



Analysis of switchgrass-derived bio-oil and associated aqueous phase generated in a semi-pilot scale auger pyrolyzer



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ABSTRACT

To efficiently utilize water-soluble compounds in bio-oil and evaluate the potential effects of these compounds on processes such as microbial electrolysis, this study investigated the physicochemical properties of bio-oil and the associated aqueous phase generated from switchgrass using a semi-pilot scale auger pyrolyzer. Combining separation and detection strategies with organic solvent extraction, an array of analytical instruments and methods were used to identify and quantify the chemical constituents. Separation of an aqueous phase from the crude bio-oil was achieved by adding water (water: crude bio-oil at 4:1 in weight), which resulted in a partition of 61 wt.% of the organic compounds into a bio-oil aqueous phase (BOAP). GC/MS analysis for BOAP identified over 40 compounds of which 16 were quantified. Acetic acid, propionic acid, and levoglucosan are the major components in BOAP. In addition, a significant portion of chemicals that have the potential to be upgraded to hydrocarbon fuels was extracted to BOAP (77 wt.% of the alcohols, 61 wt.% of the furans, and 52 wt.% of the phenolic compounds in crude bio-oil). Valorization of the BOAP may require conversion methods capable of accommodating a very broad substrate specificity. A better separation strategy is needed to selectively remove the acidic and polar components from crude bio-oil to improve economic feasibility of biorefinery operations.

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1. Introduction

The depletion of fossil fuel reserves and the increasing concern over global warming have motivated scientists and researchers to look for alternative clean energy sources. Biomass is an important and plentiful renewable resource available to make clean fuels [1]. There are several technologies for converting biomass to advanced biofuels and chemicals, for examples, pyrolysis, gasification, fermentation, and liquefaction. Among these technologies, pyrolysis has a high potential to produce drop-in, liquid hydrocarbon fuels. It is a thermochemical technology that generally conducted at temperatures ranging from 400 to 600 °C in the absence of oxygen, predominantly producing bio-oil with biochar and syngas as coproducts [2]. However, bio-oil produced from biomass pyrolysis is a carbon-based liquid product with poor physicochemical properties such as high content of water and oxygen, high acidity, and low heating value, requiring preprocessing and upgrading for fuel applications.

Due to the presence of multiple components in biomass, the pyrolysis reaction of biomass is extremely complicated involving the decomposition of cellulose, hemicellulose, lignin, and secondary decomposition with catalytic reactions of primary decomposition products catalyzed by inorganic minerals. This results in hundreds of compounds in bio-oil, which are classified as acids, alcohols, furans, aldehydes, esters, ethers, ketones, phenolics, and anhydrosugars, depending on their functional groups. Total carboxylic acids in the bio-oil were reported to be about 4–8 wt.%, with acetic acid being the most prevalent acid. High content of carboxylic acids renders corrosiveness of bio-oil, requiring special containers for bio-oil transportation and storage. Levoglucosan is a major compound in the group of anhydrosugars in crude bio-oil which contributes about 5–7 wt.% [3]. In addition to these compounds, a considerable amount of phenolics, which are decomposed from lignin, are also present in crude bio-oil. Bio-oil has been considered as a promising chemical platform for producing renewable fuels and value-added chemicals for industrial applications [4].

Simply adding water to crude bio-oil is the first step to extract valuable chemicals by fractionating crude bio-oil into an organic and an aqueous phase [5–8]. Most polar compounds such as

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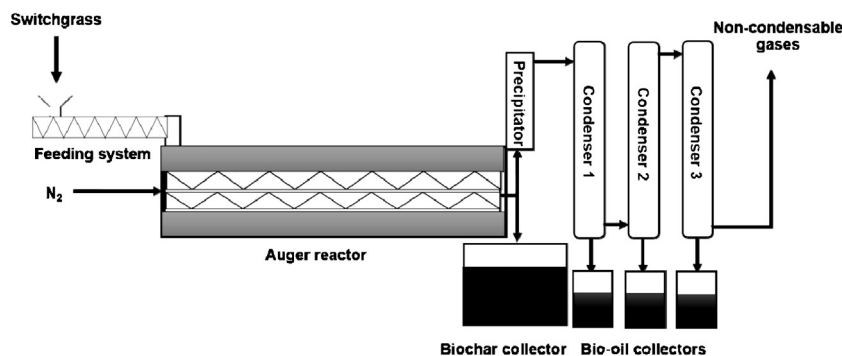


Fig. 1. Schematic diagram of semi pilot-scaled auger pyrolysis system.

carboxylic acids and anhydrosugars are extracted into the aqueous phase, while phenolic compounds contribute to the organic phase [9–12]. Due to the high water content and low amount of organic compounds, the bio-oil aqueous phase fractionated by adding water is a low-value product compared to the crude bio-oil and organic phase, and thus has little value to be upgraded to fuels. To improve the economics of biomass pyrolysis, research strategies targeted at the production of hydrogen or other value-added chemicals from the bio-oil aqueous phase (BOAP) are being investigated [9,13–20]. Recently, a novel process of converting BOAP to hydrogen via microbial electrolysis has been reported [21]. However, compounds such as furan aldehydes and phenolics presented in BOAP might be inhibitory to microbes [17,21,22]. A better understanding of bio-oil and its aqueous phase composition is, therefore, necessary to evaluate and develop new conversion technologies.

This study was to comprehensively characterize the switchgrass-derived bio-oil and its fractions, using multiple techniques, with the aim to evaluate the possibility and the potential effects of compounds presented in BOAP on new processes such as microbial electrolysis. Physicochemical properties of crude bio-oil and the associated aqueous phase were analyzed and the partition of chemicals into BOAP was evaluated.

2. Materials and methods

2.1. Materials

Air-dried switchgrass (*Panicum virgatum* L.) obtained from a local producer in eastern Tennessee was used for the bio-oil production. The water content of the biomass was 7–8 wt.%. Before pyrolysis, the material was ground to less than a 2 mm particle size. The switchgrass is composed of 34.1 wt.% cellulose, 25.7 wt.% hemicellulose, 18.8 wt.% lignin, 14.2 wt.% extractives, and 2.7 wt.% ash [23].

Ethyl acetate and chloroform purchased from Thermo Fisher Scientific (Waltham, MA) were used as organic solvents to extract organic compounds from BOAP for identifying the chemical composition of BOAP. These two chemicals were used as received. External standards used for quantifying compounds were purchased from Sigma-Aldrich (St. Louis, MO).

2.2. Bio-oil production

A semi-pilot scale auger pyrolysis system (Proton Power, Inc., Lenoir City, TN) equipped with a feeding system, a rectangular auger reactor, a pyrolysis vapor condensation section, and a biochar collector was used to pyrolyze switchgrass for bio-oil production (Fig. 1). A detailed description of the pyrolysis system was provided elsewhere [23]. In brief, bio-oil was produced under the following operation conditions. Feedstock was transferred from the

feeding hopper to the auger pyrolysis reactor by a single auger with a feeding rate of approximately 8.5 kg/h. The auger reactor (10 W × 10 H × 250 L cm) contained internal dual augers. The auger speed controlled the residence time of feedstock at 72 s. The heated zone was comprised of a 200 cm long electrical resistance furnace operating at 500 °C. The sweeping gas (nitrogen gas, 20 L/min) was introduced into the front of the auger reactor and moved with the evolved vapors to the condensation section. Before the vapors entered the condensers from the auger reactor, the particle chamber (20 cm in diameter and 100 cm long) precipitated fine particles from the vapors. The biochar produced from the feedstock was collected into the biochar drum. The condensation section was comprised of three condensers in a series (10 cm in diameter and 200 cm long, each). The temperatures of the three condensers were maintained between 10 and 15 °C using a circulation water cooling system. The bio-oils collected from the three condensers were immediately combined and mixed for homogeneity and stored in a walk-in freezer before fractionation and characterization. The non-condensable gases were burned at the end of the system. The experiment was performed in duplicate. After pyrolysis, the bio-oil and biochar were collected and weighed. The weight of non-condensable gases was calculated by difference.

2.3. Bio-oil aqueous phase separation

The crude bio-oil obtained from the pyrolysis reactor was mixed by adding deionized water (DI water) in a ratio of 1:4 (wt.%) to separate into bio-oil aqueous phase (BOAP: water soluble fraction) and an organic phase (BOOP: water insoluble fraction). The mixture was shaken vigorously on a mini vortexer (Model: MS1 S7, Fisher Scientific) until forming homogeneous solution then stored at 4 °C overnight. Then the mixture was centrifuged using an Iec Model 120 clinical centrifuge (International Equipment Company) at 5000 rpm for 30 min to accelerate phase separation. After separation, the BOAP and BOOP were collected and weighed.

2.4. Physical properties analysis

The properties of crude bio-oil and BOAP including density, pH, viscosity, water content, solid content, ash content, and total acid number were measured in triplicate. Density was measured according to the ASTM D1217 (2012) standard [24], and pH was measured with an Exttech pH meter. A Schott TitroLine Karl Fischer volumetric titrator was used to measure water content according to ASTM D4377 (2011) standard [25]. Viscosity was measured at 40 °C with serialized Schott Ubbelohde capillary viscometers according to ASTM D445 (2012) standard [26]. Ash content was measured according to ASTM D482 (2013) standard at 575 °C [27]. The solid content was determined according to Boucher et al. [28]. Total acid number (TAN) was measured by titrating bio-oil (0.1 g) and

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