



# Lignocellulose pyrolysis with condensable volatiles quantification by thermogravimetric analysis–Thermal desorption/gas chromatography–mass spectrometry method



Frank Nsaful, François-Xavier Collard\*, Marion Carrier<sup>1</sup>, Johann F. Görgens, Johannes H. Knoetze

Department of Process Engineering, Stellenbosch University, Private bag X1, Matieland 7602, Stellenbosch, South Africa

## ARTICLE INFO

### Article history:

Received 19 May 2015

Received in revised form

26 September 2015

Accepted 4 October 2015

Available online 9 October 2015

### Keywords:

Pyrolysis

Thermogravimetric analysis

Thermal desorption

Condensable volatiles

GC–MS

Biomass

## ABSTRACT

A thermogravimetric analysis technique coupled to an evolved gas analysis, namely the thermal desorption/gas chromatography–mass spectrometry method (TGA–TD/GC–MS) was developed, to identify and quantify condensable volatile compounds produced during the pyrolysis of lignocellulose. Four lignocellulose samples of different origins (i.e., pine, bamboo, corn cob and corn stover) were pyrolysed using a TGA system. Condensable volatiles released during pyrolysis were captured onto thermal desorption tubes and subsequently identified and quantified using a TD/GC–MS method. Chemical composition of condensable volatiles was statistically correlated with the original lignocellulose composition, using Principal Component Analysis (PCA). A total of 15–19 wt% (dry weight) of biomass pyrolysis products were quantified by the method, with an average Relative Standard Deviation on the high concentration condensable volatiles yield of 6.4%, a significant improvement to what has been reported in literature. The first two principal components accounted for 89.4% of the variance in the data and showed clear correlations between evolved condensable volatile compounds and compositional differences among the four biomass samples. The origin of most lignin-derived compounds could be determined, due to the limitation of secondary reactions under slow pyrolysis. The yield of levoglucosan and 5-hydroxymethylfurfural were consistent with the initial content of C<sub>6</sub> sugars in the feedstock, but also negatively correlated with the ash content. The quantification of acetic acid, the highest yielding condensable volatile product, can be used as an indicator of the number of acetyl groups in biomass.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The over dependence on fossil based fuels for energy have resulted in the depletion of such resources. Coupled to this is the issue of global warming caused by the greenhouse gases (GHG) releases associated with the consumption of these fuels. To curtail these effects, research has focussed on the search for renewable and clean alternative sources of energy such as wind, solar, tidal wave, geothermal and biomass. Among these sources, biomass is the only renewable and sustainable carbon carrier [1], with the potential to

be converted into fossil-fuel-replacing liquid fuels, chemicals and synthetic materials [2].

The conversion of biomass into chemicals and fuels through thermochemical processes such as pyrolysis, combustion and gasification has gained much attention in recent years. Bio-oil, char and gas are the main products of pyrolysis and gasification processes [3,4]. Beside the use of pyrolysis for bio-oil and char production, the process is also a very critical first step in all thermochemical processes, including gasification and combustion [5]. For this reason, an understanding of feedstock pyrolysis properties and its impact on the conversion process is essential. This will lead to the effective design of competitive thermochemical processes for the production of fuels and chemicals from biomass, or biomass in combination with other feedstock such as coal.

Many studies have been conducted on the optimization of operating conditions (temperature, pressure, heating rate, residence time and particle size) for the efficient pyrolysis of lignocellulose. Others have focussed on thermal decomposition properties and

\* Corresponding author. Fax: +27 21 808 2059.

E-mail address: [fcollard@sun.ac.za](mailto:fcollard@sun.ac.za) (F.-X. Collard).

<sup>1</sup> Present address: Technological Development Unit (UDT), Universidad de Concepción, Av. Cordillera No. 2634–Parque Industrial Coronel 4191996, Casilla 4051, Concepción, Chile.

conversion pathways of the various biomass components [6–11]. At the milligram scale, the thermogravimetric analysis (TGA) method has been used to determine the pyrolysis kinetics and thermal stability of biomass, both important for large scale applications. The mechanisms of pyrolysis conversion have been studied with analytical techniques such as TGA coupled with mass spectroscopy (MS) or Fourier transform infrared spectroscopy (FTIR) [12–16]. These techniques have led to the continuous identification of functional groups that are present in the volatiles released during biomass pyrolysis. These, however, are only useful as qualitative results, without accurate quantification of the yields of volatile components from various feedstocks. Given the complex nature of biomass [17,18], many volatiles are produced at the same time during its thermal conversion, thus making quantification very difficult.

At the lab scale, the quantification of the pyrolysis bio-oil product is usually done by gas chromatography–mass spectroscopy (GC–MS) after dilution of the bio-oil in an organic solvent. However, for study at milligram scale with small biomass sample sizes, the use of solvents to recover volatiles would lead to trace amount which would be hard to quantify. The application of pyrolysis coupled to gas chromatography–mass spectroscopy (Py-GC/MS) method has proven to effectively analyse the volatiles generated from such small sample mass without the use of solvent [19]. However, Py-GC/MS does not allow one to combine volatiles production with the kinetics of biomass pyrolysis, as captured in time-wise mass loss.

The precise quantification of bio-oil requires the preparation of individual calibration curves for all the compounds of interest to be quantified. This is a tedious task and explains why in most bio-oil analyses using GC–MS or Py-GC/MS the quantification is done based on the surface areas/normalised surface areas of the peaks corresponding to the main compounds and not on calibration curves of these compounds, which is the only method to determine the actual yields. No absolute quantities of evolved volatiles components are provided thus the need of a quantification method for the effective analysis of biomass pyrolysis volatile components even on small sample sizes.

Thermal desorption/gas chromatography–mass spectrometry (TD/GC–MS) is a technique that allows for the analysis of small sample sizes of volatile compounds and eliminates the need for solvent [20,21]. It has found wide application in several environmental and workplace air monitoring studies [22–25] as well as wood thermodegradation studies [19,20] for the analysis of volatile organic compounds (VOCs). Although the coupling of TD/GC–MS to TGA for the characterisation of VOCs has been reported [26], the application of this technique to lignocellulose pyrolysis and quantification of volatile products, is limited. The merits of the method include adaptability to smaller sample sizes (milligram scale), and provision of additional TGA information regarding the thermal stability and mass loss kinetics during the main steps of thermal conversion [26]. Other advantages are that it eliminates the effect of solvent signal on analyte peaks in sample chromatograms and it is compatible with both polar and non-polar thermally stable compounds [24]. The disadvantages are that it is ineffective for analysing thermally unstable compounds and high boiling point (>300 °C) compounds, due to reduced desorption efficiencies on thermal desorption (TD) tubes, and generation of artefacts possibly due to sorbent degradation that might influence the analysis [24].

In this study we developed a method coupling thermogravimetric analysis with thermal desorption/gas chromatography–mass spectrometry herein referred to as TGA-TD/GC–MS. This was used to study the pyrolysis profiles of four biomass feedstocks (i.e. pine, bamboo, corn cobs and corn stover) and to quantify the distribution of condensable volatile compounds from these feedstocks. TGA was used to pyrolyse the biomass and the evolved volatiles were trapped on-line into TD tubes. The tubes were then analysed off-line

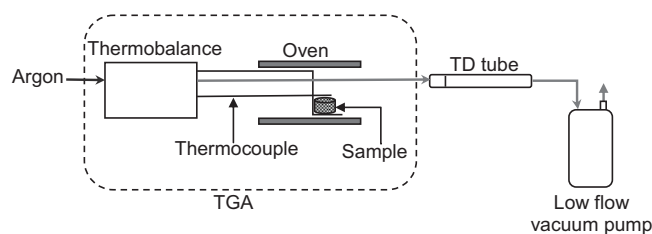


Fig. 1. Capture of volatiles generated by TGA onto TD tube.

by TD/GC–MS, enabling the identification and quantification of condensable volatile compounds (with internal calibration). The data generated were used to establish correlations between biomass composition and volatile yield among the four biomasses by means of principal component analysis (PCA).

## 2. Materials and methods

### 2.1. Feedstock preparation

The lignocellulosic biomasses used in this study were bamboo (*Bambusa balcooa*) (BB), pine (*Pinus radiata*) (PN), and two corn (*Zea mays*) residues; corn cobs (CC) and corn stover (CS). BB is often considered for energy applications because it is a fast growing species [27]. CC and CS are agricultural residues produced in large amounts in South Africa [28], while PN is also widely available in South Africa. BB was supplied from the Western Cape Province of South Africa. It was received wet and was air dried to moisture content of less than 10 wt% and then chipped into chips sizes of approximately 2 cm × 0.5 cm for further preparation. CC and CS were obtained from farms in the Northern Cape Province of South Africa. CC was obtained in whole pieces, while CS was shredded; both were received dried with about 7 wt% moisture. Pine was obtained in pellet form (5–25 mm length and 6–12 mm diameter, 4–8 wt% moisture) from EC Biomass Fuel Pellets (Pty) Limited, Eastern Cape, South Africa. The coning-and-quartering method (DD CEN/TS 14780:2005) was used to obtain sub-samples from each feedstock for experimental work. The biomass feedstocks were milled over a 2 mm screen in a Retsch mill (model ZM100) and sieved into various particle size ranges using a vibratory sieve shaker (model AS200). The 250–450 μm particle size range was selected for all TGA runs.

### 2.2. Biomass characterisation

Elemental and proximate analyses were done for all four biomass samples. A Leco TruSpec Micro CHNS was used to determine the elemental content of the samples, while proximate (volatile matter (VM), fixed carbon (FC) and ash content (AC)) analysis was determined by the ASTM method E1131 using TGA/DSC 1-LF1100 system (Mettler Toledo).

The chemical component of biomass consists of extractives, lignin and carbohydrates (mainly C<sub>6</sub> and C<sub>5</sub> sugar moieties). The standard methods NREL/TP-510-42619 and NREL/TP-510-42618 ([http://www.nrel.gov/biomass/analytical\\_procedures.html](http://www.nrel.gov/biomass/analytical_procedures.html)) were used to determine extractives, and lignin and carbohydrates respectively. For extractives, about 5 g of sample was extracted with distilled water in a Soxhlet apparatus for 24 h, after which the water extractive free sample was extracted with 95% ethanol solution (Scientific World SA) for a further 24 h. After extractives removal, approximately 0.3 g of the extractive-free sample was hydrolysed with approximately 3 mL of 72% (w/w) sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) (Fluka Analytical, Sigma–Aldrich) in a water bath at a temperature of 30 °C for an hour. The mixture was stirred intermittently

Download English Version:

<https://daneshyari.com/en/article/1197005>

Download Persian Version:

<https://daneshyari.com/article/1197005>

[Daneshyari.com](https://daneshyari.com)