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Catalytic conversion of furfural from pyrolysis of sunflower seed hulls for producing bio-based furfuryl alcohol

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Clean production of furfuryl alcohol, an industrial product used worldwide, is presented using as a raw material sunflower seed hulls, an abundant agro-industrial waste. The method involves two steps. Firstly, a fast pyrolysis of pre-treated hulls, performed washing with aqueous solutions of phosphoric acid or zinc chloride, is carried out at 400 °C under a 200 mL/min of nitrogen flow, where a bio-oil rich in furfural is obtained. In the second stage, the catalytic hydrogenation of furfural is carried out, to obtain furfuryl alcohol over palladium supported on bio-chars obtained as side products of the hull pyrolysis. High catalytic performance for the hydrogenation of furfural to furfuryl alcohol under batch conditions at 110 °C and 0.4 MPa of hydrogen is reached. A preliminary industrial scale process is presented using the laboratory data for the technical evaluation. It is concluded that it is possible to obtain furfuryl alcohol from a renewable source consisting of sunflower seed hulls.

1. Introduction

Lignocellulosicbiomass is the most economical and abundant non-fossil carbon resource that can be used for producing chemicals and fuels by applying processes that generate lower greenhouse emissions (Kajaste, 2014). Developing new and efficient technologies and processes for industrial production of chemicals and fuels is necessary for developing Bioeconomy (Giurka and Spath, 2016); Currently, there are many Waste to Energy Technologies (WTE) for treating different feedstocks (biomass among others) as a means for obtaining renewable energy and bioproducts (Ouda et al., 2016 present a case study in Saudi Arabia, Bosmans et al., 2013 study different technologies applied to enhanced landfill mining). These WTE technologies are divided into three main categories: thermochemical, physicochemical and biochemical. Thermochemical transformation uses high temperature to convert waste feedstock into energy and/or Value Added Products (VAP). Pyrolysis, incineration and gasification are examples of these types of technologies (Tozlu et al., 2016). Incineration shows an efficiency of 25–30% and produces heat with a net operational cost per ton of 1.5 USD-2.5 USD. On the other hand, pyrolysis has an energy efficiency of 80% and it is considered to be economically profitable on a large scale that minimizes environmental concerns, especially for waste minimization, carbon sequestration, soil amendment, energy/heat supply and VAP production (Higman and Tam, 2014). Finally, the gasification process presents an efficiency of around 17% producing syngas, which is a mixture of CO, H_2 and CO_2 with a net operational cost per ton of 2USD-3 USD (Ouda et al., 2016).

Biochemical transformations of lignocellulosic materials are rather difficult to carry out due to the natural resistance of plant cell walls to microbial and enzymatic deconstruction (Himmel et al., 2007). In contrast, pyrolysis can rapidly transform biomass producing liquid, gas and solid products (Lim et al., 2016). The liquid, known as bio-oil, is universally regarded as a promising source for fuels and chemicals (Bridgewater, 2012), for example furfural (Ioannidou et al., 2009).

Sunflower (*Helianthus annuus)* seed hulls are abundant lignocellulosic residues of the edible oil industry. Some studies were carried out to analyze the conversion of this waste into VAP. Rehan et al. (2017) have stated that bio-oils produced by the pyrolysis process are suitable feedstock for this purpose. As far as our knowledge is concerned, there is only one study regarding the production of furfural from sunflower hulls in which some of us concluded that bio-oil rich in furfural can be obtained from pretreated hulls (Casoni et al., 2015).

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List of acronyms

S	Raw sunflower seed hulls
SH	Seed hulls treated with 5% H_3PO_4
SZ	Seed hulls treated with 5% $ZnCl_2$
BCs	Bio-Chars
BC	Bio-Char from raw sunflower seed hulls
BCH	Bio-Char from hulls treated with 5% H_3PO_4
BCZ	Bio-Char from hulls treated with 5% $ZnCl_2$
Pd/BCs	Palladium supported on bio-char catalysts
Pd/BC	Palladium supported on bio-char from sunflower seed hulls
Pd/BCH	Palladium on Bio-Char from seed hulls treated with 5% H_3PO_4
WTE	Waste to Energy Technologies
Pd/BCZ	Palladium over Bio-char from seed hulls treated with 5% $ZnCl_2$
Pd/C_{com}	Commercial catalyst of Palladium supported on commercial Carbon
D	Mean particle size (From TEM)
D%	Percentage of Pd dispersion
FF	Furfural
FA	Furfuryl Alcohol
THF	Tetrahydrofuran
THFA	Tetrahydro Furfuryl Alcohol
FO	Furan
S_{BET}	Specific Surface Area, as measured by BET method
VAP	Value Added Products

Approximately 62% of the furfural production worldwide is converted into furfuryl alcohol by hydrogenation (Mandalika et al., 2014). Furfuryl alcohol is an intermediate in the production of lysine, ascorbic acid and lubricants. In addition, furfuryl alcohol is extensively used in the foundry industry due to its flexibility as a binder base and for drug synthesis.

With our continuing interest in valorizing sunflower seed hulls, the production of furfuryl alcohol from this residue is analyzed. The main objective is to study the catalytic conversion of biomass-derived furfural into furfuryl alcohol. In pursuing this, fast pyrolysis of sunflower seed hulls submitted to different pre-treatments is carried out at 400 °C in a vertical glass reactor to obtain bio-oils rich in furfural. The bio-oils are hydrogenated to obtain furfuryl alcohol over palladium catalysts in a Batch reactor under mild conditions (at 110 °C and 0.4 MPa). The catalysts are prepared by supporting palladium on bio-chars. The noble metal was selected due to its high activity for liquid phase hydrogenation of furfural (Lee et al., 2013). The bio-char supports were obtained as by-products of the hull pyrolysis. Finally, in order to investigate about industrial application of the production of furfuryl alcohol from sunflower seed hulls, a conceptual industrial simulation is performed.

2. Materials and methods

The biomass for pyrolysis was raw sunflower seed hulls, as well as pre-treated hulls. The pre-treatments were selected in order to increase the yield to furfural from pyrolysis. Thus two pre-treatments were performed on the hulls, consisting of washing with solutions of phosphoric acid and zinc chloride. Both acid solutions originate a partial depolymerization of holocellulose, which leads to a desired increase in furans concentration in the corresponding bio-oil (Ramirez-Corredores, 2013a; Cao, 1995).

Raw and pre-treated hulls were fully characterized in order to determine the influence of the pre-treatments on the physico-chemical properties of the hulls.

2.1. Sunflower seed hulls

Raw and pre-treated hulls were dried and milled up to particle sizes between 10 and 100 μm (determined utilizing laser diffraction equipment, HORIBA LA-950). The hulls were characterized by Thermo Gravimetric Analysis (TGA) and Differential Thermo Gravmetric Analysis (DTG) in a Discovery TGA equipment. The proximate analysis of the samples was also carried out with the same equipment. The scale was purged with nitrogen for 20 min to eliminate any trace of oxygen. Following this, approximately 10 mg of the hulls were heated at 10 °C/min from room temperature to 900 °C. Subsequently, the nitrogen flow was switched to air to determine the amount of ash. The alkaline metal concentration was measured by Induced Coupled Plasma Spectroscopy employing a Shimadzu Simultaneous 9000 apparatus, following EPA standard 200.7. Hemicellulose, cellulose and lignin contents were analyzed following the Van Soest method in an ANKON 200/220 FIBER ANALYZER (Van Soest et al., 1991).

The solutions for the pre-treatments were aqueous solutions of 5% $ZnCl_2$ (Cicarelli, 97%) and 5% H_3PO_4 (Aldrich, 85 % wt.), respectively. About 5 g of the hulls were soaked under continuous stirring for 2 h. Finally, the solutions were filtered and dried. Thus, three samples were obtained for pyrolysis: the raw hulls (S), acid washed hulls (SH) and hulls treated with zinc salt solution (SZ).

2.2. Pyrolysis and product characterization

Pyrolytic reactions of S, SH and SZ were carried out at 400 °C under a nitrogen flow (200 mL/min) in a glass down-flow reactor, provided with a porous glass disk at the bottom in order to retain the hulls and at the same time to allow vapors to escape. About 3 g of sunflower seed hulls were used in each reaction. The reactor was put into a furnace previously heated at 400 °C and the vapors were condensed, with a water/ice-bath, for collecting bio-oils. The experimental conditions were selected for achieving the maximum bio-oil yield (Casoni et al., 2015; Garg and Kuumar, 2016). The results corresponding to pyrolytic yields (to liquid, gas and solid products) were reported with a repeatability error lower than 1%.

The bio-oils from S, SH and SZ were analyzed with a GC–MS Perkin Elmer CLARUS 500 Chromatograph coupled with a mass spectroscopy detector, provided with an Elite-5 MS column (60 m, 0.25 mm ID). The quantification was carried out considering that the peak areas are proportional to the corresponding compound concentration in the sample.

Three samples of bio-chars (BCs) were obtained: one bio-char as a by-product of the pyrolysis of untreated S, named as BC, and two bio-chars obtained from the pre-treated sunflower seed hulls SH and SZ, named as BCH and BCZ, corresponding to treatments with phosphoric acid and zinc chloride, respectively. The pyrolytic BCs were heated at 500 °C for 2 h under N_2 in order to complete the activation.

The superficial acidic groups of BCs were determined following Boehm titration (Boehm, 1994, 2002). Hence, 0.1 g of BCs were soaked in 30 mL of $NaHCO_3$ 0.05 M, Na_2CO_3 0.025 M, NaOH 0.05 M and C_2H_5Na 0.05 M aqueous solutions and stirred for 24 h. Then, 10 mL of the corresponding suspension were titrated using HCl,