



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

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ARTICLE INFO

Article history:

Received 14 June 2017

Received in revised form

3 January 2018

Accepted 6 January 2018

Available online 8 January 2018

Keywords:

Furfuryl alcohol

Pyrolysis

Biomass-derived furfural

Bio-char

Pd catalyst

Sustainable process

ABSTRACT

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.

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1. Introduction

Lignocellulosic biomass 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 bio-products (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, H₂ and CO₂ 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 pre-treated hulls (Casoni et al., 2015).

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List of acronyms

S	Raw sunflower seed hulls
SH	Seed hulls treated with 5% H ₃ PO 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 ₃ PO 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 ₃ PO 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 Gravimetric 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% ZnCl₂ (Cicarelli, 97%) and 5% H₃PO₄ (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 Kumar, 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 N₂ 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 NaHCO₃ 0.05 M, Na₂CO₃ 0.025 M, NaOH 0.05 M and C₂H₅Na 0.05 M aqueous solutions and stirred for 24 h. Then, 10 mL of the corresponding suspension were titrated using HCl,

approximately 0.05 M, in a KEM AT500N Automatic Titrator.

The elemental analyses of BCs were performed on an Exeter Analytical CE-400 instrument.

2.3. Preparation of palladium supported on BCs and characterization

Palladium catalysts supported on bio-char (Pd/BCs) were prepared following the precipitation-reduction method, employing PdCl₂ as the metal precursor (Mozingo et al., 1955). The nominal weight percentage of palladium was 5% for all catalysts.

Firstly, the BCs were pretreated with a 10% nitric acid solution at room temperature for 2 h. Approximately 1 g of the sample was put in contact with a HCl aqueous solution of palladium chloride at 80 °C under stirring. A 37% formaldehyde solution was added for reducing Pd²⁺ to Pd⁰, which was precipitated on the support by adding a 30% NaOH solution up to basic pH. Afterwards, the resulting solid was filtered and washed exhaustively with de-ionized water in order to remove the chloride. Finally, the catalyst precursor was dried at 100 °C for 2 h. From the above preparation procedure, three catalysts were obtained: Pd/BC, Pd/BCH and Pd/BCZ. An extra sample, named as Pd/Ccom, was purchased from Sigma-Aldrich.

The palladium loading of the catalysts was determined by Atomic Absorption Spectrometry (AAS) in a Perkin Elmer AAnalyst 700 equipment. Before the analysis, the catalysts were pretreated according to EPA standard 200.7. Powder X-ray diffraction (XRD) patterns were recorded on a Philips PW1710 BASED Diffractometer, operating at 45 kV and 30 mA, fitted with a graphite monochromator getting Cu K α 1 radiation ($\lambda = 0.15406$ nm). The samples were characterized by Transmission Electron Microscopy (TEM), employing a Joel 100 CX2 (Tokyo, Japan) apparatus. Approximately one hundred palladium particles were measured to perform the particle size distribution in order to obtain the mean particle size (d). The percentage of palladium dispersion, D % corresponding to the (surface Pd/total Pd) ratio was calculated from d, following the Schölten equation (Schölten et al., 1985). Nitrogen adsorption/desorption isotherm at -196 °C was obtained with a Nova 1200e Quantachrome Instrument. The specific surface areas were measured following the Brunauer–Emmett–Teller (BET) method. Previously the samples were evacuated for 20 h at 110 °C. Fourier Transformed Infrared (FTIR) spectra of the BCs were obtained with a Nicolet 6700 spectrometer. Samples disks were prepared mixing the supports with KBr (Sigma-Aldrich, $\geq 99\%$).

2.4. Catalytic test: hydrogenation of furfural

All catalysts were tested for the hydrogenation of furfural. A furfural solution in isopropyl alcohol was prepared employing the real bio-oil as the furfural source. Moreover, some experiments were carried out using a model reactive mixture, with a furfural (Sigma-Aldrich, 99.5%) concentration similar to the one corresponding to the real pyrolytic oil. For both, real and synthetic mixtures, the furfural concentration was 0.01 M measured by Gas Chromatography (GC) employing a calibration curve.

The reactions were conducted in a 50 mL Batch reactor (Parr Model 4545) equipped with an electrical heating jacket and an overhead mechanical stirrer. The reactive mixture was put into the reactor with 0.10 g of the catalyst. The reactor was connected to a hydrogen cylinder for maintaining a pressure of 0.4 MPa. Before each run, the reactor was flushed five times with hydrogen in order to remove air. The temperature was set up to 110 °C and the stirring speed was 620 rpm during the reaction. The furfural conversion and the selectivity to the different products were followed by sampling aliquots of the reactive mixture over time. Turnover

Frequency (TOF) numbers, which correspond to furfural moles converted per mole of Pd at the surface and per second, were calculated using rates at the early reaction times and considering the metal dispersion, D. The furfural and the reaction products concentrations were measured by GC-Flame Ionization Detector employing an Elite-WAX capillary column. The reaction mixture was also analyzed in a Perkin Elmer CLARUS 500 GC Chromatograph provided with a Mass Spectrometry Detector. The carbon balance was checked in every run and it was higher than 95% in all cases. The results corresponding to conversion and selectivity to the different products were reported with a repeatability error lower than 1%.

2.5. Industrial simulation

A conceptual simulation of the process for producing bio furfuryl alcohol from sunflower seed hulls was carried out. The conceptual simulation yields in pyrolysis and hydrogenation step are assumed to be the same as laboratory scale. Although this is a strong assumption, this is valid at the conceptual stage design, so the technical feasibility, main equipment sizing and an economic preliminary assessment can be performed. The challenge would be to build reactors such that those yields could be obtained. Aspen Plus™ was used to simulate the process using simplified models (mass balance based on yield) for the reactors. A simplified representation of product distribution was also considered.

3. Results and discussion

Nowadays, the pyrolysis of different waste materials is an emergent WTE technology with the possibility of obtaining VAPs. According to Miandad et al. (2016a) plastic waste can be used to produce bio-oils with valuable products. These authors have also explored the quality of the bio-oils related to different catalysts. In the present study, an agro-industrial waste (sunflower seed hulls) is used as feedstock for producing VAPs by pyrolysis. In Bahia Blanca, Argentina, this residue represents 55,000 ton per year which is currently burned to produce heat, with no consideration of using it as a potential source of VAPs.

3.1. Sunflower seed hulls characterization

In Table 1 some physicochemical properties of S, SH and SZ are reported. The proximate analysis indicates that moisture, volatile matter and fixed carbon are not greatly affected by the acid pretreatment. On the other hand, the acid treated biomass presents a slight increment in the amount of ash compared to untreated hulls. Fig. 1 shows the thermal behavior studied by TGA of S, SH and SZ and it was observed that the biomass presents a first loss of mass related to moisture at temperatures below 100 °C. Then, the mass percentage of sunflower seed hulls profile shows a major decrease between 200 °C and 350 °C, which can be attributed to decomposition of hemicellulose and cellulose, whereas at the same range of temperatures, the acid washed biomass (SH) shows two clear steps due to the disruption of the linkage between hemicellulose, cellulose and lignin, as well as the cleavage of the hydrogen bonds of crystalline cellulose (Nitsos et al., 2013). Zinc chloride treated hulls present the main mass loss at a high temperature (360 °C) despite it shows a similar effect as the acid treatment. Moreover, the alkali metal concentration varies strongly when S, SH and SZ samples are compared (Table 1). It is observed that the acid and chloride treatments decrease the metal content overall, which is a remarkable result, since it is well known that alkali metals significantly affect pyrolytic reactions. For instance, Na⁺, K⁺ and Ca⁺² increase the bio-char production while decreasing the bio-oil yield

Table 1
Sunflower seed hulls characterization.

	Sunflower seed hulls	Sunflower seed hulls treated with 5% H ₃ PO ₄	Sunflower seed hulls treated with 5% ZnCl ₂
Proximate Analysis (Dry basis %)			
Moisture	6.1 ^a	5.9	5.7
Volatile Matter	79.8 ^a	83.8	83.1
Fixed Carbon	18.1 ^a	13.9	15
Ashes	2.1 ^a	2.3	1.9
Metal (mg/kg)			
Na ⁺	100	140	120
K ⁺	10400	2600	1500
Ca ⁺⁺	3200	70	1100
Mg ⁺⁺	1900	61	480
Biomass Contents %			
Hemicellulose	18.4	17.3	19.8
Cellulose	39.1	33.8	36.7
Lignin	20.4	16.9	18.7
Others ^b	22.1	32.0	34.8

^a Casoni et al., 2016.

^b Pectins, resins, extractives, etc.

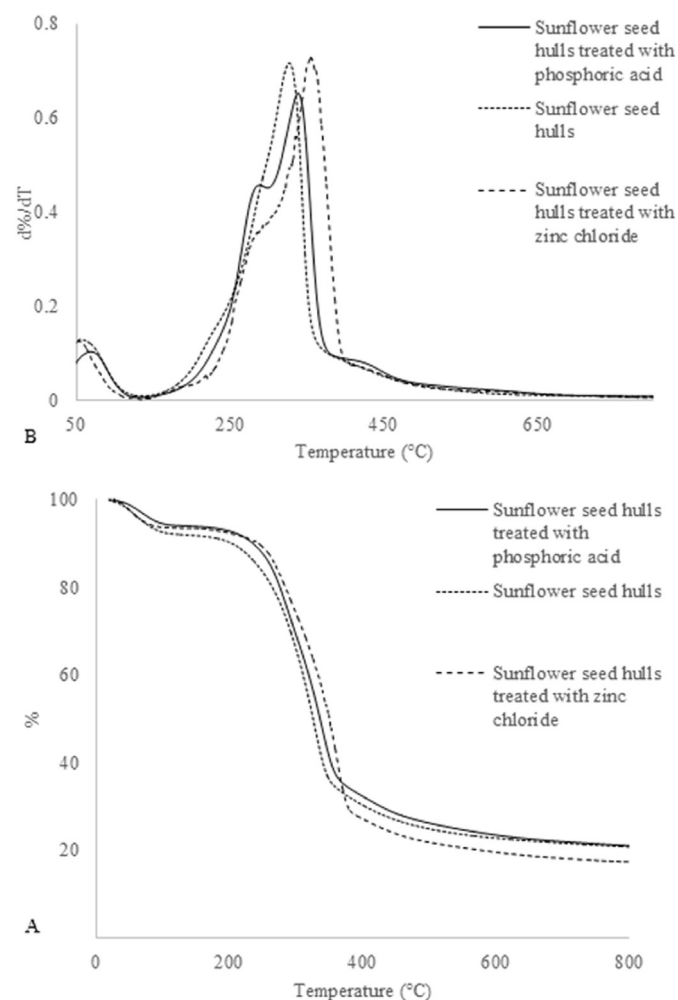


Fig. 1. (A) Thermo Gravimetric and (B) Differential Thermo Gravimetric Analysis profiles showing the different thermal degradation patterns of the biomasses under study: Sunflower seed hulls (S), Sunflower seed hulls treated with H₃PO₄ (SH) and Sunflower seed hulls treated with ZnCl₂ (SZ).

(Ramirez-Corredores, 2013a). Considering the biomass composition, it is observed that the acid pre-treatment notably affects the cellulose content, whereas the ZnCl₂ only affects it slightly. On the other hand, the hemicellulose and lignin percentages are only modified by the acid pre-treatment.

3.2. Bio-oil and bio-char characterization

The percentages of the main compounds in the bio-oil obtained from the raw sunflower seed hulls, and from the acid treated and salt washed biomass are reported in Table 2. The raw biomass generates a complex liquid, rich in acetic acid.

On the other hand, the phosphoric acid treatment leads to activation of the cellulose by depolymerization (Ramirez-Corredores, 2013b) and concomitantly, to a higher yield of furfural. Besides the liquid obtained from the acid washed material presents a much simpler composition. Although zinc chloride pretreatment leads to a slight increment in the furfural concentration of the bio-oil, this salt also favors the production of other compounds, making the corresponding liquid more complex than the one obtained from the hulls washed with phosphoric acid. This result can be attributed to the fact that the concentration of zinc chloride is not high enough to reach the same effect on the hulls than the one due to the pre-treatment with phosphoric acid. Thus the concentration of furfural in the liquid obtained from the pyrolysis of zinc chloride treated hulls is lower than the one corresponding to the bio-liquid from SH material.

Besides, it is interesting to note that if the content of hemicellulose (the main source of furfural) in the sunflower hulls is considered, the concentration of furfural in the bio-liquid from SH is extremely high (73%). However it should be taken into account that the pre-treatment with phosphoric acid leads to cellulose activation, promoting its thermal degradation to levoglucosenone, which is, in turn, a source of furfural (Lu et al., 2011).

Bio-char can be used as a source of energy or as a feedstock for activated carbon. The activated char, in the form of activated carbon can be used for industrial and municipal wastewater purification from heavy metals and disinfecting by-products, and toxic organic compounds (Miandad et al., 2016b). In the present study, bio-chars were utilized as a material for the synthesis of catalysts.

The specific surface areas of the different bio-chars are reported in Table 3. The lowest area corresponds to the material obtained from untreated hulls (BC), whereas the ZnCl₂ treatment led to the char with the highest area (98 m²/g). Phosphoric acid and zinc chloride promoted porosity of the samples, which is the main reason for the increments in the corresponding areas (Wiśniewski et al., 2001).

The information obtained from FTIR characterization revealed

Table 2
Yield to different products of pyrolysis and bio-oils^a chemical composition.

	Sunflower seed hulls	Sunflower seed hulls treated with 5% ZnCl ₂	Sunflower seed hulls treated with 5% H ₃ PO ₄
Bio-oil wt.%	45	39	33
Bio-char wt. %	27	26	31
Gas wt.%	28	35	36
% Compounds			
Acetic acid	43	17	15
Furfural	10	24	73
1-Hydroxy-2-propanone	3	—	—
Levoglucosenone	—	—	10
Others ^b	44	59	2

^a Organic phase.

^b Mainly phenolic compounds.

Table 3
Boehm titration and elemental analysis of Bio-chars from pyrolysis of sunflower seed hulls.

Boehm Titration							
Bio-char from sunflower seed hulls treated with:	Carbonyl mEq/g	Phenol mEq/g	Lactone mEq/g	Carboxyl mEq/g	Area m ² /g	Total mEq/g	Total mEq/m ²
–	0.02	13.89	0.31	0.31	5	14.53	2.90
H ₃ PO ₄ 5%	0.02	13.97	0.30	0.29	68	14.58	0.21
ZnCl ₂ 5%	0.01	14.13	0.31	0.32	100	14.77	0.15
Ultimate Analysis (wt.%)							
	C		H		O ^a		N
–	76.0		3.1		19.4		1.5
H ₃ PO ₄ 5%	58.9		2.2		37.8		1.1
ZnCl ₂ 5%	79.0		2.8		16.9		1.3
Sunflower seed hulls	46.5		6.3		46.3		0.7

^a Calculated by difference.

that the different surface functional groups were produced by the different pre-treatments. In all cases, the main characteristic absorption bands were present at: 3353 cm⁻¹, 1702 cm⁻¹, 1560 cm⁻¹ and 1230 cm⁻¹. The first one is attributed to the stretching vibrations of –OH groups from phenolic and carboxylic groups. At 1702 cm⁻¹ the spectra showed a band due to the stretching vibration of the C=O groups, whereas the band at 1560 cm⁻¹ was related to the stretching vibration of C=C in the aromatic ring. Finally, the signal at 1230 cm⁻¹ was assigned to the vibration of C–O in phenol.

The bio-char samples were characterized by Boehm titration, in order to carry out a quantification of the different functional groups normally present in the char-like material surface. The Boehm qualitative results were in line with FTIR functional group identification, since carbonyl, phenol, lactone and carboxyl groups were detected. The acidity was mainly associated with phenolic groups in the three samples. Moreover, all the bio-char samples presented similar concentrations of the total functional group expressed on a mass basis. On the other hand, if the concentration of the acidic groups is expressed per m², the acidity measurement throws different values for each support (Table 3). The BC support showed the highest total oxygenated group concentration, expressed as mEq/m². Boehm titration indicated that the acidity per m² increases following the order: BC >> BCH > BCZ.

Regarding the elemental composition (Table 3), it is observed that BCs present a lower percentage of O than the starting biomass, as would be expected. When the BCs are compared, the highest O concentration corresponds to BCH, which could be attributed to the functionalization generated by phosphoric acid.

3.3. Catalysts preparation and characterization

Palladium concentrations on Pd/BC, Pd/BCH and Pd/BCZ catalysts are reported in Table 4. All values were lower than 5% wt. (the nominal concentration) showing that Pd²⁺ ions would not be totally precipitated by sodium hydroxide or that they would be eliminated during the washing procedure of the support.

X-ray diffraction patterns of Pd/BC, Pd/BCZ and Pd/BCH showed four peaks at ca. 40.0°, 46.6°, 68.0° and 82.0°, which were ascribed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes of metallic Pd. Besides, all the catalysts exhibited a broad peak around 2θ = 26.5° indicative of the amorphous structure of bio-chars. No peaks of Pd oxide were observed, demonstrating that the Pd species are primarily metallic after reduction with formaldehyde (Fig. 2).

TEM images were employed to obtain the particle size distribution of the three catalysts prepared from bio-char and the commercial sample (Table 4). The images of different samples

demonstrated that the palladium particle size depends strongly on the nature of the bio-char supports. Particularly, Pd/BCH showed the smallest particles with a mean diameter of 2 nm (Fig. 3), showing that the bio-char obtained from the acid treated hulls would be the best support to disperse the noble metal. It could be speculated that the BCH bio-char develops a strong interaction with palladium favoring the noble metal dispersion on the surface. BCH support is even better than the commercial catalyst, which exhibits a large specific surface area. This is quite an important result, since in the course of preparation of catalysts containing noble metals, which are very expensive materials, it is expected that highly dispersed metallic particles will be obtained. A detailed description of chemical and morphological properties of BCH surface which give rise to the high noble metal dispersion is beyond the scope of the present study and is the subject of an ongoing research work.

3.4. Catalytic test: the hydrogenation of furfural

The catalytic hydrogenation of furfural (FF) leads to the desired furfuryl alcohol (FA) (pathway I, in Fig. 4) by the reduction of the carbonyl group. However furan could also be produced by decarbonylation (pathway II in Fig. 4). Moreover, the reduction of the double bonds of both, furfuryl alcohol and furan leads to tetrahydro furfuryl alcohol (THFA) and to tetrahydrofuran (THF), respectively (pathway III and IV respectively).

The influence of the solvent polarity on liquid phase hydrogenation reactions is notable. Solvent polarity increases the hydrogenation rates (von Arx et al., 1999). Besides, previous studies have shown that catalytic activity, and especially product distribution, are mainly affected by the solvent (Hronec and Fulajtarová, 2012; Ordonsky et al., 2013). In particular, polar alcohols mainly

Table 4
Physico-chemical and catalytic properties of Palladium supported on bio-chars catalysts (Pd/BCs).

Catalyst	Pd ^a (wt%)	SBET ^b (m ² /g)	d ^c (nm)	D ^d	X ^e	S ^f	TOF (s ⁻¹)
Pd/BC	3.5	4	5	22	45	41	100
Pd/BCZ	3.4	98	4	27	48	65	100
Pd/BCH	3.4	65	2	54	82	74	120
Pd/Com	2.6	700	10	11	94	0	140

^a Palladium wt.% concentration as measured by AAS.

^b Specific surface area obtained by BET method from N₂ Isotherms.

^c Means particle size from TEM.

^d Palladium metallic dispersion (D%) calculated from d following Schönten equation.

^e Conversion of furfural at 30 min of reaction.

^f Selectivity of furfuryl alcohol at 80% of conversion.

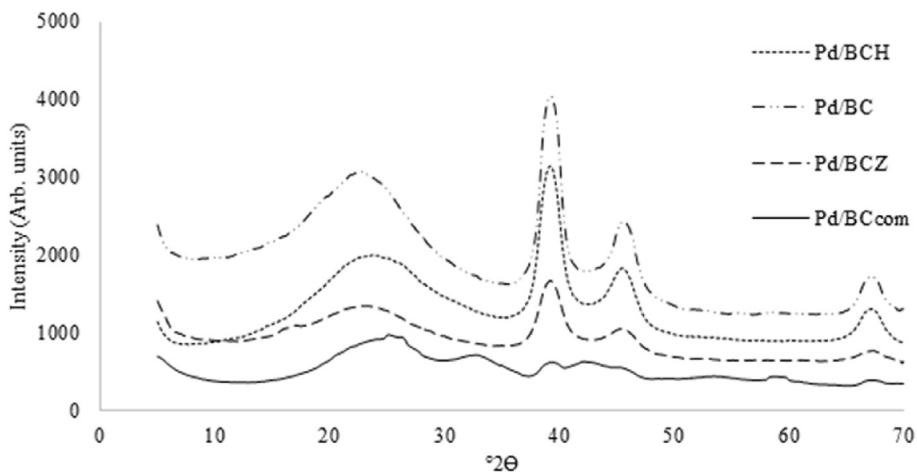


Fig. 2. XRD Pattern of catalysts Pd/BC, Pd/BCH, Pd/BCZ and Pd/BCcom.

produce furfuryl alcohol, tetrahydrofurfuryl alcohol and methyl furan (Hronec and Fulajtarová, 2012; Ordonsky et al., 2013; Hronec et al., 2012). Merlo et al. (2009) have reported that isopropanol is a suitable solvent for furfural hydrogenation because undesirable reaction products have not been observed, such as those from hydrogenolysis or decarbonylation. In addition to that, a decrease in poisoning of the selective metal support interfacial surface sites has

been reported for this solvent (Maki-Arvela et al., 2005). Moreover, Villaverde et al. (2013) have found that isopropanol increases furfuryl alcohol selectivity.

The conversion values of FF, the selectivity to FA as well as the TOF numbers, corresponding to the different Pd/BCs catalysts tested for the hydrogenation of a solution of furfural in isopropyl alcohol, are listed in Table 4. The selectivity to the desired product,

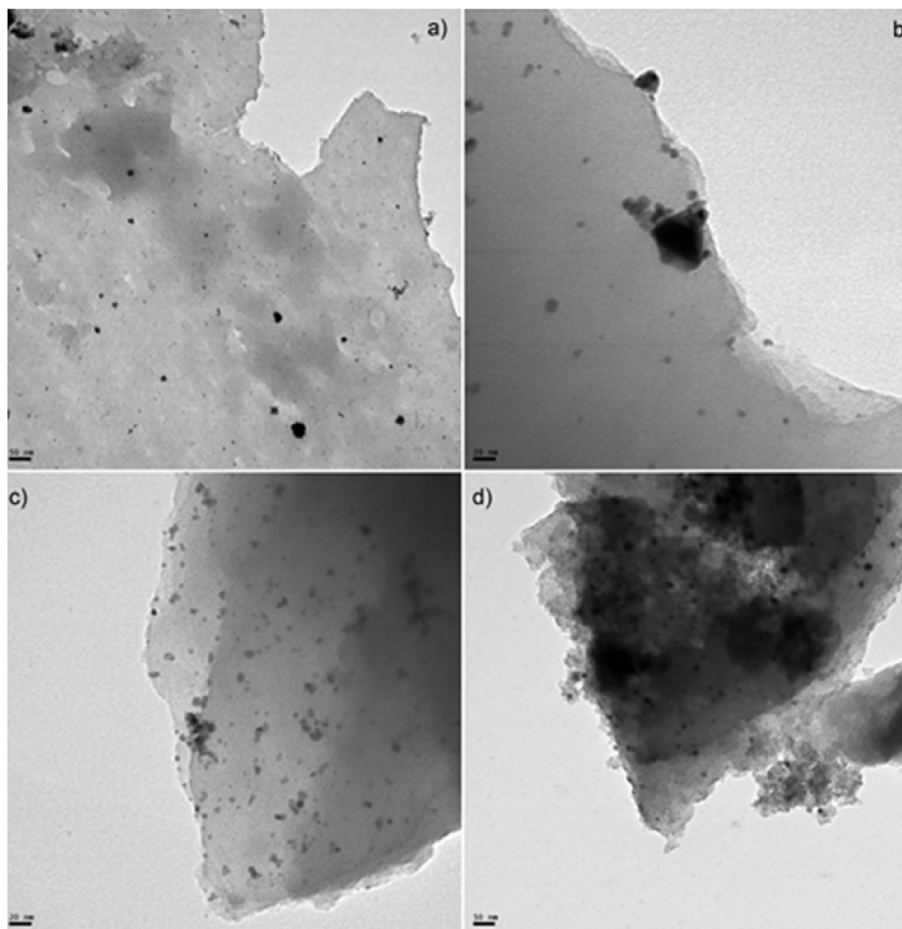


Fig. 3. Representative TEM image of palladium supported on biochar catalysts. Showing palladium particles (black) developing high contrast with the biochar support (grey). a) Pd/BCH, b) Pd/BC, c) Pd/BCZ and d) Pd/BCcom.

FA, varies for the different catalysts. THF was the main product obtained using Pd/Ccom, showing that decarbonylation and consecutive hydrogenation (in Fig. 4, pathways II and IV respectively) occur over the catalytic surface of this sample. On the contrary, the other tested catalysts prepared with the bio-chars, Pd/BCH, Pd/BCZ and Pd/BC, lead to furfuryl alcohol and tetrahydrofurfuryl alcohol (in Fig. 4, pathway I and III). The dependence of the catalytic pattern on time is shown in Fig. 5 for Pd/BCH and Pd/BCZ. The higher conversion level reached by Pd/BCH would be related to its lower Pd particle size, 2 nm compared to 4 nm for Pd/BCZ. This fact is in line with Haynes et al. (2017) who demonstrated that palladium particles size is a determining factor in the catalytic activity. Authors claimed that the smallest particles present the best activity for hydrogenation due to the fact that large particles show a weak influence on dispersion. Moreover, Bailón-García et al., 2016, have studied the Pt particle size effect on the hydrogenation of carbonyl group of citral and have concluded that particles smaller than 10 nm are highly active to hydrogenate this functional group. The selectivity of FA was quite similar (80%) for both catalysts, Pd/BCZ and Pd/BCH, measured at 60% isoconversion conditions. Thus, the yield of FA (calculated as the product between the conversion and the selectivity) shows a high value near to 50% for both Pd/BCH and Pd/BCZ, this value being reached at shorter reaction times for the former than for the later catalyst.

Normally, the catalytic hydrogenation of furfural requires severe conditions. Bhogswarao and Srinivas (2015) employed Pd(5 wt %)/Al₂O₃ at 25 °C in isopropyl alcohol at high hydrogen pressures, 2 MPa and 6.0 MPa, and long reaction times (8 h). The authors reported a TOF of 0.4 s⁻¹ and selectivity of furfuryl alcohol of about 21% as their best result with this metal. In addition, Sitthisa and Resasco (2011) employed a continuous reactor for hydrogenating furfural in the vapor phase over Pd(1 wt%)/SiO₂ under atmospheric pressure of hydrogen at 290 °C. They obtained a higher TOF of 265.8 s⁻¹ compared to those observed in our study, but the selectivity of FA was rather low, 14%. Mironenko et al. (2015) have employed Pd/CNT at 90 °C and 2.0 MPa of H₂ using water as a solvent. They observed a high conversion value of 95% with a quite high selectivity towards FA of 52%. The catalytic performance of Pd/CNT could be explained considering that the carbonaceous support became catalytically active promoting hydrogen dissociation (Lam and Luong, 2014). The catalytic performance of Pd/CNT is better than that observed in the Pd/BCs of the present study, although it should be noted that the support of the former catalyst is a commercial one, whereas the BCs are bio-based materials obtained from the residual hulls.

The Pd/BCH sample was selected for carrying out the hydrogenation of a real furfural enriched bio-oil. Thus, the bio-oil obtained

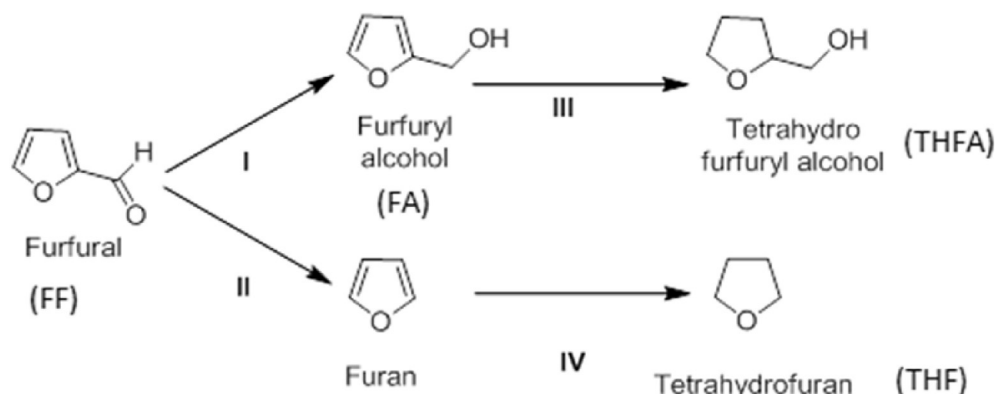


Fig. 4. Possible reaction pathways of furfural conversion to different products over Pd/BC, Pd/BCH, Pd/BCZ and Pd/Ccom catalysts.

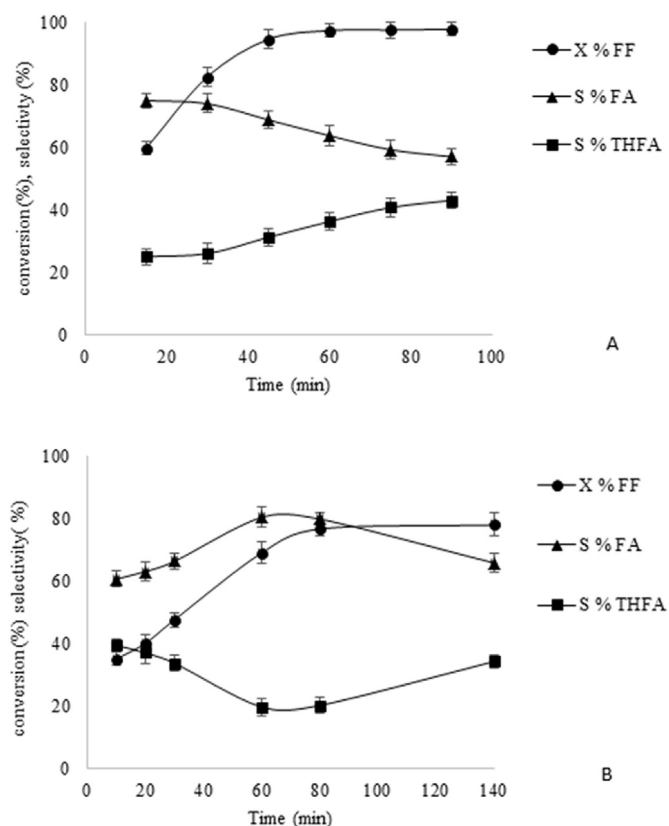


Fig. 5. Hydrogenation of furfural. Dependence of conversion of furfural (FF) and of selectivities to furfuryl alcohol (FA) and to tetrahydro furfuryl alcohol (THFA) on time for (A) Pd/BCH, (B) Pd/BCZ.

from the pre-treated hulls, with a high concentration of furfural (see Table 2, last column, which reports the composition of the bio-oil corresponding to sunflower seed hulls treated with 5% H₃PO₄) was selected for performing that catalytic transformation. The catalytic performance of Pd/BCH for the hydrogenation treatment of the real bio-oil is shown in Fig. 6. The conversion of furfural achieved by Pd/BCH was lower than that corresponding to the same catalyst when employing the synthetic mixture (Fig. 5 A). The lower conversion of furfural developed by Pd/BCH for hydrogenating the real bio-oil would be related to the complex nature of this liquid, which possesses some highly reactive molecules that partially poison the catalytic surface (Yu et al., 2011).

The selectivity to the desired product, furfuryl alcohol, is approximately 80% (see Fig. 6) and the yield of furfural into the alcohol, calculated as the product between selectivity and conversion at reaction time of 265 min is higher than 65%. If the yield of acid pre-treated biomass into bio-oil (33%), as well as the concentration of furfural in such an oil (73%) are considered, it can be established that the total yield biomass into furfuryl alcohol is approximately 12.5%. This is an important result showing that Pd based catalysts supported on bio-chars obtained from the pyrolysis of sunflower seed hulls carry out the transformation of furfural to furfuryl alcohol in a real bio-oil.

The reuse of Pd/BCH was studied, since the reusability of Pd/BCH is a property of high industrial impact. The spent catalyst was withdrawn from the reactor once the reaction was finished. Afterwards, it was submitted to a washing procedure with isopropanol and finally to a mild treatment under chromatographic air 200 °C for half an hour. The recovered and treated Pd/BCH catalyst was tested again for the hydrogenation of real bio-oil, reaching a quite similar catalytic pattern than the fresh sample (a conversion of 70% was achieved at 5 h of reaction time, with selectivity to furfuryl alcohol of 83%).

Finally, it is important to note that the biomass previously washed with phosphoric acid is at the same time the source of furfuryl alcohol (the main product) and the catalyst support (a co-product) employed for the production of furfuryl alcohol.

3.5. Relevance of the results and industrial simulation

The present study is based on global trends to replace traditional products with bio-based ones. Nowadays, almost the totality of the furfural production is based on the Quaker Oats process (1921) (USPATENT: 2140572 A “Process for producing furfural” Harold Brownlee), which presents a lot of drawbacks: low yield of, approximately 50%, along with some negative economic and environmental aspects (Marcotullio, 2011). Besides, furfural/furfuryl alcohol production is traditionally obtained from dedicated crops, for example in Argentina quebracho is exploited in the manufacturing plant of Indunor (Selvateam group). The use of land to cultivate trees for the production of chemicals represents a negative impact from environmental, social and moral point of view. This fact leads to a negative externality for the traditional process of obtaining furfuryl alcohol.

On the other hand, the use of a bio-waste as sunflower seed hulls from edible oil industry minimizes this negative externality. Regarding the economic aspects, the exploitation of null overhead

waste, such as the hulls, represents an obvious benefit of the replacement of traditional furfuryl alcohol by the bio-based product.

There are available technologies for carrying out the process. New commercial large scale pyrolysis units are based on fluidized reactors (Kajaste, 2014) A preliminary industrial production setup is presented in this section. A simplified block diagram is shown in Fig. 7.

Sunflower seed hulls are transported by truck to the facility, where they are unloaded in ground level containers. Then, the hulls are grounded using hammer mills and stored in containers until they are transported to stirred tanks where they are pretreated with phosphoric acid 5%. The hulls must be dried before being sent to the pyrolysis step.

The pretreated hulls are sent to the pyrolysis reactor, where they are mixed with hot sand (650–700 °C) and fluidized with nitrogen, where the proportions of sand/biomass should be between 10 and 20 and fluidized gas/biomass between 2 and 9. The product is sent to a series of cyclones where sand and bio-char are separated, and vapors are sent to a cooling system to condense the bio-oil with furfural.

The cooling system following the pyrolysis reactor is composed by three steps. In the first condensation step, levoglucosenone is obtained in a product containing <2% furfural. Vapor is then directed to the second step, which allows to obtain a liquid product with ~86% furfural, acetic acid and water. The third condensation step allows to obtain a liquid product with acetic acid and water while non-condensable vapors are sent to burners. The possibility of further purification of the levoglucosenone obtained in the first condensation step shown in Fig. 8 would allow for a significant improvement of the economics of the process, because the sales price for the pure product is close to 300 USD per g.

In the second reaction sector, furfural is sent to the hydrogenation sector, where furfuryl alcohol is produced. Furfural must be preheated and saturated with hydrogen in a packed tower prior to entering the catalytic reactor (Not shown in the diagram). The reactor is a fixed bed type, using Pd/BCH as catalyst. The reactor operates at 150 °C and 1 atm. Condensation of the product allows for the separation of furfuryl alcohol and unreacted hydrogen that is recycled to the packed tower. Further separation steps can be taken to obtain a laboratory grade product.

Some results of global mass balance are shown in Table 5.

For a production of furfuryl alcohol consistent with the market requirements in Argentina, approximately 20000 t/y of sunflower seed hulls need to be processed.

For the scaling up of the process some other challenges are faced as the transportation of hulls is not trivial. For example, hulls density is approximately equal to air density, and they could have traces of pips making them flammable. Other challenges posed are related to transportation of solids. The mixture of grounded hulls and phosphoric acid needs to be rheologically characterized to define the type of transportation process to be used. The reactor design is a challenge on itself. All these questions and some others are subject to further analysis and are being investigated. From the preliminary mass balance, the amount of 96% levoglucosenone produced is approximately 2075 t/y. This exceeds the global production of 99% levoglucosenone (50 t/y, only produced by Circa Group) but being this a product with high value added, efforts should be made to introduce it in the market or to find new applications that allow for the use of a higher amount of this product, to make the process more profitable.

4. Conclusions

It is possible to obtain furfuryl alcohol from sunflower seed

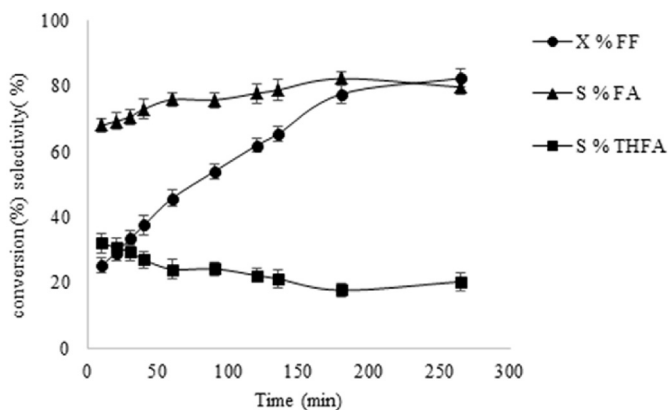


Fig. 6. Hydrogenation of bio-oil. Dependence of the conversion of furfural (FF) and of the selectivities to furfuryl alcohol (FA) and to tetrahydro furfuryl alcohol (THFA) on time for Pd/BCH.

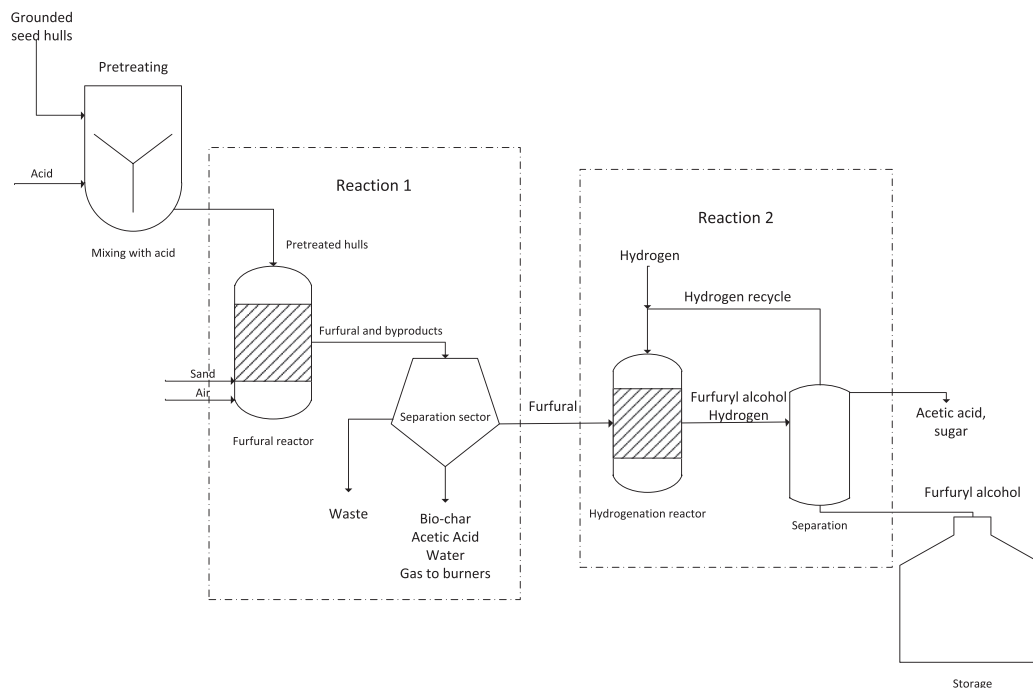


Fig. 7. Simplified schematics of the industrial furfuryl alcohol process.

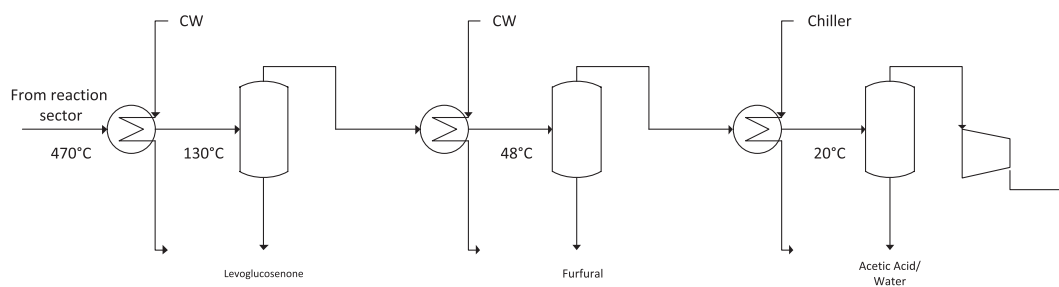


Fig. 8. Condensation steps to separate products from reaction sector 1.

hulls, an abundant agroindustrial waste. Fast pyrolysis of hulls previously washed with phosphoric acid leads to a yield of 33 wt % of furfural rich bio-oil. The co-product of the pyrolysis is a bio-char, BCH, whose properties enable its usage for supporting highly dispersed palladium metal particles, leading to a high performing hydrogenation catalyst, Pd(5 wt%)/BCH. This catalyst allows for the production of furfuryl alcohol from the bio-oil rich in furfural with

high selectivity (80% at 60% of conversion) in a batch hydrogenation process at mild conditions (100 °C and 0.4 MPa of H₂).

Besides, a conceptual simulation of the process indicates that furfuryl alcohol can be obtained from an agro-industrial residue by applying the methodology introduced in this study; thus a new green process for replacing the traditional one is presented.

Table 5

Some results of global mass balance.

Basis: Furfuryl alcohol production (t/y)	7000
(kg/h)	875
Yield Biomass to Bio-Oil (assumed from lab data)	0.33
Yield Biomass to BioGas (assumed from lab data)	0.36
Yield Furfural to Furfuryl alcohol (assumed from lab data)	0.65
Raw Biomass (kg/h)	6540
Fluidization gas/Biomass ratio	3
Fluidization gas (kg/h)	19620.02
Post treated Biomass (kg/h)	5422.18
Bio-Oil production (kg/h)	2028.71
Bio-Gas production (kg/h)	2354.40
Furfural production (kg/h)	1346.15
93% Levoglucosenone production (kg/h)	32.41
Condensation stages yield	0.94

Acknowledgements

This study was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET Argentina).

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