallate, procyanidin dimers, trimmers and procyanidins [30]. Solýom et al. have demonstrated that the polyphenol compounds are stable at temperatures as high as 70 °C. In addition, they found that the extraction kinetics increased considerably by increasing temperature. Furthermore, it was observed that an ultrasound pretreatment did not make any further improvement in the extraction process. Therefore, the sole effect of the hydrothermal treatment was enough for an efficient extraction [31]. Additionally, the thermal degradation of grape marc was studied at different temperatures and it was concluded that the total phenol content was increased at temperatures above 100 °C. In the same way, the antioxidant activity did not change at 80 °C in the liquid extract, and the degradation was observed at 150 °C. Maier et al. [32] studied yields of phenolic compounds in seven grape seeds with different solvents. The use of pure ethanol resulted in poor polyphenol extraction. The products obtained from the extraction using ethanol or methanol mixtures with water as solvents contain higher quantities of anthocyanins and polyphenols than the extraction with water. In addition, the recovered amount of these components is increased when the extraction time was raised (1, 12 and 24 h).

The objective of this work was to study the influence of temperature in the solvothermal extraction and the hydrothermal fractionation-hydrolysis process of grape seeds. It has been studied the extraction of polyphenols (in gallic acid basis) and the production of pentose and hexose sugars fractions as well as the residual lignin.

2. Materials and methods

2.1. Materials

Grape seeds from *Vitis vinifera* L. (Tempranillo) from Matarromera S.A. winery (Valbuena de Duero, Spain) campaign 2011 were used as raw material. The biomass material for this study was crushed using a mortar to a particle size between 0.5 and 1.0 mm. The chemical composition of the grape seeds was determined according to Section 2.3 obtaining the following values: 2.4 wt.% ash, 17.0 wt.% grape seed oil, 43.8 wt.% lignin and 36.8 wt.% hemicelluloses and celluloses in dry basis.

The reagents used for HPLC analysis were: cellobiose (+98%), glucose (+99%), fructose (+99%), glyceraldehyde (95%), pyruvaldehyde (40%), arabinose (+99%), 5-hydroxymethylfurfural (99%), lactic acid (85%), formic acid (98%), acrylic acid (99%), mannose (+99%), xylose (+99%) and galactose (+99%) purchased from Sigma and used without further modification.

For the structural carbohydrates and lignin determination sulfuric acid (98%) and calcium carbonate (≥99.0%) were used as reagents supplied by Sigma.

For the determination of polyphenols content the following reagents were supplied by Sigma used: ethanol (96%), sodium carbonate (≥99.0%), Folin–Ciocalteu reagent (2N), gallic acid monohydrate (≥98.0%). Distilled water and Milli-Q water were used in the experiments.

2.2. Experimental device

The fractionation process was carried out in a semi-continuous reactor. A diagram of experimental set-up is shown in Fig. 1. The reactor was charged with 4.00 ± 0.06 g of grinded grape seeds (not dried before extraction, moisture 6.00 ± 0.20 wt.%). Two metallic filters at the top and the bottom of the reactor were used to keep the fixed bed and avoid the loss of the grape seeds particles. Once the reactor was tightened up, the pump (Jasco model PU-2080) was set to 5 mL/min and the pressure was set using the Go-backpressure valve (BPV-01). The pressure was selected always to 10 bar over the bubble point at the reaction temperature, to assure liquid phase. The system was cold-checked for leaks at this point. The reactor (R-01, 20 cm length, 1/2″ O.D. SS316 piping) and preheater (E-01, 200 cm of 1/8″ AISI 316 piping) were placed inside a former chromatographic oven HP5680. The oven was then set to the desired reaction temperature and the cooling system was started up (E-02, 15 cm of concentric tube heat exchanger 1/4″–3/8″ counter-current operation).

The grape seeds were hydrothermally treated, through a multistep two-solvent and temperature profile fractionation in order to separate the value added components from hemicelluloses, celluloses and lignin. During the first 60 min of treatment, the temperature and pressure were set at 90 °C and 15 bar, respectively, using a mixture ethanol-water (70/30 wt%.) as solvent with a flow rate of 5 mL/min. The aim of this first step was to extract the polyphenols and essential oils from the raw material before the fractionation-hydrolysis process. This step was a solvothermal extraction (organosolv step), the values of temperature and percentage of ethanol were selected taking into account the highest obtained yields in previous works in the field, e.g. Lapornik et al.