



## Comparative Thermal Heating Behaviour of Selected Lignocellulosic Biomass and their Model Constituents

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**ABSTRACT:** Hardwood (*Albizia pedicellaris* and *Terminalia ivorensis*) and non-woody (*Sorghum bicolor*) biomass resources from Nigeria and biomass model constituents (xylan, glucomannan, cellulose, and lignin) were subjected to isothermal heating at 275 and 297°C using a Thermogravimetric analyser (TGA). Xylan, a hardwood hemicellulose, had a higher mass loss of 68% at 275°C, while lignin was the least degraded at both temperatures. The rate of decomposition for all the biomass samples for the initial 20 min run into the TGA were similar as temperature was ramped from ambient to isothermal temperature. At isothermal heating, the thermal decomposition profile was influenced by variation in biomass composition. Temperature also played a major role as there was an increase in weight loss at an isothermal temperature of 297°C.

**Keywords:** Biomass; Isothermal; TGA; *Sorghum bicolor*; *Albizia pedicellaris*; *Terminalia ivorensis*

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### INTRODUCTION

The quest for the deployment of renewable energy (RE) resources is being driven by the gradual decline in fossil fuel reserves, fluctuation in the international oil market price and the global rise in energy demand. Notably, several developed nations have broadened their spectrum of energy mix to include an appreciable proportion of RE, and many more are seeking ways of attaining an optimal energy mix. For instance, in the United States of America (USA) (Schnepf, 2007), RE makes up 6.7% of their total energy production in 2006, while the European Union (European Union, 2008) aims at increasing the share of RE in the region to 20% by 2020. Among the known RE sources, lignocellulosic biomass has attracted global attention because of its carbon neutrality, huge

renewable potentials, wide geographical spread, and immense abundance as waste at a relatively inexpensive price (Naik et al, 2010; van der Stelt et al, 2011).

Unfortunately, in Nigeria, the deployment of RE sources are quite marginal and in some cases non-existent (Lukman, 2003). In fact, the utilisation of lignocellulosic biomass is largely in the form of fuelwood constituting more than 50% of the overall national energy consumption; in spite of the fact that their use is characterised by low thermal efficiency and obvious health challenges (Lukman, 2003). Furthermore, fuelwood are usually obtained from tree felling activities consequently exposing the environment to diverse environmental

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degradation From biomass audit, it was estimated that  $35.50 \times 10^6$  tonnes of woody and  $10.20 \times 10^6$  tonnes of non-woody residues are available across the country (Sambo, 2009). According to Mohammed et al, (2013), an FAO 2010 data also estimated that  $11.37 \times 10^6$  tonnes of sorghum stalk wastes were produced in Nigeria. More often than not, the management of the biomass waste is daunting (Lasode and Balogun, 2010), thus this waste may serve as prospective feedstock for various bioenergy applications and chemical extraction processes. There is a clear variation in the cell wall composition (polymer fractions) among various lignocellulosic biomass resources (Naik et al, 2010). The typical polymeric structure of lignocellulosic biomass comprises of hemicellulose, cellulose and lignin fractions and these differ distinctively along the lines of woody and non-woody classification. This

variation consequently influences the thermal behaviour of biomass as each polymeric component possesses a peculiar decomposition pattern (van der Stelt et al, 2011; Moon et al, 2013). Prins et al, (2006) compared the thermal decomposition of different biomass of beech, larch, willow and straw, and some model constituents, xylan and cellulose, using isothermal thermogravimetric analysis (TGA). It was found out that the reactivity of the individual biomass sample was a function of the proportion of the model constituents that made up each biomass. In this paper, some tropical hardwood species and agricultural samples in comparison with some model constituents have been selected for isothermal TGA experiments. The primary objective of this work is to study the thermal decomposition behaviour of the biomass samples in relation to the model constituents.

## MATERIALS AND METHODS

### Sample preparation

*Sorghum bicolor* (guinea corn) glume (SBG) and stalk (SBS), non-woody samples were obtained from a farm site ( $8^{\circ} 37' N, 4^{\circ} 46' E$ ), while *Albizia pedicellaris* (AP) and *Terminalia ivorensis* (TI), hardwood samples, were obtained from a timber processing plant ( $8^{\circ} 27' N, 4^{\circ} 35' E$ ), in the city of Ilorin, Nigeria in December 2012. The samples were prepared according to the procedure outlined in an earlier publication (Balogun et al, 2014a; Balogun et al, 2014b). Model constituents namely konjac glucomannan (GLUM) (FMC Biopolymer, USA), oats spelt xylan (XYL) (MP Biomedicals, USA), microcrystalline cellulose (CEL) (FMC Biopolymer, USA) and protobind 1000 lignin (LIG) (Granit RD SA-A GreenValue, USA) were obtained commercially for use.

### Sample characterisation

The characterisation exercise, which included proximate, elemental, compositional analyses and higher heating value (HHV) determination were conducted according to a detailed description by Balogun et al, 2014a and Balogun et al, 2014b.

### Thermogravimetric analysis

TGA experiments were conducted on a Perkin Elmer TGA-7 (Massachusetts, USA) instrument under an initial dynamic and isothermal (ramped from  $30^{\circ}C$  to  $275^{\circ}C$  and  $297^{\circ}C$  at  $20^{\circ}C/min$ ) conditions purging with  $N_2$  ( $30 mL/min$ ). Data were analysed using the Pyris v8 software. Prior to TGA experiments, biomass samples were vacuum-dried at  $-762 mmHg$  for 12 h in a vacuum oven (VWR 1410) attached to a  $0.071 m^3/min$  vacuum pump.

## RESULTS AND DISCUSSION

The data from proximate, elemental and compositional analyses and HHV determination as discussed by Balogun et al, (2014b) is shown in Table 1. It was observed that the proportion of the most reactive fraction, hemicellulose, was relatively more in non-woody biomass (SBG (45.2%) and SBS (39.1%)) when compared with woody biomass (AP (14.7%) and TI (13.3)), while the reverse was found to be true for the total lignin content. Significantly, SBG had the highest ash content of 7.54% as observed by Balogun et al, (2014b). These compositional variations are expected to influence the thermal degradation process of the respective biomass species.

Figures 1 and 2 show the heating thermograms ramped from ambient temperature of about 30°C to a final heating temperature of 275°C for the model constituents and biomass samples respectively. The initial 20 min may be regarded as a warm-up phase in which moisture evaporation was largely experienced Prins et al,

(2006). The significance of the initial 20 min run into the TGA is that the samples underwent a thorough dehydration process thus providing an opportunity for comparison on dry-basis. Beyond 20 min, the samples were subjected to a constant temperature (isothermal heating) for an hour. For the model constituents in descending order, xylan (a hardwood hemicellulose) experienced the highest weight loss (68%) at 275 °C. This is because hemicellulose is the most reactive fraction of biomass. Lignin, however, experienced the least weight loss (29%) because it is the most stable of all the biomass fractions (Burhenne *et al.*, 2013).

In Figure 2, all the biomass samples showed a fairly similar thermal behaviour at the warm-up phase; here they experienced an average of 10% weight loss. SBS, a non-woody biomass, had the highest weight loss of all the biomass samples at 275°C but SBG occupied second position in the decomposition order in terms of the least weight loss. This may be due to the

**Table 1: Proximate, Elemental, and Compositional Analyses, and Heating Value of Biomass Samples**

|   | Woody Biomass |            | Non-woody Biomass |            |
|---|---------------|------------|-------------------|------------|
|   | AP            | TI         | SBG               | SBS        |
| <b>Proximate analysis</b>                     |               |            |                   |            |
| Ash Content <sup>a</sup> (%)                  | 1.68±0.01     | 0.32±0.05  | 7.54±0.21         | 3.25±0.57  |
| Fixed Carbon <sup>b</sup>                     | 5.61±0.36     | 17.40±0.57 | 13.60±0.25        | 13.80±0.96 |
| <b>Elemental Analysis <sup>a</sup></b>        |               |            |                   |            |
| Carbon (%)                                    | 51.7±0.3      | 48.6±0.3   | 42.4±0.4          | 46.2±0.1   |
| Hydrogen (%)                                  | 5.85± 0.38    | 6.00±0.20  | 5.27±0.25         | 5.85±0.44  |
| Nitrogen (%)                                  | 0.54± 0.03    | 0.44±0.00  | 0.74±0.06         | 0.44±0.01  |
| Oxygen (%) <sup>b</sup>                       | 41.9±0.7      | 45.0±0.5   | 51.6±0.7          | 47.6±0.6   |
| <b>Compositional Analysis <sup>c</sup></b>    |               |            |                   |            |
| CH <sub>2</sub> Cl <sub>2</sub> extracts (%)  | 16.9±0.1      | 1.10±0.02  | 0.31±0.55         | 0.74±0.15  |
| Hemicellulose (%)                             | 14.7±0.1      | 13.3±0.1   | 45.2±0.2          | 39.1±0.1   |
| Cellulose (%)                                 | 32.3±0.1      | 41.0±0.2   | 28.2±0.1          | 35.8±0.1   |
| Acid Insoluble (Klason) Lignin (%)            | 31.2±0.2      | 37.0±0.2   | 18.2±0.1          | 20.9±0.1   |
| Acid Soluble Lignin (%)                       | 1.2±0.1       | 2.6±0.2    | 2.3±0.1           | 1.9±0.2    |
| <b>Higher heating value [HHV]<br/>(MJ/kg)</b> | 20.1±0.5      | 18.6±0.3   | 16.4±0.1          | 17.9±0.1   |

<sup>a</sup> dry basis, <sup>b</sup> calculated by difference <sup>c</sup> dry-ash-free basis

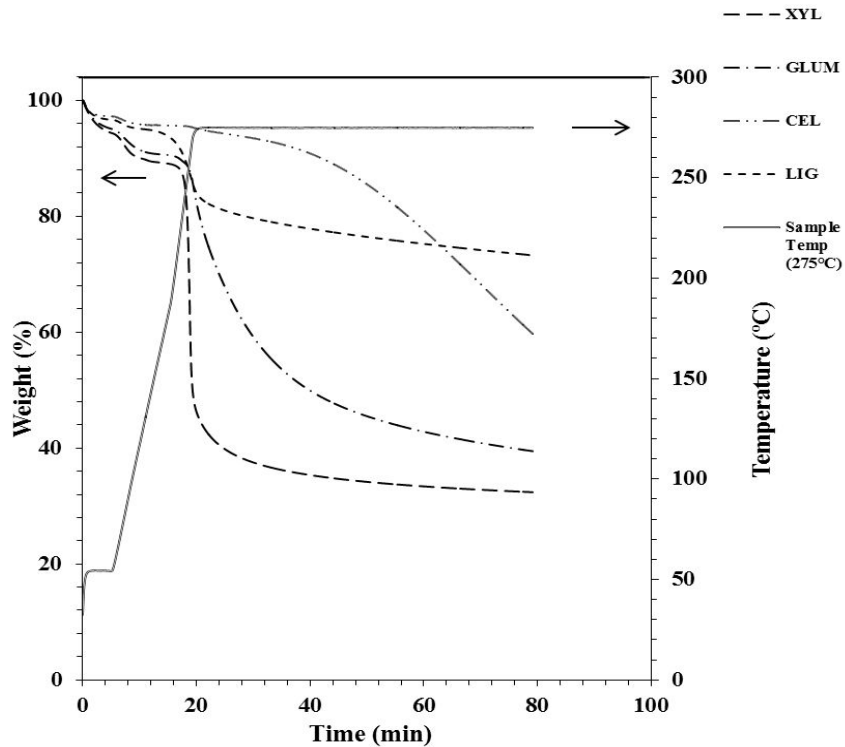


Figure 1: Thermograms of model constituents (glucomannan, xylan, cellulose, lignin) showing temperature ramped from 30°C to final heating temperature of 275°C (20°C/min)

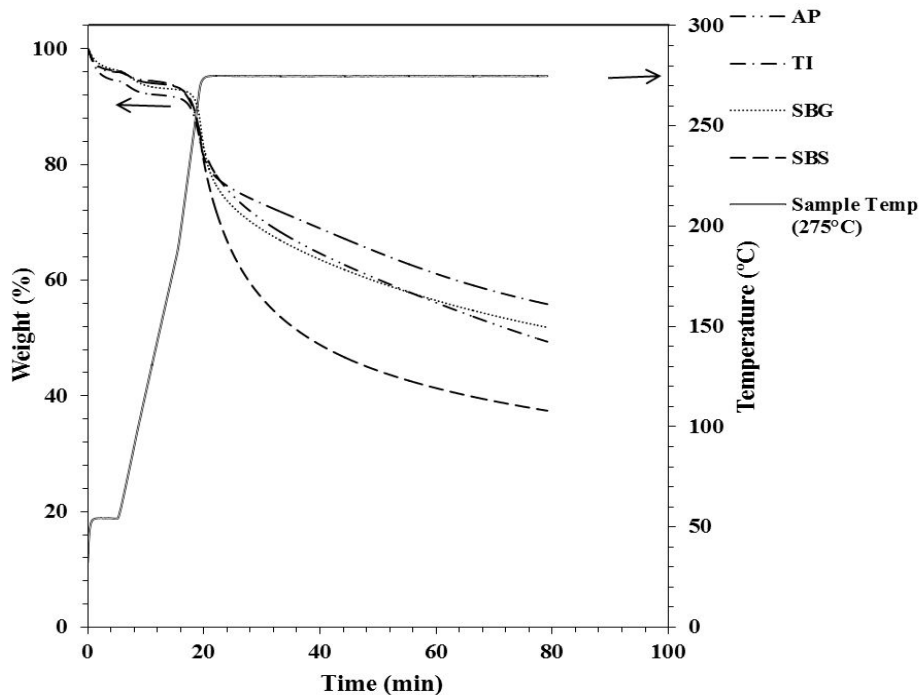


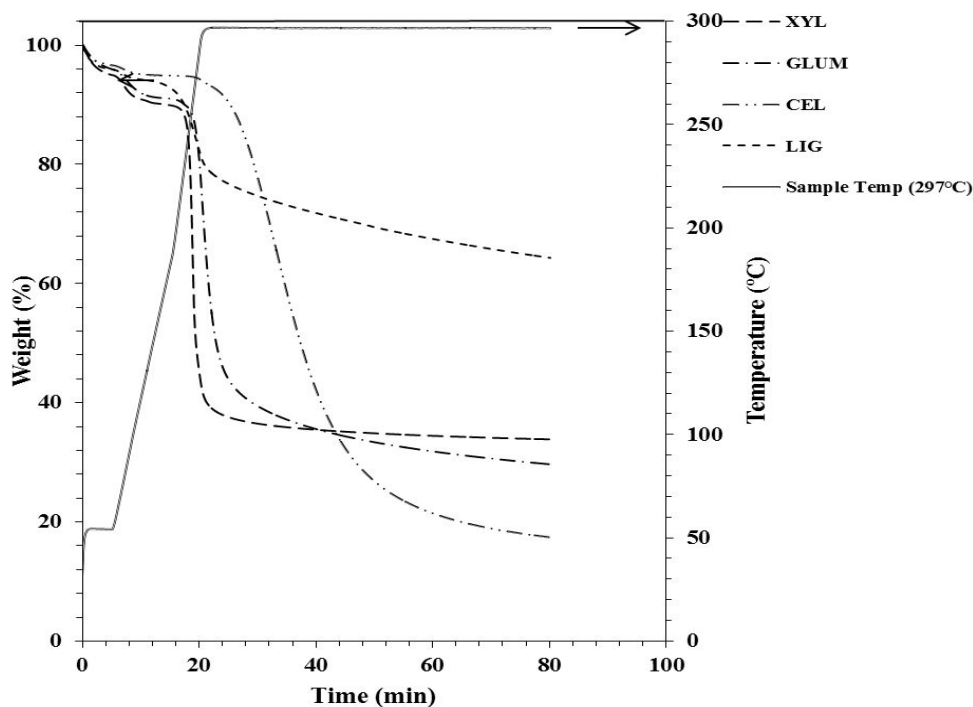
Figure 2: Thermograms of biomass samples (*Sorghum bicolor* glume, *Sorghum bicolor* stalk, *Albizia pedicellaris* and *Terminalia ivorensis*) showing temperature ramped from 30°C to final heating temperature of 275°C (20°C/min)

mineral composition of the SBG's ash content which was significantly high (Table 1). It is noteworthy that non-woody biomass' relatively high ash content makes it less suitable for energy product as compared to other woody biomass resources (Burhenne et al, 2013; Klass, 1998). TI had the least weight loss of all the biomass samples retaining about 57% weight. This may have been occasioned by its relatively higher lignin content as shown in Table 1.

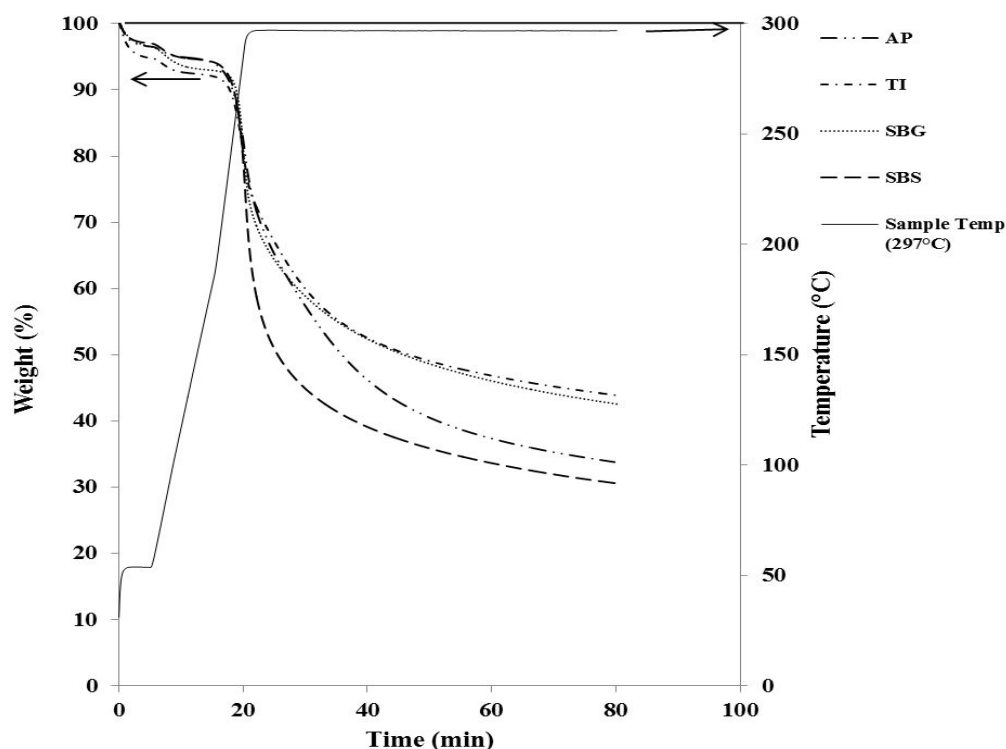
Figures 3 and 4 show the heating thermograms ramped from ambient temperature of about 30°C to the final heating temperature of 297°C for the model constituents and biomass samples respectively. The thermograms also exhibited the warm-up phase earlier discussed. Cellulose experienced the highest weight loss at 297°C. This is in agreement with findings in the literature in which it was noted that cellulose underwent rapid decomposition at temperatures above 250°C (Gaur and Reed 1998). Lignin remained

the least degraded at 297°C, retaining more than 60% weight owing to its relatively stable nature at the temperature being investigated (Burhenne et al, 2013).

In Figure 4, below the twentieth minute, a weight loss of about 10% was also observed in all the biomass samples. TI still exhibited the least reactivity recording 56% weight loss; this is much lower than 70% weight loss found in SBS. The high reactivity of SBS may not be unconnected with its relatively high hemicellulose content as shown in Table 1. Since weight loss profile is influenced by biomass composition non-woody biomass usually experiences greater weight loss during thermal decomposition (Bridgeman *et al.*, 2008). It was noted that the average weight loss, 64%, at 297 °C was much higher than at 275 °C for all the biomass samples; an indication of temperature influence on the decomposition behavior. This trend is in consonance with findings in literature (Bridgeman *et al.*, 2008).



**Figure 3: Thermograms of model constituents (glucomannan, xylan, cellulose, lignin) showing temperature ramped from 30°C to final heating temperature of 297°C (20°C/min)**



**Figure 4: Thermograms of biomass samples (*Sorghum bicolor* glume, *Sorghum bicolor* stalk, *Albizia pedicellaris* and *Terminalia ivorensis*) showing temperature ramped from 30 °C to final heating temperature of 297 °C (20 °C/min)**

#### CONCLUSION

A clear distinction between the cell wall composition of woody and non-woody biomass was observed. Among the model constituents, the hardwood hemicellulose, xylan, and cellulose had the greatest mass loss at 275 and 297 °C, respectively. Lignin, however,

experienced the least mass loss retaining about 74% and 65% at 275 and 297 °C, respectively. SBS had a higher mass loss of 62% at 275 °C. As isothermal temperature changed from 275 to 297 °C, mass loss increased to an average of 64% for all the biomass samples.

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