



Article Effects of Pretreatments on Yields, Selectivity and Properties of Products from Pyrolysis of *Phragmites australis* (Common Reeds)

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Abstract: *Phragmites australis* (PHA) is a grass-type biomass, commonly known as reed grass, which has the potential to be a valuable energy and chemical feedstock due to its high yield (4.5–7 kg biomass m⁻² year⁻¹). It is demonstrated that the physicochemical properties and composition of *phragmites* can be altered by subjecting the feedstock to a combined acid hydrolysis at various level of acid concentrations and torrefaction pre-treatment processes. In this paper, we conducted fast pyrolysis on pretreated PHA, resulting in bio-oil with significantly higher selectivity towards levoglucosenone and appreciably reduced amounts of ketones and aldehydes being produced. The experiments demonstrated that 4% H₃PO₄ acid hydrolysis and 220 °C torrefaction combined pretreatments prior to fast pyrolysis resulted in 17 times increase of relative selectivity to levoglucosenone in the bio-oil portion along with a reduction of ketones and aldehydes relative concentrations from 23% to 13%. Pyrolysis of pretreated PHA produced higher amount of biochar. The phosphorus-enriched biochar offers a potential usage for soil amendment or sorbent material. This study presents an opportunity to convert this underutilized feedstock into valuable bio-based products. Additional in-depth investigation is essential to gather more data for assessing the economic and sustainability features of the proposed process.

Keywords: *Phragmites australis;* common reed; fast pyrolysis; torrefaction; acid hydrolysis; bio-oil; biochar

1. Introduction

Lignocellulosic biomass has a tremendous potential to supply future energy requirements with many different possible sources and conversion methods. While many plants have increased their economic values due to high demand as biorenewable feedstock, other plants potentials have not yet been extensively explored. A highly potential plant to be used as a biorenewable feedstock is *Phragmites australis*, which is also known as common reed grass or phragmites, due to its abundance and potential environmental impact. Native to the United States and Europe, phragmites has proliferated on a global scale over the last 400 years [1,2]. Introductions of European strains in the 1800's to the United States with higher salt tolerance than native strains have resulted in the designation of phragmites as an invasive species [1–4]. This species is now a major concern in the Eastern United States, where these non-native strains have successfully invaded numerous sensitive wetlands and coastal salt marshes in the last 30 years due to their higher salt tolerance [3–6]. This species, while rapidly invading sensitive habitats, has potential benefits in aiding in the remediation of areas where it is already established, and are stressed by enhanced nutrients or toxic metals due to storm water runoff [7–9].

The potential of phragmites as lignocellulosic feedstock has only come to the attention of the scientific community very recently. In terms of its availability, phragmites is an especially promising energy plant and chemical feedstock due to its high production potential. It has been reported that it can provide up to 4.4–6.9 kg of biomass per meter square per year, which is aided by its ability to survive during winter months [10,11]. Also, it is one of the most widely distributed plant species on the planet, covering approximately ten million hectares [1,12]. Throughout the late fall and winter, phragmites loses its green and becomes dry under natural conditions, which makes it an ideal feedstock for biomass conversions, particularly for thermochemical processes, such as gasification and fast pyrolysis, which require the feedstock to be relatively dry (15–25 wt % moisture) [1]. Studies on the potential of phragmites as a renewable source are limited [8,9,13–15]. One study in Austria reported that, when compared to the utilization of woods and fossil fuels, the regional utilization of phragmites is potentially beneficial to the environment due to lower greenhouse gas (GHG) emissions [8]. In China, phragmites has been used industrially for paper production [16]. Other research have been primarily focused on the exploitation of its lignin content (20–25%, w/w) to produce fuel [17–19].

This study explores the potential of *Phragmites australis* as a feedstock to produce useful bio-based products, such as fuels and chemicals, via selective fast pyrolysis. Fast pyrolysis is the direct thermal decomposition of the organic components in biomass in the absence of an oxidizing agent (air or oxygen), typically at temperatures between 400 and 600 °C, to an array of useful products in the form of a liquid (bio-oil), a solid (biochar), and a mixture of non-condensable gases (synthesis gas) [20–22]. While fast pyrolysis method is feedstock "agnostic", it is known that product yield and the chemical components in the bio-oil produced are dependent on the process conditions and biomass feed composition. Liquid yields as high as 78% are possible for relatively short residence times (0.5-2 s), moderate temperatures (400-600 °C), and rapid quenching at the end of the process. Rapid quenching is essential if high-molecular weight liquids are to be condensed, rather than being further decomposed to low-molecular weight gases [23].

Bio-oil is composed of a variety of chemical compounds having diverse functionality. The primary chemical groups in bio-oil include aldehydes, anhydrosugars, carboxylic acids, furans, ketones, and phenols. The presence of this wide variety of compounds having different properties makes the utilization of bio-oil difficult. Many chemical compounds in bio-oil are valuable as specialty chemicals; however, they are present in low amounts and are difficult to recover. The ability to synthesize bio-oil having high amounts of specific targeted chemical functionalities is necessary to improve the value of bio-oil as feedstock for the production value added chemicals.

In this study, biomass was subjected to a pretreatment process prior to pyrolysis, which altered the yields and selectivity of bio-oil and biochar products. Specifically, a combination of acid hydrolysis and torrefaction process is used to modify the physicochemical properties of the biomass feedstock. Acid hydrolysis has been used intensively in biochemical processes for pretreating biomass prior to enzymatic hydrolysis for producing sugars [24–29]. Acid hydrolysis breaks the lignin-hemicellulose bonds, and disrupts the cellulose structure to make cellulose and hemicellulose more available to further breakdown [29–31]. In addition to modifying the physical structure of biomass, it is expected that acid hydrolysis can wash away most of the inorganic minerals present in the biomass. In fast pyrolysis conversion process, it has been well known that the presence inorganic matter reduces the yield of bio-oil and promotes the formation of undesired oxygenated compounds in bio-oil product. Acid hydrolysis improves the quality of bio-oil by reducing the production of these undesired oxygenated compounds. For biomass pyrolysis, an addition of phosphoric acid to biomass prior pyrolysis is known to promote the selective pyrolysis of cellulose, producing bio-oil with a high selectivity to levoglucosan [32–35].

The second pretreatment process is torrefaction. Torrefaction is a mild thermochemical process that involves heating samples for extended periods of time between 200 and 300 °C in the absence of oxygen. The resulting solid after torrefaction contains approximately 70% of the initial weight, but 80–90% of the original energy content, resulting in energy densification [36]. Since the physical

properties closely resemble coal after torrefaction, torrefied biomass is often used for combustion and gasification applications. While energy densification increases the quality and efficiency of the biomass for use in pyrolysis, torrefaction also gives the biomass other desirable qualities. Torrefaction reduces the hydroscopic property of biomass, making the biomass absorb less moisture when stored [37]. Torrefied biomass also contains improved grindability characteristics [38]. Recent studies have reported the effect of torrefaction pretreatment on biomass pyrolysis [27,39–42]. While studies on biomass pretreatment by hydrolysis and by torrefaction have been reported, studies on combined hydrolysis and torrefaction are still limited. A recent study by the authors reported the combined effect of acid hydrolysis and torrefaction pretreatment on pyrolysis of paper mill sludge [42].

Based on the pre-treatment steps that are applied to the feedstock, three process paths of converting phragmites by using fast pyrolysis approach for producing bio-oil and biochar products were evaluated. In path 1, phragmites is pyrolyzed without any pretreatment step. In path 2, phragmites is pretreated using torrefaction, followed by pyrolysis. Finally, in path 3, phragmites is pretreated using a combination of acid hydrolysis and torrefaction processes, followed by pyrolysis. The three process paths were evaluated and compared, analyzing the properties of phragmites feedstock after undergoing each treatment step and the yields and composition of the bio-oil and biochar products. Figure 1 shows the three pathways studied schematically.



Figure 1. Studied process routes for converting *Phragmites australis* to bio-oil and biochar using pyrolysis. (1) Direct fast pyrolysis, (2) torrefaction + fast pyrolysis, and (3) Acid hydrolysis + torrefaction + fast pyrolysis.

2. Materials and Methods

No animals or humans were tested on or harmed in the research performed for this study. *Phragmites australis* samples were collected in the wetland located on the West Campus of Villanova University, Villanova, PA 19085, USA. The samples were gathered in the summer, months when the stalks ranged around 2–3 m tall. The entire parts of phragmites were used. The samples were cut into 0.03 m length and used for pretreatment steps. For analytical pyrolysis, all untreated and treated samples were ground and then sifted to obtain samples with particle size less than 80 mesh (177 μm). All of the samples were dried at 105 °C to remove moisture content and carefully kept in storage to prevent decomposition

2.1. Characterization of Biomass Samples

Phragmites samples (before and after pretreatment steps) were evaluated for its proximate analysis and fiber compositions following the research group and Reckamp et al. characterization procedures [42].

Fiber analysis procedure was performed following the USDA (United States Department of Agriculture) method [43]. Hemicellulose and lignin samples were isolated using the following standard extraction steps: (1) Removal of extractives to obtain extractives-free bulk (EFB) by using ASTM (American Society of Testing Materials) D1105 standard method [44], (2) Isolation of hemicellulose from the EFB by using Wise's Chlorite Method [45], and (3) Extraction of lignin (known as Klason lignin) by using the van Soest's Method [46]. These methods are frequently accepted as standards, and have been largely applied to biomass to determine amounts of hemicellulose and insoluble lignin [47–49].

The inorganic minerals in the samples were analyzed using an Inductively Coupled Plasma (ICP) model JY 38 S following ICP (Inductively Coupled Plasma) standard operating procedure explained in Reckamp et al. [42].

2.2. Biomass Pretreatment Steps

In the study, phragmites samples were hydrolyzed using phosphoric acid of varying concentrations that were based on the studies done by Lenihan et al. [50]. In a typical experiment, 0.02 kg of dried phragmites was added to a 2 L round bottom flask, along with 1 L of phosphoric acid solution at concentrations of 0% (neutral hydrolysis), 4%, 6.5%, and 9% by weight. The solution was boiled for 60 min under reflux. After being drained, the treated biomass was washed three times with DI (deionized) water. While the sugars that were extracted from the biomass into the liquid fraction can be used for alternate biochemical uses, this study only focused on the hydrolyzed solid fraction that was remaining.

A torrefaction temperature of 220 °C was used to limit extensive degradation of carbon-containing components. Torrefaction of phragmites was performed by using a tubular furnace batch reactor (TFBR) (Blue M, New Columbia, PA, USA). The tube has an inside diameter of 0.067 m, 0.61 m long, and is heated by a Blue M tubular furnace. At the outlet of the furnace tube, two impingers were connected in series, filled with 5 mL of methanol, and were placed in an ice bath. The impingers function as condensers for the volatile vapor effluent to capture the vapors generated. A De Jaye infra-red gas analyzer (De Jaye electronics, Des Moines, IA, USA) was connected to the impinger outlet and measured concentrations of carbon monoxide, carbon dioxide, hydrogen, methane, and oxygen during operation. Nitrogen, the carrier gas at a rate of 80 mL min⁻¹, purged the TFBR. The pyrolysis temperature was 220 °C. For each run, about 0.15 kg of biomass was weighed and was placed in the bottom of a small steel tube 0.11 m long, and had an inside diameter of 0.061 m. After the furnace tube reached 220 °C, the small tube containing the biomass was pushed into the center of the furnace and was held isothermal for 30 min.

2.3. Analytical Fast Pyrolysis

The biomass pyrolysis products were determined using an analytical pyrolysis system (CDS Pyroprobe 5200, CDS Analytical, Oxford, PA, USA) connected to a gas chromatograph with mass spectrometer (HP 5890 Series II plus/HP 5972, Agilent, Wilminton, DE, USA). Performance analyses were completed by evaluating chemical product distributions of the fast pyrolysis reaction vapors. The biochar that was produced during fast pyrolysis was assessed using a thermogravimetric analyzer (TGA TA 5000, TA Instruments, New Castle, DE, USA). Error bars are the standard deviation for at least triplicate analyses in all of the results that are presented in this study. All pyrolysis experiments were performed at 500 °C. The pyrolysis vapors were directly injected into the GC/MS (gas chromatography & mass Spectrometry) using helium as the carrier gas, in which the constituents of the pyrolysis vapor were separated in the GC column and identified. The method of chromatographic separation of pyrolysis products was adapted from Patwardhan [51] and previously used in other waste biomass studies done by the research group [27,42]. Py-GC/MS analytical procedure was explained thoroughly in Reckamp et al. [42].

3. Results and Discussion

3.1. Pretreatment Effects on Physicochemical Properties of Phragmites

Experimental data from the combined acid hydrolysis and torrefaction pretreatment processes to pretreat phragmites shows significant alterations of the feedstock composition. Figure 2 presents the fiber analysis results before and after combined acid hydrolysis and torrefaction pretreatments. Figure 2a displays the compositions as a function of the initial biomass mass, showing the decrease in mass after the pretreatment processes, being predominantly attributed to the decomposition of the hemicellulose and lignin components. Torrefaction alone decreases the mass of the biomass by approximately 15%, mostly due to the decomposition of hemicellulose. The combination of acid hydrolysis and torrefaction resulted in the mass remaining approximately 60% of the original biomass. It was noted that the content of mineral matter increased as acid concentration for hydrolysis was augmented from 4% to 6.5%, it was considered that phosphorous might have been adsorbed into the biomass. Higher acid concentration did not increase the content of mineral matter anymore, suggesting a limit of how much phosphorus can be taken by the biomass feedstock.



Figure 2. (a) Fiber and inorganic mass fractions of *Phragmites australis* after combined pretreatments with respect to the mass of the original raw biomass; (b) Proximate analysis composition of *Phragmites australis* after combined pretreatments; H + T: hydrolysis and torrefaction pretreatments.

The initial phragmites feedstock consists of approximately 37% hemicellulose, 44% cellulose, 15% lignin, and the remainder inorganics. With combined 4% concentration acid hydrolysis and torrefaction pretreatments, hemicellulose was decomposed to approximately one-quarter of its original amount, while lignin was decomposed by about one-half of its amount in the initial biomass. Increasing acid concentration higher than 4 wt % did not increase the decomposition of the biomass components. As shown in Figure 2, the decomposition of hemicellulose and lignin components resulted in solid biomass containing high relative concentration of cellulose. A maximum cellulose content of approximately 71 wt % was obtained in phragmites after undergoing a combined 4% acid hydrolysis and torrefaction pretreatment. Increasing acid concentrations to 6.5 wt % and 9 wt %, while it did not affect cellulose amount, increased the number of inorganics in biomass, which reduced the relative concentration of cellulose. Having a cellulose-rich feedstock is an advantage since it could promote selective pyrolysis to produce bio-oil rich in cellulose-derived chemical components, potentially improving the bio-oil quality.

Another important property that was analyzed was proximate analysis for measuring volatiles, fixed carbon, and inorganic contents of the biomass. In general, the amount of volatiles and fixed carbon determine the maximum amount of bio-oil and the minimum amount of biochar, which can be produced from pyrolysis, respectively. Results of proximate analysis of phragmites samples before and after the pretreatment steps are shown in Figure 2b. The original PHA sample contained approximately 70%, 23%, and 7% mass fraction of volatile matters, fixed carbon, and ash (inorganic minerals), respectively. The proximate analysis composition indicated the possible maximum yield of bio-oil and gases combined (70%), and the minimum yield of biochar (~30%) that could be obtained from pyrolysis of the untreated phragmites. Torrefaction alone decreased volatile matter content to 64%, while the combined neutral hydrolysis and torrefaction increased the volatile matter content to 76% due to the reduction of inorganic content. Pyrolysis of phragmites, that underwent the combined pretreatment steps, would be expected to yield biochar with less inorganics content.

Pretreatment by acid hydrolysis followed by torrefaction resulted in significant reduction of the volatile matters content by 35–43%. The severity of volatile matter reduction increased with the acid concentration that was used in the hydrolysis pretreatment. Due to the decrease in volatile matter from pretreatments, pyrolysis of the pretreated samples was expected to have decreased bio-oil yield when compared to that of untreated material. The reduction of bio-oil yield requires a significant quality improvement to make the pretreatments worthwhile.

Analysis of inorganic components is important since the presence of inorganics in biomass affect the yields and selectivity of pyrolysis products. The effects of hydrolysis pretreatments on the composition of the selected inorganic minerals in phragmites samples are shown in Figure 3. The analyzed minerals included calcium, iron, magnesium, sodium, aluminum, potassium, and phosphorus. Apart from iron concentration, which was reduced by almost 60%, concentrations of the inorganic minerals were not affected by the neutral hydrolysis. Pretreatment by using 4% phosphoric acid reduced the concentration of all minerals, except phosphorus whose concentration increased significantly due to adsorption of phosphoric acid in biomass samples. Acid hydrolysis by using acid beyond 4% concentration did not appear to further reduce the mineral content; however, the phosphorus content increased sharply with increased acid concentration. That the concentration of phosphorus in the phragmites samples that were treated with 6.5% and 9% acid remained the same, suggested the saturation of capacity of phragmites samples for adsorbing this mineral.



Figure 3. Elemental concentrations of selected inorganics with respect to the initial biomass mass for untreated and pretreated *Phragmites australis*, H: hydrolysis (H₃PO₄).

3.2. Fast Pyrolysis of Treated and Untreated Phragmites

Fast pyrolysis of untreated and pretreated phragmites samples showed that the alteration of phragmites physicochemical properties had a significant impact on the distribution of the chemical moieties in the bio-oil product and the proximate analysis composition of the biochar products. Figure 4 shows the distribution of selected chemical components in bio-oil that was produced from fast pyrolysis of treated and untreated phragmites. Figure 4a displays the chemical components that were discovered in the GC/MS system, and then organized based on their chemical types, i.e., aldehydes, aromatics, carbohydrates, ketones, phenolics, and furans. The relative concentrations of the chemical compounds were calculated based on the integration areas/biomass of the chromatogram peaks of the respective compounds divided by total integration areas/biomass of all the peaks in the chromatograms. In Table A1, there is a list of all the components identified in this study.



Figure 4. Cont.



Figure 4. (a) Chemical component distributions of bio-oil produced from fast pyrolysis of treated and untreated *Phragmites australis;* (b) Relative concentration of selected bio-oil compounds from various chemical groups.

As shown in Figure 4a, pretreatments by torrefaction only and combined neutral hydrolysis and torrefaction did not significantly affect the chemical moieties distribution in the bio-oil products. The only significant change was the reduction of relative concentrations of ketones. The reduction of ketones was due to the reduction of hemicellulose in the biomass after the two pretreatment steps. Adding 4% phosphoric acid in the hydrolysis pretreatment resulted in biomass with high relative concentration of cellulose, which resulted in bio-oil with high relative concentration of carbohydrates. When compared to the concentration of carbohydrates in bio-oil from untreated phragmites, the increase of carbohydrate concentration in bio-oil from pyrolysis of pre-treated phragmites was almost 10 folds, i.e., from 2.8% to 32.1%. The increase of carbohydrates concentration was complemented by the reduction of ketones (from 12.6% to 1.4%), phenols (from 18.7% to 10.9%), and furans (from 8.7% to 1.4%). The reduction of these chemical moieties was due to the reduction of both hemicellulose and lignin in the biomass feedstock after pretreatments. Hydrolysis pretreatment by using phosphoric acid at concentration above 4% did not increase the selectivity towards the production of carbohydrates, however. Higher acid concentrations increased the quantities of phenolic constituents at the expense of carbohydrates. Therefore, the highest quality bio-oil is obtained with the combined 4% phosphoric acid hydrolysis and torrefaction.

Figure 4b presents noteworthy chemical moieties from some organic groups that are presented in Figure 4a. At 4% H₃PO₄ hydrolysis and torrefaction, a dramatic increase of Levoglucosan and levoglucosenone (carbohydrates) is presented with an elimination of 2-furanmethanol formations. It is known that Levoglucosan further degrades to produce furan components, such as furfural and 2-furanmethanol [52], but the addition of phosphoric acid changes the reaction mechanisms from Levoglucosan to levoglucosenone production. As a valuable pharmaceutical intermediate, levoglucosenone is a high-quality bio-oil component.

Along with bio-oil, biochar is also an important product from fast pyrolysis. In addition to its function as fuel due its energy content, biochar has an economic value in agriculture. Biochar can be applied in soils to increase soil organic carbon (SOC) content and supply nutrients to plants, which will enhance soil properties and plant growth [53,54].

Figure 5 shows the yield and the proximate analysis composition of biochar products, varying depending on the pretreatment steps that are applied to biomass feedstock. As anticipated, the addition of phosphoric acid pretreatment significantly increases the biochar yield to approximately 60–70% when compared to the 24.3% that is produced from untreated phragmites. It is worth noting that overall, biochar produced from acid-pretreated biomass have higher content of fixed carbon and lower content of inorganic matters. The inorganic matter in the acid-pretreated biomass derived biochar will

contain primarily phosphorus which was adsorbed by biomass during hydrolysis. The high content of phosphorus in biochar can potentially add the potential value of biochar for producing activated carbon and for application as soil enhancing agent. Phosphoric acid has been identified as a catalyst in the production of activated carbon from biomass [55]. Phosphorus is a well-known plant nutrient, thus additional phosphorous in biochar could provide added effectiveness as a soil enhancement agent. Reduced volatile matter with high fixed carbon in biochar from phragmites indicates that the biochar that is produced may be suitable as a soil amendment. But, further studies are needed in the remaining inorganic content still present in phragmites must be evaluated prior to commercial application of biochar as a soil amendment [50].



Figure 5. Proximate analysis mass fractions and yield of biochar produced from fast pyrolysis of pretreated phragmites.

4. Conclusions

Phragmites australis has the potential as a feedstock for thermochemical conversion to bio-oil and biochar via fast pyrolysis. Phosphoric acid hydrolysis and torrefaction pretreatments controlled the selectivity and yield of pyrolysis products by creating a cellulose-rich feedstock with reduced content of selective inorganics. Although all of the combinations of pretreatments increased carbohydrates in the products, 4% phosphoric acid hydrolysis with torrefaction produced the highest combination of yield and quality bio-oil by limiting the inorganics, producing high levels of levoglucosenone, and limiting aldehyde, ketone, and acid production. In addition, the biochar product contains minimal volatile matter with high fixed carbon and high phosphorus contents, making it potentially suitable as a soil amendment and/or precursor to produce activated carbon.

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Author Contributions: Rene A. Garrido and Justinus A. Satrio conceived and designed the experiments; Rene A. Garrido and Joseph M. Reckamp performed the experiments; all the authors analyzed the data; Charles G. Coe provided technical advice and assisted the preparation of the manuscript; Justinus A. Satrio as the principal investigator provided research facilities, including equipment, reagents/materials/supplies, and analytical tools, he also provided technical guidance along with assistance in manuscript preparation; and finally, Rene A. Garrido prepared the manuscript.

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

Appendix A

Category	Compound	Retention Time(RT) [min]
aldehyde	Butanedial	4.156
aldehyde	Furfural	5.573
furans	2-furanmethanol	6.414
aromatic	Styrene	7.379
ketone	2(5H)-Furanone	8.528
ketone	2-hydroxy-2-cyclopenten-1-one	9.011
aldehyde	5-methyl-2-furancarboxaldehyde	10.694
phenols	phenol	11.731
ketone	3-methyl-1,2-cyclopentendione	13.609
furans	5,6-dihydro-4-methoxy-2H-Furan	14.368
phenols	4-methylphenol	16.082
phenols	2-methoxyphenol	16.514
ketone	3-ethyl-2-hydroxy-2-cyclopenten-1-one	17.94
carbohydrate	Levoglucosenone	18.689
phenols	4-ethylphenol	20.362
phenols	2-methoxy-4-methylphenol	21.378
phenols	1,2-Benzenediol	22.015
furans	2,3-dihydrobenzofuran	22.785
phenols	3-methoxy-1,2-benzenediol	24.437
phenols	4-ethyl-2-methoxyphenol	25.309
aromatic	Indole	25.864
phenols	2-methoxy-4-vinylphenol	26.839
phenols	2,6-dimethoxyphenol	28.512
phenols	2-methoxy-4-(1-propenyl)phenol	32.535
carbohydrate	Levoglucosan	33.941
aldehyde	4-methyl-2,5-dimethoxy-benzoaldehyd	e 36.374
phenols	2,6-methoxy-4-(2-propenyl)phenol	39.381

Table A1. List of components.

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