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Fast pyrolysis of rice husk under vacuum conditions to produce levoglucosan

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Abstract

Levoglucosan (LG)-enriched pyrolytic oils were obtained from rice husk by lab-scale fast pyrolysis under vacuum conditions. We studied the effect of the pyrolysis temperature (300-700 °C) and the pretreatment of the biomass, on the pyrolysis product yields and the selectivity for LG formation. The maximum oil yield (47 wt.%) was obtained from hydrochloric acid-leached rice husk at 400°C, producing 1.4 times more than the amount of oil produced from untreated rice husk at the same temperature. Anhydrosugars were the predominant compounds found in bio-oils under all conditions assessed, LG being the main product. Depending on the pyrolysis conditions, LG concentration was between 9-30 wt.% considering the bio-oil mass, and between 4-60 wt.% considering the initial cellulose mass. ¹H NMR experiments were carried out as an alternative and simple technique to directly determine the amount of LG in bio-oils.

Keywords

Fast pyrolysis; rice husk; levoglucosan, acid treatment; NMR experiments

1. Introduction

As a consequence of the increase in agricultural production in recent decades, agricultural waste has become a major issue for rural system sustainability. These waste streams are generally lignocellulose materials that without adequate treatment can become sources of pollution. Rice husk (RH), which is approximately 20% of the total paddy production is normally burnt, leading to a number of environmental and health issues. According to the Food and Agriculture Organization (FAO), in 2018 the annual paddy rice production was about 770 million tons.[1,2] This means that in 2018 alone, approximately 154 million tons of rice husks were produced around the world. RH contains approximately 80% of organic compounds, mainly cellulose (25-40%), hemicellulose (20-30%) and lignin (15-25%). These percentages can change according to the variety, location, soil conditions, and other factors associated with the growth conditions.[3–5] The remaining components in RH are inorganic materials, mainly silica (18-23%), and to a lesser extent other metal ions, chlorides, phosphates, etc., that are characteristic of the particular soil type.[6,7]

A large number of studies explore the valorization of RH for applications such as fuels, syngas, absorbents, silicon precursor, among others. The transformation process has been in most cases thermochemical conversion, which is mainly gasification, combustion and pyrolysis.[3–5,8–10] Pyrolysis, that is the thermal decomposition of biomass in absence of oxygen, produces three fractions for different applications: biochar, bio-oil, and gas.[11,12] These fractions are obtained in different proportions according to the heat rate, final temperature, pressure, and residence times. According to the range of these conditions, pyrolysis can be classified into three classes as flash, fast and slow. Each

of these classes favours the production of one fraction[11–14]. The bio-oil or liquid fraction has been the subject of much research due to the organic compounds in its composition that can have several applications. Bio-oil have organic compounds that once extracted are suitable for industry. For instance, Weldekidan et al. [5] used solar pyrolysis on RH at temperatures between 500-800°C, producing yields of bio-oil between 21-43 wt.%. They observed the formation of different products that were classified in acids, alcohols, phenols and, in a lower proportion, esters, ketones and aldehydes. Although the compounds found were similar, the proportion of each varied according to the pyrolysis temperature. These RH bio-oils presented a high content of oxygen and acid, and are not suitable for application as bio-fuels.

On the other hand, Cai et al. [15] carried out fast pyrolysis on RH in a fluidized bed reactor where they optimized the yield at 500°C producing 46.9 wt.% of bio-oil. The bio-oil components were divided in nine groups and the majority fraction corresponded to phenolics. This fast pyrolysis mechanism also generates anhydrosugars derived from dehydration reactions of glucose.

Among the chemicals obtained from pyrolysis of lignocellulosic biomass, 1,6-anhydro- β -D-glucopyranose (LG) has an established market as a chiral raw material for the synthesis of oligosaccharides, biologically active compounds and pharmaceutical additives.[16,17] LG produced from lignocellulosic wastes in large scale through fast pyrolysis at a low cost has the potential to be an attractive sugar precursor for biofuels. This anhydrosugar can be upgraded into transportation fuels via fermentation to alcohols; catalytic synthesis to hydrocarbons; dehydration to furan derivatives, among other transformations.[18]

The yield of LG from pyrolysis of cellulosic biomass is known to be influenced by many factors, but temperature and the inorganic impurities are the most important.[19] A maximum yield is usually produced at around 500°C and in these pyrolytic systems, the polymerization and vaporization of LG are simultaneous and compete with one another.[20]. Among the main inhibitors of the generation of LG, alkali and alkaline earth metals are the most important because they can promote the fragmentation of cellulose into non-condensable gases. These ions also catalyze the fragmentation of LG to produce low-molecular-weight oxygenated compounds[21–23]. Pretreatment of the starting biomass with hot-water, acid, alkali or microwave irradiation have been used to eliminate these impurities and improve LG formation.[16,24–26]

LG yield increases with increasing crystallinity of cellulose. The ratio of cellulose:hemicellulose and cellulose:lignin affects the formation of anhydrosugars as well as volatile products.[27]. The generation of LG is favoured under vacuum conditions, since it effectively vaporizes before the fragmentation. Accordingly, in fast pyrolysis systems where the residence time is short and quick recovery of the product vapor can be achieved, the production of LG is higher.[28]

The formation of LG during pyrolysis of RH has not been studied in depth. Guo et al. found that LG represents 5% of the relative content in the bio-oil obtained at 520°C after distillation, predominantly in the middle and heavy fractions.[29] The chemical and thermal pretreatment of RH have significant influence in the production of LG. The combination of acid washing and torrefaction of RH before pyrolysis at 550°C, promoted a of 4x increase in LG yield respect to raw husks.[30] It is worth stating that in most of cases the

quantification of anhydrosugars is difficult and the conventional analysis requires pretreatment for HPLC or similar techniques used for determination.

The aim of this work was to evaluate the content of LG in the bio-oils obtained from fast pyrolysis of untreated and hydrochloric acid-treated rice husk under vacuum conditions. Pyrolysis carried out in vacuum media has advantages compared to other techniques. Very short residence time of the organic vapor in the reactor facilitates the formation of bio-oil and enhances the selectivity of determined compounds.[31–34] Based on these features we studied the pyrolysis of rice husk applying vacuum to improve the formation of LG. In addition, we performed ^1H NMR experiments using an internal standard as an alternative and easy method for direct quantification of LG in bio-oils.

2. Materials and methods

2.1. Materials

The rice husk used in this work was collected in June 2018 by the National Institute of Agricultural Technology (INTA) in Concepción del Uruguay, province of Entre Rios, in the Mesopotamia region of Argentina.

2.2. Characterization of rice husk materials (RH and A-RH)

The physical properties of acid treated (A-RH), and un-treated RH are listed in Table 1. Rice husk materials were analyzed for carbon, hydrogen, nitrogen and sulfur using an elemental analyzer (Elementar Analysensysteme GmbH, Germany) with an electronic microbalance. In the proximate analysis, ash

is the remnant material after complete combustion, volatile is the volatilized proportion from rice husks when it is heated in the absence of oxygen and fixed carbon is the residue after complete volatilization.

RH was hydrolyzed using TFA (flushed with Argon) at 100 °C for 4 h. Samples were evaporated completely in a centrifugal evaporator. The pellet was washed with IPA, mixed and evaporated, and re-suspended in ELGA water. The supernatant was placed in HPLC vials after filtration through 0.45µM filters. The monosaccharide composition analysis was performed using high-performance anion exchange chromatography (HPAEC) (Dionex, Camberley, UK).[35] A calibration curve containing a mixture of nine monosaccharides (Ara, Fuc, Gal, Glu, GalA, GlcA, Man, Rha, Xyl) was used for determination and quantification. For cellulose quantification, the pellet previously obtained was washed with 1.5 mL of water, stirred, centrifuged, and the supernatant was discarded. This was repeated three additional times using 1.5 mL of acetone and was left to air dry overnight. The resulting pellet (crystalline cellulose) was completely hydrolyzed by adding with 90 µl 72% sulfuric acid (Saeman hydrolysis) and incubated at room temperature for 4 h at 25 °C to break H-bonds. After incubation, water was added in order to reach 3.2% w/w sulfuric acid (1890 µL), vortexed and heated for 4 h at 120°C. The glucose content of the supernatant was assayed using the colorimetric Anthrone assay.[36]

For the lignin content analysis, the husk rice (4 mg) powder were incubated 4h at 45°C with 0.3 mL 25% (v/v) acetyl bromide/glacial acetic acid, then the mixture was cooled down to 15°C for adding 0.3 mL glacial acetic acid, followed by a 5 min vortex. 0.5 mL of reaction mixture above were added to a tube containing 0.1 mL of 0.5 M hydroxylamine and 1 mL of 2M sodium hydroxide solution. Tubes

were gently shaken after acetic acid was added to give a final volume of 10 mL. The final solutions were read in spectrophotometer at 280 nm, the percentage of total lignin content in the dry sample was calculated as [37]:

$$\% \text{ Lignin} = \{\text{abs}/(\text{coeff} \times \text{pathlength})\} \times \{(\text{total volume} \times 100\%)/\text{biomass weight}\}$$

where coefficient = 17.75; Path length = 1; total volume = 5 and biomass weight = 3.5

For the quantification of extractives one gram of each sample (milled through 1mm sieve) was washed with 96% ethanol at 100°C for 30 min and the supernatant recovered (repeated 4 times). Extractive-free residue (pellet) and supernatants (previously gathered) were dried at 45°C for 3 days. Supernatants were weighed and stored.[38]

The powder X-ray diffraction patterns (PXRD) were recorded in a diffractometer Panalytical X'Pert Pro, using a Cu K α (λ =1.5418 Å) radiation with current conditions at 40 mA and voltage at 40 kV. The patterns were collected using a pixel 1D detector with 230 canals; each pattern was recorded between 10-70° with a step of 0.026° and with a time for step of 92.95 s at room temperature. The samples were taken using a single crystal silicon sample port. The crystallinity index parameter (CI) measured by PXRD has been used to determine and compare the relative amount of crystalline cellulose in various materials.[39,40] In order to compare the relative degree of crystallinity between RH and A-RH, the crystallinity index (CrI) was determined in accordance with the reflected intensity data using the following equation [39]:

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

where I_{002} and I_{am} correspond to the maximum intensity of the lattice diffraction 0 0 2 and the minimum intensity between the peaks diffraction 0 0 2 and 1 0 1 respectively.[36,37,39,40]

FT-IR spectra of the materials were recorded as powder samples on a Nicolet iN10 (ThermoFisher Scientific) infrared microscope in the range of 4000–400 cm^{-1} using a liquid nitrogen cooled detector of Mercury Cadmium Tellurium (MCT). Measurements were obtained from 30 scans with a resolution of 4 cm^{-1} . Data were analyzed using the OMNIC software.

The content of silicon, potassium, calcium, iron, aluminum, magnesium, and phosphorus were determined by an ICP-MS Agilent 7800 equipment. Samples were diluted using a mixture of HNO_3/HCl (1 %/0.5 %) followed by digestion for 24 h. Standards and blanks were prepared using the same acid mixture. Instrumental and procedural blanks were determined together with samples, and the means of five runs were obtained for each sample. Full quantitative analysis was performed against calibration standards for each element. Precision (% CV) was below 3 % considering five measures on the same sample.

2.3. Pretreatment of rice husk

RH were washed three times with deionized water with stirring for 15 min in order to remove impurities. After washing, RH were dried in an oven at 105 °C overnight and stored at room temperature. RH were treated with hydrochloric acid (Merk 37%) in order to eliminate inorganic ions that may be present in the material. The acid leaching was done by refluxing RH in a solution of HCl (5% v/v) during 1h, with a ratio of 50g RH: 1L HCl solution. After the leaching process,

the RH were washed several times with deionized water in stirring until the final solution had a neutral pH. Subsequently, the acid treated RH (A-RH) were dried in an oven at 105 °C overnight and stored until their use in the pyrolysis process. The acid treatment caused a decrease of 30 wt% in the materials.

2.4. Fast pyrolysis procedure

The fast pyrolysis reactions were carried out in a tubular quartz reactor under Nitrogen atmosphere. The reactor was heated externally with a tubular furnace and the temperature was regulated by a thermocouple and a controller. The reactor had a length of 25 cm and an inner diameter of 2.5 cm, which was connected to a vacuum line, where a vacuum pump gave vacuum conditions inside the reactor with pressures around the 1-5 Torr. Likewise, Nitrogen flow was circulated inside the reactor for 10 minutes during and 10 minutes after the pyrolysis process at a flow of 0.1 mL/s (each reaction took 20 minutes) to ensure Oxygen absence.[32] The residence times were short (approximately 0.1 s). At the end of the hot zone in the reactor there was a condensation trap refrigerated with liquid nitrogen where the liquid products were collected. The RH were placed in a quartz boat and typical reaction was carried with 1-1.5 g of RH located inside the reactor in a cool zone until the vacuum line reached the desired conditions of pressure and temperature. The reaction time was recorded from the moment in which the material was placed in the center of the high-temperature zone. When each pyrolysis reaction ended, the solid residue remaining in the boat was recovered and weighed. Likewise, the bio-oil was removed from the trap with acetone, and later evaporated, weighed and analyzed by GC-MS. The gas fraction was calculated by the weight difference between the initial mass of RH and the solid and liquid fractions. Samples of RH and A-RH were pyrolyzed at

300, 400, 500, 600 and 700 °C. Relative standard deviation (RSD) was used to assess intra- and inter-day precisions by three replicates per pyrolysis experiment and accomplished by the same operator.

2.5. Bio-oil characterization

GC/MS analyses of the bio-oils were performed in a Shimadzu GC–MS-QP 5050 spectrometer. The injector temperature was 300°C and the separation was performed using a VF-5ms capillary column. Helium was used as a carrier gas with a constant flow rate of 0.5-1.0 µL/min. The oven temperature was programmed from 80 °C (3 min) to 280 °C (15 min) with a heating rate of 10 °C/min. The temperature of the GC/MS interface was held at 280 °C and the mass spectrometer was operated at 70 eV under electron ionization. The peak area of an individual compound was directly proportional to the concentration of such compound in the liquid pyrolysate. Thus, the peak area percentage of a compound was used to compare the change in the relative amount in the bio-oil under different conditions. The identification of chromatographic peaks corresponding to the different compounds was done using the NIST MS library (match > 85%). The identification of LG (1,6-anhydro-β-D-glucopyranose) was established by comparison with a standard.

2.6. Quantification of LG in bio-oils

The quantification of LG in pyrolytic bio-oils was carried out by ¹H NMR experiments using Presat for water suppression. Presat is a simple two-pulse experiment that utilizes a relatively long, low power RF pulse to selectively saturate the specific frequency of water, and a non-selective 45-90° pulse to

excite the desired resonances. This pulse sequence was particularly useful for aqueous samples or those with a single large solvent signal. NMR spectra were recorded with a 400 MHz Bruker spectrometer at room temperature. The samples were prepared weighing 1.0-2.0 mg of oils and 0.5-1.0 mg of pure naphthalene as internal standard, and the mixture was then dissolved in acetone- d_6 (0.5-1.0 mL) until the solution was transparent. The integration of the signal at 5.27 ppm of LG and the signals at 7.89-7.91 ppm of naphthalene were used for direct quantification of LG in bio-oils.

3. Results and discussion

3.1. Characterization of RH materials

The composition of raw and acid leached RH is shown in Table 1. Acid treatment had little impact on the ash, fixed carbon and volatiles content. Ash and fixed carbon decreased while volatiles increased by small amounts. In the ultimate analysis, moderate changes of elemental compositions could be observed. During leaching processes on RH, the carbon and hydrogen content increased while oxygen, nitrogen and sulfur content decreased. These results are in agreement with previous studies of chemical treated biomass.[33,41] Regarding the biopolymer composition, the proportion of cellulose and hemicellulose increased significantly after the acid treatment by the removal of inorganic ions. Lignin, meanwhile, decreased by a small proportion and extractives disappeared after acid impregnation.

By analyzing the composition of the matrix monosaccharides, significant changes in the concentration of several sugars were observed after acid

impregnation. The amount of glucose, rhamnose, galactose, xylose and galacturonic/glucuronic acids decreased in A-RH respect to RH. The effect was more pronounced in the case of rhamnose, galactose and galacturonic acid where the quantity decreased 12, 8 and 3.7 times respectively, relative to the raw material. On the contrary, the leaching of RH increased the quantity of fucose, arabinose and mannose 2.3, 1.9 and 1.5 times respectively. Overall the total amount of monosaccharides determined was lower after acid impregnation process of the husk. Similar variations in the sugar composition have been observed in treatments of different cellulosic materials.[42] Regarding the content of inorganic species, Si accounted for a high percentage of the total species while P and Al accounted for very small amounts in the rice husk samples. The HCl leaching of the husk removed alkali (K), alkaline earth (Ca, Mg) metallic species, and other metals such as Al and non-metallic species such as P. In the case of Si and Fe, the removal by acid leaching was on a smaller scale than for the other species. These results agree with previous studies concerning the effect of mineral and organic acids on the removal of inorganic species on rice husk.[41,43]

Table 1. Properties of raw and acid leached RH samples

Analysis		RH ^a (%)	A-RH ^b (%)
Proximate analysis ^c	Ash	15.5	14.2
	Fixed carbon	14.9	13.8
	Volatile matter	69.6	71.6

Ultimate analysis (wt.%) ^c	C	42.1	44.8
	H	6.1	6.5
	O ^f	34.9	33.4
	N	1.2	1.0
	S	0.2	0.1
Composition analysis (wt.%) ^c	Cellulose	35.7	46.2
	Hemicellulose	22.8	27.7
	Lignin	28.1	26.1
	Extractives	13.5	-
Monosaccharide composition ^d	Glucose	11.5	10.0
	Arabinose	2.8	5.3
	Rhamnose	1.2	0.1
	Galactose	8.0	1.0
	Fucose	0.6	1.4
	Xylose	5.1	4.6
	Mannose	0.6	0.9
	Galacturonic acid	4.4	1.2
	Glucuronic acid	0.4	0.3
Inorganic ions ^e	Silicon	7.49	6.89

Potassium	0.46	0.07
Iron	0.06	0.04
Calcium	0.12	0.03
Aluminum	0.03	0.02
Magnesium	0.08	0.007
Phosphorus	0.01	0.002

^aUntreated RH, ^hHydrochloric acid-treated RH, ^cDry basis, ^d Expressed as g monosaccharide per 100g biomass, ^eDetermined by ICP analysis, ^fCalculated by difference.

The PXRD profiles obtained from the RH and A-RH are shown in Figure 1. The profiles obtained have mainly amorphous structures (broad peaks and low intensity) compared with the polycrystalline materials that are the typically analyzed with PXRD. This pattern is expected because the lignin and hemicellulose present in the RH are amorphous.[44,45] Despite this, we can observe in the patterns three wide crystalline peaks around $2\theta = 16, 22$ and 35° , these peaks, according to Klemm et al. [46], correspond to cellulose crystalline structure. Likewise, in Figure 1 the pattern of A-RH showed a small increase in the intensity and definition of the peaks. The acid treatment does not affect the crystalline structure, but decreases amorphous polymers in the biomass.[44–46]

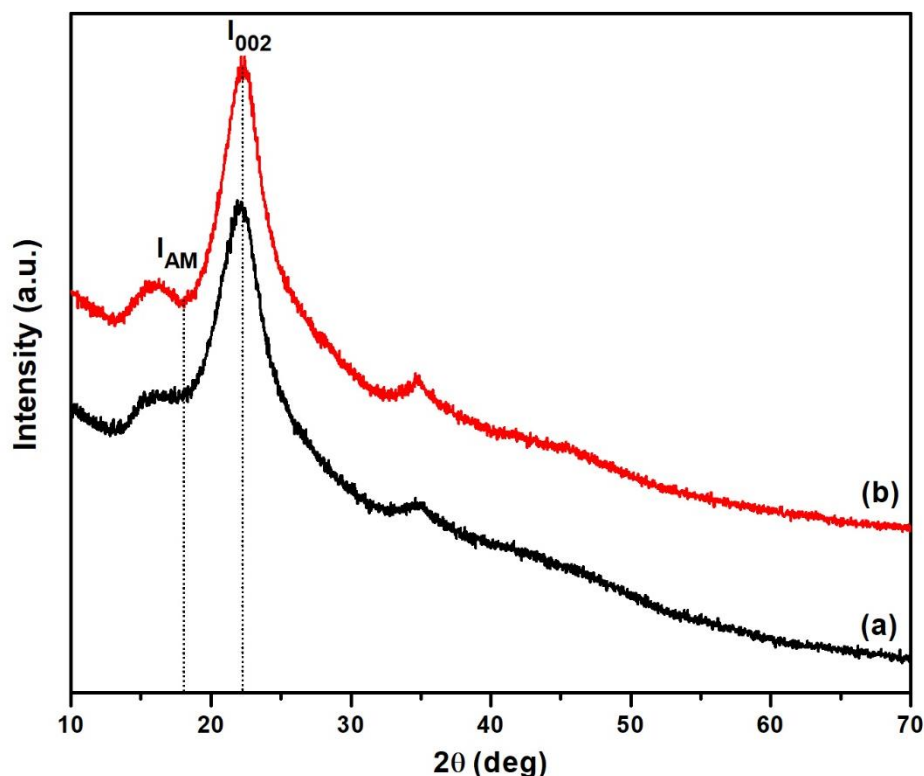


Figure 1. PXRD profiles obtained from: (a) RH and (b) A-RH samples.

The crystallinity index (Crl) calculated for the RH was 48% while the value for A-RH was 57%. This result shows that the acidic treatment of the material increased the crystallinity by approximately 10%. This effect has been observed in the acid leaching of various cellulosic materials.[32,45]

FTIR analyses of RH and A-RH samples are shown in Figure 2. For both materials wide and strong O–H and C–H stretching bands are observed between 3700 and 3000 cm^{-1} . Also, the band that appears around 1633 cm^{-1} corresponds to the adsorption of water assigned to the asymmetric stretching of O–H groups of the absorbed water molecules.[44,45,47] Both sets of peaks are ascribed to the stretching of hydrogen bonds and bending of OH groups present in the

cellulose structure. These bands indicate that the cellulose was not removed by the acid treatment applied to A-RH, in agreement with the DRX results discussed above.

The band at 2919 cm^{-1} corresponds to the stretching of C–H bonds from aliphatic CH_2/CH groups that are present in the structure of the cellulose and hemicellulose.[48] A small band at 1728 cm^{-1} attributed to the stretching vibrations of C=O bonds of carboxy groups present either in the hemicellulose or in ferulic and p-coumaric acid in lignin, is present in the spectrum of the RH sample.[44,45,47,48] The absence of this band in the A-RH sample is attributed to the elimination of amorphous hemicellulose or lignin during the acid treatment.

In both materials, bands observed at 1509 cm^{-1} and 1424 cm^{-1} are attributed to the aromatic C=C stretch from aromatic rings present in lignin.[49] The small bands at 1375 cm^{-1} could be attributed to the deformations of the C–H bond in methyl alcohol and phenols, or could be associate with $-\text{CH}_2$ groups.[44,50] Silicon dioxide in RH is confirmed by the bands at 1023 cm^{-1} and 798 cm^{-1} corresponding to the stretching and bending vibrations of bonds O–Si–O.[7,50]

RH and A-RH spectra show the characteristic bands of components such as cellulose, hemicellulose, lignin, and silica. RH presents small bands that disappear in the A-RH sample, by the effect of the acid impregnation that eliminates some amorphous structures.

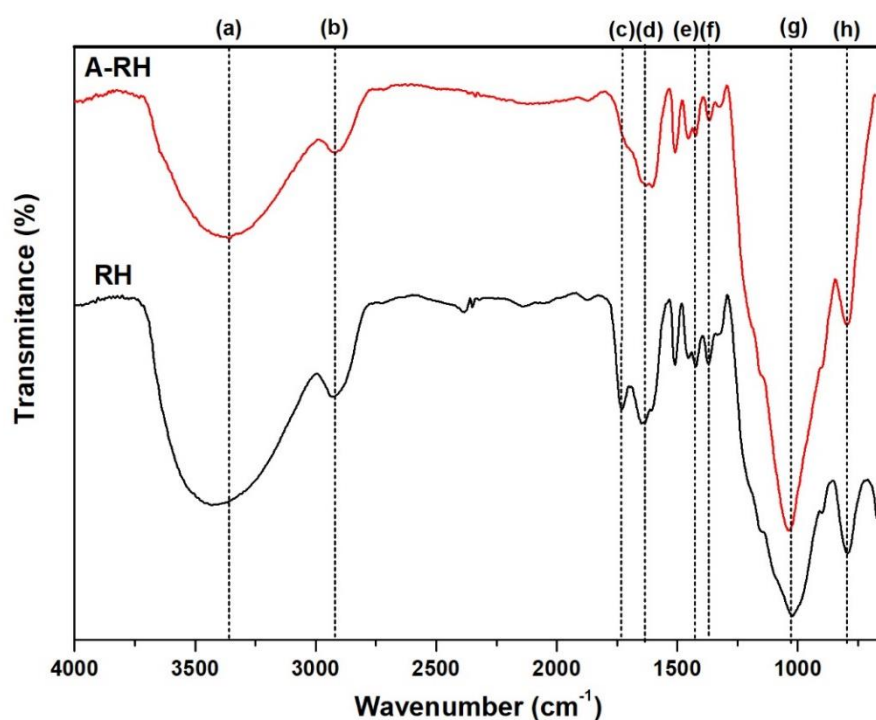


Figure 2. FTIR spectra of RH and A-RH. FT-IR spectral bands (cm^{-1}): **(a)** 3355; **(b)** 2919; **(c)** 1728; **(d)** 1633; **(e)** 1424; **(f)** 1375; **(g)** 1023; **(h)** 798

3.2. Fast pyrolysis of RH

The fast pyrolysis of RH and A-RH was carried out at 300, 400, 500, 600 and 700°C (Figure 3). In RH pyrolysis (Fig. 3a), gas products were the major component at most temperatures (37-55% yield). Solid product (biochar) was the main product at 300°C (45% yield). The liquid fraction reached the maximum yield at 400°C (34%) and remained almost constant between 500-700°C. The pyrolysis of A-RH produced a different distribution of products. The pyrolytic oil was predominant between 400-700°C, reaching maximum yield at 400°C (47 wt.% yield, 1.4 times higher compared with RH) (Fig. 3b). The yield of oils from pyrolysis of RH and A-RH at 400°C were similar to the values reported in the literature using fixed and fluidized-bed reactors at higher temperatures without

catalysts (from 450 to 650°C).[29,51–54] but lower than yield values obtained in catalytic processes.[52,55]

Biochar was the main product at the lowest temperatures evaluated, while the formation of gases increased from 400°C, and remained unchanged from 600°C.

According to these results, the acid impregnation of RH significantly improved the production of bio-oil, which would favour the production of LG.

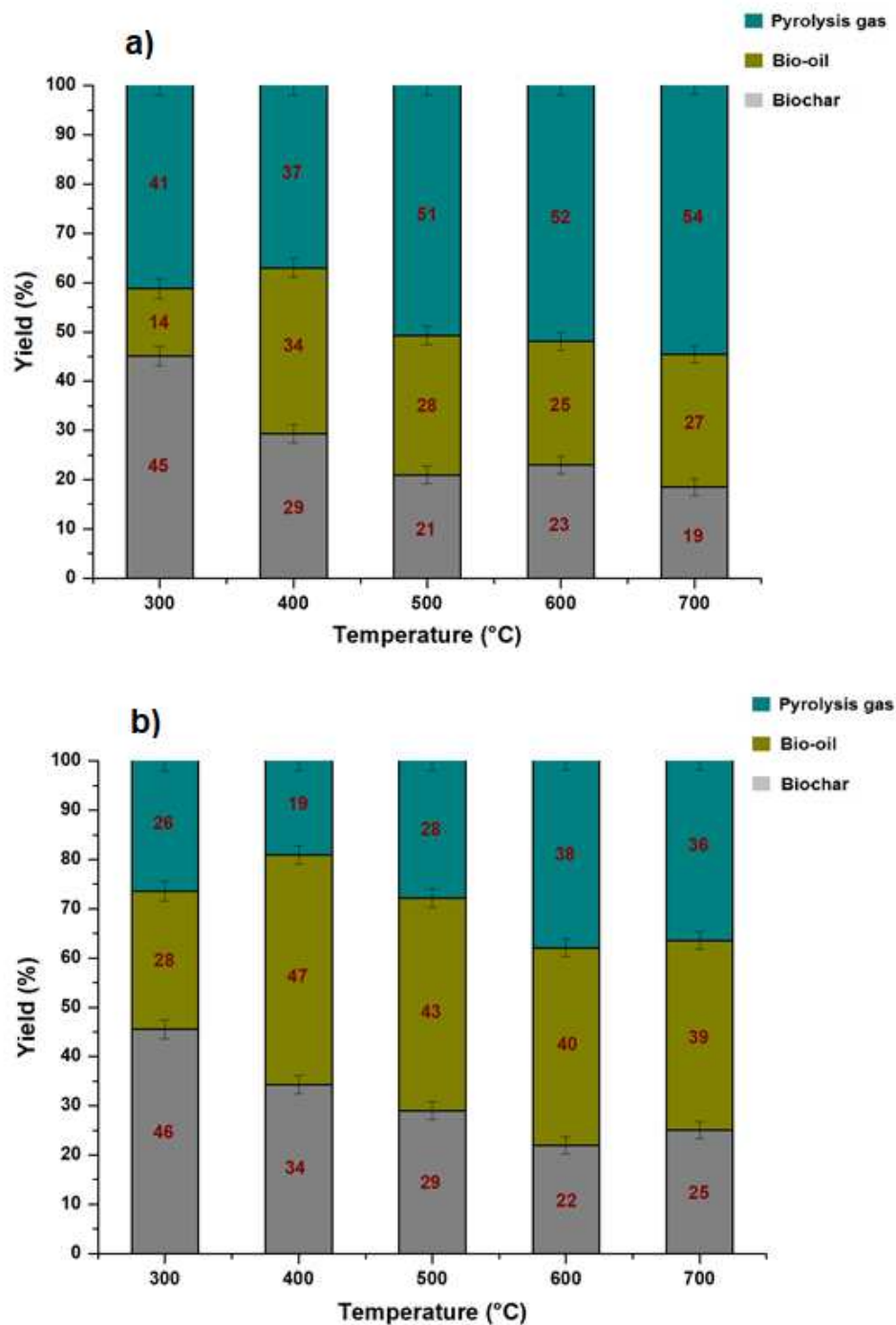


Figure 3. Product yields from pyrolysis reactions of rice husk: **(a)** RH, **(b)** A-RH

The composition of bio-oils from the pyrolysis of RH and A-RH was analyzed using GC-MS. According to the ion chromatograms and the main

families of compounds in each bio-oil, the following groups can be distinguished: aliphatic hydrocarbons (Hyd), aromatic compounds (Ar), furan derivatives (Fur), oxygenates (Oxy), anhydrosugars (Anh), and others outside in the previous groups. The variation in these types of compounds is shown in the Figure 4.

Aliphatic hydrocarbons were minority compounds in the pyrolysis of RH and A-RH. In RH reactions, the amount increased to 11% of the total area at 700°C. The bio-oils derived from A-RH had 0.4-3%, of hydrocarbons where C₈–C₁₃ alkanes were the main contributors.

Aromatic compounds (Ar) were obtained in the pyrolysis of both materials at all evaluated temperatures. For RH pyrolysis, the amount of Ar gradually increased with the increase in temperature, reaching a maximum of 27% of the total area at 700°C. In the bio-oils from A-RH, a substantial increase in aromatics was observed between 600-700°C, reaching 29% at 700°C. Within the main derivatives, xylenes, phenol, methyl-phenols, 1,2-benzendiol, 3-hydroxy-4-methoxy-benzaldehyde and guaiacols were found. It has been reported that phenolic compounds are products derived primarily from the fractionation of lignins present in the biomass. Lignins are more thermally stable than cellulose and hemicellulose during biomass pyrolysis and their degradation occurs at temperatures higher than 500°C.[56] The phenol derivatives detected in RH and A-RH-derived oils have been observed in other studies related to rice shell pyrolysis between 450-550°C. However, in several of those studies the amount of phenols was much higher, reaching 30-60% of the total peak areas calculated from GC-MS analysis, and these values increased in catalyzed reactions.[15,52,54,55]

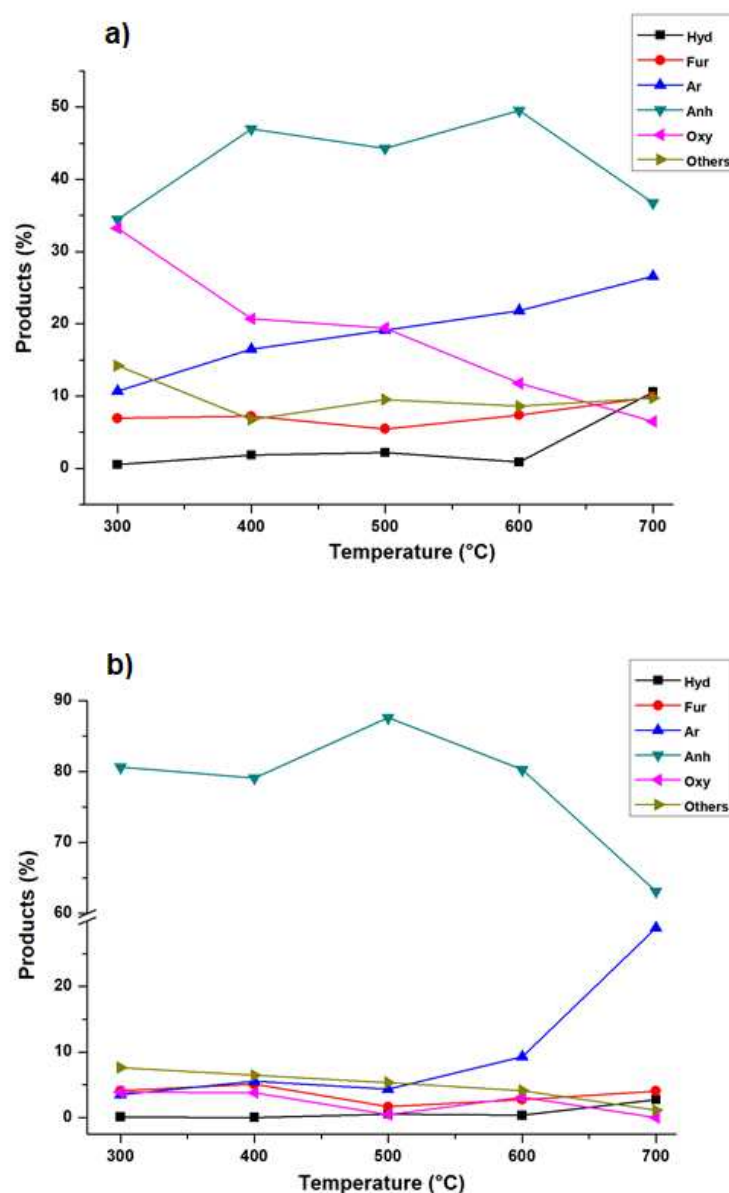


Figure 4. Composition of bio-oils from pyrolysis by GC-MS technique: **(a)** RH, **(b)** A-RH. Hyd: aliphatic hydrocarbons, Ar: aromatic compounds, Fur: furan derivatives, Oxy: oxygenates and Anh: anhydrosugars.

Furan ring-containing compounds (Fur) are formed from the pyrolysis of cellulose and hemicellulose in different pathways, such as depolymerization,

isomerization, and dehydration.[56] Based in our results, the formation of Fur took place from both RH materials under all conditions tested. In the case of RH-derived oils, the higher amount was detected at 700°C (10% of the total area) while in the A-RH oils Fur was between 2-5%. The main compounds of this group were 2,3-dihydro-benzofuran (DHBF), 5-hydroxymethyl furfural (HMF) and 4-hydroxy-dihydrofuran-2-one. DHBF has been reported as one of the main oxygenated products in pyrolytic oils obtained from RH using different fixed and fluidized bed reactors between 500-650°C.[30,55,57] Furan compounds are generated not only from the series reactions of 4-O-methyl-*D*-glucuronic acid units on the xylan branch, but also from multistep dehydration reactions after opening the ring of the D-xylose units on the xylan branch. In this last sequence, DHBF can be formed by rearrangement of poly-hydroxy-hexadienal species,[55] although other authors have proposed the formation of this compound as an intermediate in the generation of benzofuran from the degradation of lignin-derived phenols.[58]

Oxygenated compounds, such as ketones, aldehydes, carboxylic acids, alcohols and ethers, are produced in significant amounts in reactions from RH. At the lowest temperatures, the formation was significant, reaching the highest at 300°C (33% of the total area). In the pyrolysis of A-RH, the formation of oxygenates was minimized, representing less than 4% of the total area. Compounds such as 3-methylcyclopentane-1,2-dione, cyclohexanone, pentanal, cyclic ethers, acetic acid and C₄–C₁₆ carboxylic acids were predominant in the oils. According to the literature, the variation of this type of products in bio-oils from RH is very large. The quantity and quality of the oxygenated products that are obtained is determined mainly by the pyrolytic technique and the

temperature.[30,55] For example, Zhao et al. [52] found 34% of carbonyl derivatives in bio-oils from RH pyrolysis using a fixed bed reactor at 550°C, while Zhang et al. [30] obtained more than 45% of oxygenated compounds (including carbonyls and alcohols) at the same temperature. The yield of oxygenates can be reduced by using different catalysts, thus mesoporous materials have demonstrated to be efficient for deoxygenation of the product vapor due to the cracking reaction of the catalysts.[59]

Organic nitrogen-containing compounds were detected in very small quantities (1-2%) in bio-oils from both types of RH. Finding small amounts of nitrogenates agreed with the low nitrogen content in the initial biomass. We consider these products within the group of "others" along with additional derivatives such as silylated and unidentified compounds.

The sugar fraction was particularly important in the oils derived from treated and non-treated RH. In the case of RH pyrolysis, the largest quantity was obtained at 600°C (50% of the total area) although significant quantities were also obtained at lower temperatures (44 and 47% between 400-500°C). Acid treatment of RH produced a strong effect on sugar production, reaching 63-88% of the total area and maximum production at 500°C. The main components of this fraction were: LG, 1,4:3,6-dianhydro-D-glucopyranose (DGP), 2,3-anhydro-D-mannosan (AM) and 1,6-anhydro-D-glucofuranose (AGP). In the reactions of A-RH, levoglucosenone (1,6-anhydro-3,4-dideoxyhex-3-enopyran-2-ulose, LGO) was also detected between 300-400°C.

The decomposition of cellulose can occur by two competitive reactions where one is the formation of anhydrocellulose and the other is the

depolymerization to form LG, which can undergo dehydration and isomerization to form other anhydrosugars, including LGO and DGP.[32,33,60] The formation of LGO is induced in the pyrolysis of acid-treated biomass, and DGP has been proposed as an intermediate in the dehydration of LG to generate LGO.[61,62] All these anhydrosugars can react further to generate glyceraldehyde, glycolaldehyde and furans by dehydration, fragmentation, retro-aldol reactions and other rearrangements.[63]

The composition of anhydrosugars in the fast pyrolysis of RH and A-RH, shows predominantly LG under all conditions evaluated (Figure 5). Thus, LG represented between 87 and 96% of the total sugars, originating in higher amounts from acid treated husk rice. DGP and AM have also been detected in smaller amounts than LG in oils from catalytic and non-catalytic pyrolysis of RHs.[54,55]

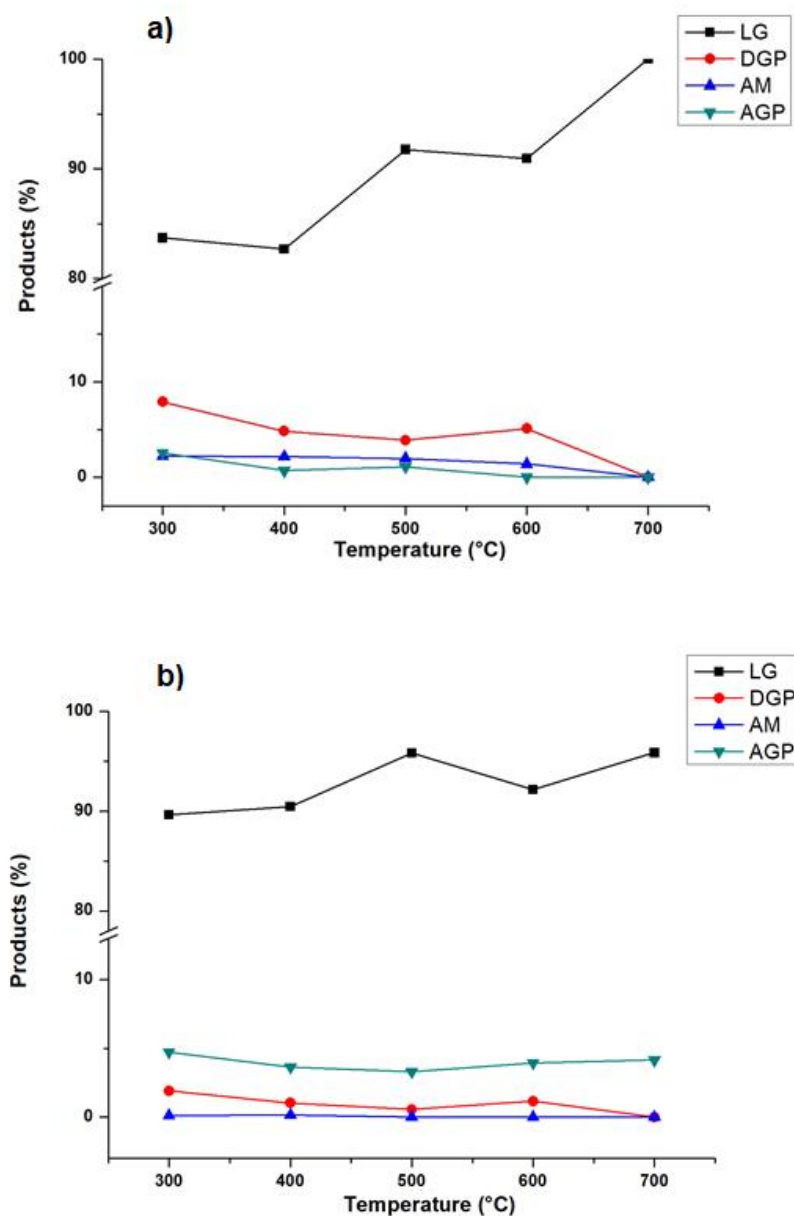


Figure 5. Variation of anhydrosugars in the oils produced from: **a)** RH and **b)** A-RH. LG: levoglucosan; DGP: 1,4:3,6-dianhydro-D-glucopyranose; AM: 2,3-anhydro-D-mannosan; and AGP: 1,6-anhydro-D-glucofuranose.

The yield of LG from the pyrolysis of lignocellulosic biomass is low, but several studies found that impregnation of biomass with a weak mineral acid solution prior to pyrolysis increased LG yields to ~60 wt%.[16,64,65] Zhang et al.

[41] found that the use of acetic acid-treated RH incremented LG content four times in comparison to untreated material.[16] In our experiments, the hydrochloric acid treatment of RH improved 1.9 times the relative content (resolved by areas in GC-MS) of LG in oils. Considering the significant LG formation in all pyrolytic reactions of RH, we carried out a quantitative determination of LG in the bio-oils obtained. We used ^1H NMR due to the ease of identifying LG proton signals and the possibility of using an internal standard such as naphthalene. The signals considered for quantification were the methine proton in LG (H_a) at 5.27 ppm and the four symmetric aromatic protons (H_b) of naphthalene at 7.89-7.91 ppm, as shown in the Figure 6.

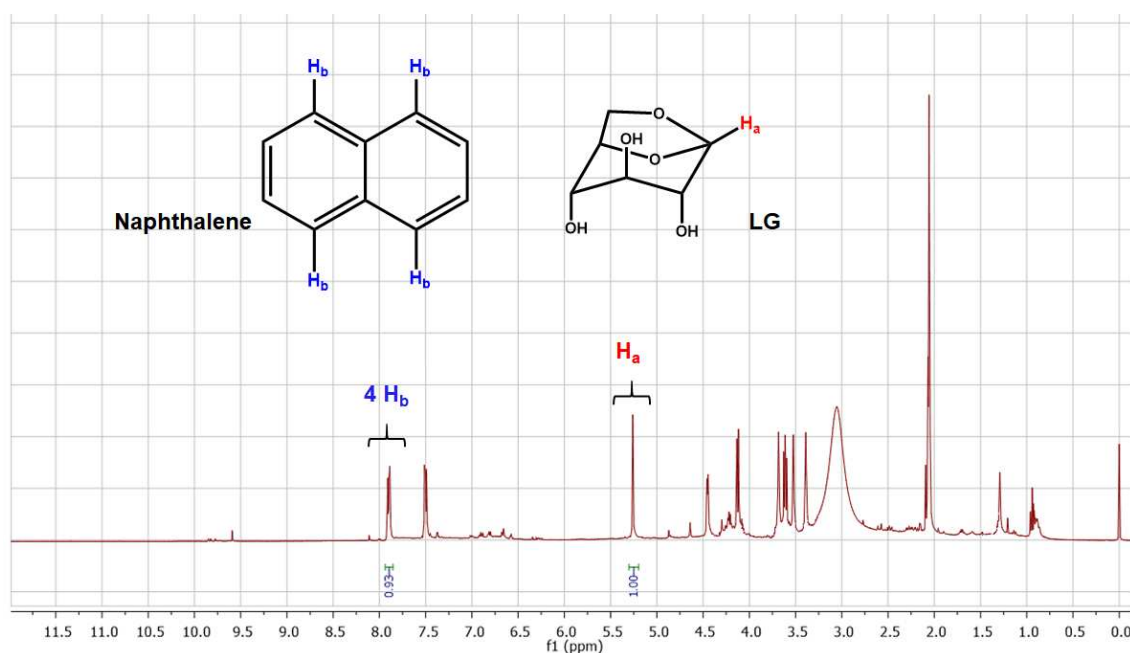


Figure 6. ^1H NMR of bio-oil (in acetone- d_6) from pyrolysis of A-RH at 500 °C containing naphthalene as internal standard. LG: levoglucosan.

The quantity of LG measured in bio-oils was in the range of 9-30 wt.% and the largest amount was obtained at 500°C from the acid treated rice husk (Table 3). In relation to the initial amount of biomass, the reactions of RH yields did not exceed 5 wt.%, while A-RH yields reached 13 wt.% at 600°C.

Table 3. Levoglucosan yields from RH and A-RH materials at different pyrolysis temperatures

T (°C)	LG (wt.%) ^a		LG (wt.%) ^b		LG (wt.%) ^c	
	RH	A-RH	RH	A-RH	RH	A-RH
300	9	19	1	5	4	23
400	10	22	3	10	11	46
500	13	30	4	13	14	60
600	19	20	5	9	18	42
700	10	17	3	7	11	32

^a Data based on the bio-oil mass, ^b Data based on the mass of starting RH, ^c Data based on the mass of cellulose.

The concentration of LG in A-RH bio-oils was comparable or larger than values found from other biomass-derived oils. According to the literature, the range in LG concentration is between 0.5-37 wt.%, depending on the pyrolysis technique, the type of starting biomass and its chemical treatment.[24,25,66] Shafizadeh et al. [67] reported up to 19 wt% LG yield for newsprint washed with mineral acids, and Scott et al. [68] obtained 17 wt% of LG yield for HNO₃-treated poplar wood.

Higher LG yields (30 wt.%) were found in the pyrolysis of poplar wood which was washed with HCl and H₂SO₄ under hydrolysis conditions.[65] Oudenhoven et al. [69] reported high yields of LG from pine wood washed with acetic acid using a staged condensation in a fluidized bed fast pyrolysis reactor.

From the initial amount of cellulose, a maximum of 60 wt.% of LG was obtained from pyrolysis of A-RH at 500°C (Table 3). According to the literature, pyrolysis of microcrystalline cellulose or cotton hydrocellulose can produce up to 70 wt.% of LG yield, depending on the process conditions and sample pre-treatment.[21,70] The high anhydrosugar yields obtained can be attributed to a combination of conditions such as the hydrochloric acid treatment of the starting material, the operating conditions of the pyrolytic process, and the vacuum system that prevent LG degradation. Vacuum pyrolysis offers advantages over other pyrolytic methods due to the short residence time of the organic vapor generated in the reactor, which reduces the occurrence and intensity of secondary reactions.[71]

4. Conclusion

This study focused on the fast pyrolysis of RH and hydrochloric acid-treated RH between 300-700°C under vacuum conditions. The chemical treatment of RH led to improving the bio-oil yields up to 47 wt.% at 400°C. The production of sugars was induced at all evaluated conditions, with LG being the predominant product. The acid leaching of RH contributed to an 88% increase in anhydrosugar yield. Direct quantification of LG in oils using ¹H NMR was used as an easy and rapid methodology. High yields of LG were obtained from A-RH in reactions at 500°C (30 wt.% yield considering the bio-oil mass and 60 wt.% yield considering the mass of cellulose in the starting material). By applying acid

treatment to RH, LG, the most abundant sugar in our pyrolysis oils, could be incremented to 1.9 times with respect to the pyrolysis of untreated RH.

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Bibliography

- [1] S.H. Javed, S. Naveed, N. Feroze, M. Kazmi, Extracting Silica from Rice Husk Treated with Potassium Permanganate, *Pakistan J. Agricultural Sci.* 45 (2008) 459–462. <http://pakjas.com.pk/papers%5C138.pdf>.
- [2] FAO, Rice Market Monitor, Food Agric. Organ. United Nations. XXI (2018).
- [3] Y. Zou, T. Yang, Rice husk, rice husk ash and their applications, Elsevier Inc., 2019. <https://doi.org/10.1016/B978-0-12-812828-2.00009-3>.
- [4] N. Soltani, A. Bahrami, M.I. Pech-Canul, L.A. González, Review on the physicochemical treatments of rice husk for production of advanced materials, *Chem. Eng. J.* 264 (2015) 899–935. <https://doi.org/10.1016/j.cej.2014.11.056>.
- [5] H. Weldekidan, V. Strezov, G. Town, T. Kan, Production and analysis of fuels and chemicals obtained from rice husk pyrolysis with concentrated solar radiation, *Fuel* 233 (2018) 396–403. <https://doi.org/10.1016/j.fuel.2018.06.061>.
- [6] H. Chen, W. Wang, J.C. Martin, A.J. Oliphant, P.A. Doerr, J.F. Xu, K.M. DeBorn, C. Chen, L. Sun, Extraction of lignocellulose and synthesis of

- porous silica nanoparticles from rice husks: A comprehensive utilization of rice husk biomass, *ACS Sustain. Chem. Eng.* 1 (2013) 254–259. <https://doi.org/10.1021/sc300115r>.
- [7] R.A. Bakar, R. Yahya, S.N. Gan, Production of High Purity Amorphous Silica from Rice Husk, *Procedia Chem.* 19 (2016) 189–195. <https://doi.org/10.1016/j.proche.2016.03.092>.
 - [8] Z. Li, E. Jiang, X. Xu, Y. Sun, Z. Wu, The complete utilization of rice husk for production of synthesis gas, *RSC Adv.* 7 (2017) 33532–33543. <https://doi.org/10.1039/c7ra04554a>.
 - [9] M. Ajmal, R. Ali Khan Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: Removal and recovery of Cd(II) from wastewater, *Bioresour. Technol.* 86 (2003) 147–149. [https://doi.org/10.1016/S0960-8524\(02\)00159-1](https://doi.org/10.1016/S0960-8524(02)00159-1).
 - [10] S.A. Abo-El-Enein, M.A. Eissa, A.A. Diafullah, M.A. Rizk, F.M. Mohamed, Removal of some heavy metals ions from wastewater by copolymer of iron and aluminum impregnated with active silica derived from rice husk ash, *J. Hazard. Mater.* 172 (2009) 574–579. <https://doi.org/10.1016/j.jhazmat.2009.07.036>.
 - [11] M.N. Uddin, K. Techato, J. Taweekun, M.M. Rahman, M.G. Rasul, T.M.I. Mahlia, S.M. Ashrafur, An overview of recent developments in biomass pyrolysis technologies, *Energies.* 11 (2018). <https://doi.org/10.3390/en11113115>.
 - [12] M.I. Jahirul, M.G. Rasul, A.A. Chowdhury, N. Ashwath, Biofuels Production through Biomass Pyrolysis—A Technological Review, *Energies.* 5 (2012) 4952–5001. <https://doi.org/10.3390/en5124952>.
 - [13] X. Cheng, B. Wang, Yield, composition, and property of biochar obtained from the two-step pyrolysis of rice husk impregnated with boric acid, *Energies.* 10 (2017). <https://doi.org/10.3390/en10111814>.
 - [14] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: A critical review, *Energy and Fuels.* 20 (2006) 848–889. <https://doi.org/10.1021/ef0502397>.
 - [15] W. Cai, L. Dai, R. Liu, Catalytic fast pyrolysis of rice husk for bio-oil production, *Energy.* 154 (2018) 477–487. <https://doi.org/10.1016/j.energy.2018.04.157>.
 - [16] L. Jiang, Z. Fang, Z. Zhao, A. Zheng, X. Wang, H. Li, Levoglucosan and its hydrolysates via fast pyrolysis of lignocellulose for microbial biofuels: A state-of-the-art review, *Renew. Sustain. Energy Rev.* 105 (2019) 215–229. <https://doi.org/10.1016/j.rser.2019.01.055>.
 - [17] D. Scott, J. Piskorz, D. Randlei, Production of Levoglucosan as an Industrial Chemical, in: Z. Witczak (Ed.), *Levoglucosenone Levoglucosans Chem. Appl.*, ATL Press, Mount Prospect, 1994: pp. 179–188.
 - [18] S. Helle, N.M. Bennett, K. Lau, J.H. Matsui, S.J.B. Duff, A kinetic model for

- production of glucose by hydrolysis of levoglucosan and cellobiosan from pyrolysis oil, *Carbohydr. Res.* 342 (2007) 2365–2370. <https://doi.org/10.1016/j.carres.2007.07.016>.
- [19] E. Leng, Y. Wang, X. Gong, B. Zhang, Y. Zhang, M. Xu, Effect of KCl and CaCl₂ loading on the formation of reaction intermediates during cellulose fast pyrolysis, *Proc. Combust. Inst.* 36 (2017) 2263–2270. <https://doi.org/10.1016/j.proci.2016.06.167>.
- [20] X. Bai, P. Johnston, S. Sadula, R.C. Brown, Role of levoglucosan physiochemistry in cellulose pyrolysis, *J. Anal. Appl. Pyrolysis.* 99 (2013) 58–65. <https://doi.org/10.1016/j.jaap.2012.10.028>.
- [21] N. Kuzhiyil, D. Dalluge, X. Bai, K.H. Kim, R.C. Brown, Pyrolytic sugars from cellulosic biomass, *ChemSusChem.* 5 (2012) 2228–2236. <https://doi.org/10.1002/cssc.201200341>.
- [22] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Influence of inorganic salts on the primary pyrolysis products of cellulose, *Bioresour. Technol.* 101 (2010) 4646–4655. <https://doi.org/10.1016/j.biortech.2010.01.112>.
- [23] A. Zheng, Z. Zhao, Z. Huang, K. Zhao, G. Wei, L. Jiang, X. Wang, F. He, H. Li, Overcoming biomass recalcitrance for enhancing sugar production from fast pyrolysis of biomass by microwave pretreatment in glycerol, *Green Chem.* 17 (2015) 1167–1175. <https://doi.org/10.1039/c4gc01724b>.
- [24] C. Branca, A. Galgano, C. Blasi, M. Esposito, C. Di Blasi, H₂SO₄-catalyzed pyrolysis of corncobs, *Energy and Fuels.* 25 (2011) 359–369. <https://doi.org/10.1021/ef101317f>.
- [25] O. Das, A.K. Sarmah, Mechanism of waste biomass pyrolysis: Effect of physical and chemical pre-treatments, *Sci. Total Environ.* 537 (2015) 323–334. <https://doi.org/10.1016/j.scitotenv.2015.07.076>.
- [26] Y. Feng, G. Li, X. Li, N. Zhu, B. Xiao, J. Li, Y. Wang, Enhancement of biomass conversion in catalytic fast pyrolysis by microwave-assisted formic acid pretreatment, *Bioresour. Technol.* 214 (2016) 520–527. <https://doi.org/10.1016/j.biortech.2016.04.137>.
- [27] T. Hosoya, H. Kawamoto, S. Saka, Cellulose-hemicellulose and cellulose-lignin interactions in wood pyrolysis at gasification temperature, *J. Anal. Appl. Pyrolysis.* 80 (2007) 118–125. <https://doi.org/10.1016/j.jaap.2007.01.006>.
- [28] C.I. De Jenga, M.J. Antal, Yields and composition of sirups resulting from the flash pyrolysis of cellulosic materials using radiant energy, *J. Appl. Polym. Sci.* 27 (1982) 4313–4322. <https://doi.org/10.1002/app.1982.070271121>.
- [29] X. Guo, S. Wang, Q. Wang, Z. Guo, Z. Luo, Properties of bio-oil from fast pyrolysis of rice husk, *Chinese J. Chem. Eng.* 19 (2011) 116–121. [https://doi.org/10.1016/S1004-9541\(09\)60186-5](https://doi.org/10.1016/S1004-9541(09)60186-5).

- [30] S. Zhang, S. Zhu, H. Zhang, X. Liu, H. Zhang, Evaluation of pyrolysis behavior and products properties of rice husk after combined pretreatment of washing and torrefaction, *Biomass and Bioenergy*. 127 (2019) 105293. <https://doi.org/10.1016/j.biombioe.2019.105293>.
- [31] Anthony V. Bridgwater, *Biomass Fast Pyrolysis*, *Bioresour. Technol.* 85 (2004) 21–49. <http://www.ncbi.nlm.nih.gov/pubmed/21232946>.
- [32] M.L. Nieva, M.A. Volpe, E.L. Moyano, Catalytic and catalytic free process for cellulose conversion: fast pyrolysis and microwave induced pyrolysis studies, *Cellulose*. 22 (2015) 215–228. <https://doi.org/10.1007/s10570-014-0484-z>.
- [33] A.I. Casoni, M.L. Nievas, E.L. Moyano, M. Álvarez, A. Diez, M. Dennehy, M.A. Volpe, Catalytic pyrolysis of cellulose using MCM-41 type catalysts, *Appl. Catal. A Gen.* 514 (2016) 235–240. <https://doi.org/10.1016/j.apcata.2016.01.017>.
- [34] M.P. Silva, E.L. Moyano, A.L. Scopel, Potential applications of biochar and terpene-enriched bio-oil produced from a semi-arid native Asteraceae, *J. Anal. Appl. Pyrolysis*. 126 (2017) 39–49. <https://doi.org/10.1016/j.jaap.2017.06.026>.
- [35] L. Jones, J.L. Milne, D. Ashford, S.J. McQueen-Mason, Cell wall arabinan is essential for guard cell function, *Proc. Natl. Acad. Sci. U. S. A.* 100 (2003) 11783–11788. <https://doi.org/10.1073/pnas.1832434100>.
- [36] F.A. Loewus, Improvement in Anthrone Method for Determination of Carbohydrates, *Anal. Chem.* 24 (1952) 219–219.
- [37] B. Liu, L.D. Gómez, C. Hua, L. Sun, I. Ali, L. Huang, C. Yu, R. Simister, C. Steele-King, Y. Gan, S.J. McQueen-Mason, Linkage mapping of stem saccharification digestibility in rice, *PLoS One*. 11 (2016) 1–13. <https://doi.org/10.1371/journal.pone.0159117>.
- [38] NREL/TP-510-42620, Preparation of Samples for Compositional Analysis Laboratory Analytical Procedure (LAP), 2008.
- [39] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer, *Text. Res. J.* (1959) 786–794.
- [40] S. Park, J.O. Baker, M.E. Himmel, P.A. Parilla, D.K. Johnson, Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance, *Biotechnol. Biofuels*. 3 (2010) 1–10.
- [41] S. Zhang, Y. Su, K. Ding, S. Zhu, H. Zhang, X. Liu, Y. Xiong, Effect of inorganic species on torrefaction process and product properties of rice husk, *Bioresour. Technol.* 265 (2018) 450–455. <https://doi.org/10.1016/j.biortech.2018.06.042>.
- [42] S.R.G. Oudenhoven, R.J.M. Westerhof, S.R.A. Kersten, Fast pyrolysis of organic acid leached wood, straw, hay and bagasse: Improved oil and sugar yields, *J. Anal. Appl. Pyrolysis*. 116 (2015) 253–262.

<https://doi.org/10.1016/j.jaap.2015.09.003>.

- [43] Karnowo, Z.F. Zahara, S. Kudo, K. Norinaga, J.I. Hayashi, Leaching of alkali and alkaline earth metallic species from rice husk with bio-oil from its pyrolysis, *Energy and Fuels*. 28 (2014) 6459–6466. <https://doi.org/10.1021/ef501748h>.
- [44] J.A. Santana Costa, C.M. Paranhos, Systematic evaluation of amorphous silica production from rice husk ashes, *J. Clean. Prod.* 192 (2018) 688–697. <https://doi.org/10.1016/j.jclepro.2018.05.028>.
- [45] N. Johar, I. Ahmad, A. Dufresne, Extraction , preparation and characterization of cellulose fibres and nanocrystals from rice husk, *Ind. Crop. Prod.* 37 (2012) 93–99. <https://doi.org/10.1016/j.indcrop.2011.12.016>.
- [46] D. Klemm, B. Heublein, H. Fink, A. Bohn, Cellulose: Fascinating Biopolymer and Sustainable Raw Material *Angewandte, Polym. Sci.* 44 (2005) 3358–3393. <https://doi.org/10.1002/anie.200460587>.
- [47] L.T. Vlaev, S.C. Turmanova, S.D. Genieva, Products and applications of pyrolyzed rise husks: Structure, morphology, thermal, kinetics and physicomechanical characteristics, in: *Pyrolysis Types, Process. Ind. Sources Prod.*, 2009: pp. 267–324.
- [48] T.P. Thao Tran, J. Bénézet, A. Bergeret, Rice and Einkorn wheat husks reinforced poly (lactic acid) (PLA) biocomposites : Effects of alkaline and silane surface treatments of husks, *Ind. Crop. Prod.* 58 (2014) 111–124. <https://doi.org/10.1016/j.indcrop.2014.04.012>.
- [49] X.F. Sun, F. Xu, R.C. Sun, P. Fowler, M.S. Baird, Characteristics of degraded cellulose obtained from steam-exploded wheat straw, *Carbohydr. Res.* 340 (2005) 97–106. <https://doi.org/10.1016/j.carres.2004.10.022>.
- [50] X. Xiao, B. Chen, L. Zhu, Transformation, Morphology, and Dissolution of Silicon and Carbon in Rice Straw-Derived Biochars under Different Pyrolytic Temperatures, *Environ. Sci. Technol.* 48 (2014) 3411–3419.
- [51] H.S. Heo, H.J. Park, J.I. Dong, S.H. Park, S. Kim, D.J. Suh, Y.W. Suh, S.S. Kim, Y.K. Park, Fast pyrolysis of rice husk under different reaction conditions, *J. Ind. Eng. Chem.* 16 (2010) 27–31. <https://doi.org/10.1016/j.jiec.2010.01.026>.
- [52] N. Zhao, B.X. Li, The effect of sodium chloride on the pyrolysis of rice husk, *Appl. Energy*. 178 (2016) 346–352. <https://doi.org/10.1016/j.apenergy.2016.06.082>.
- [53] P.T. Williams, N. Nugranad, Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks, *Energy*. 25 (2000) 493–513. [https://doi.org/10.1016/S0360-5442\(00\)00009-8](https://doi.org/10.1016/S0360-5442(00)00009-8).
- [54] M.S.A. Bakar, J.O. Titiloye, Catalytic pyrolysis of rice husk for bio-oil production, *J. Anal. Appl. Pyrolysis*. 103 (2013) 362–368.

<https://doi.org/10.1016/j.jaap.2012.09.005>.

- [55] C.X. Rong, B.X. Li, W. Liu, N. Zhao, The effect of oyster shell powder and rice husk ash on the pyrolysis of rice husk for bio-oil, *Energy Sources, Part A Recover. Util. Environ. Eff.* 40 (2018) 1291–1304. <https://doi.org/10.1080/15567036.2018.1469690>.
- [56] A. V. Bridgwater, Principles and practice of biomass fast pyrolysis processes for liquids, *J. Anal. Appl. Pyrolysis.* 51 (1999) 3–22. [https://doi.org/10.1016/S0165-2370\(99\)00005-4](https://doi.org/10.1016/S0165-2370(99)00005-4).
- [57] W.T. Tsai, M.K. Lee, Y.M. Chang, Fast pyrolysis of rice husk: Product yields and compositions, *Bioresour. Technol.* 98 (2007) 22–28. <https://doi.org/10.1016/j.biortech.2005.12.005>.
- [58] T. Hosoya, H. Kawamoto, S. Saka, Role of methoxyl group in char formation from lignin-related compounds, *J. Anal. Appl. Pyrolysis.* 84 (2009) 79–83. <https://doi.org/10.1016/j.jaap.2008.10.024>.
- [59] M.-J. Jeon, S.-S. Kim, J.-K. Jeon, S.H. Park, J.M. Kim, J.M. Sohn, S.-H. Lee, Y.-K. Park, Catalytic pyrolysis of waste rice husk over mesoporous materials, *Nanoscale Res. Lett.* 7 (2012) 18. <https://doi.org/10.1186/1556-276x-7-18>.
- [60] A. Ohnishi, K. Kunio, Crystal Structure and ¹H and ¹³C-N.M.R Studies of 1,4 : 3,6-Dianhydro- α -D-Glucopyranose Obtained from Pyrolysis of Cellulose, *Carbohydr. Res.* 96 (1981) 161–166.
- [61] F. Shafizadeh, R.H. Furneaux, T.T. Stevenson, T.G. Cochran, Acid-catalyzed Pyrolytic Synthesis and Decomposition of 1,4 : 3,6 - Dianhydro- α -D-Glucopyranose, *Carbohydr. Res.* 61 (1978) 519–528.
- [62] P. Rutkowski, Pyrolytic behavior of cellulose in presence of montmorillonite K10 as catalyst, *J. Anal. Appl. Pyrolysis.* 98 (2012) 115–122. <https://doi.org/10.1016/j.jaap.2012.07.012>.
- [63] Y. Lin, J. Cho, G.A. Tompsett, P.R. Westmoreland, G.W. Huber, Kinetics and Mechanism of Cellulose Pyrolysis, *J. Phys. Chem. C.* 113 (2009) 20097–20107.
- [64] J. Wang, Q. Wei, J. Zheng, M. Zhu, Effect of pyrolysis conditions on levoglucosan yield from cotton straw and optimization of levoglucosan extraction from bio-oil, *J. Anal. Appl. Pyrolysis.* 122 (2016) 294–303. <https://doi.org/10.1016/j.jaap.2016.09.013>.
- [65] J. Piskorz, D.S.A.G. Radlein, D.S. Scott, S. Czernik, Pretreatment of wood and cellulose for production of sugars by fast pyrolysis, *J. Anal. Appl. Pyrolysis.* 16 (1989) 127–142. [https://doi.org/10.1016/0165-2370\(89\)85012-0](https://doi.org/10.1016/0165-2370(89)85012-0).
- [66] J. Lian, M. Garcia-Perez, S. Chen, Fermentation of levoglucosan with oleaginous yeasts for lipid production, *Bioresour. Technol.* 133 (2013) 183–189. <https://doi.org/10.1016/j.biortech.2013.01.031>.

- [67] F. Shafizadeh, R.H. Furneaux, T.G. Cochran, J.P. Scholl, Y. Sakai, Production of levoglucosan and glucose from pyrolysis of cellulosic materials, *J. Appl. Polym. Sci.* 23 (1979) 3525–3539. <https://doi.org/10.1002/app.1979.070231209>.
- [68] D.S. Scott, L. Paterson, J. Piskorz, D. Radlein, Pretreatment of poplar wood for fast pyrolysis: Rate of cation removal, *J. Anal. Appl. Pyrolysis.* 57 (2001) 169–176. [https://doi.org/10.1016/S0165-2370\(00\)00108-X](https://doi.org/10.1016/S0165-2370(00)00108-X).
- [69] S.R.G. Oudenhoven, R.J.M. Westerhof, N. Aldenkamp, D.W.F. Brilman, S.R.A. Kersten, Demineralization of wood using wood-derived acid: Towards a selective pyrolysis process for fuel and chemicals production, *J. Anal. Appl. Pyrolysis.* 103 (2013) 112–118. <https://doi.org/10.1016/j.jaap.2012.10.002>.
- [70] Z. Wang, S. Zhou, B. Pecha, R.J.M. Westerhof, M. Garcia-Perez, Effect of pyrolysis temperature and sulfuric acid during the fast pyrolysis of cellulose and douglas fir in an atmospheric pressure wire mesh reactor, *Energy and Fuels.* 28 (2014) 5167–5177. <https://doi.org/10.1021/ef500999z>.
- [71] J. Ruan, J. Huang, B. Qin, L. Dong, Heat Transfer in Vacuum Pyrolysis of Decomposing Hazardous Plastic Wastes, *ACS Sustain. Chem. Eng.* 6 (2018) 5424–5430. <https://doi.org/10.1021/acssuschemeng.8b00255>.