



Relationship between thermal behaviour of lignocellulosic components and properties of biomass



Cheng Heng Pang^{a,c}, Sanyasi Gaddipatti^b, Gregory Tucker^b, Edward Lester^a, Tao Wu^{c,*}

^aDepartment of Chemical and Environmental Engineering, The University of Nottingham, University Park, NG7 2RD Nottingham, United Kingdom

^bSchool of Biosciences, Division of Nutritional Sciences, The University of Nottingham, Sutton Bonington Campus, LE12 5RD Leicestershire, United Kingdom

^cMunicipal Key Laboratory of Clean Energy Conversion Technologies, The University of Nottingham Ningbo China, Ningbo 315100, China

HIGHLIGHTS

- Biomass profiles are linked to individual lignocellulosic components.
- Biomass profiles change with the change in the lignocellulosic compositions.
- These profiles can be used as a rapid means of estimating lignocellulosic composition.

ARTICLE INFO

Article history:

Received 17 July 2014

Received in revised form 5 September 2014

Accepted 6 September 2014

Available online 21 September 2014

Keywords:

Lignocellulose

Thermal behaviour

Thermogravimetric analysis

Biomass

ABSTRACT

Five different biomass samples were selected for this study, including miscanthus, distillers dried grain (DDG), wheat shorts, wheat straw and UK wood. These samples were thermochemically treated to alter the lignin, cellulose and hemicellulose composition. Thermogravimetric tests were carried out on these samples to determine thermal behaviours of biomass and its individual lignocellulosic components. The relationship between thermal behaviour of biomass and its corresponding lignocellulosic composition was revealed. The reliability of this relationship was proved by thermogravimetric analysis of samples of artificial biomass prepared by mixing commercially obtained lignin, cellulose and hemicellulose at various blending ratios. It is shown that actual biomass profiles can be predicted with some degree of accuracy based on the lignocellulosic composition.

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1. Introduction

Biomass has the potential to be a clean and renewable source of energy (Ayhan, 2001). The organic substances in biomass can be converted into heat and power without contributing to CO₂ emission enabling biomass to function as a carbon-neutral source of energy (Ayhan, 2001; Pang et al., 2013). Therefore in the past decades, biomass has become increasingly important energy source (Pang et al., 2013) for power generation particularly in the European market where incentives and penalties have been applied through legislation due to the concerns on global warming.

Biomass differs from coal in terms of both chemical and physical characteristics including pyrolysis where biomass starts and ends more rapidly, relative to coal (Lester et al., 2007). On a dry, ash free basis, biomass can easily contain 70–80 wt% volatile matter as compared to coal with 10–50 wt% (Sami et al., 2001).

In addition, the high levels of oxygen-containing carbohydrate polymers in biomass also make its pyrolytic chemistries very different to that of coal. The pyrolysis of biomass is directly linked to the decomposition of cellulose, hemicellulose and lignin (Lester et al., 2007).

Analogous to coal having three major organic components of vitrinite, liptinite and inertinite, most biomass types have three main organic constituents: lignin, cellulose and hemicellulose. These three components make up to over 90 wt% of the plant cells dry weight (Glazer and Nikaido, 2007).

Cellulose is the principal component of plant cell walls, which is a polysaccharide with an empirical formula of (C₆H₁₀O₅)_n. Its molecules are linear chains of (1 → 4)β-linked-D-glucan and these long and thin molecules tend to hydrogen bond together to form microfibrils. Hemicellulose is a general term referring to a heterogeneous group of noncrystalline glycans or polysaccharides that are tightly bound in the cell wall. Some of the most common hemicelluloses are xylan, xyloglucan, glucomannan, arabinoxylan and glucuronoxylan. Lignin is the second most abundant organic substance in

* Corresponding author. Tel.: +86 574 88180269.

E-mail address: Tao.Wu@nottingham.edu.cn (T. Wu).

plants after cellulose. It is a highly branched polymer of phenylpropanoid groups, formed from the polymerisation of three monolignol monomers: the *p*-coumaryl, coniferyl and sinapyl alcohols.

Even though biomass has been used as an energy source in large scale for hundreds of years, there is still a need to fully understand the thermal behaviour of biomass in order to ensure its efficient and safe utilisation.

The significance of the lignocellulosic components on the behaviour of biomass can be seen in several previous works. Raveendran et al. (1996) predicted and correlated, to a good degree, the d.t.g. profiles of biomass during pyrolysis based on the amounts of lignin, cellulose and hemicellulose. Other workers (Singh et al., 2009) focused on the study of cellulose and lignin mixtures as artificial biomass. In their work, the amounts of lignin and cellulose were predicted based on the TGA (PUT) profiles. The influence of lignocellulosic components on other pyrolysis characteristics, such as gas yield, water release, reaction rates, etc. have been studied by other workers (Gani and Naruse, 2007; Worasuwannarak et al., 2007).

Currently, wet chemistry, a tedious and time-consuming method, is the only established and accepted means to determine the lignocellulosic composition (Singh et al., 2009). Other workers have also attempted to determine biomass composition via other means, including NIR spectrography (Hames et al., 2003; Kelley et al., 2004).

This study attempts to predict the lignocellulosic compositions (lignin, cellulose and hemicellulose) of biomass using the d.t.g. profiles of biomass. This would provide a quick, straight forward and cost effective means to replace wet chemistry method to characterise biomass.

More importantly, this study examines the thermal properties of lignin, cellulose and hemicellulose in biomass and their contributions to the thermal profiles of biomass using a thermogravimetric analyser (TGA). It is also one of the aims to understand and predict the characteristics of biomass during pyrolysis based on lignocellulosic composition of the biomass.

2. Methods

2.1. Sample preparation

Eleven biomass samples, including corn stover, distillers dried grains (DDG), distillers dried grains with solubles (DDGS), olive residue, wheat, wheat shorts, miscanthus, a UK soft wood, rapeseed, sunflower seed and wheat straw, were investigated in this study. These samples were chosen to show a range of lignocellulosic compositions.

Each sample was initially riffled four times, and then sieved into two size fractions: 212–300 micron and 500–1000 micron.

Miscanthus, a UK wood, DDGS, wheat straw and wheat shorts were chosen to undergo thermochemical treatment.

All profiles presented in this paper were plotted using 212–300 micron samples, although very similar trends were observed for the other size fraction tested (500–1000 micron).

2.2. Biomass pre-treatment

Lignin removal was achieved by treating the biomass samples with chlorine dioxide which was prepared in situ by mixing sodium chlorite and acetic acid at 70 °C. This method was originally described by Jayme (1942), Wise et al. (1946) and summarised by Green (1963).

Hemicellulose was removed using 17.5 wt% sodium hydroxide solution at room temperature for 1 h in a biomass to solution ratio of 1:50. Cellulose removal was achieved by treating the hemicellulose-deficient sample with acetic acid (0.1 ml to every gram of bio-

mass) and stirred for 15 min. The selective removal of cellulose was difficult without any prior pretreatment as the cellulose microfibrils tend to be encased within the hemicellulose, which in turn are closely associated with lignin (Ding and Himmel, 2006; Ishizawa et al., 2009). Mineral leaching was carried out by washing biomass samples in deionised water (1:50 ratio stirred for 1 h).

All pre-treatments in this study were done at a biomass to solution ratio of 1:50 with continuous mixing for 1 h. After which, treated samples were filtered out and washed with distilled water to remove any excessive chemicals, followed by drying at 60 °C overnight. All samples were then subjected to standard chemical assays to determine the amount of hemicellulose, cellulose and lignin (HCl). -Un was used to denote untreated sample; -L denoted lignin-deficient sample; -CH denoted cellulose and hemicellulose-deficient sample; -A denoted leached/washed sample; -H denoted hemicellulose-deficient sample.

Briefly, the amount of lignin was determined via the acetyl bromide method (Gomes et al., 2011). 10 ml of acetyl bromide in acetic acid (250 ml/l) solution was added to 100 mg of biomass samples and then heated in a water bath of 50 °C for 2 h with stirring at every 30 min interval. Upon cooling, the material was centrifuged at 2000×g for 15 min. About 0.5 ml of the solution was pipetted into a test tube containing 6.5 ml of glacial acetic acid and 2 ml of 0.3 M NaOH followed by adding 1 ml of 0.5 hydroxylamine hydrochloride solution. All contents were stirred.

Absorption spectra were determined for the samples. The absorption maxima at 280 nm were used to calculate lignin concentration using the equation suggested by Fukushima and Kerley (2011):

$$L = \frac{A - 0.0009}{23.077}$$

where L is the lignin concentration in mg/ml and A is the absorbance.

The concentrations of hemicellulose and cellulose were determined using the potassium hydroxide (KOH) fractionation method (Fang et al., 1999) after the removal of lignin (via the sodium chlorite method suggested by Ishizawa et al. (2009)). The hemicellulose was isolated by extraction using 20 ml of 4 M KOH at room temperature followed by precipitation of the hemicellulose using acetone. The hemicellulose was washed with ethanol and water, and then dried under vacuum at 60 °C. The unextracted residue is the cellulose.

It is noted that pre-treatment did not selectively remove the target component e.g. mineral leaching involves washing samples with distilled water and this can remove some extractives and hemicellulose (Couhert et al., 2009; Yang et al., 2006a). However it did appear to be a means to alter the initial lignocellulosic composition as a whole.

Commercially obtained lignin, cellulose and hemicellulose particles (Sigma Aldrich 8068-05-1, 9004-34-6, 8024-50-8) were mixed at different weight percentages to create artificial biomasses with different lignocellulosic compositions.

2.3. Thermogravimetric analysis

The thermal properties of samples were examined using the TA Q500 (TA Instruments Co.) thermogravimetric analyser (TGA). The TGA has a sampling rate of 90 readings per minute with an accuracy of ±0.5% determined by duplicate runs between samples.

All samples were heated in a TGA at a heating ramp of 10 °C/min to 900 °C. A nitrogen atmosphere was used to study the pyrolytic decomposition (volatiles loss) of biomass.

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