

## Article

# Markedly Different Decomposition Temperature and Products of Biomass Pyrolysis at Low Temperature—Differentiation of Acids in Their Effects on Pretreatment †

Peifang Yan, Xiumei Liu, Zhanwei Xu and Zongchao Conrad Zhang \* 

State Key Laboratory of Catalysis, Dalian Key Laboratory of Energy Biotechnology, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China; yanpeifang@dicp.ac.cn (P.Y.); liuxiumei@dicp.ac.cn (X.L.); xuzhanweidicp@dicp.ac.cn (Z.X.)

\* Correspondence: zczhang@yahoo.com

† Dedicated to the 70th anniversary of Dalian Institute of Chemical Physics, CAS.

**Abstract:** Pine as a softwood and poplar as a hardwood pretreated with hydrochloric acid (HCl), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), and hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>) are studied for the pyrolytic properties and products in thermogravimetry (TG) and fixed bed reactor. The pyrolysis performances are pronouncedly distinguished due to the compositional and structural changes induced by the acid pretreatments. Reduction in the mineral content in the biomass feedstocks by pretreatment with the acids results in significant changes in the pyrolytic products. The residual P in the H<sub>3</sub>PO<sub>2</sub>-pretreated biomass apparently catalyzed the biomass deeper dehydration in pyrolysis compared to the other two mineral acids. TG analysis shows a shift of the temperature of maximum mass loss ( $T_{max}$ ) by more than 40 °C to lower temperature in the decomposition of the H<sub>3</sub>PO<sub>2</sub>-pretreated biomass from that of the untreated and the HCl- and H<sub>3</sub>PO<sub>4</sub>-pretreated biomass. Inspired by the striking differences in TG profiles of biomass pretreated by the three acids, thermal pyrolysis of pretreated biomass was carried out in a fixed bed reactor aimed at producing biochemicals at low temperatures (330 °C and 400 °C). The liquid products obtained from the fixed bed reactor show remarkably different major anhydrosugars as a result of pretreatment by the three acids. While phenolics dominate in the collected pyrolysis liquid from untreated biomass samples, biomass pretreated with all three acids results in substantially reduced phenolics in the bio-oils. The reduction in phenolic compounds in the bio-oil may be attributed to the reduction in mineral content in the feedstock. Consequently, the yields of anhydrosugars, mainly levoglucosan (LG) and levoglucosenone (LGO) are increased. LG yields of 20.9–28.5% from the cellulose content are obtained from HCl- and H<sub>3</sub>PO<sub>4</sub>-pretreated pine/poplar, with very low LGO yield (less than 1.7%). However, H<sub>3</sub>PO<sub>2</sub>-pretreated biomass is selective to produce LGO, especially at 330 °C. LGO yields of 7.4% and 6.7% are obtained from H<sub>3</sub>PO<sub>2</sub>-pretreated pine and poplar, respectively.

**Keywords:** lignocellulosic biomass; acids pretreatment; hypophosphorous acid; thermal degradation; fixed bed pyrolysis; levoglucosenone; levoglucosan



**Citation:** Yan, P.; Liu, X.; Xu, Z.; Zhang, Z.C. Markedly Different Decomposition Temperature and Products of Biomass Pyrolysis at Low Temperature—Differentiation of Acids in Their Effects on Pretreatment †. *Sustain. Chem.* **2021**, *2*, 8–23. <https://doi.org/10.3390/suschem2010002>

Received: 5 November 2020

Accepted: 4 January 2021

Published: 12 January 2021

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



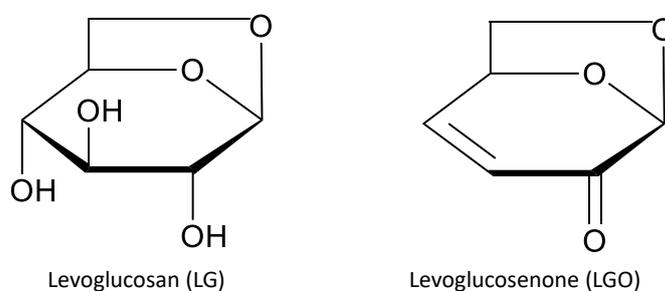
**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Due to greenhouse gas-related environmental concerns linked to fossil resources, the abundant renewable biomass has been regarded as a promising alternative for the production of sustainable biofuels and high value-added chemicals [1–3]. Pyrolysis is a thermochemical conversion process to produce bio-oils by cleavage of the lignocellulosic organic matter in an inert atmosphere. The rapid development of pyrolysis technology in recent years has made it one of the most energy efficient technologies in biomass utilization [4–7]. Among pyrolysis products, pyrolysis oil, also known as bio-oil, contains various valuable chemicals such as acids, aldehydes, ketones, furans, phenols, and anhydrosugars. However, typical pyrolysis oil of raw biomass contains a complex mix of hundreds of

organic compounds, and it is also very difficult to recover specific valuable chemicals owing to their low contents. One of the strategies for increasing pyrolysis product quality and value is to produce specific types of products with narrow distribution by developing biomass pretreatment technology [8].

Anhydrosugars are valuable chemicals that can be made from pyrolysis of biomass-derived polysaccharides [9]. Among anhydrosugars, particular interest has been placed on obtaining levoglucosan (LG) and levoglucosenone (LGO) from thermal degradation of cellulose component of biomass. LG and LGO (Figure 1) are optically active compounds suited for the synthesis of biologically active products, and accordingly, are promising monomers for the chemical and pharmaceutical industry [10,11]. However, thermal pyrolysis of untreated lignocellulose biomass typically produces phenolic-rich complex mixture of pyrolysis oil. A high level of inorganic minerals present in most biomass feedstocks has been reported to catalyze fragmentation reactions that dramatically lower the yield of simple sugars like LG [12]. In addition, some soluble inorganic species may be retained in the produced bio-oil, and may negatively impact the physical properties and the storage stability of the bio-oil [13].



**Figure 1.** The chemical structures of levoglucosan and levoglucosenone.

Biomass pretreatment is one of the key steps to improve biomass structural and compositional properties for pyrolysis process. Commonly used techniques include acid treatment [13–16], alkali treatment [14,17], steam explosion [18], hot-water extraction [19,20], etc. Acid pretreatment as a chemical method is effective in removing minerals from lignocellulosic biomass and can significantly increase the bio-oil yield in thermal pyrolysis [17,21,22]. Previous studies also demonstrated that the removal or passivation of minerals in biomass by mineral acid is an effective method for improving the yields for anhydrosugars from the pyrolysis of biomass [21,23]. Hence, biomass pretreatment with dilute acidic chemicals have been considered an advantageous approach to improve the bio-oil quality.

In this work, we systematically studied the effect of hydrochloric acid (HCl), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>) in biomass pretreatment on the biomass composition, the thermal decomposition profile, and the pyrolysis oil composition and quality. Pine as a softwood and poplar as a hardwood are studied as representative forest biomass feedstocks. Although two typical mineral acids HCl and H<sub>3</sub>PO<sub>4</sub> have been used for biomass pretreatment [24,25], there is no report on the effect of H<sub>3</sub>PO<sub>2</sub> pretreatment on biomass pyrolysis. H<sub>3</sub>PO<sub>2</sub> is a phosphorus oxyacid; its formula is generally expressed as H<sub>3</sub>PO<sub>2</sub>. A more intuitive presentation of H<sub>3</sub>PO<sub>2</sub> is HOP(O)H<sub>2</sub> to highlight its monoprotic and P-H bond characters. In addition to its acid functionality, the two P-H bonds in H<sub>3</sub>PO<sub>2</sub> are reactive to organic groups such as aldehyde [26]. Therefore, the dual acid and reactive P-H functions of H<sub>3</sub>PO<sub>2</sub> may effectively modify the physicochemical properties of biomass and hence may offer unique pyrolysis product compositions.

Because TG analysis offers the unique advantages of rapid assessment and precise determination of the decomposition temperature profile, it has been used as one of the most important techniques in investigating thermal behavior of biomass during combustion, gasification, and pyrolysis processes [27,28]. However, limited by a small amount of sample mass, TG experiment is not suited to collect the solid, liquid, and gaseous products for unambiguously determining the mass balance. Therefore, a fixed or fluidized bed reactor

can complement the study in order to obtain detailed information on product composition, distribution, and properties.

In this study, three acids (HCl, H<sub>3</sub>PO<sub>4</sub>, and H<sub>3</sub>PO<sub>2</sub>) are used in the acid pretreatment of pine and poplar. The pyrolysis characteristics of the pretreated biomass are then investigated in detail using TG-DTG and a fixed bed reactor. The objective of this work is to study the effect of different acid pretreatments on the structure and composition of softwood and hardwood biomass and on their corresponding thermal decomposition profiles and pyrolysis oil compositions.

## 2. Experimental

### 2.1. Materials

Two biomass species were chosen to represent two types of forestry feedstocks: pine for softwood and poplar for hardwood. The pine and poplar were obtained from China National Pulp and Paper Research Institute. The samples were ground using a mill (SM200 Rostfrei, Retsch, Frankfurt, Germany) to pass through a 40 mesh (~1 mm) screen. The moisture contents of pine and poplar were 8.7 wt % and 7.4 wt %, respectively, in reference to the oven-dry material. A 50 wt % H<sub>3</sub>PO<sub>2</sub> solution in water and the other reagents and solvents were obtained from commercial suppliers and were used without further purification.

### 2.2. Biomass Composition Analysis

The compositions of biomass before and after acid pretreatment were analyzed via a two-step acid hydrolysis according to the National Renewable Energy Laboratory (NREL) protocol [29]. Each sample was treated with 72% (*w/w*) sulfuric acid in a water bath at 30 °C for 1 h. Upon completion of the 60-min hydrolysis, the 72% sulfuric acid was diluted to 4% by adding deionized water. The sample tube was then placed in the autoclave for hydrolysis at 121 °C for 1 h. The hydrolysis solution was filtered and analyzed for sugar content. The hydrolysis products, glucose and xylose, were quantified by HPLC equipped with a refractive index detector (Agilent 1260 series, Anaheim, CA, USA) and an HPX-87H column (300 × 7.8 mm, Bio-Rad, Hercules, CA, USA). The HPLC running temperature was 65 °C, and a 5 mM sulfuric acid solution was used as the mobile phase at a flow rate of 0.6 mL/min. The injection volume was 25 µL with a run time of 60 min. According to the method of “Determination of Structural Carbohydrates and Lignin in Biomass” from the National Renewable Energy Laboratory (NREL) [29], the concentration of the polymeric sugars from the concentration of the corresponding monomeric sugars was calculated, using an anhydro correction of 0.88 (or 132/150; the molecular weight of xylose is 150, the dehydrated xylose has a molecular weight of 132) for C-5 sugars (xylose and arabinose) and a correction of 0.90 (or 162/180; the molecular weight of glucose is 180) for C-6 sugars (glucose, galactose, and mannose).

### 2.3. Biomass Acid Pretreatment

A 3 g (dry basis) portion of biomass was treated with acid (typical dosage is 5 mmol acid/g biomass) in 30 mL solvent (contain 28 mL 1, 4-dioxane and 2 mL water) in a 100 mL flask at 80 °C for 5 h. We have also evaluated different acid concentrations in the range of 3.3–10 mmol acid/g biomass. The results were not affected by the acid concentration in this range. In order to compare the pretreatment differences of these three acids, 5 mmol acid/g biomass was used as the pretreatment acid concentration. The content in the flask was hot filtered after pretreatment. The solid part was washed with water until the solution turned neutral. The biomass with and without acids pretreatment was dried according to the National Renewable Energy Laboratory (NREL) protocol [29]. All the biomass samples were dried at 105 °C for 24 h to a constant weight. We also determined that there was no loss of water in TG up to 200 °C.

The pretreated biomass composition was calculated as follows:

$$\text{Cellulose (wt \%)} = \left( \frac{m_{Cp}}{m_O} \right) \times 100$$

$$\text{Hemicellulose (wt \%)} = \left( \frac{m_{Hp}}{m_O} \right) \times 100$$

$$\text{Lignin (wt \%)} = \left( \frac{m_{Lp}}{m_O} \right) \times 100,$$

where  $m_P$  and  $m_O$  are recovered mass (g) of the acid-pretreated biomass and the mass (g) of raw biomass, respectively.  $m_{Cp}$ ,  $m_{Hp}$ , and  $m_{Lp}$  are the mass (g) of cellulose, hemicellulose, and lignin in the pretreated biomass, respectively.

#### 2.4. Characterization Methods

**X-ray fluorescence (XRF) method:** The mineral compositions of the samples were determined using a PANalytical AxiosmAX X-ray fluorescence spectrometer with a 4 KW water-cooled X-ray tube with Rh anode, 75  $\mu\text{m}$  Be window, and 60 KV maximum acceleration voltage. The recorded spectra were evaluated with the precalibrated/standardless software Super Q (PANalytical, delivered with the XRF instrument) for analysis of approximately 70 elements from F to U.

**CHNS analysis:** Ultimate analysis of the biomass (CHNS) was performed using an elemental analyzer (Vario EL cube, Elementar, Hesse, Germany). The oxygen content was calculated by the difference method.

**The morphology of biomass and biochar:** The biomass and biochar samples were exposed in a helium ion microscope (HIM (Orion Nano Fab, Carl Zeiss, Jena, Germany) to a 25 keV focused helium ion beam at a working distance of 8–10 mm. Helium pressure was maintained at  $2 \times 10^{-6}$  Torr during the exposure and a 10  $\mu\text{m}$  beam-limiting aperture was selected. A beam current of 1.66–2.19 pA was used.

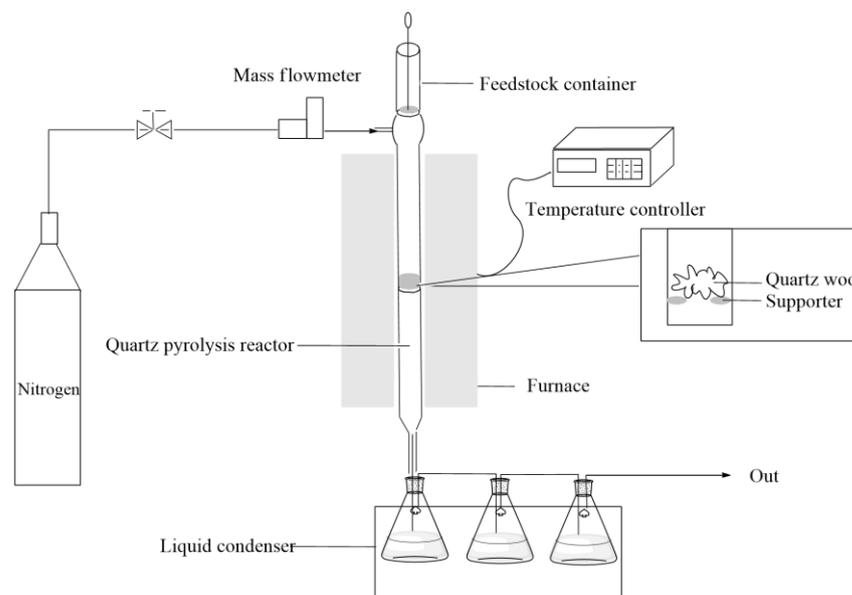
#### 2.5. Pyrolysis

##### 2.5.1. Thermogravimetric Analysis (TGA)

Thermogravimetric profiles were obtained on a thermal analyzer (STA 449 F3, NET-ZSC, Germany). The untreated biomass and acid-pretreated biomass samples were heated from room temperature to 800  $^{\circ}\text{C}$  at a rate of 10  $^{\circ}\text{C}/\text{min}$  under  $\text{N}_2$  at a flow rate of 20 mL/min. Prior to the measurement, the samples were extensively dried for 24 h in an oven at 105  $^{\circ}\text{C}$  to eliminate water.

##### 2.5.2. Pyrolysis in Fixed Bed Reactor

Rapid pyrolysis experiments of untreated and acid-pretreated biomass samples were performed using a fixed bed pyrolysis reactor, as shown in Figure 2. The pyrolysis assembly consists of the following components: a nitrogen cylinder, a mass flowmeter, a thermocouple, a feedstock container, a quartz reactor, an electric furnace, a temperature controller, and a three-flask condenser unit. High-purity nitrogen was used as carrier gas with a flow rate of 200 mL/min. When the temperature of the tubular quartz pyrolysis reactor steadily reached 400  $^{\circ}\text{C}$  or 330  $^{\circ}\text{C}$ , a biomass sample was directly drop-fed into the reactor from the feedstock container. The feedstock container has a specially designed seal from the reactor, preventing the pyrolysis gas stream from leaking through the container. The quartz tube has a diameter of 2 cm and a length of 60 cm. One gram of sample was used for each experiment and the pyrolysis time was controlled for 15 min at the set pyrolysis temperature. The volatile pyrolysis matter in the product stream passed through the condensers where the condensed liquid was collected. The solid residue (biochar) was removed from the reactor and weighted. The yields of biochar and liquid products were obtained by weighing while that of noncondensable gas was calculated by difference.



**Figure 2.** Schematic of fixed bed pyrolysis unit.

The liquid product was analyzed with a gas chromatography–mass spectrometry instrument (GC-MS, Agilent, 7890B-5975C, Palo Alto, Santa Clara, CA, USA) equipped with a capillary column, HP-5MS (length 30 m, i.d. 0.25 mm, and film thickness 0.25  $\mu\text{m}$ , Düren, Germany). The temperatures of the injection port and ion source were held at 280 and 250  $^{\circ}\text{C}$ , respectively. The GC oven temperature was initially held at 50  $^{\circ}\text{C}$  for 3 min, ramped up to 280  $^{\circ}\text{C}$  at a rate of 10  $^{\circ}\text{C}/\text{min}$ , and maintained at 280  $^{\circ}\text{C}$  for 2 min. The ion chromatographic peaks were identified according to NIST MS library 2.0 and the peak areas of identified products from different pyrolysis conditions were recorded. The LG and LGO yields in the liquid products were quantitatively determined using external calibration by GC. The yields of LG and LGO are calculated based on the masses of cellulose fractions in the biomass feedstocks on dry basis. The GC instrument (Agilent, 7890A, Santa Clara, CA, USA) was equipped with a capillary column, DB-1 (length 60 m, i.d. 0.32 mm, and film thickness 0.50  $\mu\text{m}$ ). Nitrogen was used as carrier gas. The injector temperature and detector (FID) temperature were 280 and 300  $^{\circ}\text{C}$ , respectively. The oven program was the same with the GC-MS.

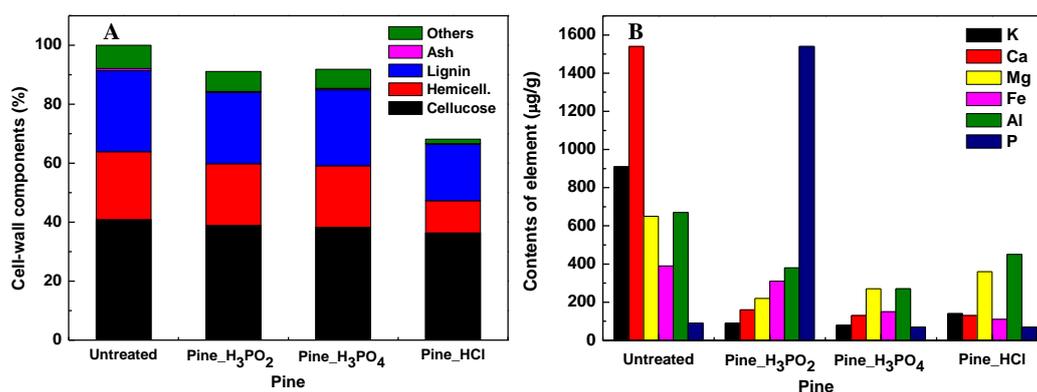
### 2.6. Experiment Repeatability

All experiments were replicated three times, and the averaged analytical data were used. The relative error was generally less than 5%.

## 3. Results and Discussion

### 3.1. Compositional and Morphology Changes of the Biomass Resulting from the Acid Pretreatments

The compositions of pine and poplar from proximate and ultimate analyses before and after acid pretreatments are given in Table S1 (see Supplementary File). After pretreatment with the three acids, changes in composition and ash content for pine and poplar are similar. For clarity of data presentation and discussion, we only display the results on pine in Figure 3A to illustrate the effect of acid pretreatments. Similar changes due to acid pretreatment on poplar are shown in Figure S1.

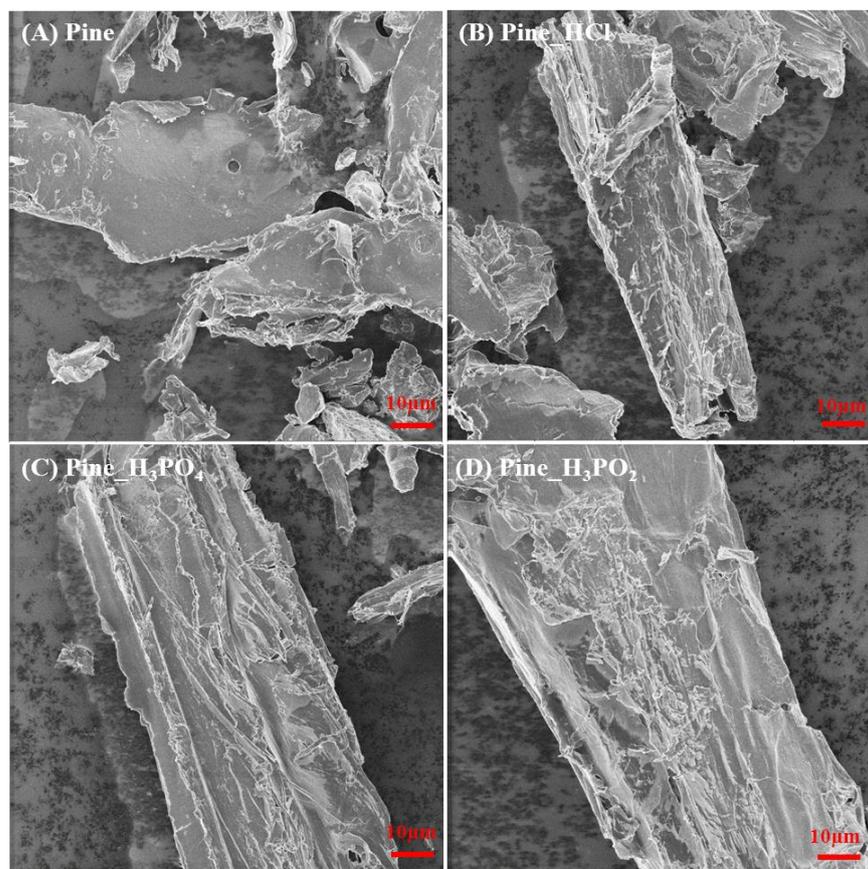


**Figure 3.** (A) Cell wall compositions of untreated and acid-pretreated pine, corrected for the measured solid recovery rate and (B) mineral species and contents of untreated and acid-pretreated pine.

For untreated pine (Figure 3), the major plant cell wall components are 40.9% cellulose, 23.0% hemicellulose, 27.5% lignin, and 0.7% ashes. Solid recovery refers to the mass in weight percentage recovered after each pretreatment of the untreated biomass (dry weight). After HCl pretreatment of pine, the solid recovery was about 68% (Figure 3A). Most of hemicellulose (52.6%) and some lignin (30.0%) were removed. The removal of portions of biomass constituents, mostly hemicellulose and lignin, led to an increase in the cellulose content in the HCl-pretreated biomass. In comparison, the solid recoveries after H<sub>3</sub>PO<sub>4</sub> or H<sub>3</sub>PO<sub>2</sub> pretreatment of both pine and poplar were much higher (>90%). The relative mass of the three major cell wall components, cellulose, hemicellulose, and lignin, and the C/H/N/S contents for the H<sub>3</sub>PO<sub>4</sub>- and H<sub>3</sub>PO<sub>2</sub>-pretreated biomass did not show substantial change compared to the untreated biomass.

Biomass typically contains mineral elements, such as K, Ca, Na, Mg, etc. The mineral species are known to affect the yield and composition of pyrolysis oils by catalytically altering the biomass pyrolytic decomposition pathways [8]. Significant impact of mineral species on the characteristics of pyrolysis products has been reported in thermal decomposition of biomass [12,30,31]. These minerals, particularly K, Na, Ca, Mg, and Cl elements, are known to catalyze the secondary reactions of the primary pyrolysis products, with increased biochar, syngas, and water yields by suppressing the bio-oil yield. The ash content and mineral species of pine before and after the acid pretreatment are presented in Table S1 and Figure 3B. After HCl, H<sub>3</sub>PO<sub>4</sub>, and H<sub>3</sub>PO<sub>2</sub> pretreatments, the ash content of the samples was markedly decreased. The levels of K and Ca elements, as two most prominent mineral species, were significantly reduced in all acid-pretreated biomass samples. The levels of Mg, Al, and Fe elements were also reduced in all acid-pretreated biomass samples, but the removal efficiency of these elements was lower than that of K and Ca. Among the three acids, the H<sub>3</sub>PO<sub>2</sub>-pretreated biomass showed the most prominent residual P element content, indicative of a strong interaction between H<sub>3</sub>PO<sub>2</sub> and biomass.

The morphology changes of the biomass samples were investigated by helium ion microscope (HIM). The HIM micrographs of untreated pine and acids-pretreated pine are shown in Figure 4. The results show that the untreated pine has a highly fibrillar and intact morphology. The cell wall structure was disrupted in the samples from the pretreatment of acids. It was found that holes and loose structure appeared on the surface of the acids-pretreated pine, although there are no discernable differences in the pretreated samples by the three acids (Figure 4B–D). The observation phenomenon implies that the connection between the three major components of biomass is disrupted during the acid pretreatment.

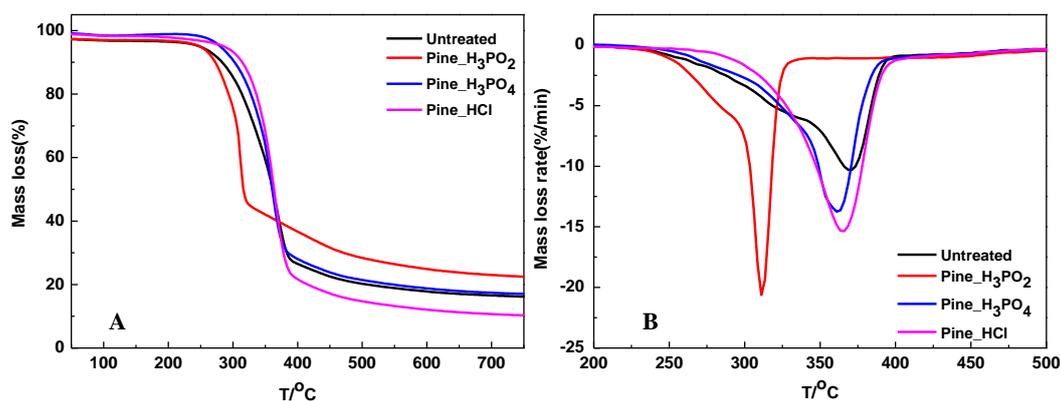


**Figure 4.** Helium ion microscope (HIM) images of pine with or without acid pretreatment. (A) Virgin pine sample and (B–D) pine pretreated with HCl (aqueous),  $\text{H}_3\text{PO}_4$ , and  $\text{H}_3\text{PO}_2$ , respectively.

### 3.2. TG-DTG Decomposition Profiles of Untreated and Acid-Pretreated Biomass

Thermogravimetry (TG) and differential thermogravimetry (DTG) studies provide thermal decomposition profiles of the biomass components. The TG and DTG profiles have been used to understand the changes in biomass from biomass pretreatment [27].

The thermal decomposition profiles for untreated and acid-pretreated pine are shown in Figure 5A (TG results) and Figure 5B (DTG results). Compared to untreated pine, the main decomposition temperature of HCl- and  $\text{H}_3\text{PO}_4$ -pretreated pine did not significantly change. However, the decomposition peaks shifted to substantially lower temperatures for the  $\text{H}_3\text{PO}_2$ -pretreated pine. A shoulder peak corresponds to the decomposition of hemicelluloses, and the main peak has been assigned to the decomposition of cellulose and lignin [32]. For the biomass pretreated with HCl, the shoulder peak disappeared due to loss of bulk hemicellulose, in agreement with the compositional change for pine in Figure 3A and Table S1. Although some lignin was also removed through the HCl pretreatment, the temperature at which maximum mass loss did not substantially change. The TG and DTG profiles of untreated and acids-pretreated poplar (Figure S2) again show similar changes as with the pine samples.



**Figure 5.** (A) Thermogravimetry (TG) profiles and (B) differential thermogravimetry (DTG) profiles of untreated and acid-pretreated pine.

For the convenience of comparison on quantitative basis, the DTG characteristic parameters for the pine sample derived from Figure 5 are listed in Table 1 (pine) and that for the poplar samples derived from Figure S2 are listed in Table S2. The parameters are defined as follows: the initial decomposition temperature  $T_i$ , the final decomposition temperature  $T_f$ , which is the termination temperature beyond the maximum weight loss peak, and the maximum mass loss rate  $(dW/dt)_{max}$  corresponding to temperatures  $T_{max}$ . The results in Table 1 indicate that decomposition of untreated biomass occurred across a wide range between  $T_i$  (~200 °C) and  $T_f$  (400 °C, Table 1, entry 1). Although HCl pretreatment of pine resulted in substantial loss of both hemicellulose and lignin (Figure 3A) compared to  $H_3PO_4$  pretreatment, the DTG characteristic parameters of HCl- and  $H_3PO_4$ -pretreated pine (Table 1), also for identically pretreated poplar (Table S2), did not appreciably differ from that of untreated biomass. However, for the  $H_3PO_2$ -pretreated pine and poplar, the range of  $T_i$  and  $T_f$  was significantly shifted to lower values, e.g., to the range of 200–335 °C for the  $H_3PO_2$ -pretreated pine (Table 1, entry 2), which was a decrease in 71 °C in the decomposition temperature range as a result of  $H_3PO_2$  pretreatment of the pine. The changes in  $T_{max}$  followed the decomposition temperature range (Table 1). For example, the  $T_{max}$  (310 °C) of  $H_3PO_2$ -pretreated pine shifted by 60 °C to lower temperature compared to the  $T_{max}$  of the untreated pine. The maximum mass loss rate, i.e., the  $(dW/dt)_{max}$  value, of pine is 10.3%/min. The  $(dW/dt)_{max}$  value of  $H_3PO_2$ -pretreated pine is about two times that of untreated pine (Table 1, entry 1 and 2). The  $H_3PO_2$  pretreatment on the poplar caused a similar effect. It should be noted that the rate  $(dW/dt)_{max}$  and  $T_{max}$  are indicative of the reactivity of the sample during pyrolytic degradation; a higher  $(dW/dt)_{max}$  value reflects rapid decomposition, and a lower  $T_{max}$  reflects higher reactivity of the sample. Therefore, compared to HCl- and  $H_3PO_4$ -pretreated samples, the  $H_3PO_2$ -pretreated biomass exhibited a lower  $T_{max}$  and higher  $(dW/dt)_{max}$ , indicating high degradation reactivity of the  $H_3PO_2$ -pretreated sample during the temperature programmed decomposition process [33]. In view of the P content, 1540 ppm for pine and 650 ppm for poplar, from the  $H_3PO_2$ -pretreated biomass, the distinctively lowered  $T_{max}$  values (Figures 5A and S2) compared with untreated biomass could be ascribed to catalytic effect of residual acidic phosphorous species on the decomposition of a specific component of the sample during pyrolysis, while the residual phosphorous content may also be responsible for the increased char yields as phosphorus compounds are well-known flame-retardants resulting in increased char yield [26].

**Table 1.** Characteristic parameters derived from thermogravimetric profiles.

Entry	Samples	$T_i$	$T_f$	$T_{max}$	$(dW/dt)_{max}$
			°C		%/min
1	Pine	198	404	370	10.3
2	Pine_H <sub>3</sub> PO <sub>2</sub>	200	335	310	20.4
3	Pine_H <sub>3</sub> PO <sub>4</sub>	198	402	363	13.7
4	Pine_HCl	210	405	366	15.4

$T_i$ : initial decomposition temperature;  $T_f$ : final decomposition temperature (in this study, it is the termination temperature of maximum weight loss peak);  $T_{max}$ : the temperature of maximum mass loss;  $(dW/dt)_{max}$ : the maximum mass loss rate.

### 3.3. Pyrolysis Product Selectivity of Untreated and Acid-Pretreated Biomass

The results for pine in Figure 3B, and that for poplar in Figure S1B, showed that the HCl, H<sub>3</sub>PO<sub>4</sub>, and H<sub>3</sub>PO<sub>2</sub> acid pretreatment removed most of the mineral ions. While the solid recoveries (>90%) and the recovered biomass compositions from H<sub>3</sub>PO<sub>4</sub> and H<sub>3</sub>PO<sub>2</sub> pretreatments are similar (Figure 3A), the recovered biomass sample pretreated by H<sub>3</sub>PO<sub>2</sub> showed dramatically enhanced thermal decomposition reactivity compared to that pretreated by H<sub>3</sub>PO<sub>4</sub>, as evidenced by the TG profiles and DTG parameters (Figure 5 and Table 1). The dramatically reduced decomposition temperature by H<sub>3</sub>PO<sub>2</sub> pretreatment inspired us to investigate whether it could be advantageous to produce anhydrosugars at a low temperature. We then investigated the production of anhydrosugars by conducting pyrolysis in a fixed bed reactor at low pyrolysis temperatures (330 and 400 °C), which may be beneficial to achieve high anhydrosugar selectivity. We carried out pyrolysis experiments in the fixed bed pyrolysis reactor (Figure 2) systematically for pine samples pretreated by the three mineral acids, followed by detailed characterization of the pyrolysis products.

The results on product distributions are shown in Table 2. At 400 °C, pretreatment with HCl enhanced bio-oil yield over the untreated pine (Table 2, entry 4). The bio-oil yield was 55.7%, an increase by 4.1% over that of the untreated pine (51.6%). In addition, HCl pretreatments also reduced the biochar yield from 23.6% to 21.6%. First, removal of the minerals through acid pretreatment is expected to reduce the amount of biochar during pyrolysis reaction. In addition, another important reason is the removal of a substantial portion of biomass constituents (68 wt % solid recovery), especially hemicellulose and lignin, with little loss of cellulose, resulting in increased cellulose content in the HCl-pretreated biomass (Figure 3A and Table S1). It has been reported that a higher cellulose content is responsible to obtain higher liquid product yield, while high hemicellulose favors the production of higher gaseous products and higher lignin content results in more solid residues [8]. Therefore, the reduced biogas yield for HCl-pretreated pine may be ascribed to the largely reduced hemicellulose content. Although the liquid yield was increased and the biochar yield was decreased for the HCl-pretreated pine and poplar, the poor solid recovery due to the loss of 32% biomass makes the HCl pretreatment unattractive in terms of economics as the overall liquid yield is much less based on the untreated feedstock. In contrast, the high solid recovery (92%) by H<sub>3</sub>PO<sub>4</sub> pretreatment makes it particularly interesting to compare the pyrolysis product yields with the untreated biomass. As shown in Table 2, the biochar yield also decreased after H<sub>3</sub>PO<sub>4</sub> pretreatment of pine. The bio-oil yield of H<sub>3</sub>PO<sub>4</sub>-pretreated pine (entry 2, Table 2) showed insignificant difference compare with that of the untreated pine. Interestingly, results in Table 2 reveal that the product distribution of H<sub>3</sub>PO<sub>2</sub>-pretreated biomass is largely different from that pretreated with HCl and H<sub>3</sub>PO<sub>4</sub>, although the solid recovery and the composition of the H<sub>3</sub>PO<sub>2</sub>-pretreated pine are similar to that of H<sub>3</sub>PO<sub>4</sub>-pretreated pine. The higher P content in the H<sub>3</sub>PO<sub>2</sub>-pretreated pine (Figure 3B) is likely responsible for the increased biochar formation by catalyzing condensation reactions and for the reduced bio-oil yield (Table 2). It is well known that phosphorus compounds are flame-retardants and promote char yield [26]. The high char yield is also consistent with the TG results (Figure 5A). It has been reported that pyrolysis

of cellulose at low temperatures results in the main products being carbon dioxide, carbon monoxide, water, and char [34]. The higher phosphorus content from  $\text{H}_3\text{PO}_2$ -pretreated pine, unlike the  $\text{H}_3\text{PO}_4$ -pretreated pine, reduced the temperature of pyrolysis (Figure 5) by favoring a dehydration pathway.

**Table 2.** Yields of the products obtained from pyrolysis of untreated and acids pretreated pine in the fixed bed reactor.

Entry	Samples	Solid Recovery/wt %	T <sup>a</sup> /°C	Liquid/wt %	Biochar/wt %	Syngas/wt %
1	Pine	100	400	51.6	23.6	24.8
			330	35.0	31.9	33.0
2	Pine_ $\text{H}_3\text{PO}_2$	91	400	44.9	30.4	24.6
			330	33.0	38.6	24.1
3	Pine_ $\text{H}_3\text{PO}_4$	92	400	51.9	19.9	24.9
			330	48.5	31.9	17.3
4	Pine_HCl	68	400	55.7	21.6	19.9
			330	52.5	29.6	17.8

<sup>a</sup>: pyrolysis temperature.

Pyrolysis at 330 °C produced more char and less bio-oil than at 400 °C (Table 2). This is expected as char is the dominant product of pyrolysis at such a low temperature [15]. The higher P content in the  $\text{H}_3\text{PO}_2$ -pretreated pine again promoted higher biochar formation at this temperature compared with untreated and HCl- and  $\text{H}_3\text{PO}_4$ -pretreated pine. A difference on the reaction conditions in biomass pyrolysis between TG analysis and the fixed bed reactor should be noted: TG analysis shows the transient evolution of gaseous products in biomass decomposition in response to rapid temperature ramping, while the pyrolysis of biomass in a fixed bed reactor reflects the effect of longer residence time at a specified temperature during the decomposition of biomass. Therefore, although the TG results in Figure 5B indicate less decomposition of the untreated and HCl- and  $\text{H}_3\text{PO}_4$ -pretreated pine compared with  $\text{H}_3\text{PO}_2$ -pretreated pine at 330 °C, long residence time at 330 °C in the fixed bed reactor helped to obtain high conversions of untreated and all acid-pretreated biomass. The higher P content in the  $\text{H}_3\text{PO}_2$ -pretreated pine also appeared to suppress the decomposition of the lignin component in the biomass.

After HCl and  $\text{H}_3\text{PO}_4$  pretreatment, the pyrolysis product yields of poplar showed the similar trend of changes as with the pine samples (Table S3). While the liquid product yield of  $\text{H}_3\text{PO}_2$ -pretreated poplar was not noticeably changed from that of untreated poplar, a small increase in biochar yield may be ascribed to the presence of P content in  $\text{H}_3\text{PO}_2$ -pretreated poplar.

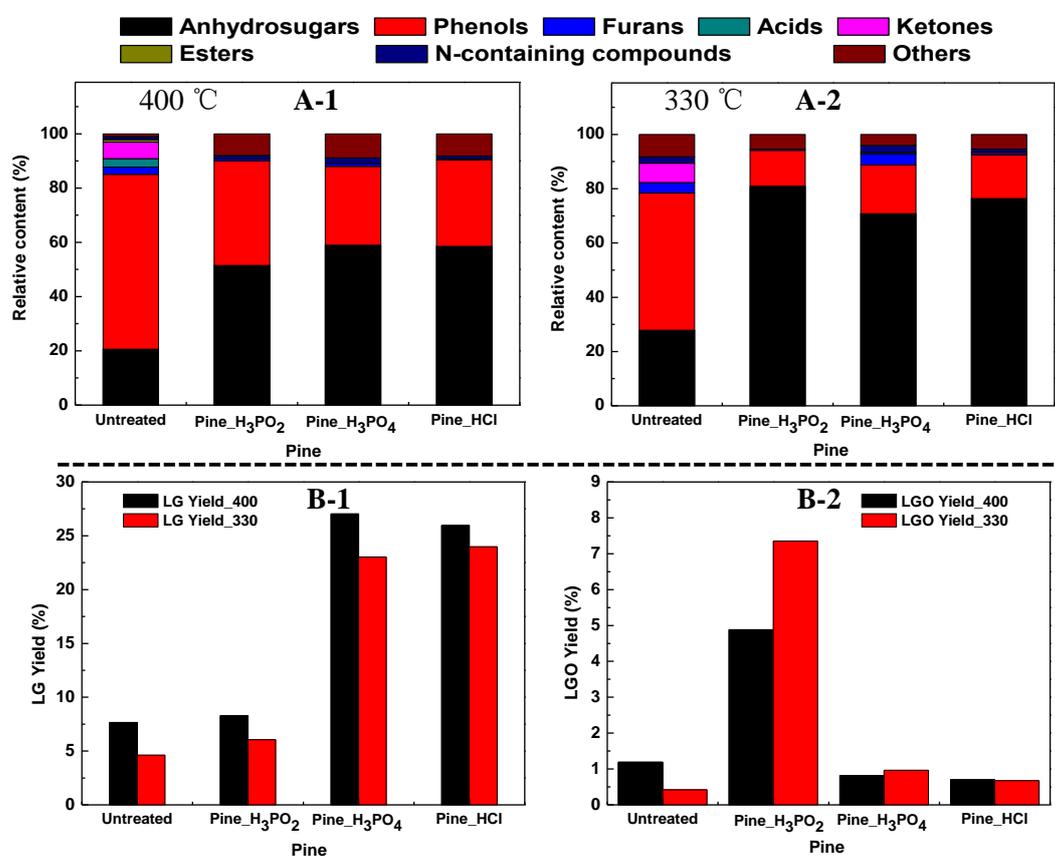
### 3.4. Analysis of Bio-Oils from Untreated and Acid-Pretreated Biomass

It has been well established that the biomass types and pyrolysis conditions affect the composition of biomass pyrolysis products. Cellulose is a macromolecule composed of semicrystalline arrays of  $\beta$ -1,4 glucan chains associated with one another through extensive hydrogen bonding. Depolymerization of cellulose leads to the formation of a high proportion of anhydro-oligosaccharides and anhydro-saccharides [35], as well as a small portion of glucose-derived compounds such as furans, furfural, and furfuryl alcohol. Hemicelluloses are complex polysaccharides in the cell wall, consisting of branched structures that vary with biomass types. Acids, ketones, and furans are the main types of compounds in bio-oils from hemicellulose pyrolysis [36]. Lignin are polymers of highly branched, substituted, monoaromatics in the cell walls of most biomass. Lignin tends to produce chars in high yield and its depolymerization leads to various phenolics [37].

The possible differences in the chemical compositions of the bio-oils from HCl-,  $\text{H}_3\text{PO}_4$ -, and  $\text{H}_3\text{PO}_2$ -pretreated pine and poplar were investigated by detailed characterization of the oils using GC/MS. Figure S3 shows the identified products from fixed-bed pyrolysis of untreated and acid-pretreated biomass at 400 and 330 °C. For untreated biomass, the composition of the pyrolysis oil is a characteristic mixture of many compounds (Figure S3, black lines). The most striking observation revealed by the GC-MS results in Figure S3 is

the distinctively different anhydrosugar, dominantly levoglucosenone (LGO), produced from the  $H_3PO_2$ -pretreated pine and poplar, compared with dominantly levoglucosan (LG) from the HCl- and  $H_3PO_4$ -pretreated pine and poplar.

Figure 6A shows the relative contents of different groups of bio-oils. The identified compounds are divided into seven groups according to their functional groups, anhydrosugars, phenols, furans, acids, ketones, esters, and N-containing compounds (Figure 6A, Tables S4–S7). The detailed components of the bio-oils are listed in Tables S4–S7. As shown in Figure 6(A-1),(A-2), phenolics anhydrosugars are the dominant products of pyrolysis at 400 and 330 °C for untreated pine. The main products of pyrolysis at 400 °C are 64.4% phenolic compounds and 20.6% anhydrosugars. The phenolic compounds include 2-methoxyphenol, creosol, 4-ethyl-2-methoxyphenol, 2-methoxy-4-vinylphenol, 2,6-dimethoxyphenol, 1,2,4-trimethoxybenzene, 2-methoxy-4-(1-propenyl)-(Z)phenol, etc. The anhydrosugars include the following main compounds, levoglucosan (LG), levoglucosenone (LGO), 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose, and D-(+)-melezitose.

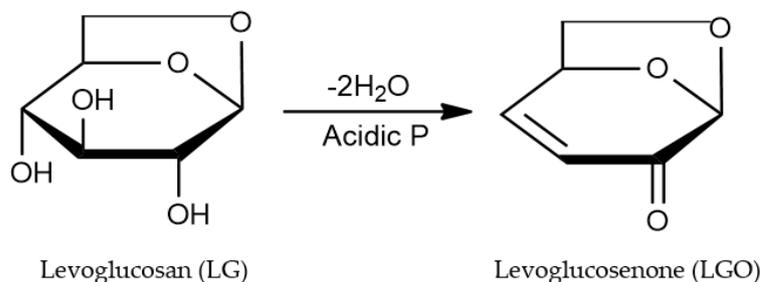


**Figure 6.** (A) Relative content of major groups of compounds in bio-oils from pyrolysis of untreated and acid-pretreated pine. (The data are also given in Tables S4 and S6) (B) Levoglucosan (LG) and levoglucosenone (LGO) yields of liquid products from pyrolysis of untreated and acid-pretreated pine. The yields of LG and LGO are calculated mass ratio of the products to the masses of corresponding cellulose fractions in the biomass feedstocks on dry basis.

Despite of the small amounts of K, Ca, Mg, and Fe (Figures 3B and S1B), these minerals have a significant effect on the fast pyrolysis oil composition. Removal of the minerals by pretreatments with all these acids was found to enhance the yield of anhydrosugars relative to the untreated pine by reducing phenolic products (Figure 6(A-1),(A-2)). After HCl,  $H_3PO_4$ , and  $H_3PO_2$  pretreatment, the anhydrosugars content range was increased to between 51.5% and 59.0% (Figure 6(A-1), 400 °C) and phenolic content in the bio-oil was much decreased. Patwardhan et al. reported that the added minerals (K and Na), even at a very low mineral/biomass ratio, significantly inhibited the formation of levoglucosan during the pyrolysis of cellulose [8].

With an objective to produce anhydrosugars, lowering the pyrolysis temperature to 330 °C is found to favor the formation of anhydrosugars products (Figure 6(A-1),(A-2)). The relative content to anhydrosugars of 70.8% at 400 °C was increased to 80.9% at 330 °C, with a decrease in the relative content of phenolic compounds to a minimum of 13.2%.

The anhydrosugars in the products are mainly composed of LG and LGO. LG is of potential interest for the production of pharmaceuticals, surfactant, and biodegradable polymers [10]. LGO has been regarded as a promising building block with high versatility in modern organic synthesis, for the preparation of various bioactive compounds, disaccharides, chiral inductors, and so on [11]. Figure 6(B-1),(B-2) show the intriguing LG and LGO yield as results of the acid pretreatments of the pine. For the HCl- and H<sub>3</sub>PO<sub>4</sub>-pretreated pine, pyrolysis at 400 and 330 °C produced LG yields in 23.0% and 27.0% based on the cellulose content, respectively, while the LGO yield is considerably low (<0.9%). However, for the H<sub>3</sub>PO<sub>2</sub>-pretreated pine, although the LG yield is slightly higher than that for untreated pine, it is substantially lower than that of HCl- and H<sub>3</sub>PO<sub>4</sub>-pretreated pine. Most strikingly, the LGO yield was most pronounced for the H<sub>3</sub>PO<sub>2</sub>-pretreated pine, especially at the low pyrolysis temperature of 330 °C, reaching the LGO yield of 7.4% based on cellulose content (Figure 6(B-2)). The H<sub>3</sub>PO<sub>2</sub>-pretreated biomass showed more P residual, which resulted in the LGO as the main dehydrated sugar products. As LGO is the product of LG dehydration by losing two molecules of water (Figure 7), the residual P in the H<sub>3</sub>PO<sub>2</sub>-pretreated biomass apparently catalyzed the deeper dehydration of biomass. It has been reported that the acidic phosphorus is effective in catalyzing the dehydration process and in lowering pyrolysis temperature [26,38]. Although H<sub>3</sub>PO<sub>4</sub> and H<sub>3</sub>PO<sub>2</sub> are both P-containing inorganic acid, their different interaction with the biomass is attributed to the difference in thermal decomposition characteristics of cellulosic biomass and in the degree of dehydration.



**Figure 7.** Acidic phosphorus in H<sub>3</sub>PO<sub>2</sub>-pretreated biomass catalyzed the LG to LGO.

Compared with untreated poplar, the acid-pretreated poplar also greatly promoted the generation of anhydrosugars with reduced phenolics. The results are shown in Figure S4. The HCl- and H<sub>3</sub>PO<sub>4</sub>-pretreated poplar produced LG with the yield of 27.8% (HCl, 400 °C) and 28.5% (H<sub>3</sub>PO<sub>4</sub>, 400 °C). Similar to pretreated pine, the H<sub>3</sub>PO<sub>2</sub>-pretreated poplar produced the LGO with the yield of 6.7% from pyrolysis at 330 °C.

The observed effect of acid pretreatment as reported in this work is reproducibly acid specific, irrespective of biomass feedstock materials. The most pronounced differences of the acid-pretreated samples in TG and in pyrolysis products are shown to be associated with the nature of the acids, although different feedstocks were used. Some biomass pretreatments with water and acids have been reported to remove the ashes [21–23]. However, these pretreatment methods showed that the temperature of cellulose pyrolysis shifts to high temperature because of the removal of ashes by dilute acids or hot water [23]. In addition, the reported pyrolysis experiments were typically run at high temperatures in the range of 450–650 °C with the objective of producing pyrolysis oils. Although the ash removal increased the relative content of anhydrosugars in bio-oil, LG is the main anhydrosugar product, and there is almost no or very little LGO in the bio-oils [21,23,25].

### 3.5. Analysis of Biochars from Untreated and Acid-Pretreated Biomass

Biochar is a solid product obtained from the pyrolysis of biomass samples, which has gained attention because of its potential economic value [39]. Helium ion microscope (HIM) images of biochar from untreated and acid-pretreated pine samples are shown in Figure S5. The images revealed that the surfaces of biochars from acid-pretreated pine samples appear more destructed and have the large pore structure compared with biochar from untreated pine. Especially,  $\text{H}_3\text{PO}_2$ -pretreated pine shows large pores and rough surfaces in the structure, which may be related to the rapid catalyzed pyrolysis of biomass components at low temperature by residual P.

Table 3 shows the results of ultimate analysis and the mineral species of biochars obtained from the pyrolysis of untreated and acid-pretreated pine samples. For the untreated pine (Table 3), the C content in the biochar was higher when the pyrolysis temperature was high (data of 400 °C compare with that of 330 °C), while the considerable decreases in mass percent of H and O may be ascribed to increased dehydration at a higher temperature. Table 3 also shows that the ash content in the biochar decreased due to the acids pretreatment of pine samples, which was also reflected by the results of the ultimate analysis (Table S1 and Figure 3). Furthermore, the high P content in the biochar obtained from the  $\text{H}_3\text{PO}_2$ -pretreated pine is also consistent with the results of the ultimate analysis (Table S1 and Figure 3). The increased P content after pyrolysis at higher temperature is related to the higher conversion of the carbohydrate components.

**Table 3.** Ultimate analysis and mineral species of biochars obtained from the pyrolysis of untreated and acid-pretreated pine.

Samples	T <sup>a</sup> °C	Ultimate Analysis/wt %					Mineral Species and Contents/ppm					
		N	C	H	S	O	K	Ca	Mg	Al	Fe	P
Pine _biochar	330	–	64.8	4.9	0.13	30.1	730	1110	740	680	140	60
	400	–	73.7	3.5	0.02	22.8	310	170	260	990	140	50
Pine_ $\text{H}_3\text{PO}_2$ _biochar	330	–	67.8	4.2	–	28	100	200	210	360	240	2810
	400	–	73.3	3.4	–	23.3	120	240	200	570	140	3920
Pine_ $\text{H}_3\text{PO}_4$ _biochar	330	0.01	65	4.9	–	30.1	120	120	210	460	90	50
	400	0.02	72.9	3.6	–	23.5	150	240	270	650	150	80
Pine_HCl _biochar	330	–	62	4.9	0.06	33	150	60	190	540	50	40
	400	–	71.5	3.3	–	25.2	310	170	260	990	140	50

<sup>a</sup>: pyrolysis temperature.

## 4. Conclusions

We report the dramatic differences in the pyrolysis products and biomass decomposition temperature by pretreatments with the three mineral acids. The effect of  $\text{H}_3\text{PO}_2$  is most striking and is reported in this work for the first time. The  $\text{H}_3\text{PO}_2$  pretreatment not only induced a considerably lowered pyrolysis temperature (by 40 °C), but also catalyzed the formation of LGO as a distinctively different product from LG which dominates in products from HCl,  $\text{H}_3\text{PO}_4$  pretreatments. Removal of minerals (especially K and Ca) by the acid pretreatment strongly enhanced the formation of anhydrosugars and inhibited the formation of phenolics in pyrolysis at low temperatures. In TG-DTG characterization, the thermal decomposition profiles of the HCl- and  $\text{H}_3\text{PO}_4$ -pretreated pine and poplar showed little difference from that of unpretreated samples. In contrast,  $\text{H}_3\text{PO}_2$ -pretreated pine and poplar exhibited a distinctively lowered  $T_{\text{max}}$  values. Pyrolysis results in a fixed bed reactor showed that HCl and  $\text{H}_3\text{PO}_4$  pretreatment led to a high yield (27.0% for pine, 28.5% for poplar) of LG in pyrolysis at 400 °C. However, HCl pretreatment is disadvantageous due to significant degradative loss of the biomass during demineralization. A higher P content in the  $\text{H}_3\text{PO}_2$ -pretreated biomass, as compared to the  $\text{H}_3\text{PO}_4$  pretreatment, indicates a stronger interaction of  $\text{H}_3\text{PO}_2$  with the biomass than  $\text{H}_3\text{PO}_4$ . The residual P species following the  $\text{H}_3\text{PO}_2$  pretreatment is proposed to have a catalytic effect on the decomposition

of cellulose at low temperature and on the formation of LGO. The low phenolic products yield from the pyrolysis of the  $\text{H}_3\text{PO}_2$ -pretreated biomass is consistent with the low level of lignin decomposition, which accounts for the high biochar. For the purpose of selectively producing anhydrosugars from cellulose component, the production of reduced phenolics is beneficial. Therefore, to obtain LG as the main anhydrosugar product, biomass pretreatment with  $\text{H}_3\text{PO}_4$  is preferred. The biomass pretreatment with  $\text{H}_3\text{PO}_2$  is identified to be unique for the selective production of LGO at low pyrolysis temperature, as demonstrated at 330 °C.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/2673-4079/2/1/2/s1>, Table S1: Characterization of raw and acids-pretreated biomass. Table S2: Characteristic parameters from thermogravimetric analysis. Table S3: Yields of the products obtained from pyrolysis of untreated and acids-pretreated poplar. Table S4 to Table S7: GC/MS analysis of bio-oil obtained from the fixed-bed pyrolysis of untreated and acids-pretreated pine/poplar samples. Figure S1: (A) Cell-wall compositions of untreated and acids-pretreated poplar, corrected for the measured solid recovery rate and (B) mineral species and contents of untreated and acids-pretreated poplar. Figure S2: (A) TG profiles and (B) DTG profiles of untreated and acids-pretreated poplar. Figure S3: GC–MS chromatograms of liquid products from untreated and acid-pretreated biomass pyrolysis: (A) pine, (B) poplar. Figure S4: (A) Relative content of main groups of bio-oil from pyrolysis of untreated and acids-pretreated poplar and (B) levoglucosan (LG) and levoglucosone (LGO) yields of liquid products from pyrolysis of untreated and acids-pretreated poplar. Figure S5: Helium ion microscope (HIM) images of biochar from untreated and acids-pretreated pine: (1)–(4): pyrolysis at 330 °C and (5)–(8): pyrolysis at 400 °C.

**Author Contributions:** P.Y. performed all experiments, analyzed the results, wrote the original draft of the manuscript and improved its final version. X.L. and Z.X. helped guide the analysis and critically revised the manuscript. Z.C.Z. was responsible for the conception of the studies, guided the analysis, and carried out major revisions of the manuscript. He is the corresponding author. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported by the National Natural Science Foundation of China (21932005, 21721004 and 21690084) and by DICP I201936.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

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

## References

1. Li, C.-Z.; Zhao, X.-C.; Wang, A.-Q.; Huber, G.-W.; Zhang, T. Catalytic transformation of lignin for the production of chemicals and fuels. *Chem. Rev.* **2015**, *115*, 11559–11624. [PubMed]
2. Mao, L.-Y.; Li, Y.-X.; Zhang, Z. Conrad. Upgrading of derived pyrolysis vapors for the production of biofuels from corncobs. *Front. Chem. Sci. Eng.* **2018**, *12*, 50–58. [CrossRef]
3. Lynd, L.R.; Liang, X.-Y.; Bidy, M.J.; Allee, A.; Cai, H.; Foust, T.; Himmel, M.E.; Laser, M.S.; Wang, M.; Wyman, C.E. Cellulosic ethanol: Status and innovation. *Curr. Opin. Biotechnol.* **2017**, *45*, 202–211. [CrossRef] [PubMed]
4. Zhang, C.; Zhang, Z. Conrad. Essential quality attributes of tangible bio-oils from catalytic pyrolysis of lignocellulosic biomass. *Chem. Rec.* **2019**, *19*, 1–15. [CrossRef] [PubMed]
5. Bridgwater, A. Renewable fuels and chemicals by thermal processing of biomass. *Chem. Eng. J.* **2003**, *91*, 87–102. [CrossRef]
6. Ranzi, E.; Cuoci, A.; Faravelli, T.; Frassoldati, A.; Migliavacca, G.; Pierucci, S.; Sommariva, S. Chemical kinetics of biomass pyrolysis. *Energy Fuel* **2008**, *22*, 4292–4300. [CrossRef]
7. Meier, D.; van de Beld, B.; Bridgwater, A.V.; Elliott, D.C.; Oasmaa, A.; Preto, F. State-of-the-art of fast pyrolysis in IEA bioenergy member countries. *Renew. Sustain. Energy Rev.* **2013**, *20*, 619–641.
8. Kumar, R.; Strezov, V.; Weldekidan, H.; He, J.; Singh, S.; Kan, T.; Dastjerdi, B. Lignocellulose biomass pyrolysis for bio-oil production: A review of biomass pre-treatment methods for production of drop-in fuels. *Renew. Sustain. Energy Rev.* **2020**, *123*, 109763. [CrossRef]
9. Cao, F.-Z.; Xia, S.-P.; Yang, X.-W.; Wang, C.-Y.; Wang, Q.; Cui, C.-X.; Zheng, A.-Q. Lowering the pyrolysis temperature of lignocellulosic biomass by  $\text{H}_2\text{SO}_4$  loading for enhancing the production of platform chemicals. *Chem. Eng. J.* **2020**, *385*, 123809.
10. Longley, C.J.; Fung, D.P.C. Potential applications and markets for biomass-derived levoglucosan. *Adv. Thermochem. Biomass Convers.* **1993**, *2*, 1484–1494.

11. Sarotti, A.M.; Zanardi, M.M.; Spanevello, R.A.; Suarez, A.G. Recent applications of levoglucosenone as chiral synthon. *Curr. Org. Synth.* **2012**, *9*, 439–459. [[CrossRef](#)]
12. Patwardhan, P.R.; Satrio, J.A.; Brown, R.C.; Shanks, B.H. Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresour. Technol.* **2010**, *101*, 4646–4655. [[CrossRef](#)] [[PubMed](#)]
13. Oudenhoven, S.R.G.; Westerhof, R.J.M.; Aldenkamp, N.; Brilman, D.W.F.; Kersten, S.R.A. Demineralization of wood using wood-derived acid: Towards a selective pyrolysis process for fuel and chemicals production. *J. Anal. Appl. Pyrolysis* **2013**, *103*, 112–118. [[CrossRef](#)]
14. Wang, X.-D.; Leng, S.; Bai, J.-Q.; Zhou, H.; Zhong, X.; Zhuang, G.-L.; Wang, J.-G. Role of pretreatment with acid and base on the distribution of the products obtained via lignocellulosic biomass pyrolysis. *RSC Adv.* **2015**, *5*, 24984–24989.
15. Messina, L.I.G.; Bonelli, P.R.; Cukierman, A.L. Effect of acid pretreatment and process temperature on characteristics and yields of pyrolysis products of peanut shells. *Renew. Energy* **2017**, *114*, 697–707. [[CrossRef](#)]
16. Xue, Y.; Bai, X.L. Synergistic enhancement of product quality through fast co-pyrolysis of acid pretreated biomass and waste plastic. *Energy Conv. Manag.* **2018**, *164*, 629–638. [[CrossRef](#)]
17. Wang, H.; Srinivasan, R.; Yu, F.; Steele, P.; Li, Q.; Mitchell, B. Effect of acid, alkali, and steam explosion pretreatments on characteristics of bio-oil produced from pinewood. *Energy Fuel* **2011**, *25*, 3758–3764. [[CrossRef](#)]
18. Biswas, A.K.; Umeki, K.; Yang, W.-H.; Blasiak, W. Change of pyrolysis characteristics and structure of woody biomass due to steam explosion pretreatment. *Fuel Process. Technol.* **2011**, *92*, 1849–1854. [[CrossRef](#)]
19. Tarves, P.C.; Serapiglia, M.J.; Mullen, C.A.; Boateng, A.A.; Volk, T.A. Effects of hot water extraction pretreatment on pyrolysis of shrub willow. *Biomass Bioenergy* **2017**, *107*, 299–304. [[CrossRef](#)]
20. Roux, É.L.; Diouf, P.N.; Stevanovic, T. Analytical pyrolysis of hot water pretreated forest biomass. *J. Anal. Appl. Pyrolysis* **2015**, *111*, 121–131. [[CrossRef](#)]
21. Wang, H.; Srinivasan, R.; Yu, F.; Steele, P.; Li, Q.; Mitchell, B.; Samala, A. Effect of acid, steam explosion, and size reduction pretreatments on bio-oil production from sweetgum, switchgrass, and corn stover. *Appl. Biochem. Biotechnol.* **2012**, *167*, 285–297. [[CrossRef](#)] [[PubMed](#)]
22. Mohammed, I.Y.; Abakr, Y.A.; Kazi, F.K.; Yusuf, S. Effects of pretreatments of Napier Grass with deionized water, sulfuric acid and sodium hydroxide on pyrolysis oil characteristics. *Waste Biomass Valor.* **2017**, *8*, 755–773. [[CrossRef](#)]
23. Chen, D.-Y.; Wang, Y.; Liu, Y.-X.; Cen, K.-H.; Cao, X.-B.; Ma, Z.-Q.; Li, Y.-J. Comparative study on the pyrolysis behaviors of rice straw under different washing pretreatments of water, acid solution, and aqueous phase bio-oil by using TG-FTIR and Py-GC/MS. *Fuel* **2019**, *252*, 1–9. [[CrossRef](#)]
24. Das, P.; Ganesha, A.; Wangikar, P. Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products. *Biomass Bioenergy* **2004**, *27*, 445–457. [[CrossRef](#)]
25. Hassan, E.M.; Steele, P.H.; Ingram, L. Characterization of fast pyrolysis bio-oils produced from pretreated pine wood. *Appl. Biochem. Biotechnol.* **2009**, *154*, 182–192. [[CrossRef](#)]
26. Liu, L.-X.; Pan, Y.; Wang, Z.; Hou, Y.-B.; Gui, Z.; Hu, Y. Layer-by-layer assembly of hypophosphorous acid-modified chitosan based coating for flame-retardant polyester–cotton blends. *Ind. Eng. Chem. Res.* **2017**, *56*, 9429–9436.
27. Chen, W.-H.; Peng, J.-H.; Bi, X.T.T. A state-of-the-art review of biomass torrefaction, densification and applications. *Renew. Sustain. Energ. Rev.* **2015**, *44*, 847–866. [[CrossRef](#)]
28. Chen, Q.; Yang, R.-M.; Zhao, B.; Li, Y.; Wang, S.-J.; Wu, H.-W.; Zhuo, Y.-Q.; Chen, C.-H. Investigation of heat of biomass pyrolysis and secondary reactions by simultaneous thermogravimetry and differential scanning calorimetry. *Fuel* **2014**, *134*, 467–476. [[CrossRef](#)]
29. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass*; NREL Laboratory: Golden, CO, USA, 2008; LAP, NREL/TP-510-42618.
30. Nan, H.-Y.; Zhao, L.; Yang, F.; Liu, Y.; Xiao, Z.-Y.; Cao, X.-D.; Qiu, H. Different alkaline minerals interacted with biomass carbon during pyrolysis: Which one improved biochar carbon sequestration. *J. Clean. Prod.* **2020**, *255*, 120162. [[CrossRef](#)]
31. Lin, Y.; Munroe, P.; Joseph, S.; Henderson, R.; Ziolkowski, A. Water extractable organic carbon in untreated and chemical treated biochars. *Chemosphere* **2012**, *87*, 151–157. [[CrossRef](#)]
32. Stefanidis, S.D.; Kalogiannis, K.G.; Iliopoulou, E.F.; Michailof, C.M.; Pilavachi, P.A.; Lappas, A.A. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 143–150. [[CrossRef](#)]
33. Gil, M.V.; Casal, D.; Pevida, C.; Pis, J.J.; Rubiera, F. Thermal behaviour and kinetics of coal/biomass blends during co-combustion. *Bioresour. Technol.* **2010**, *101*, 5601–5608. [[CrossRef](#)] [[PubMed](#)]
34. Granzow, A. Flame retardation by phosphorus compounds. *Acc. Chem. Res.* **1978**, *11*, 177–183. [[CrossRef](#)]
35. Zhang, H.-J.; Meng, X.; Liu, C.; Wang, Y.; Xiao, R. Selective low-temperature pyrolysis of microcrystalline cellulose to produce levoglucosan and levoglucosenone in a fixed bed reactor. *Fuel Process. Technol.* **2017**, *167*, 484–490. [[CrossRef](#)]
36. Yang, H.-P.; Li, S.-J.; Liu, B.; Chen, Y.-Q.; Xiao, J.-J.; Dong, Z.-G.; Gong, M.; Chen, H.-P. Hemicellulose pyrolysis mechanism based on functional group evolutions by two-dimensional perturbation correlation infrared spectroscopy. *Fuel* **2020**, *267*, 117302. [[CrossRef](#)]
37. Zhao, C.-X.; Jiang, E.-C.; Chen, A.-H. Volatile production from pyrolysis of cellulose, hemicellulose and Lignin. *J. Energy Inst.* **2017**, *90*, 902–913. [[CrossRef](#)]

- 
38. Ye, X.-N.; Lu, Q.; Wang, X.; Guo, H.-Q.; Cui, M.-S.; Dong, C.-Q.; Yang, Y.-P. Catalytic fast pyrolysis of cellulose and biomass to selectively produce levoglucosenone using activated carbon catalyst. *ACS Sustain. Chem. Eng.* **2017**, *5*, 10815–10825. [[CrossRef](#)]
  39. Alvarez, J.; Lopez, G.; Amutio, M.; Bilbao, J.; Olazar, M. Physical activation of rice husk pyrolysis char for the production of high surface area activated carbons. *Ind. Eng. Chem. Res.* **2015**, *54*, 7241–7250. [[CrossRef](#)]