



# Article Biomass Behavior upon Fast Pyrolysis in Inert and in CO<sub>2</sub>-Rich Atmospheres: Role of Lignin, Hemicellulose and Cellulose Content

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Abstract: The present work focuses on the quality of char and primary tar produced from fast pyrolysis in N<sub>2</sub> and CO<sub>2</sub> of lignocellulosic biomasses: walnut shells (lignin-rich), straw (hemicelluloserich) and pinewood (cellulose-rich). Heat treatments are carried out in a heated strip reactor (HSR) at 1573 and 2073 K for 3 s, with a heating rate of  $10^4$  K/s. The equipment allows for quenching the volatiles as soon as they are emitted. Chars are analyzed by thermogravimetric analysis in air. Results are compared with the products obtained from raw lignin, pure cellulose and pure hemicellulose. Cellulose and hemicellulose tars are dominated by anhydrous monosaccharides, which are scarce in straw tar and abundant in walnut shells tar. Polycyclic aromatic hydrocarbons PAHs are present in the primary products, in particular for walnut shells. The most reactive char is the one obtained from straw and the least reactive is the walnut shells char. Severe heat treatment and a CO<sub>2</sub> atmosphere generate additional char components with higher and lower reactivity. The more reactive char component may arise from cross-linking reactions involving the monosaccharides (for which the result decreased in tar), whereas the less reactive component arises from thermal annealing and graphitization. Thus, the pyrolytic behavior of biomasses cannot be reconstructed with a mere addition of the lignin/cellulose/hemicellulose contribution, taking into account their content in the biomass.

Keywords: pyrolysis; oxy-fuel; coal; biomass; lignin; hemicellulose and cellulose

## 1. Introduction

The present work aims to characterize char and primary tar produced from biomasses with different contents of lignin/cellulose/hemicellulose upon heating under the following conditions:

- 1. with very fast heating rates  $(10^4 \text{ K/s})$ ;
- 2. at very high temperature (up to 2000 K);
- 3. in inert or CO<sub>2</sub> rich atmospheres.

It must be emphasized that, even though pyrolysis of biomass has been the object of extensive research over the past few decades, experimental studies, which combine the conditions reported in 1 to 3 points, are relatively scarce. In the present work, these conditions are achieved by means of a special heated strip reactor, which allows not only heating the solid samples with temperature (up to 2073 K) and heating rates (up to  $10^4$  K/s) similar to those of laminar flow reactors, but also quenching the volatiles as soon as they are emitted. The focus is posed on primary tar, i.e., on condensable volatile products collected immediately after their ejection from the particles, and before they undergo secondary reactions in the gas phase. This is indeed an important feature addressed by the present work.



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**Copyright:** © 2022 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/). Several papers so far addressed the role of heating rate and temperature on the yields and composition of solid (char), liquid (tar) and gaseous products from pyrolysis of raw biomass and of single lignocellulosic fractions. A review is provided in [1]. At a low heating rate, pyrolysis of hemicellulose and cellulose occurs in the range of 470–530 K and 510–620 K [2,3], respectively, starting with depolymerization into oligosaccharides and proceeding through bond cleavage and rearrangement of the produced molecules [4]. Lignin pyrolysis is more complex: it occurs over a broader temperature range (550–770 K) and proceeds through free radical reactions, chain propagation and termination [5,6]. Interactions between the components are, however, possible throughout pyrolysis, as investigated in [7].

A parallel research line addressed the role of  $CO_2$  in pyrolysis/gasification of biomasses [8–22] and lignocellulosic components [10]. It was shown that in a thermogravimetric apparatus, at a low heating rate ( $\approx 1$  K/s), the presence of  $CO_2$  in the atmosphere does not affect thermolysis, and also, the Boudouard reaction is negligible. At a fast heating rate (100 K/s), in a fluidized bed at 800 K, Zhang et al. [11] observed that  $CO_2$  favored the yield of acid products and instead decreased phenols in tar. At very fast heating rates ( $10^4$  K/s), in a drop tube reactor at 1600 K, Senneca et al. [20] observed that  $CO_2$  modified the degree of aromaticity of the tar and also the quality of char. A role of single lignocellulosic components was suspected, but not clarified yet.

In a recent work [22], the same group carried out an experimental campaign similar to the one presented in the present paper, focusing only on single biomass components: cellulose, hemicellulose and lignin. A cellulose sample was in the form of microcrystalline cellulose supplied by JRS Pharma, the hemicellulose sample was a xylooligosaccharide extracted from Corncob supplied by Roth, while lignin was a dealkaline lignin supplied by Fisher Scientific. A very different behavior was observed during fast pyrolysis of hemicellulose and lignin  $(10^4 \text{ K/s})$ : the former produced only light tars, almost solely anhydrous monosaccharides, and the latter produced oxo-aromatics but also polycyclic aromatic hydrocarbons (PAHs), high molecular weight species (named heavy tar), soot and char. Cellulose resembled hemicellulose, regarding the chemical composition of light tar, being largely constituted by anhydrous monosaccharides. CO<sub>2</sub> in the gaseous environment did not affect the composition of "light tar" from cellulose and hemicellulose, which was in fact largely dominated by chain scission and formation of anhydrous monosaccharides. On the contrary, it affected the size of large molecules present in heavy tar produced from cellulose at a very high temperature. All the products of lignin pyrolysis were affected by  $CO_2$ .

The results of the single components will be compared in the present work with the results for raw biomasses with different ratios of lignin/cellulose/hemicellulose to verify if the pyrolytic behavior of biomasses can be simply reconstructed, adding the contribution of lignin/cellulose/hemicellulose, taking into account their content in the biomass. Previous work [7] has indeed already underlined that such simplification is not so easy to realize due to the presence of other constituents, including extractives and mineral matters and to the occurrence of the mutual interactions among the components.

## 2. Materials and Methods

# 2.1. Materials

Three biomass samples were used for the experiments: walnut (Juglans regia) shells (WS) (already used also for [20,21]), pinewood (Pinus Sylvestris) (PW) (provided by LUT and already used in paper [23]) and straw pellets (Triticum aestivum) (ST). WS and PW were used in the form of powder of granulometry smaller than 120 and 600  $\mu$ m, respectively; the ST sample was obtained from the straw pellets upon hand grinding in a mortar and had a size smaller than 300  $\mu$ m. Table 1 reports the ultimate analysis calculated according to the ASTM D5373 standard and the composition of the biomasses in terms of hemicellulose/cellulose/lignin from previous works [23,24].

	<b>Volatile<sub>db</sub></b>	Fix Carbon <sub>db</sub>	Ash <sub>db</sub>	C <sub>db</sub>	H <sub>db</sub>	N <sub>db</sub>
WS	81.1	18.5	0.4	51.9	5.7	0.3
PW	83.1	16.8	0.1	49.3	6.6	b.i.s. <sup>1</sup>
ST	77.8	16.2	6.1	45.9	6.5	0.6
	Hemicelluloses (%)		Cellulose (%)		Lignin (%)	
WS	22.2		25.5		52.3	
PW <sup>2</sup>	17.8		38.3		31.4	
ST	40.8		29.8		19.4	

 Table 1. Composition of selected biomasses.

<sup>1</sup> Beyond instrument sensitivity; <sup>2</sup> extractives 8.8%, additives 0.6%.

#### 2.2. Thermogravimetric Analysis (TGA) of Raw Samples

A first set of thermogravimetric experiments was carried out on the raw biomasses in order to characterize their behavior upon heating under standard TGA conditions in N<sub>2</sub> and air. Approximately 20 mg of sample was loaded in a NETZSCH 409CD apparatus. A gas flow of 200 mL/min of either N<sub>2</sub> of chromatographic grade or air (STP) was used. Double determinations were performed to ensure the reproducibility of the results.

## 2.3. Fast Pyrolysis in N<sub>2</sub> and CO<sub>2</sub>

## 2.3.1. Heat Treatment in the Heated Strip Reactor (HSR)

The three different feedstocks were subjected to severe heating conditions in the  $N_2$  and  $CO_2$  atmosphere, using a special heated strip reactor (HRS), where the metal grid, usually employed as a sample holder, was replaced by a pyrolytic graphite foil thermally stabilized for use up to 2800 K (Figure 1). For the experimental campaign, a heating rate of  $10^4$  K/s was used [22,25]. The apparatus was enclosed in a stainless-steel vessel with a volume of 2 L. The temperature of the grid was set by changing the value of the voltage at the two ends of the strip and was measured using a Pyrometer (Land System 4). For each test, about 100 mg of fine particles were placed on the strip in a thin layer. The reactor was flushed with the test gas (either  $N_2$  or  $CO_2$ ) for 10 min to remove any air traces. The strip was then heated up to 1573 or 2073 K for 3 s. Internal particles' temperature gradients are modest, as evaluated in previous works [22,25]. A Pyrex glass bridge was located above the strip to collect the emitted volatiles. The Pyrex bridge remained fairly cool, as it was nearly transparent to thermal radiation; hence, tars condensed on its surface.



**Reactor chamber** 

Figure 1. Heated Strip Reactor (HSR).

#### 2.3.2. Analysis of Primary Tar

The tar samples condensed on the Pyrex bridge located above the HSR were recovered by washing the bridge with acetone in an ultrasonic bath. The acetone volume was reduced to 0.5 mL under vacuum for analysis by gas chromatography–mass spectrometry (GC–MS). The GC–MS employed was an AGILENT GC 6890—MSD 5975C. The mass spectrometer operating in electron ionization mode was scanned from m/z = 50 to 400. GC–MS measurements showed a relative standard deviation (RSD) of less than 10%. In some conditions, acetone was unable to dissolve all the material deposited on the bridge. In these cases, the insoluble fraction was dissolved in N-methyl pyrrolidone (NMP) and named heavy tar. UV-Visible (UV-Vis) spectra of the samples, dissolved in NMP, were measured on an HP 8453 Diode Array spectrophotometer using 1 cm quartz cuvettes. Size Exclusion Chromatography (SEC) of heavy tar samples was carried out on a HPLC system HP1050 series by elution with NMP on a Jordi Gel DVB Solid Bead column 300 × 7.8 10<sup>-3</sup> m for the molecular weight (MW) determination in the 2000–400,000,000 u range. A HP1050 UV-Vis diode array detector was used for online detection of species eluted from the SEC column. The absorbance signal was measured at the fixed absorption wavelength of 350 nm.

#### 2.3.3. Analysis of Char

Char samples were collected from the graphite strip and analyzed by thermogravimetric analysis (TGA) using a Perkin-Elmer Pyris 1 Thermogravimetric Analyzer suitable for operation with small samples. Approximately 1–2 mg was used, indeed, for each test. After a dehumidification step, samples were heated up to 1150 K in a flow of air of 50 mL/min (STP) at a constant heating rate of 10 K/min. Double determinations were performed to ensure the reproducibility of the results, obtaining a maximum experimental uncertainty of  $\leq$ 5–10%. Notably, the ST sample presented a much higher amount of ashes than the other two biomasses and, markedly, a large portion of alkali.

## 3. Results

## 3.1. TG Pyrolysis of Raw Fuels

Figure 2 reports the preliminary analysis of the three biomasses (WS, PW, ST) upon heat treatments in TGA. Figure 2 shows the differential thermogravimetric curves (DTG) of biomass pyrolysis in  $N_2$  (a) and of biomass combustion in air (b), where  $w_0$ , w and  $w_f$  are the actual, initial and final weight of the sample.

Figure 2a shows that pyrolysis of ST spans over the temperature interval 500–600 K with a main peak at 570 K, PW between 500 and 650 K with a main peak at 640 K and WS in the same temperature range of 500–650 K with two distinct peaks at 530 and 630 K. The presence of air facilitates pyrolysis of ST, PW and WS, anticipating and enhancing the first peaks. In particular, the ST sample appeared the most reactive, probably also associated with its highest content of mineral matter. The PW char combustion stage appeared with a peak at 740 K, while ST and WS char combustion peaks appeared around 680 K. The effects of oxygen concentration on the course of pyrolytic processes was investigated by Senneca et al. [26]. For fuels with high volatile matter content, such as biomass, the devolatilization process was enhanced by the parallel occurrence of heterogeneous char oxidation [26].





Figure 2. Cont.



Figure 2. Derivative thermogravimetric (DTG) curves of biomasses in: (a) N<sub>2</sub>, (b) air.

3.2. Heat Treatment in HRS in N<sub>2</sub> and CO<sub>2</sub>

## 3.2.1. Tar Analysis

Figures 3 and 4 report the results of the analyses carried out on the fraction of tars soluble in acetone (light tar) and on the fraction of tar, which was insoluble in acetone and required further treatment with NMP (heavy tar).

Five classes of chemical species were identified in the light tar: aliphatics (alkanes and alkenes, aliphatic acid), oxo-aromatics (aromatic aldehydes and alcohols), anhydrous monosaccharides and PAHs with C < 16 (light PAHs) and C > 16 (heavy PAHs).

Senneca et al. [22] report that anhydrous monosaccharides are by far the largest component in light tar of cellulose and hemicelllose, while oxo-aromatics are the most abundant species in lignin tar, followed by anhydrous monosaccharides and light PAHs. In Figure 3, it can be observed that in the light tar produced at 1573 K from both WS and PW, oxo-aromatics and anhydrous monosaccharides were present in comparable amounts, followed by aliphatics and small PAHs present in much smaller amounts. In the light tar produced from ST at 1573 K, instead, the oxo-aromatics definitely prevailed, followed by aliphatics and light PAHs in a comparable amount. When the heat treatment temperature increased from 1573 to 2073 K, anhydrous monosaccharides were completely lost and PAHs, in particular the heavy PAHs, largely increased. The latter were more abundant when pyrolysis was carried out in N<sub>2</sub> than in CO<sub>2</sub>, in the case of WS, whereas the opposite occured in the case of ST. PAHs concentration (both light and heavy) was independent from the atmosphere for PW light tar. A particularly relevant concentration of large PAHs was found in tar produced from WS at 2073 K in N<sub>2</sub>.



Figure 3. Cont.





**Figure 3.** Gas Chromatography Mass Spectrometry (GC–MS) analysis on light tar samples of: (a) walnut shells (WS); (b) pinewood (PW); (c) straw (ST).

Figure 4a reports the chromatograms obtained by SEC for heavy tar fractions. The heavy tar fraction was present only after the pyrolysis tests at 2073 K. The column was calibrated by using polystyrene and carbonaceous particles in order to correlate retention time with MW. The MW distribution of all the samples were spread in the  $10^4$  (~7.5 min)– $10^7$  (~6.5 min) u range. For ST samples in CO<sub>2</sub>, a third peak can be observed at very high MW values (at about  $4 \times 10^8$  u, which corresponds to dimensions of about 100 nm). The peak at  $4 \times 10^8$  u was observed for both ST and WS samples in N<sub>2</sub>. This peak was already found in [22] in the heavy tar from pyrolysis at 2073 K of cellulose in both N<sub>2</sub> and CO<sub>2</sub> and of lignin only in N<sub>2</sub>. Indeed, it was not observed when lignin was pyrolyzed in CO<sub>2</sub>, where, however, a not negligible amount of soot (5 w%) was collected. In the present work, high MW species are also more abundant when pyrolysis is carried out in N<sub>2</sub> than in CO<sub>2</sub>, even though soot was not obtained.

The normalized UV-Vis spectra features of the heavy tar fraction, reported in Figure 4b, are consistent with SEC results; indeed, they show that the highest absorption in the visible part of the spectrum ( $\lambda > 400$  nm) was registered for the tar produced from ST pyrolysis, which means that it is composed of species with a higher aromatic character, i.e., characterized by a larger aromatic extension. Tars produced in N<sub>2</sub> are for all samples more absorbing than tars produced in CO<sub>2</sub>. This effect is particularly evident in WS tar.





**Figure 4.** Analysis of heavy tar samples: (**a**) Size exclusion chromatography (SEC) chromatograms; (**b**) UV-Vis spectra.

## 3.2.2. Char Analysis

The ash content of chars is reported in Table 2. The mass balance on ash content allows for the estimation that the volatile loss occurred in the HSR ranged between 80 and 96%. Comparison of such values with the proximate analysis of raw biomasses confirms the completion of pyrolysis in all the heated strip treatments.

Figure 5 reports differential thermogravimetric curves obtained from combustion tests of the char samples. The patterns of most samples result from the superposition of multiple peaks. Within a first order approximation, each peak identified one component, and the temperature of the peak provided an indication of its combustion reactivity. The peak temperatures are reported in Table 2. Notably, they were all higher than the peak temperatures obtained in the differential thermogravimetric curves of the raw biomasses, confirming that no residual undevolatilized matter was included in the char samples.

Samples	Raw Biomass	HSR 1573 K N <sub>2</sub>	HSR 1573 K CO <sub>2</sub>	HSR 2073 K N <sub>2</sub>	HSR 2073 K CO <sub>2</sub>		
Ash <sub>dry</sub> (%)							
WS	0.4 (±0.1)	5.8 (±0.6)	8.8 (±1)	5.4 (±0.6)	17 (±2)		
PW	0.1 (±0.3)	$3.9(\pm 0.4)$	4.3 (±0.4)	$4.4 (\pm 0.4)$	4.9 (±0.5)		
ST	6.1 (±0.5)	29.8 (±3)	32.2 (±3)	36.8 (±4)	42.8 (±4)		
DTG peaks (K, ±5)							
WS	520; 560; 690	720	650; 710	820	760		
PW	590; 720	750	750 (±5)	630; 720 *; 760	630; 720; 810		
ST	530; 680	690; 710 *	690; 710	710; 810	810		

Table 2. Results of combustion tests in TGA on raw biomass and Heated Strip Reactor (HSR) chars.

\* Appearing as a shoulder in the DTG plot.



(c)

Figure 5. TGA combustion tests of char samples: (a) WS, (b) PW; (c) ST.

In the char produced from PW at 1573 K, only one component with a peak at 750 K was identified. After heat treatment of PW at 2073 K in N<sub>2</sub>, three char components were observed with peaks at 630, 720 and 810 K. After heat treatment of PW at 2073 K in CO<sub>2</sub>, two main components were observed: the first at 630 and the second with two contributions at 720 K and 760 K. The question whether the early components appeared at 630 K after severe heat treatment could be due to tar deposited on the char surface was addressed by extraction in ethanol of the char, according to the procedure already described in [25], as a means to separate char particles from soot or lighter species eventually mixed with the sample collected from the strip. The char after extraction was again analyzed by TGA, and all the peaks remained unchanged, indicating that they cannot be ascribed to undevolatilized or condensed phases.

Chars produced from ST at 1573 K in  $N_2$  and  $CO_2$  exhibited two partly overlapped peaks at 690 and 710 K. Increasing the temperature of heat treatment in  $CO_2$ , the first component decreased, while a new one appeared with a peak around 810 K. The phenomenon was more remarkable in  $CO_2$ .

WS chars produced in N<sub>2</sub> at 1573 K had a main component with a peak at 710–720 K. In the char produced in CO<sub>2</sub> at 1573 K, a more reactive component below 650 K was also present. Increasing the temperature resulted in chars with much lower reactivity: the WS 2073 N<sub>2</sub> char had the lowest reactivity, with a pronounced component peaking at 820 K. The char produced in CO<sub>2</sub> at 2073 K also exhibited a single component peaking at 760 K.

#### 4. Discussion and Conclusions

The results of the present work clearly indicate the presence of multiple components in the biomass chars. The relation of such components with lignocellulosic constituents of biomass (lignin, cellulose and hemicelluloses) and the impact of biomass components on tar composition are now open to discussion. In a parallel work [22], where similar experimental procedures were applied to lignin, cellulose and hemicelluloses, a complex picture emerged. Fast pyrolysis of hemicellulose and cellulose produced light tars mainly made of anhydrous monosaccharides, while light tar from lignin pyrolysis included also important amounts of oxo-aromatics and PAHs. High molecular weight species were recovered in heavy tar produced at a high temperature from lignin and cellulose. Char was produced only from lignin. Its reactivity was rather low, with DTG peaks above 700 K. The least reactive char was produced at 2073 K in N<sub>2</sub>. Results of the three biomasses investigated in the present work are summarized in Table 3. Results from [22] on the individual biomass components are summarized in Table 4.

Atmosphere	T (K)	Light Tar (GC–MS)	Heavy Tar (SEC)	Char DTG Peaks (K)	
Walnut Shells					
N <sub>2</sub>	1573	Anhydrous monosaccharides: 40%	None	720	
CO <sub>2</sub>	1573	Aliphatics: 40% Light PAHs: 10%	1010	650; 710	
N <sub>2</sub>	2073	Heavy PAHs: 60% Light PAHs: 30% Anhydrous monosaccharides: 5% Oxo-aromatics: 5%	Trimodal	820	
CO <sub>2</sub>	2073	Light PAHs: 55% Oxo-aromatics: 20% Heavy PAHs: 15% Anhydrous monosaccharides: 10%	(higher MW)	760	

Table 3. Summary of results for walnut shells, pinewood and straw.

Atmosphere	T (K)	Light Tar (GC–MS)	Heavy Tar (SEC)	Char DTG Peaks (K)
N <sub>2</sub>	1573	Oxo-aromatics: 40% Anhydrous monosaccharides 30%		750
CO <sub>2</sub>	1573	Aliphatics:15% Light PAHs: 15%	None	
N <sub>2</sub>	2073	Oxo-aromatics:40% Light PAHs: 30% Heavy PAHs: 10% Anhydrous monosaccharides 10% Aliphatics 10%	Trimodal	630; 720; 760
CO <sub>2</sub>	2073	Oxo-aromatics:30% Light PAHs: 30% Aliphatics: 20% Heavy PAHs: 10% Anhydrous monosaccharides: 10%	(higher MW)	630; 720; 810
		Straw		
N <sub>2</sub>	1573	Oxo-aromatics: 50%		
CO <sub>2</sub>	1573	Aliphatics: 20% Aliphatics: 20% Anhydrous monosaccharides: 10%	None	690; 710
N <sub>2</sub>	2073	Oxo-aromatics: 50% Light PAHs: 30% Aliphatics: 15% Heavy PAHs: 5%	Trimodal distribution (higher MW)	710; 810
CO <sub>2</sub>	2073	Light PAHs: 40% Oxo-aromatics: 35% Aliphatics: 15% Heavy PAHs: 10%	Trimodal distribution (higher MW)	810

Table 3. Cont.

The analysis of pyrolysis products from pyrolysis of WS, PW and ST is often not consistent with the results obtained for single lignocellulosic components in [22], as summarized in the following points:

- In ref. [22], anhydrous monosaccharides were found to dominate tar from cellulose and hemicellulose. At odds, in the present work, anhydrous monosaccharides are scarce in ST, the biomass with the highest content of cellulose and hemicelluloses, and most abundant in tar from WS, the biomass with the largest fraction of lignin.
- In ref. [22], PAHs were found to be the most abundant species in tar from lignin pyrolysis, especially in CO<sub>2</sub>-rich atmospheres. Consistently, in the present work, PAHs are present in tars from all the examined biomasses but are particularly abundant in WS tar.
- In ref. [22], heavy tars were obtained from pyrolysis of both cellulose and lignin at high temperature. Consistently in the present work, they are produced from pyrolysis of all the examined biomasses at high temperature.
- In [22], cellulose and hemicelluloses did not produce relevant char residues, while lignin did. Its char appeared to be constituted by one or two components. Differently, all the biomasses investigated in the present work produced char. Chars were quite different from each other in terms of combustion reactivity and appeared to be constituted by several components. After heat treatment in N<sub>2</sub> at 1573 K, the most reactive char was the one from ST, followed by WS and PW. However, the char of WS, the biomass with larger lignin content, appeared the most similar to the char produced from lignin in [22].
- In [22], lignin char had DTG combustion peaks in the range of 700–770 K. More severe heat treatment resulted in higher peak temperature values (lower combustion reactivity) and a higher degree of structural order/thermal annealing of the char. The presence of CO<sub>2</sub> in the atmosphere upon heat treatment, however, hindered thermal

annealing of lignin char; in fact,  $CO_2$  chars were more reactive than  $N_2$  chars. In the present work, severe heat treatment and the presence of  $CO_2$  in the atmospheres generated additional char components, which were both more reactive (with peaks at temperature as low as 630 K) and less reactive (with peak temperatures as high as 830 K). It is possible that the newly formed high reactive char component arose from interactions and cross-linking reactions within the solid matrix at the expense of anhydrous monosaccharides (which decrease sensibly in the corresponding tars), whereas the less reactive component arose from thermal annealing of the solid phase.

Light Tar Heavy Tar Char -T (K) Atmosphere (GC-MS) (SEC) DTG Peaks (K) Cellulose \* 1573  $N_2$ None CO<sub>2</sub> 1573 Anhydrous monosaccharides >90% None Trimodal 2073  $N_2$ distribution CO<sub>2</sub> 2073 (higher MW) Hemicellulose (Xylan) \*\* 1573  $N_2$  $CO_2$ 1573 Anhydrous monosaccharides >90% None None 2073  $N_2$ 2073  $CO_2$ Lignin \*\*\* Oxo-aromatics: 50%  $N_2$ 1573 Anhydrous monosaccharides: 30% 700; 750 Light PAHs: 20% Bimodal distribution Anhydrous monosaccharides: 40%  $CO_2$ 1573 Oxo-aromatics: 30% 700 Light PAHs: 30% Anhydrous monosaccharides:60% Aliphatics: 20% Trimodal  $N_2$ 2073 Light PAHs: 15% distribution 760 Oxo-aromatics: 10% (higher MW) Heavy PAHs: 5% Light PAHs: 40% Oxo-aromatics: 30% Bimodal  $CO_2$ 2073 700; 720 Aliphatics: 20% distribution Anhydrous monosaccharides:10%

**Table 4.** Summary of results for single biomass components. Adapted with permission from Ref. [22]2022, Elsevier.

\* The cellulose sample was in the form of microcrystalline cellulose supplied by JRS Pharma. \*\* The hemicellulose sample was a xylooligosaccharide extracted from Corncob supplied by Roth. \*\*\* The lignin was a dealkaline lignin supplied by Fisher Scientific.

Altogether, the emerging scenario suggests that it is not possible to predict the quality of primary tar and char produced from fast pyrolysis of lignocellulosic biomasses simply by taking into account the behavior of cellulose, hemicelluloses and lignin. Interactions among primary volatile products do exist. Furthermore, it is worth noting that extraction processes for separating cellulose, hemicellulose and lignin from lignocellulosic biomass induce several structure modifications [27–29], thus making it more and more inefficient to predict the biomass pyrolysis behavior on account of the cellulose /hemicellulose /lignin commercially available. In particular, cellulose extraction methods influence the cellulose crystallinity degree [27]. Extraction processes of hemicellulose generate a lower degree of polymerization, mineral impurities and partial breakage of side chains [28], while lignin extraction methods produce low aromatic products [29].

Additional effects of extractives, proteins and minerals further complicate the phenomena and deserve future work and investigation. **Author Contributions:** Conceptualization, O.S. and B.A.; investigation, C.R. and F.C.; data curation, C.R. and F.C.; writing—original draft preparation, O.S., B.A., C.R. and F.C.; writing—review and editing, O.S., B.A., C.R. and F.C. All authors have read and agreed to the published version of the manuscript.

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