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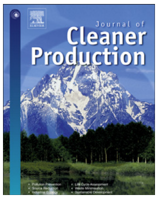

The green biorefinery concept for the valorisation of pistachio shell by high-pressure CO_2/H_2O system

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ABSTRACT

The use of high-pressure CO_2/H_2O in valorisation of pistachio shell to produce hemicellulose-derived, oligomeric and monomeric sugars and their further transformation to furfural as well as enzymatic transformation of cellulose-rich solids is presented in this work. Different pre-treatment conditions *i.e.* temperature ranged from 160 to 200 °C; reaction time varied between 0 and 30 min and liquid to solid mass ratio between 4 and 8 with constant initial pressure of CO_2 of 50 bars were examined. At the optimal pre-treatment conditions, the concentrations of xylose and xylo-oligosaccharide were of 1.7 and 35.5 g/L. Furthermore, this work demonstrates the high-pressure CO_2 catalysed production of furfural in an aqueous/tetrahydrofuran system. For model solution containing a mixture of xylose and acetic acid, the optimised furfural yield was as high as 53.3 mol%, while for real sample of hemicellulose hydrolysate, the furfural yield of 39.6 mol% and the selectivity of 40.0 mol% were obtained. Additionally, quantitative glucan to glucose conversion by enzymatic hydrolysis of pre-treated cellulose-rich biomasses was achieved.

The promising results achieved confirm that the valorisation of food residues such as pistachio shell using greener alternative methods involving high-pressure CO_2 is an efficient technology, which can be integrated into the biorefinery concept.

1. Introduction

Social, economic and environmental concerns regarding the global energy supplies have been driving to seek for alternative feedstocks and for novel and more sustainable technologies for the production of fuels and chemicals. In this context, the use of a sustainable supply chain of renewable lignocellulosic food industry residues is a potential alternative (Arshadi et al., 2016). Pistachio shell (PS) is one of such examples and is generated in considerable amounts, as the annual world production of pistachios in the last 10 years oscillates between 800 and 900 ktonnes (FAO, 2018). Thus, the valorisation of PS is crucial on the way to achieve sustainable processing of such considerable scale residue. Pre-treatment step is one of the most important and critical stages for the deconstruction of PS in order to make biomass available for further conversion to fermentable sugars and other value-added products (Zhao et al., 2017). Several chemical, physical and biological methods of biomass pre-treatment have been developed in last years (Silveira et al., 2015). Among them, the special attention has been focused on the development of more sustainable and greener technologies of biomass pre-treatment (Brandt et al., 2017; Silveira et al., 2015). High-pressure CO_2/H_2O pre-treatment is advanced in comparison to hydrothermal processes because, the presence of pressurised liquid CO_2 favours a series of reactions including carbonic acid formation, which supports the hydrolysis of the biomass hemicellulose fraction into corresponding sugars and simultaneously increases the enzymatic cellulose digestibility (Morais et al., 2014). Furthermore, the use of CO_2, contrary to pre-treatments with *e.g.* mineral acids, does not cause the environmental problem because during the depressurisation, the effect of acidic character of CO_2 formed *in-situ* disappear rising the pH of the reaction mixture (Morais et al., 2015). Besides the chemical character, a physical

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effect of this gas on the processed solid is notorious also. Additionally, due to own properties, CO_2 can penetrate the porous structure of the recalcitrant lignocellulosic biomass causing the swelling effect of biomass and changing its internal constitution (Liu et al., 2014; Zhang and Wu, 2014). This, in turn, has a direct effect on the cellulose hydrolysis as reported in literature (Magalhães da Silva et al., 2014; Zhao et al., 2017). Beside the numerous aforementioned advantages of the CO_2/H_2O technology in the biomass processing, one of the main drawbacks is a need of special reactors able to stand high pressure generate during reactions. This, in turn, may influence the capital expenditure of such processes (Morais et al., 2015).

Furfural is one of the top value-added chemicals possible to be obtained from biomass (Bozell and Petersen, 2010). At industrial scale, furfural is produced by the acid-catalysed hydrolysis of biomass with subsequent dehydration of pentose sugars to furfural (DalinYebo, 2016). Since the current industrial processes demonstrate rather limiting furfural yields (∽50%) and involve corrosive media (*e.g.* mineral acids), alternative processes are strongly desired. To accomplish this challenge many alternative approaches of furfural production were proposed (da Costa Lopes et al., 2017; Danon et al., 2014; Peleteiro et al., 2015). Among them are also those with high pressure CO_2 (Morais and Bogel-Lukasik, 2016; Morais et al., 2016). The use of CO_2 in furfural production is focused on the creation of acidic environment, based on the same phenomenon as in case of pre-treatment. Additionally, in the presence of other solvent, *e.g.* tetrahydrofuran (THF), CO_2 generates biphasic H_2O/THF system, in which furfural produced in the aqueous phase is automatically stripped out to the CO_2 + THF phase in order to prevent its further degradation to *e.g.* humins.

Although the use a high-pressure CO_2/H_2O in pre-treatment of many biomasses has been proven already (McWilliams and van Walsum, 2002; Morais et al., 2015; van Walsum, 2001; Van Walsum et al., 2007), this technology was never applied to feedstocks with high hemicellulose contents such as PS. This work fills this gap and demonstrates the efficiency of the cleaner CO_2/H_2O processing of PS. Therefore, the presented work is focused on the valorisation of hemicellulose fraction by production of high concentration oligosaccharides in hydrolysates and provides alterative way to valorise the hemicellulose-rich hydrolysate to furfural. At the same time, the produced solid leftover was subject to enzymatic hydrolysis to produce a monosaccharide-rich (pentose and hexose) stream ready for further valorisation to e.g. biofuels or other value added products. The illustrative representation of the explored concept is shown in Fig. 1.

2. Experimental section

2.1. Raw material preparation and chemicals

Pistachio shell was kindly provided by Altin Fistik Gida Mad. San. Ve Tic. Ltd. Şti., Gaziantep, Turkey. The raw material was ground to particles smaller than 1.5 mm using a knife mill (IKA® WERKE, MF 10 basic, Germany) and stored at room temperature. CO_2 used in pre-treatment and in furfural production was acquired from Air Liquide, AlphaGaz™ gamma, Paris, France with a purity ≥99.99% (w/w). Distilled water (18.2 MΩ/cm) was produced by the PURELAB Classic Elga system. Aqueous solution of 72% (w/w) H_2SO_4 was prepared from 96% (w/w) H_2SO_4 (Panreac Química, Barcelona, Spain). THF and sodium azide were bought from Merck, Darmstadt, Germany. Cellic Ctec2 and Cellic Htec2 enzymes used for enzymatic hydrolysis assays were kindly provided by Novozymes A/S, Bagsværd, Denmark.

2.2. Reaction system

2.2.1. High-pressure CO_2/H_2O hemicellulose extraction

Hemicellulose extraction experiments from PS with CO_2 were performed in a 500 mL stainless steel high-pressure reactor (series 4576B, Parr Instruments Company, Moline, IL, USA) equipped with Parr 4848 unit used to monitor and control the reaction conditions, such as temperature, pressure and stirring speed. An external fabric mantle was used to heat the reactor, while an internal stainless steel loop was used to either maintain desired temperature during the isothermal step of the reaction or to cool down the reactor rapidly to quench the reaction. The extraction experiments were carried out at different temperature (T), time (t) and liquid (water)/solid (biomass) mass ratio (LSR) as defined by the design of experiments. All experiments were performed with a constant initial CO_2 pressure of 50 bar. The stirring speed of 200 rpm and an initial mass loading of 120 g (sum of masses of water and PS) were kept constant in all experiments.

Once water and PS were placed into the reactor, the reaction mixture was pressurised with 50 bar of CO_2 introduced at −9 °C with aim to reduce the variation of density of introduced CO_2. Next, the reaction mixture was heated under continuous stirring until the desired reaction temperature was achieved. Depending on the pretreatment conditions, the isothermal stage of the process designated by the reaction time (t), was considered as well. Next, the reaction was quenched using an internal loop as well as cooling the reaction by placing it into the ice and water bath. When temperature of the mixture was close to room temperature, the reactor was slowly depressurised. The depressurisation step was carried out at controlled temperature and flow rate to minimise losses of volatile products (Magalhães da Silva et al., 2014). The obtained liquid (rich in hemicellulose-derived sugars) and solid (cellulose-enriched) fractions were separated by vacuum filtration. The recovered processed solid materials were washed with distilled water and stored at 4 °C while the liquid was stored at −20 °C. The chemical analyses of both liquid and solid fractions were performed according to the procedures presented in section below.

2.2.2. Dehydration reactions for furfural production

The CO_2-catalysed dehydration reactions were carried out in aqueous media in the presence of THF as stripping out solvent. A series of preliminary experiments were carried out with xylose and acetic acid, as a model system, before the produced hemicellulose hydrolysate was used in dehydration reactions for furfural production. All dehydration reactions were performed in the same high-pressure reactor described in the previous section. The furfural production reactions were carried out at different temperature, time and volume of aqueous solution in mixture with THF as defined by the design of experiments. The reactions were performed in the same reactor used for the hemicellulose hydrolysis described above. First reactor was loaded with known volume of aqueous solution and THF to maintain total volume of 40 mL in experiments. Next a reactor was closed and pressurised to constant initial pressure of CO_2 of 50 bar. To decrease the CO_2 density variations due to changes of initial temperature, the reactor was pressurised with CO_2 with initial temperature of −9 °C and the reaction was started when the temperature of mixture was 22 °C. Next system heated up to the desired temperature and then time at isothermal stage was considered. After that, the reactor was immediately cooled down in the similar manner as described above for hemicellulose extraction. A slow depressurisation of reaction mixture was performed when temperature was lower than 20 °C minimise losses of volatile products.

The hemicellulose hydrolysate dehydration reactions were