

Upgrading of Tall Fescue Grass Pyrolytic Bioliquid and Catalytic Valorization of The Biofurfural Obtained

Juan J. Musci,^[a, b] Andrés I. Casoni,^[c] Victoria S. Gutiérrez,^[c] Marco A. Ocsachoque,^[d] Andrea B. Merlo,^[d] María A. Volpe,^[c] Ileana D. Lick,^{*[d]} and Mónica L. Casella^{*[a, d]}

The production of added value products following catalytic hydrogenation reactions of bioliquids was studied. These bioliquids were obtained from the pyrolysis of raw and acid-treated (H₃PO₄) Tall Fescue (*Fescue arundinacea*) waste. Before the pyrolytic test, the biomass samples were analyzed by a micro thermogravimetric analysis coupled with FTIR spectroscopy (TGA-IR), which enables the chemical identification of functional groups of gaseous molecules originated by solid/gas

transformations. From these results, the pyrolysis temperature was selected, and bench scale pyrolysis reactions were carried out. The pyrolysis bioliquids showed high furfural concentration, 46 and 70% for fescue and acid washed fescue, respectively. The bioliquid with the highest furfural concentration was catalytically hydrogenated in aqueous phase. A batch reactor was employed, with Ru/C and Ru–Sn/C catalysts to produce high added value alcohols.

Introduction

Lignocellulosic biomass is the most economical and abundant non-fossil carbon resource that can be used to produce chemicals and fuels, applying processes that generate fewer greenhouse gas emissions.^[1] The lignocellulosic biomass is composed of cellulose, hemicellulose and lignin and, in addition, it contains components such as extractives (resins, tannins and fatty acids) and ash-forming elements (inorganic). Cellulose, the main chemical component of lignocellulosic biomass, is a linear polymer of β -D-glucose units linked by β -(1-4)-glycosidic bonds. Its degree of polymerization can be close to 10,000 in lignocellulosic biomass.^[2] On the other hand, hemicellulose is a heterogeneous copolymer of β -D-glucose units and other sugar units, such as arabinose, xylose, galactose and mannose, linked together through glycosidic bonds. Monomers composing hemicellulose are hexoses and/or pentoses, and the sugars present depend on the plant species. Hemicellulose polymer chains are much shorter than cellulose

ones and, in addition, they are branched and more labile.^[3] The third main component of lignocellulosic biomass is lignin, which is a three-dimensional heteropolymer made up of substituted phenylpropane units.^[4–6]

Waste from agricultural activity is an important biomass resource. Buenos Aires Province (Argentina) is an important area of agricultural and livestock production. Livestock feeding requires high-quality forages of high nutritional value (digestible proteins and fibers, holocellulose). A grass, rich in holocellulose that tolerates cold climates, widely used for grazing in extensive livestock production worldwide, and very abundant in Argentina, is Tall Fescue (*Fescue arundinacea*).^[7] When this forage reaches its state of maturity, it becomes a lignocellulosic residue not suitable for livestock. Nevertheless, it is still a biomass with a high content of cellulose and hemicellulose, which can be valorized by, for example, thermochemical and catalytic treatments.

Among other biomass conversion processes, the thermochemical route known as fast pyrolysis is considered one of the most promising technologies.^[8–11] Fast pyrolysis is a thermochemical process carried out at middle temperature (350–600 °C) in an inert atmosphere and short residence times. This process allows obtaining three valuable fractions, bioliquid, biochar and biogas,^[12–14] with potential applications in various fields. Changing operational conditions such as heating rate, temperature and residence time leads to modification of the fraction yields. Under the operating conditions used in fast pyrolysis, the yield towards the liquid fraction is maximized.^[15–17]

Bioliquids consist of a complex mixture of water (15–30% by mass) and different valuable oxygenated molecules including hydroxy aldehydes, hydroxyketones, sugars, carboxylic acids and phenols.^[18] The chemical composition of the bioliquid is significantly influenced by the chemical composition of the used biomass and, furthermore, by the experimental conditions under which the pyrolytic reaction takes place.^[16,19] Thus, from the pyrolysis of biomass, different families of compounds can

[a] Dr. J. J. Musci, Dr. M. L. Casella

Departamento de Ciencias Básicas y Experimentales
Universidad Nacional del Noroeste de la Provincia de Buenos Aires
Roque Sáenz Peña 456, (6000) Junín, Argentina
E-mail: casella@quimica.unlp.edu.ar

[b] Dr. J. J. Musci

Centro de Investigaciones y Transferencia del Noroeste de la Provincia de Buenos Aires (CITNOBA) – UNNOBA-UNSA-CONICET
Monteagudo 2772, 2700 Pergamino, Argentina

[c] Dr. A. I. Casoni, Dr. V. S. Gutiérrez, Dr. M. A. Volpe

Planta Piloto de Ingeniería Química (PLAPIQUI) (CCT CONICET-Bahía Blanca)

Camino La Carrindanga Km 7, CC 717, 8000 Bahía Blanca, Argentina

[d] Dr. M. A. Ocsachoque, Dr. A. B. Merlo, Dr. I. D. Lick, Dr. M. L. Casella

Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. Jorge J. Ronco" (CINDECA) (CCT CONICET–La Plata)
Universidad Nacional de La Plata
Calle 47 No.257, 1900 La Plata, Argentina
E-mail: ilick@quimica.unlp.edu.ar



Supporting information for this article is available on the WWW under <https://doi.org/10.1002/slct.202202233>

be eco-friendly obtained, such as hydrocarbons, oxygenates (phenols, anhydro sugars, furanics, etc.) and nitrogen-containing compounds. The obtainment of a certain group of compounds, for example furan compounds, can be oriented by a correct choice of the starting substrate, the pyrolysis temperature, and the use of certain pretreatments.^[20–26] In general, the use of biomass containing a low lignin content will give rise to bioliquids with a higher content of sugar derivatives and a lower content of phenolic compounds.

In this work, it is of particular interest to obtain furfural from residual biomass pyrolysis. This furan molecule, which is industrially obtained by the acid-catalyzed dehydration of pentosan-containing lignocellulose, can also be obtained from the thermal degradation of cellulose and hemicelluloses.^[27] Among the compounds that derive from the thermochemical degradation of cellulose are anhydrosugars, mainly levoglucosan, which are formed by cleavage of unstable glycosidic bonds and dehydration reactions. Then, levoglucosan can be transformed into levoglucosenone and glucopyranose, and from these molecules, furans, hydroxyacetone, glycolaldehyde, and glyceraldehydes can be obtained.^[24,28–30] In this sense, Sarotti *et al.* have shown that it is possible to obtain levoglucosenone from crystalline cellulose pre-treated with dilute phosphoric acid by microwave-assisted pyrolysis.^[31] In this same sense, M. Shibagaki *et al.* obtained a levoglucosenone-rich bio oil from the pyrolysis of cellulose pre-treated with phosphoric acid, furfural was found as the major impurity, at levels between 5–10%.^[32,33] Regarding the degradation of pure hemicellulose, it is worth mentioning that there are few studies dealing with this issue, because it is very difficult to separate hemicellulose from cellulose without causing its degradation. Even so, hemicellulose can be degraded to sugar monomers (such as xylan), from which both anhydroasugars and low molecular weight molecules such as acetic acid, acetone, acetol, formic acid, furfural, 5-hydroxymethylfurfural, anhydroxylopyrans, among others are obtained. In biomass substrates of diverse nature, the selective obtention of a particular product depends on various factors, such as process temperature, presence of alkaline metals, moisture content, length of the chains, cellulose-hemicellulose or cellulose-lignin interactions, among others. In addition, competitive reactions generally occur that can generate unwanted by-products in the form of low molecular weight molecules.^[28,34–37]

An effective way to promote selectivity towards a certain family of products is by choosing the pretreatments to which the biomass is subjected, prior to the pyrolysis process.^[17,20,21,25,38–40] In several bibliographic studies it has been proposed that an acidic pretreatment makes the biomass polymers more accessible by opening up the polymer fibers to enhance the conversion of cellulose, hemicellulose and lignin. The more labile chains of hemicellulose could be hydrolyzed first, and part of the light hydrolysis products could be extracted. In this sense, it has been reported^[5,41] that pretreatments with acids (H_2SO_4 , HCl, CH_3COOH , H_3PO_4) cause changes not only in the structure, but also in the relative composition of the biomass (changing the concentration of the lignocellulosic components). Some acids, such as phosphoric acid, are capable

of hydrolyzing the hemicellulose chains without causing a high solubilization of it,^[5] which allows having a pre-treated biomass, with a certain degree of hydrolysis, and with a high content of sugars (C5 and C6). In this way, compounds that can be transformed during pyrolysis into dehydration products and their derivatives are preserved, among which are furans. This is a key factor to take into account when the starting biomass is “soft” or very rich in holocellulose. Thus, for example, Casoni *et al.* enhanced the yield of levoglucosenone and furfural from fast pyrolysis of sunflower seed hulls treated with 5% H_3PO_4 .^[42] A similar result was found by Zhang *et al.*, who obtained bioliquids rich in anhydrosugars and furans by fast pyrolysis of eucalyptus pre-treated with diluted H_2SO_4 ^[43] and by Sui *et al.* who obtained bioliquids with high contents of levoglucosenone from acid pre-treated bagasse.^[40] In addition, to promote the cleavage of glycosidic bonds, the role of acid treatments could be associated with the passivation of alkali and alkaline earth metals present in the biomass. These metals act as catalysts of the pyranose ring fragmentation and, as a result, decrease the yield of anhydrosugars and increase the yield of low molecular compounds (e.g., CO_2 , acetol, furfural, 5-hydroxymethylfurfural, aldehydes and ketones of short chain, etc.).^[43] Another factor that should be taken into account is the change in the degree of crystallinity of the cellulose with the pretreatments, since an acid wash can cause a loss of crystallinity and thus promote the formation of furfural.^[44]

On the other hand, bioliquids enriched in furan derivatives of sugar monomers can be subjected to upgrading reactions, to obtain products with high added-value. Biofurans such as furfural and 5-hydroxymethylfurfural (FUR and 5-HMF) can be transformed through different catalytic routes into products of high industrial interest.^[47,48] In this sense, catalytic hydrogenations are revealed as high potential pathways^[42,49–52] being furfuryl alcohol, tetrahydrofurfuryl alcohol, dimethyl tetrahydrofuran and methyl tetrahydrofuran some of the reduced derivatives of interest.^[46] In this work, it is of particular interest the production of alcohols, furfuryl alcohol and tetrahydrofurfuryl alcohol, from the selective hydrogenation of bio-furans. Previous research of our group has demonstrated that tin-modified ruthenium supported catalysts are very effective for the selective reduction of the carbonyl group of furfural in the aqueous phase.^[49,50] These results are promising for the application of these catalysts in the treatment of substrates rich in water, such as crude bioliquids.^[47] There are very few studies that report results on the hydrogenation of furans-rich raw bioliquids coming from biomass pyrolysis.^[42,51–53] Furthermore, little is known about the effect of the presence of other compounds usually found in bioliquids on the conversion of furfural. It has been reported, for example, that the presence of acetic acid can cause a decrease in activity and selectivity towards alcohols.^[54]

Therefore, a deep investigation of the pyrolysis of wastes of Tall Fescue was carried out, including the effect of pretreatment with phosphoric acid on the chemical composition of the pyrolysis bioliquid. The raw bioliquid, rich in furfural, was subjected to a catalytic up-grading process to obtain high added-value alcohols. The reaction selected for this purpose is

the selective hydrogenation of the bioliquid, using tin-modified ruthenium catalysts, obtained by techniques derived from Surface Organometallic Chemistry on Metals (SOMC/M). SOMC/M is a set of tools for the design and preparation of well-defined catalysts having a very good catalytic performance.^[55,56] To meet the objectives, preliminary experiments were carried out using a TGA-FTIR microreactor. The pyrolysis reactions were carried out in flow reactors and the composition of the obtained bioliquids was analyzed by means of GC-MS.

Results and Discussion

Characterization

The cellulose, hemicellulose and lignin content ashes and moisture content of raw fescue (RF) and pre-treated fescue (APF) samples are given in Table 1. As can be seen, the starting substrate, RF, has high cellulose and hemicellulose content and very low lignin content. At this point, it is worth mentioning that the biomass samples analysed contain other components that are solubilized during the treatment with detergent in the Van Soest method (neutral detergent soluble fraction), such as starch, lipids, pigments, pectin, proteins, soluble non-nitrogenous organic compounds and sugars (designated as "Others" in Table 1), so the reported values for cellulose and hemicellulose may be slightly lower.^[57] The treatment with H₃PO₄ (APF sample) caused a slight change in the composition of the biomass. The biomass fractions are slightly solubilized, observing a loss of approximately 11, 17 and 18%, for cellulose, hemicellulose and lignin, respectively. These results agree with others reported in the literature.^[5,42] On the other hand, it can be observed that the extractable percentage increased, probably due to the increase in the content of derivatives of the original polymers (hydrolyzed short chains of sugars, monomers, alcohols, etc.).

On the other hand, it can be seen that the acid treatment also modifies the content of inorganic components, since the ash content is lower in the APF sample. A dissolution of these components is likely to be generated during the acid wash.

In order to analyse the effect of acid treatment on the structure of the samples at a microscopic level, scanning electron micrographs of fescue samples were performed. The results obtained (see Supplementary Material) indicate that the acid-washed sample shows that the fibres maintain a certain

structure, however its surface appears cleaner and more compact, probably due to a separation of the cellulose fibres from the hemicellulose polymers.

Besides, microscopy and SEM-EDS analysis of the ashes of both samples (RF and APF) were performed, with the aim of analysing whether the acid treatment led to a decrease in inorganic compounds in the samples. The results obtained (Table 2) indicate that the H₃PO₄-washed samples contain a lower amount of silicon and other elements (K, Na, Ca, Mg, Fe, Al, etc.). It is evident that the acid dissolves the compounds that contain them and extracts them from the samples. On the other hand, it is worth mentioning that the ashes contain P, which obviously comes from the acid. The results obtained are important since it is known that the presence of alkaline and alkaline-earth metals in the substrates condition the quality of the bioliquids.^[28,42,43]

The removal of crystalline inorganic components was also observed by XRD (see Supplementary Material). The diffractogram of the RF sample shows diffraction lines associated with the presence of inorganic salts, which are not present in the diffractogram of the APF sample. The XRD spectra show weak and broad signals located at $2\theta = 15.14, 16.22$ and 22.6° that could be associated with cellulose crystal structure.^[44] It should be noted that, although both samples have very low crystallinity, the signals from the APF sample are slightly broader, denoting a lower degree of crystallinity relative to the RF sample.

The thermal degradation of raw (RF) and H₃PO₄-pretreated (APF) fescue samples were studied thermogravimetrically. Figure 1 shows the evolution of the mass loss as a function of temperature, TGA curves, obtained with both substrates in an inert atmosphere, using a typical heating ramp (20 °C/min). In the same figure, the derivatives of each curve (DTGA curves) are also observed. These experiments were carried out in order to choose the pyrolysis temperature.

This figure clearly shows the effect of the acid pretreatment on the thermogravimetric profile. Both the final yield towards the solid fraction and the temperatures at which the main thermochemical events occur are modified. Both thermograms present a first stage of mass loss at temperatures below 100 °C, associated with the loss of adsorbed water. The sample treated with phosphoric acid presents a greater loss at this stage, probably due to retained water from pretreatment. Decompositions appearing at higher temperatures involve thermochemical changes of the main biomass constituents (extractables, hemicellulose, cellulose, and lignin). Hemicellulose, made up of amorphous chains of saccharides, is the easiest polymer component to decompose and its degradation occurs between 150–200 and 350 °C, generating a high concentration of volatile

Table 1. Chemical composition of raw fescue (RF) and pre-treated fescue (APF).

| Sample | Cella ^[a] | HCella ^[a] | Liga ^[a] | Others ^[a] | Ashesa ^[a] | Moisture content |
|--------------------------|----------------------|-----------------------|---------------------|-----------------------|-----------------------|------------------|
| Raw Fescue (RF) | 65.0 | 21.7 | 6.2 | 7.1 | 10.9 | 3.0 |
| Pre-treated Fescue (APF) | 58.1 | 18.1 | 5.1 | 18.7 | 5.5 | 14.6 |

Cell: Cellulose, HCell:Hemicellulose, Lig: Lignin
[a] Dry mass

Table 2. Content of elements present in the ashes, measured by EDS.

| Element | Na | K | Si | Ca | Mg | Al | Ti | Fe | Cl | P |
|-------------------------|-----|-----|------|-----|-----|-----|-----|-----|-----|------|
| Raw Fescue (RF) | 2.1 | 5.9 | 43.0 | 2.1 | 0.8 | 5.2 | 1.3 | 2.4 | 0.2 | – |
| Pretreated Fescue (APF) | 0.7 | 4.0 | 9.7 | 0.8 | 0.3 | 0.2 | – | – | – | 34.1 |

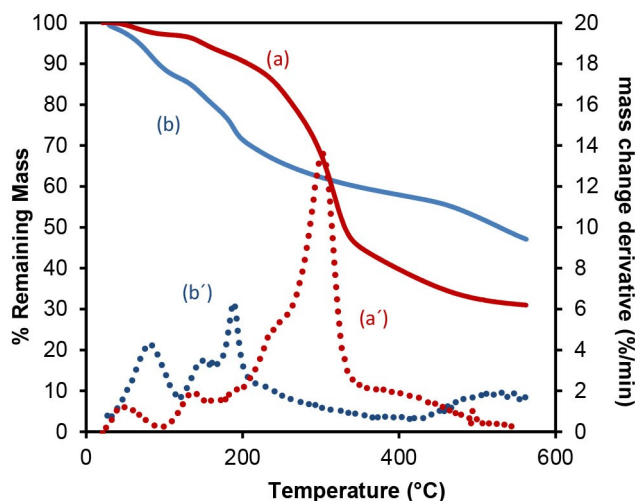


Figure 1. TGA plots of Tall fescue samples: a) raw fescue (RF) and b) H_3PO_4 -pre-treated fescue (APF). a') and b') correspond to the derivatives.

components (acetic acid, CO, CO_2 , light hydrocarbons, etc.). Cellulose, whose ordered structure is formed by a long polymer of glucose is more stable, degrades rapidly between 200 and 450 °C, and normally its maximum degradation rate is between 290 °C–380 °C, depending strongly on the speed of the heating ramp.^[58] This signal is usually the most intense in the thermograms of different biomass substrates. Finally, lignin, with its complex structure, degrades slowly over a wide temperature range between 180 °C and 900 °C. The so-called refractory lignin is the most difficult fraction to decompose ($T > 450$ °C–500 °C), due to the presence of strong carbon-carbon and carbon-oxygen bonds in its tridimensional structure.^[59] The fact that the degradation phenomena of the fractions overlap, makes it difficult to assign the signals to the processes associated with each particular fraction.^[5,58,60,61]

In the thermogram of the RF sample (Figure 1), in addition to the initial mass loss corresponding to water (3%), unresolved processes are observed between 100 and 550 °C, as clearly indicated by the derivative curve. The temperatures where each of these processes occur faster are 132, 237 °C (as a shoulder) and 298 °C, and these signals could be associated with the degradation of extractables, hemicellulose and cellulose, respectively. In addition, a slow basal process can be seen with a maximum at 410 °C and it can be associated with the degradation of lignin. Between RT and 550 °C a mass loss of 70% is achieved. The mass loss calculated between 100 °C and 170 °C, probably coming from the degradation of extractables and light substances, is 4%, while that calculated in the zone where the degradation of hemicellulose and cellulose predominates (170 °C–370 °C) is 50%.

The thermogravimetric profile of the APF sample is substantially different to the profile obtained with the RF sample (Figure 1). In principle; this sample shows a greater mass loss at temperatures below 130 °C, indicating the loss of water and volatile and low molecular weight compounds, most likely generated during acid hydrolysis. Furthermore, the most

important thermochemical processes occur at temperatures below 350 °C, indicating that the acid hydrolysis treatment was successful in terms of generating lability in the depolymerization of holocellulose (hemicellulose and cellulose). The mass loss between 120 and 350 °C is 28%. Above 350 °C, the mass loss detected can be associated with the degradation of lignin.

The APF sample presented a lower yield towards the gas fraction than the RF sample, a fact that can be associated with a slight dissolution of biomass components in the washing acid, in accordance with the results obtained from the analysis of the composition of the fractions (Table 1). Probably, during the acid pretreatment there is a leaching of some extractable compounds and of small (and probably polar) molecules from the hydrolysis of the biopolymers. In general terms, for both substrates the degradation processes of the hemicellulose and cellulose fractions end at temperatures below 450 °C. Therefore, this temperature can be selected to perform the pyrolytic tests to obtain the maximum yield to bioliquid.

Figure 2 shows the FTIR spectra of the gases released during the thermal degradation of both samples, RF and APF. It is remarkable how the pretreatment with phosphoric acid not only modifies the thermal profile but also alters the nature of the gases (e.g., CO_2 , CO, CH_4 , etc.) and condensable vapors that are generated during the thermal treatment in a nitrogen atmosphere (Figure 2B).

The TGA-FTIR spectra exhibited a great variety of superimposed energy absorption signals corresponding to the different functional groups of the species present in the gas phase. However, spectral zones associated with different functional groups characteristic of biomass degradation can be identified (Table 3).^[62,63]

The TGA-FTIR spectra of the gases released during the pyrolysis of both substrates differ substantially in many aspects. The first one of these is related to the time (or temperature) in which the absorbance signals begin to be observed, the second one is related to the intensity of these signals and finally, with

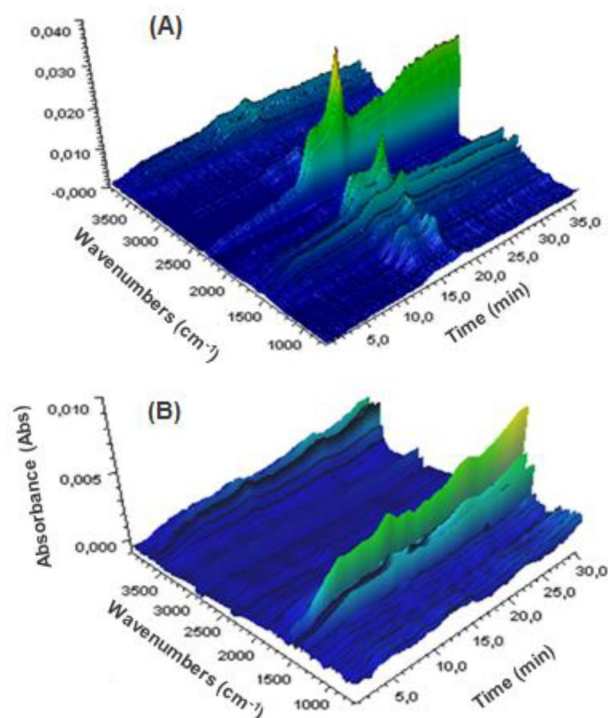


Figure 2. TGA-FTIR diagrams obtained: (A) RF and (B) APF.

| Table 3. FTIR bands of the main functional groups of molecules derived from biomass. | | |
|--|--------------------------|------------------------------------|
| Wave number (cm ⁻¹) | Assignment | Compound |
| 3650–3580 | O–H stretching | Alcohols |
| 3100–3500 | O–H stretching | H ₂ O, carboxylic acids |
| 3050–3150 | C–H stretching | CH ₄ |
| 2850–3030 | C–H stretching | Hydrocarbons |
| 3010 | Aromatic C–H stretching | aromatic ring |
| 2250–2500 | C=O stretching | CO ₂ |
| 2100–2200 | C–O stretching | CO |
| 1680–1750 | Aliphatic C=O stretching | aldehydes |
| 1595–1715 | Aromatic C=O stretching | Aldehydes |
| 1725–1705 | Aliphatic C=O stretching | ketones |
| 1700–1680 | Aromatic C=O stretching | ketones |
| 1680–1800 | C=O stretching | carboxylic acids |
| 580–730 | C–O stretching | carboxylic acids |
| 1080–1260 | C–O stretching | alcohols, aldehydes |

the wave number where the strongest signals appear. In general, it can be observed that the evolution of gaseous products begins at higher temperature during the heat treatment of the RF sample, but a wide variety of signals at different wave numbers are also observed, the most intense being those located in the zone of 2200–2500 cm⁻¹. Instead, the spectra of the APF sample show a lower number of signals and lower intensity (lower absorbance). These results would indicate the presence of a smaller number of compounds generated during the thermal degradation of the substrates, and this result can be associated with the fact that part of the most labile compounds is lost with acid washing, as evidenced also with TGA results.

In this sense, it can be seen that in the RF spectra (Figure 2A) the greatest evolution of gaseous products occurs between 15 and 20 min (270 and 370 °C). In this time/ temperature range, the absorption bands of greater intensity appear, located at 2200–2500 cm⁻¹, but some also appear in the lower part of the spectrum (1100–1300 cm⁻¹), which can be associated with the evolution of light gases (CO₂, CO, CH₄, short chain hydrocarbons, etc.). Signals related to compounds containing carbonyl groups (1400–1750 cm⁻¹) such as aldehydes, ketones and carboxylic acids also appear. The area of the spectra where absorption bands of phenolic compounds appear (~3000 cm⁻¹) does not show very strong signals, which would indicate a low content of the main lignin degradation compounds.

On the other hand, in the spectra of the gas mixture obtained with APF (Figure 2B) the signals begin to evolve at a lower temperature and the spectra are cleaner and dominated by typical absorption bands of carbonyl group-containing species (~1750–1600 cm⁻¹). In addition, energy absorption is observed in the range of 3500–3700 cm⁻¹, an area of the spectra where signals of -OH groups appear. Furthermore, the decrease in signals associated with evolution of light gases is marked. These results indicate that the acid pretreatment has directed the pyrolysis towards a bioliquid of simpler composition, rich in compounds with carbonyl bonds, which can be of furan or acid family.

Considering the preliminary results obtained in TGA-FTIR, the pyrolysis tests were carried out in a batch reactor at 450 °C. Figure 3 shows the yields obtained with both samples, and Table 4 shows the composition of the bioliquids obtained. The acid pre-treatment does not significantly change the distribution of the obtained fractions; it only slightly decreases the yield towards the bioliquid. Instead, the pretreatment substantially affects the distribution of compounds that make up the bioliquid, as predicted from the TGA-FTIR preliminary results.

The pyrolysis liquid of the RF sample has a complex composition that includes short and long chain acids, furans, aldehydes, ketones, etc. It is noted that the acid pretreatment of the fescue leads to pyrolysis liquids of much simpler composition (Table 3). Furthermore, in both liquids' molecules typical of lignin degradation such as phenol, 4-vinyl phenol,

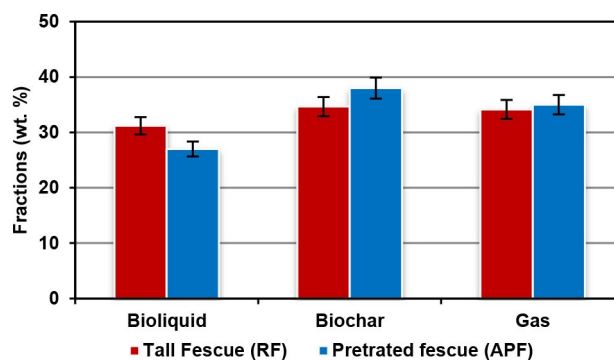


Figure 3. Percentage yield to each fraction obtained by pyrolysis.

Table 4. Composition of the bioliquids obtained by biomass pyrolysis. (wt.%) by GC-MS.

| Fraction ^[a] | Fescue | Pre-treated |
|---|--------|-------------|
| Furfural | 46 | 70 |
| Acetone | 15 | – |
| Acetic acid | – | 11 |
| Vinyl acetate | 4 | – |
| Levogluconan | – | 7 |
| 2-Propanone, 1-(acetyloxy) | 11 | – |
| Glycidyl acetate | 4 | – |
| Cyclopentanone | 4 | – |
| 3-Octin-1-ol | 4 | – |
| Heptane | 3 | – |
| L-Alanine, N-methoxycarbonyl-, tridecyl ester | 4 | – |
| Ethanone, 1-(2-furanyl)- | 3 | – |

[a] Compounds whose proportion is ≥ 3 wt.% are shown.

cresol, guaiacol, vanillin, are not found in concentrations higher than 3%. These results are associated with the low lignin content of the original biomass and the choice of the relatively low pyrolysis temperature, which allowed the degradation of the holocellulose and avoided an extensive transformation of the lignin.

Furthermore, the fast pyrolysis leading to the degradation of polymeric cellulose and hemicellulose is known to take place in several steps, the most important being the cleavage of the chains to give monomers or dimers. Polysaccharide particles not only undergo depolymerization reactions when submitted to an increase in temperature, but also undergo phase change processes (melting and volatilization). This reaction stage is conditioned by the cellulose-hemicellulose and cellulose-lignin interactions. Hosoya *et al.* proposed that the hemicellulose melt during pyrolysis, and it could cover the cellulose before the pyrolysis reaction of the cellulose itself begins.^[34] That is, the hemicellulose-derived products volatilize more easily than cellulose derivatives and could inhibit the formation of volatiles from cellulose. Other compounds that have a low melting point and have this same effect are the monomers or dimers of sugars. Then various secondary reactions can occur in the liquid or gas-phase. Products (liquid or vapor) are then transferred to the gas surrounding cellulose particles. Then, other reactions occur generating volatile compounds and light gases. Also, these secondary reactions promote isomerization, dehydration of sugars as well as the ring opening of sugars. The most common depolymerization/dehydration products include mainly monomers and dimers (e.g., glucose and cellobiose) and levoglucosan. Then, by secondary reactions of them, 5-HMF, levoglucosone, dianhydroxylose and furfural can be obtained, among other products.^[64] Small oxygenated molecules such as acetone, 3-pentanone, acetol, glycolaldehyde and acetic acid are obtained by ring opening and bond cleavage. The relative content of anhydrous sugars, furanic compounds and/or low molecular weight products depends on various factors: *i*) Degree of depolymerization of the chains. The initial length of polysaccharide chains, mainly cellulose, present a strong influence on the yields of levoglucosan and low molecular weight products. In general, long chains promote

the formation of levoglucosan while the concentration of non-condensable gases and low molecular weight molecules increase with a reduction in the chain length of the carbohydrate. The increase in the concentration of linear compounds of five carbon atoms, anhydrosugars and dehydrated glucose, suggests that the secondary reactions of these compounds could be responsible for the higher yield of furfural obtained from short cellulose oligomers. Furthermore, the formation of furanics (e.g., HMF, furfural, etc.) involves the pyranose-furanose transformation of glucose through an intermittent open structure.^[65] *ii*) Degree of crystallinity of the cellulose. Bibliographic reports indicate that a decrease in the degree of crystallinity of cellulose leads to an increase in the concentration of furanics in bioliquids.^[44] *iii*) Content of alkali and alkaline earth metals: As already mentioned in the Introduction section, the presence of these species generates a rupture of the rings and an increase in low molecular weight products.^[28,42,43] In a recent work, Zhou *et al.*^[66] showed how the variation in the concentration of sulfuric acid in the biomass pretreatment modified the product distribution in bioliquids from pyrolysis of the raw biomass. These authors reported that with intermediate and strong acid treatments, the opening-breaking of rings is avoided. On the other hand, as the acid concentration increases during pretreatment, the conversion of anhydrosugars to dehydration products such as furfural is promoted.

From the analysis of the results shown in Table 4 it is inferred that the pretreatment of the Tall Fescue samples has been successful.

On the other hand, the quantitative measurement of the major component, furfural, was carried out by gas chromatography using the external standard method. The furfural concentration found for the bio-oils from raw and pre-treated fescue was 47.8 and 72.5 wt.%, respectively.

It can be seen that it decreases the opening of the rings and with it the number of lower molecular weight compounds, promoting the isomerization-dehydration sugar monomers pathway (C6 and C5) to generate levoglucosan and furan derivatives. These facts are explained according to what was mentioned in the previous paragraphs. Evidently, with the acid treatment, it has been possible to direct the reaction towards furfural, achieving a high degree of depolymerization, a decrease in alkali and alkaline earth metals in the APF sample, and a certain decrease in the crystallinity of the cellulose, according to EDS, TGA and XRD results. In this sense, since furfural has been found as the main component in both bioliquids, the results are highly promising because this compound is a platform molecule for biorefineries.

Hydrogenation of the bio furfural obtained

As already mentioned, one of the challenges of biomass conversion is to obtain target molecules that can then be converted into higher added-value products. Furfural (FA) is an important building block that can be converted, through catalytic hydrogenation, into different products of interest, such as furfuryl alcohol (FAL: widely used in the foundry

industry and in the production of cosmetics), or tetrahydrofurfuryl alcohol (THFA). THFA is a biodegradable compound that is used in various applications, from solvent for printing inks to precursor of intermediates for the pharmaceutical industry (i.e., 3,4-dihydro-2H-pyran). The use of their derivatives (i.e., ethers or acetals) has also been proposed as precursors of surfactants and even as fuel additives, as they significantly reduce particulate emissions.^[53]

In Table 4 it can be seen that, although furfural has been found in both bioliquids as the major component, in the bioliquid (B_{APF}) that comes from acid-washed fescue, this product is found in greater proportion. Considering these results, the B_{APF} was selected for the hydrogenation tests shown in Table 5. B_{APF} reduction was performed at H_2 pressure of 1.25 MPa and $90^\circ C$, using a monometallic ruthenium catalyst, Ru/C, and a ruthenium-tin bimetallic catalyst, $RuSn_{0.4}/C$. The systems selected in this work have been previously studied in the aqueous phase hydrogenation of commercial furfural.^[49,50] These catalysts proved to be active, selective and stable in this reaction, without leaching of the metallic phase into the reaction medium. For these reasons, the hydrogenation of bio furfural was tested with them.

As it can be observed, both catalysts resulted active in the B_{APF} hydrogenation under the tested experimental conditions, reaching conversion values of 100% and 80% after 30 min of reaction (Table 5). The higher conversion observed for the Ru/C catalyst could be due to the fact that this system presented smaller metal particles size (see Supplementary Material).

On the other hand, it can be said that the systems turned out to be highly selective to two main reaction products: THFA (in higher percentage) and FAL. These results are highly satisfactory given that high levels of selectivity have been achieved in a crude bioliquid, in the presence of the other molecules, mainly acetic acid and levoglucosan, produced during the pyrolytic process. These obtained results allow inferring that the mechanism of the complete and selective

hydrogenation reaction, FAL to THFA, in the presence of supported Ru catalysts occurs in two stages (Figure 4).

Finally, when analyzing the addition of tin, it can be said that during the bioliquid hydrogenation, the presence of this second metal led to an increase in selectivity to FAL, for the bioliquid hydrogenation. This result can be attributed to the fact that the presence of ionic Sn acts as Lewis acid polarizing the C=O bond of furfural, with the consequent increase in the selectivity towards FAL.^[49] Nevertheless, it must be taken in account that there is a compromise between the dilution of the Ru sites, active for the hydrogenation reaction, and the Sn promoting effect. That is why the tests were carried out using a ratio Sn/Ru = 0.4. The RuSn phase is very important for activity in FA hydrogenation. When the proportion of Sn(0) increases, the activity decreases, so the formation of the RuSn phase must be kept relatively low with respect to the active metal, so that the catalytic performance is not affected (see XPS results in the supplementary material).

Conclusion

This work shows the effect of an acid pretreatment with diluted phosphoric acid on the quality of a bioliquid obtained from the acid pyrolysis process of waste from Tall Fescue, lignocellulosic biomass. To meet the objective, a cascade process was proposed, consisting of a pretreatment stage of the lignocellulosic substrate, obtaining the pyrolysis operating variables through analytical techniques (TGA and TGA-FTIR), obtaining and characterizing bioliquids pyrolytic by GC-MS and, finally, a stage of catalytic up-grading of the obtained bioliquid was proposed.

The results obtained clearly demonstrated that the acid pretreatment with H_3PO_4 of these residues is an effective method to maximize bio furfural production during the pyrolytic process, obtaining a high concentration of this platform molecule (70%) in the bioliquid (B_{APF}). In addition, a bioliquid with a simpler composition than that found with the crude substrate (B_{RF}) is obtained.

In a later stage, the furfural-rich bioliquid was subjected to catalytic hydrogenation in the presence of ruthenium and ruthenium-tin catalysts supported on carbon. The results obtained in this stage were highly promising since high conversions of bio furfural into products with high added value were obtained. On the other hand, it is noteworthy that high selectivity was obtained in the hydrogenation of FA present in the bioliquid towards alcohols (FAL and THFA), mainly in the presence of the bimetallic catalyst Ru–Sn/C. The high selectivity obtained with the bimetallic catalyst is noteworthy, given that it was found in a pyrolytic bioliquid that, besides furfural, contained other typical concomitants.

The present manuscript allows carrying out a conceptual simulation of the process for obtaining bio-based products from Tall Fescue residues, being the results obtained very interesting.

Table 5. Furfural conversion and selectivity obtained with Ru/C and $RuSn_{0.4}/C$ catalysts in catalytic hydrogenation of the bioliquid.

| Catalyst | X% | Selectivity % ^[a] | | |
|----------------|-----|------------------------------|---------------------------|-----------------------------|
| | | S_{FAL} ^[b] | S_{THFA} ^[c] | S_{others} ^[d] |
| Ru/C | 100 | – | 95 | 5 |
| $RuSn_{0.4}/C$ | 80 | 23 | 53 | 24 |

[a] Selectivity towards the products calculated at the maximum conversion. [b] Furfuryl alcohol. [c] Tetrahydrofurfuryl alcohol. [d] cyclopentanone, 1,5-pentanediol, 2,2'-difurfuryl ether, 2-methoxymethylfuran.

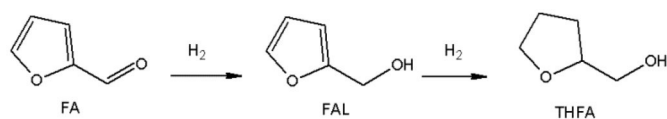


Figure 4. Reaction scheme and main products obtained in the hydrogenation of furfural (FA) with supported Ru catalysts.

Supporting Information Summary

The supporting information contains details of the experimental techniques used for the preparation and characterization of the catalysts, as well as experimental characterization results. Figures S2 and S3 show SEM micrographs and DRX profiles of raw fescue and acid-pre-treated Fescue samples, respectively. Supporting Information file include Section 1. Catalyst Preparation, Section 2. Characterization, Section 3. Characterization result of supports and catalysts, Figure S1 and Table S1. Section 4. Characterization results of raw and acid-pre-treated Tall Fescue samples, Figure S2 and Figure S3, Section 5. References

Experimental Section

Pre-treatment and analysis of the biomass fractions

Tall Fescue residues (Seed Cluster, Pergamino, Argentina) were used as starting substrates in this study. Before the preliminary TGA-FTIR experiments or pyrolysis reactions, the samples were ground and sieved to a particle size of 80–100 mesh, and then dried at 60 °C for 12 h. These samples were designated as *raw fescue* (RF).

To obtain the phosphoric acid pre-treated sample, a sample of Tall Fescue (10 g) was washed with 100 mL of a phosphoric acid solution (15 wt.%) in a beaker for 2 h at room temperature, under magnetic stirring. Phosphoric acid (85%) was purchased from Aldrich. The phosphoric acid-washed fescue sample was then crushed to 80–100 mesh and dried at 60 °C for 12 h. This sample was named acid-pre-treated fescue (APF).

Hemicellulose, cellulose and lignin contents both in RF and APF samples were analyzed following the Van Soest method^[67] in an ANKON 200/220 FIBER ANALYZER. Moisture was determined gravimetrically, after drying the samples at 105 °C for 24 h. The mineral components were determined as ash, after incineration of aliquots of the materials in muffle at 900 °C. The effect of pre-treatment on the morphology of the samples was analyzed by SEM microscopy in a Philips 505 SEM equipment (Philips Co, Amsterdam, The Netherlands). On the other hand, a semi-quantitative elemental analysis of the ashes from both samples was performed by EDS using a Genesis APEX 2-Apollo X 60 Imaging device. XRD spectra were acquired using a Philips PW1710 BASED equipment.

Preliminary Pyrolysis experiments by TGA coupled with FTIR

The thermal behaviour of both raw (RF) and acid pre-treated fescue (APF) samples was followed using the TGA coupled with FTIR technique. The instrument consisted of a thermobalance (TA Instruments, model Q50) coupled with a FTIR spectrometer (Thermo Scientific, model Nicolet is10, DTGS detector and KBr windows). This equipment allows analysing the mass loss of the fescue samples and the formation of gaseous products at the same time. To reduce errors associated with heat and mass transfer, a small amount of sample (12 mg) was loaded into the platinum pan. The analysis was carried in an inert atmosphere (pure N₂) with a flow rate of 100 mL/min from RT to 600 °C at a heating rate of 20 °C/min. To prevent combustion reactions, before carrying out the experiments, the thermogravimetric reactor was purged with N₂ for 20 min to obtain an oxygen-free atmosphere. The gases generated during the pyrolysis in the thermobalance furnace were

swept to the gas cell of the FTIR. The transfer line and the gas cell were heated and kept at a temperature of 300 °C, to avoid condensation of the gaseous products. Each IR spectrum was obtained in the spectral range of 4000–400 cm⁻¹.

With this TGA-FTIR technique, information is obtained from two interfaces, one is thermogravimetric and the other, spectroscopic. From the thermogravimetric interface, results of mass loss are obtained as a function of time (or temperature). These data are represented in a two-dimensional x-y graph, where the mass loss is plotted on the primary y axis and the derivative of the mass loss (DrTGA) on the secondary y axis, both as a function of temperature. On the other hand, from the interface related to the FTIR spectroscopic analysis of the gas phase, a three-dimensional graph is obtained, where the x, y and z axes are time, wave number and absorbance, respectively. Temperature is obtained from the analysis time, initial temperature, and heating ramp.

Pyrolysis of biomass

Pyrolytic experiments of RF and APF samples were carried out at 450 °C under a N₂ flow (Q_{N₂} = 200 mL/min) in a glass down-flow reactor, provided with a porous glass disk at the bottom, to retain the solid products generated and at the same time to allow vapours to escape. The experimental conditions were selected from the preliminary results of TGA-FTIR. The pyrolytic reactor was heated by a vertical electric oven provided with a temperature programmer-controller. About 1.5 g placed inside a porous mesh basket before being rapidly introduced into the isothermal zone of the reactor, which was at a temperature of 450 °C, with a heating rate of 450 °C s⁻¹. The vapours were condensed using a water/ice-bath, for collecting the bioliquid. After the reaction, the reactor was removed from the furnace and cooled in an inert atmosphere to avoid the combustion of the solid. After the experiment, three products were obtained: the bioliquid (collected in the condenser), the biochar (residual in the reactor) and the biogas. The yield of biochar was estimated as the mass difference of the reactor before and after the experiment. The yield of bioliquid was determined by the mass difference of the condenser and connecting tubes before and after the experiment. Finally, the yield of gas products was calculated as the difference from the initial mass of feedstock and the mass of bioliquid plus biochar obtained.^[68] The estimated pyrolytic yields were reported with a repeatability error lower than 1%.

The bioliquids obtained from pyrolysis of RF and APF samples were identified and semi quantitatively determined 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. Data were reported considering a relative error of 2%.

The quantitative measurement of furfural concentration in the studied bio-oils, was carried out with a Varian CP-3800 gas chromatograph equipped with a CP Wax 52 CB (30 m and 0.3 mm) capillary column and a FID detector. A calibration curve, employing a furfural chromatographic standard (Furfural analytical standard, Merck CAS 98-01-1) was used for preparing solutions.

Catalyst Preparation

The monometallic catalyst Ru/C was prepared by impregnation with excess solution on a commercial activated carbon (C) (NORIT, ground and sieved at 60–100 mesh). The ruthenium salt solution had such a concentration to obtain 3 wt.% Ru impregnated on the carbon support. The bimetallic RuSn/C catalyst was prepared using Surface Organometallic Chemistry on Metals techniques (SOMC/M). The experimental details of the preparation methods are gathered in the Supplementary Material. Monometallic and bimetallic catalysts were characterized by temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The characterization procedures are found in the Supplementary Material.

Valorization of the bioliquids obtained by catalytic hydrogenation

The hydrogenation of the crude bioliquid obtained from the pyrolysis of RF and APF samples, was performed in a high-pressure reactor (Berghof BR-100) at a H₂ pressure of 1.25 MPa and 90 °C. The operating conditions were chosen from the results found in a previous work of our research group.^[49] For the experiments, 85 mg catalyst (60–100 mesh) were placed into the reactor, together with 0.15 mL of bioliquid and 50 mL of water. To follow the reaction, a series of microsamples were taken at certain times and analysed by GC. A Varian CP-3800 gas chromatograph equipped with a FID detector was used. The capillary column employed was a CP Wax 52 CB (30 m and 0.3 mm i.d.). The reaction products were identified by GC-MS (GCMS QP-2010 ULTRA, Shimadzu, Japan). The conversion of furfural and the selectivity to the reaction products were calculated using the following expressions (Eq. 1 and 2):

$$X (\%)_{FF} = (C_{FF}^0 - C_{FF}^t) / C_{FF}^0 \cdot 100 \quad (1)$$

$$S (\%)_i = C_i^t / \sum_{i=1}^n C_i^t \cdot 100 \quad (2)$$

Where X_{FF} is the conversion of furfural, C_{FF}^0 is the initial molar concentration of furfural and C_{FF}^t its molar concentration at t (min). S_i is the selectivity and C_i^t s the molar concentration of compound i at t (min).

Acknowledgements

The authors would like to acknowledge the following institutions of Argentina for the financial support, UNNOBA (project SIB 2022), UNLP (project X903, Expte 100–1282/19), CONICET (project PUE 2018, EXP. 8085/17) and ANPCyT FONCyT (PICT 2019/1962).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Biomass · Furfural · Heterogeneous catalysis · Hydrogenation · Pyrolysis

- [1] R. Kajaste, *J. Cleaner Prod.* **2014**, *75*, 1–10.
- [2] Y. Z. Zhang, J. Liu, P. Gao, *Acta Biophys Sin.* **1997**, *13*(3), 375.
- [3] S. Willför, R. Sjöholm, C. Laine, M. Roslund, J. Hemming, B. Holmbom, *Carbohydr. Polym.* **2003**, *52*, 175–187.
- [4] E. Sjöström, *Wood Chemistry: Fundamentals and Applications*, 2nd edition, Academic Press, Inc., San Diego, USA, **1992**.
- [5] P. B. Saynik, V. S. Moholkar, *Bioresour. Technol. Rep.* **2020**, *11*, 100545.
- [6] E. Zadeh, A. Abdulkhani, O. Aboelazayem, B. Saha, *Processes* **2020**, *8*, 799.
- [7] J. O. Scheneiter, I. I. Kaufmann, A. R. Ferreyra, R. T. Llorente, *J. Br. Grassl. Soc.* **2015**, *71*(3), 403–412.
- [8] H. Yang, R. Yan, H. Chen, C. Zheng, D. H. Lee, D. T. Liang, *Energy Fuels* **2006**, *20*, 388–393.
- [9] A. Aho, N. Kumar, K. Eränen, B. Holmbom, M. Hupa, T. Salmi, D. Yu. Murzin, *Int. J. Mol. Sci.* **2008**, *9*, 1665–1675.
- [10] S. Stephanidis, C. Nitsos, K. Kalogiannis, E. F. Iliopoulou, A. A. Lappas, K. S. Triantafyllidis, *Catal. Today* **2011**, *167*, 37–45.
- [11] C.-H. Zhou, X. Xia, C.-X. Lin, D.-S. Tong, J. Beltramini, *Chem. Soc. Rev.* **2011**, *40*, 5588–5617.
- [12] D. C. Elliott, *Hydrothermal processing. In: Thermochemical Processing of Biomass*, (Ed. R. C. Brown), **2011**.
- [13] T. Dickerson, J. Soria, *Energies* **2013**, *6*, 514–538.
- [14] A. V. Bridgwater, D. Meier, D. Radlein, *Org. Geochem.* **1999**, *30*, 1479–1493.
- [15] A. V. Bridgwater, *Biomass Bioenergy* **2012** *38*, 68–94.
- [16] D. Mohan, C. U. Pittman, P. H. Steele, *Energy Fuels* **2006**, *20*, 848–889.
- [17] Z. E. Zadeh, A. Abdulkhani, O. Aboelazayem, B. Saha, *Processes* **2020**, *8*, 799.
- [18] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098.
- [19] D. Carpenter, T. Westover, S. Czernick, W. Jablonski, *Green Chem.* **2014**, *16*, 384.
- [20] G. Dobeles, T. Dizhbite, G. Rossinskaja, G. Telysheva, D. Meier, S. Radtke, O. Faix, *J. Anal. Appl. Pyrolysis* **2003**, *68*, 197–211.
- [21] A. I. Casoni, V. S. Gutierrez, M. A. Volpe, *J. Environ. Chem. Eng.* **2019**, *7*, 102893.
- [22] M. L. Nieva Lobos, P. Campitelli, M. A. Volpe, E. L. Moyano, *J. Anal. Appl. Pyrolysis* **2016**, *122*, 216–223.
- [23] L. Dai, Y. Wang, Y. Liu, R. Ruan, C. H. Z. Yu, L. Jiang, Z. Zeng, X. Tian, *Renewable Sustainable Energy Rev.* **2019**, *107*, 20–36.
- [24] L. Dai, Y. Wang, Y. Liu, C. He, R. Ruan, Z. Yu, L. Jiang, Z. Zeng, Q. Wu, *Sci. Total Environ.* **2020**, *749*, 142386.
- [25] Q. Lu, C.-q. Dong, X.-m. Zhang, H.-y. Tian, Y.-p. Yang, X.-f. Zhu, *J. Anal. Appl. Pyrolysis* **2011**, *90*(2), 204–212.
- [26] Q. Lu, Z. Wang, C.-q. Dong, Z.-f. Zhang, Y. Zhang, Y.-p. Yang, X.-f. Zhu, *J. Anal. Appl. Pyrolysis* **2011**, *91*(1), 273–279.
- [27] C. B. T. Loong Lee, T. Y. Wu, *Renewable Sustainable Energy Rev.* **2021**, *137*, 110172.
- [28] Y. Zhang, J. Wang, P. Lv, N. Bie, P. Cao, Y. Bai, X. Song, G. Yu, *Fuel* **2022**, *317*, 123557.
- [29] Y. Lin, J. Cho, G. A. Tompsett, P. R. Westmoreland, G. W. Huber, *J. Physical Chem. C* **2009**, *113*(46), 20097–20107.
- [30] S.-J. Oh, G.-G. Choi, J.-S. Kim, *Energy* **2015**, *88*, 697–702.
- [31] A. M. Sarotti, R. A. Spanevello, A. G. Suárez, *Green Chem.* **2007**, *9*, 1137–1140.
- [32] M. Shibagaki, K. Takahashi, H. Kuno, I. Honda, H. Matsushita, *Chem. Lett.* **1990**, *19*, 307–310.
- [33] M. B. Comba, Y.-h. Tsai, A. M. Sarotti, M. I. Mangione, A. G. Suárez, R. A. Spanevello, *Eur. J. Org. Chem.* **2018**, 590–604.
- [34] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2007**, *80*, 118–125.
- [35] X. Wang, Y. Liu, X. Cui, J. Xiao, G. Lin, Y. Chen, H. Yang, H. Chen, *Waste Manage.* **2020**, *114*, 43–52.
- [36] D. Zhang, Y. Fan, A. Zheng, Z. Zhao, F. Wang, H. Li, *Catalysts* **2018**, *8*(12), 609.
- [37] Z. Gao, N. Li, M. Chen, W. Yi, *Fuel Process. Technol.* **2019**, *193*, 131–140.
- [38] D. L. Dalluge, T. Daugaard, P. Johnston, N. Kuzhiyil, M. M. Wright, R. C. Brown, *Green Chem.* **2014**, *16*, 4144–4155.
- [39] S. Zhou, D. Mourant, C. Lievens, Y. Wang, C.-Z. Li, M. Garcia-Perez, *Fuel* **2013**, *104*, 536–546.
- [40] X. W. Sui, Z. Wang, B. Liao, Y. Zhang, Q. X. Guo, *Bioresour. Technol.* **2012**, *103*, 466–469a.

- [41] X. Meng, Q. Sun, M. Kosa, F. Huang, Y. Pu, A. J. Ragauskas, *ACS Sustainable Chem. Eng.* **2016**, *4*, 4563–4572.
- [42] A. I. Casoni, P. M. Hoch, M. A. Volpe, V. S. Gutierrez, *J. Cleaner Prod.* **2018**, *178*, 237–246.
- [43] D. Zhang, Y. Fan, A. Zheng, Z. Zhao, F. Wang, H. Li, *Catalysts* **2018**, *8*, 609.
- [44] J. Zhang, J. Luo, D. Tong, L. Zhu, L. Dong, Changwei Hu, *Carbohydr. Polym.* **2010**, *79*, 164–169.
- [45] F. Deng, A. S. Amarasekara, *Ind. Crops Prod.* **2021**, *159*, 113055.
- [46] M. Kabbour, R. Luque, in *Furfural As a Platform Chemical: From Production to Applications, Biomass, Biofuels, Biochemicals*. Elsevier, Amsterdam, **2020**, pp. 283–297.
- [47] Y. Wang, D. Zhao, D. Rodríguez-Padrón, C. Len, *Catalysts* **2019**, *9*, 796.
- [48] A. B. Merlo, V. Vetere, J. F. Ruggera, M. L. Casella, *Catal. Commun.* **2009**, *10*, 1665–1669.
- [49] J. J. Musci, A. B. Merlo, M. L. Casella, *Catal. Today* **2017**, *296*, 43–50.
- [50] J. J. Musci, M. Montaña, A. B. Merlo, E. Rodríguez-Aguado, J. A. Cecilia, E. Rodríguez-Castellón, I. D. Lick, M. L. Casella, *Catal. Today* **2022**, *394–396*, 81–93.
- [51] M. J. Zhang, W. Li, S. Zu, W. Huo, X. Zhu, Z. Wang, *Chem. Eng. Technol.* **2013**, *36* (12), 2108–2116.
- [52] S. Fulignati, C. Antonetti, D. Licursi, M. Pieraccioni, E. Wilbers, H. J. Heeres, A. M. Raspolli Galletti, *Appl. Catal. A* **2019**, *578*, 122–133.
- [53] V. Sánchez, P. Salagre, M. D. González, J. Llorca, Y. Cesteros, *J. Mol. Catal.* **2020**, *490*, 110956.
- [54] M. Pirmoradi, N. Janulaitis, R. J. Gulotty, Jr., J. R. Kastner, *ACS Omega* **2020**, *5* (14), 7836–7849.
- [55] M. K. Samantaray, E. Pump, A. Bendjeriou-Sedjerari, V. D'Elia, J. D. A. Pelletier, M. Guidotti, R. Psaro, J.-M. Basset, *Chem. Soc. Rev.* **2018**, *47*, 8403–8437.
- [56] O. A. Ferretti, M. L. Casella, in *Modern Surface Organometallic Chemistry*, (Eds: J. M. Basset, R. Psaro, D. Roberto, R. Ugo), Wiley-VCH, Weinheim, **2009**, Chapter 6.
- [57] J. Balthrop, B. Brand, R. A. Cowie, J. Danier, J. De Boever, L. de Jonge, F. Jackson, H. P. S. Makkar, C. Piotrowski, *Quality assurance for animal feed analysis laboratories*, FAO Animal Production and Health Manual No. 14, FAO, **2011**.
- [58] A. Anca-Couce, C. Tsekos, S. Retschitzegger, F. Zimbardi, A. Funke, S. Banks, T. Kraia, P. Marques, R. Scharler, Wiebren de Jong, N. Kienzl, *Fuel* **2020**, *276*, 118002.
- [59] M. G. Teixeira, S. De Paiva Silva Pereira, S. A. Fernandes, M. J. Da Silva, *Ind. Crops Prod.* **2020**, *154*, 112680.
- [60] G. Özsin, A. E. Pütün, *Waste Manage.* **2017**, *64*, 315–326.
- [61] H. Yang, R. Yan, H. Chen, D. Ho Lee, C. Zheng, *Fuel* **2007**, *86*, 1781–1788.
- [62] S. Singh, C. Wu, P. T. Williams, *J. Anal. Appl. Pyrolysis* **2012**, *94*, 99–107.
- [63] K. Lazdovica, V. Kampars, L. Liepina, M. Vilka, *J. Anal. Appl. Pyrolysis* **2017**, *124*, 1–15.
- [64] I. Itabaiana Junior, M. Avelardo Nascimento, R. O. Mendonça Alves de Souza, A. Dufour, R. Wojcieszak, *Green Chem.* **2020**, *22*, 5859–5880.
- [65] R. Vinu, L. J. Broadbelt, *Energy Environ. Sci.* **2012**, *5*, 9808–9826.
- [66] S. Zhou, Y. Xue, J. Cai, C. Cui, Z. Ni, Z. Zhou, *Chem. Eng. J. (Amsterdam, Neth.)* **2021**, *411*, 128513, and other there reported.
- [67] P. J. Van Soest, J. B. Robertson, J. B. Lewis, *J. Dairy Sci.* **1991**, *74*, 3583–3597.
- [68] I. Y. Mohammed, Y. Abdalla, Abakr, S. Yusup, P. Adeniyi Alaba, K. Isima Morris, Y. Muhammad Sani, F. Kabir Kazi, *J. Cleaner Prod.* **2017**, *162*, 817–829.

Submitted: June 10, 2022

Accepted: October 14, 2022