

## Article

# Effect of Acid Pretreatment on the Primary Products of Biomass Fast Pyrolysis

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**Abstract:** A high load of inorganics in raw lignocellulosic biomass is known to inhibit the yield of bio-oil and alter the chemical reactions during fast pyrolysis of biomass. In this study, palm kernel shell (PKS), an agricultural residue from palm oil production, and two other woody biomass samples (mahogany (MAH) sawdust and iroko (IRO) sawdust) were pretreated with distilled water or an acidic solution (either acetic, formic, hydrochloric (HCl) or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)) before fast pyrolysis in order to investigate its effect on the primary products and pyrolysis reaction pathways. The raw and pretreated PKS, MAH and IRO were pyrolysed at 600 °C and 5 s with a micro-pyrolyser connected to a gas chromatograph–mass spectrometer/flame ionisation detector (GC-MS/FID). Of the leaching solutions, HCl was the most effective in removing inorganics from the biomass and enhancing the primary pyrolysis product formed compared to the organic acids (acetic and formic acid). The production of levoglucosan was greatly improved for all pretreated biomasses when compared to the original biomass but especially after HCl pretreatment. Additionally, the relative content of the saccharides was maximised after pretreatment with H<sub>2</sub>SO<sub>4</sub>, which was due to the increased production of levoglucosone. The relative content of the saccharides increased by over 70%. This increase may have occurred due to a possible reaction catalysed by the remaining acid in the biomass. The production of furans, especially furfural, was increased for all pretreatments but most noticeable when H<sub>2</sub>SO<sub>4</sub> was used. However, the relative content of acids and ketones was generally reduced for PKS, MAH and IRO across all leaching solutions. The relative content of the phenol-type compound decreased to a large extent during pyrolysis after acid pretreatment, which may be attributed to dehydration and demethoxylation reactions. This study shows that the production of valuable chemicals could be promoted by pretreatment with different acid solutions.



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**Keywords:** fast pyrolysis; primary products; pretreatment of biomass; Py-GC/MS/FID

## 1. Introduction

Biomass, which is abundant in nature, is renewable and regarded as carbon dioxide neutral. Lignocellulosic biomass, such as wood, forestry residues and agricultural waste, is of special interest due to its wide availability, low cost and low negative impact on food production [1]. Lignocellulosic biomass is composed of cellulose, hemicellulose and lignin, as well as minor amounts of extractives and inorganic constituents, and can be transformed into biofuel and chemicals, such as bio-oil, phenols and anhydrous sugars, by thermochemical conversion [2]. Among the different thermochemical conversion routes, fast pyrolysis has been identified as a promising technique for converting biomass into bio-oil and chemicals [3]. This is because fast pyrolysis favours the production of bio-oil that can be upgraded to transportation fuels compared to slow pyrolysis, which favours the production of bio-char and gas [4]. However, the produced bio-oil is of low quality due to its high water and oxygen content, high viscosity, poor volatility, corrosiveness and instability (i.e., ageing) during storage [5]. This has been attributed to the biomass composition and the presence of inorganic constituents in the biomass feedstock [1,6]. The inorganic constituents in the biomass are in the form of alkaline and alkaline earth metals (AAEMs), which have

catalytic effects on the thermal decomposition behaviour [1,7]. Thus, they will affect the conversion rate of biomass. This may result in a changed yield of the volatile compounds formed and a change in the reaction pathway during biomass pyrolysis.

The presence of inorganic substances in the biomass has been reported to hinder the formation of sugars, especially levoglucosan, during pyrolysis of biomass; instead, it promotes the formation of lower molecular weight compounds, such as hydroxyacetaldehyde [8–10]. Usino et al. [8] showed that the interaction between cellulose, xylan and lignin in virgin birch wood strongly inhibited the formation of saccharides (especially levoglucosan), while the yield of hydroxyacetaldehyde was promoted when compared with the pyrolysis of the combined individual compounds. This was suggested to be due to the presence of inorganic materials and covalent bonds between cellulose, hemicellulose and lignin in the native biomass. Furthermore, Patwardhan et al. [11] studied the effects of inorganic salts on the yield of levoglucosan from primary pyrolysis of cellulose by impregnating it with switchgrass ash, NaCl and MgCl<sub>2</sub>. The result showed that mineral salts present in the biomass lowered the activation energy of the reactions, promoting the formation of the low molecular weight compounds from the cellulose, while, at the same time, hindering the production of levoglucosan. The presence of inorganic substances in biomass and the interaction between cellulose, xylan and lignin, thus, have a significant effect on bio-oil composition during fast pyrolysis [8]. Additionally, the presence of inorganic substances favours both the formation of char and water via dehydration reactions and, also, the formation of light oxygenate compounds by ring fragmentation of the biomass constituents [10,12]. The inorganic substances not only catalyse the depolymerisation reactions of the biomass macromolecules, but also promote the secondary degradation of the biomass, which results in the formation of compounds of lower molecular weight [13].

To improve the quality of the pyrolysis products and minimise the negative effect of inorganic constituents during fast pyrolysis of biomass, pretreatment of raw biomass is needed. This is because pretreatment can be used to isolate the effect of inherent or externally added AAEMs on the pyrolysis reaction pathways [14]. Some of the pretreatment methods use water (both at room temperature and hot water) [15,16], torrefaction [17,18], acids (both organic and inorganic) [7,19] or a combination of these methods [20–22]. Using pretreatment techniques on biomass could weaken the macromolecular structure of the initial biomass [23] and dissolve most of the hemicellulose [24]. This will increase the surface area, the energy density and the porosity of the biomass, as well as reduce the cellulose crystallinity [23] and lead to reduced content of hydroxy acids, aldehydes and ketones in the bio-oil. Among the pretreatment methods, the use of inorganic acids has been reported to be the most effective method to remove inorganic substances, as well as to improve the yield and quality of the bio-oil produced from fast pyrolysis of biomass [7,25]. During acid leaching of biomass, AAEM salts react with the acid to form water-soluble compounds, as these cations are ion exchanged by a proton from the strong acid [10]. Thus, it results in increased bio-oil yield and a reduction in the water content and the amounts of light oxygenate compounds [23].

Chen et al. [26] observed a significant increase in levoglucosan content and decreased yield of the phenolic compounds (especially phenol) when corn straw was treated with 0.1 mol/L hydrochloric acid (treatment at room temperature for 4 h). The increased yield of the sugars was attributed to the removal of AAEMs. However, they observed a decreased yield of furfural for the acid-treated sample. Zhang et al. [19] investigated the influence of pretreatments with different solutions: water, formic acid, acetic acid, oxalic acid, phosphoric acid, nitric acid, hydrochloric acid and sulphuric acid at room temperature on the pyrolysis of the reed pole. They observed an increased yield of levoglucosan for all pretreated samples compared to the raw biomass. However, the yield of furfural, phenol and acetic acid was decreased. The increased yield of levoglucosan from the acid-treated (especially after treatment with sulfuric acid) sample was attributed to the presence of a small amount of acid that remained in the biomass after washing with deionised water [27]. Washing with water alone does not completely remove the acid from the pore structure

of the biomass after acid pretreatment [28]. This small amount of acid could act as a catalyst when converting cellulose to anhydrosugars, while also hindering the production of carboxylic acid and ketone products [27,28].

Most studies on pyrolysis of pretreated biomass showed enhanced production of levoglucosan, while the production of phenolic and furans compounds have been decreased [23,26,29]. However, a few studies have reported otherwise for the phenolic [30,31] or furan (especially furfural) compounds [25,32]. The higher yield of the phenolic compounds from the untreated biomass compared to the pretreated biomass is attributed to the inorganic constituents in the biomass, which may catalyse cracking of lignin and oligomers and thereby enhance the formation of phenolic monomers [1]. With the differing results, it is worth noting that the success of different leaching methods depends on the composition of the raw biomass, the leaching conditions, the particle size of the biomass, the water/acid-to-biomass ratio, the temperature and the leaching time [6].

This study aims to investigate the effect of water and acid pretreatment on the primary products of fast pyrolysis of palm kernel shells (PKS), mahogany (MAH) and iroko (IRO) sawdust, as well as provide insight into their decomposition mechanism. Additionally, the volume of waste emanating from PKS and sawdust in a tropical region, such as Nigeria, is estimated at 2.5 million tonnes of PKS [33] and 1.8 million tonnes of sawdust annually [34]. Moreover, both PKS and MAH and IRO sawdust are usually stacked in piles to compost or burned in the open to supply energy or as a waste management technique, thus resulting in environmental problems. Hence, a more controlled use of such waste is important, and one possibility is the production of bio-oil and chemicals.

## 2. Materials and Methods

### 2.1. Materials and Sample Preparation

To investigate the fast pyrolysis of raw and pretreated biomass, samples of iroko (*Chlorophora excelsa*) and mahogany (*Khaya ivorensis*) were collected from sawmills in the western part of Nigeria, while palm kernel shell was obtained from a palm oil production site in the southern part of Nigeria. The biomass samples were then milled with a Retsch SM 100 cutting mill to pass through a 6 mm screen. They were further sieved by a Haver (EML 200 pure) test sieve shaker, and sample sizes of 1–2 mm were used for further studies after drying in an oven at 105 °C overnight to a constant weight.

### 2.2. Acid Pretreatment

To remove inorganic materials from the raw PKS, IRO and MAH, dilute acid pretreatments and Milli-Q water were used. The acid solutions were prepared with acetic acid (99.7 wt.%), formic acid (95 wt.%), hydrochloric acid (37 wt.%), sulfuric acid (95 wt.%) and Milli-Q water. A 5.0 M solution was used for the mild acids: acetic (Ace) and formic (For) acids, while both 3.0 and 5.0 M solutions were used for the strong acids: hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Leaching of the biomasses was carried out by immersing 1 g of the sample in 15 mL solution of water/acids in a 100 mL blue cap screw bottle. These were then placed on an Innova platform shaker for 4 h at room temperature and set at a speed of 220 rpm. The leached samples were then filtered and washed continuously with Milli-Q water until a neutral pH value was achieved. The washed samples were then dried in an oven at 105 °C for 24 h and, thereafter, cooled in a desiccator before being stored for further use. Additionally, the weight of the cooled samples were used to determine the weight loss during the leaching procedure.

### 2.3. Compositional Analysis of Raw and Pretreated Biomass Sample

The carbohydrate and lignin contents of the raw and pretreated PKS, MAH and IRO were characterised according to the NREL protocol (NREL/TP-510-42618) [35]. This was conducted by adding 3 mL solution of 72% H<sub>2</sub>SO<sub>4</sub> to 0.3 g of the raw and pretreated biomass sample and stirring every 10 min for 1 h in a water bath at 35 °C. It was then hydrolysed by adding 84 mL of Milli-Q water before placing them in an autoclave at

121 °C for 60 min. The sample was thereafter cooled to room temperature and filtered. The filtrate was collected and stored in a 50 mL bottle for analysis of acid-soluble lignin and carbohydrate, while the residue was used to determine the acid-insoluble lignin. The acid-soluble lignin was analysed by spectrophotometry, while the residue was dried overnight at 100 °C and then kept in a desiccator. Determination of the carbohydrate content, glucose, xylan, arabinose and galactose, was carried out with the use of high-performance liquid chromatography (HPLC). This was achieved with a lead-(II)-based column (Aminex HPX-87P, Bio-Rad, Hercules, CA, USA) operating at 85 °C and with 0.6 mL/min of ultrapure water as the eluent [36]. The amount of glucan present in the sample was used to determine the cellulose content, while the amount of xylan, arabinose and galactose correspond to the amount of hemicellulose. All analysis was carried out in duplicate, and the values are reported as average values.

#### 2.4. Proximate Analysis

The moisture content and volatile matter of the biomass were determined according to the ASTM standard test methods: ASTM E 871–82 and ASTM E872–82. The moisture content was determined by drying 3.0 g of each biomass sample in an oven at 105 °C for 16 h. The difference in weight between the raw and the dried samples was used to determine the weight loss of the biomass. The volatile matter of the raw biomass was determined by heating 1.0 g of each biomass sample in a furnace at a constant temperature of  $950 \pm 20$  °C for 7 min and cooled thereafter in a desiccator. The difference in weight was then used to determine the volatile matter of the sample. The ash content was determined by drying 4.0 g of raw biomass overnight at 105 °C and then heating it in a furnace (Nabertherm B 150) at 550 °C for 4 h. The remaining residue in the crucible, after combustion in the furnace, was then used to estimate the ash content of each biomass. The fixed carbon content of the biomasses was determined by calculating the difference between 100 and the sum of the percentages of volatile matter, ash and moisture content of the biomass.

#### 2.5. FTIR Spectroscopy

In order to investigate the effect of acid pretreatment on the biomass structure before and after pretreatment, a Fourier transform infrared spectroscopy (FTIR) was used to analyse the functional groups present. The samples were scanned 64 times in the spectrum range of  $4000\text{--}400\text{ cm}^{-1}$  with a resolution of  $4\text{ cm}^{-1}$  by a Nicolet iS10, Thermo Fisher Scientific FTIR spectrometer and using the OMNIC 4.1 software.

#### 2.6. TGA Experiment

Thermogravimetric analysis was used to investigate the thermal degradation behaviour of the raw and pretreated PKS, MAH and IRO using a Mettler-Toledo TGA/DSC 3<sup>+</sup> thermogravimetric analyser. About 5.0 mg of the sample was placed on a microbalance and heated from 25 to 600 °C, with a heating ramp of 10 °C/min under a nitrogen flow rate of 20 mL/min, and then held for 30 min after reaching the final temperature [8]. Each experiment was carried out at least two times to ensure repeatability.

#### 2.7. Determination of Inorganic Material Present in the Biomass

The content of inorganic material present in PKS, MAH and IRO was determined by drying 4.00 g of raw or pretreated biomass overnight at 105 °C to remove water and then heating in a furnace (Nabertherm B 150) at 550 °C for 4 h. The residue left in the crucible after combustion in the furnace was used to determine the content of inorganic constituents. Each analysis was carried out in duplicate.

#### 2.8. Py-GC-MS/FID

Fast pyrolysis of the samples was carried out in a micro-pyrolyser (Pyrola2000 (Pyrolab)) connected to a gas chromatograph (GC), a mass spectrometer (MS) and a flame ionisation detector (FID), so-called Py-GC-MS/FID. Close to 500 µg of the biomass sample

was weighed on an analytical balance (KERN ABT 320-4M) and placed at the centre of the platinum filament in the micro-pyrolyser. The platinum filament had been calibrated to the desired temperature range before the experiment. The fast pyrolysis was performed at a temperature of 600 °C for 5 s. The selected operating condition agrees with previous studies [37,38] to achieve the maximum yield of released volatile compounds.

Both the micro-pyrolyser chamber temperature and the transfer tube were set to 150 °C. The released pyrolysis products were directly transferred by a continuous flow of helium gas to the GC (Trace GC Ultra, Thermo Scientific, Waltham, MA, USA). The separated pyrolysis product was then identified by an MS (ISQ™, Thermo Scientific) and quantified by an FID (Thermo Scientific). The assigned GC operating parameters were injector temperature (200 °C); capillary column (Zebron™ ZB-5MS, 30 m × 0.25 mm × 0.25 µm); and oven temperature (60 °C for 1 min, heated at 8 °C/min to 265 °C and held for 20 min), and helium gas was used as carrier gas (1.5 mL min<sup>-1</sup>) in split mode with 1:7 ratio to the GC.

The MS transfer line and the FID base temperatures were set to 250 °C, while the ion source temperature was kept at 200 °C. The mass spectrometer operated in electron ionisation mode (EI) of 70 eV and scanned from 25 to 250 *m/z*. Identification of the pyrolysis product was based on the retention time and with reference to the NIST Library (NIST MS Search 2.0). Experiments were repeated at least three times to demonstrate replicability and to minimise errors. A drawback of this technique is that not all released volatile compounds can be identified based on their mass spectra [5]. This is due to the low concentration of some compounds, coelution of compounds on the GC column and limitations of the mass spectral database [5]. Additionally, this technique is unable to give a quantitative analysis of the produced volatile compounds because of the complex mass spectrum and the lack of available standards [39]. Additionally, since the MS detector responds differently to different compounds and the response is not always linear with respect to concentration [5], the FID peak area with consideration of the response factor was used for comparison between different volatile compounds obtained from the GC-MS, as described in a previous study [8].

### 3. Results and Discussion

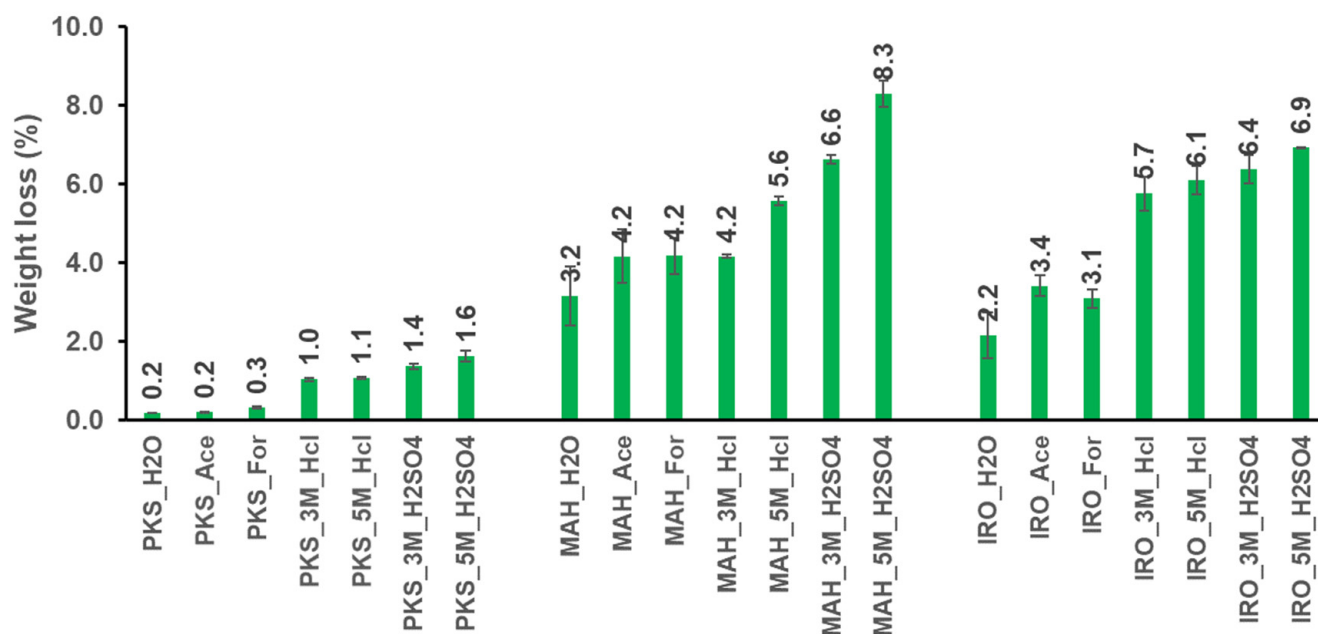
#### 3.1. Weight Loss of Pretreated Biomass

Pretreatment of biomass is an effective way to remove dirt, dust and inorganic materials from the biomass before thermal degradation. However, the pretreatment can affect the initial material, as some material could be released and others might suffer structural changes. The percentage weight loss of material after pretreatment with different acids and water is shown in Figure 1.

After pretreatment of the three biomasses, the percentage of material loss varied from 0.2 ± 0.0% to 1.6 ± 0.1% for PKS, 3.2 ± 0.8% to 8.3 ± 0.3% for MAH sawdust and 2.2 ± 0.6% to 6.9 ± 0.0% for the IRO sawdust. Less material loss was observed for the PKS compared to the IRO and MAH sawdust. This may be due to the complexity and robust structure as well as the recalcitrant nature of the lignin-rich PKS to acid degradation [40,41]. The differences in material loss observed for PKS, MAH and IRO may be attributed to the structure and composition of these biomasses and not the leaching method used [1]. In comparison with the woody biomasses (MAH and IRO), PKS has also been shown to have a higher density (1.19–1.32 g/cm<sup>3</sup>) [42] than MAH and IRO (0.52 and 0.61 g/cm<sup>3</sup>, respectively) [43]. As observed in Figure 1, more material loss occurs with increasing severity of the acid pretreatment for all three biomass samples. Pretreatment with water and mild acid (5 M of acetic acid and formic acid) resulted in less material loss compared to pretreatment with the strong acids (3 and 5 M of HCl and H<sub>2</sub>SO<sub>4</sub>), where the highest loss of 6.9% and 8.3% was found for the 5 M H<sub>2</sub>SO<sub>4</sub> pretreatment of IRO and MAH sawdust, respectively. This could be attributed to the harshness of the acid solution and, also, because more fines were generated for the biomass samples, which led to higher material loss after washing with Milli-Q water. This result is similar to a previous study where the loss of fines was lesser



for PKS leached with distilled water compared to that pretreated with 5% dilute acetic acid [44].



**Figure 1.** Percentage of weight loss after pretreatment of palm kernel shell (PKS), mahogany (MAH) and iroko (IRO) sawdust.

### 3.2. Compositional Analysis of Pretreated Biomass

Table 1 provides an overview of the content of cellulose, hemicellulose and lignin in the raw and pretreated PKS, MAH and IRO. As observed in Table 1, the lignin content in the untreated PKS (57.2 wt.%) was high, while its cellulose content was low (8.3 wt.%) compared to the content of these substances in untreated MAH and IRO. The cellulose contents in untreated MAH and IRO were similar ( $\approx 25$ – $28$  wt.%), while the lignin content had a larger variation (31.9 wt.% in MAH and 38.4 wt.% in IRO). The remaining fractions of PKS, MAH and IRO not accounted for in Table 1 may include proteins, oils and ash [45]. After pretreatment, a slight increase in the cellulose content was observed for PKS leached with water or strong acids. The highest content of cellulose (11.2 wt.%) was observed for PKS pretreated with 3 M HCl. The content of cellulose for the woody biomasses was increased for all pretreatment conditions and most pronounced for the IRO sawdust. The highest composition of cellulose for MAH and IRO was obtained at 5 M HCl, with a cellulose content of 32.0 wt.% and 30.8 wt.%, respectively. A similar increment has also been reported when reed pole was pretreated with different mild and strong acids at room temperature [19]. The lignin content for most of the pretreated biomass was slightly decreased for PKS and IRO. However, the case of MAH sawdust was different, with increased content of lignin for most of the pretreated biomass samples. The highest lignin content in all materials was observed after pretreatment with 3 M H<sub>2</sub>SO<sub>4</sub> for PKS (58.1 wt.%) and MAH (40.9 wt.%) and 5 M H<sub>2</sub>SO<sub>4</sub> for IRO (43.1 wt.%). Moreover, the content of xylan was mostly decreased after this pretreatment. A similar result was presented by Jiang et al. [46], who observed an obvious decrease in the hemicellulose content after pretreatment of sugarcane bagasse with 0.1 wt.% dilute sulfuric acid solution and a slight decrease when pretreated with water. This may be due to hydrolysis of hemicellulose to its monomeric constituents; therefore, its interaction with lignin is partially disrupted during acid pretreatment [47].

**Table 1.** Compositional analysis of palm kernel shell (PKS), mahogany (MAH) and iroko (IRO) sawdust.

Sample Type	Cellulose (wt.%)	Lignin (wt.%)	Xylan (wt.%)	Arabinose (wt.%)	Galactose (wt.%)
PKS_Untreated	8.4 ± 1.3	57.2 ± 0.7	3.3 ± 0.0	0.0 ± 0.0	0.4 ± 0.0
PKS_H <sub>2</sub> O	9.2 ± 1.0	57.6 ± 0.8	2.9 ± 0.2	0.0 ± 0.0	0.3 ± 0.0
PKS_Ace	7.8 ± 0.9	55.7 ± 0.0	3.4 ± 0.0	0.0 ± 0.0	0.3 ± 0.0
PKS_For	8.0 ± 1.2	55.6 ± 0.1	3.2 ± 0.0	0.0 ± 0.0	0.4 ± 0.0
PKS_3M_HCl	11.2 ± 1.2	53.7 ± 3.2	2.8 ± 0.0	0.0 ± 0.0	0.3 ± 0.0
PKS_5M_HCl	11.0 ± 1.1	53.0 ± 0.2	3.0 ± 0.3	0.0 ± 0.0	0.2 ± 0.0
PKS_3M_H <sub>2</sub> SO <sub>4</sub>	10.4 ± 1.1	58.1 ± 0.3	2.6 ± 0.0	0.0 ± 0.0	0.3 ± 0.0
PKS_5M_H <sub>2</sub> SO <sub>4</sub>	10.0 ± 0.2	56.7 ± 1.3	3.0 ± 0.4	0.0 ± 0.0	0.3 ± 0.0
MAH_Untreated	27.5 ± 0.6	31.9 ± 1.6	2.0 ± 0.6	0.1 ± 0.0	0.2 ± 0.1
MAH_H <sub>2</sub> O	28.9 ± 0.7	32.0 ± 1.3	2.0 ± 0.5	0.1 ± 0.0	0.2 ± 0.0
MAH_Ace	30.4 ± 0.2	30.7 ± 1.5	2.1 ± 0.4	0.2 ± 0.0	0.1 ± 0.1
MAH_For	29.3 ± 1.3	32.2 ± 0.0	1.6 ± 0.0	0.2 ± 0.0	0.1 ± 0.0
MAH_3M_HCl	29.9 ± 0.3	33.4 ± 0.8	2.5 ± 0.1	0.1 ± 0.0	0.2 ± 0.0
MAH_5M_HCl	32.0 ± 0.3	30.5 ± 0.1	2.6 ± 0.0	0.1 ± 0.0	0.2 ± 0.0
MAH_3M_H <sub>2</sub> SO <sub>4</sub>	28.0 ± 1.4	40.9 ± 2.3	1.5 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
MAH_5M_H <sub>2</sub> SO <sub>4</sub>	27.9 ± 1.3	37.1 ± 0.8	1.6 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
IRO_Untreated	25.0 ± 0.3	38.4 ± 0.9	2.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
IRO_H <sub>2</sub> O	28.8 ± 0.1	34.6 ± 0.3	2.2 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
IRO_Ace	26.9 ± 0.3	36.4 ± 1.0	2.3 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
IRO_For	27.1 ± 0.1	38.3 ± 0.1	2.2 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
IRO_3M_HCl	29.2 ± 0.1	40.9 ± 1.2	2.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
IRO_5M_HCl	30.8 ± 0.1	36.4 ± 0.1	2.2 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
IRO_3M_H <sub>2</sub> SO <sub>4</sub>	27.7 ± 0.7	42.6 ± 0.3	1.3 ± 0.4	0.1 ± 0.0	0.1 ± 0.1
IRO_5M_H <sub>2</sub> SO <sub>4</sub>	27.4 ± 0.7	43.1 ± 3.1	1.4 ± 0.1	0.1 ± 0.0	0.1 ± 0.0

Table 2 shows the moisture content, ash, volatile matter, fixed carbon and heating value of the raw PKS, MAH and IRO. PKS had the lowest moisture content (2.2 wt.%), ash content (0.9 wt.%) and volatile matter (76.7 ± 1.0 wt.%) compared to the MAH and IRO, while IRO had the highest ash content (4.8 wt.%) and MAH had the highest volatile matter content (82.5 ± 1.0 wt.%).

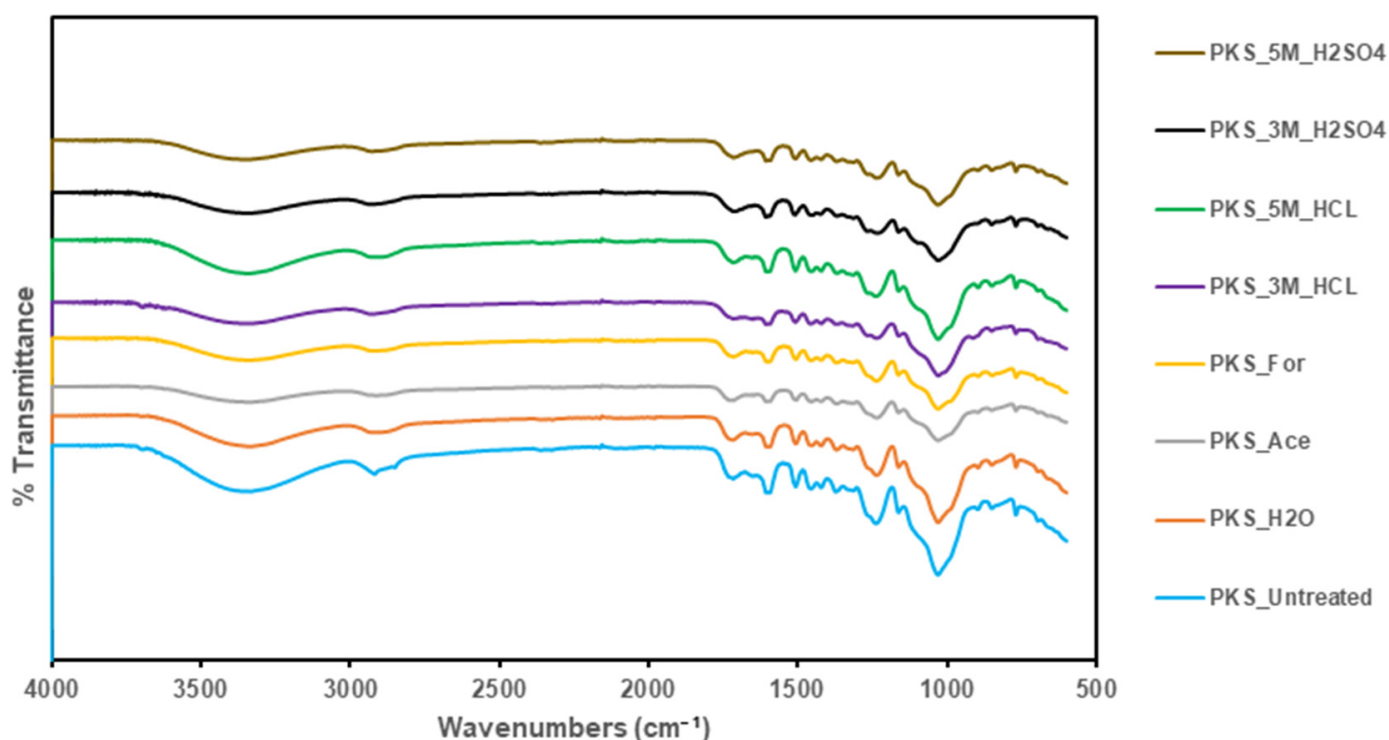
**Table 2.** Proximate analysis and characterisation of raw PKS, MAH and IRO.

Feedstock	PKS (wt.%)	MAH (wt.%)	IRO (wt.%)
Proximate analysis			
Moisture content	2.2 ± 0.0	3.9 ± 0.0	3.8 ± 0.1
Ash	0.9 ± 0.0	2.6 ± 0.1	4.8 ± 0.0
Volatile matter	76.7 ± 1.0	82.5 ± 0.6	78.6 ± 0.1
Fixed carbon	20.3	11.1	12.9
Calorific value (HHV, MJ/kg)	20.7 ± 0.2	18.9 ± 0.1	19.5 ± 0.2

### 3.3. FTIR Analysis of the Biomass Samples

FTIR analysis for the raw and pretreated PKS, MAH and IRO was carried out to investigate the impact of the pretreatment on the chemical structures of the biomass. The FTIR spectra presented in Figure 2 show that the acid-washed PKS was slightly affected by the acid pretreatment compared to that of the untreated PKS. The deviation was most notable at the absorption band of 1000 cm<sup>-1</sup> for the PKS treated with H<sub>2</sub>SO<sub>4</sub>, acetic and formic acid, which corresponds to the C-O stretching of polysaccharides. However, only small differences were observed for the woody biomasses (MAH and IRO) for all the leaching treatment, as shown by the FTIR spectra in Figure S1. The slight deviations in the peak intensities are mostly observed for the peak bands between 3600–3200, 3000–2800, 1800–1200, and 1100–800 cm<sup>-1</sup> for the PKS, MAH and IRO. However, the deviations were stronger for the woody biomass (MAH and IRO) and especially in the region of 1800–1200 cm<sup>-1</sup>.

Furthermore, the deviations in the peak intensities could mean that some functional groups in the biomass were disrupted to a certain extent after acid pretreatment [7]. The broad band at  $3600\text{--}3200\text{ cm}^{-1}$  corresponds to the O-H stretching vibration of phenolic, alcoholic and carboxylic functional groups [48]. The reduced intensity observed at  $3326\text{ cm}^{-1}$ , especially for the strong-acid-pretreated woody biomass, can be attributed to the disruption of hydrogen bonds of cellulose in the sample after acid pretreatment [7,49]. The deviation at  $2922\text{ cm}^{-1}$  corresponds to C-H stretching vibrations of  $-\text{CH}_2$  and  $-\text{CH}_3$  functional groups and is interpreted as cellulose being present in the biomass [48,50]. The disruption of this band could be due to changes in the cellulose crystallinity [51]. The absorption band at  $1713\text{ cm}^{-1}$  and  $1735\text{ cm}^{-1}$  corresponds to the hemicellulose content [48]. The reduction in the peak intensity, especially for the woody biomass, can be attributed to the hydrolysis of hemicellulose during pretreatment [52]. Additionally, the bands at  $1601$ ,  $1509$  and  $1455\text{ cm}^{-1}$  are due to the C=C stretching vibrations and correspond to the presence of lignin. The reduction in peak intensity after acid washing of the different biomasses can be attributed to condensation reactions and/or splitting of lignin aliphatic side chains [7]. The absorption band at  $1370\text{--}1235\text{ cm}^{-1}$  indicates the presence of alkanes and is due to the C-H stretching vibration of cellulose [53,54]. The strong absorption band at  $1031\text{ cm}^{-1}$  corresponds to the C-O stretching of polysaccharides [7]; for this study, there was no deviation in peak intensity for any of the three biomasses investigated. Finally, the band at  $897\text{ cm}^{-1}$  is associated with the C-O-C bond from the cellulose, and its enhancement can be attributed to an increase in the relative content of cellulose due to the release of the hemicellulose fraction during pretreatment [55].



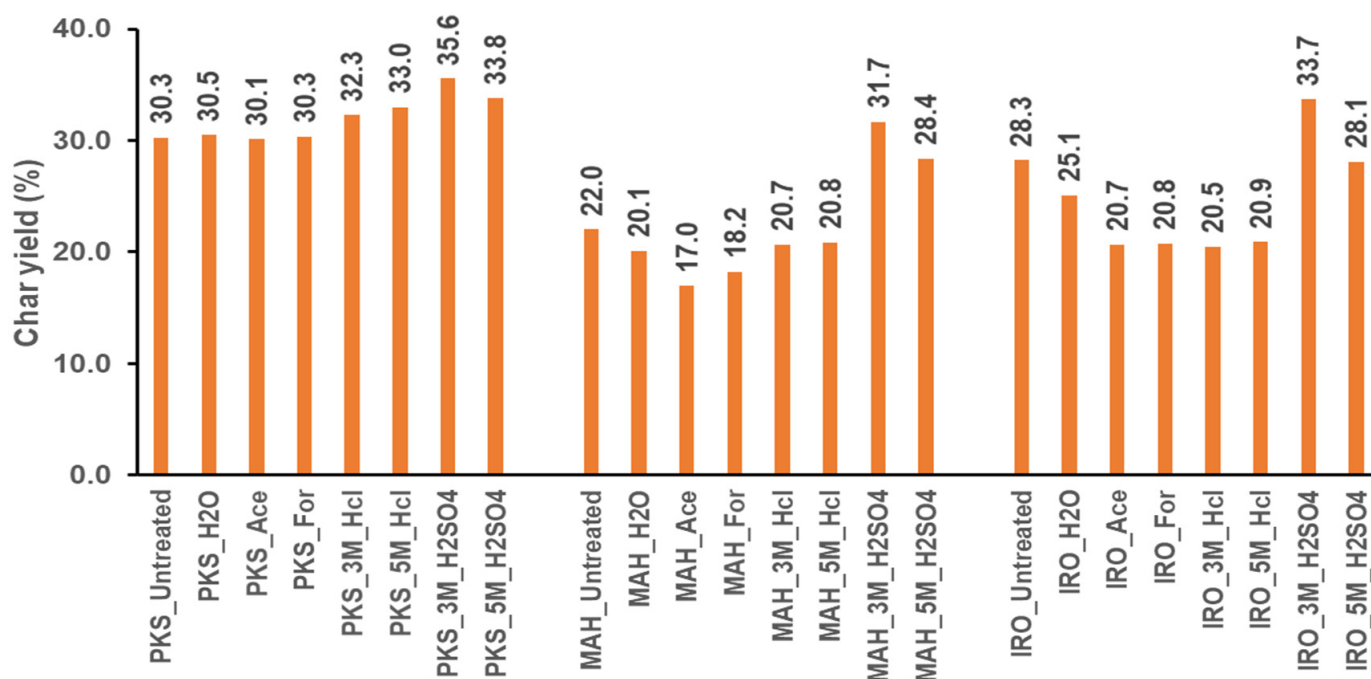
**Figure 2.** FTIR spectra of the raw and pretreated palm kernel shell.

### 3.4. Thermogravimetric Analysis of Raw and Pretreated Biomass

Figure 3 shows the char yield from the thermogravimetric analysis for untreated and pretreated PKS, MAH and IRO. The char yield obtained at  $600\text{ }^{\circ}\text{C}$  describes the degradation behaviour of the raw and pretreated biomasses. As observed, the char yield from the PKS residue showed higher char yield than the untreated PKS for the demineralised biomass when compared to those of MAH and IRO. This is because demineralisation increases devolatilisation and the initial decomposition temperature of the biomass pyrolysis, which



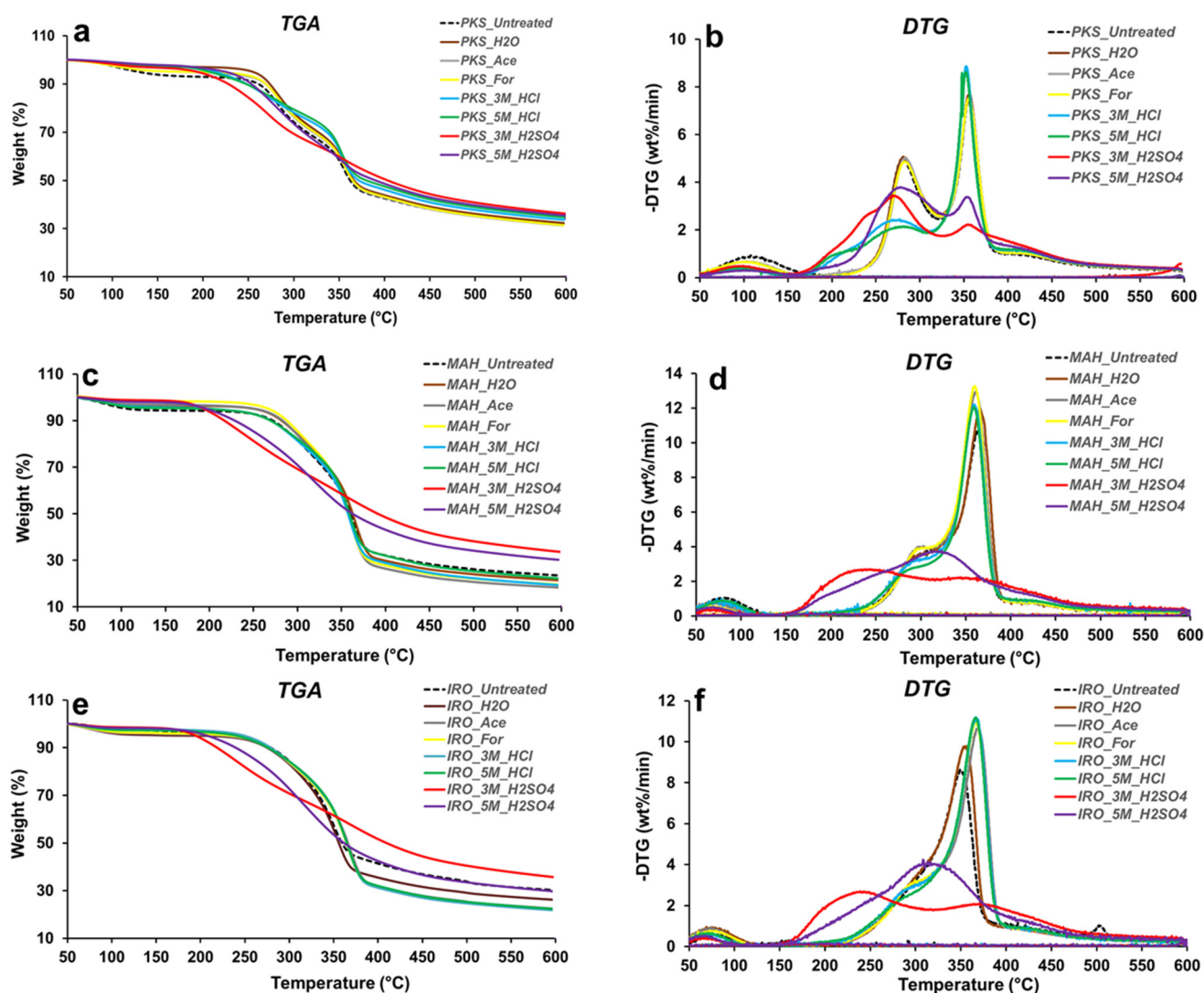
can be attributed to the high potassium and lignin content of PKS [3,56]. Additionally, potassium, which is one of the main inorganic constituents in PKS (150 mg/kg), has been reported to be a strong catalyst for char gasification [3,56]. The char yield for the PKS was almost equal for the untreated, water and mild acid treatment and with a slight increase in the char yield from 30.3 wt.% of the untreated PKS to 33.0 and 35.6 wt.% for PKS treated with 5 M HCl and 3 M H<sub>2</sub>SO<sub>4</sub>, respectively, which may be due to the slow degradation and thermal stability of the lignin molecule [14]. This trend was, however, different for the woody biomasses (MAH and IRO). They showed an initial decrease in char yield compared to the untreated sample when using mild acids and then an elevated char yield for the H<sub>2</sub>SO<sub>4</sub> pretreated samples. The result is in agreement with previous studies [57,58], even though other species were used: *Pinus radiata* wood chips [58] and Douglas fir and hybrid poplar wood [57]. The increased char yield can be attributed to the increased presence of sulphur in the biomass after leaching with H<sub>2</sub>SO<sub>4</sub>, which shows that some sulphur remained in the biomass after washing with water. This may have catalysed the char formation by polymerisation of the primary vapours [58].



**Figure 3.** Schematic of the raw and pretreated PKS, MAH and IRO final residue obtained from the TGA analysis in nitrogen atmosphere at 600 °C. Average standard deviation for all samples was <1.1%.

The TGA and DTG curves for the raw and pretreated PKS, MAH and IRO are shown in Figure 4a–f. The TGA/DTG curves for the raw and pretreated biomasses showed three main degradation steps for PKS, MAH and IRO feedstock. Generally, as observed from the TGA/DTG curves in Figure 4, the first stage of the biomass degradation involves the removal of the moisture and the decomposition of light organic compounds in the biomass (50–150 °C) [21]. This is followed by the devolatilisation of the biomass material: devolatilisation of hemicellulose (150–320 °C); cellulose (330–380 °C); and lignin (150–500 °C) [48]. The DTG curve presented in Figure 4 also shows that the majority of the compounds were released at a temperature of 320–380 °C. The weight loss observed for the three biomasses, as shown in Figure 4, ranges from 64 to 70%, 68 to 83% and 66 to 80% for the PKS, MAH and IRO biomasses, respectively. The final stage is mainly due to carbonisation (500–550 °C) of the biomass, as shown by the flattened line in the TGA/DTG curve. Compared to the wood biomass, the DTG curve for the PKS (Figure 4b) shows a more pronounced shoulder peak at 280 °C, with a clear separation of the hemicellulose and cellulose decomposition peak.

This may be due to the wide temperature range associated with the lignin decomposition during pyrolysis and the high lignin content of the PKS [59].



**Figure 4.** Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves of raw and pretreated PKS (a,b), MAH (c,d) and IRO (e,f).

The DTG curves for the pretreated biomasses showed a distinctive thermal degradation behaviour compared to that of the untreated PKS, MAH and IRO, especially for the  $\text{H}_2\text{SO}_4$ -pretreated biomasses. Figure 4b,d,f show a rapid devolatilisation of hemicellulose, cellulose and lignin for PKS, MAH and IRO pretreated with 3 M and 5 M  $\text{H}_2\text{SO}_4$ . The 5 M  $\text{H}_2\text{SO}_4$  pretreatment showed a slightly higher peak than the 3 M  $\text{H}_2\text{SO}_4$  pretreatment for the cellulose decomposition part for all three biomasses, as seen in Figure 4b,d,f. This is an indication of a higher biomass reactivity from the increased severity of the acid pretreatment. This might explain the slight decrease in the char yield observed for the 5 M  $\text{H}_2\text{SO}_4$ -pretreated PKS, MAH and IRO shown in Figure 3 compared to that of the 3 M  $\text{H}_2\text{SO}_4$ -pretreated biomasses. A similar observation was also made by Zhou et al. [57], where a decrease in the char yield with increased concentration of sulfuric acid for Douglas fir and hybrid poplar wood was observed. Additionally, the rapid reaction that occurred for the 3 M and 5 M  $\text{H}_2\text{SO}_4$ -pretreated biomasses may be due to the dehydration, hydrolysis and crosslinking reactions [57]. The  $\text{H}_2\text{SO}_4$  pretreatment of all three biomasses may have led to lowering/shifting of the reaction temperature (160–450 °C) for the lignin decomposition compared to the other acid-pretreated biomasses. This may also be responsible for

the increased lignin composition observed for the PKS, MAH and IRO washed with the  $H_2SO_4$ -pretreated biomasses, as shown in Table 1, compared to the untreated and the other washed biomasses.

A closer look at the effect of HCl pretreatment shown in Figure 4b,d,f reveals that HCl pretreatment resulted in lowering of the hemicellulose decomposition peak for PKS compared to the woody biomass (MAH and IRO) for 3 and 5 M HCl. This can be attributed to the removal of a considerable portion of the hemicellulose content during the HCl acid pretreatment [24]. The DTG curves shown in Figure 4b,d for PKS and IRO show that the cellulose decomposition peak shifted to a slightly higher temperature for the feedstock pretreated with HCl compared to the untreated biomass and other acid pretreatments. It can be summarised from Figure 4b,d,f and Table 1 that the HCl acid pretreatment had a greater effect on the biomass degradation, given the increased cellulose content which is due to the hydrolysis of hemicellulose into its monomers as a result of the destruction of the polymeric bonds [60]. This might also be responsible for the decreased char yield observed in Figure 3 for the HCl-acid-pretreated biomasses, especially for MAH and IRO compared to the untreated biomass. This indicates that inorganic constituents, such as calcium, responsible for the promotion of char formation are no longer present or have been decreased [61]. The increased lignin and cellulose content associated with the  $H_2SO_4$  and HCl acid washing, respectively (Table 1), showed that acid pretreatment of biomasses prior to pyrolysis is suitable for removing most of the AAEMs and releasing of the volatile compounds in the biomass [22]. However, while the  $H_2SO_4$ - and HCl-pretreated biomasses showed a large effect on the structure of the biomass, mild acids (acetic and formic acid) and water leaching only showed a minimal effect on the biomass structure, as seen from the DTG curve presented in Figure 4b,d,f.

### 3.5. Effects of Pretreatment on the Contents of Inorganic Materials

The inorganic material present in woody and agricultural biomass could vary depending on the chemical composition and region where the plant is grown [62]. As seen from Figure 5, PKS had the lowest amount of inorganic materials and IRO had the highest. The inorganic content is mainly composed of potassium, calcium, silicon, sodium, phosphorus, magnesium and chlorine [62].

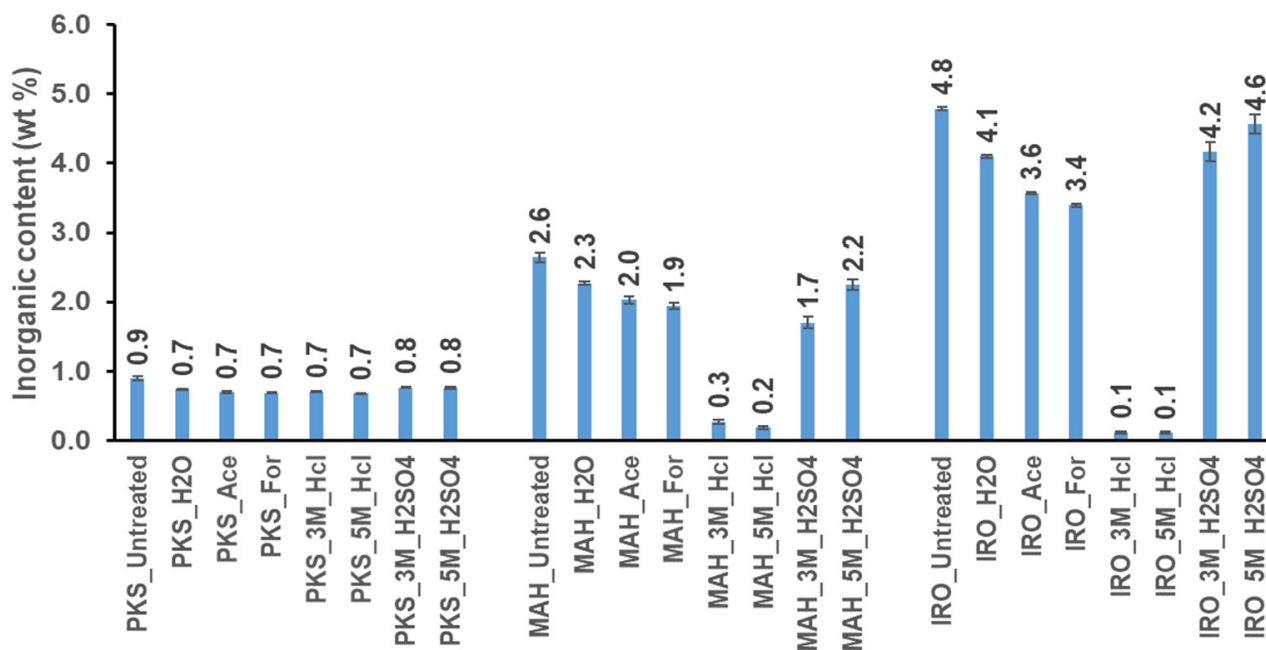


Figure 5. Inorganic content in weight (%) of raw and pretreated PKS, MAH and IRO.

The amount of inorganic materials can influence thermal degradation and chemical reaction pathways during pyrolysis [8]. The removal of inorganic material slightly reduces the formation of crosslinks between the biomass polymers [58]. In this work, the removal of inorganic material from the raw PKS by washing/leaching was very low, an indication of lower ash content in the PKS compared to the MAH and IRO, as shown also in Table 2. As observed from Figure 5, the untreated PKS, MAH and IRO had the highest amount of inorganic substances, while MAH and IRO pretreated with 3 and 5 M HCl gave the lowest amount of inorganic material, with about 90% and 98% removal efficiency for MAH and IRO, respectively. This shows that HCl was highly effective in removing inorganic substances present in the biomass, which may be as a result of the biomass structure being opened up by the acid [1]. However, the result was different for PKS, with only about 24% removal of inorganic materials after leaching with HCl. This may be due to the stability and high lignin content of the PKS compared to that of the woody biomass [48]. The degree to which lignin is present in a biomass sample can influence its digestibility [63,64]. This is because lignin is closely bound to cellulose microfibrils, which prevents enzyme accessibility [63]. The high removal of inorganic substances by HCl in the woody biomasses (MAH and IRO) is similar to the result presented by Ma et al. [25]. They observed over 90% removal of AAEMs for rice husk pretreated with 0.5 to 4 M solution of HCl.

The removal efficiency was about 15% for water and that of the mild acid pretreatment was approximately 25% for all three biomass samples investigated. Also noteworthy is the high amount of inorganic material still present in the different biomasses after pretreatment with H<sub>2</sub>SO<sub>4</sub>. Pretreatment with H<sub>2</sub>SO<sub>4</sub> gave the lowest removal rate of inorganic materials, with a removal efficiency of 15% for PKS and MAH and 5% for IRO pretreated with 5 M solution of the acid. This may be due to the sulphur content in the biomass linked to the sulphate radical residual [7].

### 3.6. Effect of Pretreatment on the Primary Pyrolysis Products

Figure 6a–c provide the FID chromatogram for the product distribution of the untreated PKS, MAH and IRO fast pyrolysis at 600 °C and 5 s, while Figure 7a–c show the effect of pretreatment on the primary pyrolysis product of raw and pretreated PKS, MAH and IRO. The identified compounds from the GC-MS were grouped into six categories, namely phenols, ketones, aldehydes, saccharides, furans and acids. Detailed information on the chemical compounds and their product distribution is given in Tables S1–S3 in the Supplementary Material. In terms of quantification, Figure 7a, the acids are the main group of compounds found in PKS, with a relative content ranging from 30 to 50% of the total yield of product formed, followed by phenol in the range of 18–21% and aldehydes 11–19%. However, for MAH and IRO (Figure 7b,c), aldehydes constitute the major group of chemical compounds found in the woody biomass and the range of 39–62%, followed by acids and phenols in the range of 7–16% and 10–18%, respectively.

#### 3.6.1. Effect of Pretreatment on the Product Distribution of the Phenolic Compounds

Phenolic compounds originate from the lignin polymer and are obtained by depolymerisation during pyrolysis [38]. Figure 7a shows a slight increase in the relative content for PKS pretreated with H<sub>2</sub>O and 3M HCl for the phenols compared to that of the untreated and the other acids. This may be attributed to the stability of the lignin molecule and minimal catalytic effect of the inherent inorganic species on the depolymerisation of lignin-rich biomass [23]. Dong et al. [7] also reported an increase in the relative content of the phenols after leaching with HCl and with no major difference in the content of the phenols for Moso bamboo treated with H<sub>2</sub>SO<sub>4</sub>. They attributed the increased yield of the phenols to an increase in the lignin content after washing with HCl. Phenols are important chemicals, as they can be used as building blocks for synthetic bioplastics [65] and can also be used to replace phenolic resins from fossil fuels [66].

The relative content of the phenolic compounds produced from woody biomass (MAH and IRO), found in Figure 7b,c, increased for all the acid pretreatments. The increase was

more pronounced for MAH pretreated with either 5 M formic acid or 5 M HCl, while that of IRO was most pronounced with either 5 M H<sub>2</sub>SO<sub>4</sub> or 5 M formic acid pretreatment. The relative content of the phenols increased from 10 to 18% for formic acid and from 10 to 17% for HCl-acid-pretreated MAH and from 11 to 14% for the formic and H<sub>2</sub>SO<sub>4</sub> pretreatment of IRO. This increase in the relative content of the phenols could be attributed to the removal of the inorganic components for the HCl-washed biomass and the presence of sulphur for the H<sub>2</sub>SO<sub>4</sub>-pretreated biomass (Figure 5). The increase in the relative content of the phenols after acid pretreatment is in agreement with the previous literature [7].

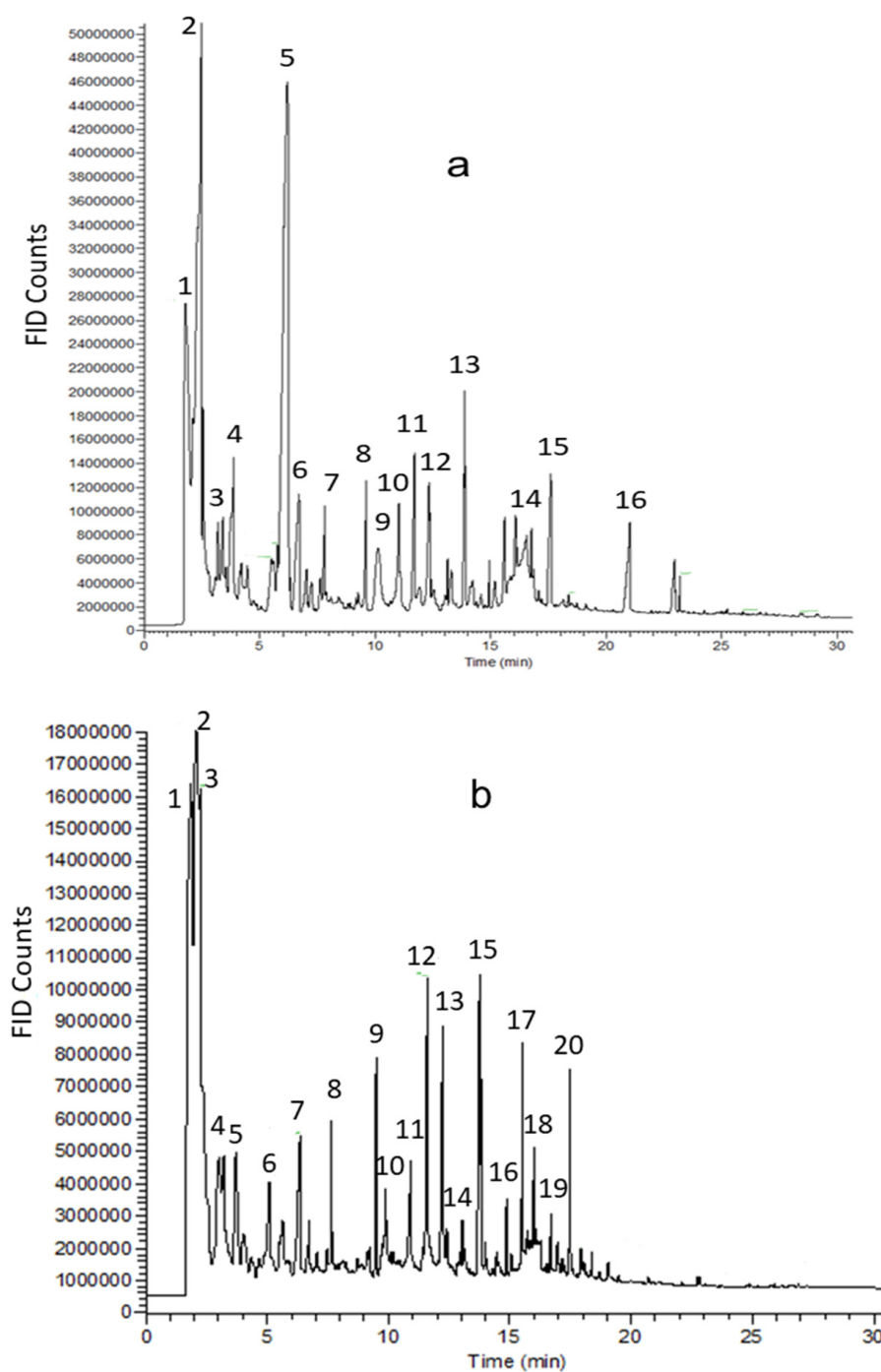
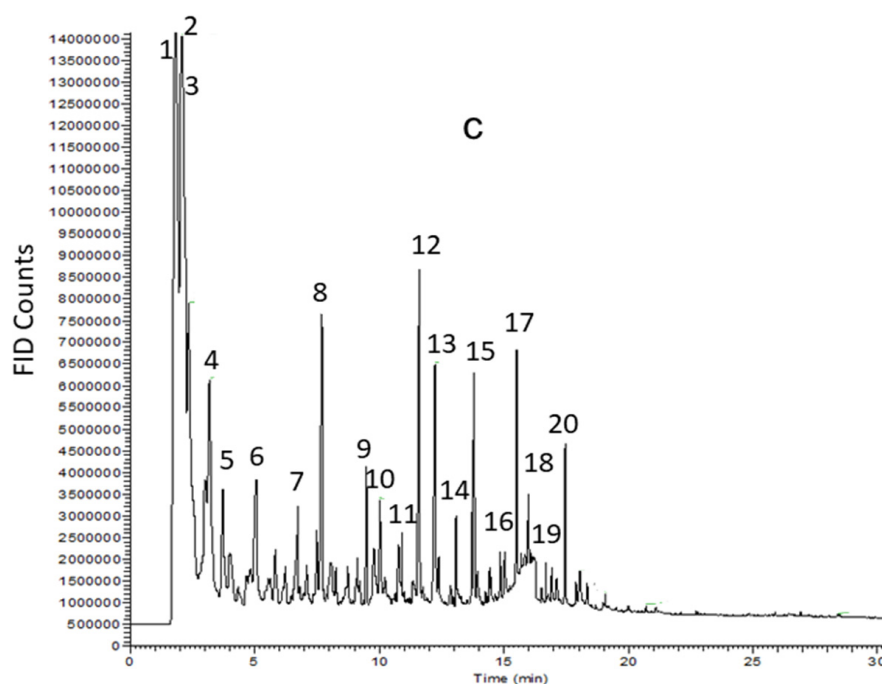


Figure 6. Cont.





**Figure 6.** (a) Chromatogram of untreated PKS pyrolysis at 600 °C at 5 s. The main components of the untreated PKS pyrolysis: (1) acetaldehyde; (2) acetic acid; (3) 2,3-pentanedione; (4) furfural; (5) phenol; (6) 4-hydroxy-5,6-dihydro-2H-pyran-2-one; (7) 2-methoxyphenol; (8) 4-methyl-2-methoxyphenol; (9) 1,2-benzenediol; (10) 4-ethyl-2-methoxyphenol; (11) 4-vinyl-2-methoxyphenol; (12) 4-(1-propenyl)-2-methoxyphenol; (13) 4-methoxy-3-(methoxymethyl)phenol; (14) 4-acetoxybenzoic acid; (15) 4-(2-propenyl)-2,6-dimethoxyphenol; (16) oleic acid. (b,c) Chromatogram of untreated MAH (b) and IRO (c) pyrolysis at 600 °C at 5 s. The main components of the untreated MAH and IRO pyrolysis: (1) acetaldehyde; (2) hydroxyacetaldehyde (3) acetic acid; (4) 2,3-pentanedione; (5) furfural; (6) 2-methylcyclopentanone; (7) 4-hydroxy-5,6-dihydro-2H-pyran-2-one; (8) 2-methoxyphenol; (9) 4-methyl-2-methoxyphenol; (10) 3-methoxy-1,2-benzenediol; (11) 4-ethyl-2-methoxyphenol; (12) 4-vinyl-2-methoxyphenol; (13) 2,6-dimethoxyphenol (14) 4-(1-propenyl)-2-methoxyphenol; (15) 4-methoxy-3-(methoxymethyl)phenol; (16) 5-tert-butylpyrogallol; (17) 3-tert-butyl-4-hydroxyanisole; (18) levoglucosan; (19) 4-(2-propenyl)-2,6-dimethoxyphenol; (20) 4-(2-propenyl)-2,6-dimethoxyphenol-trans.

Figure 8a–c and Tables S4–S6 show a grouping of the phenols into phenol-type, guaiacol-type, syringol-type, catechol-type and pyrogallol-type compounds, respectively. Phenol-type compounds include phenol, 2-methylphenol and 4-methylphenol, while guaiacol-type compounds include 2-methoxyphenol, 4-methyl-2-methoxyphenol, 4-vinyl-2-methoxyphenol, etc. Syringol-type compounds are mainly made up of 2,6-dimethoxyphenol and 4-(2-propenyl)-2,6-dimethoxyphenol, while catechol-type compounds mainly consist of 1,2-benzenediol and 3-methoxy-1,2-benzenediol. Pyrogallol-type compounds are composed of only 5-tert-Butylpyrogallol. The primary product distribution for PKS showed the presence of mainly guaiacol- and phenol-type compounds, while the woody biomass is composed of mainly guaiacol- and syringol-type compounds (Figure 8a–c). Phenol is the main chemical compound present not only in the phenol-type compounds, but it is also the main chemical compound derived from the lignin depolymerisation of PKS, as seen in Tables S1 and S4. Figure 8a shows a reduction in the relative content of the phenol-type compounds to a large extent for all pretreated samples compared to that of the untreated sample. The main decrease was observed for the PKS sample pretreated with either of the two H<sub>2</sub>SO<sub>4</sub> solutions, which decreased its relative content from 46 to 20%. The decreased yield of phenol observed in the current study strongly indicates that the presence of inorganic constituents in the untreated PKS is the primary catalyst for cracking the lignin structure in the biomass and promoting of cross-linking and decomposition reactions [1,14,30]. The

removal or reduction in metal ions, such as silica and potassium, in the washed PKS may have led to the reduction in phenols observed in Figure 8a during pyrolysis and, thus, given rise to dehydration and demethoxylation reactions [14,67]. Previous study had shown that the most abundant metal ions in PKS are silica and potassium [33], while calcium and potassium constitute the main metal ion present in iroko wood [68].

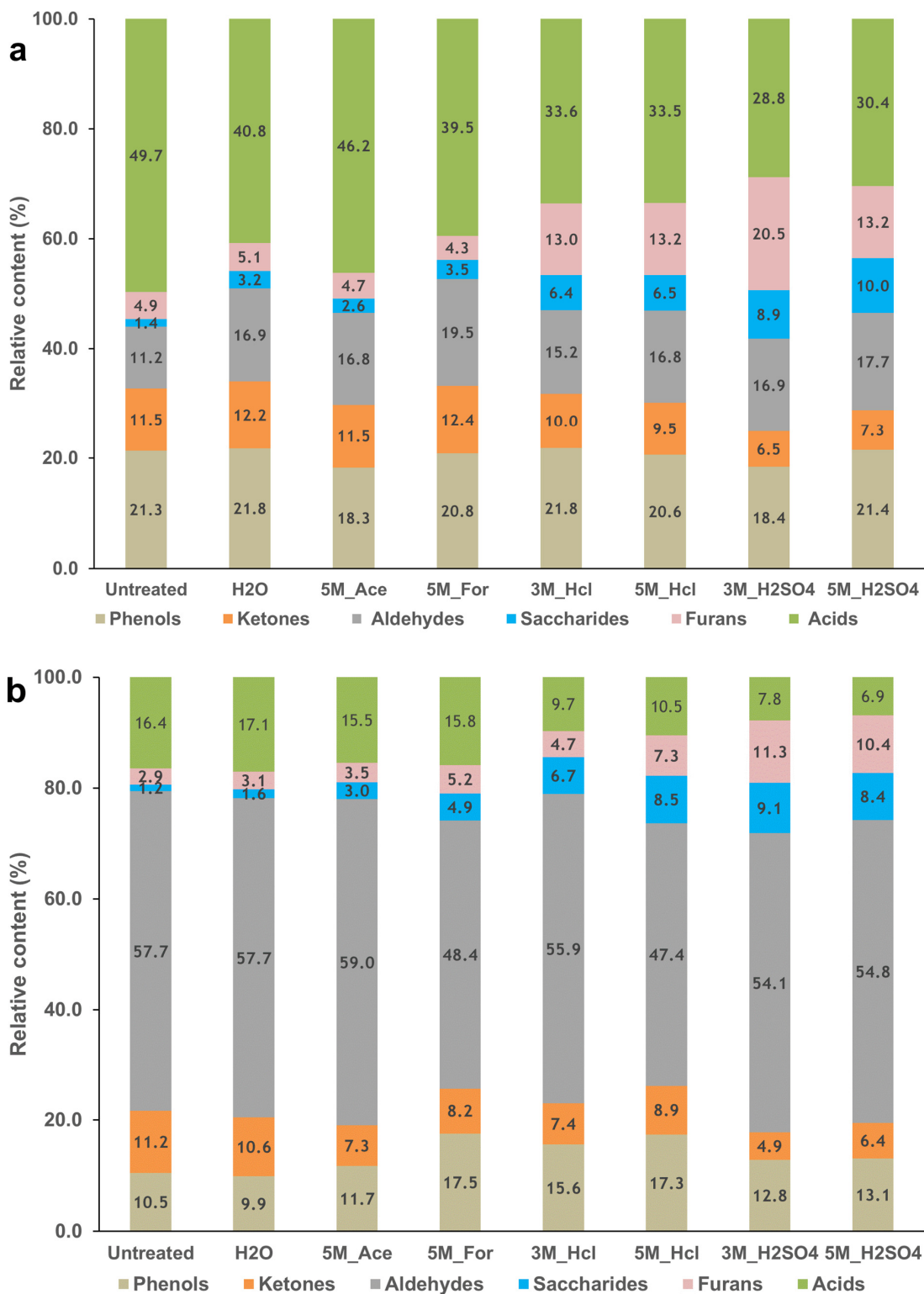


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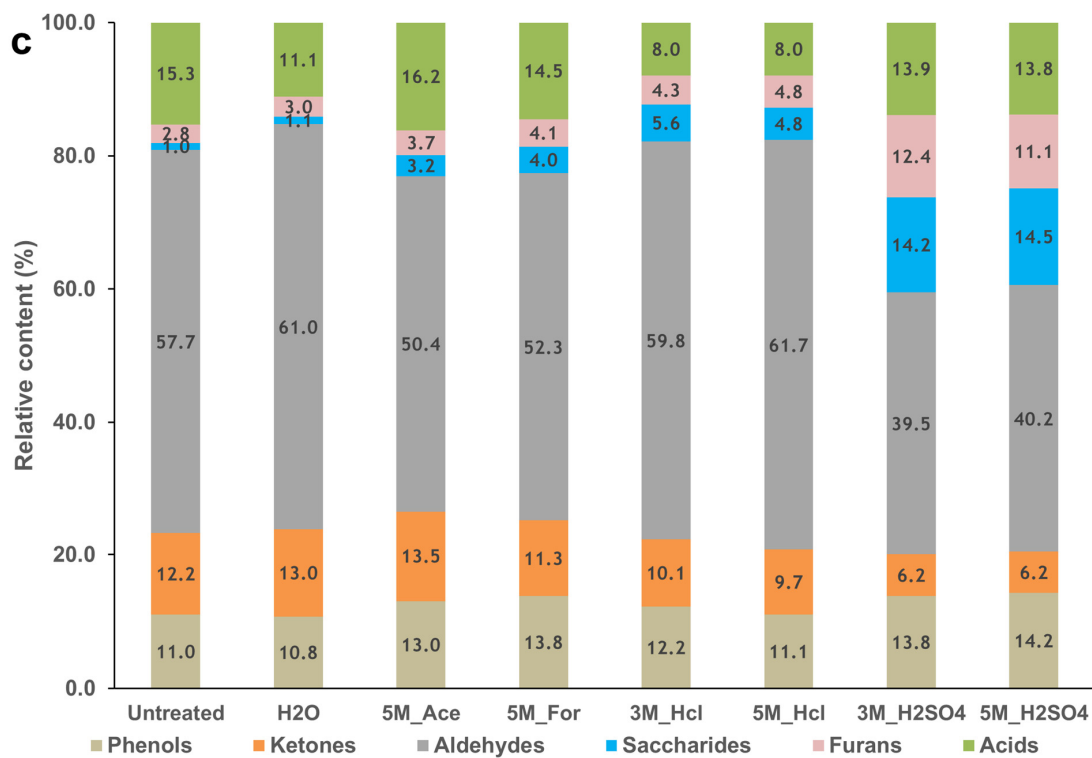


Figure 7. Effect of pretreatment on the pyrolytic products of PKS (a), MAH (b) and IRO (c).

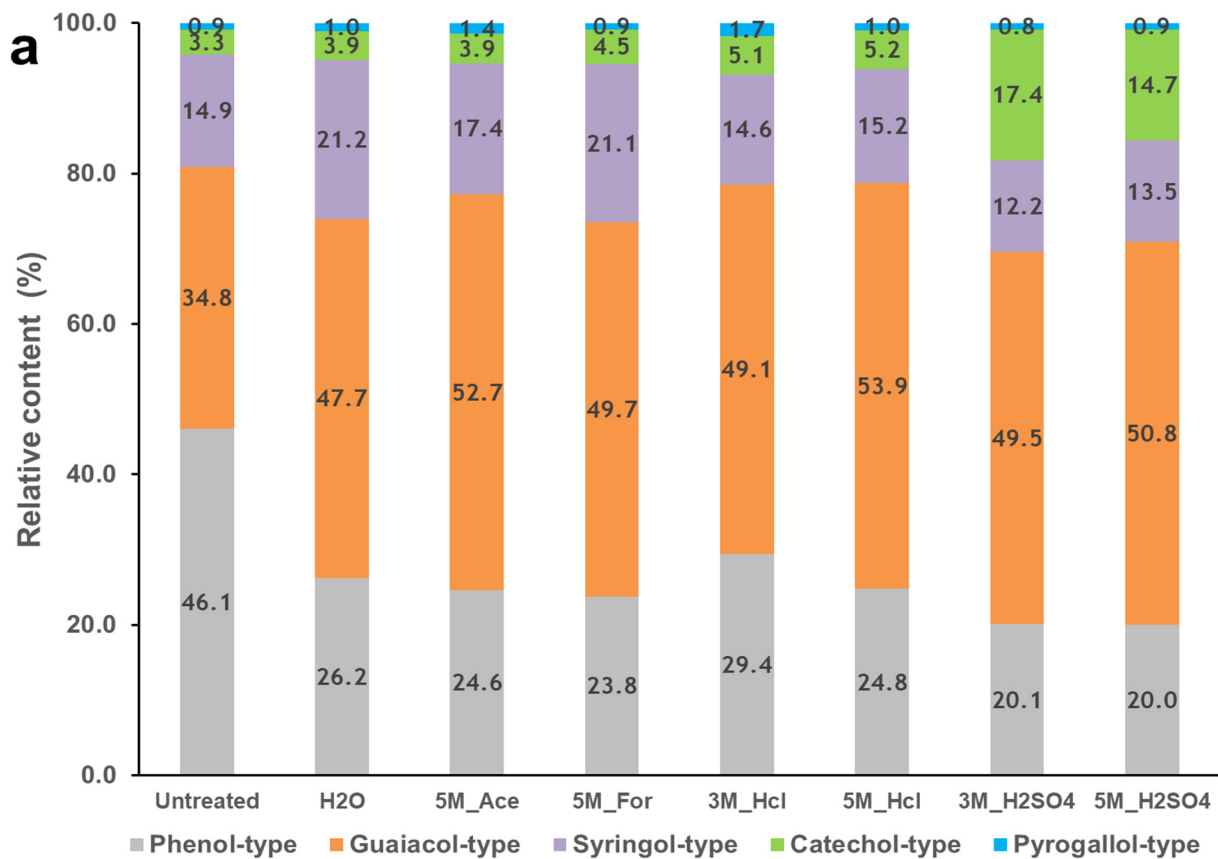
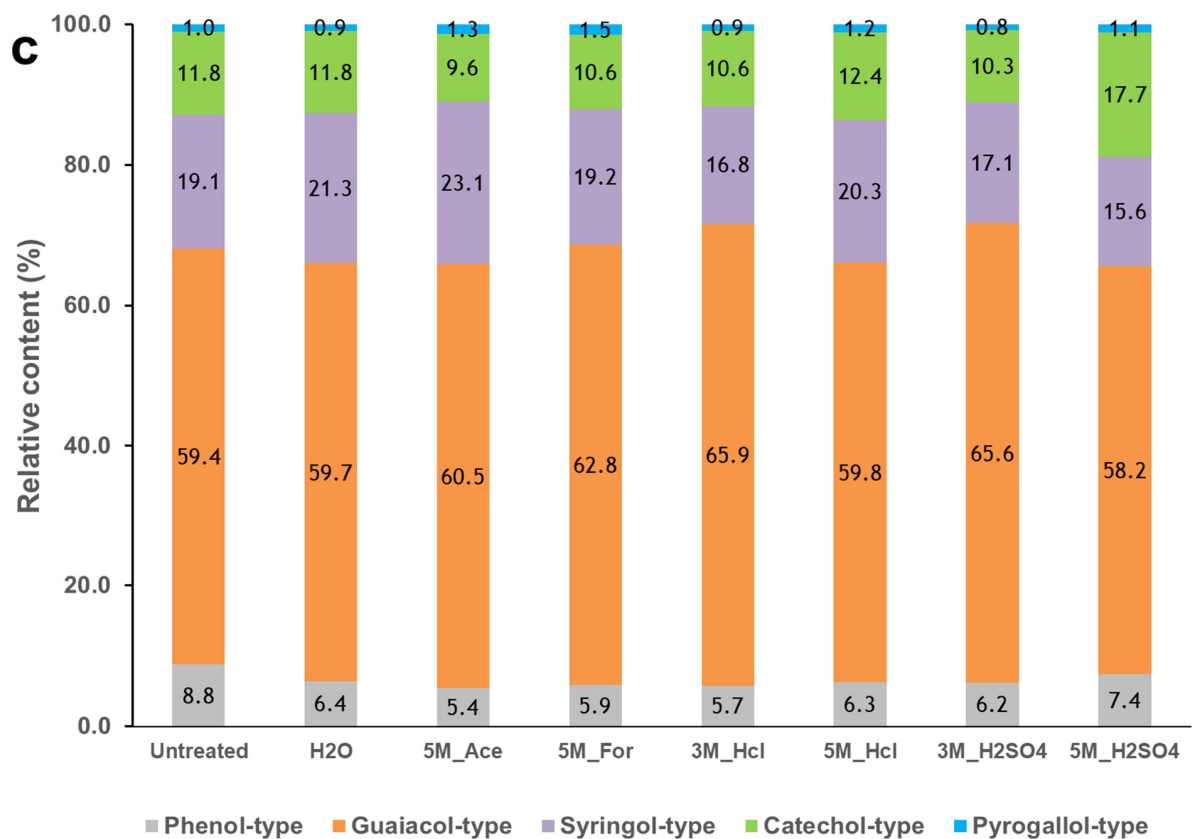
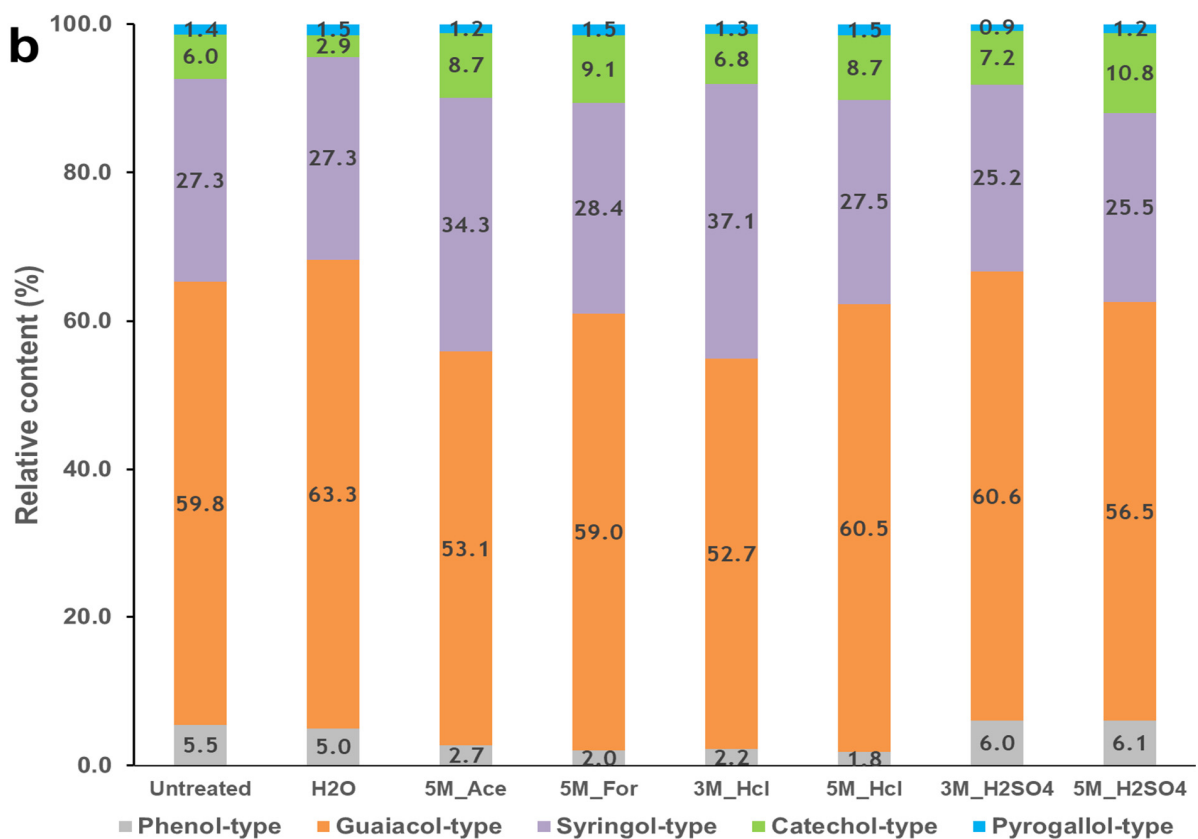


Figure 8. Cont.



**Figure 8.** Effect of water and acid leaching on the lignin-derived products of PKS (a), MAH (b) and IRO (c).

However, the guaiacol- and catechol-type compounds showed an increase in the relative content of the primary products for both the water- and acid-leached biomass samples. Figure 8a shows that the relative content of the guaiacol-type phenols increased from 35% (untreated PKS) to an average of 50% for the pretreated PKS, while the relative content of catechol-type phenols increased from 3% (untreated PKS) to about 5% for the mild-acid- and HCl-pretreated PKS. Additionally, a significant increase from 3 to 17% was observed for the 3 M H<sub>2</sub>SO<sub>4</sub>-pretreated PKS. The syringol-type compounds also showed an increase in the volatile compounds for PKS pretreated with water and mild acid solutions. However, the H<sub>2</sub>SO<sub>4</sub>-leached biomass decreased from 15% (untreated PKS) to 13% (5 M H<sub>2</sub>SO<sub>4</sub>-pretreated PKS). The increase in the relative content of the guaiacol-, catechol- and syringol-type compounds observed in this study indicates minimal degradation of these units in the lignin and may be attributed to the promotion of decarboxylation or decarbonylation reactions, along with the removal of unsaturated alkyl branch chains [14,69]. Peng et al. [69] observed that the addition of K<sub>2</sub>CO<sub>3</sub> and KOH to commercial alkali lignin and purified lignin from black liquor resulted in the promotion of the methoxy phenol and production of alkyl-phenols. The decreased yield of the syringol-type observed in this study for the H<sub>2</sub>SO<sub>4</sub>-pretreated PKS is in line with another study [57]. They observed a reduction in the production of the syringol-type compounds, especially for 2,6-dimethoxy-phenol after washing with H<sub>2</sub>SO<sub>4</sub>. This was attributed to the negative influence of potassium on the formation of 2,6-dimethoxy-phenol [7].

Figure 8b,c show that the woody biomass had the lowest amount of phenol-type compounds, which decreased from 6 to 2% for the mild-acid- and HCl-pretreated MAH, while no major difference was observed in the relative content for the H<sub>2</sub>SO<sub>4</sub>-pretreated MAH. These results are in agreement with a study by Zhou S. et al. [57]. They reported that the H<sub>2</sub>SO<sub>4</sub>-washed hybrid poplar wood did not change their production due to the low removal of the inorganic material. Similar to MAH, the IRO sample also showed a decrease in the relative content of the phenol-type compounds but, unlike the MAH pretreated biomass, the decrease was observed for all the pretreatment conditions investigated. These results are in general agreement with the previous literature [27]. There, it was observed that the yield of phenol significantly decreased after demineralisation of poplar wood with water, HCl and HF, and the same behaviour was shown for Douglas fir leached with H<sub>2</sub>SO<sub>4</sub>. Additionally, no major difference was observed in the relative content for the guaiacol-type compounds for both MAH and IRO, except for IRO pretreated with 3 M HCl and H<sub>2</sub>SO<sub>4</sub>, which increased from 59 to 66%, respectively. The difference in the result for the phenol-type and guaiacol-type compounds pretreated with H<sub>2</sub>SO<sub>4</sub> could be attributed to the difference in the relative content of the lignin [57] observed for MAH and IRO, as seen in Table 1. The syringol-type compounds showed a slight increase in the relative content for MAH and IRO pretreated with the mild and HCl acid solutions, while the relative content decreased for the H<sub>2</sub>SO<sub>4</sub>-pretreated biomass. The reduction in the primary product observed for the syringol-type compounds is in line with the previous literature [57]. The catechol-type compounds slightly increased in the relative content for MAH when using acid pretreatment, while no major difference was observed across the different pretreatment conditions for IRO, except for 5 M H<sub>2</sub>SO<sub>4</sub>-treated biomass, which showed a significant increase.

The decomposition of the lignin molecule for the PKS, MAH and IRO can thus be summarised by dehydration and depolymerisation (guaiacol type), demethoxylation (phenols), side-chain scission and demethylation (catechol-type) and alkylation (syringol-type) [38,70].

### 3.6.2. Effect of Pretreatment on the Product Distribution of Anhydrous Sugar and Other Low-Molecular-Weight Compounds

- Anhydrous sugar

Cellulose pyrolysis is known to proceed through two main pathways, either depolymerisation of cellulose to anhydrous sugar or ring breaking of light oxygenated compounds [37]. The depolymerisation of cellulose to anhydrous sugar results in an increased



production of levoglucosan at higher temperatures due to cleavage of the 1,4-glycosidic bond of the cellulose molecule. However, the presence of inorganic material in the biomass hinders the formation of levoglucosan, as was indicated when a sample of native biomass was compared to a sample mixed of pure cellulose, xylan and lignin [8]. Figure 7a–c show that the formation of sugars (saccharides) increased to a large extent after leaching with acids for all three biomass samples. This shows that even a slight removal of inorganic material could improve the production of sugars. Saccharides, here, are mainly composed of levoglucosenone, 1,4-dideoxy-D-glycerohex-1-enopyranos-3-ulose and levoglucosan. As observed in Figure 7a–c, the highest relative content of saccharides was obtained when 3 and 5 M H<sub>2</sub>SO<sub>4</sub> acid were used as pretreatment, and these increased from 1 to 10% for PKS, 1 to 8% for MAH and 1 to 15% for IRO for the 5 M H<sub>2</sub>SO<sub>4</sub>-pretreated sample. The increase in the relative content of the saccharides can be attributed to the increased yield of levoglucosenone and 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose, as shown in Tables S1–S3, which may have been catalysed by the presence of free sulfuric acid [57]. The increased production of sugars after pretreatment with different acids is in agreement with previous studies [7,57]. Levoglucosenone has been reported [37] to be formed together with levoglucosan by cleavage of the glycosidic bond, and the H<sub>2</sub>SO<sub>4</sub> pretreatment tends to enhance this mechanism. Additionally, the formation of levoglucosan (Tables S1–S3) increased across all pretreatment conditions and was more pronounced for the samples pretreated with 3 and 5 M HCl for all three biomasses. This result is in agreement with previous studies [7]. Previously, it was observed that the use of HCl increased the yield of levoglucosan more than the pretreatment with other acids. The promotion of levoglucosan can be attributed to the fact that HCl is more effective in the removal of inorganic materials, as observed in Figure 5, compared to other acids.

The improved yield of levoglucosan and the other anhydrous sugars, as shown in Tables S1–S3, can be attributed to the removal of inorganic constituents from the raw PKS, MAH and IRO. The presence of inorganic constituents has previously been reported to decrease the yield of levoglucosan due to decreased stability of the glycosidic bond and the promotion of hydroxyl group during pyrolysis [14]. The weakening of the glycosidic bond thus leads to dehydration reactions, cleavage of the glycosidic bond and ring scission reactions that result in the formation of low-molecular-weight compounds and inhibition of levoglucosan formation [14]. However, in this study, the removal of inorganic constituents via leaching of the biomass minimised the catalytic effect of the inorganic constituents in inhibiting the formation of the sugars and led to the promotion of the depolymerisation and cleavage of the glycosidic bond of the cellulose molecule and gave rise to an increase in the relative content of levoglucosan [1,37].

- Furans

Furan compounds, such as furfural and 5-(hydroxymethyl)-2-furancarboxaldehyde (5HMF), have been reported to be formed by depolymerisation, dehydration and rearrangement from both cellulose and hemicellulose pyrolysis [37]. The response of the furans (count/ $\mu$ g sample), as shown in Tables S1–S3, and the relative content of the furans in Figure 7a–c show a general increase for all samples after pretreatment with both water and acids, and this increase was most pronounced for the samples treated with H<sub>2</sub>SO<sub>4</sub>. The most enhanced production of furans, in terms of their relative content, as well as their response (count/ $\mu$ g sample), was observed when leaching with 3 M H<sub>2</sub>SO<sub>4</sub>. Specifically, the increase was from 5 to 21%, 3 to 11% and 3 to 12% for PKS, MAH and IRO, respectively. Additionally, the increased yield (taken as the response) of the furans can be attributed to the production of furfural, Tables S1–S3. The increased yield of furfural is in agreement with previous studies [7,57]. Specifically, Dong et al. [7] and Zhou et al. [57] reported a significant increase in the average peak area/ $\mu$ g sample of furfural after washing Moso bamboo and hybrid poplar wood with H<sub>2</sub>SO<sub>4</sub>.

The production of furfural has been reported to be catalysed by strong acids, especially by H<sub>2</sub>SO<sub>4</sub> [7,71]. This suggests that leaching with H<sub>2</sub>SO<sub>4</sub> can be used to improve the yield of furfural. Additionally, the removal of inorganic constituents from the biomass by acid

washing may have inhibited the homolysis of the pyranose ring structure and enhanced the ring-opening and depolymerisation reactions [1,72], leading to the increased formation of furfural for all three biomasses. Furfural is a very versatile chemical compound for the chemical industry and can be used for the production of resin [73] and making inks, plastics, adhesives, fungicides, fertilisers and flavouring compounds [74]. It can also be used as a starting chemical to produce other high-value products, such as furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, tetrahydrofuran and diols [71,73,74]. However, the production of the other furan compounds in this study, such as 2-furan methanol, decreased with increasing severity of the acid pretreatment for PKS and a general decrease was observed for MAH and IRO, Tables S1–S3. The yield of 3-butylidihydro-2(3H)-furanone was increased for the water and mild acid pretreatment but decreased with H<sub>2</sub>SO<sub>4</sub> pretreatment.

- Ketones, Aldehydes and Acids

Figure 7a–c show that the relative content of the ketones was generally decreased after leaching with the different acids. However, no major impact was observed for the samples pretreated with water and the mild acids, especially for PKS and MAH, while the decrease was high for the strong acids (HCl and H<sub>2</sub>SO<sub>4</sub>) pretreatment for all materials. The result is similar to that reported by Dong et al. [7]. They observed a similar reduction in the formation of the ketones for Moso bamboo sawdust pretreated with H<sub>2</sub>SO<sub>4</sub>, HCl, HF and HNO<sub>3</sub>.

The aldehydes constitute a significant portion of all the volatile compounds identified from fast pyrolysis of the woody biomasses, as observed in Figure 7b,c. However, for the PKS, as seen in Figure 7a, acids constitute the largest portion of the volatile compounds. This is mainly due to the strong presence of acetic acid in PKS compared to that of MAH and IRO. However, hydroxyacetaldehyde was the main volatile compound formed from the pyrolysis of MAH and IRO, and their chromatogram was observed to coelute with acetic acids during the analysis of the chemical compounds for the wood biomasses. The significant portion of aldehydes still present in the pretreated biomass suggests that some inorganics remain even after pretreatment [75]. Figure 7a shows that the relative content of aldehydes was generally increased after leaching with water and the acids for PKS. Contrary to the increase in the relative content of the aldehydes observed for the PKS, the content of the aldehydes decreased for the woody biomass, especially for the H<sub>2</sub>SO<sub>4</sub>-pretreated sample. The relative content of the aldehydes was 58% for the untreated MAH and IRO but decreased to 54% and 40%, respectively, for MAH and IRO pretreated with 3 and 5 M H<sub>2</sub>SO<sub>4</sub>. The different results observed for the relative content of aldehydes could be attributed to the composition and nature of the biomass. The increased yield of the aldehydes (hydroxyacetaldehyde and aldehyde), especially for the PKS pretreated biomass, may be attributed to the presence of inorganic constituents, which may have catalysed the decomposition of glucosidic units by a heterolytic mechanism and favour the depolymerisation and fragmentation of the cellulose and hemicellulose molecule, as well as cracking of the lignin side chain [37,38,61]. However, the reduced content of the aldehydes observed for the woody biomass (MAH and IRO), especially for the H<sub>2</sub>SO<sub>4</sub> pretreatment, may be as a result of the depolymerisation of the pyrolysis product occurring to a lesser extent due to the slightly reduced inorganic content, as seen in Figure 4 [23].

Acetic acid, which is formed mainly by ring opening and cracking reactions, is promoted in the presence of alkali metals [61]. Figure 7a–c show that the relative content of acid for PKS and the woody biomasses decreased for all pretreatment conditions and was more pronounced for the strong acids, especially the H<sub>2</sub>SO<sub>4</sub> pretreatment. This is in agreement with Zhou et al. [57], who observed a lower yield of acetic acid after leaching Douglas fir with H<sub>2</sub>SO<sub>4</sub>. The acid decreased from 50 to 30% for PKS, 16 to 8% for MAH and 15 to 14% for IRO pretreated with 3 M H<sub>2</sub>SO<sub>4</sub>. This decrease is important for improving the quality and stability of the bio-oil. The high content of acetic acid in the untreated biomass suggests that the compounds have been catalysed by the presence of inorganics [57]. Tables S1–S3 show that the acids are mainly composed of aliphatic acetic acids, together with other

aromatic acids, such as 4-hydroxybenzoic acid, 4-acetoxybenzoic acid and oleic acid for the PKS, while those of the woody biomasses are only composed of aliphatic acetic acids.

Additionally, the reduction in the relative content observed for the acids for all three biomasses can be attributed to the decreased composition of the hemicellulose content after pretreatment [76], as seen in Table 1.

### 3.6.3. Comparison of the Pyrolysis Product from PKS and the Woody Biomasses (MAH and IRO)

The main group of compounds formed from the pyrolysis of PKS are acids, phenols and aldehydes, while the main group of compounds formed from the woody biomasses (MAH and IRO) are the aldehydes, phenols and the acids in descending order, as shown in Figure 7a–c. It can be observed from Figure 7a–c that the yield of the acids was decreased for PKS and the woody biomasses when any leaching pretreatment was applied, except for MAH leached with H<sub>2</sub>O and IRO leached with 5 M acetic acid. This may be attributed to the removal of inorganic substances from the biomasses during pretreatment. The formation of aldehydes in the woody biomasses was also mostly decreased across the different leaching medium, except for the MAH sample washed with acetic acid and IRO washed with either H<sub>2</sub>O or HCl acid. However, the yield of the aldehydes was increased across the different leaching medium for the PKS, as seen in Figure 7a. It can also be observed from Figure 8a–c that the main phenolic compounds found in PKS are the guaiacol- and phenol-type compounds, while those of the woody biomasses are guaiacol- and syringol-type compounds. The relative content of the ketones was also observed to decrease for all three biomasses studied, especially after washing with the strong acids (HCl and H<sub>2</sub>SO<sub>4</sub>).

## 4. Conclusions

The effect of distilled water and both mild and strong acid pretreatment on fast pyrolysis of PKS, MAH and IRO was examined to promote the production of valuable primary products. All pretreatment solutions investigated were shown to remove inorganic material to a different degree. This, in turn, enhanced the production of some volatile compounds during pyrolysis. The relative content of levoglucosan was increased across all pretreatment conditions, especially for the HCl pretreatments, which also gave the highest removal of inorganic material from the biomass. The highest total relative content for the sugar was observed for the biomass sample pretreated with H<sub>2</sub>SO<sub>4</sub>, which was due to the increased yield of levoglucosenone that may have been catalysed by the presence of free H<sub>2</sub>SO<sub>4</sub>. Additionally, the relative content of furans was also increased for all biomass samples investigated in this study, especially after the H<sub>2</sub>SO<sub>4</sub> pretreatment, which could be attributed to the increased yield of furfural. Increase in relative content for the phenols was mainly influenced by washing with water and 3 M HCl for the PKS, while that of the woody biomasses was generally promoted across all the washing media. However, the phenol-type compounds were reduced to a large extent for the PKS, while the reduction was only observed for water- and mild acid pretreated MAH and IRO. Additionally, the relative content of ketones and acids was generally decreased for almost all pretreatment conditions, while the relative content of aldehydes was increased for PKS across all the pretreatment conditions investigated. However, the yield of the aldehydes for the woody biomass decreased mostly across the different leaching conditions. The difference between PKS and the woody biomasses may be attributed to the lack of hydroxyacetaldehyde in the PKS compared to the woody biomass.

The main reaction pathways for cellulose and hemicellulose were suggested to be by cleavage of the glycosidic bond, giving rise to fragmentation and depolymerisation reactions to form levoglucosan, furfural and hydroxylacetaldehyde, while lignin decomposition was mainly due to depolymerisation and demethoxylation to form guaiacol- and phenol-type compounds, respectively.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16052377/s1>, Figure S1: FTIR spectra of raw and pretreated MAH and IRO; Table S1: Product distribution of fast pyrolysis of untreated and pretreated palm kernel shell at 600 °C, 5 s; Table S2: Product distribution of fast pyrolysis of untreated and pretreated mahogany (MAH) sawdust at 600 °C, 5 s; Table S3: Product distribution of fast pyrolysis of untreated and pretreated iroko (IRO) sawdust at 600 °C, 5 s; Table S4: Grouping of the phenols obtained from the fast pyrolysis of untreated and pretreated PKS at 600 °C, 5 s; Table S5: Grouping of the phenols obtained from the fast pyrolysis of untreated and pretreated MAH at 600 °C, 5 s; Table S6: Grouping of the phenols obtained from the fast pyrolysis of untreated and pretreated IRO at 600 °C, 5 s.

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