



Multi-technique characterization of fast pyrolysis oils



Nadège Charon^{a,*}, Jérémie Ponthus^a, Didier Espinat^a, François Broust^b, Ghislaine Volle^b,
Jérémy Valette^b, Dietrich Meier^c

^a IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP3, 69 360 Solaize, France

^b CIRAD, TA B-DIR/09, Avenue Agropolis, 34 398 Montpellier Cedex 5, France

^c Thünen Institute of Wood Research (TI), Leuschnerstr. 91, D-21031 Hamburg, Germany

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ABSTRACT

In this study an analytical multi-technique approach was developed in order to describe as fully as possible the composition of several fast pyrolysis oils. Six bio-oils were produced at CIRAD (centre de Coopération Internationale en Recherche Agronomique pour le Développement) and TI (Thünen Institute of Wood Research) using the same three lignocellulosic biomass materials (*i.e.* hardwood, softwood and wheat straw). Different and complementary analytical tools were used to characterize these samples. Whole bio-oils were first directly analyzed by gas chromatographic (GC) hyphenated techniques with flame ionization detector (FID) and mass spectrometry (MS) (Headspace-GC-FID/MS, GC-FID/MS) and by a high resolution mass spectrometry technique (Fourier transform ion cyclotron resonance mass spectrometry FT-ICR/MS) without any pre-separation step. The GC analyses provide a detailed molecular description (more than 90 compounds) of the composition of the six bio-oils. To achieve a better understanding of the chemical composition of this set of bio-oils, the samples were fractionated into aqueous fractions and water-insoluble fractions (also called pyrolytic lignins). Detailed analysis of sugars was performed by GC-FID/MS after a solid-phase extraction (SPE) and a subsequent derivatization performed on the aqueous fractions. Moreover, FT-ICR/MS analyses show that species having molecular weights up to 900 Da are present in the aqueous phases. The originality of this work is based on the development of complementary analytical tools (*i.e.*, chromatographic and spectrometric techniques) to describe the composition from volatiles (monomeric) to non-volatiles (oligomeric) species of several bio-oils that were produced and stored under controlled conditions.

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1. Introduction

Nowadays diversifying energy supplies has become a major issue to tackle the greenhouse effect causing climate change as well as to alleviate the transport sector's reliance on oil. Transformation of biomass offers a promising alternative route to produce fuels, chemical intermediates and energy. Fast pyrolysis is such a thermochemical pathway that enables the liquefaction of lignocellulosic material (wood, straw, ...) to produce bio-oils which might be potentially upgraded into biofuels by further processing [1,2]. Production of fast pyrolysis oils at an industrial scale has been demonstrated, but nevertheless it has so far not been adopted in commercial practice [3]. Chemical characterization of such liquids is still a challenge today although a high number of papers

dealing with this topic have been published for many years now. Several round robins have been organized in the past [4–6], revealing difficulties to get consistent results to describe the oil's chemical composition. There is a lack of standard method being available to date for that kind of products. A large number of chromatographic and spectroscopic techniques has been used in literature to describe the chemical properties of biomass fast pyrolysis oils. For instance high resolution mass spectrometry has demonstrated that bio-oils are composed of oxygenated compounds distributed over a wide range of polarities and molecular weights. In recent years increasing attention has been paid to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS), a high resolution mass spectrometry technique that provides comprehensive information about bio-oils composition through measurement of double bonds equivalents (DBE), molecular weights and chemical formulas [7–14].

Gas chromatography (GC) and more recently comprehensive gas chromatography (GC × GC) have been also widely investigated to

* Corresponding author.

E-mail address: nadege.charon@ifpen.fr (N. Charon).

get a molecular description of bio-oils [15–21]. On the contrary the use of headspace-SPME (solid phase micro-extraction) as a sample preparation step, not combined with pyrolysis, to measure volatile compounds present in bio-oils is rather scarce [22–26]: study performed by Tessini et al. deserves interest as they focused on quantitative determination of the main aliphatic aldehydes (*i.e.*, formaldehyde, acetaldehyde and propionaldehyde) in a bio-oil by using GC/MS analysis preceded by on fiber derivatization SPME [25].

Even if gas chromatography is now largely used, however few data are available to compare the detailed and quantified composition of bio-oils produced in different pyrolysis conditions or from different biomass feedstocks such as wheat straw, hardwoods and softwoods. Published some years ago, the review from Milne et al. established based on literature data a detailed list of compounds that have been quantified in bio-oils at levels greater than 0.1% on wet basis using several analytical techniques and pyrolysis systems [31]. The authors indicated that combined effects of feed, pyrolysis method and pyrolysis conditions (assuming collection, storage and methods of analysis are comparable) do lead to reported differences of factors of 5–10. More recently, a round robin organized by IEA-EU provided molecular and quantitative results of four bio-oils but focused on the analytical results and not on the comparison of chemical compositions [6]. Nevertheless, to our knowledge, the relationship between pyrolysis conditions, biomasses and products quality has not been yet clearly described in literature. To go further on, in this work six bio-oils have been produced using two different pyrolysis systems. In both configurations, the same feedstocks were used: a hardwood material, a softwood material and a wheat straw material. In this way production and storage conditions of the pyrolysis liquids are well documented. A multi-technical approach involving complementary analytical tools (*i.e.*, gas chromatographic hyphenated techniques with flame ionization detector (FID) and mass spectrometry (MS): headspace-GC-FID/MS, GC-FID/MS and FT-ICR/MS) has been applied on the six bio-oils and the chemical compositions are compared and discussed.

2. Material and methods

2.1. Lignocellulosic materials

Three feedstocks were used to produce the bio-oils: hardwood (beech wood), softwood (spruce wood) and wheat straw. Both woody biomasses were purchased from Rettenmaier & Söhne GmbH (Germany): a hardwood mixture with 1.2–1.8 mm particle size (Lignocel Grade HBK 750–2000) and a softwood mixture with 0.2–3.15 mm particle size (Lignocel S 8/15 Granulat). Wheat straw was supplied by KIT Karlsruhe (Germany). Moisture contents measured at 105 °C were 7.3 wt%, 8.3 wt% and 7.8 wt% (on a raw basis) for hardwood, softwood and wheat straw materials, respectively. Ash contents measured at 600 °C were 0.76 wt%, 0.44 wt% and 5.3 wt% (on a dry basis) for hardwood, softwood and wheat straw materials, respectively.

2.2. Fast pyrolysis systems for bio-oil production

From each biomass, bio-oils were produced with two different bench-scale fast pyrolysis units. Both consisted of fluidized bed reactors, with continuous biomass feeding system, cyclone char-separator system, bio-oil condenser, light-organic trap and finally gas to vent.

The first unit (based at CIRAD and called FP1 in the paper) was 1 kg/h throughput. The reactor consisted of a stainless steel fluidized bed (80 mm i.d. and 530 mm height), with silica sand (600–700 µm particle size) as bed material. The reactor was heated

to 500 ± 10 °C by three adjustable electric heaters and was fed by a continuous and controlled flowrate of biomass, through a two-screws feeding system. The fluidizing gas was nitrogen (1.9–2.4 m³/h at standard temperature and pressure depending on the feedstock), pre-heated to the reactor temperature. The char particles were separated from the hot gas stream by two cyclones traced at 400 °C and collected in vessels which were weighed after experiment. The bio-oils were collected from a condensation train consisting of a quenching column (using Isopar™ as cooling agent) and an electrostatic precipitator. A dry-ice condenser and a cotton wool filter trapped the remaining light vapors. The non-condensable gases were finally sampled and analyzed by micro-GC to determine their composition and mass. At the end of the experiment, the bio-oil was separated by decantation from the Isopar™ V and weighted.

The operating conditions were the same for all runs, except the biomass flowrate which was decreased for straw (0.25 kg/h against 1 kg/h for wood) due to its lower bulk density. As a consequence, the required quantity of bio-oil could be produced from one single run of each wood feedstock while three successive runs were necessary to accumulate enough bio-oil from straw (Table 1); the bio-oil yields were higher for wood biomass (69 and 74 wt% respectively for hardwood and softwood) than for straw (58 wt%, cumulated yield). Such a yield decrease is typical of agricultural residues, due to their high ash content, as already reported in the literature. Water contents measured for bio-oils produced from hardwood, softwood and straw were 30.4, 30.0 and 42.8 wt%, respectively.

The second fast pyrolysis unit (based at TI and called FP2 in the paper) has a throughput capacity of 0.3 kg/h. The fluidized bed reactor was a stainless tube (41 mm i.d. and 305 mm height). The bed material was silica sand (particle size 300–500 µm) which was fluidized by preheated nitrogen. The reactor was first preheated to 475 °C and then continuously fed with about 250 g/h through a vibrator-agitated hose connected to a small screw conveyor. During pyrolysis, the reactor temperature was controlled and maintained at predetermined optimum temperature of 465–470 °C, with pressure drop of 8000 Pa. The char was separated from the vapors in a heated cyclone and collected in a glass flask. The vapors were rapidly quenched in the first condenser (ethanol-cooled at 2 °C) and the remaining aerosols were trapped in an electrostatic precipitator operated –5 kV. Both condensates were collected together in a single flask to give the bio-oil. The outlet gases passed through a second jacketed coil condenser held at –30 °C with ethylene glycol to further trap condensable light organic components. The non-condensable gas was passed into vent without analysis. The condensers, reactor sand, electrostatic precipitator, and all product collectors were weighed before and after pyrolysis. Due to the lower maximum throughput of this unit, several consecutive runs (5–10) were necessary to produce from each feedstock enough bio-oils for analyses.

Hardwood and softwood-based bio-oils from both systems were homogeneous single phase liquids, while straw-based bio-oils were heterogeneous, with apparent phase-separation. This is also a well-known property of bio-oils produced from high ash-content feedstocks such as agricultural residues: alkali metals can act as catalyst for secondary cracking reactions, resulting in increased water

Table 1

Product yields (wt%, raw basis) measured on FP1 unit with hardwood, softwood and wheat straw. Straw-results are summed values obtained out of three runs.

Feedstock	Hardwood	Softwood	Straw
Bio-oils and condensates (incl. H ₂ O)	69.2	74.1	58.5
Char (incl. ash)	15.1	14.4	25.8
Gas	12.3	9.5	15.8
Total	96.6	98.1	101.3

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