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Research paper

# Fast pyrolysis of hot-water-extracted and soda-AQ-delignified okra (*Abelmoschus esculentus*) and miscanthus (*miscanthus* x *giganteus*) stalks by Py-GC/MS

Maryam Ghalibaf*, Saleem Ullah, Raimo Alén

*Laboratory of Applied Chemistry, Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014, Jyväskylä, Finland*

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ABSTRACT

The thermochemical behavior of various samples of okra (*Abelmoschus esculentus*) and miscanthus (*Miscanthus* x *giganteus*) stalks (initial, hot-water-extracted, and those from sulfur-free delignification) were studied by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). In all cases, major GC-amenable condensable products were measured semi-quantitatively and classified into several product groups. The formation of these product groups from different feedstock samples with varying mass portions of their structural constituents (carbohydrates and lignin) was investigated at 500 °C and 700 °C with a residence time of 5 s and 20 s. The main product groups were aliphatic compounds, such as lactone, furan, and cyclopentenone derivatives from carbohydrates (mainly hemicelluloses) and aromatic compounds, such as guaiacol, phenol, and syringol derivatives from lignin. Additionally, the formation of aliphatic and aromatic products (e.g., the ratio of aliphatic compounds to aromatic compounds) was found to be characteristically dependent on feedstock composition and pyrolysis conditions. This kind of approach is of practical importance concerning efforts not only to uncover new integrated biorefinery possibilities to manufacture value-added products but also to develop rapid characterization tools for lignocellulosics.

## 1. Introduction

Due to many reasons, the rapidly increasing utilization of lignocellulosic feedstocks for producing renewable energy and chemicals, especially a variety of various non-wood materials, is in progress [1–7]. At the same time, more effective use of more versatile biomass resources is of great importance. One of the most promising integrated biorefining approaches, mainly utilized for the partial recovery of wood-derived carbohydrates, is based on different pre-treatment processes [8–14], such as hot-water extraction conducted prior to delignification [15–22]. Typically, by such pre-treatments, it is possible to obtain potential by-streams and simultaneously increase the reactivity of feedstock material, resulting in enhanced pulping performance together with spent liquors that have attractive chemical compositions. Hence, by these kinds of integrated biorefinery concepts, the efficient utilization of all major feedstock constituents (cellulose, hemicelluloses, and lignin) can be considered when planning target-oriented economic processes for the manufacture of useful products from fibrous lignocellulosics.

Non-wood based raw materials, such as annual crops, can be applied as an effective fibrous alternative to the decreasing forest wood resources in most developing regions [5,23]. Potential agricultural feedstocks, such as okra (*Abelmoschus esculentus*) and miscanthus (*Miscanthus* x *giganteus*, a hybrid of *M. sinensis* and *M. sacchariflorus*) stalks, may offer interesting raw materials for lignocellulosic biorefineries. Okra is one of the most important vegetables and is widely grown from Asia to Africa, Southern Europe, and America. Its edible green seed pods play an essential role in the human diet by supplying carbohydrates, minerals, and vitamins [24–26]. Post-harvest okra stalk residues have traditionally been an unused fraction of the total harvest, although their utilization for fiber in pulps [27,28], composites [29], and ethanol production [30] has been studied to some extent. In contrast, miscanthus, as a commercial energy crop, is currently of great importance in the sustainable production of biofuel products and chemicals due to its vast production worldwide and its high dry-matter yield [31–36]. Hence, its thermochemical behavior has also been studied [37–40], for example, together with the suitability of its fiber for paper production [41,42]. However, only a limited amount of data on the detailed chemical composition of okra and miscanthus stalk is still available.

Pyrolysis is one of the thermochemical conversion methods of

* Corresponding author.
*E-mail address:* maryam.m.ghalibaf@jyu.fi (M. Ghalibaf).

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biomass carried out in the complete or near complete absence of an oxidizing agent (air or oxygen), typically at 500–700 °C to provide complex fractions of gases, condensable liquids (tars), and char (solid residue) [43]. In our earlier papers, we studied the thermochemical behavior of silver birch (*Betula pendula*) [44] and Norway spruce (*Picea abies*) [45] sawdust, both untreated and after various chemical treatments (hot-water extraction, delignification, and hot-water extraction followed by delignification), by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). In each case, major GC-amenable condensable products were determined and classified into several compound groups, characteristically originated from the main structural constituents (cellulose, hemicelluloses, and lignin) of these wood materials. In this comparative study, the aim was to use the untreated and analogously treated non-wood feedstocks, okra, and miscanthus stalks for the same purpose by utilizing the treatment conditions suitable for these raw materials. Also, in this case, the suitability of this analytical pyrolysis method was investigated under varying pyrolysis conditions as a rapid tool for roughly detecting changes that took place during different treatments in the relative content of each constituent of the feedstock samples.

## 2. Materials and methods

### 2.1. Feedstock materials and their analyses

The untreated (okra, $O_{ref}$ and miscanthus, $M_{ref}$) and hot-water-extracted (HWE) okra and miscanthus stalks ($O_{HWE}$ and $M_{HWE}$, respectively) (< 5 mm) and the soda-anthraquinone (AQ)-cooked pulps of these feedstocks ($PO_{ref}$, $PO_{HWE}$, $PM_{ref}$, and $PM_{HWE}$) were investigated.

Hot-water extraction (140 °C for 60 min) and the soda-AQ cooking experiments were carried out in a laboratory-scale, oil-heated batch digester (CRS Autoclave System 420, CRS Reactor Engineering AB, Stenkullen, Sweden) equipped with 1.25-L rotating stainless-steel autoclaves [46–48]. The HWE feedstock obtained was thoroughly washed with tap water, and the amount of the solid residue ("yield") was calculated on the basis of oven-dried (o.d.) initial and HWE material. The yields of hot-water extraction were 85.6% ($O_{ref} \rightarrow O_{HWE}$) and 95.2% ($M_{ref} \rightarrow M_{HWE}$).

The cooking conditions were as follows: alkali (NaOH) charge 20% (okra) and 15% (miscanthus) on o.d. feedstock, AQ charge 0.05% on o.d. feedstock, cooking temperature 165 °C, cooking time 180 min (okra) and 60 min (miscanthus), and liquor-to-feedstock ratio 5 L $kg^{-1}$. At the end of each cook, the autoclaves were removed from the oil bath and cooled rapidly with cold tap water. The spent cooking liquor (black liquor) was then separated from the pulp by pressing it into a nylon-woven fabric bag. The pulp obtained was thoroughly washed with water, and the amount of removed organic material was calculated on the basis of o.d. initial and cooked feedstock. Pulp yields of the material charged into the reactors were 40.2% ($O_{ref} \rightarrow PO_{ref}$), 37.8% ($O_{HWE} \rightarrow PO_{HWE}$), 57.5% ($M_{ref} \rightarrow PM_{ref}$), and 60.3% ($M_{HWE} \rightarrow PM_{HWE}$).

For the chemical analyses, air-dried untreated and HWE samples and pulps were ground with a Retsch SM 100 cutting laboratory mill (Retsch GmbH, Haan, Germany) equipped with a bottom sieve with trapezoidal holes (perforation size < 1.0 mm) and stored in plastic bags. Prior to analyses, the moisture content was determined according to TAPPI T264 cm-97 standard in an oven at 105 °C. All analyses were carried out with two parallel samples, and the results were calculated as percentages of the dry sample.

The extractives content of the ground samples (about 1.5 g) was determined according to TAPPI T280 pm-99 standard with acetone in a Soxhlet apparatus (extraction time 4 h with 6–10 percolations per hour). The extract was concentrated nearly to dryness by vacuum evaporation with a rotary evaporator (Heidolph VV2000, Gemini BV Laboratory, Apeldoorn, The Netherlands), and drying was finalized before weighing using a gentle nitrogen stream.

Acid hydrolysis of the extractives-free ground samples was performed according to TAPPI T249 cm-00 standard. The lignin content of the extractives-free ground samples was calculated as the sum of the "acid-insoluble (Klason) lignin" and the "acid-soluble lignin" according to TAPPI T222 om-98, T249 cm-00, and T250 UM standards. The acid-soluble lignin content was determined with a Beckman DU 640 UV/Vis spectrophotometer (Beckman Instruments Inc., Fullerton, CA, USA) at 205 nm after quantitative dilution of the sulfuric acid hydrolysate; the absorptivity value was 120 L $(gcm)^{-1}$ [49].

The content of different monosaccharides (i.e., arabinose, galactose, glucose, mannose, and xylose) in the Klason hydrolysates and free monosaccharides in the hot-water-extraction hydrolysates were analyzed with high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD, from the Dionex Corp., Sunnyvale, CA, USA) [50]. A Dionex CarboPac PA-1 column (250 mm × 4 mm inner diameter) was applied to the separation of different monosaccharides at a flow rate of 1.0 mL $min^{-1}$. A post-column alkali (300 Mm NaOH) addition was utilized at a flow rate of 0.2 mL $min^{-1}$ to increase the performance of PAD. The peak identification and the mass-based response factors between an internal standard (L-fucose) and each monosaccharide were collected from separate runs with model monosaccharides. The content of the carbohydrates in acid hydrolysates was determined based on the anhydro forms of the measured monosaccharides. Moreover, a slight decrease (about 5%) in the yield of monosaccharides during acid hydrolysis, which resulted from different side reactions (e.g., the formation of furans), was considered.

### 2.2. Pyrolysis experiments and product analysis

About 0.5 mg of samples were pyrolyzed in a quartz tube (3.0 cm × 1.0 mm inner diameter, between quartz wool) at a heating rate of 20 °C $(ms)^{-1}$ using a CDS Pyroprobe 1000 resistively heated coil filament pyrolyzer coupled to an HP 5890 II gas chromatograph (Py-GC, Hewlett Packard Company, Wilmington, NC, USA). The column was a ZB-35HT (Inferno) capillary GC column (30 m × 0.25 mm with a film thickness of 0.25 μm). The GC oven temperature program in the analyses of pyrolysis products was as follows: 2 min at 40 °C, 4 °C $min^{-1}$ to 190 °C, 10 °C $min^{-1}$ to 320 °C, and 10 min at 320 °C. Helium was used as carrier gas with a gas flow rate of 1 mL $min^{-1}$ and as an inert atmosphere in the pyrolysis interface. The pyrolysis temperatures were 500 °C and 700 °C, and, in each case, the temperature was kept constant for both 5 s and 20 s. Detection was carried out with an HP 5970 mass spectrometric detector under electron ionization (70 eV). In addition, mass spectra were recorded at a rate of 2.92 scan files per second in the 30–550 m/*z* interval.

For the identification of chromatogram peaks, the proper interpretation of the mass spectra (based on the National Institute of Standards and Technology [NIST] mass spectral library) was used. Quantitative analysis was conducted based on duplicated injections according to our earlier study [44] so that pure compounds (the total number was 27) were used as external standards to relatively quantify all the 60 identified peaks from pyrolysis products (Py-GC/MS) by comparing the products to a set of standard samples of known concentration.

## 3. Results and discussion

### 3.1. Raw materials

The main chemical components (and their building blocks) in non-wood feedstocks are basically the same as those in wood feedstocks (resembling primarily hardwoods) and can be found in varying amounts depending on species (genetic differences), growing conditions, and presence of specialized tissues within individual plants [5]. However, it is still possible to detect considerable differences, for example, in both the content and composition of hemicelluloses between