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Selective pyrolysis of paper mill sludge by using pretreatment processes to enhance the quality of bio-oil and biochar products

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ABSTRACT

Paper mill sludge (PMS) is a residual biomass that is generated at paper mills in large quantities. Currently, PMS is commonly disposed in landfills, which causes environmental issues through chemical leaching and greenhouse gas production. In this research, we are exploring the potential of fast pyrolysis process for converting PMS into useful bio-oil and biochar products. We demonstrate that by subjecting PMS to a combination of acid hydrolysis and torrefaction pre-treatment processes it is possible to alter the physicochemical properties and composition of the feedstock material. Fast pyrolysis of pretreated PMS produced bio-oil with significantly higher selectivity to levoglucosenone and significantly reduced the amount of ketone, aldehyde, and organic acid components. Pretreatment of PMS with combined 4% mass fraction phosphoric acid hydrolysis and 220 °C torrefaction processed prior to fast pyrolysis resulted in a 17 times increase of relative selectivity towards levoglucosenone in bio-oil product along with a reduction of acids, ketones, and aldehydes combined from 21 % to 11 %. Biochar, produced in higher yield, has characteristics that potentially make the solid byproduct ideal for soil amendment agent or sorbent material. This work reveals a promising process system to convert PMS waste into useful bio-based products. More in-depth research is required to gather more data information for assessing the economic and sustainability aspects of the process.

1. Introduction

This study explores the use of paper mill sludge (PMS) as a potential feedstock for the production of useful bio-based products. Paper mill sludge (PMS) is a type of residual biomass that is generated at every paper mill as a solid byproduct of pulping and papermaking operations [1]. On average, 35% of a paper mill's feed material becomes undesired materials in the forms of wastes, mainly PMS [2]. Paper mills generate PMS at a daily rate of 15 Mg up to 200 Mg or more depending on the capacity of the mills [1]. In North America, the United States of America and Canada, respectively produce 5 Tg and 1.5 Tg of PMS annually [1,3]. These numbers expand worldwide to approximately 10,000 paper mills in operation, creating an abundant supply of the sludge.

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Currently, PMS is commonly disposed in landfills, causing environmental problems through chemical leaching and greenhouse gas production. Studies show that the disposal of PMS has negatively affected plant growth in the area [4]. Adding to the problem, landfills are becoming increasingly difficult to site and more expensive due to increased regulations, decreased land availability, and public oppositions. The number of landfills is also decreasing rapidly in the United States from 8000 in 1988 to an estimated 1900 in 2010 [5]. These problems have caused remediation of PMS to be as high as 60% of a plant's operating costs [6]. Rising costs have made alternative methods of use or disposal for PMS an economic priority.

Research and development efforts on utilizing PMS efficiently and economically are being done in many different areas although still limited. PMS has found use for improving the quality of soils, i.e. as composting materials [3] and as feed for soil-dwelling earthworms [7]. Converting PMS to activated carbons and biocatalysts for adsorption purposes is also gaining interest [8–10]. In addition, the use of PMS as fuel for combustion process has been explored [11]. For the production of biofuels, PMS has been reported as an attractive source for biomass conversion to ethanol since it is a pre-processed biomass that is more readily accessible for enzymatic hydrolysis [12,13]. A recent economic analysis study on the conversion of PMS to ethanol has indicated that the process is economically profitable [14]. The present study explores the potential of fast pyrolysis for converting PMS into high-quality bio-oil and biochar products since reported studies on conversion of PMS by pyrolysis are still limited [9,15].

Fast pyrolysis is a thermochemical conversion process in which biomass is decomposed to produce a liquid (bio-oil), a solid (biochar), and a non-condensable gas mixture (syngas) by exposing biomass to heat, typically at 500 °C, in the absence of oxygen [16]. Liquid bio-oil is composed of hundreds of chemical constituents from various chemical groups, primarily anhydrosugars, phenols, furans, ketones, aldehydes, and carboxylic acids, whose compositions affect the physicochemical properties of bio-oil. Among its many potential uses, bio-oil is most economically attractive to be used as intermediate feedstock for the production of transport liquid fuels and value added chemicals. Quality bio-oil as intermediate feedstock for transport liquid production requires a reduction in ketones, aldehydes, and carboxylic acids, since high presence of these oxygenated compound cause bio-oil to be highly acidic, highly polar, chemically unstable, and low in heating value [17]. The high polarity of bio-oil makes it immiscible with crude oil, making it difficult for using bio-oil as a co-feedstock in petroleum refineries. Furthermore, while many chemical constituents in bio-oil are valuable, their contents are low, making their recovery technically difficult and costly. As feedstock for the production of value-added chemicals, specific bio-oils that have high contents of target chemical products, need to be produced.

Among various factors that affect biomass pyrolytic pathways and their subsequent products, the selection of biomass could be the most important one. Although fast pyrolysis is 'agnostic' to the biomass feedstock, the selectivity and yield of fast pyrolysis bio-oil and biochar products and their quality and properties are dependent on biomass' physicochemical properties, particularly the amounts of its three primary components (cellulose, hemicellulose, and lignin) and inorganic matter [18]. It is well-known that inorganic minerals in biomass have significant impact on pyrolytic pathways, altering the pyrolysis products. Specifically, alkali metals are important in selective decomposition, from which more organic acids are formed, lowering bio-oil quality [19]. Therefore, controlling the content of inorganic components in biomass feedstock is important in producing quality bio-oil yield and composition.

In addition to bio-oil, this study also focuses on the biochar product. Biochar is the solid product of fast pyrolysis, which only recently has gained attention for its economic value. While biochar can also be valued as a fuel due to its energy content, research has shown that biochar application to increase soil organic carbon (SOC) and improve the supply of nutrients to plants, enhancing plant growth and soil properties, may be economically preferred [20,21]. The carbon component in biochar is primarily fixed in aromatic form, making it resistant to decomposition as a soil amendment as a carbon sequestration agent [22]. Similar to the bio-oil product, the physicochemical properties and composition of biochar also vary depending on the biomass feedstock and the conditions of the pyrolysis used for producing the biochar [23].

This study aims to demonstrate the feasibility of producing high quality PMS-derived bio-oil from by subjecting the PMS feedstock with a pre-treatment process, specifically a combined acid hydrolysis and torrefaction process, to modify the physicochemical properties of paper mill sludge prior to pyrolysis. Fig. 1 shows three process paths of converting PMS by using fast pyrolysis approach for producing bio-oil and biochar products. The three process paths are based on the pretreatment steps applied to the PMS feedstock prior to fast pyrolysis. In Path I, PMS is pyrolyzed without any pretreatment step. In Path II, PMS is pretreated by torrefaction followed by pyrolysis. Finally, in Path III, PMS is pretreated by using a combination of acid hydrolysis and torrefaction processes followed by pyrolysis. The three process paths were evaluated and compared by analyzing the properties of PMS feedstock after undergoing each treatment step and the yields and composition of the bio-oil and biochar products.

In this study acid hydrolysis and torrefaction processes were selected for modifying biomass structure. In biochemical processes, lignocellulosic biomass is recalcitrant to enzymatic hydrolysis because of the heterogeneous character of biomass particles, the crystalline structure of cellulose, the low surface area, the protective seal of lignin, and the sheathing of hemicellulose [24]. Chemical pretreatment by acid hydrolysis breaks the lignin seal and disrupts the cellulose structure to make cellulose and hemicellulose more accessible to further decomposition [25]. In addition to its structural modification of biomass, acid hydrolysis also modifies/reduces the content of inorganic minerals to improve the quality of pyrolysis products by eliminating the production of undesired oxygenated compounds. Various acids, such as sulfuric acid, hydrochloric acid, and phosphoric acid, have been used for hydrolyzing biomass [26]. For the production of sugars, the use of these strong acids causes severe decomposition of biomass resulted in the production of furfural and organic acids [27]. In this work, phosphoric acid was used for pretreating PMS. In