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Determination of volatile organic compounds in eucalyptus fast pyrolysis bio-oil by full evaporation headspace gas chromatography

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ABSTRACT

This paper reports a full evaporation (FE) headspace gas chromatographic (HS-GC) method for the determination of the volatile organic compounds (VOCs) in bio-oil (i.e. methanol, ethanol, acetone, acetic acid and furfural). The method uses a 4 μL sample of bio-oil in a headspace vial (ca. 20 mL). Complete evaporation of the compounds was achieved after seven minutes at 90 °C. The method showed good precision and accuracy for methanol, ethanol, acetone and acetic acid. The recovery of furfural was low (74.3%). The results showed that the protocol can be applied for the determination of methanol, ethanol, acetone and acetic acid in bio-oil. Detection limits ranged from 0.13 to 0.16 μg. Acetic acid was the dominant analyte in the heavy bio-oil and light bio-oil analysis (113. 3 and 85.1 μg mg^{-1}, respectively), followed by methanol, ethanol, and acetone. The polymerisation of furfural was suspected as the cause of its poor quantification.

1. Introduction

Technologies for the use of plant biomass in the production of liquid fuels and the acquisition of new inputs are increasingly being developed. Among existing technologies, fast pyrolysis has been gaining prominence in bio-oil production. In Brazil, the fast pyrolysis process has been studied in pilot scale units, and eucalyptus (hardwood) biomass residues from the pulp and paper industry comprise the great majority of the raw materials used [1].

Fast pyrolysis is a process where thermal degradation of biomass occurs in the absence of oxygen, forming products in three fractions: solid (ash and charcoal); liquid (bio-oil); and gas (synth gas). The recovery and applications of some organic compounds of bio-oil have been studied for the production of energy, phenol-formaldehyde resins, nitrogen fertilizers, and for the recovery of chemicals (e.g. carboxylic acids, furfural, eugenol and syringol) for the petrochemical and food industries. The high abundance of VOCs (e.g. methanol, ethanol and acetic acid) may add a great value in the bio-oil (e.g. calcium salts of acetic acid may be used as environmentally friendly road de-icers), which makes their characterisation and absolute quantification important [1,2].

The identification and quantification of VOCs in bio-oil by gas chromatography (GC) with liquid injection requires highly technical sample preparation due to the complexity of the matrix (i.e. compounds with different molecular mass and physico-chemical properties). The full evaporation (FE) headspace (HS) technique is an interesting approach, since it may completely eliminate sample matrix effects [3], it is easy and quick to operate, and has great sensitivity [3]. In fact, the full evaporation technique has already been used for the determination of VOCs in different biomass matrices, although it has not yet been optimised [3].

Thus, the objective of the present work was to develop and optimise a simple FE-HS-GC method for the rapid determination of methanol, ethanol, acetone, acetic acid and furfural in bio-oil produced by the fast pyrolysis of eucalyptus mulch.

2. Experimental

2.1. Chemicals and samples

All chemicals used in the experiment were of analytical grade: ethanol (99.9%, Merck), methanol (99.8%, Vetec), acetone (99.9%, Vetec), acetic acid (99.9%, Merck) and furfural (99.0%, Sigma - Aldrich). Heavy bio-oil and light bio-oil were produced from eucalyptus mulch in a pilot-scale fluidised-bed fast pyrolysis (20 kg/h, 500 °C, 5 s, BioWare)

2.2. Apparatus and operations

All measurements were carried out using a 22.5 mL headspace vial, injecting 0.5 mL of vapour into an automatic headspace sampler (AOC-

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5000 Shimadzu), which was analysed by a capillary gas chromatograph (GC) with a flame ionization detector (FID, GC-2010 Shimadzu). The GC conditions were as follows: DB-624 UI capillary column (30 m × 0.25 mm × 1.40 μm), flame ionization detector at 300 °C, injector temperature of 200 °C using a split mode of 1:25. The GC oven was programmed from 40 °C (held for 7 min) to 70 °C at 10 °C min^{-1} (held for 6 min), to 110 °C at 10 °C min^{-1} (held for 5 min) and to 220 °C at 20 °C min^{-1} (held for 5 min). Helium was used as the carrier gas with a constant flow of 2 mL min^{-1}.

2.3. Optimisation and validation

The first goal was to assess the effects of temperature and time incubation during FE-HS-GC analysis using 5 μL of bio-oil. A central composite design (CCD) with three central points was used for the two factors: (i) headspace oven temperature in the range of 90 – 110 °C, and (ii) headspace incubation time in the range of 1 – 5 min (X10.2, Unscrambler). According to the screening evaluation results, time incubation (1 – 9 min) and sample size (1–25 μL) optimisation were performed separately. Linearity was assessed using external analytical curves (n = 2) prepared in water by adding different concentrations of a standard solution (final volume 4 μL) to a set of headspace sample vials and performing the FE HS-GC measurements for the contents in each vial. The limit of detection (LOD = 3 × Sσ) and the limit of quantification (LOQ = 10 × Sσ) were calculated from blanks (n = 7). The trueness was assessed using fortified oven dried bio-oil samples (60 °C, 2 weeks, n = 4, free-VOCs bio-oil samples were confirmed by FE analysis), since no standard method or certified reference material exists. The intra-day and inter-day validations were estimated by analysing three replicates at two QC levels for each compound on three different runs. The repeatability was assessed during the bio-oil analysis (n = 3).

3. Results and discussion

3.1. Initial characterisation of bio-oil by FE

Fig. 1A shows a chromatogram of the eucalyptus VOCs using the FE-HS-GC analysis of a 5 μL bio-oil sample. Good peak symmetry and resolution were obtained for the active components such as acetic acid, indicating the inertness and stability of the 6% cyanopropyl-phenyl stationary phase (DB-624 UI) for bio-oil analysis. This was not possible with other stationary phases tested (i.e. 70% cyanopropyl polysilphenylene-siloxane, 5% phenyl-methylpolysiloxane, 50% phenyl-methylpolysiloxane, polyethylene-glycol, 50% cyanopropyl-phenyl, results not shown). The presence of the target compounds was certified using standards and the comparison chromatogram is shown in Fig. 1B.

3.2. Conditions for FE headspace analysis

To study the parameters (time x temperature), headspace was used in the CCD with three central points (100 °C, 3 min). Among the parameters tested, it was observed that temperature and its interaction (time x temperature) was not significant for any of the

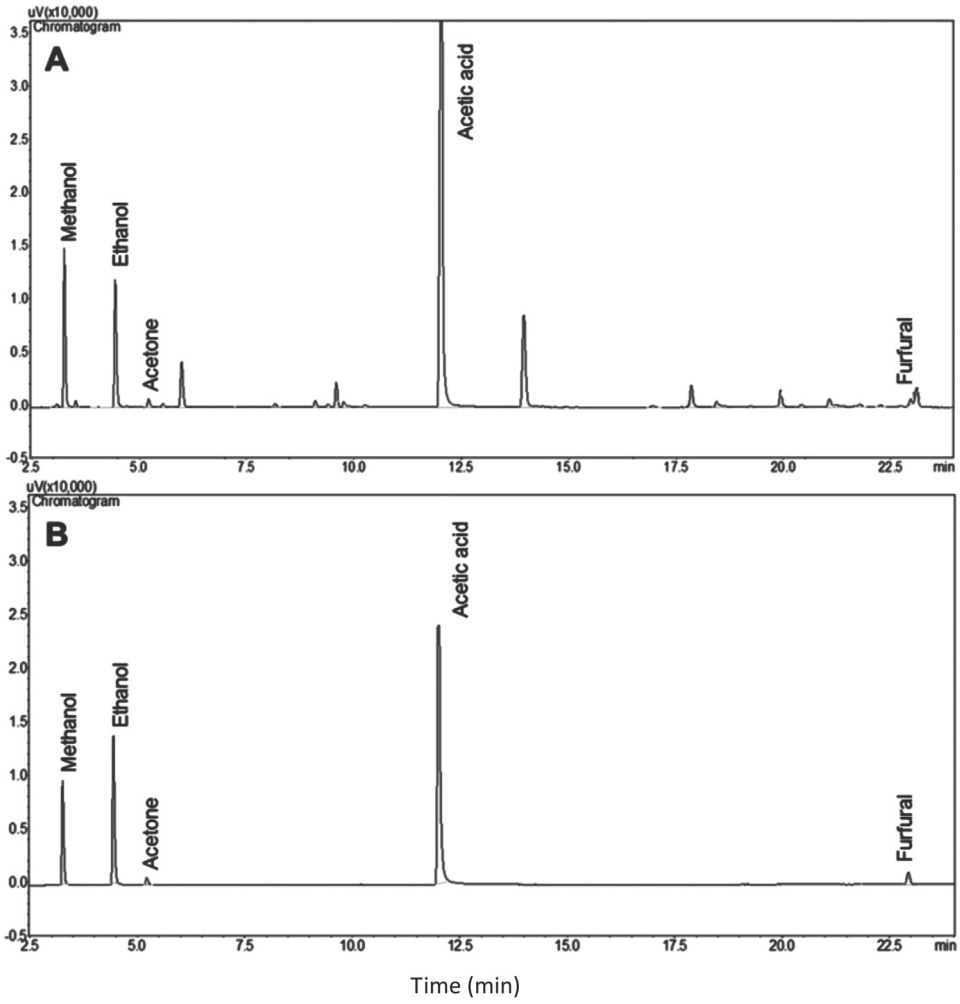

Fig. 1. Partial FE - HS - GC chromatograms of bio-oil (A) and standard mixture (B) samples. The standard solution consisted of methanol, ethanol, acetone, acetic acid and furfural in the following concentrations (v/v): 0.5; 0.5; 0.5; 5.0% and 0.1%. Headspace operating conditions were 5 min incubation at 110 °C.