Thermo-Analytical and Physico-Chemical Characterization of Woody and Non-Woody Biomass from an Agro-ecological Zone in Nigeria

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Woody (*Albizia pedicellaris* and *Terminalia ivorensis*) and non-woody (guinea corn (*Sorghum bicolor*)) glume and stalk biomass resources from Nigeria were subjected to thermo-analytical and physico-chemical analyses to determine their suitability for thermochemical processing. They were found to have comparably high calorific values (between 16.4 and 20.1 MJ kg^{-1}). The woody biomass had very low ash content (0.32%), while the non-woody biomass had relatively high ash content (7.54%). Thermogravimetric analysis (TGA) of the test samples showed significant variation in the decomposition behavior of the individual biomasses. Gas chromatography/mass spectrometry (GC/MS) of fatty acid methyl esters (FAMEs) derivatives indicated the presence of fatty and resin acids in the dichloromethane (CH_2Cl_2) extracts. Analytical pyrolysis (Py-GC/MS) of the samples revealed that the volatiles liberated consisted mostly of acids, alcohols, ketones, phenols, and sugar derivatives. These biomass types were deemed suitable for biofuel applications.

Keywords: Ash; Biomass; Nigeria; TGA; Calorific value; GC/MS

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INTRODUCTION

The persistent upswing in energy consumption due to increased urbanization and industrialization in developed and developing nations has led to environmental consequences and a gradual decline in fossil fuel sources (Klass 1998; Fornasiero and Graziani 2012). In an attempt to reverse this trend, there has been growing interest in the development and exploitation of an array of renewable energy sources. As compared to fossil fuels, renewable energy sources possess lower environmental risks if used in a sustainable manner. Lignocellulosic biomass, in particular, holds an immense advantage because of its enormous availability as a byproduct from agricultural and timber processing activities. Lignocellulosic biomass is more environmentally friendly than fossil fuels because the gaseous emission from biomass combustion is relatively low in nitrogen and sulfur oxides (Klass 1998).

Biomass-based technology for energy-related purposes in Europe and the United States of America is at an advanced stage where its utilization is on a steady rise. Unfortunately, a developing country like Nigeria, with acute energy challenges, has yet to take advantage of this new development in renewable energy in spite of the availability of biomass resources (Mohammed *et al*. 2013). The prevalent practice in Nigeria is to fell trees for firewood and charcoal. However, it has been established from biomass audits that both woody and non-woody residues (35.5 and 10.20 million tonnes, respectively) are available across the country, which presents disposal challenges (Sambo 2009). More often than not, the waste management practices employed, such as open-air burning and disposal into river channels or drainages, constitute environmental nuisances and health risks (Lasode and Balogun 2010).

The complex matrix of organic and mineral contents of biomass resources makes characterization a necessary preliminary process (Naik *et al.* 2010). The physical properties and calorific value of fuel are known to vary for different biomass types. Agricultural residues have relatively higher ash contents and lower calorific values than forestry residues (van der Stelt *et al.* 2011). It is also common to find variation among similar species, as biomass characteristics are significantly influenced by environmental conditions in their respective geographical locations; weather variations, soil types, and chemical applications are among such factors (Demeyer *et al*. 2001; McKendry 2002). Furthermore, the polymeric structures of lignocellulosic materials differ between woody and non-woody feedstocks. This distinction plays a pivotal role in the product yield distribution and quantity. For instance, it has been observed that in a thermal pretreatment technology like torrefaction, different yield distributions due to the polymeric structure can be expected (van der Stelt *et al*. 2011), as each component possesses a peculiar decomposition mechanism (Moon *et al*. 2013). The above information demonstrates the importance of biomass feedstock characterization as a fundamental step prior to deployment for any bioenergy application.

Biomass is sometimes subjected to biochemical and/or thermochemical conversion techniques to produce biofuels, chemicals, and other value-added products (Klass 1998). During such conversion processes, biomass undergoes very complex decomposition patterns owing to its heterogeneity. Thermogravimetric analysis (TGA) is a veritable method that has helped to give insight into the decomposition mechanism of lignocellulosic biomass (Burhenne et *al.* 2013). In comparison to coal, lignocellulosic biomass possesses relatively higher volatile organic matter, which varies for diverse biomass materials (Naik *et al.* 2010). Hence, thermochemical reactions lead to devolatilization. Analytical pyrolysis gas chromatography/mass spectrometry (Py–GC/MS) is a characterization technique that can be deployed to prospect and identify some of the volatile components (Gao *et al.* 2013). It has also been noted that high-value low-volume chemicals can be obtained from lignocellulosic biomass, mainly from the extractive contents (Klass 1998).

In the current study, types of biomass broadly classified into woody and non-woody were selected for thermo-analytical, physical, and chemical characterization. The tropical hardwoods, *Terminalia* and *Albizia* species, considered in this study belong to the families of Combretaceae and Fabaceae, and they are commonly found in sub-Saharan Africa (RNGR, Wadsworth 1997, Okai *et al*. 2003). According to Fengel and Wegener (1984) many tropical plants can be expected to have high extractives and ash contents owing to an abundance of soil minerals. *Sorghum bicolor*, a non-woody biomass, is also native to Africa and it possesses agronomic properties that make it drought tolerant (Ali and Hasnain 2012, Serna-Saldívar *et al.* 2012). Sorghum, a C4 plant, is highly resistant to both abiotic and biotic factors and has relatively low water requirement (Serna-Saldívar *et al.* 2012). Furthermore, it has been identified as an energy crop with a 3 to 5 month growth cycle; thus it can be cropped about twice a year.

The two groups of biomass resources chosen generate huge wastes across Nigeria. In Lagos State, 267,436 tonnes of wood residues were estimated to be generated annually with 91.1 tonnes d^{-1} in Ilorin, Kwara State (Dosunmu and Ajayi 2002; Lasode and Balogun

2010). In addition, according to FAO 2010 data, sorghum stalks were estimated to produce 11.37 million tonnes of waste (Mohammed *et al.* 2013), while Azeez *et al.* (2010) reported that 7,000,000 m^3 of wood wastes are produced annually from logging and sizing operations in Nigeria. The literature is replete with data on the characterization of woody and non-woody biomass; Naik *et al.* (2010) evaluated the potentials of some Canadian biomass for biofuel production, Viana *et al.* (2012) studied the fuel and ash characteristics and combustion properties of selected native shrubs of central Portugal and northwestern Spain, and Kataki and Konwer (2001), and Umamaheswaran and Batra (2008) carried out characterization work on Northeast Indian indigenous woody species and Indian biomass ash, respectively. Other researchers who have worked on biomass characterization include Nordin (1994), Demirbas (2004), Jenkins *et al.* (1998), and Butler *et al.* (2013). There is, however, little information on the characterization of lignocellulosic biomass of Nigerian origin, particularly thermo-analytical data. Therefore, the primary objective of this study was to carry out experimental analyses of some Nigerian biomass resources comprising GC/MS analysis of fatty acid methyl esters (FAMEs) derivatives of organic extractives, analytical Py-GC/MS, and TGA under dynamic conditions in addition to providing data on proximate, compositional, and elemental analyses, and heating values.

EXPERIMENTAL

Materials

Biomass source

Biomass resources categorized into agricultural (non-woody) and forestry (woody) were obtained from a farm site (8º 37´ N, 4º 46´ E) and a timber processing plant (8° 27´ N, 4º 35´ E) in the city of Ilorin, Nigeria, respectively, in December 2012. The agricultural resource was *Sorghum bicolor* (guinea corn), while the forestry samples were tropical hardwoods, namely *Albizia pedicellaris* (AP) and *Terminalia ivorensis* (TI).

Harvesting and handling

The maturity period of the *Sorghum bicolor* plant is about six months. After harvesting the panicles, stems were taken, leaves were stripped off the stems, and stalks were cut into a length of 0.305 m. The panicles were threshed and the glumes handpicked. *Sorghum bicolor* glumes (SBG) and stalks (SBS) were air dried in the laboratory for about one month. Woodchips (15 x 10 x 10 mm^3) from tree lumbers, aged between 40 and 45 years, were also produced. The woody and non-woody biomass were packed in separate polythene bags and stored.

Sizing, sieving, and storage

The biomass resources described above were further milled in a Thomas Wiley Laboratory Mill Model 4 (New Jersey, USA) and sieved into particle sizes ranging between 0.25 and 1.0 mm. Thereafter, they were all kept in Ziploc® bags and stored at room temperature.

Methods

Proximate and elemental analyses

The British standard method BS EN 15148 (2009) was used to determine the volatile matter (VM) content. The ash content was determined in a muffle furnace at 580 °C according to ASTM D1102-84 (2007), while the moisture content (MC) was determined using a HB 43-S Mettler Toledo moisture analyzer (Ohio, USA). The fixed carbon (FC) content was calculated by difference. Elemental analysis was conducted using a CE 440 elemental analyzer (Massachusetts, USA) to determine C, H, and N content, with O being calculated by difference.

Compositional analysis

Compositional analysis was conducted using both wet chemistry and instrumental analytical methods to obtain the dichloromethane (CH_2Cl_2) extracts, lignin, hemicellulose, and cellulose contents of the biomass resources. The biomass was extracted using a Soxhlet apparatus with CH_2Cl_2 for 16 h (in duplicate); the extract was concentrated to dryness, and the yield was determined gravimetrically according to ASTM D1108-96 (2007). This procedure only extracts lipophilic compounds at low temperature to minimize compound degradation. The lignin content of extractive free biomass (200 mg, in duplicate) was determined using acid insoluble (Klason) lignin and acid soluble lignin procedures according to ASTM D1106-96 (2007) and Schoening and Johansson (1965), respectively. The carbohydrate analysis (hemicellulose and cellulose determination) was determined by High Performance Liquid Chromatography (HPLC) according to the modified ASTM E1758-01 (2007). The Waters HPLC (Waters; Milford, MA) consisted of two Rezex RPM columns in series (7.8 x 300 mm, Phenomenex; Torrence, CA) at 85 °C, that were eluted with water (0.5 mL $min^{-1)}$ and a differential refractive index detector (ERC-5710, ERMA). Data were acquired and analyzed using N2000 chromatography software.

Higher heating value (HHV) determination

The HHV of biomass samples, in triplicate, was determined using a Parr oxygen bomb calorimeter model 1341 (Illinois, USA) according to ASTM D5865-04 (2004). Biomass samples (1.0 g) were pelletized (6 mm Ø) on a Carver Laboratory hydraulic press (Indiana, USA) using a pressure of 13.8 MPa and dried prior to charging the bomb.

GC/MS analysis of fatty acid methyl esters (FAMEs) derivatives

A detailed procedure described in the literature was used in the preparation of the FAMEs derivatives of CH_2Cl_2 extracts (Osman *et al.* 2012). The FAMEs derivatives were analyzed by GC-MS_{EI} (FOCUS-ISQ, Thermo Scientific; USA) with a temperature profile of 40 °C (1 min) to 300 °C at 5 °C min^{-1} and a GC capillary column: (RTx5, 30 m, 0.25 mm Ø, Restek). Eluted compounds were identified by comparison with authentic standards and by spectral matching with the 2008 NIST mass spectral library.

Analytical Py-GC/MS experiment and Thermogravimetric Analysis (TGA)

Analytical Py-GC/MS experiments and thermogravimetric analysis (TGA) were carried out on a Perkin Elmer TGA-7 instrument (Massachusetts, USA) (30 to 900 °C at 20 °C/min) according to the detailed description reported by Balogun *et al.* (2014).

RESULTS AND DISCUSSION

Proximate, Elemental, and Compositional Analyses, and Heating Value Determination

Table 1 gives a summary of the proximate, elemental, and compositional analyses, and the heating values for the biomass resources in comparison with results from the literature (Prins *et al.* 2006). Chemical analyses are important preliminary steps to the application of biomass as feedstock for energy-related purposes because they give valuable information regarding the correlation between their structural profile and energy content.

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

	Woody Biomass			**Non-woody Biomass**		
	AP	TI	Beech[d]	SBG	SBS	straw[d]
Proximate analysis						
Volatile Matter [a] (%)	92.7±0.3	82.30±0.36	82.7	78.90±0.43	82.90±0.21	79.0
Ash Content [a] (%)	1.68±0.01	0.32±0.05	1.2	7.54±0.21	3.25±0.57	7.1
Fixed Carbon [b]	5.61±0.36	17.40±0.57	-	13.60±0.25	13.80±0.96	-
Elemental Analysis [a]						
Carbon (%)	51.7±0.3	48.6±0.3	47.2	42.4±0.4	46.2±0.1	44.3
Hydrogen (%)	5.85±0.38	6.00±0.20	6.0	5.27±0.25	5.85±0.44	5.8
Nitrogen (%)	0.54±0.03	0.44±0.00	0.4	0.74±0.06	0.44±0.01	0.4
Oxygen (%) [b]	42.0±0.1	45.0±0.5	45.2	51.6±0.7	47.6±0.6	42.4
Compositional Analysis [c]						
CH_2Cl_2 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	
Higher heating value [HHV] (MJ/kg)	20.1±0.5	18.6±0.3	18.3	16.4±0.1	17.9±0.1	17.4

[a]dry basis, [b] calculated by difference [c]dry-ash-free basis [d]Prins *et al.* (2006)

Table 1 shows that the woody biomass had the lowest ash content (< 2%), and consequently the highest HHV. The ash content value obtained in this study for tropical hardwoods agrees with that reported for an albizia species (1.8%) but was relatively lower than the value for iroko (3.5%) (Azeez *et al.* 2010). Agricultural biomass, on the other hand, had relatively high ash content (3.25 to 7.54%). This result was similar to that obtained by Boateng and Mullen (2013), in which the ash contents of raw hardwood species and switch grass were 0.63% and 7.33%, respectively. The ash content in this study for sorghum straw is much higher than the value obtained by Serna-Saldívar *et al.* (2012). Climatic and environmental conditions may be responsible for this variation. The high ash content of the agricultural sample makes it less desirable for energy application purposes because its high mineral content lowers its energy value (Klass 1998). TI had the lowest ash content (0.32%) and the highest FC content (17.40%). It has been noted that ash content influences the quality of organic yield (Das *et al.* 2004). In addition, the inorganic elements in biomass ash eventually become part of a process waste stream in bio-based chemical extraction systems, which need to be disposed of in an environmentally compatible way (Pan *et al.* 2013). Hence, biomass materials with lower ash contents are more attractive for thermochemical conversion processes.

The data in Table 1 show that the C, H, N, and O for the biomass samples ranged from 42.4 to 51.7%, 5.3 to 6.0%, 0.44 to 0.74%, and 42.0 to 51.6%, respectively. This compares well with results from the literature (Prins *et al.* 2006). The carbon content for woody biomass was the highest. For instance, AP had 51.7%, while SBG had the least, 42.4%. A similar trend was reported in which pinewood had 49.0% and barley straw had 41.4% carbon content (Naik *et al*. 2010). The nitrogen content for all the samples was less than 1%; this corresponds well with results from the literature (Prins *et al*. 2006, Azeez *et al.* 2010). This is a positive sign, as there would be significant reduced emissions of nitrogen oxides during combustion. With woody biomass possessing the least ash content and the highest carbon content, it may be expected to have a comparably higher HHV than non-woody samples.

Table 1 shows that AP has an exceptionally high amount of CH_2Cl_2 extracts (~17%), which corresponds with other *Albizia* species (Azeez *et al*. 2011; Palmer *et al.* 1983) and tropical hardwoods (Fengel and Wegener 1984). TI had an extractives content comparable to other *Terminalia* species (Palmer *et al.* 1983). The amount of CH_2Cl_2 extracts for SBG and SBS was 0.31% and 0.74%, respectively. There was a clear distinction in the distribution of the lignocellulosic fractions between woody and non-woody samples, which is indicative of structural differences. For instance, the carbohydrate content (hemicellulose ± cellulose, ≥ 70%) for non-woody samples was much higher than that for woody samples (< 55%). Kim *et al.* (2011) reported a difference in the compositional analysis of pinewood and switch grass, alluding to differences in their structural makeup. It is also noteworthy that TI had the highest Klason lignin content at 37%, which is higher than that reported for *Terminalia superba* at 32% (Palmer *et al.* 1983); however, this value falls within the range reported for other woody biomass (Pan *et al.* 2013). The high lignin content cannot be explained, but it is speculated that the presence of lignin derivatives, which have been found in *T. tropophylla* (Cao *et al.* 2010), *T. bellerrica* (Valsaraj *et al.* 1997), and tannins (Srivastava *et al.* 1999), may contribute to this high value.

The HHV obtained in this study compared well with the calorific values compiled in the Phyllis database for some woody and non-woody biomasses (Phyllis2). For instance, the database recorded 20.2 MJ/kg (teak), 20.66 MJ/kg (*Gmelina arborea*), and 18.77 MJ/kg (*Casuarina*) for tropical hardwood and 17.86 MJ/kg (sorghum stalk) for non-woody on dry basis. The comparably higher HHV for woody biomass may be linked to its higher FC, C, and lower ash content. SBG had a relatively lower HHV of 16.4 MJ/kg when compared with SBS (17.9 MJ/kg); this may be as a result of its relatively higher ash and lower C contents earlier mentioned. Residue from these biomass samples holds great promise for co-firing applications or conversion into biofuels. In summary, the woody biomass feedstocks under investigation showed better potential than non-woody biomass for bioenergy purposes.

Analysis of FAMEs Derivatives

The CH_2Cl_2 extracts were derivatized to FAMEs through acidic methanolysis and analyzed by GC-MS (Osman *et al.* 2012). Table 2 shows the identities and relative abundance of the compounds found in the derivatized extracts. The derivatized CH_2Cl_2 extract from AP was remarkably different in content, composition, and quantity, as it had very low area peaks for fatty acids but two prominent peaks at 20.87 and 40.40 min. The latter peak, being the highest (55.08 mg g^{-1} of biomass), was *p*-anisoin, while the former (32.83 mg g^{-1} of biomass) was methoxy-α-methyl-benzene propanoic acid, methyl ester based on mass spectral assignment (Table 2). Unlike in other biomass samples, the GC-MS did not detect the presence of oleic acids in the derivatized extract from AP. Significantly, all the fatty acids tested for were present in the derivatized extract from the non-woody biomass. The most abundant fatty acids were palmitic and oleic acids; this is consistent with findings from literature (Osman *et al.* 2012). The highest quantity of palmitic acid was found in non-woody biomass (SBS; 0.93 mg $g^{-1}$of biomass), while oleic acid was highest in woody biomass (TI; 0.84 mg g^{-1} of biomass). It has been reported in literature that some fatty and resin acids could be used as biodiesel additives and bio-lubricant after transesterification (Nagy *et al.* 2009; Xiang and Amin 2011).

Table 2. Compounds Identified and Quantified by GC/MS Analysis of FAMEs Derivatives

RT (min)	**COMPOUND**	**M^+ (m/z)**	**AP**	**TI**	**SBG**	**SBS**
			mg g^{-1} (biomass)			
20.87	methoxy-α-methyl-benzene propanoic acid, methyl ester	194	32.83	-	-	-
22.19	Dodecanoic acid, methyl ester (lauric acid)	214	-	-	0.01	0.37
30.76	Hexadecanoic acid, methyl ester (palmitic acid)	270	0.55	0.68	0.58	0.93
33.91	9,12-Octadecadienoic acid, methyl ester (linoleic acid)	294	0.99	0.11	0.17	0.26
34.03	9-Octadecenoic acid (Z)-, methyl ester (oleic acid)	296	-	0.84	0.38	0.81
34.47	Octadecanoic acid, methyl ester (stearic acid)	298	0.30	0.04	0.08	0.22
40.40	2-hydroxy-1,2-bis(4-methoxyphenyl) ethanone (*p*-anisoin)	272	55.08	-	-	-
42.63	Unknown	302		-	-	-
RT = retention time, M+ = molecular ion						

Thermogravimetric Analysis (TGA)

The TGA and the first derivative TGA (DTG) curves provide useful information concerning the decomposition mechanism of the respective components of biomass complex structures.

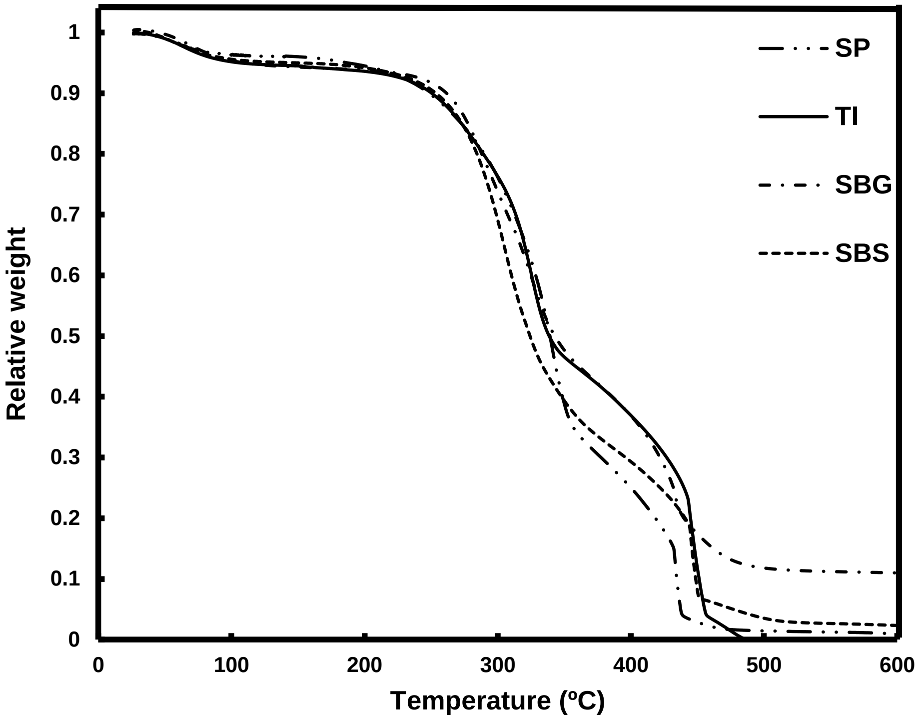

Fig. 1. TGA thermograms for biomass samples at 20 °C min^{-1}

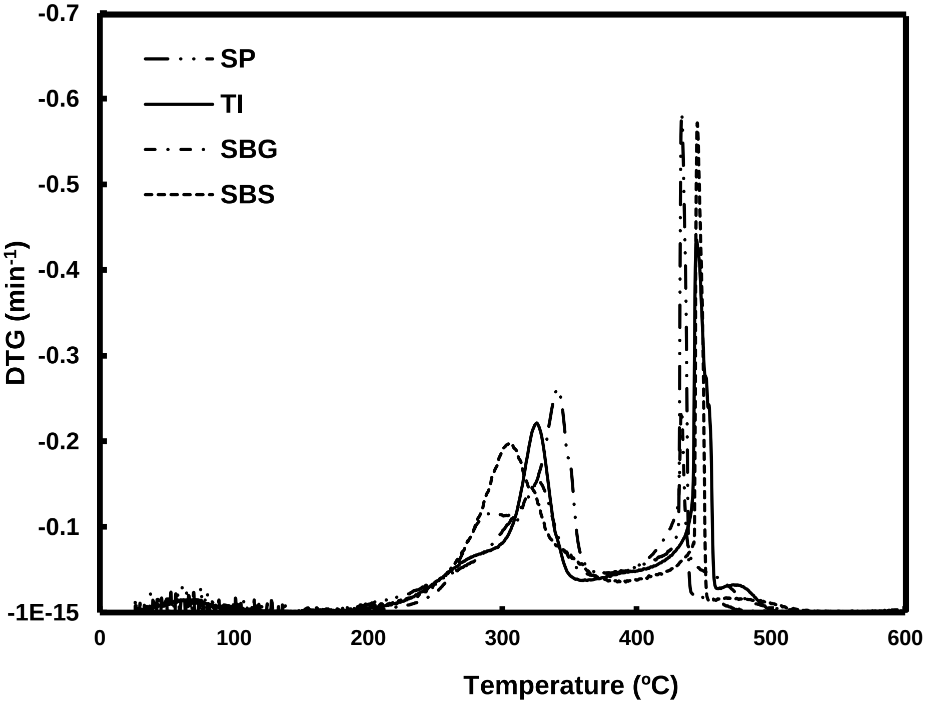

Fig. 2. DTG thermograms for biomass samples at 20 °C min^{-1}

Figures 1 and 2 present the TGA and DTG curves for the biomass samples, respectively, demonstrating that the devolatilization trend differed significantly for each lignocellulosic biomass. Evidently, decomposition started below 200 °C, as shown in Fig. 2. This corresponded to less than a 10% weight loss (Fig. 1) and was essentially due to loss of moisture and some light volatile organic fractions. Significantly, Fig. 1 also shows that the solid residue left in decreasing order was as follows: SBG > SBS > AP > TI. This matched the trend portrayed in the proximate analysis for ash content (Table 1). The main weight loss began with characteristic shoulders that ended at 340 to 365 °C for all biomass samples. This is indicative of primary devolatilization, in which the vast majority of volatile species is liberated, leading to more than 50% weight loss (Fig 1). The shoulders which spanned 250 and 300 °C lie within the hemicellulose degradation region (Burhenne *et al.* 2013). The next stage (295 to 350 °C) shows peaks emerging with maxima first derivative TGA at 318, 321, 322, and 339 °C, respectively, for SBS, TI, SBG, and AP. In comparison to published studies, this degradation stage can be assigned to cellulose decomposition (Yang *et al.* 2006). Subsequently, a steady and continuous weight loss that may be assigned to lignin decomposition followed. The appearance of some maxima DTG peaks at the secondary devolatilization stage could have been a result of the degradation of some chemical species in the biomass structure; this is consistent with findings from the literature (Fisher *et al.* 2002; Naik *et. al.* 2010).

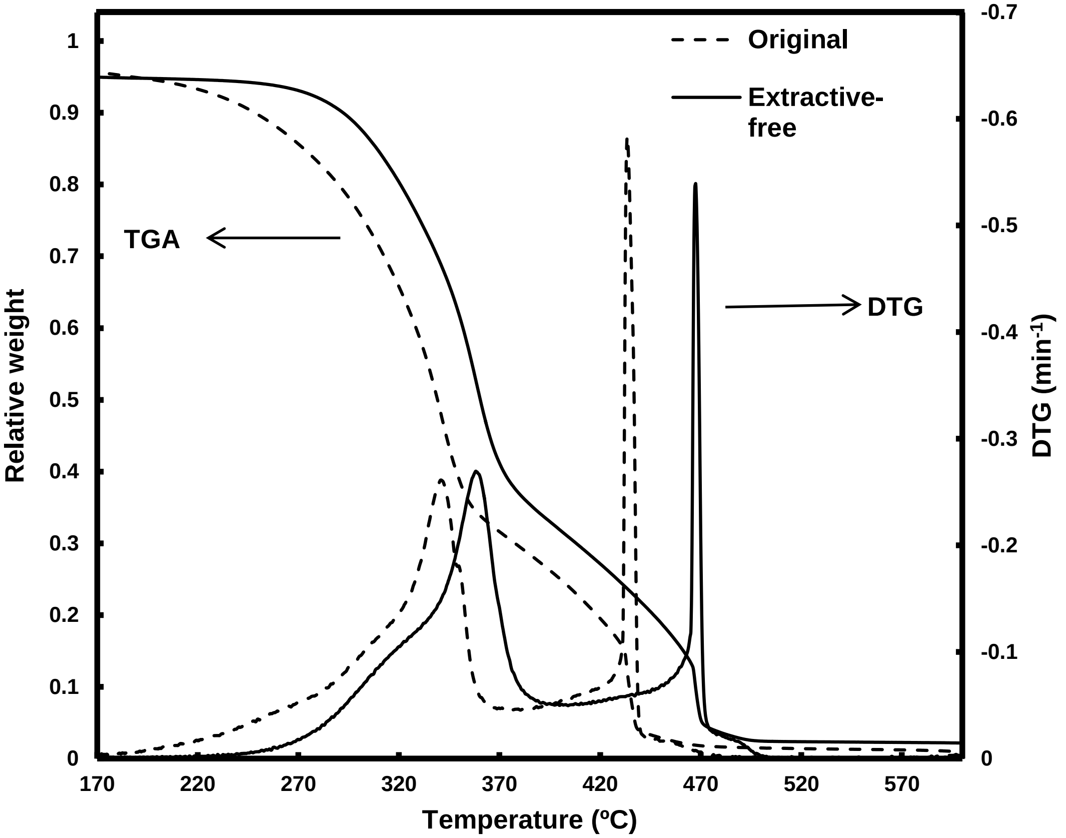

Fig. 3. TGA and DTG thermograms for original and CH_2Cl_2 extractive-free biomass samples (AP) at 20 °C min^{-1}

Figure 3 shows the TGA/DTG thermograms for AP (original biomass and CH_2Cl_2 extractive-free biomass), which were typical of all biomass samples under consideration. The thermal degradation profiles were essentially the same with the three decomposition phases identifiable, except for a peak shift of about 20 °C observed in the extractive-free sample. The isolation of the CH_2Cl_2 extracts (low-molecular weight component), which leaves behind relatively heavier molecular weight organics that require higher energy to degrade, may have been responsible. It is noteworthy that the quantity of AP extracts was significant: approximately one-fifth of the polymeric structure as shown in the compositional analysis (Table 1). Its composition was also of great importance (Table 2). Therefore, the extracts could be isolated for the production of some high-value low-volume chemicals prior to the thermal decomposition process for energy applications.

Analytical Pyrolysis (Py-GC/MS) at 500 °C

Analytical Py-GC/MS is a potent technique that is useful in the qualitative determination of the range of volatile species that may be liberated from biomass thermal degradation, such as torrefaction and pyrolysis (Azeez *et al*. 2010).

Table 3. Chemical Constituents Identified during Analytical Pyrolysis (Py-GC/MS) at 500 °C

RT (min)	**COMPOUND**	**MW (m/z)**	**AP**	**TI**	**SBG**	**SBS**
			% Peak Area			
1.16	Carbon dioxide	44	8.4	6.0	8.2	13.4
1.34	Furan + 2-butanone	68, +72	2.5	1.2	3.0	3.2
1.65	Acetic acid	60	4.3	1.3	2.1	6.3
2.06	1-hydroxy-2-propanone	74	3.8	0.6	1.6	5.8
3.17	1-hydroxy-2-butanone + unknown	104	1.8	-	1.1	2.4
3.36	Butanedial	86	1.1	-	0.5	1.8
3.47	Methyl pyruvate	102	1.0	-	0.5	1.0
4.25	Furfural	96	1.8	1.7	-	2.1
4.71	Furfural alcohol	98	-	-	0.4	1.1
4.98	Acetyl-1-hydroxy-2-propanone	98	0.7	0.2		
6.06	2(5)-Furanone	84	0.8	-	1.2	1.0
6.32	1,2-Cyclopentanedione	98	1.4	0.6	3.4	1.5
7.85	Phenol	94	0.9	-	4.0	1.9
9.07	3-methyl-1, 2-cyclopentanedione-	112	-	-	1.4	1.8
9.85	3-methyl-phenol	108	0.6	-	0.5	0.8
10.43	4-methyl-phenol	108	1.0	-	1.7	0.8
10.77	Guaiacol	124	2.1	1.0	0.8	1.8
10.94	4-methyl 1,2-benzenediol + unknown	124	0.6	-	1.2	1.1
11.62	3-ethyl-2-hydroxy-2-cyclopenten-1-one	126	0.3	-	0.4	0.6
13.02	4-ethyl-phenol	122	0.6	-	-	0.8
13.49	Unknown	142	0.6	0.4	0.8	-
13.67	Methyl guaiacol	138	1.4	0.7	0.7	0.4
14.08	1,2 benzenediol	110	1.1	-	-	-
14.15	1,4:3,6 dianhydro-glucpyranose	144	-	-	1.2	0.7
14.44	2,3 or 3,4 anhydro-hexosan	144	-	0.3	-	-
14.48	4-vinylphenol	120	1.5	-	9.3	7.0
14.65	2,3 or 3,4 anhydro-hexosan	144	-	-	0.5	-
15.58	3-methoxy-1,2-Benzenediol,-	140	0.5	1.0	-	-
15.71	3-methyl-1,2-Benzenediol,-	124	0.7	-	-	-
16.03	Ethyl guaiacol	152	0.9	-	-	0.6
16.98	4-vinylguaiacol	150	2.9	0.9	4.4	2.9
18.01	Syringol	154	2.0	0.8	0.4	2.2
18.11	Eugenol	164	0.8	-	-	-
19.25	Vanillin	152	0.9	-	0.8	0.6
20.39	Methyl-syringol	168	-	1.0	-	-

20.45	Isoeugenol	164	3.3	-	0.7	1.4
20.72	Propylguaiacol	166	-	0.5	-	-
21.13	$C_{10}H_{10}O_2$	162	0.2			0.2
21.30	$C_{10}H_{10}O_2$	162	0.2			0.2
21.40	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	166	0.6	-	1.6	-
21.62	levoglucosan	162	1.0	1.3	4.5	0.8
23.27	Vinyl-syringol	180	2.2	0.9	0.4	1.4
23.47	cis-Coniferyl alcohol	180	0.1	0.1	-	-
23.66	propioguaiacone	180	0.3	0.1	0.2	0.2
24.09	trans-Propenylsyringol	194	0.7	0.2		0.3
25.43	syringaldehyde	182	0.6	-	0.2	0.2
25.75	$C_{11}H_{12}O_3$	192	0.2	0.1	-	0.3
25.93	$C_{11}H_{12}O_3$	192	0.2	0.1	0.1	0.1
26.30	cis-propenyl-syringol	194	1.7	-	-	0.8
26.40	homosyringaldehyde	196	-	0.3	0.3	0.1
27.00	acetosyringone	196	1.1	0.4	0.1	0.3
27.12	Trans-Coniferyl alcohol	180	1.3	-	-	-
27.27	Propiosyringone	210	-	0.1	-	-
27.81	Syringyl acetone	210	0.4	0.4	0.1	0.2
31.45	Hexadecanoic acid	256	0.4	0.4	0.8	0.9
40.44	p-Anisoin	272	-	10.6	-	0.6
45.7-51.0	diterpene hydrocarbons		1.05	32.5	3.6	1.63
	Unknown		37.5	34.3	37.8	26.8
RT = Retention time, MW = Molecular ion						

Table 3 shows the result of analytical pyrolysis (Py-GC/MS at 500 °C) for the biomass resources being investigated (Faix *et al.* 1990). A total of 56 compounds were identified in the analysis. Furan plus 2-butanone, acetic acid, and 1-hydroxy-2-propanone were among the earliest chemical components eluted in the four samples, and SBS recorded the highest proportion of each: 3.2, 6.3, and 5.8%, respectively. Guaiacol, methyl guaiacol, 4-vinylguaiacol, syringol, and other lignin derivatives were found in all four biomass samples. The non-woody biomass, SBG, had the highest yield of 4-vinylguaiacol (4.4%) and levoglucosan (4.5%), which are products of lignin and cellulose decomposition, respectively. In their study of comparative pyrolytic products from woody and non-woody biomass, Greenhalf *et al.* (2013) observed that switch grass (a non-woody biomass) had the highest yield of the same compounds. Significantly, of all the compounds identified, it was only TI that produced a significant yield of *p*-anisoin (10.6%). In addition, the highest proportion (32.5%) of the chemical species eluted in TI emerged between 45.7 to 51.0 min and was tentatively assigned as diterpenoid hydrocarbons.

CONCLUSIONS

1. The physico-chemical analysis showed that the biomass resources had a comparably high energy value. Woody biomass recorded the least ash and the highest C, lignin, and CH_2Cl_2 extracts; consequently, it had the highest HHV. Woody biomass is thus an attractive fuel source for thermochemical conversion systems.
2. Data for TI showed that it had the most favorable properties; the highest value for fixed carbon and the lowest ash content.

3. Non-isothermal heating also showed that the thermal behavior of both CH_2Cl_2 extractive-free and original biomass samples were essentially the same, while FAMEs analysis identified the presence of fatty and resin acids in the extractive contents. Therefore, extractives can be isolated from biomass prior to thermal treatment purposes for the production of additives and adhesives.

4. The analytical Py-GC/MS indicated the presence of phenolic organic compounds in the volatile species from biomass, in addition to some gases, acids, ketones, and alcohols.

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