



Organosolv processing of vine shoots: Fractionation and conversion of hemicellulosic sugars into platform chemicals by microwave irradiation

S. Rivas^{a,b,*}, L. López^{a,b}, C. Vila^{a,b}, J.C. Parajó^{a,b}

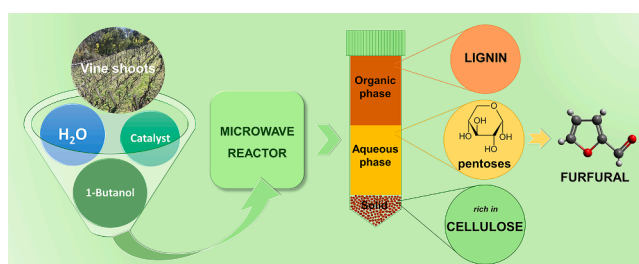
^a Chemical Engineering Department, University of Vigo (Campus Ourense), Faculty of Science, Polytechnical Building, As Lagoas, 32004 Ourense, Spain

^b CINBIO, University of Vigo (Campus Lagoas-Marcosende), 36310 Vigo, Spain

HIGHLIGHTS

- Cellulose, hemicelluloses and lignin were separated in a single reaction.
- Water/1-butanol/catalyst media were employed for vine shoot fractionation.
- Optimal conditions for lignin and cellulose recovery were identified.
- The recovered lignin showed 85% purity, and the solid contained 75% cellulose.
- Furans were produced from the aqueous phase obtained in fractionation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Vine shoots
Fractionation
Lignin
Microwave heating
Furfural

ABSTRACT

Vine shoots were subjected to a mild aqueous extraction (to remove water-soluble extractives), and the extracted solids were reacted in catalyzed media (containing water and 1-butanol) to achieve the one-stage solubilization of lignin and hemicelluloses, yielding a cellulose-rich solid. Operating in a microwave-heated reactor under optimized conditions (190 °C in media containing 2% of catalyst and 52% 1-butanol), 67.8% lignin was dissolved, and solids containing 75% cellulose were obtained. Lignin was recovered from the reaction medium and characterized, whereas the hemicellulose-derived products present in the aqueous phase (obtained under conditions leading to maximum concentrations of 17.7 g pentoses/L) were converted into furfural at 64.6% molar yield by acidic processing in the presence of recycled 1-butanol.

1. Introduction

The current needs of society require the development of economic and energy-efficient processes for a sustainable manufacture of fuels and chemicals. These technologies must be able to solve critical problems related to the intensive utilization of fossil resources, replacing them by renewable and sustainable alternatives such as the lignocellulosic biomass (Beig et al., 2021).

The biorefinery approach for lignocellulosic biomass utilization considers the selective separation of the structural constituents, and their further transformation in a scope of bioproducts. The lignocellulosic residues from agricultural crops and agroindustries are abundant and low cost feedstocks for biorefineries. Viticulture is an important agricultural practice in Spain, where approximately 970,000 ha are dedicated to vineyards (OIV, 2019). Vine shoots (VS) are agricultural wastes generated in vineyards at an estimated annual rate around 2–4

* Corresponding author.

E-mail address: sandrarivas@uvigo.es (S. Rivas).

<https://doi.org/10.1016/j.biortech.2021.125967>

Received 7 August 2021; Received in revised form 12 September 2021; Accepted 14 September 2021

Available online 20 September 2021

0960-8524/© 2021 The Author(s).

Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

tonnes/ha, which are used in the fields as fertilizers or burned (Nabais et al., 2010; Sánchez-Gómez et al., 2014). However, products of higher added-value could be obtained using VS as feedstocks for biorefineries (Rivas et al., 2007).

The chemical utilization of lignocellulosic materials is difficult because of their heterogeneous structure, defined by the presence of polysaccharides (cellulose and hemicelluloses) and non-saccharide fractions (including lignin, extractives, proteins and ash). VS are mainly composed of cellulose (32.9–36%), lignin (27.1–29.6%), hemicelluloses (19–22.8%) and extractives (7.1–13.7%) (Rivas et al., 2007; Jesús et al., 2017; Alves Filho et al., 2020).

The recalcitrance of lignocellulose to chemical conversion is one of the major problems for its utilization as a raw material for biorefineries. Lignocellulose fractionation can be achieved taking benefit from the diverse chemical properties of the major components. For example, mild acidic or hydrothermal pretreatments promote the selective hydrolysis of hemicelluloses, while lignin can be converted into soluble fragments by alkaline or organosolv processing (OP). A number of methods have been considered in literature for VS fractionation, including autohydrolysis (Dávila et al., 2016), acidic treatments (Rivas et al., 2007), steam explosion (Buratti et al., 2015), alkaline pretreatment (Cotana et al., 2015), combined autohydrolysis-delignification (alkaline or organosolv) (Dávila et al., 2017), combined acid hydrolysis-alkaline treatments (Alves Filho et al., 2020), or two-stage autohydrolysis (Jesús et al., 2017).

OP involves the utilization of organic solvents (such as acetone, glycerol, or ethanol), in catalyzed or uncatalyzed media, to cause the dissolution of lignin (and hemicelluloses, if a suitable catalyst is employed), leaving cellulose in the solid phase (Thoresen et al., 2020).

Alternatively, OP can be performed using solvents partially immiscible in water, such as 1-butanol, which can be obtained from biomass (Romo et al., 2018; Thoresen et al., 2020). This type of reaction media enable the one-step separation of the major lignocellulosic constituents in different phases: the soluble lignin fragments are transferred to the organic phase, the products derived from hemicelluloses are accumulated in the aqueous one, and cellulose is kept in the processed solid. Teramura et al. (2016 and Teramura et al. (2018) considered the OP of sorghum bagasse in water-butanol media catalyzed with H₂SO₄, whereas Schmetz et al. (2019) followed the same approach with different types of biomass. Del Río et al. (2009) compared different catalysts in OP using 1-butanol: water 65:35 (v/v). Lancefield et al. (2017) and Panovic et al. (2019) used a higher proportion of 1-butanol (95%), while Wang et al. (2014) and Kawamata et al. (2019) reported on the utilization of alkaline or solid acidic catalysts.

Lignin, cellulose and hemicellulose-derived products from OP can be valorized individually to obtain an array of bioproducts. The lignin can be easily recovered from the phase rich in 1-butanol, and employed, for example, in the manufacture of phenolic compounds (Kawamata et al., 2019), adhesives or polyolefins (Wang et al., 2014).

VS hemicelluloses are mainly made up of xylose chains, which can be substituted with arabinosyl, galactosyl, mannosyl and/or acetyl groups (Dávila et al., 2016). Upon acidic treatments, VS pentosans are converted into pentoses (xylose and arabinose) and/or in higher saccharides, which can be dehydrated into furfural (F) (Cai et al., 2014).

Simultaneously, hexosans can be hydrolyzed into hexoses (glucose, galactose or mannose), which can be dehydrated into hydroxymethylfurfural (HMF). This compound can be further rehydrated into levulinic and formic acids (LA and FA, respectively). F, HMF and LA are important platform chemicals, from which a number of fuels and bioproducts can be obtained (Cai et al., 2014; Choi et al., 2015; Rivas et al., 2019).

The yields of F, HMF and LA are limited by side reactions leading to the formation of humins (black, resinous and insoluble byproducts), which take place in the aqueous phase. Humin formation can be limited if the reaction is carried out in biphasic reaction media, because the target products are transferred from the aqueous to the solvent phase

just when generated (Cai et al., 2014; Rivas et al., 2016). Among the solvents used for furan manufacture, 1-butanol led to favorable results (Romo et al., 2018; Esteban et al., 2020; Hu et al., 2021; Amiri et al. 2010; Zhang et al., 2012).

Microwave-heated reactors are receiving a growing attention, as they can improve the efficiency of many processes (Aguilar-Reynosa et al., 2017), particularly when the target product yields are enhanced by fast heating profiles. Rivas et al. (2015) and López et al. (2020) cited a number of advantages of microwave-heated reactors for processing cellulosic materials, including easy operation, homogeneous heating and efficient control.

In this study, the structural VS constituents (cellulose, hemicelluloses and lignin) were fractionated in media containing 1-butanol/water/catalyst mixtures. An in-depth study was performed to assess the fractionation effects achieved under diverse operational conditions. The manufacture of F (from pentoses) and HMF (from hexoses) from the aqueous phase obtained in the fractionation treatments was performed in the presence of recycled 1-butanol.

2. Materials and methods

2.1. Feedstocks

Vine shoots (VS) were collected in Arnoia, a geographical zone that belongs to the Designation D.O. Ribeiro (Galicia, Spain) holding about 2500 ha of vineyards. The VS samples employed in this study were mixtures of varieties (Godello, Treixadura, Mencía, Caño...) harvested in the region. VS were pruned in November-December, air-dried until reaching a constant moisture, milled to obtain a particle size in the range 0.25–2 mm, and stored in a dry place until use.

2.2. Aqueous extraction

Water-soluble extractives were removed from VS by water extractions performed in a stirred reactor (Parr Instrument Co., Moline, Illinois, USA), operating under the following conditions: liquid to solid ratio (LSR), 10 g/g of dry VS; heating from room temperature up to 130 °C, with immediately cooling to 40 °C (without isothermal stage). The extracted solids (pretreated VS, denoted PVS) were separated by vacuum-filtration through glass fiber filters (Fisher Scientific) at room temperature, washed, air-dried until reaching constant moisture and stored until use.

2.3. Organosolv processing

VS or PVS samples were mixed with water and 1-butanol, in the presence or absence of catalyst (H₂SO₄), and processed in a MARS 6 (Microwave Accelerated Reaction System, CEM Corporation, Matthews, NC, USA) for 20 min. LSR was fixed at 12 mL of liquid phase/ g of dry solid substrate (VS or PVS). The treated solids (S_{OP}) were separated from the liquid phases by vacuum filtration through glass fiber filters (Fisher Scientific), washed with 1-butanol and water, and assayed for solid yield (SY) and composition (see below). The aqueous and organic phases (denoted Aq_{OP} and Org_{OP}, respectively) were separated using a separatory funnel, and analyzed by HPLC (see below).

Org_{OP} was subjected to partial evaporation under vacuum to recover 1-butanol, which was reused (see below). The concentrate was mixed with water to induce lignin precipitation. The precipitate was recovered by centrifugation and vacuum-dried at 40 °C to yield lignin-derived products, denoted L_{OP}.

2.3.1. Preliminary experiments

Preliminary experiments were made to compare the behaviour of VS and PVS as substrates for OP. The operational conditions were as follows: butanol/water volume ratio, 30/70%; catalyst charge, 0, 1, or 2 wt % H₂SO₄ (measured respect to the dry solid); and temperature, 160, 175

Table 1

Operational conditions proposed for the experimental design, expressed as dimensionless and dimensional variables.

Exp.	Dimensionless variables			Dimensional variables		
	%cat (x_1)	%org (x_2)	T (x_3)	%cat (wt%)	%org (v/v)	T (°C)
1	-1	-1	-1	0	0	160
2	-1	1	-1	0	60	160
3	-1	-1	1	0	0	190
4	-1	1	1	0	60	190
5	1	-1	-1	2	0	160
6	1	1	-1	2	60	160
7	1	-1	1	2	0	190
8	1	1	1	2	60	190
9	-1	0	0	0	30	175
10	1	0	0	2	30	175
11	0	-1	0	1	0	175
12	0	1	0	1	60	175
13	0	0	-1	1	30	160
14	0	0	1	1	30	190
15	0	0	0	1	30	175
16	0	0	0	1	30	175
17	0	0	0	1	30	175

or 190 °C. The effects of treatments were evaluated on the basis of the results determined for the solid yield (SY), % hemicellulose solubilization and % delignification. These variables were calculated as follows:

$$\%SY = 100 \times \frac{DS_{AOP}}{DS_{BOP}} \quad (1)$$

where DS_{AOP} and DS_{BOP} stand for the dry weights of solids after and before OP, respectively;

$$\% \text{ hemicellulose solubilization} = 100 \times \frac{H_{BOP} - H_{AOP} \times \frac{SY}{100}}{H_{BOP}} \quad (2)$$

where H_{BOP} and H_{AOP} are the percentages of hemicelluloses in the solid before and after OP, respectively;

$$\% \text{ delignification} = 100 \times \frac{TL_{BOP} - TL_{AOP} \times \frac{SY}{100}}{TL_{BOP}} \quad (3)$$

where TL_{BOP} and TL_{AOP} are the percentages of total lignin (calculated as the sum of acid soluble lignin and Klason lignin) in the solids before and after OP, respectively.

2.3.2. Optimization of organosolv processing

The Response Surface Methodology (RSM) was employed to assess the organosolv processing, using a centered, incomplete, three-level, factorial experimental design. The experimental variables, their nomenclature, and variation ranges were: catalyst concentration (%cat), 0–2 wt% H_2SO_4 respect to dry solid; volume percentage of 1-butanol respect to the total volume of liquid (%org), 0–60%; and temperature (T), 160–190 °C. These independent variables were transformed into normalized ones, denoted x_1 , x_2 , x_3 , with ranges of variation (-1,1), using the following equations:

$$x_1(\text{dimensionless \%cat}) = 2 \times [\%cat \text{ (wt\%)} - 1] / 2 \quad (4)$$

$$x_2(\text{dimensionless \%org}) = 2 \times [\%org \text{ (v/v)} - 30] / 60 \quad (5)$$

$$x_3(\text{dimensionless T}) = 2 \times [T \text{ (°C)} - 175] / (190 - 160) \quad (6)$$

Table 1 lists the experimental conditions considered for the 17 runs included in the experimental design, expressed in terms of dimensional and dimensionless independent variables. These experiments were performed in the microwave reactor indicated above. The effects of treatments were measured in terms of the following dependent variables:

- y_1 : % cellulose content of S_{OP}.
- y_2 : % delignification.

- y_3 : concentration of pentoses in Aq_{OP} (g/L).

The experimental data in Table 1 were employed to deduce the values of the regression coefficients participating in empirical equations expressing the dependent variables as the sum of the 1st order, interactions, and 2nd order contributions of the independent variables:

$$y_j = b_{0j} + \sum_i b_{ij}x_i + \sum_i \sum_k b_{ikj}x_i x_k \quad (7)$$

where y_j (j : 1–3) stands for the dependent variables, x_i or x_k (i or k : 1–3, $k \geq i$) are the independent, dimensionless variables, and b_{0j} ... b_{ikj} are the regression coefficients, which were calculated from the experimental data using the least-squares method.

In order to allow a comparative evaluation of the performances of reactors with conventional or microwave heating, a second set of fractionation experiments was performed with the same Parr reactor employed in the aqueous extraction step (see section 2.2). Some of these assays were performed under conditions (liquid to solid ratio, temperature, duration, organic solvent content and catalyst concentration) already explored with the microwave reactor, whereas the rest of experiments correspond to longer reaction times (see below).

2.4. Acidic treatments of Aq_{OP} in biphasic systems

The Aq_{OP} sample obtained in the experiment leading to the maximal concentration of pentoses (and minor amounts of hexoses) was considered for further valorization, based on the manufacture of furans (F from pentoses and HMF from hexoses) in biphasic media. For this purpose, Aq_{OP} was supplemented with 1 wt% H_2SO_4 (respect to the Aq_{OP} volume), and mixed with the organic solvent (1-butanol) at a solvent: Aq_{OP} volume ratio (OAR) of 2:1. The media were reacted in a MARS 6 (Microwave Accelerated Reaction System, CEM Corporation, Matthews, NC, USA) at 170 °C for selected reaction times. Time zero was assigned when the media reached the target temperature (so, the reaction times corresponded to the duration of the isothermal stage). The 1-butanol recovered from OP (see section 2.3) was employed in the formulation of the reaction media, and fresh solvent was added when necessary. For comparison, additional experiments were performed using fresh 1-butanol instead of the recycled solvent.

The molar yields of HMF and F were calculated as:

$$\% \text{HMF molar yield} = 100 \times \frac{FM_{HMF} - IM_{HMF}}{IM_{hexoses}} \quad (8)$$

$$\% \text{F molar yield} = 100 \times \frac{FM_F - IM_F}{IM_{pentoses}} \quad (9)$$

where FM_{HMF} and FM_F , are the moles of HMF and F present in the reaction medium, respectively; IM_{HMF} and IM_F are the initial moles of HMF and F in the aqueous phase, respectively; and $IM_{hexoses}$ and $IM_{pentoses}$ are the moles of hexoses and pentoses before reaction, respectively.

2.5. Analytical procedures

2.5.1. Compositional analysis of solid substrates

Aliquots of VS and PVS were assayed for composition using the following standard methods: extractives (NREL/TP-510-42619), ash (NREL/TP-510-42622), structural carbohydrates, acetyl groups, Klason lignin, and acid soluble lignin (NREL/TP-510-42618) (Sluiter et al., 2008a, Sluiter et al. (2008b) and Sluiter et al. (2012)). The NREL/TP-510-42618 standard method involved a two-step quantitative acid hydrolysis, that provided an insoluble fraction (considered as Klason lignin, denoted KL), and a liquid phase containing acid soluble lignin (ASL), sugars and organic acids. KL was determined gravimetrically at 105 °C until constant weight, whereas ASL was determined by spectrophotometry at 205 nm. The sum of KL and ASL provided the total lignin content.

Sugars and acetic acid in the liquid phase from the second acid hydrolysis were analyzed by HPLC using an Agilent 1200 Series instrument equipped with a Refractive Index Detector (RID) and a Diode Array Detector (DAD), as described by Rivas et al. (2019). A second aliquot was assayed for monosaccharides (xylose, arabinose, glucose, galactose and mannose), using a CARBOsep CHO-682 column following the procedure reported by Rivas et al. (2016). Solids from OP (S_OP) were assayed for composition using the same methodology employed for VS and PVS. The protein content was determined as per Yáñez et al. (2009).

The analyses were made in triplicate.

2.5.2. Composition of liquid phases

Samples from Aq_OP, Org_OP and media from furfural manufacture were analyzed by HPLC using the method cited above. Additionally, samples from Aq_OP were supplemented with 4% sulfuric acid and treated in autoclave at 121 °C for 20 min to convert the poly- and oligosaccharides into the respective monomers (sugars and acetic acid). The concentration of the resulting solutions were quantified by HPLC to calculate the amounts of polysaccharides, oligosaccharides and acetyl groups generated from hemicelluloses.

2.5.3. Biomass, solids from organosolv processing and characterization of lignin-derived products

Fourier Transform Infrared Spectroscopy (FTIR) of VS, PVS and S_OP was performed as per Míguez et al. (2020). The lignin recovered from the fractionation media (L_OP) was characterized by FTIR and Nuclear Magnetic Resonance Spectroscopy (NMR). L_OP (50 mg approximately) was dissolved in deuterated DMSO and analyzed by HSQC 2D NMR using a Bruker Advance 400 MHz at 25 °C, equipped with a z-gradient 5-mm QNP probe. The molecular weight distribution of products in L_OP was studied by Gel Permeation Chromatography (GPC), employing an HPLC 1200 instrument equipped with RI and DAD detectors and two 300x7.5 mm PolarGel-M columns. The mobile phase (DMSO containing 1% LiBr) was eluted at 0.6 mL/min. Agilent InfinityLab standards (EasiVial PS-L from 162 to 5000 g/mol) were used for calibration. Chromatograms were recorded at 280 nm and processed using the Agilent GPC software. The thermogravimetric analysis (TGA) of L_OP was carried out using a SETSYS Evolution 1750 Thermal Analyzer (Setaram), operating at a heating rate of 10 °C/min from 25 to 900 °C in air or N₂.

3. Results and discussion

3.1. Composition of vine shoots and pretreated vine shoots

The composition of VS (expressed as average wt% in oven-dry basis ± standard deviation) was as follows: cellulose, 31.2 ± 0.3; xylan, 11.7 ± 0.3; galactan, 2.6 ± 0.2; mannan, 0.9 ± 0.1; arabinan, 0.9 ± 0.0; acetyl groups, 3.2 ± 0.1; KL, 22.2 ± 0.1; ASL, 3.2 ± 0.1; protein, 6.2 ± 0.5; extractives, 3.9 ± 0.4; ash, 3.4 ± 0.1; and other components (by difference), 11%. For the purposes of this study, the most important fractions were lignin, cellulose, and hemicelluloses. These latter, measured as the joint contributions of xylan, galactan, arabinan, mannan and acetyl groups, accounted for 19.2 wt% of the feedstock. The compositional data obtained in this study are in the range reported in other studies (Rivas et al., 2007; Jesús et al., 2017; Alves Filho et al., 2020).

The aqueous extraction at 130 °C solubilized 13.7% of the VS mass, yielding a pretreated solid (PVS) with the following composition (expressed as average wt% in oven-dry basis ± standard deviation): cellulose, 36.0 ± 0.3; xylan, 13.8 ± 0.2; galactan, 2.5 ± 0.3; mannan, 1.0 ± 0.1; arabinan, 0.8 ± 0.0; acetyl groups, 3.3 ± 0.1; KL, 24.4 ± 0.2; ASL, 2.4 ± 0.1; extractives, 2.7 ± 0.2; protein, 2.8 ± 0.2; ash, 2.0 ± 0.1; and other components (by difference), 8.4.

A comparison of the compositional data determined for VS and PVS showed that the aqueous extraction increased the percentages of

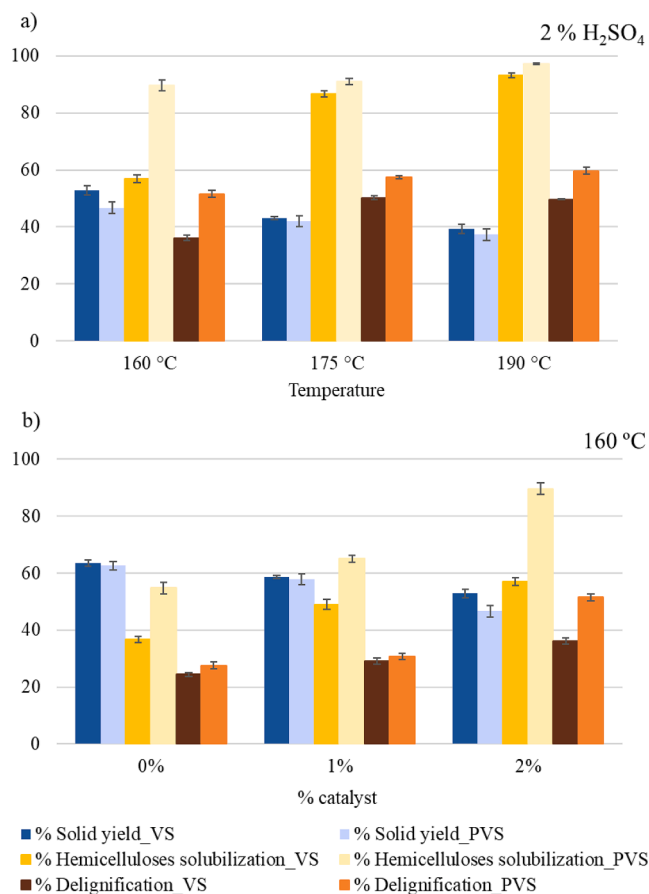


Fig. 1. Solid yields, % of hemicellulose solubilization, and % delignification obtained in the fractionation of VS and PVS. a) Experiments performed with 2% catalyst at 160, 175 or 190 °C; b) experiments performed at 160 °C in media containing 0, 1 or 2% of catalyst.

cellulose, hemicelluloses and lignin, a fact ascribed to the selective removal of non-structural components from the solid phase. This is expected to improve the further fractionation, due both to the easier accessibility of catalysts to polymers, and to the decreased amounts of compounds acting as contaminants (particularly extractives).

3.2. Organosolv processing

3.2.1. Preliminary experiments

In order to assess the behavior of VS and PVS as substrates for OP, preliminary experiments were performed to measure the SY, degree of hemicelluloses solubilization and extent of delignification. Fig. 1 shows the results obtained in experiments carried out at diverse temperatures using a fixed catalyst concentration (2%) (Fig. 1.a), and at a fixed temperature (160 °C) using diverse catalyst concentrations (Fig. 1.b).

As expected, SY was lower for PVS than for VS (owing to the presence in this latter of water soluble material), and decreased with the severity of the operational conditions (i.e., higher temperatures and/or higher catalyst concentrations). Oppositely, the percentages of delignification and hemicellulose solubilization were higher in experiments performed with PVS, a fact ascribed to physicochemical and chemical alterations induced by the aqueous extraction. The degrees of delignification and hemicellulose solubilization increased with temperature (see Fig. 1.a), which also affected to the differences in the results achieved with the two substrates: for example, in experiments performed at 160 °C with 2% of catalyst, markedly different percentages of hemicelluloses solubilization were achieved for PVS (89.7%) and VS (57%); but closer results (about 4% difference) were achieved for the same variable at

Table 2

Results determined for the experimental variables solid yield (SY), percentage of cellulose in S_OP (y_1), % delignification (y_2), and pentose concentration in Aq_OP (y_3).

Run.	Solid Yield (%)	y_1 (%)	y_2 (%)	y_3 (g/L)
1	67.5	44.7	4.5	6.4
2	72.0	41.9	21.6	4.5
3	55.4	47.5	0.0	3.5
4	50.5	60.3	46.5	11.9
5	58.6	45.7	13.8	10.5
6	48.2	61.9	50.4	17.0
7	53.6	49.6	0.5	0.1
8	39.8	72.0	63.5	8.6
9	54.6	49.3	35.9	13.2
10	42.1	62.5	57.4	14.1
11	57.6	48.2	7.9	8.6
12	54.3	53.7	43.2	11.2
13	57.8	52.2	30.8	11.6
14	39.3	75.9	60.7	3.3
15	46.5	58.2	47.4	11.5
16	47.8	61.3	46.1	12.1
17	46.9	58.5	45.3	12.9

190 °C. A similar pattern was observed for the delignification percentage: the differences between experiments performed with PVS or VS reached 15.5% at 160 °C, in comparison with 10% at 190 °C. This result is in agreement with studies reported for wheat straw (Wildschut et al., 2013).

Fig. 1b shows the effects caused by the catalyst concentration on VS and PVS. When the catalyst charge increased from 0 to 2%, SY decreased owing to the higher removal of hemicelluloses and lignin. These effects were more important for PVS than for VS. The most noticeable finding was the different degree of hemicellulose solubilization achieved with PVS and VS in media containing 2% of catalyst, conditions under which PVS behaved especially well. A similar behavior was reported by Teramura et al. (2018).

3.2.2. Optimization of organosolv processing using the microwave reactor

Based on the above findings, PVS was selected as a substrate for an in-depth fractionation study made up of 17 experiments, which were carried out in the microwave reactor. The experimental conditions considered are listed in Table 1. Table 2 includes the experimental data determined for the dependent variables SY, y_1 (cellulose content in S_OP, wt%), y_2 (delignification percentage, %), and y_3 (concentration of pentoses in Aq_OP, g/L).

The experimental results in Table 2 indicated that SY decreased with the severity of treatments (defined by temperature and catalyst concentration): for example, SY of 67.5 and 72.0% were achieved in experiments 1 and 2, respectively, which corresponded to the mildest conditions assayed; but dropped below 40% in runs 8 and 14, which were carried out at 190 °C with 1–2% catalyst. The cellulose content of S_OP (variable y_1) was favored by temperature and by the presence of organic solvent and catalyst, reaching a maximum value (75.9%) in experiment 14 (performed at 1% of catalyst and 190 °C in media containing 30% of organic solvent). Poor delignification (y_2 below 14%) was reached in absence of solvent (assays 1, 3, 5, 7, and 11), but the presence of catalyst and organic solvent boosted y_2 , which reached values above 50% in runs 6, 10 and 14. The concentration of pentoses in Aq_OP (variable y_3) achieved its maximum experimental value (17 g/L) in experiment 6, which was performed at 160 °C in media containing the highest concentrations of both catalyst and organic solvent. Experiments 3, 7 and 14, performed at the highest temperature considered (190 °C), resulted in near total hemicelluloses solubilization with little concentrations of pentoses, which were converted into furfural (which appeared in the aqueous and organic phases) and condensation products.

Scarce information has been reported on the OP of lignocellulose using partially immiscible organic solvents. Teramura et al. (2016 and

Table 3

Regression coefficients and statistical parameters that measure the correlation and significance of models developed for cellulose content in S_OP (y_1), % delignification, (y_2) and pentose concentration (y_3).

Parameter	y_1 (%)	y_2 (%)	y_3 (g/L)
b_{0j}	59.2 ^a	46.4 ^a	11.9 ^a
b_{1j}	4.8 ^a	7.7 ^a	1.1
b_{2j}	5.4 ^a	19.8 ^a	2.4 ^a
b_{3j}	5.9 ^a	5.0 ^b	-2.3 ^a
b_{12j}	3.6 ^c	4.5 ^c	1.0
b_{13j}	-0.9	-2.6	-2.9 ^a
b_{23j}	2.7	6.9 ^b	1.5 ^b
b_{11j}	-3.2	0.2	1.9
b_{22j}	-8.1 ^b	-20.8 ^a	-1.8
b_{33j}	4.9	-0.7	-4.2 ^a
R^2	0.91	0.96	0.92
F_{exp}	7.89	19.59	10.16

Coefficients significant at confidence levels of:

^a 99%,

^b 95%,

^c 90%.

2018) treated sorghum bagasse for 30–90 min at 160–220 °C in media containing 0–37.5% 1-butanol and 0.25–2% H₂SO₄, to achieve 64.7% lignin removal and solids containing 59.1% cellulose. Schmetz et al. (2019) treated diverse biomasses (bagasse, herbaceous material, hardwood and softwood) with butanol/water mixtures, and reported satisfactory delignification and increases in the cellulose content of solids, particularly when bagasse was used as a substrate. Salapa et al. (2017) employed diverse organic solvents (ethanol, methanol, butanol, and acetone) for wheat straw fractionation. Del Rio et al. (2010) treated *Pinus contorta* with butanol/water mixtures under acidic conditions, and obtained solids more susceptible to hydrolysis than the ones coming from ethanol/water processing. In all these studies, OP was carried out in reactors with conventional heating. To our knowledge, no literature was reported on the fractionation of lignocelluloses in butanol/water/catalyst mixtures using microwave-heated reactors.

Focusing on the RSM assessment of OP, Table 3 lists the regression coefficients resulting from data analysis, the statistical significance of the various terms participating in the empirical model (based on a *t*-test), the R^2 coefficient measuring the correlation, and the Fische's parameter (F_{exp}) measuring the statistical significance of the empirical models. The regression coefficients in Table 3 and eq. (7) were employed to assess the interrelationships between dependent and independent variables.

The empirical model predicted a maximum cellulose content (75%) for S_OP treated at 190 °C with 2% catalyst and 51% organic solvent. Fig. 2.a presents the response surface describing the dependence of y_1 on %cat and %org at 190 °C. The maximum delignification percentage achievable at 190 °C ($y_2 = 67.8\%$, see Fig. 2.b) was predicted for operation in media containing 52.5% organic solvent and 2% catalyst. The RSM assessment confirmed the compatibility of the optimal conditions determined for both cellulose content and delignification percentage, which enabled a selective fractionation of S_OP.

Concerning the aqueous phase, Fig. 2.c shows the dependence of the pentose concentration (variable y_3) on T and %cat when the concentration of the organic solvent was fixed at 52%. The maximum pentose concentration in Aq_OP (17.5 g/L) was predicted for treatments performed at 168 °C with 2% catalyst.

3.2.3. Results obtained in a Parr reactor (with conventional heating) and comparative analysis

In order to assess the performance of reactors with microwave or conventional heating on a comparative basis, additional OP experiments were using the Parr reactor employed in the aqueous extraction stage. In this set of experiments, the amounts of biomass and the liquor to solid ratio (12 mL liquid/g of dry biomass) were the same employed in the

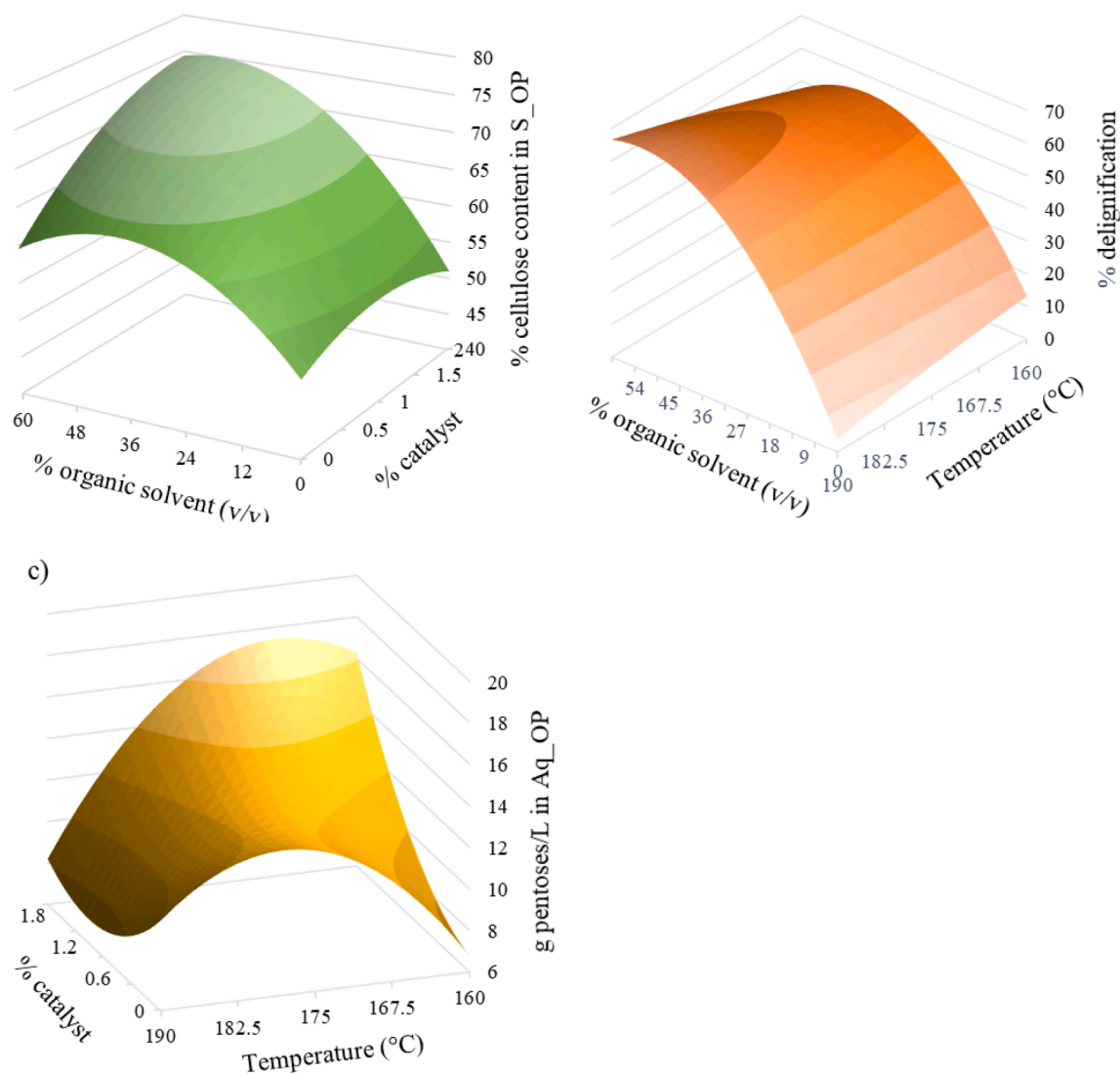


Fig. 2. Response surfaces calculated from the experimental data: a) dependence of y_1 on % catalyst and % of organic solvent at 190 °C; b) dependence of y_2 on T and % of organic solvent in media containing 2% of catalyst; c) dependence of y_3 on T and % catalyst for operation in media containing 52% of organic solvent.

Table 4

Conditions assayed in the Parr reactor (conventional heating), and results achieved in experiments.

Exp.	Operational conditions			Reaction time (min)	Experimental results			
	T (°C)	% Catalyst concentration	% Organic solvent		Solid Yield (%)	% cellulose in S_OP	Deligni-fication (%)	Pentose concentration (g/L)
18	160	0	0	20	80.2	37.1	2.7	1.5
19	160	2	60	20	67.4	43.9	18.8	14.0
20	190	2	60	20	43.2	65.4	62.2	14.4
21	175	2	30	20	61.2	54.3	32.7	12.5
22	175	1	30	20	60.1	48.9	33.3	9.2
23	190	2	52	20	44.5	68.5	62.8	16.4
24	168	2	52	20	56.5	52.7	41.7	15.0
25	168	2	52	40	48.8	59.7	51.4	17.2
26	168	2	52	50	46.6	61.1	58.3	17.6
27	168	2	52	60	44.0	62.3	61.0	17.1

experiments performed in the MARS reactor (with microwave heating).

Table 4 lists the operational conditions considered in experiments 18–27, performed in the Parr reactor, as well as the experimental results achieved. The values of the operational variables (temperature, catalyst concentration, content of organic solvent and reaction time) were selected as follows:

a) Conditions corresponding to assays already performed in the

microwave reactor:

a.1) experiment 18 was performed under the conditions of experiment 1, which correspond to the mildest treatment (lowest temperature, catalyst concentration and organic solvent content).

a.2) experiment 19 was performed under the conditions of experiment 6 (lowest temperature, highest catalyst concentration and organic solvent content).

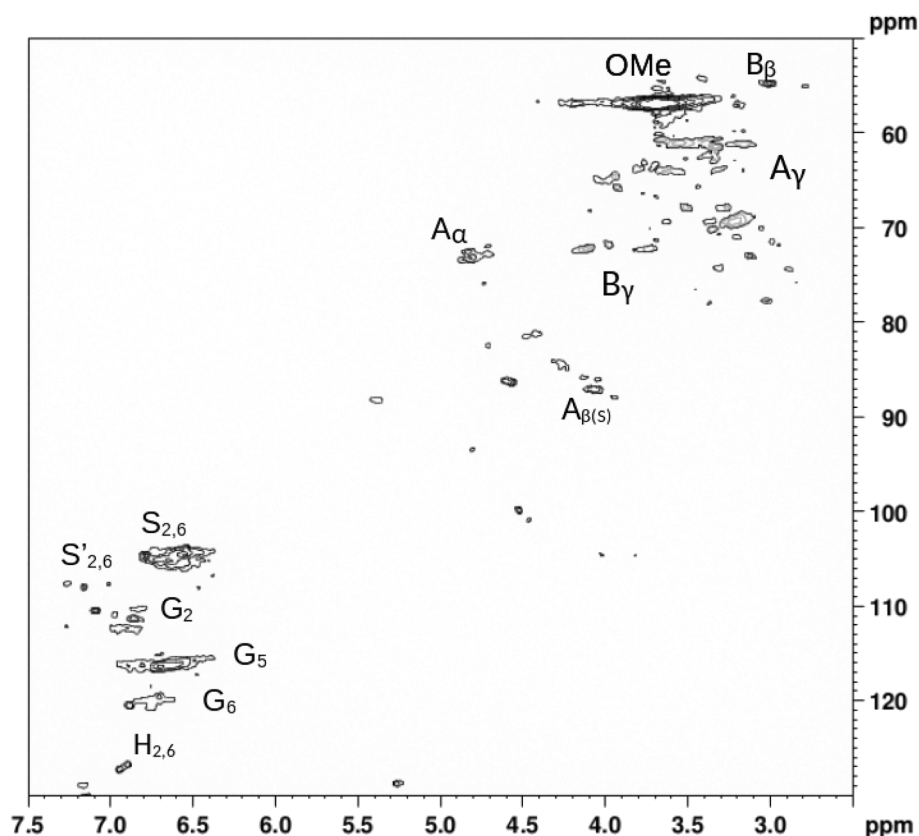


Fig. 3. HSQC 2D NMR spectra recorded for the recovered lignin.

a.3) experiment 20 was performed under the conditions of experiment 8, which corresponded to the harshest conditions (highest temperature, catalyst concentration and organic solvent content).

a.4) experiment 21 was performed under the conditions of experiment 10 (intermediate temperature and organic solvent content, highest catalyst concentration).

a.5) experiment 22 was performed under the conditions of experiment 15 (intermediate temperature, organic solvent content and catalyst concentration).

b) Conditions considered optimal for operation in the microwave reactor:

b.1) experiment 23 was performed under the conditions leading to optimal delignification and cellulose content of treated solids.

b.2) experiment 24 was performed under the conditions leading to optimal concentration of pentoses in the aqueous phase from fractionation.

c) Conditions not considered for operation in the microwave reactor:

c.1) experiments 25 to 27 were performed at the temperature and organic solvent concentration employed in experiment 24, but at longer reaction times.

The performance of the microwave and Parr reactors can be compared on the basis of the experimental results listed in Table 2 for experiments 1, 6, 8, 10 and 15, and the results listed in Table 4 for runs 18–22. These experiments are selected to cover diverse zones of the experimental domain. In all cases the MARS reactor provided lower solid yields (67.5 vs. 80.2%; 48.2 vs. 67.4%, 38.9 vs. 43.2%, 42.1 vs. 61.2%, and 46.5 vs. 60.1%) than the Parr reactor, a finding indicative of faster fractionation kinetics. Moreover, the solids treated in the MARS reactor under these conditions presented higher cellulose contents (44.7 vs. 37.1%, 61.9 vs. 43.9%, 72.0 vs. 65.4%, 62.5 vs. 54.3%, and 58.2 vs. 48.9%) resulting from a more intense delignification (4.5 vs. 2.7%, 50.4 vs. 18.8%, 63.5 vs. 62.2%, 57.4 vs. 32.7%, 47.4 vs. 33.3% and 65.4 vs.

62.8). On the other hand, the highest pentose concentration obtained in the aqueous phases under these conditions (17.0 g/L) was obtained in experiment 6, performed with the microwave reactor.

It can be noted that experiment 23 (performed with the Parr reactor under conditions leading to optimal delignification in the MARS reactor) provided a sample with good cellulose content and delignification degree (68.5 and 62.8, respectively), values slightly lower than the ones obtained with microwave heating; together with a noticeable pentose concentration (16.4 g/L). Experiment 24, performed under conditions leading to the maximum pentose concentration with the MARS reactor, provided worse results than experiment 23.

The data obtained in experiments 18–24 suggested that the results could be improved by increasing the duration of experiments performed in the Parr reactor, in order to compensate (at least, in part) the slower kinetics. The results obtained in experiments 25 to 27 confirmed that longer reaction times resulted in decreased yields, higher cellulose contents (up to 62.3%), extended delignification (up to 61.1%) and pentose concentrations in the range 17.1–17.6 g/L. However, none of these results improved the best ones obtained with the microwave reactor, which showed a superior performance for the purposes of this study.

3.3. FTIR characterization of vine shoots, pretreated vine shoots and solids from organosolv processing

The FTIR spectra of VS and PVS presented closely related patterns (with some differences caused by the presence or absence of water-soluble extractives). The FTIR spectra of the S_{OP} obtained under the conditions leading to both high cellulose content and extensive solubilization showed peaks characteristic for hemicelluloses and lignin of decreased intensities, for example the ones related to the carbonyl group (1730 cm⁻¹), the aromatic skeleton of lignin (1596, 1515 and 1452

Table 5
 ^{13}C - ^1H peak assignments for the 2D-HSQC spectra of L_OP.

Label	Assignments	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm) ^a
B $_{\beta}$	C $_{\beta}$ -H $_{\beta}$ in β - β (resinol) (B)	54.7/3.01
O _{Me}	C-H in methoxyl groups	56.8/3.63
A $_{\gamma}$	C $_{\gamma}$ -H $_{\gamma}$ in β -O-4 substructures (A)	60.6/3.35–3.66
C $_{\gamma}$	C $_{\gamma}$ -H $_{\gamma}$ in phenylcoumaran (C)	63.8/3.61
B $_{\gamma}$	C $_{\gamma}$ -H $_{\gamma}$ in β - β resinol (B)	71.8/3.97–4.12
A $_{\alpha}$	C $_{\alpha}$ -H $_{\alpha}$ in β -O-4 unit (A)	72.5/4.83
A $_{\beta(S)}$	C $_{\beta}$ -H $_{\beta}$ in β -O-4 linked to S (A)	87.1/4.07
S $_{2,6}$	C $_{2,6}$ -H $_{2,6}$ in syringyl units (S)	104.8/6.62
S' $_{2,6}$	C $_{2,6}$ -H $_{2,6}$ in oxidized S units (S')	108.1/7.16
G $_{2}$	C $_{2}$ -H $_{2}$ in guaiacyl units (G)	110.5/7.10
G $_{5}$	C $_{5}$ -H $_{5}$ in guaiacyl units (G)	116.2/6.64
G $_{6}$	C $_{6}$ -H $_{6}$ in guaiacyl units (G)	119.6/6.70
J $_{\beta}$	C $_{\beta}$ -H $_{\beta}$ in cinnamyl aldehyde end-groups (J)	126.8/6.90
H $_{2,6}$	C $_{2,6}$ -H $_{2,6}$ in H units (H)	127.3/6.94

^a The signals were assigned according reported data (Del Río et al., 2009; Wen et al., 2013).

cm^{-1}) and those assigned to C-C, C-O and C=O stretching of lignin and hemicelluloses (1237 cm^{-1}). Oppositely, the S_OP spectra showed higher intensities in the peaks related to cellulose (at 1158 and 1104 cm^{-1}), to the peaks corresponding to C-OH stretching and C-O deformation of cellulose (1053 cm^{-1}), and to C-O stretching of cellulose (1025 cm^{-1}).

3.4. Characterization of lignin derived products from organosolv processing

This study was carried out using the L_OP fraction resulting from OP processing under the optimal conditions predicted by the RSM methodology (190 °C, 52% of organic solvent and 2% of catalyst). L_OP presented a satisfactory purity (85.3 \pm 0.3 wt% of the material), with minor amounts of cellulose (0.4 \pm 0.0%), xylan (2.6 \pm 0.1%), acetyl groups (1.0 \pm 0.0%), and ash (0.6 \pm 0.0%).

The HSQC 2D NMR data of L_OP (Fig. 3) showed signals in the regions corresponding to the side chains (50–95/2.5–6.0) and aromatic areas (95–135/5.5–7.5). Within the side chain region, L_OP showed signals related to β -O-4 ether linkages (A regions) in the $\delta_{\text{C}}/\delta_{\text{H}}$ listed in Table 5. Additionally, small signals were found for the resinol linkages ($\delta_{\text{C}}/\delta_{\text{H}}$ of 54.7/3.01 and 71.8/3.97–4.12) and phenylcoumaran linkages ($\delta_{\text{C}}/\delta_{\text{H}}$ 63.8/3.61), with a strong signal for methoxyl groups. β -O-4 are the main interunit bonds with an estimated relative abundance of 61%. Respect to the aromatic region, the signals corresponded to the *p*-hydroxyphenyl (H), syringyl (S) and guaiacyl (G) units. Strong signals were noted for S-lignin units at $\delta_{\text{C}}/\delta_{\text{H}}$ of 104.8/6.62, and oxidized S-lignin units at $\delta_{\text{C}}/\delta_{\text{H}}$ of 108.1/7.62. In addition, small signals for carbohydrates that corresponded with acetylated xylopyranoside units were noted at $\delta_{\text{C}}/\delta_{\text{H}}$ 99.8/4.5. This indicates that L_OP is of high purity, with a low content of carbohydrates and low condensation. The G-lignin units demonstrated different correlations for C $_{2}$ -H $_{2}$, C $_{5}$ -H $_{5}$ and C $_{6}$ -H $_{6}$, as listed in Table 5. G $_{2}$ and G $_{6}$ signals were lower than G $_{5}$ indicating minor condensations of the lignin at these positions of the G units. A small signal ascribed to H units was noticed in the $\delta_{\text{C}}/\delta_{\text{H}}$ spectra of 127.3/6.94. From the integration of the HSQC 2D NMR spectra, the value of the S/G ratio was estimated to be 2.2.

The FTIR spectra of L_OP showed a broad band at 3400 cm^{-1} , corresponding to phenolic and aliphatic hydroxyl groups. The bands at 2929 and 2872 cm^{-1} corresponded to the stretching of C-H in methyl and methylene groups; whereas the band at 2850 cm^{-1} was assigned to methoxyl groups. The fingerprint region showed bands at 1595, 1513 and 1456 cm^{-1} , slightly more intense than the peak at 1595 cm^{-1} , a feature typical for lignins of high S/G ratios (Faix, 1991). The band at 1114 cm^{-1} , assigned to the aromatic C-H in plane deformation of G and S units, was dominant in the spectra; whereas the bands at 1267 and 1326 cm^{-1} , corresponding to G rings and S units plus condensed G rings,

presented similar intensities. The intensities of the deconvoluted signals appearing at 1326 cm^{-1} (corresponding to the C-O stretching of S rings) and 1267 cm^{-1} (corresponding to the C-O stretching of G rings) allowed an additional estimate of the S/G ratio (2.1). Sammons et al. (2013) reported results for hardwood organosolv lignins in the range of the ones determined in this work.

The GPC data recorded for L_OP provided values of Mw and Mn of 3180 and 699 g/mol, respectively, with a polydispersity (Mw/Mn) of 4.55. These values are in the range reported for organosolv lignins (Son et al., 2019; Kangas et al., 2015). Within the broad molecular weight distribution, the compounds of lowest molecular weights may correspond to monomeric units (Andreo-Martínez et al., 2020).

The thermogravimetric analysis (TGA) of L_OP under oxidative conditions indicated 7.8% mass loss at 150 °C, 58.6 % between 200 °C and 400 °C, and 29.4% from 400 up to 550 °C. Concerning the derivative of mass loss, two maximums (at 278 and 478 °C) and a shoulder (at 360 °C) were observed under oxidative conditions, whereas only a peak (at 283 °C) was noticed in the absence of oxygen. When operation was performed in N $_2$ the total mass loss in the range 200 to 800 °C was of 72 %, with 19.3% of char generation. L_OP showed a slow thermal decomposition, related to its complex structure. Under oxidative conditions, the cleavage of the β -O-4 linkages took place between 250 °C and 350 °C, with a shoulder ascribed to C-C bonds at 360 °C (Kim et al., 2013); whereas the second maximum (at 458 °C) corresponded to oxidative reactions of the char formed previously. In general, L_OP showed a good thermal stability, similar to the ones of other lignins scarcely susceptible to degradation, but lower than the ones reported for condensed lignin.

3.5. Processing of the aqueous phase from organosolv fractionation

The acidic processing of hexoses and pentoses in aqueous media led to their dehydration into HMF and F, respectively. Moreover, depending on the severity of the operational conditions, HMF may undergo rehydration to yield equimolecular amounts of LA and FA. In stoichiometric terms, 1 mol of a hexose or a pentose yields 1 mol of HMF or F, respectively. The furan yields can be improved using biphasic reaction media water/solvent, in which the furans are transferred when generated from the aqueous phase (where the side reactions take place) to the organic one.

Following this idea, the 1-butanol recovered from OP media was used as a solvent for an improved production of the target products (F from pentoses, and HMF from hexoses), starting from the Aq_OP solution obtained in fractionation treatments leading to maximum concentrations of furfural precursors (pentose and higher saccharides made up of pentoses). The composition of Aq_OP (measuring the oligomeric compounds as monomer equivalents, in mmol/L) was as follows: glucose, 42.7 \pm 0.9; galactose, 13.2 \pm 0.6; mannose, 5.1 \pm 0.2; xylose, 111.9 \pm 2.0; arabinose, 6.0 \pm 0.2; acetic acid, 84.1 \pm 1.7; HMF, 1.2 \pm 0.2; and F, 2.8 \pm 0.3. Aq_OP also contained 1-butanol (73 g/L) from the fractionation treatment. These data corresponded to 117.9 mmol of F precursors/L, and 60.9 mmol of HMF precursors/L.

The concentration profiles obtained in the acidic processing of Aq_OP in media containing 1-butanol are displayed in Fig. 4. Pentoses and hexoses were partially converted during heating. The dehydration kinetics were different for pentoses and hexoses: when almost complete conversion of pentoses was reached, only 64% of hexoses were consumed. The maximum F concentrations in organic and aqueous phases (reached after 16 min) were 34.8 and 9.41 mmol/L, respectively; and the partition coefficients (calculated as the ratio between the F concentration in organic and aqueous phases) were in the range 3.5–3.8. The maximum F yield was 64.7%, whereas HMF was generated at low concentrations, owing to the limited amounts and/or the limited conversions of its precursors. Under the conditions tested, HMF did not undergo significant rehydration into LA.

To assess the possible influence of contaminants in furan

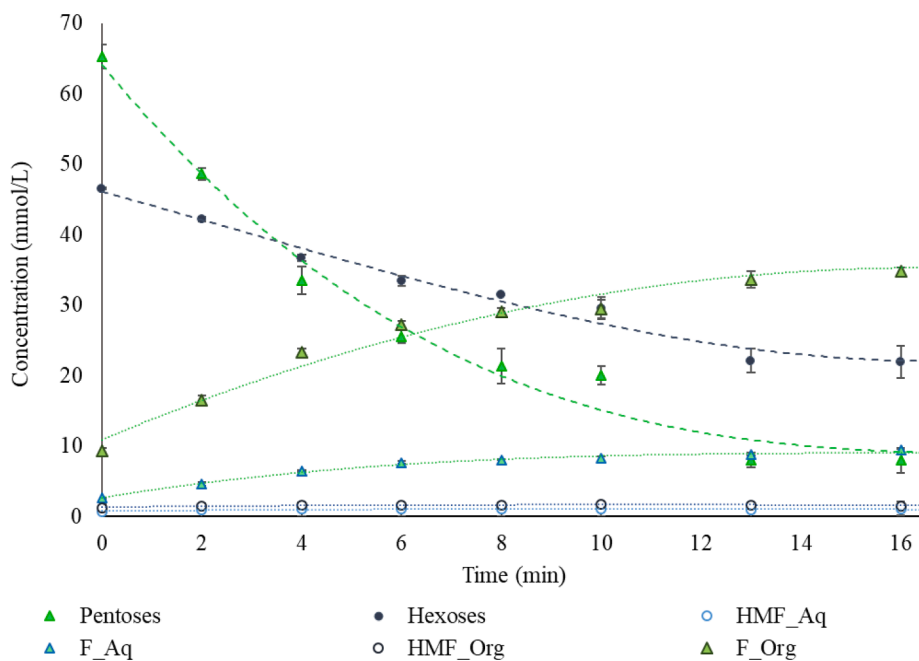


Fig. 4. Concentration profiles determined for the acid-catalyzed treatments of the aqueous phase from organosolv fractionation.

manufacture, additional experiments were performed using fresh (and not recycled) 1-butanol. The results obtained in both sets of experiments were identical, confirming that solvent recycling is a suitable approach for F production in catalyzed, biphasic 1-butanol/water reaction media. Li et al. (2015) studied the production of furfural from pentoses using 1-butanol in batch and continuous processes, and reported F yields of 48% and 59%, respectively. Zhang et al. (2012) considered that butanol is a green, renewable, and efficient solvent for F extraction. Amiri et al. (2010) suggested that the use of 1-butanol in biphasic systems may reduce the costs of separation, since most of the F generated can be separated during the process.

4. Conclusions

Fractionation of water-extracted vine shoots in water/1-butanol/ H_2SO_4 media using a microwave reactor provided solids with cellulose contents up to 75%; an organic phase containing lignin of good purity (85%) with a polydispersity of 4.55, a S/G ratio close to 2 and good thermal stability; and an aqueous phase containing hemicellulose-derived saccharides. This latter was mixed with recycled 1-butanol from the previous delignification stage, and employed to convert hemicellulose-derived saccharides into furans. The furfural yields (up to 64.6%), and the amounts and properties of the products resulting from fractionation, confirmed the suitability of the approach considered in this study for vine shoot valorization.

The comparative evaluation of organosolv processing by microwave and conventional heating demonstrated a superior performance on the valorization of vine shoots by microwave irradiation, when operating under the same conditions.

CRedit authorship contribution statement

S. Rivas: Conceptualization, Formal analysis, Investigation, Data curation, Writing – review & editing; Funding acquisition. **L. López:** Methodology. **C. Vila:** Analysis, Writing. **J.C. Parajó:** Writing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was funded by “Universidade de Vigo” and “Deputación de Ourense” (INO20-03A grant). S. Rivas thanks to MINECO for the research contract with reference IJC2018-037665-I. Authors are grateful to “Universidade de Vigo” and CISUG for the financial support of Open Access publication.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2021.125967>.

References

- Aguilar-Reynosa, A., Romaní, A., Rodríguez-Jasso, R.M., Aguilar, C.N., Garrote, G., Ruiz, H.A., 2017. Microwave heating processing as alternative of pretreatment in second-generation biorefinery: An overview. *Energy Convers. Manag.* 137, 50–65. <https://doi.org/10.1016/j.enconman.2017.01.004>.
- Alves Filho, E.G., Maciel, T.C., Gudiña, E., Miguel, E.C., Rodrigues, L.R., Rodrigues, S., 2020. Multivariate analysis as a tool for selecting the vine pruning pretreatment towards the highest enzymatic hydrolysis yield. *Biomass Bioenerg.* 140, 105653. <https://doi.org/10.1016/j.biombioe.2020.105653>.
- Amiri, H., Karimi, K., Roodpeyma, S., 2010. Production of furans from rice straw by single-phase and biphasic systems. *Carbohydr. Res.* 345 (15), 2133–2138. <https://doi.org/10.1016/j.carres.2010.07.032>.
- Andreo-Martínez, P., Ortiz-Martínez, V.M., García-Martínez, N., Hernández-Fernández, F.J., de los Ríos, A.P., Quesada-Medina, J., 2020. A simple fractionation method and GPC analysis of organosolv extracts obtained from lignocellulosic materials. *Biomass Conversion and Biorefinery.* 11 (5), 1807–1821.
- Beig, B., Riaz, M., Raza Naqvi, S., Hassan, M., Zheng, Z., Karimi, K., Pugazhendhi, A., Atabani, A.E., Thuy Lan Chi, N., 2021. Current challenges and innovative developments in pretreatment of lignocellulosic residues for biofuel production: A review. *Fuel.* 287, 119670. <https://doi.org/10.1016/j.fuel.2020.119670>.
- Buratti, C., Barbanera, M., Lascaro, E., 2015. Ethanol production from vineyard pruning residues with steam explosion pretreatment. *Environ. Prog. Sustain. Energy.* 34 (3), 802–809. <https://doi.org/10.1002/ep.v34.310.1002/ep.12043>.
- Cai, C.M., Zhang, T., Kumar, R., Wyman, C.E., 2014. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. *J. Chem.*

- Technol. Biotechnol. 89 (1), 2–10. <https://doi.org/10.1002/jctb.2014.89.issue-110.1002/jctb.4168>.
- Choi, S., Song, C.W., Shin, J.H., Lee, S.Y., 2015. Biorefineries for the production of top building block chemicals and their derivatives. *Metab. Eng.* 28, 223–239. <https://doi.org/10.1016/j.ymben.2014.12.007>.
- Cotana, F., Barbanera, M., Foschini, D., Lascaro, E., Buratti, C., 2015. Preliminary optimization of alkaline pretreatment for ethanol production from vineyard pruning. *Energy Procedia*. 82, 389–394. <https://doi.org/10.1016/j.egypro.2015.11.814>.
- Dávila, I., Gordobil, O., Labidi, J., Gullón, P., 2016. Assessment of suitability of vine shoots for hemicellulosic oligosaccharides production through aqueous processing. *Bioresour. Technol.* 211, 636–644. <https://doi.org/10.1016/j.biortech.2016.03.153>.
- Dávila, I., Robles, E., Andrés, M.A., Gullón, P., 2017. Delignification alternatives of spent solid from autohydrolysis of vine shoots. *Chem. Eng. Trans.* 57, 85–90. <https://doi.org/10.3303/CET1757015>.
- Del Río, J.C., Rencoret, J., Marques, G., Li, J., Gellerstedt, G., Jiménez-Barbero, J., Martínez, A.T., Gutiérrez, A., 2009. Structural Characterization of the Lignin from Jute (*Corchorus capsularis*) Fibers. *J. Agric. Food Chem.* 57 (21), 10271–10281. <https://doi.org/10.1021/jf900815x>.
- Del Río, L.F., Chandra, R.P., Saddler, J.N., 2010. The effect of varying organosolv pretreatment chemicals on the physicochemical properties and cellulolytic hydrolysis of mountain pine beetle-killed lodgepole pine. *Appl. Biochem. Biotechnol.* 161 (1–8), 1–21. <https://doi.org/10.1007/s12010-009-8786-6>.
- Esteban, J., Vorholt, A.J., Leitner, W., 2020. An overview of the biphasic dehydration of sugars to 5-hydroxymethylfurfural and furfural: a rational selection of solvents using cosmo-rs and selection guides. *Green Chem.* 22 (7), 2097–2128. <https://doi.org/10.1039/c9gc04208c>.
- Faix, O., 1991. Classification of linins from different botanical origins by FT-IR spectroscopy. *Holzforchung* 45, 21–27. <https://doi.org/10.1515/hfsg.1991.45.s1.21>.
- Hu, D.i., Zhang, M., Xu, H., Wang, Y., Yan, K., 2021. Recent advance on the catalytic system for efficient production of biomass derived 5-hydroxymethylfurfural. *Renew. Sustain. Energy Rev.* 147, 111253. <https://doi.org/10.1016/j.rser.2021.111253>.
- Jesús, M.S., Romani, A., Genisheva, Z., Teixeira, J.A., Domingues, L., 2017. Integral valorisation of vine pruning residue by sequential autohydrolysis stages. *J. Clean. Prod.* 168, 74–86. <https://doi.org/10.1016/j.jclepro.2017.08.230>.
- Kangas, H., Liitiä, T., Rovio, S., Ohra-aho, T., Heikkinen, H., Tamminen, T., Poppius-Levlin, K., 2015. Characterization of dissolved lignins from acetic acid Lignofibre (LGF) organosolv pulping and discussion of its delignification mechanisms. *Holzforchung* 69 (3), 247–256. <https://doi.org/10.1515/hf-2014-0070>.
- Kawamata, Y., Yoshikawa, T., Nakasaka, Y., Koyama, Y., Fumoto, E., Sato, S., Tago, T., Masuda, T., 2019. Organosolv treatment using 1-butanol and degradation of extracted lignin fractions into phenolic compounds over iron oxide catalyst. *J. Japan. Pet. Inst.* 62 (1), 37–44. <https://doi.org/10.1627/jpi.62.37>.
- Kim, J., Oh, S., Hwang, H., Kim, U., Choi, J.W., 2013. Structural features and thermal degradation properties of various lignin macromolecules obtained from poplar wood (*Populus alba* L.). *Polym. Degrad. Stabil.* 98 (9), 1671–1678. <https://doi.org/10.1016/j.polymdegradstab.2013.06.008>.
- Lancefield, C.S., Panovic, I., Deuss, P.J., Barta, K., Westwood, N.J., 2017. Pre-treatment of lignocellulosic feedstocks using biorenewable alcohols: towards complete biomass valorisation. *Green Chem.* 19 (1), 202–214. <https://doi.org/10.1039/C6GC02739C>.
- Li, X.-L., Pan, T., Deng, J., Fu, Y., Xu, H.-J., 2015. Catalytic dehydration of D-xylose to furfural over a tantalum-based catalyst in batch and continuous process. *RSC Adv.* 5, 70139–70146. <https://doi.org/10.1039/c5ra11411j>.
- López, M., Santos, V., del Río, J.C., Rencoret, J., Parajó, J.C., 2020. One-pot processing of Eucalyptus globulus Wood under microwave heating: simultaneous delignification and polysaccharide conversion into platform chemicals. *ACS Sustain. Chem. Eng.* 8 (27), 10115–10124. <https://doi.org/10.1021/acssuschemeng.0c0202310.1021/acssuschemeng.0c02023.s001>.
- Míguez, B., Vila, C., Venema, K., Parajó, J.C., Alonso, J.L., 2020. Potential of high- and low-acetylated galactoglucomannooligosaccharides as modulators of the microbiota composition and their activity: a comparison using the model of the human colon TIM-2. *J. Agric. Food Chem.* 68 (29), 7617–7629. <https://doi.org/10.1021/acs.jafc.0c02225>.
- Nabais, J.M.V., Laginhas, C., Carrott, P.J.M., Carrott, M.M.L.R., 2010. Thermal conversion of a novel biomass agricultural residue (vine shoots) into activated carbon using activation with CO₂. *J. Anal. Appl. Pyrolysis*. 87 (1), 8–13. <https://doi.org/10.1016/j.jaap.2009.09.004>.
- OIV, 2019. Statistical Report of World Vitiviniculture. International Organisation of Vine and Wine (visualized 04/06/2021).
- Panovic, I., Lancefield, C.S., Phillips, D., Gronnow, M.J., Westwood, N.J., 2019. Selective primary alcohol oxidation of lignin streams from butanol-pretreated agricultural waste biomass. *ChemSusChem*. 12, 542–548. <https://doi.org/10.1002/cssc.201801971>.
- Rivas, B., Torrado, A., Rivas, S., Moldes, A.B., Domínguez, J.M., 2007. Simultaneous lactic acid and xylitol production from vine trimming wastes. *J. Sci. Food Agric.* 87 (8), 1603–1612. [https://doi.org/10.1002/\(ISSN\)1097-001010.1002/jsfa.v87:810.1002/jsfa.2923](https://doi.org/10.1002/(ISSN)1097-001010.1002/jsfa.v87:810.1002/jsfa.2923).
- Rivas, S., Raspolli-Galletti, A.M., Antonetti, C., Santos, V., Parajó, J.C., 2015. Sustainable production of levulinic acid from the cellulosic fraction of pinus pinaster wood: operation in aqueous media under microwave irradiation. *J. Wood Chem. Technol.* 35 (5), 315–324. <https://doi.org/10.1080/02773813.2014.962152>.
- Rivas, S., Vila, C., Alonso, J.L., Santos, V., Parajó, J.C., Leahy, J.J., 2019. Biorefinery processes for the valorization of Miscanthus polysaccharides: from constituent sugars to platform chemicals. *Ind. Crop. Prod.* 134, 309–317. <https://doi.org/10.1016/j.indcrop.2019.04.005>.
- Rivas, S., Vila, C., Santos, V., Parajó, J.C., 2016. Furfural production from birch hemicelluloses by two-step processing: a potential technology for biorefineries. *Holzforchung*. 70 (10), 901–910. <https://doi.org/10.1515/hf-2015-0255>.
- Romo, J.E., Bollar, N.V., Zimmermann, C.J., Wettstein, S.G., 2018. Conversion of sugars and biomass to furans using heterogeneous catalysts in biphasic solvent systems. *ChemCatChem*. 10 (21), 4805–4816. <https://doi.org/10.1002/cctc.v10.2110.1002/cctc.201800926>.
- Salapa, I., Katsimpouras, C., Topakas, E., Sidiras, D., 2017. Organosolv pretreatment of wheat straw for efficient ethanol production using various solvents. *Biomass Bioenerg.* 100, 10–16. <https://doi.org/10.1016/j.biombioe.2017.03.011>.
- Sammons, R.J., Harper, D.P., Labbé, N., Bozell, J.J., Elder, T., Rials, T.G., 2013. Characterization of organosolv lignins using thermal and ft-ir spectroscopic analysis. *Bioresources* 8 (2), 2752–2767.
- Sánchez-Gómez, R., Zalacain, A., Alonso, G.L., Salinas, M.R., 2014. Vine-shoot waste aqueous extracts for re-use in agriculture obtained by different extraction techniques: phenolic, volatile, and mineral compounds. *J. Agric. Food Chem.* 62 (45), 10861–10872. <https://doi.org/10.1021/jf503929v>.
- Schmetz, Q., Teramura, H., Morita, K., Oshima, T., Richel, A., Ogino, C., Kondo, A., 2019. Versatility of a dilute acid/butanol pretreatment investigated on various lignocellulosic biomasses to produce lignin, monosaccharides and cellulose in distinct phases. *ACS Sustainable Chem. Eng.* 7 (13), 11069–11079. <https://doi.org/10.1021/acssuschemeng.8b0584110.1021/acssuschemeng.8b05841.s00110.1021/acssuschemeng.8b05841.s002>.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., 2008b. Determination of ash in biomass, NREL/TP-510-42622. Laboratory Analytical Procedure (LAP). National Renewable Energy Laboratory (NREL), Golden, CO, USA. <https://www.nrel.gov/docs/gen/fy08/42622.pdf>.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2012. Determination of structural carbohydrates and lignin in biomass, NREL/TP-510-42618. Laboratory Analytical Procedure (LAP). National Renewable Energy Laboratory (NREL), Golden, CO, USA. <https://www.nrel.gov/docs/gen/fy13/42618.pdf>.
- Sluiter, A., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., 2008a. Determination of extractives in biomass, NREL/TP-510-42619. Laboratory Analytical Procedure (LAP) National Renewable Energy Laboratory (NREL), Golden, CO, USA. <https://www.nrel.gov/docs/gen/fy08/42619.pdf>.
- Son, D., Gu, S., Choi, J.-W., Suh, D.J., Jae, J., Choi, J., Jeong-Myeong Ha, J.-M., 2019. Production of phenolic hydrocarbons from organosolv lignin and lignocellulose feedstocks of hardwood, softwood, grass and agricultural waste. *J. Ind. Eng. Chem.* 69, 304–314. <https://doi.org/10.1016/j.jiec.2018.09.009>.
- Teramura, H., Sasaki, K., Oshima, T., Kawaguchi, H., Ogino, C., Sazuka, T., Kondo, A., 2018. Effective usage of sorghum bagasse: Optimization of organosolv pretreatment using 25% 1-butanol and subsequent nanofiltration membrane separation. *Bioresour. Technol.* 252, 157–164. <https://doi.org/10.1016/j.biortech.2017.12.100>.
- Teramura, H., Sasaki, K., Oshima, T., Matsuda, F., Okamoto, M., Shirai, T., Kawaguchi, H., Ogino, C., Hirano, K., Sazuka, T., Kitano, H., Kikuchi, J., Kondo, A., 2016. Organosolv pretreatment of sorghum bagasse using a low concentration of hydrophobic solvents such as 1-butanol or 1-pentanol. *Biotechnol. Biofuels*. 9 (1), 27. <https://doi.org/10.1186/s13068-016-0427-z>.
- Thoresen, P.P., Matsakas, L., Rova, U., Christakopoulos, P., 2020. Recent advances in organosolv fractionation: Towards biomass fractionation technology of the future. *Bioresour. Technol.* 306, 123189. <https://doi.org/10.1016/j.biortech.2020.123189>.
- Wang, K., Yang, H., Guo, S., Yao, X.i., Sun, R.-C., 2014. Comparative characterization of degraded lignin polymer from the organosolv fractionation process with various catalysts and alcohols. *J. Appl. Polym. Sci.* 131 (1), n/a–n/a. <https://doi.org/10.1002/app.39673>.
- Wen, J.L., Sun, S.L., Xue, B.L., Sun, R.C., 2013. Recent Advances in Characterization of Lignin Polymer by Solution-State Nuclear Magnetic Resonance (NMR) Methodology. *Materials (Basel)*. 6 (1), 359–391. <https://doi.org/10.3390/ma6010359>.
- Wildschut, J., Smit, A.T., Reith, J.H., Huijgen, W.J.J., 2013. Ethanol-enzymed organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose. *Bioresour. Technol.* 135, 58–66. <https://doi.org/10.1016/j.biortech.2012.10.050>.
- Yáñez, R., Romani, A., Garrote, G., Alonso, J.L., Parajó, J.C., 2009. Processing of *Acacia dealbata* in aqueous media: first step of a Wood biorefinery. *Ind. Eng. Chem. Res.* 48 (14), 6618–6626. <https://doi.org/10.1021/ie900233x>.
- Zhang, J., Zhuang, J., Lin, L., Liu, S., Zhang, Z., 2012. Conversion of D-xylose into furfural with mesoporous molecular sieve MCM-41 as catalyst and butanol as the extraction phase. *Biomass Bioenerg.* 39, 73–77. <https://doi.org/10.1016/j.biombioe.2010.07.028>.