

Article

Microwave-Assisted Pyrolysis of Pine Wood Sawdust Mixed with Activated Carbon for Bio-Oil and Bio-Char Production

Anissa Khelfa *, Filipe Augusto Rodrigues, Mohamed Koubaa *  and Eugène Vorobiev

TIMR (Transformations Intégrées de la Matière Renouvelable), Université de Technologie de Compiègne, École Supérieure de Chimie Organique et Minérale, Centre de Recherche Royallieu, CS 60319, 60203 Compiègne CEDEX, France; filipe_augusto22@hotmail.com (F.A.R.); eugene.vorobiev@utc.fr (E.V.)

* Correspondence: a.khelfa@escom.fr (A.K.); m.koubaa@escom.fr (M.K.)

Received: 15 October 2020; Accepted: 5 November 2020; Published: 10 November 2020



Abstract: Pyrolysis of pine wood sawdust was carried out using microwave-heating technology in the presence of activated carbon (AC). Experimental conditions were of 20 min processing time, 10 wt.% of AC, and a microwave power varying from 100 to 800 W. The results obtained showed that the microwave absorber allowed increasing the bio-oil yield up to 2 folds by reducing the charcoal fraction. The maximum temperature reached was 505 °C at 800 W. The higher heating values (HHV) of the solid residues ranged from 17.6 to 30.3 MJ/kg. The highest HHV was obtained for the sample heated at 800 W with 10 wt.% of AC, which was 33% higher than the non-charged sample heated at the same power. Furthermore, the addition of AC allowed showing the probable catalytic effect of the AC in the charged sample pyrolysis bio-oils.

Keywords: activated carbon; biomass; microwave absorber; pine wood sawdust; pyrolysis

1. Introduction

Fossil fuels are the most widely used energy sources nowadays and comprise over 80% of the world's energy supply. However, the reserves' depletion and the carbon fingerprint impact on the environment require finding alternative energy resources. This includes the use of virgin and waste biomasses due to their widespread availability and low impact on the greenhouse effect.

Lignocellulosic biomass (e.g., wood, crops, agricultural and forestry residues, etc.) would be preferable due to its high density (i.e., high energy content per volume), its low amount of ash, and its very low amount of nitrogen. It consists of 35–50 wt.% cellulose, 25–30 wt.% hemicelluloses, 15–20 wt.% lignin, 2–20 wt.% extractable components, and some minerals [1]. Different lignocellulosic materials were subjected to microwave pyrolysis. They include, among others, the treatment of willow chips and straw [2], oil palm shell [3], pine wood sawdust and corn stover [4], barley dust and macroalgae [5], coffee hulls [6], rice straw and rice husk [7], sugarcane bagasse and sugarcane peel [7], and bamboo leaves [7]. One of the main thermochemical conversion routes for the conversion of biomass resources into value-added products is pyrolysis. This process consists of heating the biomass in the absence of air. It allows the production of three valuable fractions: a bio-oil fraction called “condensable liquid”, a volatile fraction, and a carbon-rich solid residue (biochar). Maximizing the yield of one of these fractions requires the optimization of several parameters that include the temperature, the residence time and/or the heating rate [8]. The solid biochar has a wide range of applications such as activated carbon precursors for wastewater treatment [9], soil additive [10], and solid fuel for energy generation [11]. Otherwise, applications as liquid fuel after refining [12] and as valuable chemicals [13] have been considered for bio-oil liquid fraction. Moreover, gas fraction, as the light molecular weight gases, has shown great potential in fuel application [14], electricity generation [15], and as feedstock for H₂ production [16].

The application of microwave technology in biomass pyrolysis has increased from the mid-1990s. This process's advantages over conventional heating include selective and rapid heating, non-contact and volumetric heating, energy saving, easy to control, and environmentally friendly. The heat transfer in conventional heating is governed by conduction and convection compared to microwave heating, where ionic conduction and dipole polarization occur between feedstock and microwave radiation [17]. Applying microwave radiations in a pyrolysis process is a new concept that could be an interesting way of biomass waste pyrolysis. Microwave action during biomass pyrolysis is reflected by the value of the dielectric loss tangent ($\tan \delta = \epsilon''/\epsilon'$), where ϵ'' corresponds to the dielectric loss factor, and ϵ' is the dielectric constant. The latter refers to the ratio between the absorbed microwave irradiations and the reflected ones, whereas ϵ'' measures the efficiency of the heat energy converted from the received microwave energy [18]. A high value of $\tan \delta$ is the main condition to convert microwave energy into thermal one. Thus, while some materials are transparent to microwaves, other materials such as carbon and activated biochar are excellent microwave absorbers. Indeed, the loss tangents of coal ($\tan \delta = 0.02 - 0.08$) [19], carbon black ($\tan \delta = 0.35 - 0.83$) [20], charcoal ($\tan \delta = 0.11 - 0.29$) [21], and activated carbon ($\tan \delta = 0.57 - 0.80$) [22], are comparable to the loss tangent of distilled water (0.118 at room temperature and 2.45 GHz). Therefore, carbon materials are good microwave absorbers that show a high capacity to absorb and convert microwave energy into heat.

In this study, pine wood sawdust (PWS) biomass was pyrolyzed under microwave irradiation using activated carbon (AC) as a microwave absorber. The effect of AC on the potential energy use of heating fractions, bio-oil composition, and solid characteristics was studied. Results related to temperature profiles, product yields, and pyrolyzed biomass behavior were discussed and compared to conventional pyrolysis described in the literature for the same operating conditions.

2. Materials and Methods

2.1. Materials

PWS was kindly provided by the Lecopin Company (Sore, France) and was used in this study as the raw material for the thermochemical conversion experiments. Some physicochemical properties of PWS are listed in Table 1. Activated carbon with similar particle density (0.113 g/cm^3) than PWS biomass and having a specific surface area of $500 \text{ m}^2/\text{g}$ was supplied by CECA S.A. Company (Parentis-en-Born, France) and was used as a microwave radiation absorber. It was then mixed with the biomass before the heat treatment. Relatively high moisture content is a desirable characteristic in microwave biomass pyrolysis as it plays a role in the initial microwave absorption and allows increasing the raw material temperature to the water boiling point [23]. The proximate analysis of biomass is of paramount importance for biomass energy use. Indeed, the high value of volatile matter (81.1%) and the low value of ash content (0.2%) show its higher calorific value potential and better heating rate [24].

Table 1. Properties of pine wood sawdust.

Property	Value
Higher heating value (MJ/kg)	16.6
Density of particles (g/cm^3)	0.113
Proximate analysis (wt.%):	
Moisture	9
Volatile matter	81.1
Fixed carbon	9.7
Ash	0.2

2.2. Proximate Analysis

The moisture contents (MC) of the samples (untreated and treated PWS biomass) were determined based on the measurements of weight loss after oven-drying at $105 \text{ }^\circ\text{C}$ for 24 h. "Ash content (AshC)" and "volatile matter content (VMC) were determined according to the ISO 1171 standard procedures.

Each measurement was carried out in triplicate, and the mean values are reported. Then, ≈ 3 g of a sample was weighed, put into a crucible, and then placed in a muffle furnace (Cerhec, Lacroix-Saint-Ouen, France) at $815\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$ to determine the ash content. After 2 h incineration, all organic materials were carbonized, and the ash content was calculated on a percentage dry weight basis. Similarly, VMC was obtained by incinerating ≈ 7 g of a sample in a muffle furnace at $815\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$. After 10 min, the sample weight remaining in the crucible was recorded, and the VMC was calculated on a percentage dry weight basis. The “fixed carbon content (FCC)” was then calculated according to Equation (1).

$$\text{FCC (wt\%)} = 100 - (\text{MC (wt.\%)} + \text{AshC (wt.\%)} + \text{VMC (wt.\%)}) \quad (1)$$

The higher heating values (HHV) were determined using an adiabatic IKA-calorimeter C200 (IKA, Staufen, Germany).

2.3. Pyrolysis Process

A 900 W, 2.45 GHz microwave system (NEOS-Milestone, Sorisole, Italy) was used to perform the thermal treatment experiments. Each sample of ≈ 35 g, introduced in a round-bottom quartz flask, was placed in the microwave system, as shown in Figure 1. A flow of N_2 (800 mL/min) was used as an inert gas to carry out the volatile compounds released during biomass heating. The obtained carbonaceous residue (char) and the condensable fraction (bio-oil) were weighed, and the non-condensable vapors (gas) were evacuated. The gas yield was estimated by the difference of weight between bio-oil and char fraction. The mass loss percentages were calculated according to Equation (2). m_0 and m_f represent the initial mass of the sample before heating and the final mass after heating, respectively.

$$\text{Mass loss (\%)} = \frac{m_0 - m_f}{m_0} * 100 \quad (2)$$

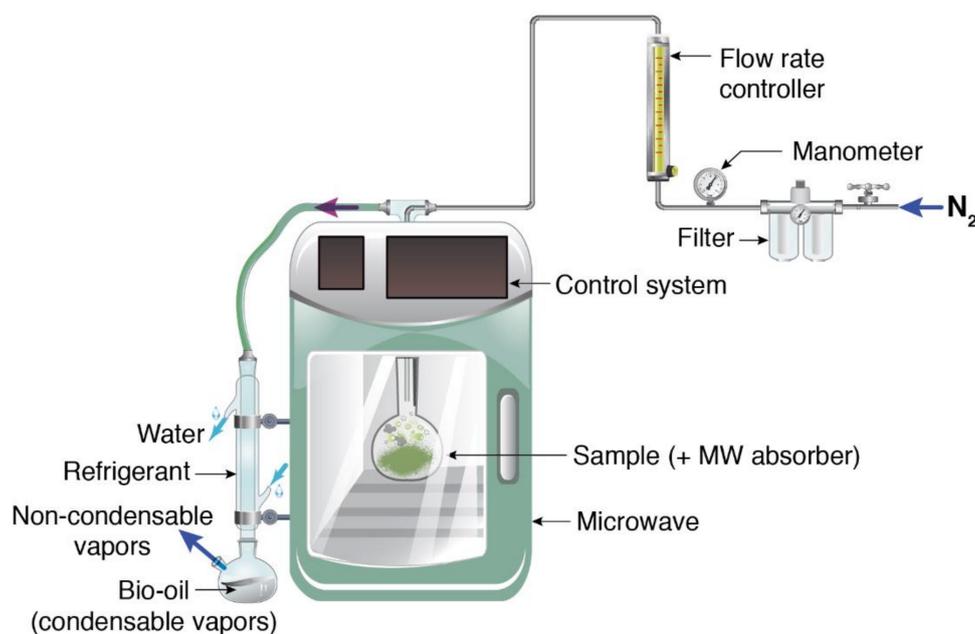


Figure 1. Experimental set-up for microwave-assisted pyrolysis of pine wood sawdust biomass.

Given the low dielectric loss tangent of pine wood sawdust ($\tan \delta = 0.11$ for wood and $\tan \delta = 0.18$ for pine bark [25]), the feedstock has to be mixed with a suitable microwave absorber (here activated carbon (AC)) to reach high temperatures that are necessary for pyrolysis. 10 wt.% of AC was added to

the biomass, mixed, and then exposed to microwave treatment. The desired pyrolysis and torrefaction temperatures were reached by setting the microwave power from 100 to 800 W for 20 min.

The device was switched off for each measurement, and a temperature probe was immediately introduced in the center of the sample to have appropriate and accurate measurements of the temperature during thermal treatment. The duration of each temperature measurement was less than 30 s, which is required to not disturb the temperature increasing and the sample's heating-up. The monitoring was done to see the effects of both microwave power and AC on the temperature evolution during the thermal treatment.

The different samples were labeled as follows: "S (=sample) – microwave power value - activated carbon mass percentage". For example, "S-300-10" was for the sample heated at 300 W and charged with 10 wt.% of AC, "S-100-N" corresponds to the sample heated at 100 W without AC. Two categories of samples were then treated; the 1st category grouped the samples without AC, heated at 100 W, 300 W, 500 W, and 800 W, and the 2nd category grouped the samples charged with 10 wt.% AC and heated at 100 W, 300 W, 500 W, and 800 W.

2.4. Chromatographic Analysis

The compositions of the oil fractions obtained were analyzed using the gas chromatography-mass spectrometry (GC-MS) technique. The analyses were carried out using an Agilent 7820A chromatograph equipped with an Agilent-MS 5975 mass spectrometer (Agilent, Santa Clara, United States). High purity helium was used as carrier gas at a 1 mL/min flow rate with a split ratio of 1:10. The separation was performed using an HP-5 capillary column (5% diphenyl + 95% dimethylpolysiloxane) (30 m length, 250 μm inner diameter, and 0.25 μm film thickness). The initial column temperature set at 45 $^{\circ}\text{C}$ was maintained for 4 min; the temperature was then increased at a rate of 3 $^{\circ}\text{C}/\text{min}$ until reaching 280 $^{\circ}\text{C}$. The sample (1 μL) was injected under high pressure (50 kPa), and the injector temperature was kept at 280 $^{\circ}\text{C}$. The mass spectra were operated in EI mode at 70 eV and obtained from 20 to 150 (m/z). The chromatographic peaks were identified according to the NIST MS (National Institute of Standards and Technology Mass Spectral) library. Before analysis, the oil fraction's moisture was removed by heating for ≈ 12 min using a heating plate. The organic fraction remaining (≈ 1 g) was dissolved in 5 mL acetone, put in a GC-MS vial, and then injected. The obtained chromatograms were normalized against the peak of the solvent to allow the quantitative analysis.

2.5. Statistical Analysis

Average values and standard deviations were calculated using three biological replicates.

3. Results and Discussion

3.1. Temperature Profiles

The temperature profiles recorded over the time for the different microwave (MW) powers applied during 20 min of thermal treatment of PWS samples, and with 10 wt.% of AC, are shown in Figure 2.

Results in Figure 2 show that the temperatures tend to increase proportionally to the MW power applied. After approximately 12 min, except for the sample S-100-N, the temperature values almost reached a plateau. Beyond this time, the vapors' release had almost stopped, thereby indicating that the heating process had reached a steady state.

Figure 2 shows that for the 1st category of samples, the maximum temperature value reached after 20 min was 210 ± 2 $^{\circ}\text{C}$ (for the sample S-800-N). This temperature corresponds to the torrefaction conditions (200–300 $^{\circ}\text{C}$). For the 2nd category of samples, pyrolysis temperatures (estimated in the range of 300–700 $^{\circ}\text{C}$ [26]) were reached at 505 ± 2 $^{\circ}\text{C}$ (for the sample S-800-10). These results show that the desired pyrolysis temperature could be obtained using 10 wt.% of MW absorber with a MW power up to 500 W. Usually, temperature values higher than 550 $^{\circ}\text{C}$ lead to the occurrence of secondary reactions and hence it could favor the release of gaseous products [27].

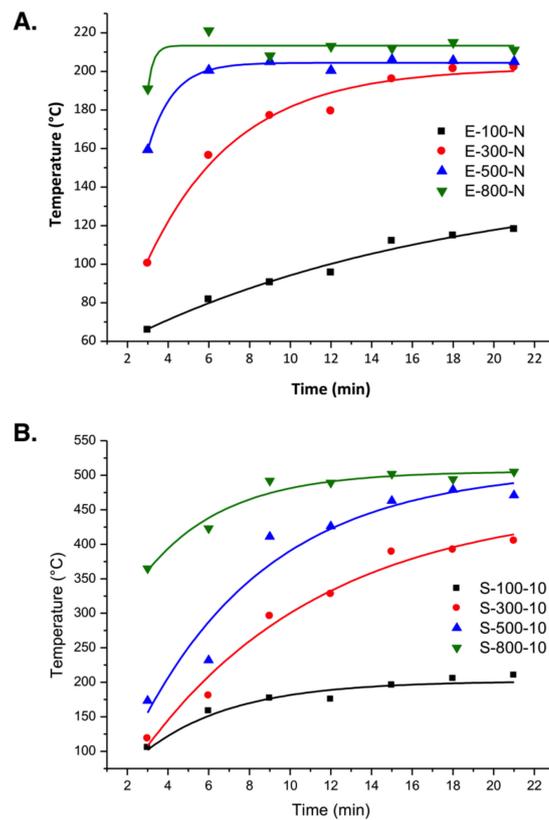


Figure 2. Real-time temperature profiles of the PWS samples. (A) 1st category of samples. (B) 2nd category of samples.

Macroscopic changes in the solids obtained after the MW treatments could be observed in Figure 3. Gradual changes were noticed in the samples' color, which was mainly due to the uniform heating provided by the addition of the activated carbon and the increase of MW power. In fact, uniform carbonization was observed clearly for all the samples of the 2nd category.

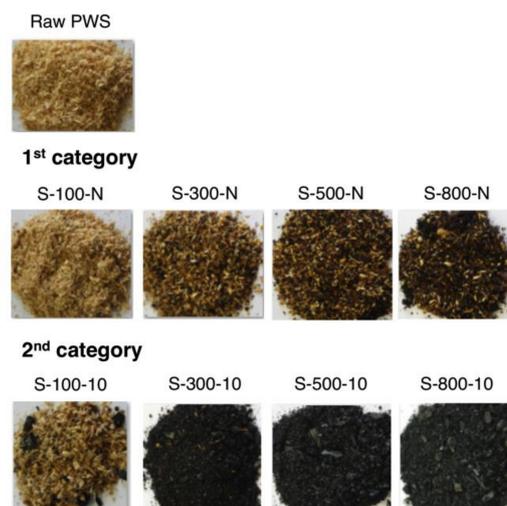


Figure 3. Aspects of the resulting chars obtained after microwave heating at different experimental conditions.

3.2. Pyrolysis Products' Yields

Char residue, bio-oil, and gas fraction were the three main fractions of the pyrolysis process. The yields, in mass percentage, obtained using the different process conditions are presented in Figure 4. The increase of MW power leads to enhanced gas production, which implies systematically decreasing the yield of the solid fraction (char). Indeed, the decrease in char yield with the increase of temperature can be explained by removing volatile material during devolatilization of the organic material with the likely presence of partial gasification of the char [6]. The highest oil yield (24 wt.%) was reached at 505 ± 2 °C for the sample heated at 800 W with 10 wt.% of AC.

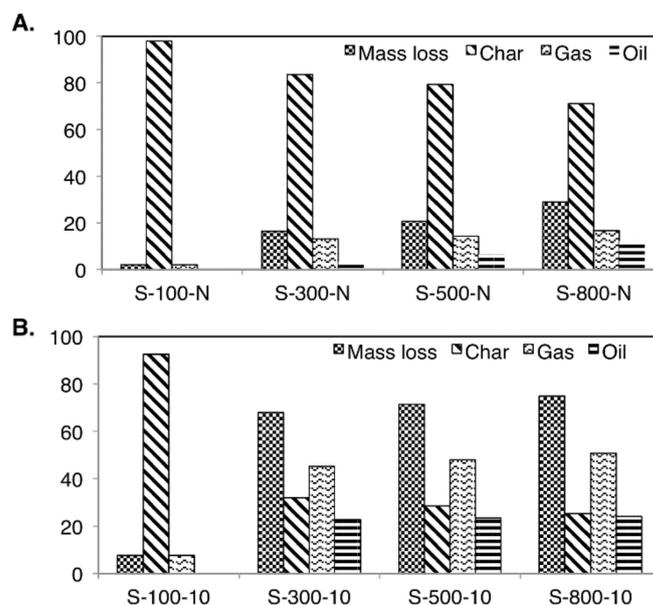


Figure 4. Mass losses and fraction yields of MW-treated samples for the 1st category (A) and the 2nd category (B). No oil fraction recovery was observed for the samples S-100-N and S-100-10.

Moreover, the mass loss percentages were equivalent to the yields of volatiles (condensable (oil), non-condensable (gas) fractions, and moisture); it is, therefore, higher in the presence of AC and when increasing the microwave heating power. The addition of 10 wt.% AC (except for the sample S-100-10) involves reaching the highest values of mass loss, which is very likely due to the high temperatures reached in these experiments. Indeed, a temperature beyond 250 °C induces a higher reactivity and a greater degradation of the biomass components (i.e., cellulose, hemicelluloses, and lignin) [28,29]. On the other hand, the mass loss observed below this temperature range is largely due to the evaporation of water and low molecular weight volatile compounds. Gao et al. reported different trends in mass loss percentage for pine sawdust conventional pyrolysis [30]. They reported that 81.3 wt.% of weight loss was noted for the samples of conventional pyrolysis compared to 71.4 and 74.8 wt.% for microwave pyrolysis samples (S-500-10 and S-800-10, respectively) obtained in this work. Moreover, the solid residue that remained was equal to 14.8 wt.% and 17.5 wt.% of the original mass in slow and fast conventional pyrolysis, respectively, compared to 26.9 wt.% on average in microwave pyrolysis. These differences could be related to the difference in the mass loss rate, which is much higher in microwave pyrolysis than that in conventional pyrolysis [30,31].

Microwave pyrolysis produces much larger gas yields than conventional fast pyrolysis over the entire temperature range [31]. The oil yield, however, was lower in the case of microwave heating (33.5 wt.% for conventional fast pyrolysis against 24.0 wt.% for S-800-10 sample heated under MW conditions), which suggests that microwave heating favors secondary cracking reactions leading to obtaining lighter products compared to that of conventional heating [5,31,32].

3.3. Characterization of the Solid Fraction

The chemical composition of the obtained chars from PWS microwave thermochemical conversion under various conditions is shown in Table 2. As expected, increasing the temperature values (or microwave power) leads to an increase of the fixed carbon content (*FCC%*), a decrease of the volatile matter content (*VMC%*), and a slight increase of the ash content (*AshC%*). In fact, the increase of *FCC* by approximately five times was observed for the sample S-800-10, compared to the sample S-100-N. This is the consequence of the significant removal of hydrogen and oxygen atoms from the raw biomass and the low amount of carbon in the form of hydrocarbons in the raw biomass. On the other hand, the char resulting from microwave pyrolysis has slightly lower carbon content compared to that obtained from conventional pyrolysis [5,32]. However, the resulting char from both pyrolysis has the potential to be used as precursor of AC due to its high carbon content (e.g., 78.7, 78.1, and 79.2 wt.% of *FCC*, respectively, for the S-300-10, S-500-10, and S-800-10 samples).

Table 2. HHV and proximate analysis results for the different MW-treated samples.

	Sample	HHV (MJ/kg)	AshC (wt.%)	VMC (wt.%)	FCC (wt.%)
	Raw PWS	16.6	0.2	81.1	9.7
1st category	S-100-N	17.7	0.3	80.9	14.8
	S-300-N	19.4	0.5	77.4	22.1
	S-500-N	19.4	0.7	73.7	25.6
	S-800-N	22.8	0.6	69.6	29.8
2nd category	S-100-10	21.5	0.4	74.4	25.2
	S-300-10	29.3	1.7	19.6	78.7
	S-500-10	30.2	6.1	15.8	78.1
	S-800-10	30.3	10.0	10.8	79.2

Low ash content in raw pine sawdust is an indicator that this biomass could be a good candidate for fuel production via the thermochemical process. According to De Bhowmick et al. [32], the ash content of pine sawdust char obtained by conventional slow pyrolysis (at 500 °C) was lower than that of the chars obtained in this work by microwave-assisted pyrolysis at the same temperature (chars from the samples of the 2nd category; S-500-10 and S-800-10). These chars' relatively high ash content could be related to the increased mineral concentrations and organic combustion residues. For the same reasons, it can be seen that the content of volatile matter decreases as either the temperature or the amount of AC increase. In fact, the heated material has a lower O/C ratio compared to that of the untreated biomass and thereby a higher calorific value [28]. For the 1st category samples, the increase in temperature allowed the increase of higher heating values (HHV) (Table 2). The same behavior was observed for the samples of the 2nd category. The chars produced in this work had the heating values ranging from 17.7 to 30.3 MJ/kg, which is lower than the transportation grade diesel fuels (≈ 36.5 MJ/kg) and natural gas (≈ 42.5 MJ/kg), and approximately similar to that of coal (≈ 34.1 MJ/kg), lignite (≈ 26 MJ/kg) or ethanol (≈ 29 MJ/kg) [33]. Moreover, by comparing the results obtained in the current work to those from conventional slow pyrolysis, similar values of PWS HHV were observed for similar pyrolysis conditions [32].

3.4. GC-MS Characterization of the Liquid Fraction

The liquid fractions (bio-oils) obtained after the thermal treatment of PWS biomass were analyzed using gas chromatography-mass spectrometry. Total ion chromatograms obtained for the two categories of samples are given in Figure 5. Among 32 identified compounds, organic products resulting from the decomposition of the three main biomass components were identified. In fact, hemicelluloses can be decomposed into furfural and acetic acid [34–37]. The products resulting from its degradation showed in Figure 5 are acetic acid, (acetyloxy)- (#3), acetic acid, hydroxy-, ethyl ester (#5),

and furfural (#6). The cellulose can be decomposed into furans, aldehydes, and ketones [38,39]. The products of Figure 5 resulting from its degradation are thereby: 2-propanone-1-hydroxy (#1), succinaldehyde (#4), 3,4-furandiols, tetrahydro-trans (#8), 2(5H)-furanone (#9), 2,5-furandione, dihydro-3-methylene- (#11), 3-methyl-1,2-cyclopentanedione (#12), 1,3-cyclopentanedione (#14), octan-2-one-, 3,6-dimethyl (#22) and 5-octen-2-one, 3,6-dimethyl (#27). Lignin can be decomposed into phenols and guaiacols [40–44], leading to the degradation of the products: guaiacol (#16), creosol (#20), catechol (#21), 4-ethenyl-2-methoxyphenol (#23), 4-ethylcatechol (#24), vanillin (#28), apocynin (#30), and guaiacyl acetone (#32). Moreover, a small relative yield of polysaccharide product (D-mannose #25) was observed in the bio-oils of two categories of samples.

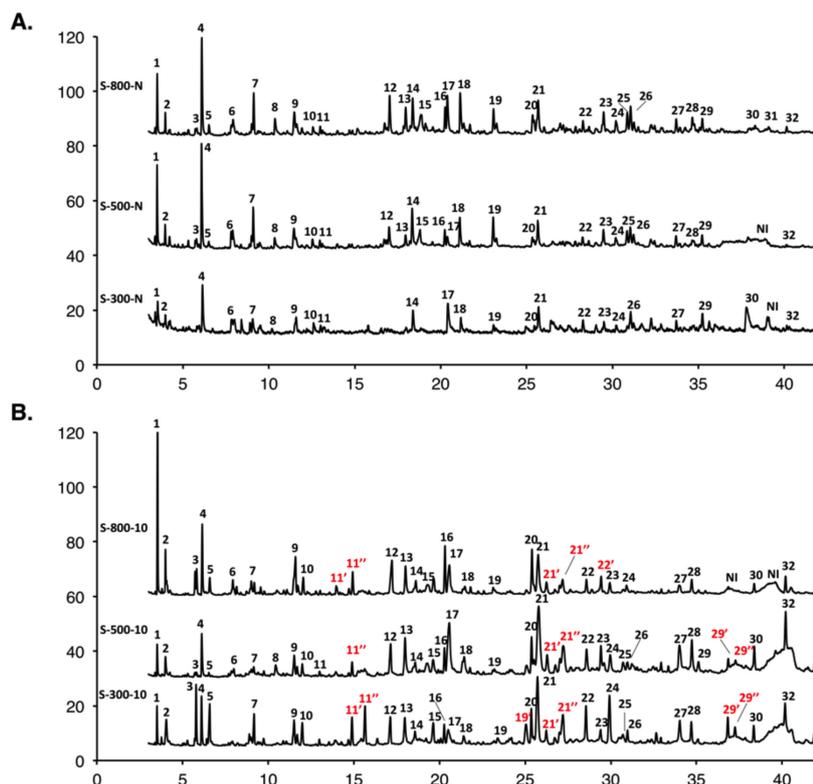


Figure 5. Total ion chromatograms for the liquid fractions of the samples of the 1st category (A) and the 2nd category (B).

1: 2-Propanone-1-Hydroxy, 2: 1,3-Dioxolane-2,2-dimethyl-, 3: Acetic acid, (acetyloxy)-, 4: Succinaldehyde, 5: Acetic acid, hydroxy-, ethyl ester, 6: Furfural, 7: 1-Propen-2-ol-, acetate, 8: 3,4-Furandiols, tetrahydro-trans, 9: 2(5H)-Furanone, 10: 4-Hydroxy-2-butanone, 11: 2,5-Furandione, dihydro-3-methylene-, 11': 4-Ethyl-3-methylenedihydrofuro [3,4-b]furan-2,6(3H,4H)-dione, 11'': Phenol, 12: 3-Methyl-1,2-cyclopentanedione, 13: 2-Allyl-1,3-dioxolane, 14: 1,3-Cyclopentanedione, 15: Pentanoic acid, 4-oxo-, 16: Guaiacol, 17: Hydroperoxide, 1-methylhexyl, 18: 4-Hydroxy-4-methyltetrahydro-2H-pyran-2-one, 19: 3-Acetyl-cyclopentanone, 19': 2-Nonen-1-ol, 20: Creosol, 21: Catechol, 21': 1,4:3,6-Dianhydro- α -d-glucopyranose, 21'': 5-Hydroxymethylfurfural, 22: Octan-2-one-, 3,6-dimethyl, 23: 4-Ethenyl-2-methoxyphenol, 24: 4-Ethylcatechol, 25: D-Mannose, 26: Vinyl cyclopentylacetate, 27: 5-Octen-2-one, 3,6-dimethyl-, 28: Vanillin, 29: 3,7-Dimethyl-2,6-nonadien-1-ol, 29': Trans-isoeugenol, 29'': Dihydroeugenol, 30: Apocynin, 31: 5,8-Epoxy-3H-2-benzopyran, 4,4a,5,8-tetrahydro-5,8-dimethyl-, 32: Guaiacyl acetone. NI: non identified compound.

Considering the non-charged samples (Figure 5A), the MW power variation did not significantly modify the chemical composition of the resulting bio-oils. In fact, the identified products were approximately the same regardless of the heating power applied. However, ketone yields (#1, #9

and #14), which are mainly derived from cellulose decomposition, and compounds #20, #23 and #24, which are mainly derived from lignin decomposition, increased relatively with the increase of MW power (or temperature). Some other compounds (phenolic compounds) appeared with the increase of temperature (e.g., guaiacol (#16) and vanillin (#28)). In general, the yields of chemicals derived from pine wood sawdust decomposition were proportional to the microwave power applied. The results obtained concur with those reported in the literature [38,45].

The addition of AC allowed modifying the quantitative and qualitative composition of bio-oils (Figure 5B). Variations in the intensity of the product peaks were observed. Moreover, the presence of a MW absorber in the heated samples allowed the formation of new products that were labeled in red color. The analysis of these new compounds allowed the identification of new phenolic compounds (phenol #11", trans-isoeugenol #29', and dihydroeugenol #29'') and a new furan compound (5-hydroxymethylfurfural (HMF) #21''). An increase in the content of phenolic compounds might be due to the addition of AC that plays a catalytic role in the mechanism of lignin degradation, whereas the formation of 5-hydroxymethylfurfural could happen due to the presence of continuous secondary degradation reactions with an increase in the temperature. Phenols, derived mainly from lignin's decomposition, are widely useful chemicals in pharmacy, synthesis, and the food industry [44,46,47]. One of the pine wood pyrolysis polysaccharide products is HMF. It can also be a catalytic pyrolysis product; for example, zeolites catalyze the dehydration of levoglucosan to 5-hydroxymethylfurfural [48,49]. Unlike conventional pyrolysis, levoglucosan is not observed in the bio-oil of our work [30]. This may be due to the high heating rate in microwave pyrolysis. In fact, the microwave technique is one of the most promising methods of enhancing and accelerating chemical reactions. Thus, this mechanism prevents the appearance of levoglucosan, which breaks down into HMF.

The main compounds obtained in microwave pine sawdust pyrolysis oil were also found in bio-oil obtained at high temperatures conventional slow pyrolysis [30] (e.g., acetic acid, (acetyloxy)-(#3), succinaldehyde (#4), 2(5H)-furanone (#9), 3-methyl-1,2-cyclopentanedione (#12), Guaiacol (#16), 4-ethenyl-2-methoxyphenol (#23), trans-isoeugenol (#29'), and dihydroeugenol (#29'')). Moreover, in conventional fast pyrolysis, the chemical composition of liquid fraction can be classified into sugars (levoglucosan), acids (acetic acid, etc.), phenols (1,2-benzenediol, etc.) and with lower yields; aldehydes (hydroxyacetaldehyde, etc.), furans (furfural, etc.) and ketones (2-cyclopenten-1-one, etc.) [31], which is close to that of microwave pyrolysis at the same temperature. Otherwise, Wang et al. obtained, from pine sawdust conventional fast pyrolysis, more phenols with almost the same composition for other prevalent compounds [50].

4. Conclusions

Potential gains from the use of microwave technology, both on the efficiency of pyrolysis process and on the decrease in time analysis, have been illustrated in this work. The main goal was to study the efficiency of activated carbon on the final product properties—the addition of activated carbons allowed unifying biomass heating and increases of heating temperatures. Calorific values of solid residues ranged from 17.6 to 30.3 MJ/kg and were higher in the pyrolysis conditions of 800 W microwave power. Moreover, activated carbon's addition allowed the formation of new organic products (e.g., phenolic compounds) and then modifying the quantitative and qualitative composition of the bio-oils generated. The activated carbon probably plays a catalytic role in the pyrolysis of PWS biomass. An increase in microwave irradiation power allowed the intensification of mass loss percentages, the increase of the fixed carbon content, and solids' calorific value. These behaviors were most likely due to the increase of the treatment temperature. Indeed, the temperatures tend to increase proportionally to the MW power applied. Moreover, microwave pyrolysis of PWS produces an abundant solid fraction, in which the amount decreases with the pyrolysis temperature. Additionally, the variation of the MW power did not significantly modify the chemical composition of the resulting bio-oils.

The comparison made between the results obtained in this work and conventional heating has shown that microwave heating allowed obtaining a solid pyrolysis fraction with similar characteristics to solids obtained from conventional heating treatment, but with shorter residence time. This shows the potential of this technology to reduce energy consumption and, therefore, the production cost. Microwave pyrolysis produces much larger gas yields, less oil, and similar char yields than conventional pyrolysis over the entire range of temperatures. The char resulting from microwave pyrolysis has slightly lower carbon content than that obtained from conventional pyrolysis. In general, the main compounds analyzed in microwave pine sawdust pyrolysis oil were found, at higher temperatures, in conventional pyrolysis bio-oil. It can be concluded from this work that microwave technology can reduce the pyrolysis reaction time and increase the quality of value-added products obtained from PWS biomass.

Author Contributions: Conceptualization, A.K.; methodology, F.A.R.; validation, A.K., M.K. and E.V.; formal analysis, A.K.; resources, E.V.; writing—original draft preparation, A.K.; writing—review and editing, A.K., M.K., and E.V.; supervision, A.K.; project administration, A.K.; funding acquisition, E.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bajpai, P. *Pretreatment of Lignocellulosic Biomass for Biofuel Production*; Springer: Singapore, 2016; ISBN 978-981-10-0686-9.
2. Mašek, O.; Budarin, V.; Gronnow, M.; Crombie, K.; Brownsort, P.; Fitzpatrick, E.; Hurst, P. Microwave and slow pyrolysis biochar—Comparison of physical and functional properties. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 41–48. [[CrossRef](#)]
3. Salema, A.A.; Ani, F.N. Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer. *J. Anal. Appl. Pyrolysis* **2012**, *96*, 162–172. [[CrossRef](#)]
4. Zhang, B.; Zhong, Z.; Chen, P.; Ruan, R. Microwave-assisted catalytic fast pyrolysis of biomass for bio-oil production using chemical vapor deposition modified HZSM-5 catalyst. *Bioresour. Technol.* **2015**, *197*, 79–84. [[CrossRef](#)] [[PubMed](#)]
5. Ferrera-Lorenzo, N.; Fuente, E.; Bermúdez, J.M.; Suárez-Ruiz, I.; Ruiz, B. Conventional and microwave pyrolysis of a macroalgae waste from the Agar-Agar industry. Prospects for bio-fuel production. *Bioresour. Technol.* **2014**, *151*, 199–206. [[CrossRef](#)] [[PubMed](#)]
6. Domínguez, A.; Menéndez, J.A.; Fernández, Y.; Pis, J.J.; Nabais, J.M.V.; Carrott, P.J.M.; Carrott, M.M.L.R. Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. *J. Anal. Appl. Pyrolysis* **2007**, *79*, 128–135. [[CrossRef](#)]
7. Huang, Y.-F.; Chiueh, P.-T.; Kuan, W.-H.; Lo, S.-L. Microwave pyrolysis of lignocellulosic biomass: Heating performance and reaction kinetics. *Energy* **2016**, *100*, 137–144. [[CrossRef](#)]
8. Yanik, J.; Stahl, R.; Troeger, N.; Sinag, A. Pyrolysis of algal biomass. *J. Anal. Appl. Pyrolysis* **2013**, *103*, 134–141. [[CrossRef](#)]
9. Han, L.; Qian, L.; Liu, R.; Chen, M.; Yan, J.; Hu, Q. Lead adsorption by biochar under the elevated competition of cadmium and aluminum. *Sci. Rep.* **2017**, *7*, 1–11. [[CrossRef](#)]
10. Mohamed, B.A.; Kim, C.S.; Ellis, N.; Bi, X. Microwave-assisted catalytic pyrolysis of switchgrass for improving bio-oil and biochar properties. *Bioresour. Technol.* **2016**, *201*, 121–132. [[CrossRef](#)]
11. Bazargan, A.; Rough, S.L.; McKay, G. Compaction of palm kernel shell biochars for application as solid fuel. *Biomass Bioenergy* **2014**, *70*, 489–497. [[CrossRef](#)]
12. Dai, L.; Fan, L.; Duan, D.; Ruan, R.; Wang, Y.; Liu, Y.; Zhou, Y.; Yu, Z.; Liu, Y.; Jiang, L. Production of hydrocarbon-rich bio-oil from soapstock via fast microwave-assisted catalytic pyrolysis. *J. Anal. Appl. Pyrolysis* **2017**, *125*, 356–362. [[CrossRef](#)]
13. Czernik, S.; Bridgwater, A.V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **2004**, *18*, 590–598. [[CrossRef](#)]

14. Huang, Y.-F.; Chiueh, P.-T.; Kuan, W.-H.; Lo, S.-L. Effects of lignocellulosic composition and microwave power level on the gaseous product of microwave pyrolysis. *Energy* **2015**, *89*, 974–981. [[CrossRef](#)]
15. Lanzini, A.; Madi, H.; Chiodo, V.; Papurello, D.; Maisano, S.; Santarelli, M.; Van Herle, J. Dealing with fuel contaminants in biogas-fed solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) plants: Degradation of catalytic and electro-catalytic active surfaces and related gas purification methods. *Prog. Energy Combust. Sci.* **2017**, *61*, 150–188. [[CrossRef](#)]
16. Guerrero, M.R.B.; Salinas Gutiérrez, J.M.; Meléndez Zaragoza, M.J.; López Ortiz, A.; Collins-Martínez, V. Optimal slow pyrolysis of apple pomace reaction conditions for the generation of a feedstock gas for hydrogen production. *Int. J. Hydrog. Energy* **2016**, *41*, 23232–23237. [[CrossRef](#)]
17. Lam, S.S.; Chase, H.A. A Review on waste to energy processes using microwave pyrolysis. *Energies* **2012**, *5*, 4209–4232. [[CrossRef](#)]
18. Zhang, X.; Hayward, D.O. Applications of microwave dielectric heating in environment-related heterogeneous gas-phase catalytic systems. *Inorg. Chim. Acta* **2006**, *359*, 3421–3433. [[CrossRef](#)]
19. Marland, S.; Merchant, A.; Rowson, N. Dielectric properties of coal. *Fuel* **2001**, *80*, 1839–1849. [[CrossRef](#)]
20. Atwater, J.E.; Wheeler, R.R. Temperature dependent complex permittivities of graphitized carbon blacks at microwave frequencies between 0.2 and 26 GHz. *J. Mater. Sci.* **2004**, *39*, 151–157. [[CrossRef](#)]
21. Wu, K.H.; Ting, T.H.; Wang, G.P.; Yang, C.C.; Tsai, C.W. Synthesis and microwave electromagnetic characteristics of bamboo charcoal/polyaniline composites in 2–40 GHz. *Synth. Met.* **2008**, *158*, 688–694. [[CrossRef](#)]
22. Atwater, J.E.; Wheeler, R.R. Complex permittivities and dielectric relaxation of granular activated carbons at microwave frequencies between 0.2 and 26 GHz. *Carbon* **2003**, *41*, 1801–1807. [[CrossRef](#)]
23. Ellison, C.R.; Hoff, R.; Mărculescu, C.; Boldor, D. Investigation of microwave-assisted pyrolysis of biomass with char in a rectangular waveguide applicator with built-in phase-shifting. *Appl. Energy* **2020**, *259*, 114217. [[CrossRef](#)]
24. Kumar, M.; Sabbarwal, S.; Mishra, P.K.; Upadhyay, S.N. Thermal degradation kinetics of sugarcane leaves (*Saccharum officinarum* L.) using thermo-gravimetric and differential scanning calorimetric studies. *Bioresour. Technol.* **2019**, *279*, 262–270. [[CrossRef](#)] [[PubMed](#)]
25. Torgovnikov, G.I. *Dielectric Properties of Wood and Wood-Based Materials*; Springer: Berlin/Heidelberg, Germany, 1993.
26. Hu, X.; Gholizadeh, M. Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage. *J. Energy Chem.* **2019**, *39*, 109–143. [[CrossRef](#)]
27. Luque, R.; Menéndez, J.A.; Arenillas, A.; Cot, J. Microwave-assisted pyrolysis of biomass feedstocks: The way forward? *Energy Environ. Sci.* **2012**, *5*, 5481–5488. [[CrossRef](#)]
28. Medic, D.; Darr, M.; Shah, A.; Potter, B.; Zimmerman, J. Effects of torrefaction process parameters on biomass feedstock upgrading. *Fuel* **2012**, *91*, 147–154. [[CrossRef](#)]
29. Koukios, E.G. Progress in thermochemical, solid-state refining of biofuels—From research to commercialization. In *Advances in Thermochemical Biomass Conversion*; Bridgwater, A.V., Ed.; Springer: Dordrecht, The Netherlands, 1993; pp. 1678–1692.
30. Gao, N.; Li, A.; Quan, C.; Du, L.; Duan, Y. TG–FTIR and Py–GC/MS analysis on pyrolysis and combustion of pine sawdust. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 26–32. [[CrossRef](#)]
31. Yildiz, G.; Ronsse, F.; Venderbosch, R.; Duren, R.; van Kersten, S.R.A.; Prins, W. Effect of biomass ash in catalytic fast pyrolysis of pine wood. *Appl. Catal. B Environ.* **2015**, *168–169*, 203–211. [[CrossRef](#)]
32. De Bhowmick, G.; Sarmah, A.K.; Sen, R. Production and characterization of a value added biochar mix using seaweed, rice husk and pine sawdust: A parametric study. *J. Clean. Prod.* **2018**, *200*, 641–656. [[CrossRef](#)]
33. Raveendran, K.; Ganesh, A. Heating value of biomass and biomass pyrolysis products. *Fuel* **1996**, *75*, 1715–1720. [[CrossRef](#)]
34. Ponder, G.R.; Richards, G.N. Thermal synthesis and pyrolysis of a xylan. *Carbohydr. Res.* **1991**, *218*, 143–155. [[CrossRef](#)]
35. Shafizadeh, F.; McGinnis, G.D.; Philpot, C.W. Thermal degradation of xylan and related model compounds. *Carbohydr. Res.* **1972**, *25*, 23–33. [[CrossRef](#)]
36. Antal, M.J.; Leesomboon, T.; Mok, W.S.; Richards, G.N. Mechanism of formation of 2-furaldehyde from d-xylose. *Carbohydr. Res.* **1991**, *217*, 71–85. [[CrossRef](#)]
37. Shen, D.K.; Gu, S.; Bridgwater, A.V. Study on the pyrolytic behaviour of xylan-based hemicellulose using TG–FTIR and Py–GC–FTIR. *J. Anal. Appl. Pyrolysis* **2010**, *87*, 199–206. [[CrossRef](#)]

38. Shen, D.K.; Gu, S. The mechanism for thermal decomposition of cellulose and its main products. *Bioresour. Technol.* **2009**, *100*, 6496–6504. [[CrossRef](#)] [[PubMed](#)]
39. Lu, Q.; Yang, X.; Dong, C.; Zhang, Z.; Zhang, X.; Zhu, X. Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: Analytical Py-GC/MS study. *J. Anal. Appl. Pyrolysis* **2011**, *92*, 430–438. [[CrossRef](#)]
40. Nowakowski, D.J.; Bridgwater, A.V.; Elliott, D.C.; Meier, D.; de Wild, P. Lignin fast pyrolysis: Results from an international collaboration. *J. Anal. Appl. Pyrolysis* **2010**, *88*, 53–72. [[CrossRef](#)]
41. Windt, M.; Meier, D.; Marsman, J.H.; Heeres, H.J.; Koning, S. de Micro-pyrolysis of technical lignins in a new modular rig and product analysis by GC-MS/FID and GC × GC-TOFMS/FID. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 38–46. [[CrossRef](#)]
42. Klein, M.T.; Virk, P.S. Modeling of Lignin Thermolysis. *Energy Fuels* **2008**, *22*, 2175–2182. [[CrossRef](#)]
43. Murwanashyaka, J.N.; Pakdel, H.; Roy, C. Step-wise and one-step vacuum pyrolysis of birch-derived biomass to monitor the evolution of phenols. *J. Anal. Appl. Pyrolysis* **2001**, *60*, 219–231. [[CrossRef](#)]
44. Pandey, M.P.; Kim, C.S. Lignin depolymerization and conversion: A review of thermochemical methods. *Chem. Eng. Technol.* **2011**, *34*, 29–41. [[CrossRef](#)]
45. Ren, S.; Lei, H.; Wang, L.; Bu, Q.; Chen, S.; Wu, J.; Julson, J.; Ruan, R. Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 163–169. [[CrossRef](#)]
46. Effendi, A.; Gerhauser, H.; Bridgwater, A.V. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. *Renew. Sustain. Energy Rev.* **2008**, *12*, 2092–2116. [[CrossRef](#)]
47. Proestos, C.; Chorianopoulos, N.; Nychas, G.-J.E.; Komaitis, M. RP-HPLC analysis of the phenolic compounds of plant extracts. investigation of their antioxidant capacity and antimicrobial activity. *J. Agric. Food Chem.* **2005**, *53*, 1190–1195. [[CrossRef](#)] [[PubMed](#)]
48. Wang, K.; Kim, K.H.; Brown, R.C. Catalytic pyrolysis of individual components of lignocellulosic biomass. *Green Chem.* **2014**, *16*, 727–735. [[CrossRef](#)]
49. Xin, X.; Pang, S.; de Miguel Mercader, F.; Torr, K.M. The effect of biomass pretreatment on catalytic pyrolysis products of pine wood by Py-GC/MS and principal component analysis. *J. Anal. Appl. Pyrolysis* **2019**, *138*, 145–153. [[CrossRef](#)]
50. Wang, J.-X.; Cao, J.-P.; Zhao, X.-Y.; Liu, T.-L.; Wei, F.; Fan, X.; Zhao, Y.-P.; Wei, X.-Y. Study on pine sawdust pyrolysis behavior by fast pyrolysis under inert and reductive atmospheres. *J. Anal. Appl. Pyrolysis* **2017**, *125*, 279–288. [[CrossRef](#)]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 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 (<http://creativecommons.org/licenses/by/4.0/>).