

Article

# Activated Carbons from Fast Pyrolysis Biochar as Novel Catalysts for the Post-Treatment of Pyrolysis Vapors, Studied by Analytical Pyrolysis

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**Abstract:** Biochars are attractive materials for carbon catalysts since their carbon content and surface area are relatively high and minerals present in biochar can act as active sites for catalytic reactions. In this study, biochars from the fast pyrolysis of birch, pine, and unbarked willow were activated and acid washed. These materials were tested as catalysts for a post-treatment of pine wood pyrolysis vapors, aiming at stabilizing the vapors before their condensation. All the unmodified biochars had high content of minerals, those being highest in willow due to the bark. After the activation treatments, the surface areas and pore volumes of all biochars significantly increased. All studied biochars and activated carbon catalysts reduced the oxygen content of the pyrolysis degradation products. This effect was more pronounced for compounds derived from polysaccharides vs. lignin. The most promising catalyst for vapor upgrading was unwashed activated carbon from willow, having high surface areas and pore volumes together with high mineral contents. These properties together promoted the high conversion of polysaccharide-derived products (anhydrosugars, acids, and pyrans) into CO<sub>2</sub>. Release of highly oxidized degradation products may indicate that reductive stabilization takes place via hydrogen migration from the polysaccharide-derivatives to lignin derivatives, mediated by the carbon catalyst.

**Keywords:** biochar; activated carbon; steam activation; sulfonation; catalyst; pyrolysis vapors; post-treatment

## 1. Introduction

Carbon materials are widely used as catalyst supports or as heterogeneous catalysts. They have many good properties required for a catalyst. In particular, they have very high surface areas reaching thousands of m<sup>2</sup>/g [1], enabling a high density of active sites and thus high activity. Carbons are also chemically stable and in fact relatively inert materials [2]. Activated carbon is one of the main types of carbons used as catalysts. Activated carbon is prepared through an activation treatment of a carbonaceous material. In activation treatment, typically acid or basic groups are created on the carbon surface. Activation treatments can be divided into physical and chemical treatments, and they typically also increase the surface area and porosity of the material. Acidic or basic surface groups can act themselves as active sites (heterogeneous acid/base catalysis) or they can act as anchoring sites if an active metal is deposited on the carbon surface [2].

Activated carbons have been traditionally produced from charcoal. Today, many other raw materials, including bio-based feedstocks such as coconut husk and wood, are applied [3]. In addition to activated carbons and carbon black produced from solid raw materials, carbonaceous nanomaterials such as nanotubes and nanofibers have recently raised attention as

catalytic materials. For these nanomaterials, the typical production method utilizes gaseous or liquid carbon substrates. Of these, chemical vapor deposition (CVD) is the most often applied method, in which gaseous carbon precursors such as methane are used as raw materials [4].

Char is a by-product in many thermochemical conversion processes of biomass, where the main product fractions are liquids or gases typically targeting for applications in transportation fuels or chemicals. Such processes include, e.g., fast pyrolysis, hydrothermal liquefaction, and gasification. There are also thermochemical processes where the solid product char is the main product fraction, including slow pyrolysis, hydrothermal carbonization, and torrefaction [5,6]. The biochars are interesting and sustainable materials for solid carbon catalyst manufacturing, as their carbon content is typically high (~50–95 wt.% for woody biomasses, depending on production temperature) and they can have relatively high surface areas, up to several hundred m<sup>2</sup>/g [7]. However, the biochars typically contain various mineral impurities such as Ca, K, P, Si, Mg, Na, Fe, and Zn, limiting their direct use in activated carbon catalytic applications. These minerals, typically reported as the biochar ash, may also block the pore structure. On the other hand, these minerals can also exhibit some catalytic activity. Therefore raw biochars have been used for catalytic cracking or reforming of hydrocarbon conversion of pyrolytic vapor to hydrocarbons, and for hydrogen production [6]. Acid washing is favored to remove minerals, but it is also desirable to increase the carbon content of biochars by removing hydrogen and oxygen (tar compounds) from the biochar structure. Activation treatments are performed to increase the surface area and porosity and create acidic/basic active sites or anchoring sites for active metal deposition [6]. Activation treatments typically also increase the carbon content. Both physical and chemical activation treatments can be applied for biochars. In physical activation, the char is typically exposed to heat > 700 °C in the presence of steam or CO<sub>2</sub>. In chemical activation, biochars are treated by acids (e.g., H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>) or bases (e.g., KOH, NaOH) before thermal treatment typically performed in the range 400–900 °C [6,8]. In recent years, fast pyrolysis of biomass for the production of fuels and chemicals has attracted the attention of researchers working in academia and industry.

Bio-oil production plants have been commissioned in recent years and new plants are under construction [9]. However, the greatest challenge to the further technological development of a fast pyrolysis process is the quality of bio-oil and its application for production of fuel components and chemicals. Bio-oils obtained from fast pyrolysis have poor stability due to acidity, high content of oxygenated functional groups, and several impurities [9]. Therefore, treatments stabilizing the fast pyrolysis bio-oil are needed to prevent its undesired reactions already before the condensation stage.

In this paper, biochars produced by fast pyrolysis of birch, pine, and willow biomasses are applied for the production of activated carbon catalysts by different activation and purification treatments. The produced catalysts are used to study post-treatment of biomass fast pyrolysis vapors applying analytical pyrolysis to observe the effects of the catalyst on gaseous degradation product composition.

## 2. Materials and Methods

### 2.1. Biochars Production

Biochars from birch, pine, and unbarked willow biomasses were prepared by fast pyrolysis using bench scale bubbling fluidized bed pyrolyser. The pyrolysis temperature was 480 °C and the vapor phase residence time 0.8 s. The particle sizes of the raw materials were 0.5–1 mm and aluminium oxide was used as bed material. A more detailed description of the equipment can be found in Oasmaa et al. 2010 [10].

### 2.2. Activation

The biochars were activated by steam and sulfonation. Steam activation was performed using a 115 L batch retort at 800 °C for 3.5 h. The water flow during the activation was 0.85 mL/min. The formed steam was flushed inside the retort using nitrogen flow at a rate of 2 L/min. Nitrogen was also used during the heating and cooling periods of the activation. Sulfonation procedure is described in [11].

In this procedure, diatsonium salts were used for the activation. The method is safer than more commonly used methods that apply sulfuric acid or oleum for sulfonation. In the Samulski method used here, diatsonium salt is prepared by mixing 460 mg of sulfanile acid ( $C_6H_7NO_3S$ ), 5 mL 1 M hydrochloric acid, 100 mL ice-cold Milli-Q water and 180 g sodium nitrate. This mixture is mixed overnight with the catalyst (750 g) in an ice bath. The final steps in the catalyst preparation are washing and filtration yielding ~ 450 g of catalyst. The detailed method is described by Jaatinen [12]. To remove ash, biochars were acid washed with 1% HCl using 3 h shaking time followed by DI water wash and drying at 105 °C.

### 2.3. Analysis of Biochar and Activated Carbons

The unmodified biochars and activated biochar catalysts were characterized for surface area and porosity (Micromeritics 3Flex, Norcross, GA, USA), elemental and mineral composition, and surface groups. The surface oxygen group characterization for phenolic, lactonic, and carboxylic surface groups was performed by a Boehm titration [13,14]. Briefly, approximately 0.1 g of biocarbon was extracted using 50 mL of 0.01 N  $NaHCO_3$ ,  $Na_2CO_3$  or NaOH. The biochar/catalyst and base mixtures were shaken for 24 h after which 10 mL of each sample was filtered using a syringe and mixed with 20 mL of 0.01 N HCl for the titration. All titrations were performed using 0.01 N  $Na_2CO_3$ . The extractions and the titrations were done in triplicate.  $NaHCO_3$  determines the carboxylic groups,  $Na_2CO_3$  the sum of carboxylic and lactonic groups, and NaOH the sum of carboxylic, lactonic and phenolic groups. Lactonic and phenolic groups were calculated by subtraction, e.g., phenolic groups were determined by subtracting the amount of carboxylic and lactonic groups from the NaOH extraction result. Unmodified biochars were also characterized for their metal composition using ICP-OES and ICP-MS at Eurofins Labtium Oy (Jyväskylä, Finland). The elemental analysis was performed using a Flash 2000 series analyzer (Thermo Scientific, Waltham, MA, USA) and with a Variomax 785-500 analyzer (Elementar, Langensfeld, Germany).

### 2.4. Post-Treatment

Pyrolysis experiments applying biochar catalysts were performed with a Pt-filament pulse pyrolyzer connected to a gas chromatography (GC) with flame ionization (FID) and mass spectrometry detectors (MSD). Pyrolysis was performed at 500 °C for 4 s using a pine biomass load of 0.1 mg. Formed degradation products were led to gas chromatography and mass spectrometry for separation and detection. A more detailed description of the analysis method is described in [15]. The catalyst bed was located in the gas chromatography (GC) inlet liner adjusted to temperature of 250 °C. A thin layer of catalyst, about 2–4 mg (0.15–0.25 cm) was packed in the liner between glass wool. In the reference run, pure glass wool was used. After the GC-FID-MSD analysis, peak areas of lignin and polysaccharide pyrolysis derivatives were integrated from GC-FID data and normalized to the weight of the sample and average of three parallel measurements was calculated. Results are presented as peak areas or peak areas normalized to 100%. Gas compounds ( $CO$  and  $CO_2$ ) and water were calculated using GC-MS data.

### 2.5. Data Analysis

Multivariate data analysis for pyrolysis data (Table A1), using principal component analysis (PCA), was carried out with SIMCA-15 (Umetrics AB, Umeå, Sweden), according to the same procedures that have been reported elsewhere [16]. Two principal components were calculated for the data set. The obtained score plot shows how the biochar and activated carbon catalyst treatments differ from each other and from the thermal pyrolysis (no catalyst).

### 3. Results

#### 3.1. Chemical Characteristic of the Biochars and Activated Carbons

##### 3.1.1. Elemental Composition

The biochars were activated using steam and analyzed for their elemental composition, surface oxygen groups, surface area, and porosity. In addition, the unwashed willow biochar and steam activated willow biochar were chemically activated by sulfonation and analyzed for their physical and chemical characteristics, similarly to the unsulfonated biochars. The elemental results (Table 1) show high carbon contents for the biochars, which increased further due to the high temperature steam activation treatment. All untreated biochars had approximately the same distribution of oxygen, nitrogen, and sulfur. The biggest difference was found with the nitrogen content, which was higher for willow biochar. The willow nitrogen content was also highest among the ACs. The steam activation treatment reduced the amount of oxygen in the carbons, with willow AC retaining the highest amount. The high nitrogen and oxygen contents of the biochars and ACs probably originate from the willow bark, which was not removed prior to the fast pyrolysis. Because of the bark, the willow biochar also had higher ash content compared to the other biochars. Based on the elemental analysis results of nitrogen (N) and oxygen (O), willow was found to be the most promising candidate for the catalytic pyrolysis experiments, and selected for the sulfonation treatment as both N and O have been found to increase the catalytic performance, e.g., through enhanced electron transfer at the carbon surface [17,18]. The sulfonation treatment increased the amount of sulfur (S) slightly, indicating successful addition of sulfur containing surface groups to the willow biochar and AC surface.

**Table 1.** The elemental and ash results of the unwashed biochars and ACs.

Sample	C, wt.%	H, wt.%	N, wt.%	S, wt.%	O, wt.%	Ash, wt.%
Willow biochar	76.2	3.5	0.9	0.019	19.1	7.4
Willow AC	87.4	0.6	0.8	0.06	6.3	8.6
Willow biochar S	72.5	3.3	0.9	0.08	18.7	n.m.
Willow AC S	89.6	0.8	1.0	0.06	6.3	n.m.
Birch biochar	76.7	3.5	0.3	0.016	18.8	2.2
Birch AC	93.7	0.6	0.5	0.02	3.8	3.1
Pine biochar	77.7	3.7	0.1	0.01	18.1	1.5
Pine AC	94.6	0.6	0.4	<0.02	2.7	2.3

AC = Activated carbon, S = sulfonated, n.m. = not measured.

Minerals in biochars were measured before acid washing (Table 2). Unwashed willow biochars contained more alkaline (K) and earth alkaline metals (Ca) and phosphorous (P) than birch and pine due to the unbarked willow used as feedstock (Table 2). Biochars having high contents of K and Ca have been found to promote syngas production in biomass pyrolysis and gasification [19–21], but they also enhance phenolics formation in biomass pyrolysis [21,22]. Interestingly, the content of minerals (K, Ca) and phosphorus in willow biochars resembles biochar from corn stover [23], which has been found to enhance the formation of phenolics and hydrocarbons in bio-oil and the gas compounds H<sub>2</sub>, CO, and CH<sub>4</sub> in microwave pyrolysis of biomass [22]. Heteroatoms such as P, N, and S have been reported to create catalytically beneficial sites on carbon catalyst surfaces. However, this depends on which form these heteroatoms are present in within the catalyst. High oxygen content can also indicate high residual tar content in the pore system [6,24]. Pine biochar contained more iron than the other biochars. Iron-impregnated biochars have been shown to be efficient in the conversion of acetic acid [25].

**Table 2.** Minerals content in unwashed biochars.

	<b>Pine</b>	<b>Birch</b>	<b>Willow</b>
	mg/kg	mg/kg	mg/kg
As	<0.5	<0.5	<0.5
Cd	0.15	0.3	0.83
Co	<0.5	0.69	<0.5
Cr	17	4.6	32
Cu	20	9.7	13
Hg	<0.02	<0.02	<0.02
Mn	390	780	120
Mo	2.3	<0.5	4.2
Ni	11	3.5	20
Pb	3.8	3.9	0.5
Sb	2.5	0.92	<0.5
Tl	2	1.5	<0.5
V	<0.5	<0.5	<0.5
Zn	61	180	320
Ca	3800	5900	10,300
Mg	970	1700	2100
Na	150	97	530
K	3500	5100	17,400
P	530	640	4900
S	130	110	500
Fe	460	160	240
Al	240	74	330
Si	280	100	360
Ti	13	4.7	8.3
Mn	430	840	na
Ba	43	140	14

### 3.1.2. Surface Properties

As surface oxygen groups are important in determining catalytic activity, Boehm titration was conducted for the biochars and ACs. The method can be used to quantify the carboxylic, lactonic, and phenolic surface groups. The results (Table 3) show that the steam activation treatment reduces the amount of acidic surface groups on carbon surfaces and changes the surface group composition. The decrease of total amount of acidic surface groups can be related to the general decrease of oxygen and hydrogen content, which occurs during steam activation treatments. Prior to the steam activation, all biochars had approximately the same functional group composition consisting mostly of phenolic groups. The steam treatment reduced the amount of phenolic groups and increased the amount of carboxylic groups with pine and birch, but not with willow. With willow, the amount of phenolic groups was further enhanced and the carboxylic groups remained at the same level as in the biochar. The amount of lactonic groups was lowered in all prepared activated carbon catalysts.

Sulfonation increased the total acidity of both biochar and AC, and changed the group composition to resemble those of pine and birch after activation, where the carboxylic group is the most dominant.

The surface area results (Table 4) are given for the acid-washed and sulfonated biochars and activated carbons due to difficulties in analyzing the unwashed carbons. The analytic difficulties probably originate from the high ash content of the biochars causing pore clogging.

The surface area and porosities were significantly increased by the steam activation treatment. Comparable results have been reported for different types of biochars activated with steam [26,27]. Sulfonation performed on the willow biochar and willow AC further increased the surface areas of willow BC and AC, as sulfonation was performed in acidic conditions with longer treatment duration than that used in the acid washing. Therefore, sulfonation appeared more effective in opening the biochar pore structure. The biochars were originally mostly mesoporous with small amounts

of macropores. The steam activation increased the micropore volume. Sulfonation increased the meso- and macroscale pore volumes in both BC and AC willow, probably due to enhanced pore opening during the treatment (Table 4 and Figure A1). Previous study has shown that high amount of mesopores in activated carbons exhibit high catalytic activity for the oxygen reduction reactions [26].

**Table 3.** The surface oxygen group results of the biochars and ACs.

Sample	Carboxylic Groups, %	Lactonic Groups, %	Phenolic Groups, %	Total Acidity, mmol/g
Willow biochar AW	16	39	45	1.02
Willow AC AW	15	13	71	0.10
Pine biochar AW	10	35	55	0.58
Pine AC AW	65	10	26	0.13
Birch biochar AW	11	35	54	1.01
Birch AC AW	58	15	27	0.20
Willow biochar S	28	32	41	1.40
Willow AC S	41	24	35	0.34

AW = Acid washed, AC = Activated carbon, S = sulfonated.

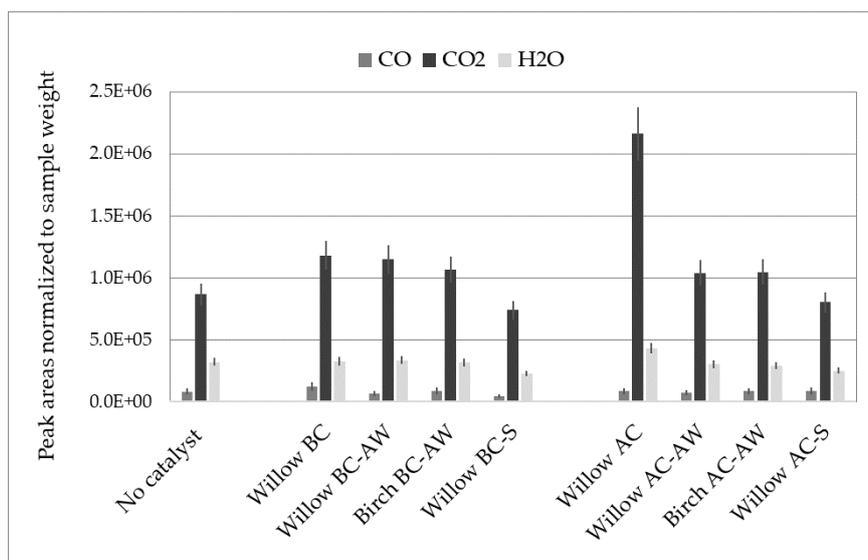
**Table 4.** Surface area and porosity results of the acid-washed and sulfonated biochars and ACs.

Sample	BET Surface Area m <sup>2</sup> /g	Total Pore Volume cm <sup>3</sup> /g	Micropores (<2 nm)	Mesopores (2–50 nm)	Macropores (>50 nm)
Willow biochar AW	5.1	0.004	10%	76%	13%
Willow AC AW	295	0.13	88%	12%	0.5%
Willow biochar S	23	0.033	0%	87%	13%
Willow AC S	382	0.18	64%	34%	2%
Birch biochar AW	24	0.03	0%	96%	4%
Birch AC AW	329	0.13	87%	12%	0.2%
Pine biochar AW	26	0.03	0%	97%	3%
Pine AC AW	340	0.15	84%	16%	0.1%

AW = Acid washed, AC = Activated carbon, S = sulfonated.

### 3.2. Post-Treatment of Pyrolysis Vapors

Post-treatment of pine wood pyrolysis vapors applying analytical pyrolysis was performed with selected biochars and activated carbons as catalyst (Figure 1). In post-treatment, the vapors formed in pyrolysis (500 °C) passed through the catalyst, which was kept at elevated temperature (250 °C) and ended up at GC-FID-MS for analysis. Activity of the biochars and activated carbons was determined based on the vapor composition and the results were compared with the results of thermal pyrolysis (no catalyst), applying analytical pyrolysis with the same set-up. Pine wood pyrolysis vapors including gas compounds (CO and CO<sub>2</sub>), water, and both lignin- and polysaccharide-derived products were analyzed by GC-FID-MS (list of compounds in Table A1). Polysaccharide pyrolysis derivatives were grouped to acids, alcohols, hydroxyacetaldehyde, aldehydes, ketones, lactones, dihydropyranoses, and anhydrosugars, and to lignin pyrolysis derivatives having an oxygen functional group (C=O, OH) in side chain and those having a hydrocarbon side chain. Hydroxyacetaldehyde was monitored separately from the other aldehydes, because it was the major pyrolysis degradation product of pinewood.



**Figure 1.** Gas and water release in thermal pyrolysis and after post-treatment. Compounds determined by GC/MSD. BC = biochar, AW = acid washed, S = sulfonated, AC = activated carbon.

Based on the preliminary test, there were minor changes on vapor formation if the same catalyst was repeatedly used. Therefore, the catalyst was replaced after every run. Results of thermal pyrolysis run and four pine pyrolysis vapors post-treatments using the same original willow AC are presented in Supplementary Material (Figures S1 and S2). It was noticed, in particular, that willow BC, willow, and birch acid-washed BCs and sulfonated willow BC contained organic components that were released in post-treatment together with pyrolysis vapors. Some of the compounds (guaiacol, 4-methylguaiacol, vanillin, homovanillin, 1,5-Anhydro-4-deoxypent-1-en-3-ulose, 1,6-anhydroglucopyranose) were the same as the compounds present in pine wood vapors. Hence, two pyrolysis runs without biomass were performed as a pretreatment for biochars and ACs, to remove the unwanted components before the actual post-treatments. Total ion chromatograms of post-treated pine pyrolysis vapors using pretreated willow BC and willow AC as catalysts are presented in the Supplementary Material (Figures S3 and S4).

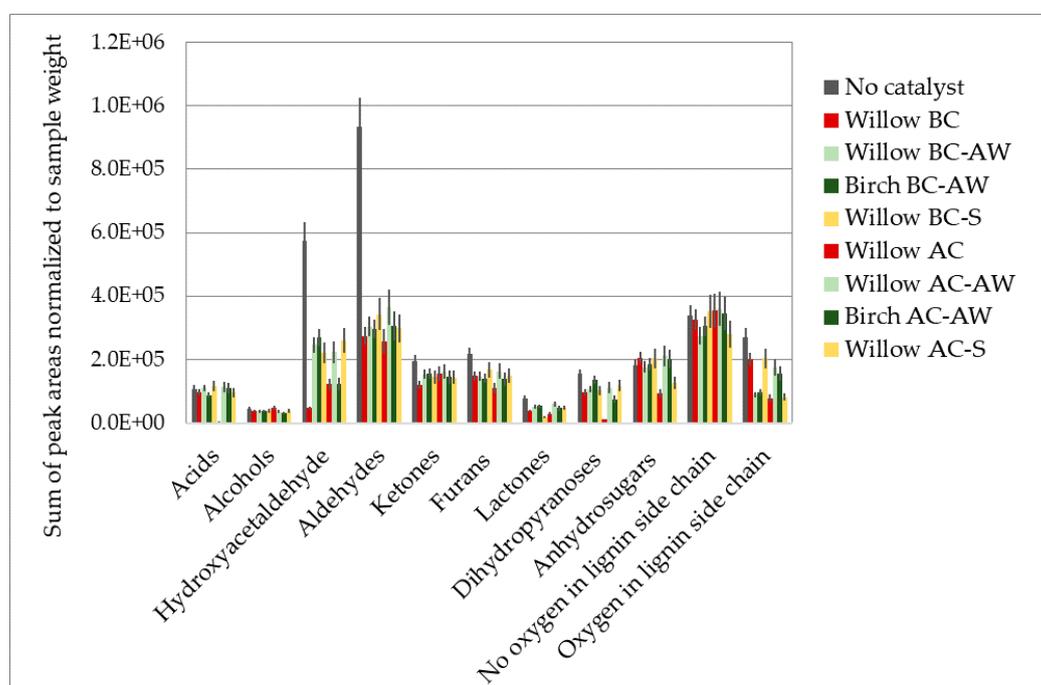
### 3.2.1. Gas and Water

Post-treatment changed the formation of gas and water from pyrolysis vapors compared to thermal pyrolysis (Figure 1). Biochars and activated carbons enhanced CO<sub>2</sub> formation in comparison to the reference, whereas sulfonated BC and AC slightly lowered its yield (Figure 1). The most significant increase in CO<sub>2</sub> yield was obtained with unwashed willow AC, which also had high content of minerals before activation (Table 2). Hence, steam activation increased the catalytic effectiveness of willow BC. The steam activation enhanced the surface area and porosity that together with high mineral contents seem to promote CO<sub>2</sub> formation. Conversely, mineral leaching by acid decreased the CO<sub>2</sub> formation. Formation of water followed the same order as CO<sub>2</sub>, being also highest with unwashed willow AC. A slight increase in CO yield was observed with willow BC, but the other catalysts gave similar result as reference (no catalyst). Biochars having high contents of minerals have shown similar activity as willow BC [22]. Acid washing of BC reduced the CO formation being in accordance with studies found in literature [20]. After the acid washing, wood species (willow, birch) seem to have a minor influence on catalytic activities of biochar and activated carbon.

### 3.2.2. Condensable Gases

All catalytic post treatments changed both lignin and polysaccharide pyrolysis derivatives' composition and yield (Figure 1). Decrease in yields was higher for the polysaccharide pyrolysis derivatives than lignin. Polysaccharide derivatives (hydroxyacetaldehyde, aldehydes, ketones,

furans lactones, dihydropyranses) having a carbonyl group were more altered than those having the acid or hydroxyl group (acids, alcohols, and anhydrosugars), except with willow AC. Aldehydes including hydroxyacetaldehyde were the major compounds formed in pyrolysis of pinewood. Their conversion was significantly high in all catalytic post treatments varying from 60 to 80%. Oxygen was released from the lignin pyrolysis derivatives with carbonyl or alcohol in side chain, decreasing the yields of those products. On the contrary, lignin pyrolysis derivatives with hydrocarbon side chains were less altered in catalytic post treatments. The reduction of carbonyls to corresponding alcohols has been found to be the main reaction in mild catalytic hydrotreatments used for the stabilization of bio-oil [28], but also in electro-catalytic hydrogenation using ruthenium on activated carbon [29]. In our study, new alcohols were not detected, but alcohols present in the vapors were less altered than the aldehydes. Hence, the decrease of carbonyl compounds in vapors was a clear indication of the activity of the catalyst. Adsorption of vapors on biochar and ACs might to a certain extent encounter a decrease in the component yields. Based on the results there was also an increase in the yields of certain compounds inside the compound groups and increased gas formation (Figures 1 and 2 and Table A1). Thus, the overall effect of the adsorption on the results in this study was thought to be minor.

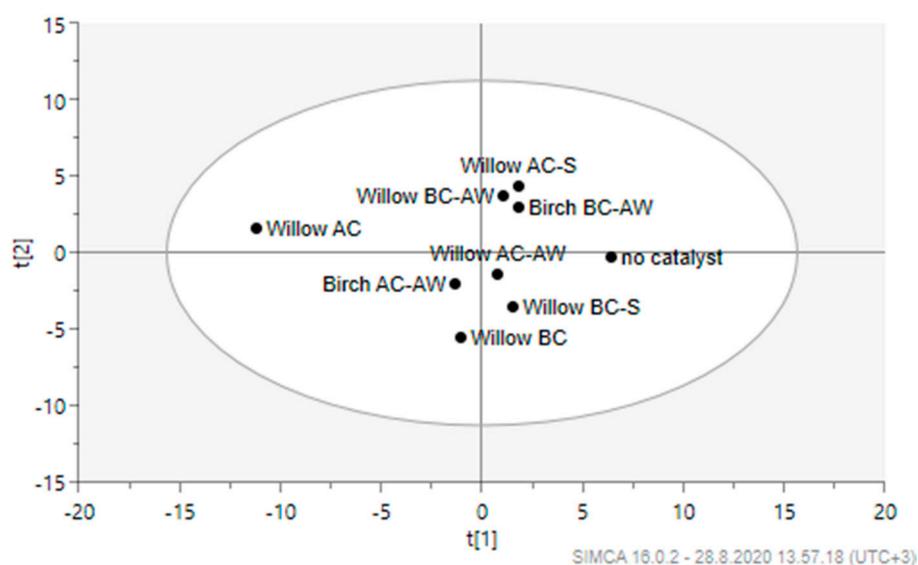


**Figure 2.** Polysaccharide and lignin pyrolysis derivatives from pine wood with and without catalytic post-treatment determined by gas chromatography with flame ionization (GC-FID). BC = biochar, AW = acid washed, S = sulfonated, AC = activated carbon.

AC willow had clearly the highest catalytic activity, and its performance differed from the other biochars and activated carbons. It can be suggested that minerals, together with high surface area and porosity, serve as the active sites for vapor stabilization. AC willow promoted the conversion of acid (97%) and dihydropyranses (93%) almost fully, and 50% of anhydrosugars, simultaneously increasing formation of CO<sub>2</sub> and water (Figure 1). As a minor detail, dianhydrosugars were formed as new compounds when unwashed willow AC was used as catalyst. The result indicated dehydration of anhydrosugars (Table A1). Similar changes in vapor composition were not observed with other biochars and activated carbons. The high formation of CO<sub>2</sub>, observed with unwashed willow AC, is a typical reaction when carbon materials loaded with noble metals have been used as a catalyst [26]. High formation of CO<sub>2</sub> has been found in conversion of pure acetic acid with the biochar catalyst loaded with iron [25]. Decrease of acids in bio-oil also reduces its acidity and thus

prevents repolymerization reactions in storage [30]. The formation of CO<sub>2</sub> may be an indication of oxidation of the carbohydrate components, related to reduction of the lignin-derived compounds via hydrogen migration. Availability of molecular hydrogen was low despite the fact that some hydrogen may have been released in post-treatment reactions. On the other hand, it is possible that some transfer hydrogenation might have taken place through hydrogen migration from polysaccharide-derivatives to lignin derivatives. The residuals of minerals left in the chars and catalysts creating metal active sites might have catalyzed these reactions, especially with unwashed willow AC.

The multivariate analysis using PCA was used to evaluate to what extent the catalyst treatments differed from each other and from the non-catalytic treatment based on the pyrolysis data (Table A1). Two principal components that described the variance of the data were calculated, a score plot (Figure 3). The first principle component described the highest variance (45%) and the second component the second highest variance (24%) of the data.



**Figure 3.** Principal component analysis (PCA) of the pyrolysis data for catalyst and no catalyst treatments (Table A1). The score plot of the two principle components shows how the samples are related to each other. BC = biochar, AW = acid washed, S = sulfonated, AC = activated carbon.

All catalytic post-treatments changed the composition of pine pyrolysis vapors in comparison to the non-catalytic treatment (Figure 3). Unwashed AC willow clearly had the highest impact on vapor composition, as discussed earlier. However, some minor differences in activity were observed among the other biochars and activated carbons. Acid washing changed the activity of willow biochar and activated carbon. After acid washing, activation method (biochar, activated carbon) had a higher influence than feedstock type (willow, birch). Sulfonated biochar showed similar activity to acid-washed activated carbons, whereas sulfonated activated carbon had a similar effect to acid-washed biochar.

#### 4. Conclusions

Biochars obtained from fast pyrolysis of willow, birch, and pine were first activated with steam. The biochars and activated carbons were purified by hydrochloric acid and willow biochar and the steam-activated willow biochar were activated by sulfonation. These materials were tested as catalysts in post-treatment of pinewood pyrolysis vapors, aiming at a more stable product. The steam activation increased the porosity of the all biochars, producing activated carbons with high microporosity. Based on the high oxygen and nitrogen contents, willow was found to be the most promising candidate for the ex situ catalytic pyrolysis experiments, therefore it was selected for the sulfonation treatment, which further increased the number of active acidic sites of the materials. All catalytic post-treatments changed the composition of pine pyrolysis vapors in comparison to the non-catalytic treatment, especially with

unwashed steam-activated biochar willow. The major observation was the decrease of compounds having carbonyl groups, which is advantageous for bio-oil stability. The high mineral content and porosity together served the active sites on steam-activated biochar willow for the high conversion of polysaccharide-derived products into CO<sub>2</sub>. This indicated oxidation of the carbohydrate components, related to reduction of the lignin-derived compounds, enhancing their stability.

**Supplementary Materials:** The following Figures are available online at <http://www.mdpi.com/2311-5629/6/4/0065/s1>; Figure S1: Gas and water release in thermal pyrolysis of pine (pyrolysis\_No catalyst) and in post-treatment of pine pyrolysis vapours using four times the same original willow activated carbon (AC) as catalyst. Compounds analyzed by GC/MSD; Figure S2: Polysaccharide and lignin pyrolysis derivatives released in thermal pyrolysis pine and in post-treatment of pine pyrolysis vapours using four times the same original willow activated carbon (AC) as catalyst. Compounds analyzed by GC-FID; Figure S3: Total ion chromatograms of two pyrolysis runs with willow BC without biomass (a) pretreatment 1 and (b) pretreatment 2 and (c) post-treatment of pine pyrolysis vapors using pretreated willow BC as catalyst; Figure S4: Total ion chromatograms of two pyrolysis runs with willow AC without biomass (a) pretreatment 1 and (b) pretreatment 2 and (c) post-treatment of pine pyrolysis vapors using pre-treated willow AC as catalyst.

**Author Contributions:** Conceptualization, T.T. and J.L.; methodology, T.O.-a., C.L., J.L., and V.S.; writing—original draft preparation, T.O.-a., V.S., J.L.; writing—review and editing, T.T.; funding acquisition, T.T. All authors have read and agreed to the published version of the manuscript.

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

## Appendix A

Supporting information section related to cumulative pore volume and pore size distribution plots obtained using density functional theory (DFT) function.

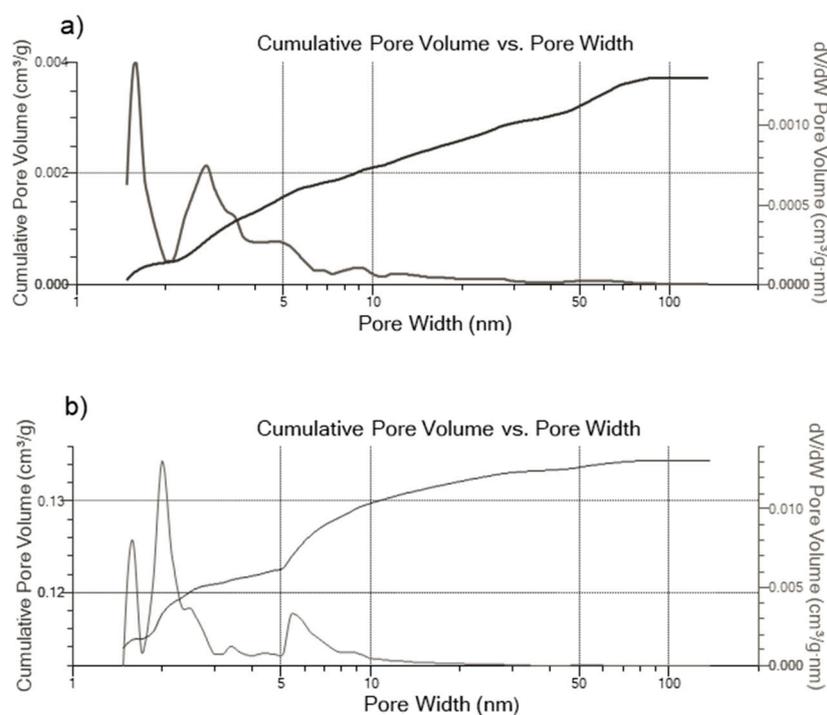
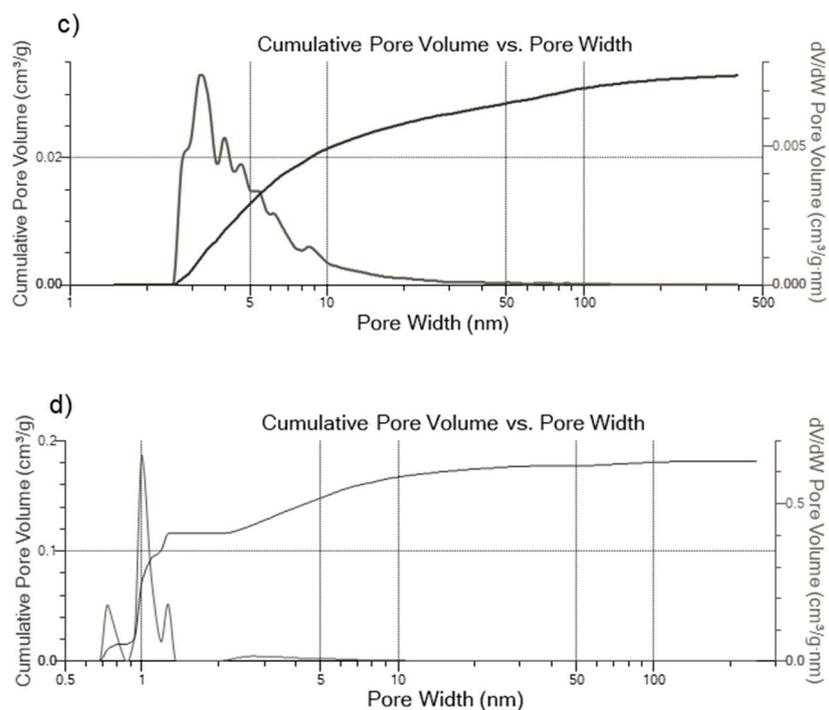


Figure A1. Cont.



**Figure A1.** Cumulative pore volume and pore size distribution plots obtained using DFT function for (a) willow BC acid washed (b) willow AC acid washed (c) willow BC sulfonated (d) willow AC sulfonated.

## Appendix B

Supporting information section related to the compounds detected by GC-MS in post-treatment of pinewood pyrolysis vapors and in reference run (no catalyst).

**Table A1.** Lignin and polysaccharide derivatives (peak areas normalized to 100%) formed in pyrolysis of pinewood.

Compound	Type	No Catalyst	Willow BC	Willow BC-AW	Birch BC-WC	Willow BC-WC	Willow AC	Willow AC-AW	Birch AC-WC	Willow AC-S
Acetic acid	Ac	4.3	6.1	6.5	5.0	6.1	0.3	5.7	6.5	5.9
Methanol	Al	1.8	2.3	2.1	2.1	2.0	3.8	1.8	1.9	2.3
Acetaldehyde	A	1.3	2.1	2.1	1.9	1.8	2.7	1.8	2.0	2.1
2-Propenal	A	1.0	1.2	1.4	1.2	1.4	1.8	1.3	1.3	1.3
Propanal-2-one	A	4.8	7.2	7.2	7.1	7.5	6.6	7.8	7.5	8.0
Hydroxyacetaldehyde	A	22.8	3.0	14.5	15.2	11.6	9.6	11.3	7.3	15.9
3-Hydroxypropanal	A	2.5	3.0	3.2	3.0	3.1	3.9	3.2	3.3	3.1
3-Butenal-2-one	A	2.1	0.7	0.4	0.2	1.2	0.2	1.2	0.6	0.5
Butanedial	A	2.5	3.1	3.6	3.4	3.0	5.2	3.2	3.4	3.2
1-Hydroxy-2-propanone	K	3.7	3.9	4.7	4.6	3.8	8.8	4.3	4.7	4.2
2-Hydroxy-3-methyl-2-cyclopenten-1-one	K	0.6	0.9	0.9	0.8	0.6	1.6	0.6	0.8	0.8
Cyclopentanedione	K	2.0	2.0	2.4	2.7	2.1	1.9	2.4	2.6	2.6
5,6-dihydropyran-2,5-dione	K	1.5	0.8	1.0	0.8	1.0	0.0	0.9	0.5	1.1
Furan	F	0.2	0.4	0.4	0.3	0.5	0.4	0.4	0.4	0.4
2-Furaldehyde	F	1.7	2.8	1.5	1.3	2.5	2.6	2.1	2.3	2.0
2-Furanemethanol	F	0.9	1.1	0.8	0.8	0.5	1.3	0.7	0.7	0.7
5-Methylfurfural	F	0.2	0.9	0.5	0.7	0.9	0.3	0.9	0.8	0.8
5-Hydroxymethyl-2-furaldehyde	F	3.0	0.7	1.2	0.9	1.1	0.9	1.0	0.7	1.1
Furan derivative from cellulose	F	2.6	3.5	4.3	4.0	3.2	3.2	3.1	3.4	4.0
2(5H)-Furanone	L	1.6	1.4	2.0	1.7	0.4	2.1	2.2	2.0	2.0
Unidentified lactone derivative	L	1.5	0.9	1.0	1.3	0.6	0.2	0.8	0.8	0.9
1,5-Anhydro-4-deoxypent-1-en-3-ulose	P	1.8	2.5	2.7	3.0	2.0	0.9	2.2	1.9	3.1
1,4-Dideoxy-D-glycero-hex-1-enopyranos-3-ulose	P	4.4	3.6	3.6	4.7	3.3	0.0	3.4	2.6	4.1
1,5-Anhydroarabinofuranose	As	0.7	1.0	0.9	1.0	0.9	1.1	0.9	0.8	0.6
1,4-Anhydroxylopyranose	As	0.5	0.7	0.5	0.6	0.5	0.7	0.6	0.6	0.4
1,6-Anhydromannopyranose	As	0.5	1.6	0.7	0.6	0.8	0.4	0.8	1.0	0.4
1,6-Anhydroglucopyranose	As	5.0	8.6	7.9	7.5	7.7	4.9	7.8	8.9	5.8
1,6-Anhydroglucofuranose	As	0.5	1.0	0.4	0.8	0.8	0.0	0.7	0.7	0.5
Dianhydrosugars	As	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
Phenol	H	0.1	0.2	0.2	0.2	0.2	0.3	0.2	0.3	0.3
2-Methylphenol	H	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
4-Methylphenol	H	0.2	0.3	0.2	0.2	0.2	0.4	0.3	0.3	0.2
Guaiacol	G	2.6	3.7	3.3	3.3	3.0	5.4	3.0	3.4	3.3
4-Methylguaiacol	G	2.9	4.3	3.9	3.8	3.5	6.5	3.7	4.3	5.0
4-Ethylguaiacol	G	0.4	0.6	0.6	0.5	0.5	0.7	0.5	0.6	0.5
4-Propylguaiacol	G	0.1	0.3	0.2	0.2	0.2	0.3	0.2	0.3	0.2
4-Vinylguaiacol	G	3.1	4.6	2.6	3.0	3.6	5.4	3.5	4.0	2.5
Eugenol	G	0.9	1.4	1.0	1.2	1.2	2.0	1.2	1.4	1.0
cis-Isoeugenol	G	0.4	0.7	0.4	0.5	0.6	0.9	0.6	0.7	0.4
trans-Isoeugenol	G	2.4	4.1	3.3	4.0	4.3	5.6	4.1	4.7	3.2
Guaiacylpropyne	G	0.2	0.3	0.3	0.3	0.9	0.4	0.6	0.7	0.6
Vanillin	G	2.2	2.1	1.7	1.6	2.0	1.4	2.0	1.9	1.6
Acetoguaiacone	G	0.8	1.1	0.7	0.7	0.9	1.1	0.9	0.9	0.7
4-(oxyallyl)guaiacol	G	0.6	0.8	0.3	0.3	1.1	0.4	0.6	0.6	0.5
Homovanillin	G	1.0	1.2	0.8	0.9	1.1	0.6	1.1	1.2	0.7
Guaiacylacetone	G	0.5	0.7	0.3	0.4	0.5	0.7	0.5	0.6	0.4
4-(1-hydroxyprop-2-enyl)guaiacol	G	0.7	0.8	0.3	0.3	1.2	0.5	0.6	0.6	0.5
Dihydroconiferyl alcohol	G	0.9	1.4	0.5	0.6	0.9	1.1	1.0	1.2	0.3
cis-Coniferyl alcohol	G	0.6	0.8	0.2	0.2	0.5	0.1	0.5	0.5	0.0
trans-Coniferyl alcohol	G	1.7	1.8	0.0	0.1	1.1	0.2	0.7	0.9	0.0
Coniferaldehyde	G	1.9	1.7	0.4	0.3	1.3	0.1	1.0	1.0	0.3

Ac = acid, Al = alcohol, A = aldehyde, K = ketone, F = furan, L = lactone, P = dihydropyranose, As = anhydrosugars, H = *p*-hydroxyphenyl, G = guaiacyl, BC = biochar, AW = acid washed, AC = activated carbon, S = sulfonated.

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