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Characterization of fast pyrolysis oil from short-rotation willow by high-resolution Fourier transform ion cyclotron resonance mass spectrometry

Ilja Miettinen[a], Suvi Kuittinen[b], Ville Paasikallio[c], Marko Mäkinen[a], Ari Pappinen[b], Janne Jänis[a,*]

[a] Department of Chemistry, University of Eastern Finland, P.O. Box 111, FI-80101 Joensuu, Finland
[b] School of Forest Sciences, University of Eastern Finland, P.O. Box 111, FI-80101 Joensuu, Finland
[c] VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland

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ABSTRACT

Fast pyrolysis oil (FPO) produced from short-rotation willow was characterized by using high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and various bulk chemical analyses. The pyrolysis experiments were carried out on a bench-scale bubbling fluidized bed pyrolysis reactor operating at the temperature of 500 °C. The resulting pyrolysis oil was a single-phase liquid with relatively low oxygen content and had pH and total acid number values of 3.0 and 129 mg/g, respectively. A wealth of compositional information of the willow FPO was obtained using FT-ICR MS in combination with electrospray ionization (ESI) and atmospheric-pressure photoionization (APPI) techniques. While ESI preferentially ionized acidic extractives, small phenolics and anhydrosugars, APPI ionized clearly larger compounds, including neutral lipophilic extractives, triterpenoids and high molecular mass pyrolytic lignin, most of which are beyond conventional gas chromatography–mass spectrometry analyses.

1. Introduction

Short-rotation willow *Salix schwerinii* is a member of *Salix* genus, which comprises about 350–500 tree species distributed all over the world [1]. Different willow species possess suitable properties for being utilized as biomass crop, including high yield when grown in short rotation cycles, easiness in vegetative propagation and ability to resprouting [2]. These are among the features characteristic for short-rotation woody crops, which will have a significant role in biomass production for sustainable chemicals, materials and energy in the future. Besides biomass production, willow species are also explored as a promising alternative for stabilization of disturbed landscapes, phytoremediation and erosion control [3,4]. Different *Salix* clones have been studied in the UK and Sweden, where *S. schwerinii* has demonstrated high biomass productivity and good rust resistance [5,6]. *Salix* species can be used for phytoremediation by enabling rapid biomass production on contaminated land areas with simultaneous purification of the soil [7]. When heavy metal containing biomass is converted, most impurities end up in charcoal and the obtained bio-oil contains no significant amounts of contaminants [8].

Thermochemical conversion via fast pyrolysis has been successfully utilized with wood biomass [9–11], such as softwood spruce (*Picea abies*) and pine (*Pinus sylvestris*). In addition, a lot of research work has been conducted using hardwood, herbaceous plants and different waste streams as alternative feedstocks. Even though agricultural and municipal waste can be used, they usually give lower oil yields, and other conversion methods (e.g., hydrothermal liquefaction) are therefore applied [11,12]. Fast pyrolysis process is the most efficient way to convert lignocellulosic biomass to liquid biofuel, but the quality of the resulting bio-oil can be a challenge. Acidity, chemical instability and high oxygen content of bio-oils are the main reasons for their further upgrading [13]. Undesired properties of fast pyrolysis bio-oils can be decreased by well-chosen raw material or appropriate pretreatment, but pyrolysis parameters have an effect on the bio-oil composition as well [14–17].

Fast pyrolysis bio-oils are complex mixtures of small and large oxygenated compounds with a varying range of polarity. Thus, their molecular-level analysis is rather challenging. Gas chromatography-mass spectrometry (GC–MS) is widely used in the bio-oil analysis [14,18,19]. Even though this method is quite useful, it can only detect small, sufficiently volatile analytes. In recent years, high-resolution mass spectrometry (HRMS) has been increasingly used for bio-oil analysis due to its versatility and

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* Corresponding author.
E-mail address: janne.janis@uef.fi (J. Jänis).

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comprehensiveness [20–36]. Atmospheric pressure ionization techniques, such as electrospray ionization (ESI), atmospheric pressure photoionization (APPI) and atmospheric pressure chemical ionization (APCI), allow direct detection of less polar (non-volatile) and thermolabile compounds present in bio-oils (e.g., low and high molecular weight pyrolytic lignin, anhydrosugars and different extractives), thus well complementing the data from GC–MS [23]. Moreover, complicated mixtures, having thousands of molecular constituents, can be directly analyzed using HRMS.

In this study, chemical composition of fast pyrolysis oil (FPO) produced from short-rotation willow (*S. schwerinii*) was characterized by using high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, coupled with negative-ion ESI or positive-ion APPI methods. In addition, bulk physicochemical properties of the produced FPO (i.e., CHNOS and water content, pH, total acid number, and heating value) were also determined. Moreover, the feedstock material was characterized in terms of its overall chemical composition (i.e., holocellulose, lignin and extractives content), elemental composition as well as moisture and ash content.

2. Materials and methods

2.1. Feedstock material and analysis

2.1.1. Feedstock material

Short-rotation coppice willow (*S. schwerinii*) was harvested at the age of 5 years from the field in Siikasalmi (North Karelia, Finland). After harvesting, the feedstock material was chopped (with bark) and transported to the laboratory and stored at 4 °C. Before further analysis, the wood material was air-dried (30 °C) and milled to a particle size of <1 mm.

2.1.2. Chemical composition and trace elemental analysis

The moisture content of the feedstock material was determined after drying in an oven (105 °C) overnight. The ash content was determined by using a Nabertherm L-240H1SN muffle furnace (Nabertherm GmbH, Lilienthal, Germany) with a ramped heating program up to the temperature of 575 °C and maintained for 3 h [37]. For extractives removal, both ethanol and water were used. A Dionex Accelerated Solvent Extractor (ASE) (Thermo Fisher Scientific, Bremen, Germany) was employed [37]. Briefly, the 11-mL ASE cells were used at a pressure of 1500 psi, a temperature of 100 °C, and a heating time of 5 min was applied with a static cycle time of 7 min. A total flush volume was 150% for three static cycles of each sample. The total amount of extractives was determined as the loss in a dry weight after air-drying of the samples on a Petri dish for two days following continuous extraction. The samples for the total nutrient analysis were digested in a CEM MDS 2000 microwave owen (CEM Corporation, Matthews, USA) with a closed wet HNO_3–H_2O_2 digestion method. The extract was analyzed by using an iCAP 6500 DUO inductively-coupled plasma–optical emission spectrometry (ICP-OES) instrument (Thermo Fisher Scientific).

2.1.3. Carbohydrate and lignin content

For feedstock hydrolysis, to determine its carbohydrate and lignin content, an Uppsala method was used for acid hydrolysis [38]. First, 3 mL of 72% H_2SO_4 was added to the milled wood sample (ca. 300 mg), followed by incubation for 1 h at 30 °C with stirring the mixture in every 5 min. After the incubation period of 1 h, the mixture was diluted to 4% by adding water and autoclaved at 121 °C for 60 min. Together with the sample, 10 mL of sugar standards in water and 348 μL 72% H_2SO_4 were also autoclaved to determine sugar loss during autoclaving. The autoclaved mixtures were filtered through pre-weighted filter crucibles using vacuum suction. The resulting filtrates were stored for sugar composition and acid soluble lignin analysis. A chromatographic analysis was done as previously described [37]. The hydrolysates were diluted 5 times with a solution containing a known concentration of the internal standard (l-fucose) in deionized water, filtered through 0.2 μm Teflon syringe filters, and analyzed on a Dionex ICS-3000 high-performance ion chromatography system (Thermo Fisher Scientific), comprising an electrochemical detector (pulsed amperometric detector), a gradient pump, a temperature controlled column, and an AS50 autosampler. The injection volume was 10 μL, and a sugar separation was achieved with the use of Dionex CarboPac PA1 guard and analytical columns, connected in series. Hydrophobic materials were removed via in-line solid phase extraction, comprising a Dionex NG1 guard column placed between the injection valve and the PA1 guard column. The eluent flow was diverted to bypass this guard column 2 min after injection. The sugar separation occurred in 16 min with deionized water as the eluent, a flow rate of 1.1 mL/min, and a column/detector temperature of 18 °C. The standard Dionex "Carbohydrates" waveform was used for detection. After 16 min, the column was regenerated and re-equilibrated for the next sample. This involved a 30 s ramp to an eluent containing 240 mM sodium acetate and 400 mM NaOH in water. These conditions were held for 2 min after which there was a 30 s ramp to deionized water as the only eluent. This elution was maintained for 15 min prior to the injection of the next sample. Since PAD requires alkaline conditions for carbohydrate detection, NaOH (300 mM) was added to the post-column eluent stream, using a Dionex GP40 pump operating at a flow rate of 0.3 mL/min. The chromatographic conditions allowed a baseline resolution between fucose, arabinose, galactose, rhamnose, glucose, xylose, and mannose. Relative response factors used for quantitation were determined via sugar standard samples injected at regular intervals in the analytical sequence.

2.2. Pyrolysis experiments

Fast pyrolysis was carried out on a bench-scale bubbling fluidized bed (BFB) pyrolysis unit, located at the VTT Technical Research Centre of Finland (Espoo, Finland). The unit, which has been previously described by Oasmaa et al. [11], consists of a feed hopper, a twin-screw feeding system, a stainless steel BFB reactor (height 57 cm, inner diameter 5.2 cm) containing 300 g of Al_2O_3 as heat transfer material, two cyclones for char separation, and a three-stage liquid recovery system. The liquid recovery system includes a water-cooled condenser, an electrostatic precipitator (ESP), and a glycol-cooled condenser. The fast pyrolysis experiment was carried out at a reaction temperature of 500 °C. The reactor was fluidized with a N_2 flow of 35 L/min (NTP), which resulted in a calculated vapour residence time of approximately 0.8 s. The feeding rate of willow was 700 g/h on dry basis, and the duration of the experiment was 3 h. The particle size of the willow feedstock was 0.55–0.92 mm, and its moisture content was 6.6 wt%. After separating the char in the cyclones, the pyrolysis vapours were condensed in the liquid recovery system. The water-cooled condenser was operated at 40 °C, the ESP at ambient temperature, and the glycol-cooled condenser at 10 °C. The pyrolysis bio-oil was obtained by collecting the individual liquid products from the water-cooled condenser and the ESP, which were combined after the experiment. A separate aqueous product was also recovered from the glycol-cooled condenser, but was not further characterized in this study. The overall dry basis product distributions for the fast pyrolysis experiment were 58 wt% of organic liquids, 8 wt% of pyrolytic water, 13 wt% of char and 13 wt% of non-condensable gases. The overall mass balance closure was 93 wt%.