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At-line characterisation of compounds evolved during biomass pyrolysis by solid-phase microextraction SPME-GC-MS

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ABSTRACT

At-line sampling by solid phase microextraction (SPME) followed by GC-MS analysis was investigated as a fast analytical method to identify and quantify the compounds evolved during intermediate pyrolysis of biomass. A 75 μm carboxen/polidimethylsiloxane (CAR/PDMS) coated fiber in retracted configuration was inserted at-line during pyrolysis at 500 °C with a bench scale fixed bed pyrolyzer of different biomass substrates, lignocellulosic feedstock, agricultural wastes, animal residues and algal biomass. The molecular composition resulting from SPME sampling was compared to the chemical composition of collected pyrolysis liquid, which included the aqueous and organic phase (bio-oil). The storage capacity of the SPME fiber was tested 48 and 96 h after sampling under air atmosphere and vacuum-packed plastic bags. The SPME-GC-MS profiles could be utilized to gather information on the characteristics of pyrolysis process, such as the efficiency of vapor condensation.

1. Introduction

Pyrolysis oil also known as bio-oil is a complex mixture of hundreds of polar and non-polar compounds formed during the thermal degradation of the main biomass components. Bio-oil composition varies depending on feedstock and process conditions [1–3].

Bio-oil contains approximately 20% water, 40% GC-detectable compounds, approximately 15% non-volatile HPLC-detectable compounds and 25% high molecular lignin [4–7]. Bio-oil from lignocellulosic biomass is mainly constituted by pyrolysis products originated from plant biomolecules (cellulose, hemicellulose, and lignin). Pyrolysis of lignin produces phenols and methoxyphenols (guaiacyl and syringyl moieties) while cellulose and hemicellulose give furans, aldehydes, ketones and anhydrous sugars (i.e. levoglucosan and anhydro xylopyranose, from cellulose and hemicellulose, respectively). This mixture of polar and non-polar compounds makes the chemical characterisation extremely difficult and laborious and requires the use of several analytical techniques (i.e. GC-MS, HPLC-MS, and GPC) and chemical procedures (e.g. derivatisation [8,9], solvent fractionation [10]).

The chemical characterisation at a molecular level is often accomplished by direct GC-MS of the oil (condensed organic fraction) dissolved in an appropriate solvent after pyrolysis has occurred. However, the large variety of constituents ranging from polar hydrophilic to highly hydrophobic compounds may render the choice of the appropriate solvent difficult as certain solvents are immiscible with certain constituents of the bio-oil. Moreover, the distribution of the pyrolysis products in different liquid fractions, generally a bio-oil and an aqueous solution is an additional analytical complication. This leads to inefficiencies in the spectrum of detectable compounds during GC-MS analysis. Therefore, knowledge of hot pyrolysis vapors could be useful to obtain information on the complete composition of the liquids before their condensation in the cold traps. A solvent-less technique capable of hot gas phase analysis such as solid phase microextraction (SPME) is ideally suited for this purpose.

Solid phase microextraction is a sample preparation and sampling technique developed by Pawlizny in 1990 [11,12] which has been employed on a wide range of analytes and for several applications in various research fields, such as environmental chemistry, forensic chemistry and pharmaceutical and food industries [13–17]. It allows a fast and solvent-free sampling and it is mainly applied coupled with GC-MS or other chromatographic techniques [18].

Previous works have shown SPME can be applied downstream of pyrolysis (Py-SPME) evolved by thermal desorption and pyrolysis, which de-couples the thermal conversion process and the GC-MS analysis, thus providing information on the actual composition of native vapors with simple and solventless technique [9,16]. Other works showed SPME application by derivatisation headspace SPME (D-HS-SPME) followed by GC-MS for determination of low molecular mass aldehydes in bio-oil [8].

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Several studies investigated the application of SPME for direct sampling of gaseous streams from thermochemical conversions, showing the potential of this technique for the on-line monitoring of plant operations [19–23]. This could be quite useful in the case of a distributed biomass/waste conversion schemes based on small scale intermediate pyrolysis where continuous quality control checks are necessary to ensure consistent final product.

Then, SPME sampling turns out to be a useful method as it is fast, solventless and able to give detailed information on the chemical composition of bio-oil. In addition, SPME could be coupled with several analytical techniques. Direct SPME-GC-MS analysis can give information on the volatiles and semi volatiles compounds. However, by proper derivatisation on headspace, SPME is also able to detect polar compounds (e.g. anhydrous sugars) [9].

Finally, being the fiber reusable, the costs can be reduced in high sample throughput [24].

The aim of this study is to evaluate the SPME sampling directly within the bench scale pyrolysis reactor in order to apply the SPME as *at-line* fast method for the characterisation of several pyrolysis products evolved during the pyrolysis process.

An in-depth literature review revealed that there are no studies using SPME-GC-MS as an analytical technique applied to a bench scale pyrolysis in order to evaluate the pyrolysis in order to obtain a comprehensive spectrum of pyrolysis vapors formed with detailed comparisons made condensate bio-oil post pyrolysis.

Furthermore, the storage capacity has been tested to evaluate its ability to accurately analyze products post experimentation.

In this study, captured products were stored for periods of 48 and 96 h in order to determine the accuracy of analysis after extended periods of time in storage, determined on a qualitative and quantitative basis.

2. Experimental

2.1. Feedstock

A pelletized solid digestate deriving from an anaerobic digestion plant operated by Neue Energie Steinfurt GmbH, Germany (NESt) using a mixture of maize silage (62%), cattle slurry (17%), pig slurry (17%) and cereals (4%) was used as a feedstock [25].

Other biomass samples were from woody (pine sawdust), herbaceous (switchgrass, cornstalk) [26], microalgae (Spirulina, *Arthrospira platensis*), animal residues (poultry litter) from a local poultry farm and agricultural wastes (olive residues).

2.2. At-line SPME sampling in a bench scale reactor

The SPME fiber tested was a 75 μm Carboxen/polidimethylsiloxane (CAR/PDMS) coated fiber (Supelco) used in retracted fiber configuration. Biomass samples (approximately 6–7 g) were pyrolyzed using a fixed bed tubular quartz reactor previously described [27] modified with the addition of a quartz T-junction for the SPME sampling (Fig. 1).

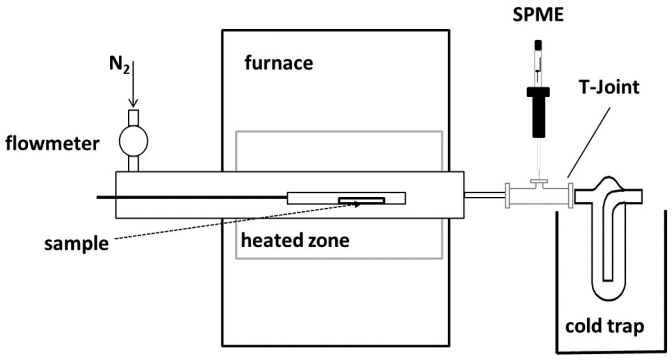

Fig. 1. Bench scale reactor with the addition of a quartz T-junction for the SPME sampling.

The SPME fiber was placed through a tee-joint in quartz upstream of the cold salt-ice trap (ca. −15 °C) where the oil was condensed. The pyrolysis experiments were performed at 500 °C for 5 min under nitrogen flow set a 1000 mL min^{-1}. At the end of the pyrolysis run the SPME fiber was promptly subjected to GC-MS analysis.

The pyrolysis liquid collected in the cold trap was centrifuged at 3000 rpm for 15 min to separate the low viscous aqueous phase (AP) from the tarry dark brown bio-oil (BO). The yields of the various fractions (char, aqueous phase and bio-oil) were determined by weight difference.

2.3. Analysis of pyrolysis liquid

The chemical composition of pyrolysis liquid was determined by solvent fractionation according to the method by Oasmaa and E. Kuoppala [28] slightly modified (ethyl acetate in place of ethyl ethers and lower sample amount).

After the separation into aqueous phase and bio-oil, 1 mL of aqueous phase was taken and added 9 mL of water. Then, the mixture was placed in the centrifuge at 3000 rpm for 10 min. The water insoluble fraction was determined by weight of the formed precipitate after centrifuge. The water soluble fraction was further extracted with 10 mL of ethyl acetate (1:1 *v/v*) in a separation funnel and let the solution to settle. The ethyl acetate solution was decanted from the bottom and evaporated in a rotary-evaporator at 40 °C. Concentration of the water soluble-ethyl acetate insoluble fraction was determined by BRIX method [10]. The same procedure was applied to the bio-oil using 1 g diluted into 10 mL of water.

The following fractions were quantified: water solubles, WS, divided into ethyl acetate soluble, EAS, (furans, phenols etc.) and insoluble, EAI, (sugars determined by the Brix method) and water insoluble, WIS, (pyrolytic lignin, extractives). The water content was determined by Karl Fischer titration.

Bio-oil elemental analysis was performed by combustion using a Thermo Scientific Flash 2000 series analyzer.

For bio-oil, GC-MS analysis was performed on 1% solution *w/v* in acetone/cyclohexane 1/1 *v/v* spiked with 0.1 mL internal standard solution (100 mg/L 1,3,5-tri-*terz*-butylbenzene), for the aqueous phase a 10% solution *v/v* in acetonitrile spiked with 0.05 mL internal standard solution (5000 mg/L butanoic acid, 2-ethyl).

2.4. GC-MS analysis

SPME and bio-oil analysis were performed with a 6850 Agilent HP gas chromatograph connected to a 5975 Agilent HP quadrupole mass spectrometer (EI 70 eV, at a frequency of 1.55 scan s^{-1} within the 10–450 *m/z* range). Analytes were separated by a HP-5 fused-silica capillary column (stationary phase poly [5% diphenyl/95% dimethyl] siloxane, 30 m, 0.25 mm i.d., 0.25 mm film thickness) using helium as carrier gas with the following thermal program: 50 °C with a hold for 5 min, then ramping up with a heating rate of 10 °C min^{-1} until 325 °C followed by a column cleaning at 325 °C for 10 min. SPME desorption was performed at 280 °C in the injection port in splitless mode.

The total sum area of GC detectable compounds was quantified in terms of absolute concentration using the internal standard.

A set of 27 compounds was quantified in terms of percentage relative abundance (% peak area to the total area).

All the experiments were run in duplicate. The precision was assessed by triplicate runs of SPME and bio-oil analysis of digestate sample and assumed to be representative of all biomass feedstock.

Percentage relative standard deviations (%RSD) were calculated for each pyrolysis product.

Aqueous phase analyses were performed with a Varian 3400 gas chromatograph equipped with a polar GC column (Agilent Q7221 J&W