



Application of off-line pyrolysis with dynamic solid-phase microextraction to the GC–MS analysis of biomass pyrolysis products

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ARTICLE INFO

Article history:

Received 19 April 2009

Received in revised form 30 May 2009

Accepted 30 May 2009

Available online 7 June 2009

Keywords:

SPME

Analytical pyrolysis

Biomass

Corn stalk

Sorghum

Poplar

Switchgrass

ABSTRACT

Pyrolysis coupled with dynamic solid-phase micro extraction (Py-SPME) followed by GC–MS analysis was applied to the determination of volatile compounds evolved by a micro-scale off-line pyrolysis apparatus, in order to extend the information affordable with this type of analytical equipment. The Py-SPME method with a carboxen/PDMS fiber working in the retracted mode was tested on four biomass samples (switchgrass, sweet sorghum, corn stalk and poplar) for qualitative analysis of semi-volatile pyrolysis products and quantitative determination of main volatiles (C_1 – C_4) pyrolysis products. The developed procedure allowed capturing and analysis of all GC analyzable compounds, without memory effects and with good peak resolution also for early GC-eluting compounds. Twelve main volatile pyrolysis products, including hydroxyacetaldehyde and acetic acid, were successfully quantified; in spite of the intrinsic variability introduced by dynamic SPME sampling, results were relatively accurate and consistent with literature data on bench pyrolysis reactors.

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1. Introduction

Pyrolysis allows the conversion of biomass into a liquid product, named bio-oil, pyro-oil and so forth, which can be used as feedstock for fuels and valuable chemicals [1,2]. Bio-oil is a very complex mixture containing many organic compounds which are formed by the thermal degradation of cellulose, hemicellulose, lignin and other bio-molecules originally present in vegetable biomass. The knowledge of the chemical composition of bio-oil is important for its use destination and eco-toxicological properties. A large portion of bio-oil (about 55%) is composed of semi-volatile products which are quantifiable through GC–MS, derivatization/GC–MS and HPLC [3]. These compounds are present at concentrations ranging from a few units percent by weight, such as acetic acid and hydroxyacetaldehyde, down to parts per million (e.g. polycyclic aromatic hydrocarbons), so that different analytical methods were developed to achieve a complete chemical characterization of bio-oil [4].

On-line pyrolysis, with the pyrolyser directly interfaced to GC–MS or MS systems, is the preferred configuration to study the pyrolytic behavior of biomass. This is a well assessed technique to quantify semi-volatile compounds evolved from pyrolysis [5,6]. The quantification of more volatile compounds is possible by means of a cryogenic trap [7], in order to avoid peak broadening caused by the intrinsic duration of the pyrolytic reaction (particularly longer with low temperature pyrolysis).

Main drawbacks of the on-line configuration are mass discrimination (mass transfer of heavier compounds is more difficult), poor chromatographic behavior of polar compounds, deterioration of GC column and memory effects caused by the presence of non-volatile compounds in the aerosol produced by pyrolysis [8].

Previous works have shown that off-line techniques, whereby pyrolysis products are captured by a sorbent and solvent eluted prior to instrumental analysis, can overcome memory effects, allow the application of different analytical procedures on the same pyrolysate and improve absolute quantification [9]. For example, silylation of pyrolysis products enabled accurate quantification of anhydrosugars which are important pyrolysis products of polysaccharides [10]. However, solvent elution needs time consuming steps (e.g. preconcentration), hampers quantification of most volatile compounds (e.g. methanol) and instable molecules (e.g. small aldehydes) [11].

Solid-phase microextraction (SPME) could be used as a solvent free technique for sampling pyrolysis products. Moldoveanu has recently investigated the use of SPME combined with pyrolysis [8]. Pyrolysis was conducted with a heated coil pyrolyser inside a glass sampling vial that was closed to perform SPME (static SPME). This method provided qualitative information on the pyrolysis products avoiding the use of solvents in the off-line configuration and GC column deterioration typical of on-line pyrolysis–GC/MS. The main drawback was the necessity of long sampling time in order to detect heavier pyrolysis products.

Sampling the gas flow in an open system could be an alternative approach of SPME yet to be investigated in analytical pyrolysis. This technique does not need the complete trapping of volatiles and

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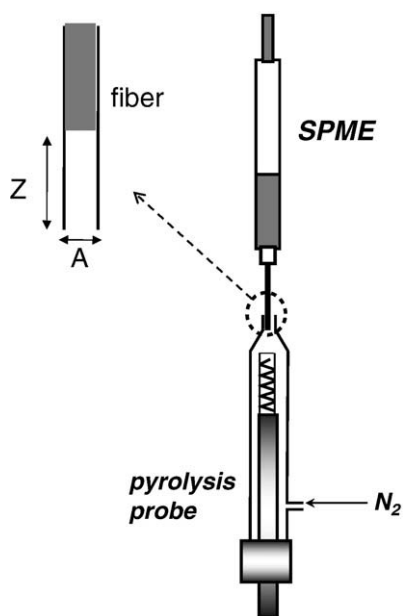


Fig. 1. Scheme of off-line pyrolysis equipment with SPME sampling and related dimensional parameters (Z , A see Materials and methods).

eliminates some of the problems of static SPME, like matrix effects, interaction with inner surface of the vial and long exposure times. This method has been applied for qualitative analysis of products evolved from synthetic polymers pyrolysed with a bench scale pyrolyser [12].

In order to perform a quantitative analysis, both equilibrium SPME and dynamic SPME can be used. In the former case the partition equilibrium of the analyte between the fiber and the gas is reached. On the contrary, in dynamic SPME, equilibrium must be avoided as long as possible, and calibration is performed using Fick diffusion law. The basic assumption when using Fick law is that the amount of analyte on the fiber is negligible with respect to that expected at equilibrium, and this condition should be respected during all sampling time (“zero sink” hypothesis) [13].

Equilibrium SPME was used for sampling the flue gas of a bench scale pyrolyser and different SPME fibers were tested with good results [14]. The main problem of equilibrium SPME, when applied to analytical off-line system, is the short sampling time needed in a small and discontinuous pyrolysis equipment. Dynamic SPME techniques, in spite of the “zero sink” hypothesis, need gas/fiber concentration ratios as much as possible far from equilibrium conditions; for this reason it is potentially more appropriate for the off-line pyrolysis configuration.

The aim of this work is to investigate the performance of SPME applied to off-line pyrolysis in the analysis of pyrolysis products of

biomass. Besides qualitative determination of all pyrolysis products amenable to GC analysis, the attention was focused on the quantitative determination of the more volatile fraction, that is C_1 – C_4 compounds.

2. Materials and methods

2.1. Biomass samples and chemicals

Biomass samples were kindly provided by Dr. Andrea Monti DISTA (Dipartimento di Scienze e Tecnologie Agroambientali) of the University of Bologna. All solvents, chemicals and standard were purchased from Sigma-Aldrich.

Table 1

Volatile products evolved from off-line pyrolysis of biomass samples quantified after SPME sampling and GC–MS analysis.

t_r^a	m/z^b	Structure	Compound name	D_i/D_{AA}^c	sensitivity ^d
1.32	30	<chem>O=O</chem>	Formaldehyde	1.41	57
1.38	31	<chem>O=O</chem>	Methanol	1.37	13
1.38	44	<chem>CC=O</chem>	Acetaldehyde	1.17	38
1.39	58	<chem>O=C=O</chem>	Glyoxal	1.02	14
1.55	58	<chem>CC(=O)C</chem>	Acetone	0.91	19
1.56	72	<chem>CC(=O)C=O</chem>	Methylglyoxal	0.91	6
1.86	31	<chem>O=CCO</chem>	Hydroxyacetaldehyde	1.00	47
2.16	60	<chem>CC(=O)O</chem>	Acetic acid	1.00	18
2.06	57	<chem>CC(=O)CC</chem>	3-pentanone	0.84	35
2.16	43	<chem>CC(=O)CO</chem>	Hydroxyacetone	0.90	37
5.23	43	<chem>CC(=O)OCC=O</chem>	Acetoxy-acetaldehyde	0.77	74
5.52	58	<chem>O=CCCC=O</chem>	Butanedial	0.84	17

^a Retention time in minutes.

^b Quantitation ion.

^c Ratio of molecular diffusion coefficient of analyte and acetic acid.

^d Sensitivity in M count s mg^{-1} is given by $\alpha_{AA} (D_{AA}/Fr(i) D_i)$ (see Materials and methods section).

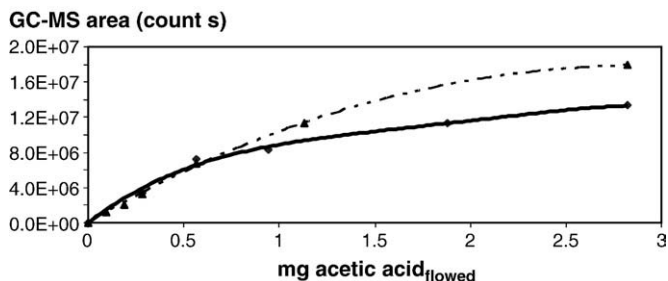


Fig. 2. Saturation behaviour of the CAR/SPME fiber in acetic acid spiked nitrogen flow (100 ml min^{-1} with acetic acid concentration of $2 \mu\text{g ml}^{-1}$) at room temperature (dotted line) and with heating coil at $700 \text{ }^\circ\text{C}$ (full line).

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