



# Article Coffee Husks Valorization for Levoglucosan Production and Other Pyrolytic Products through Thermochemical Conversion by Fast Pyrolysis

Euripedes Garcia Silveira Junior <sup>1</sup><sup>(1)</sup>, Victor Haber Perez <sup>1,\*</sup><sup>(1)</sup>, Solciaray Cardoso Soares Estefan de Paula <sup>1</sup><sup>(1)</sup>, Thays da Costa Silveira <sup>1</sup>, Fabio Lopes Olivares <sup>2</sup><sup>(1)</sup> and Oselys Rodriguez Justo <sup>3</sup>

- <sup>1</sup> Center of Sciences and Agricultural Technologies (CCTA), State University of Northern of Rio de Janeiro, Campos dos Goytacazes 28013-602, RJ, Brazil; euripedes@uenf.br (E.G.S.J.)
- <sup>2</sup> Bioscience and Biotechnology Center (CBB), State University of Northern of Rio de Janeiro, Campos dos Goytacazes 28013-602, RJ, Brazil
- <sup>3</sup> Industrial Engineering School, Estácio de Sá University, Campos dos Goytacazes 28020-740, RJ, Brazil
- \* Correspondence: victorh@uenf.br; Tel.: +55-(22)-27486085

Abstract: Levoglucosan is an anhydrosugar from biomass that has important applications as a platform for obtaining many value-added derivatives with high demand in the chemical industry and bioproducts by fermentation, including biofuels, among others. Thus, the experimental strategy was to intensify the levoglucosan production in the condensable fraction (bio-oil) from pyrolysis gases using different biomass pretreatments before fast pyrolysis according to the following conditions: (a) biomass washing with 10% acetic acid; (b) biomass washing with 0.1% HNO<sub>3</sub>, followed by impregnation with 0.1% H<sub>2</sub>SO<sub>4</sub>; and (c) biomass impregnation with 0.1% H<sub>2</sub>SO<sub>4</sub>. The pyrolysis was carried out in a pyroprobe reactor, coupled to GC/MS to verify the progress of the chemicals formed at 400, 500, and 600 °C. Although levoglucosan was the main target, the programs showed more than 200 pyrolytic compounds of which more than 40 were identified, including organic acids, ketones, aldehydes, furans, and phenols. Then, principal component analysis (PCA) allowed for the discrimination of the simultaneous effect of biomass acid treatment and pyrolysis temperature on the formation of the pyrolytic products. All treated biomasses with acids resulted in a levoglucosan yield increase, but the best result was achieved with acetic acid at 500 °C which resulted from 7-fold higher levoglucosan production with changes in the profiles by-products formed concerning untreated biomass. This result was attributed to the alkali and alkaline earth metals reduction and partial removal of lignin content and extractives by acid washing, increasing the cellulose and hemicellulose relative content in the treated biomass. This hypothesis was also confirmed by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) qualitative analysis. Thus, the results achieved in this work show the potential of this biomass for levoglucosan production and other pyrolytic products, thereby being able to mitigate the environmental impact of this agricultural residue and contribute to the development of the coffee agro-industrial chain and the production of bioenergy from lignocellulosic biomass.

Keywords: coffee husk; fast pyrolysis; levoglucosan; value-added byproducts

## 1. Introduction

Coffee is one of the main agricultural crops in the world, reaching a production of 175.347 million bags of 60 kg (10.52 billion tons of coffee) during the 2020/2021 coffee harvest. In addition, data already report that at the beginning of 2022, coffee exports have already reached 651,756 tons worldwide. In this scenario, Brazil is the world's largest producer with 4.140 million tons in the 2020/2021 coffee harvests whose exportation reached 2.344 million tons until January 2022 [1].



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). During coffee processing, a large quantity of residues is produced. The production of these residues is equivalent to half of the processed coffee [2]. Although coffee husk is used for composting, fertilizer production, and animal feed, among others, there is still a large fraction that ends up being inappropriately discarded into the environment [3].

Some strategies have been explored to propose alternatives to the disposal of this agricultural waste, such as the production of ecological polymeric materials via extrusion [4], particle board with polymers via pressing [5], energy production [2], magnetic hydrochar via the hydrothermal carbonization method [6], activated carbon [7], biogas [8–10], bio-oil via slow pyrolysis [11–14], bio-char via slow pyrolysis [3,11–17], hydrochar by a two-step hydrothermal carbonization process [18,19], ethanol [20,21], briquette and pellet production [22,23], and xylooligosaccharide production [24].

An interesting way to process this residue can be by thermochemical conversion of biomass through fast pyrolysis into biochar, bio-oil, and non-condensable gases. Among these three products, the bio-oil produced contains a complex mixture of phenolic compounds, organic acids, ketones, aldehydes, and furans, as well as a pyrolytic sugars fraction [25–28]. Pyrolytic sugars consist of 1,3-Di-O-acetyl- $\alpha$ - $\beta$ -d-ribopyranose; D-(+)-melezitose, 1,6-anhydro- $\beta$ -D-glucofuranose, and mainly levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) derived from cellulose that can be used as a raw material for biofuel production and other bioproducts of agricultural, chemical, and pharmaceutical interest [29–34].

In general, fast pyrolysis of in-nature feedstocks can produce levoglucosan yields around 4 wt%, however, the production of this anhydrosugar can be intensified using different strategies to remove alkali and alkaline earth metals (AAEMs) present in the biomass. During pyrolysis, these elements have catalytic effects that are unfavorable for anhydrosugar formation and change the pyrolytic chemical profile [25,27,35,36]. Several methods for biomass pretreatment, such as acid washing or passivation, have been tested and shown to be effective in either partial or total removal of AAEMs from biomass, consequently increasing levoglucosan production. Thus, weak organic acids, such as acetic acid [32,36,37], strong (inorganic) acids, such as sulfuric acid [25,37,38], phosphoric and nitric acid [37], and hydrochloric acid [39], have been evaluated. On the other hand, in some cases, passivation procedures via acid impregnation have also been used to reduce the catalytic effects of AAEMs on biomass [25].

Although there are some proposals for the use of coffee husks due to the large residual volumes available, this biomass has not yet been fully explored in relation to all compounds formed by thermochemical transformation. Thus, the novelty of this work is to verify the potential of coffee husks as a source of lignocellulosic biomass for levoglucosan production, as well as other pyrolytic compounds obtained by fast pyrolysis at different temperatures (400, 500, and 600 °C) and pre-treatment conditions, seeking to mitigate the environmental impact of these agricultural residues and, thus, contribute to the development of the coffee agro-industrial chain and the bioenergy production from lignocellulosic biomass.

#### 2. Materials and Methods

#### 2.1. Coffee Husks Biomass Collection and Characterization

The coffee husks from *Coffea arabica* of the red "catuaí" variety were collected after the coffee processing process on a farm located in the Varre-Sai region of Northern Rio de Janeiro, Brazil.

#### 2.2. Experimental Procedures

### 2.2.1. Coffee Husks Biomass Acid Pretreatments

Prior to fast pyrolysis, milled coffee husk (30 mesh) was pretreated in a jacketed glass-stirred tank reactor at lab scale according to the following conditions: (a) acetic acid (10%) at 90 °C for 10 min under 200 rpm; (b) nitric acid (0.1%) with sulfuric acid (0.1%) at room temperature for 2 h under 200 rpm; (c) sulfuric acid (0.1%) at room temperature for 2 h under 200 rpm. The acid-pretreated biomass was washed with deionized water until

it reached pH 7 and finally dried at 60 °C under a vacuum oven (model Q819V2, Quimis, Brazil) at 0.085 MPa until it reached a constant weight [32]. The untreated biomass was also used in the study as a control for comparative purposes.

#### 2.2.2. Fast Pyrolysis of Coffee Husks Biomass

The biomass samples were subjected to fast pyrolysis in a Single-Shot Pyrolyzer (Frontier Laboratories Ltd., Fukushima, Japan) connected to a GC-2010 Plus system with a GCMS-QP2010 Ultra spectrometer (Shimadzu, Kyoto, Japan) and valve interface at 290 °C. The fast pyrolysis was conducted at 400, 500, and 600 °C. The GC operating parameters were: injector temperature (250 °C); Rtx-5MS column (30 m × 0.25 mm × 0.25  $\mu$ m) (Restek, Bellefonte, PA, USA); initial oven temperature of 40 °C for 1 min, heated 6 °C/min to 280 °C and held for 15 min; and helium carrier gas (1 mL/min) in split mode at a 20:1 ratio [27,28]. Experiments were carried out in duplicate, and the pyrolytic compounds formed were identified using the NIST library for Mass Spectral Search Program (2.0) coupled with the NIST/EPA/NIH Mass Spectral Database (NIST 11) and the Wiley 7v100 Mass Spectral Data Library. The percent yield of all pyrolytic products formed was calculated based on the amount of pyrolyzed biomass (around 0.5 mg) for standardization of the content of the formed compound and followed by the "Internal Normalization of Peak Areas Method" for quantitative analysis, as described by Guiochon and Guillemin [40], considering the area of the target component peak as a proportion of the total area from all detected peaks.

#### 2.3. Analytical Methods

## 2.3.1. Coffee Husk Characterization

Initially, the coffee husks were dried in a vacuum oven at 70 °C until constant weight and milled using a mill model TE-650 Willey from Tecnal (Piracicaba, SP, Brazil). Then, samples were analyzed according to particle size distribution by ASTM D5644-01, moisture content by ASTM D4442-07, and ash content by NREL/TP-510-42622 (2008). Finally, the cellulose, hemicellulose, and lignin content were determined according to the methods described by Van Soest et al. [41].

#### 2.3.2. Elemental Analysis (CHN-O)

The elemental analysis of the biomass treated and untreated was also determined using a PerkinElmer Series II CHNS/O Analyzer 2400, weighing around 3 mg of samples on a PerkinElmer AD6 Autobalance.

#### 2.3.3. FTIR Spectroscopy Analysis

Fourier transform infrared spectroscopy (FTIR) was carried out using a Shimadzu IRAffinity-1 spectrophotometer in the wavenumber range of 4000–400 cm<sup>-1</sup>. The spectrophotometer was programmed for 40 scans per reading. Potassium bromide (KBr) pellets were used for obtaining the IR spectra, whereas the IR Solution software was used to record and process the obtained spectra.

#### 2.3.4. Scanning Electron Microscopy (SEM) Analysis

Treated and untreated coffee husks (50 mg of dried biomass powder each) were prepared on carbon adhesive tape affixed to aluminum stubs and subsequently coated with platinum in a sputter coater device (BAL-TEC SCD 005 Cool Sputter Coater, BAL-TEC AG., Liechtenstein). The samples were viewed using a LEO EVO 40 XVP SEM (Carl Zeiss, Jena, Germany) at 15 kV. Micrographs were obtained at a magnification between 1300 to  $6300 \times$  for a comparative structural analysis of vegetal cell units and tissue patterns.

#### 2.4. Principal Component Analysis

Principal component analysis (PCA) was used to identify the main factors affecting the yield of products obtained by Py-GC/MS. In this analysis, the number of principal components should be equal to or less than the number of variables in such a way that the

first principal component has the largest possible variance, and each succeeding component in turn has the highest variance possible under the restriction that it be orthogonal to the preceding components [42]. Then, PCA was conducted according to the matrix containing 12 cases by 38 variables, where each case represents combined data of biomass kind (untreated and treated by different acids)  $\times$  pyrolysis temperature and the semiquantitative estimation of the yield of each pyrolytic compound formed (see Table A1 in Appendix A). The PCA was then carried out using statistical software "Statistica" 8.0 at a 95% confidence level.

## 3. Results and Discussion

## 3.1. Compositional Analysis of Untreated Biomass

Firstly, proximate analysis considering cellulose, hemicellulose, lignin, extractives/volatiles, and ash, as well as an elemental analysis (CHN/O) of untreated coffee husk were determined before any biomass pretreatment and/or pyrolysis procedure (Table 1). As can be seen, the analysis of the elemental composition of this biomass resulted in a carbon-hydrogen ratio of 9:1, carbon-oxygen of 1:1, and oxygen-hydrogen of 10:1. This is important information because it is related to the yield and formation profile of the pyrolysis products [43] since higher values of H/C and C/O may result in more attractive pyrolytic compounds. On the other hand, it was possible to verify that the relative contents of cellulose, hemicellulose, and lignin showed some differences compared to data reported in the literature [5,21,23,44]. Probably, however, the differences observed were due to the type of coffee variety and climatic factors during cultivation and also to its post-harvest processing. It is known that edaphoclimatic effects impact the specific physicochemical properties of a given plant and cause variations in the cellulose, hemicellulose, and lignin contents, making it difficult to attain very similar data comparable to published works referring to coffee husks from different sources and agricultural regions.

Biomass Components	Composition (wt%)					
Moisture	$14.56\pm0.20$					
Cellulose	$24.51\pm0.18$					
Hemicellulose	$13.42\pm0.21$					
Lignin	$11.47\pm0.01$					
Carbon	$43.08\pm0.42$					
Hydrogen	$4.53\pm0.08$					
Nitrogen	$4.02\pm0.41$					
* Oxygen	$48.12\pm0.76$					
Ash	$0.27\pm0.02$					
Extractives	$28.90\pm0.01$					

Table 1. Compositional and elemental analysis results from untreated coffee husk.

\* Oxygen content determined by difference.

#### 3.2. Coffee Husk Pretreatment Prior Pyrolysis

The coffee husk was subjected to pre-treatments through acid washing using acids from different sources (acetic, sulfuric, and nitric/sulfuric) as a strategy to change the formation profiles of the pyrolytic products and intensify the levoglucosan formation as a target product, although other value-added by-products are also important for their several applications in the industrial sector. In this context, Figure 1 illustrates in a simplified form a diagram of coffee husk pretreatment procedures with different acids prior to fast pyrolysis at different pyrolysis temperatures. These procedures were adopted based on satisfactory results observed with biomass from several sources exposed to acid washing to improve, for instance, the levoglucosan production at different pyrolysis conditions [25,27,28,32,36,45].



**Figure 1.** Block diagram of coffee husk pretreatment with different types of acids prior to fast pyrolysis at different temperatures.

According to SEM (Figure 2) and FTIR (Figure 3) analysis, it is possible to verify that acid treatment changed the morphology and structure of coffee husk compared to the untreated biomass. Thus, Figure 2a shows through a longitudinal section of untreated biomass that the plant material composed of parenchyma and sclerenchyma cells is well-preserved, with a thick, intact, and well-ordered appearance whose structures are chemically interconnected with calcium pectates and magnesium (middle lamella). However, after pretreatment of the biomass with acetic acid (Figure 2b), it is possible to observe morphological changes associated with cell wall distortion, thus suggesting evidence of partial removal of the middle lamella and starch. Meanwhile, the effect of inorganic acids on biomass was stronger (Figure 2c,d), resulting in the intensification in the middle lamella

removal with clear damage to the cell wall for both parenchyma and sclerenchyma cells. In some cases, it can be observed that cells of plants are detached from each other, suggesting that the entire plant tissue responsible for the structural support between the cells was damaged. In fact, Jiang et al. [46] already reported that leaching by strong acids has a high mineral removal efficiency but simultaneously induces a non-negligible impact on the physicochemical structure of the biomass compared to water and/or weak acids washing.



**Figure 2.** Micrographs attained for: (**a**) untreated biomass; (**b**) pretreated biomass with acetic acid (10 wt%); (**c**) pretreated biomass with HNO<sub>3</sub> (0.1 wt%)/H<sub>2</sub>SO<sub>4</sub> (0.1 wt%); (**d**) pretreated biomass with H<sub>2</sub>SO<sub>4</sub> (0.1 wt%).



**Figure 3.** FTIR spectra of coffee husks. Symbols: – untreated biomass; – pretreated biomass with acetic acid (10 wt%); – pretreated biomass with  $HNO_3$  (0.1 wt%)/ $H_2SO_4$  (0.1 wt%); – pretreated biomass with  $H_2SO_4$  (0.1 wt%).

Regarding FTIR analysis (Figure 3), the adsorption bands were associated with the functional groups of the aromatics, ketones, and alcohols compounds, and comparing the FTIR spectra showed a reduction in the bands intensity of treated biomass with respect to untreated biomass, suggesting qualitative changes in the biomass structure after acid pretreatment. This could be attributed to partial removal of extractives and lignin.

## 3.3. Fast Pyrolysis of Coffee Husks

After the biomass treatments by acid washing, fast pyrolysis experiments were carried out at 400, 500, and 600 °C. Then, chemicals derived from cellulose, hemicellulose, and lignin were analyzed quantitatively by GC-MS (Appendix A) and grouped in two pyrolytic fractions containing volatile and non-condensable product families, which include phenolics, organic acids, ketones, aldehydes, and furans, as well as pyrolytic sugars (Figures 4–6) and non-condensable gases ( $CO_2$ ,  $CH_4$ , among others) as a function of biomass acid treatment adopted and pyrolysis temperature. For comparative purposes, untreated biomass was also considered.



**Figure 4.** Pyrolytic compounds in the liquid fraction obtained from untreated and acetic acid (10%) washed coffee husks after fast pyrolysis at: (a) 400 °C; (b) 500 °C; (c) 600 °C. Symbols: ■ untreated biomass; ■ treated biomass.



**Figure 5.** Pyrolytic compounds in the liquid fraction obtained from untreated and HNO<sub>3</sub> (0.1 wt%)/H2<sub>S</sub>O<sub>4</sub> (0.1 wt%) washed coffee husks after fast pyrolysis at: (a) 400 °C; (b) 500 °C; (c) 600 °C. Symbols:  $\blacksquare$  untreated biomass;  $\blacksquare$  treated biomass.

Observing the results in Figures 4–6, it becomes evident how complex the pyrolysis process is, in which the reaction and pretreatment conditions favor the heterogeneous formation of pyrolytic derivatives of a family of compounds to the detriment of the others. Thus, in an attempt to interpret and correlate the families of compounds formed as a function of biomass treatment conditions using different types of acids and fast pyrolysis parameters of coffee husks, a principal component analysis (PCA) was performed to identify the main factors that affect the distribution of the pyrolytic products. Table 2 presents the variances accounting for the principal components, with the first and second principal components (PC1 = 45.83% and PC2 = 16.06%) representing 61.89% of the total variance. Then, the results obtained for the projection of cases and variables in the factorial plane (PC1  $\times$  PC2) are shown in Figure 7. Through these graphs, the importance of the original variables and their contribution to the principal components (PC) model can be verified.



**Figure 6.** Pyrolytic compounds in the liquid fraction attained from untreated and  $H_2SO_4$  (0.1 wt%) washed coffee husks after fast pyrolysis at: (a) 400 °C; (b) 500 °C; (c) 600 °C. Symbols:  $\blacksquare$  untreated biomass;  $\blacksquare$  treated biomass.

<b>Table 2.</b> Percentage of explained varia	ance of the PCA model.
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Principal Component	Variance (%)	Cumulative Variance (%)				
PC1	45.82533	45.8253				
PC2	16.05843	61.8838				
PC3	13.41248	75.2962				
PC4	10.72452	86.0208				

Figure 7a suggests that each type of used acid in the biomass treatment favored more or less the formation of different groups from pyrolytic compounds. Thus, the samples were grouped into four different groups corresponding to the acid treatments, as well as untreated biomass. Biomass treated with acetic acid, as it is a milder treatment that affects the structure and morphology of the biomass less, resulted in a group very close to the untreated biomass in the PCA graph, positively correlated with PC1 with emphasis on the condition that most favored the formation of levoglucosan, which, being closer to the origin, presents less influence in the PC model. The samples treated with strong acids  $(HNO_3/H_2SO_4$  negatively correlated with PC1, probably due to the greater impact on the biomass structure and morphology after the treatments. These groups in the PCA graph were very close, but in different quadrants and more distant from the origin. Consequently, their influence on the PC model can be higher than the other groups.



Projection of the cases on the factor - plane  $(1x^2)$ 



**Figure 7.** PCA analysis of pyrolysis sugarcane bagasse untreated and treated with different acids at 400, 500, and 600 °C: (**a**) score plot; (**b**) loading plots for the PCA model with all the compounds.

Figure 7b shows the results obtained for the projection of the variables on the factor plane (1 × 2), and this plot can be used to visualize the relationship between the principal components PC1 and PC2 and the pyrolytic chemicals formed. The numbers inside the graph correspond to chemicals listed in Appendix A that were determined by Py-GC/MS. It is noted that the pyrolytic derivates were found to group in two major clusters, apart in different quadrants too, but only correlated with PC2 in such a way that the greater the distance from the origin, the greater the influence of the variable, and the more grouped the variables, the greater the correlation between them (p < 0.05), positive (in the left superior quadrant) and/or negative (in the lower left quadrant) would be. Thus, the pyrolytic products formed seem to have a strong relationship with the acid treatment of the biomass and the pyrolysis temperature. Essentially, however, strong acids seem to have contributed to the formation of products with greater heterogenicity due to their impact probably being more harmful to the morphology and biomass structure.

#### 3.3.1. Levoglucosan Production

Levoglucosan (1, 6-anhydro- $\beta$ -D-glucopyranose) is the main compound obtained from cellulose during pyrolysis, and it is already known that its formation takes place through dehydration and depolymerization reactions of cellulose [27,28,32,37,47–49]. The focus on this product is due, among other applications, to its importance as a source of carbon for obtaining biofuels. In this context, it should be noted that this pyrolytic sugar must be removed from the volatile fraction as part of the bio-oil purification before the stages of reduction of oxygenated compounds that aim to improve the quality of the bio-oil for applications such as green fuel. Depending on the type of lignocellulosic biomass and the operating conditions used in the pyrolysis, the resulting bio-oil from the volatile fraction may contain more than a 10 wt% of levoglucosan [50]. According to Wang et al. [49], the composition and yield of the pyrolytic products from cellulose can be affected by several structural properties, such as polymerization degree and crystallinity index, among others. Thus, for example, a high crystallinity can intensify depolymerization reactions, leading to greater levoglucosan formation and less biochar quantity [49].

Figure 8 shows the levoglucosan production as a function of temperature and the type of acid used in the biomass treatment. The best results were attained with acetic acid at 400 and 500 °C, exceptionally resulting in 7-fold higher levoglucosan production than untreated biomass at 500 °C. This result was attributed to the alkali and alkaline earth metals reduction (K, Mg, and Ca) present in the biomass, which are known for their catalytic effect which favors the cellulose fragmentation reactions which strongly affects the levoglucosan yield of the untreated biomass [25,28,36,37,47], as well as by partial removal of the lignin content and extractives by acid washing, increasing the relative cellulose and hemicellulose content in the treated biomass.

Organic (CH<sub>3</sub>COOH) and inorganic acids (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>3</sub>PO<sub>4</sub>) have been used as a strategy to intensify the production of levoglucosan, and it actually seems to be a good alternative since the acids partially or totally remove the alkali and alkaline earth metals from biomass [49]. In addition, Silveira Junior et al. [32] reported that acetic acid is not only responsible for the removal of AAEMs from elephant grass, but also for the partial removal of hemicellulose and lignin, consequently pre-concentrating the cellulose, thus obtaining an increase from 4.96 to 54.27% in the production of levoglucosan. In addition to elephant grass, the authors also observed an increase in levoglucosan production from 3.88 to 35% when peanut husks were pyrolyzed under similar conditions [27], while for guava seeds, the effect of acetic acid provided more than a 14-fold increase of anhydrous sugar, i.e., from 2.64% to 37% [28]. On the other hand, the results of using inorganic acids are quite diverse. As an example, we have the evaluation of different concentrations of hydrochloric acid (4, 8, 12, and 16%) in cotton straw by Wang et al. [39] which resulted in an increase from 12.67 to 19.45% in levoglucosan production, whereas Dobele et al. [51], after impregnating wood with phosphoric acid at concentrations of 0.5 and 1%, obtained a levoglucosan yield of up to 15.3%.



**Figure 8.** Production of levoglucosan from untreated and treated coffee husks with acetic acid (10 wt%); HNO<sub>3</sub> (0.1 wt%)/H<sub>2</sub>SO<sub>4</sub> (0.1 wt%); H<sub>2</sub>SO<sub>4</sub> (0.1 wt%) at 400, 500, and 600 °C.

#### 3.3.2. Oxygenated Compounds Production

Figures 9 and 10 show the formation profiles of formed oxygenated compounds during the pyrolysis of coffee husks. In untreated biomass, the formation profiles of these compounds consist of 21.07% aldehydes (acetaldehyde, diethyl acetaldehyde, acetyl formaldehyde), 30.22% acids (acetic acid), 6.62% esters (vinyl methanoate, methyl 2 oxopropanoate, ethyl acetate), 6.40% furans (furfural, 2-furanmethanol), 1.40% glycols (3-methyl-2,4-pentanediol), and 34.28% of ketones (hydroxyacetone, 2,3-butanedione, 2,3pentanedione, 2methyl-3-pentanone, cyclopentenone, 2-methyl -5-hexanone). The formed condensable gas during the fast pyrolysis process can be condensed in two fractions, the first consisting of the bio-oil and the second consisting of an aqueous phase. Oxygenated compounds containing 5 or more carbons, such as 2,3-pentanedione, 2-methyl-3-pentanone, 2-methyl-5-hexanone, cyclopentenone, methylacetylacetone, guaiacylacetone, diethylacetaldehyde, among others, are present in the bio-oil fraction. These compounds contribute to the low quality of bio-oil and must therefore be reduced to improve its calorific value, stability, corrosivity, and viscosity, among others [52]. Some alternatives include: heterogeneous catalytic hydrodeoxygenation [53,54], catalytic co-pyrolysis of biomass and waste plastics [55–57], and pretreatment of biomass with organic acids [32].



Figure 9. Cont.



**Figure 9.** Formed oxygenated pyrolytic compounds (>5 Carbons) from coffee husks as a function of pyrolysis temperature and pretreatment acid type. Symbols:  $\Box$  Untreated biomass;  $\blacksquare$  biomass pretreated with acetic acid;  $\blacksquare$  biomass pretreated with HNO<sub>3</sub> (0.1%)/H<sub>2</sub>SO<sub>4</sub> (0.1%);  $\blacksquare$  biomass pretreated with H<sub>2</sub>SO<sub>4</sub> (0.1%).



Pyrolysis temperature (°C)

**Figure 10.** Formed oxygenated pyrolytic compounds (<5 Carbons) from coffee husks as a function of pyrolysis temperature and pretreatment acid type. Symbols:  $\Box$  Untreated biomass;  $\blacksquare$  biomass pretreated with acetic acid;  $\blacksquare$  biomass pretreated with HNO<sub>3</sub> (0.1%)/H<sub>2</sub>SO<sub>4</sub> (0.1%);  $\blacksquare$  biomass pretreated with H<sub>2</sub>SO<sub>4</sub> (0.1%).

As can be seen in Figures 9 and 10, all the acids used in the pre-treatment of the biomass favored the production of the oxygenated compounds. However, this increase is excessively greater when the biomass is treated with inorganic acids combined with high pyrolysis temperatures (500 and 600 °C). Among the oxygenated compounds, the methylacetylacetone stands out. Its production was around 13 and 15.5 times greater when the biomass was treated with 0.1% HNO<sub>3</sub>/0.1% H<sub>2</sub>SO<sub>4</sub> and 0.1% H<sub>2</sub>SO<sub>4</sub>, respectively, at 600 °C, and cyclopentenone, whose production increased 99 times when the biomass was treated with 0.1% H<sub>2</sub>SO<sub>4</sub> and pyrolyzed at 500 °C. also stands out. Compounds containing between 1 and 4 carbons (hydroxyacetone, 2, 3-butanedione, acetaldehyde, acetylformaldehyde, vinyl methanoate, and acetic acid) are present in the aqueous phase. Among these compounds, acetic acid is a compound of great importance and also the main compound derived from hemicellulose, and its formation occurs from the fractions of o-acetyl xylan and 4-o-methylglucuronic acid [37]. The formation of acetic acid must be highlighted, as this product has commercial value, and its production had a substantial increase of 22 times when the biomass was treated with inorganic acids and pyrolyzed at 500 °C.

#### 3.3.3. Phenolic Compounds Production

Lignin is the third major component of biomass and has a highly cross-linked threedimensional network [58–61]. Lignin is formed by the disordered polymerization of three primary phenylpropane units with hydroxyl or methoxy substituents through various carbon and oxygen bridges between alkylated methoxyphenol rings. These primary phenylpropane units are guaiacyl, syringyl, and p-hydroxyphenyl synthesized via the dehydrogenation oxidation of three typical alcohol precursors also known as monolignols with different degrees of methoxylation in aromatic rings which are referred to as coniferyl, sinapyl, and p-coumaryl alcohols, respectively [62].

Figure 11 shows the profiles of phenolic compounds derived from coffee husk lignin when the biomass was subjected to different acid treatments and pyrolysis temperatures. The profile of the formation of phenolic compounds is constituted with 58.52% guaiacols (guaiacol, p-ethylguaiacol, p-vinylguaiacol, isoeugenol, guaiacylacetone, and methoxyeugenol), 23% syringols (syringol, methyl vanillyl ether, and 2,5-dimethoxy-4–methyl benzaldehyde), 6.18% alkylphenols (phenol and o-cresol), and 12.30% alcoholic precursor compounds (methylbenzene, p-xylol, and p-xylenol).

In general, after the acid treatment of the biomass, there was a reduction in the phenolic compounds formation of 26.35% when the biomass was treated with acetic acid (10%), 8.4% when the biomass was treated with HNO<sub>3</sub> (0.1%) followed by impregnation with  $H_2SO_4$  (0.1%), and 57.56% when the biomass was treated with  $H_2SO_4$  (0.1%). However, the phenolics reduction effect from acid treatment was more noticeable when the biomass was washed with acetic acid because guaiacols and syringols were reduced in 51.92% and 48.09%, respectively.

The phenol reduction should be seen as relevant to the extraction and purification of levoglucosan from bio-oil because when these compounds are present in liquid extracts, greater detoxification efforts must be made to remove them [30,32,47,63]. On the other hand, a more detailed analysis of Figure 11 allowed for verifying a reduction in the formation of the phenolic with the pyrolysis temperature increase for both untreated and treated biomass with acetic acid. In general, however, an opposite effect was observed for those treated samples with strong acids, whose pyrolysis showed an increase in the formation of phenolics as a function of the pyrolysis temperature. However, in some cases, no obvious trend was observed in the yield of phenolic compounds, showing the complexity of the fast pyrolysis process of this lignocellulosic waste. In fact, this behavior seems to be consistent with the results between the pyrolysis conditions and the formation of pyrolytic compounds, including, obviously, the phenols observed in this case by the PCA model.



Figure 11. Cont.



**Figure 11.** Formed phenolic compounds from coffee husks as a function of pyrolysis temperature and pretreatment acid type. Symbols:  $\Box$  Untreated biomass;  $\blacksquare$  biomass pretreated with acetic acid;  $\blacksquare$  biomass pretreated with HNO<sub>3</sub> (0.1%)/H<sub>2</sub>SO<sub>4</sub> (0.1%);  $\blacksquare$  biomass pretreated with H<sub>2</sub>SO<sub>4</sub> (0.1%).

## 4. Conclusions

Coffee husks were treated with different acid solutions before thermochemical conversion via fast pyrolysis to intensify levoglucosan production and other pyrolytic compounds at different pyrolysis temperatures. Strong acids seem to have contributed to the formation of pyrolytic products with greater heterogenicity due to their impact being probably more harmful in the morphology and biomass structure. The maximum levoglucosan yield was achieved when the biomass was treated with acetic acid and pyrolyzed at 500 °C, resulting in a 7-fold higher anhydrosugar production concerning untreated biomass. In addition, acetic acid also had a greater impact on the reduction of phenolic compounds, a fact that may be relevant in the reduction of levoglucosan recovery and purification steps. Thus, the results of this work can be considered satisfactory and point to new opportunities for coffee husk use in the biofuel production chain and other value-added bioproducts. However, further studies concerning the environmental impact and a techno–economic analysis should be carried out to evaluate the benefits of this technology objectively.

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## Appendix A

**Table A1.** Cases and variables used in principal component analysis (PCA) to discriminate the effect of pyrolysis temperature and acid type during biomass pretreatment.

Variables		Study Cases											
	Variables	1	2	3	4	5	6	7	8	9	10	11	12
N°	Name	Untreated 400 °C	Untreated 500 °C	Untreated 600 °C	Acetic Acid 400 °C	Acetic Acid 500 °C	Acetic Acid 600 °C	1%HNO3/ 0.1 H <sub>2</sub> SO <sub>4</sub> 400 °C	1%HNO <sub>3</sub> / 0.1 H <sub>2</sub> SO <sub>4</sub> 500 °C	1%HNO <sub>3</sub> / 0.1 H <sub>2</sub> SO <sub>4</sub> 600 °C	0.1 H <sub>2</sub> SO <sub>4</sub> 400 °C	0.1 H <sub>2</sub> SO <sub>4</sub> 500 °C	0.1 H <sub>2</sub> SO <sub>4</sub> 600 °C
1	Carbon dioxide	$6.78 \times 10^{6}$	$2.69 \times 10^{4}$	$3.75  imes 10^7$	$4.02 \times 10^7$	$3.70 \times 10^{7}$	$2.73 \times 10^{7}$	$5.20 \times 10^{7}$	$7.17 \times 10^7$	$8.68 \times 10^{7}$	$3.52 \times 10^7$	$6.61 \times 10^{7}$	$1.78 \times 10^{8}$
2	Acetaldehyde	$6.06  imes 10^6$	$6.92  imes 10^6$	$2.67  imes 10^7$	$7.34  imes 10^7$	$4.27  imes 10^7$	$1.35 \times 10^7$	$2.61  imes 10^8$	$9.51  imes 10^7$	$1.00  imes 10^8$	$5.37 \times 10^7$	$1.31 \times 10^8$	$2.10  imes 10^8$
3	Vinyl methanoate	$2.12  imes 10^6$	$2.16 imes10^4$	$1.10  imes 10^7$	$6.07 imes10^7$	$1.57  imes 10^7$	$2.55  imes 10^7$	$1.69 imes10^8$	$1.61  imes 10^8$	$2.30  imes 10^8$	$4.40 imes10^7$	$1.89  imes 10^8$	$6.55 imes10^7$
4	Hydroxyacetone	$7.35  imes 10^6$	$9.76 imes10^6$	$1.39 \times 10^7$	$3.66 \times 10^{7}$	$2.39  imes 10^7$	$7.64  imes 10^6$	$2.26  imes 10^8$	$6.32  imes 10^7$	$1.34  imes 10^8$	$1.48  imes 10^7$	$2.62 \times 10^8$	$8.91 imes10^7$
5	2,3-Butanedione	$2.62 \times 10^7$	$2.43 imes10^6$	$2.84  imes 10^7$	$1.12  imes 10^8$	$5.40  imes 10^7$	$6.84  imes 10^6$	0	$9.96  imes 10^7$	$2.51 \times 10^8$	$2.13 \times 10^{7}$	$4.04  imes 10^8$	$4.02  imes 10^8$
6	Diethylacetaldehyde	$7.55 imes10^6$	$3.04 imes10^6$	$1.85  imes 10^7$	$1.70  imes 10^8$	$1.36 imes10^8$	$1.51  imes 10^7$	0	$5.55  imes 10^8$	$2.44 imes10^8$	$8.21  imes 10^7$	$5.04 imes10^8$	$9.43 imes10^7$
7	Acetylformaldehyde	$3.97 \times 10^7$	$9.18 imes10^6$	$2.07  imes 10^7$	$2.70  imes 10^7$	$2.88  imes 10^7$	$2.82 \times 10^7$	$5.75  imes 10^7$	$4.22  imes 10^7$	$9.22 \times 10^7$	$3.80 \times 10^7$	$1.06 \times 10^7$	$2.31  imes 10^7$
8	Acetic acid	$9.80  imes 10^7$	$2.67  imes 10^6$	$9.45  imes 10^7$	$1.91  imes 10^7$	$1.29  imes 10^7$	$2.52 \times 10^{7}$	$2.62  imes 10^7$	$4.00  imes 10^7$	$2.13  imes 10^7$	$1.69 \times 10^{7}$	$4.15  imes 10^7$	$4.64 imes10^7$
9	2,3-Pentanedione	$2.26  imes 10^7$	$6.38  imes 10^5$	$2.78  imes 10^7$	$1.24  imes 10^7$	$1.12  imes 10^7$	$2.28  imes 10^7$	0	$4.41  imes 10^7$	$2.42 \times 10^7$	$2.86  imes 10^6$	$4.49  imes 10^7$	$4.90 imes10^7$
10	Methylbenzene	$8.19 imes10^6$	$1.27  imes 10^7$	$1.94  imes 10^7$	$3.04  imes 10^7$	$1.04  imes 10^7$	$8.39  imes 10^6$	0	$6.60  imes 10^7$	$4.57 \times 10^7$	$8.96  imes 10^6$	$7.48  imes 10^7$	$2.52  imes 10^7$
11	Pyridine	$2.26  imes 10^6$	$1.56 \times 10^{7}$	$8.93 imes10^6$	$8.02  imes 10^6$	$1.84 imes10^7$	$2.02 \times 10^7$	0	$1.21  imes 10^8$	$9.62  imes 10^6$	$7.31  imes 10^6$	$6.22 \times 10^{6}$	$3.55  imes 10^7$
12	2-Methyl-3-pentanone	$7.34 imes10^6$	$7.26  imes 10^6$	$1.05  imes 10^7$	$2.31  imes 10^7$	$1.40 imes10^7$	$1.13  imes 10^7$	$2.82  imes 10^6$	$4.58 imes10^7$	$8.65  imes 10^7$	$3.82 \times 10^6$	$7.06 \times 10^7$	$5.50  imes 10^7$
13	2-Methyl-5-Hexanone	$2.31  imes 10^6$	$3.23  imes 10^6$	$5.81  imes 10^6$	$1.99  imes 10^7$	$1.51  imes 10^7$	$6.38  imes 10^6$	0	$6.53  imes 10^7$	$1.89  imes 10^7$	$8.72  imes 10^6$	$5.15  imes 10^6$	$3.73  imes 10^7$
14	Methyl 2-oxopropanoate	$1.57  imes 10^6$	$5.47  imes 10^6$	$6.60  imes 10^6$	$1.10  imes 10^7$	$9.18 imes10^6$	$3.86  imes 10^6$	0	$1.75  imes 10^8$	$2.78  imes 10^7$	$5.86  imes 10^6$	$6.19 imes10^7$	$1.22  imes 10^7$
15	2- Furancarboxaldehyde	$3.40 imes10^6$	$3.26  imes 10^6$	$1.33  imes 10^7$	$3.72 \times 10^7$	$8.78  imes 10^6$	$3.82  imes 10^6$	0	$6.42 \times 10^7$	$3.37  imes 10^7$	0	$7.88  imes 10^7$	$5.84  imes 10^7$
16	Cyclopentenone	$2.15  imes 10^6$	$2.71  imes 10^6$	$7.55  imes 10^6$	$1.99 imes10^7$	$8.01 imes10^6$	$5.29  imes 10^6$	0	$2.42  imes 10^7$	$5.12  imes 10^7$	0	$1.91  imes 10^8$	$4.08 imes10^7$
17	p-xylol	$4.52  imes 10^6$	0	$5.09 imes10^6$	$4.51  imes 10^7$	$2.36  imes 10^7$	$1.27 \times 10^7$	$2.46 imes10^6$	0	$1.39  imes 10^7$	0	$3.84  imes 10^7$	$1.89 imes10^7$
18	Methylacetylacetone	$2.81  imes 10^5$	0	$4.38 imes10^6$	$1.62  imes 10^7$	$5.69  imes 10^6$	$5.82  imes 10^6$	0	0	$5.57  imes 10^7$	0	$3.06  imes 10^7$	$6.77  imes 10^7$
19	2-Furanmethanol	$8.57  imes 10^6$	0	$6.77  imes 10^6$	$3.36 imes10^7$	$7.00  imes 10^6$	$3.17 imes10^6$	0	0	$3.08  imes 10^7$	0	$2.26  imes 10^7$	$9.39  imes 10^7$
20	Ethylene acetate	$1.55 imes10^6$	0	$3.08 imes10^6$	$2.10 imes10^7$	$6.94 imes10^6$	$3.76  imes 10^6$	0	0	$3.23  imes 10^7$	0	$2.51  imes 10^7$	$4.72  imes 10^7$
21	Phenol	$6.38  imes 10^6$	$2.76  imes 10^6$	$7.32  imes 10^6$	$2.99  imes 10^7$	$1.77  imes 10^7$	$8.23  imes 10^6$	$8.06 imes10^6$	$1.39  imes 10^8$	$4.92  imes 10^7$	0	$5.70  imes 10^6$	$3.74 imes10^7$
22	Cycloten	$1.65  imes 10^7$	$1.93 imes10^6$	$1.32  imes 10^7$	$2.73  imes 10^7$	$5.66  imes 10^6$	$6.44 imes10^6$	0	$4.55  imes 10^7$	$9.52  imes 10^7$	0	$7.16 imes10^6$	$1.36  imes 10^7$
23	o-Cresol	$1.75  imes 10^7$	$2.08 imes10^6$	$6.01 imes10^6$	$2.03 imes10^7$	$2.32  imes 10^7$	$7.28 imes10^6$	0	$3.94 imes10^7$	$8.57 imes10^7$	0	$1.05 imes10^8$	$3.33 imes10^7$
24	Guaiacol	$1.03  imes 10^7$	$1.49 imes10^6$	$4.56  imes 10^7$	$1.37  imes 10^7$	$2.01  imes 10^7$	$3.21  imes 10^6$	$1.47 imes10^7$	$2.83  imes 10^7$	$4.61  imes 10^7$	$1.15  imes 10^7$	$1.29  imes 10^8$	$2.15  imes 10^7$
25	p-Xylenol	$3.56  imes 10^6$	$5.77  imes 10^5$	$2.02  imes 10^6$	$2.11  imes 10^7$	$1.69  imes 10^7$	$6.66  imes 10^6$	0	$4.13  imes 10^7$	$3.68  imes 10^7$	0	$1.18  imes 10^7$	$1.99  imes 10^7$
26	Creosol	$6.37 imes10^6$	$8.90 imes10^5$	$8.42  imes 10^6$	$1.92  imes 10^7$	$7.08 imes10^6$	$5.23 imes10^6$	0	$2.64 imes10^7$	$4.02  imes 10^7$	0	$8.18 imes10^6$	$5.87  imes 10^7$
27	p-Ethylguaiacol	$5.27  imes 10^6$	$2.10 imes10^6$	$4.76  imes 10^6$	$2.03  imes 10^7$	$1.68  imes 10^7$	$6.39 imes10^6$	0	$7.45  imes 10^7$	$6.39  imes 10^7$	0	$9.52  imes 10^7$	$1.02  imes 10^8$

Table A1. Cont.

Variables		Study Cases											
		1	2	3	4	5	6	7	8	9	10	11	12
N°	Name	Untreated 400 °C	Untreated 500 °C	Untreated 600 °C	Acetic Acid 400 °C	Acetic Acid 500 °C	Acetic Acid 600 °C	1%HNO3/ 0.1 H <sub>2</sub> SO <sub>4</sub> 400 °C	1%HNO <sub>3</sub> / 0.1 H <sub>2</sub> SO <sub>4</sub> 500 °C	1%HNO <sub>3</sub> / 0.1 H <sub>2</sub> SO <sub>4</sub> 600 °C	0.1 H <sub>2</sub> SO <sub>4</sub> 400 °C	0.1 H <sub>2</sub> SO <sub>4</sub> 500 °C	0.1 H <sub>2</sub> SO <sub>4</sub> 600 °C
28	Syringol	$1.62 \times 10^7$	$1.03  imes 10^7$	$2.18  imes 10^7$	$3.51 \times 10^7$	$3.14  imes 10^7$	$5.12 \times 10^{6}$	$1.10 \times 10^7$	$6.91  imes 10^7$	$7.30 \times 10^7$	$7.29  imes 10^6$	$2.29  imes 10^7$	$1.20 \times 10^7$
29	Isoeugenol	$1.75  imes 10^7$	$1.53 imes10^7$	$2.22  imes 10^7$	$2.04 imes10^7$	$1.83 imes10^7$	$6.10 imes10^6$	$1.90 imes10^7$	$1.51  imes 10^8$	$1.34 imes10^7$	0	$6.92 imes10^7$	$9.47 imes10^7$
30	Guaiacylacetone	$6.55  imes 10^6$	$2.06  imes 10^6$	$5.81  imes 10^6$	$1.32  imes 10^7$	$2.56  imes 10^7$	$6.87  imes 10^6$	0	$3.12  imes 10^7$	$8.68 imes10^7$	$1.28  imes 10^7$	0	$1.95  imes 10^7$
32	2,5-Dimethoxy-4- methylbenzaldehyde	0	$8.64\times 10^6$	$1.93  imes 10^7$	$9.23  imes 10^6$	$3.11  imes 10^6$	$4.53 imes10^6$	0	0	$4.10  imes 10^7$	0	0	$6.33 imes10^7$
33	Levoglucosan	$7.70 imes10^5$	$1.06  imes 10^5$	$2.70  imes 10^7$	$2.13 imes10^8$	$9.33 imes10^7$	$4.81 imes10^7$	$2.51 \times 10^7$	$1.31  imes 10^8$	$1.33 imes10^8$	$1.69 imes10^7$	$1.07 imes10^8$	$1.82  imes 10^8$
34	Methoxyeugenol	$2.59  imes 10^6$	$5.17 imes10^6$	$1.57 \times 10^7$	$3.78  imes 10^7$	$1.72  imes 10^7$	$1.54 imes10^7$	$1.33  imes 10^7$	$1.18 imes10^7$	$5.80  imes 10^7$	$3.95 imes10^6$	$5.93 imes10^6$	$3.49  imes 10^7$
35	Caffeine	$1.11 \times 10^7$	$1.04 imes10^7$	$6.01  imes 10^7$	$1.09 imes10^8$	$5.28  imes 10^7$	$1.71  imes 10^7$	$7.46 imes10^6$	$5.19  imes 10^7$	$6.57  imes 10^7$	$1.76  imes 10^7$	$1.12  imes 10^7$	$1.49 imes10^8$
36	Palmitic acid	$2.16  imes 10^7$	$2.15  imes 10^7$	$3.37  imes 10^7$	$4.45 imes10^7$	$5.67  imes 10^7$	$2.77 imes10^6$	$2.65  imes 10^7$	$1.13 imes10^7$	$5.91  imes 10^7$	$7.27 imes10^6$	$7.72  imes 10^7$	$2.07 imes10^8$
37	Linoleic acid	$3.80  imes 10^6$	$6.23  imes 10^6$	$2.94  imes 10^7$	$6.11  imes 10^7$	$3.57 \times 10^7$	$5.47 imes10^6$	$2.06  imes 10^7$	$8.30  imes 10^7$	$3.16  imes 10^7$	$3.79  imes 10^7$	$4.10 imes10^6$	$1.94 imes10^8$
38	Stearic acid	$7.11  imes 10^4$	$1.68  imes 10^6$	$4.18  imes 10^6$	$2.92  imes 10^7$	$1.81  imes 10^7$	$1.22 \times 10^7$	$6.96  imes 10^6$	$1.00 \times 10^8$	$1.67  imes 10^7$	$9.94 imes10^6$	$7.32  imes 10^6$	$1.09  imes 10^8$

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