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ORIGINAL RESEARCH

Comparative study on pyrolysis and combustion behavior of untreated *Matooke* biomass wastes in East Africa via TGA, SEM, and EDXS

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Abstract

Biomass has several benefits due to its novel behavior among energy sources. This study aims to characterize a unique form of biomass from two varieties of *Matooke* peel, namely, untreated *Mbwazirume* waste peel (UM-WP) and untreated *Nakyinyika* waste peel (UN-WP). The analysis of the characteristics of these biomasses was carried out using TGA, SEM, and EDXS. TG and DTG analysis showed an almost identical trend between UM-WP and UN-WP. The UM-WP exhibited a high VC 69.988 wt%, MC 13.125 wt%, O 48.02 wt%, and HHV 15.52 MJ-kg^{-1} with a low ash content 5.957 wt%, sulfur 0.64 wt%, and N 1.13 wt% compared to UN-WP. As compared to pretreated biomass, it was found that the smaller particle sizes had only minor intra-particle gradients and the bigger particle sizes had more of a linear pattern variation. The pyrolysis behavior obtained revealed three distinct regions at elevated temperatures related to the elimination of cellulose, hemicellulose, and lignin. During carbonization, high fluidity and bubbles were produced due to the release of a large amount of volatile matter and forms porous structure which flowed through the fluid mass and produced a non-homogeneous vacuolated structure. These might cause the oxygen to easily disperse inside the particles during combustion. In addition, white spots were observed which are elements from different categories. The findings of this study indicate that UM-WP biomass could be an ideal material source for the production of biofuel and photovoltaic.

Keywords Biomass · Energy · Intra-particle · Micrographs · Biofuel

Abbreviations

UM-WP	Untreated *Mbwazirume* waste peel
UN-WP	Untreated *Nakyinyika* waste peel
TGA	Thermogravimetric analysis
SEM	Scanning electron microscopes
EDXS	Energy-dispersive X-ray spectroscopy
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
HHV	Higher heating value
MP	*Matooke* peel
VM	Volatile matter
FC	Fixed carbon
MC	Moisture content
LCB	Lignocellulosic biomass

Introduction

The increase in demand for energy and identifying appropriate resources for energy production are key issues for most countries in the Africa. For instance, Uganda is highly vulnerable to oil price shocks in East Africa, because it imports almost all of its 31,490 barrels per day (5006.5 m^3/day) of oil from Kenya [1]. This causes problems for the transportation sector. In addition, the country has one of the lowest per capita electricity consumption rates in the world with 215 kWh per capita per year [2]. Such limited and unreliable energy access represents an underutilization of the large amount of biomass waste available in the country. For this reason, more attention should be paid to renewable energy,

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especially biomass energy, which is the case now in many countries [3, 4]. A number of different forms of biomass and waste can be used as fuels to be burned, digested, or co-combusted with coal to produce energy [5]. Examples of these energy sources include wood, straw, bagasse, *matooke* peels, agro-residues, municipal solid waste, etc.

Matooke (*Musa-AAA-EA*) is a variety of banana indigenous to Uganda, and is the most common staple food crop for human consumption in that country. It comes from the family of bananas known as East African highland bananas [6, 7]. The waste residue of *Matooke* is the peels, and a large amount of *Matooke* peel (MP) is generated every year; so, it is the most abundant agricultural biomass in East Africa, especially Uganda. This is due to the lack of sufficient structure to process this waste; so there is indiscriminate dumping, resulting in environmental pollution and loss of economic opportunities [8]. Although little amount of peel is used as animal feed and as local briquettes. Besides, biowastes of various origins are utilized despite the number of negative side effects they introduce to environment. This type of waste resource can be converted into energy recovery by means of thermochemical conversion processes, since it does not compete with the human food chain, and in turn improves the CO_2 balance [9].

The calorific values, high volatility, and fixed carbon contents indicate that this biomass waste could be an excellent energy source through various technologies such as combustion, gasification and pyrolysis [10]. Pyrolysis is a thermal and degradation technique performed under N_2 atmosphere [11], while combustion takes place under severe oxidative conditions with the aid of an ignition system. There are many reports on the effect of combustion and pyrolysis conditions on the physical and chemical properties of biomass. These properties of biomass char are generally characterized by thermogravimetric analysis (TGA), scanning electron microscopes (SEM), energy-dispersive X-ray spectroscopy (EDXS), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

The objective of this study was to characterize the unique biomass from two varieties of *Matooke* peel, namely, UM-WP and UN-WP with TGA, SEM, and EDXS. According to the available literature, there is only one published article on characterization of pretreated *Mbwazirume* and *Nakyinyika* biowaste [7]. Therefore, there is a need for additional experiments on pyrolysis and the combustion behavior of untreated *Mbwazirume* and *Nakyinyika* biowaste, and for comparison of the samples. The contributions from these various technological processes are described to verify the mechanism of combustion and thermal degradation of biowaste and visualize the feasible recovery of biofuels by means of the thermochemical conversion process.

Materials and methods

Characterization of UM-WP and UN-WP samples

These characterization analyses include: proximate, ultimate, TGA, SEM and EDXS. The biomass sample in this study had a particle size of 0.7 mm after grinding because high-energy output depends on the particle size and reduction in crystallinity of the LCB. The UM-WP and UN-WP samples are shown in Fig. 1a, b.

Proximate and ultimate analyses

The proximate and ultimate analyses are essential methods of characterization. The proximate analysis determines the composition of a biomass in terms of wt% of volatile matter (VM), fixed carbon (FC), moisture content (MC), and ash. In this study, these compositions were obtained according to ASTM standards (DIN 51718, DIN 51719, and DIN 51720). The method was that 1 g of each of the biomass samples was weighed on two different dried aluminum dishes and placed in a furnace at a required temperature under N_2 atmospheric conditions. For ultimate analysis, the chemical elements such as C, H, O, N and S were determined. The method was that 1.00–2.00 mg of the UM-WP and UN-WP samples was placed separately inside a muffle furnace according to

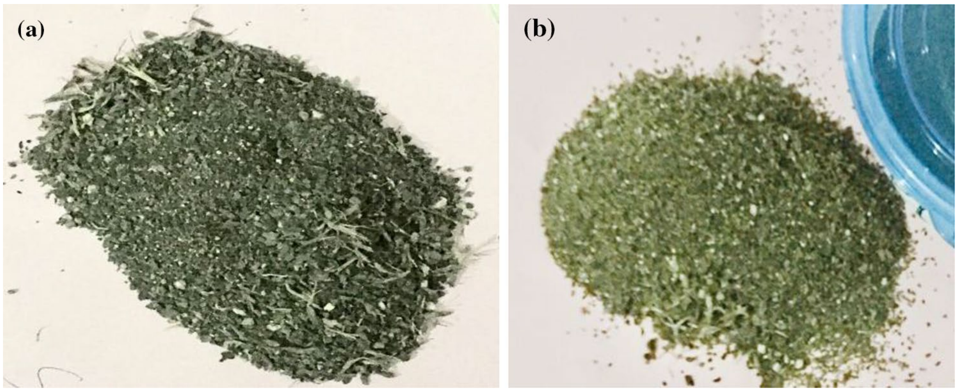

Fig. 1 **a**, **b** The UM-WP and UN-WP samples

ASTM E775-78 standards using PerkinElmer 2400 Series II as described by [7]. The HHV was determined using the known elemental composition with Eq. (1), which is acceptable for engineering calculations:

$$\begin{aligned} \mathrm{HHV}\ \left[\mathrm{MJ/kg}\right] = {} & 0.3491x\ (\%\mathrm{C})\ +\ 1.1783x\ (\%\mathrm{H}) \\ & -\ 0.1034x\ (\%\mathrm{O}) +\ 0.1005x\ (\%\mathrm{S}) \\ & -\ 0.0151x\ (\%\mathrm{N})\ -\ 0.0211x\ (\%\mathrm{Ash}) \end{aligned} \tag{1}$$

Thermogravimetric analysis (TGA)

The thermal analysis was to determine the change in the sample mass under certain conditions of temperature, time and atmosphere. These analyses were carried out on UM-WP and UN-WP biomass samples with a TGA thermostep analyzer manufactured by ELTRA, Germany. 5 mg and 10 mg portion of the samples were prepared and heated from ambient temperature to 1000 °C at 10 °C min^{-1} under N_2 as described by [7]. The weight loss, fixed carbon, ash content, moisture, and heating rate were monitored and recorded.

SEM and EDXS analysis

The change in micrographs of the UM-WP and UN-WP samples was examined under SEM (VEGA 3 TESCAN-LMH). In this experiment, the sample was coated with a thin layer of carbon as a non-conducting adhesive at 50/60 Hz, 230 V and 1300 VA.

Elemental compositions of the UM-WP and UN-WP samples were analyzed using energy-dispersive X-ray. In this experiment, the energy is dispersed to determine the individual elements and to point out the lateral variation of its composition from chosen areas.

Results and discussions

Proximate analysis

As observed in Figs. 2 and 3 and Table 1, the compositions of UM-WP and UN-WP found are slightly different from the pretreated biomass. This happens due to the pretreatment technique and the composition of the original biomass. For proximate analysis, the thermal degradation of UM-WP and UN-WP in an inert atmosphere at different rates of heating showed a peak temperature of 35–108 °C which corresponds to the moisture loss with percentage content of 13.125 wt% and 13.011 wt%. The second peak was observed between 105 and 915 °C as shown in the TG-DTG curves, which is associated with VM content with a mass loss of 69.901 wt% and 69.723 wt%. The high VM found in the UM-WP suggests the high potential of this residue for energy production by pyrolysis [12].

The significant amount of FC for UM-WP and UN-WP was found to be 11.017 wt% and 11.278 wt% which corresponds to 715–750 °C, respectively. The ash content was found to be low at 5.957 wt% and 5.988 wt%, respectively. As previously presented, any biomass with an ash content

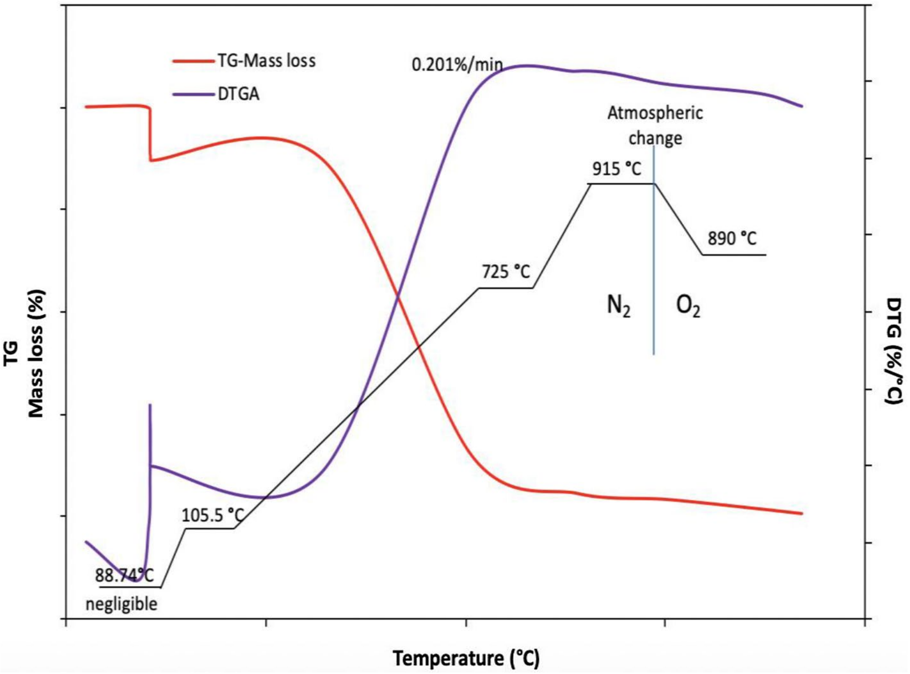

Fig. 2 TG-DTG curve of UM-WP

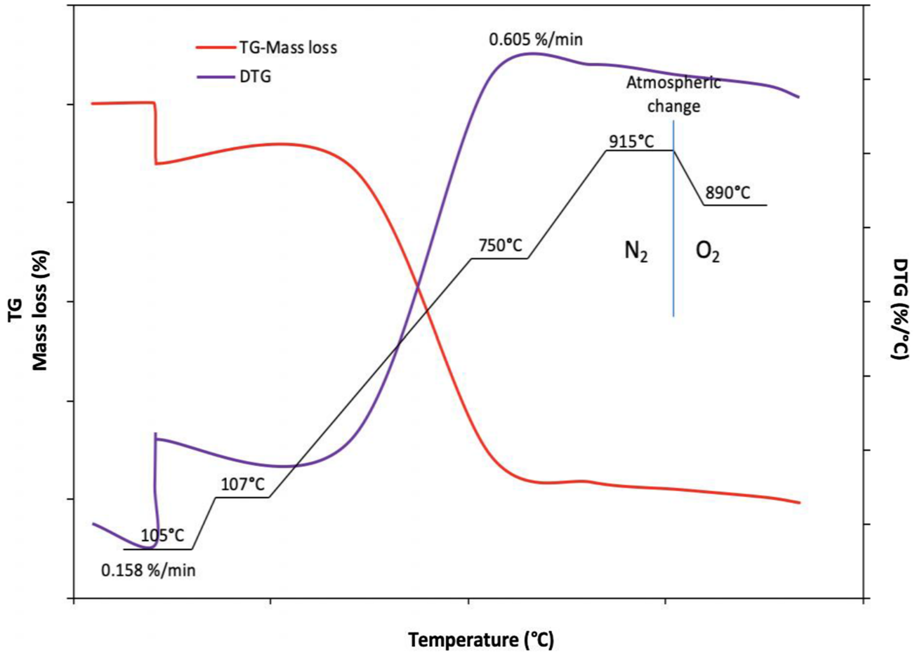

Fig. 3 TG-DTG curve of UN-WP

Table 1 Fuel composition of UM-WP and UN-WP biomass

Samples	Particle size (mm)	Proximate analysis				Ultimate analysis					HHV* (MJ/kg)
		MC	VM	Ash	FC	C	H	N	O	S	
		(wt. %) on db				(wt. %)					
UM-WP	0.7	13.125	69.901	5.957	11.017	45.95	4.26	1.13	48.02	0.64	15.52
UN-WP		13.011	69.723	5.988	11.278	43.49	4.51	3.16	47.91	0.93	15.49

[a] Calculated HHV (MJ/kg)

db dry basis

less than 5–6% does not undergo knocking trends [7, 13, 14]. The temperature range of thermal degradation of untreated waste peel is wider than that for pretreated waste peel. This trend is due to thermal stability and requires a longer retention time during the pyrolysis process. A residual mass of ~ 18% was observed from the samples that did not thermally degrade even at 1000 °C as similarly observed by [7, 11].

Ultimate analysis

As shown in Table 1 (ultimate analysis), the C, H, and O contents of UM-WP were found to be 45.95 wt%, 4.26 wt%, and 48.02 wt%, respectively; while the UN-WP was found to be 43.49 wt%, 4.51 wt%, and 47.91 wt%, respectively. The UM-WP has higher oxygen content which indicates a higher thermal reactivity than char [15]. This is essential because the more the oxygen content in a fuel, the easier it is to ignite [7, 16]. The decrease in O and H content in biomass fuels can be associated with the scission of weak bonds within the char structure [7]. These resources (UM-WP and UN-WP) might be environmentally friendly with a certain amount of S (0.64 wt% and 0.93 wt%, respectively) and N (1.13 wt% and 3.16 wt%, respectively). The HHVs were found to be 15.52 MJ-kg^{-1} and 15.49 MJ-kg^{-1}, respectively, which might be high enough for consideration as a source of energy. However, the ignition of such high volatile fuels may lead to high flame length unlike low volatile fuels which ignite less readily [7]. The higher the volatile content in a fuel, the higher the HHV and the less heat is required for the thermochemical reactions [7, 17].

Thermal analysis

The thermal pyrolysis behavior obtained reveals the three different regions at elevated temperatures, which is related to elimination of hemicellulose (100–250 °C), cellulose (350–520 °C), and lignin (500–640 °C). The maximum mass loss rate was about 0.201% min^{-1}, which corresponds to a peak temperature of about 639.46 °C in UM-WP. The maximum mass loss rate was about 0.605% min^{-1}, which corresponds to a peak temperature of about 770.8 °C in UN-WP (see Figs. 2 and 3).

The TG-DTG curves showed the presence of endothermic peaks with corresponding temperatures of 88.74 °C and 105 °C. These show that the endothermic peaks obtained refer to the onset of combustion, which is associated with the presence of hydrated or adsorbed water [18]. The UM-WP showed an obvious decrease during the exothermic reaction, confirming the presence of a few organic compounds which were exothermic.

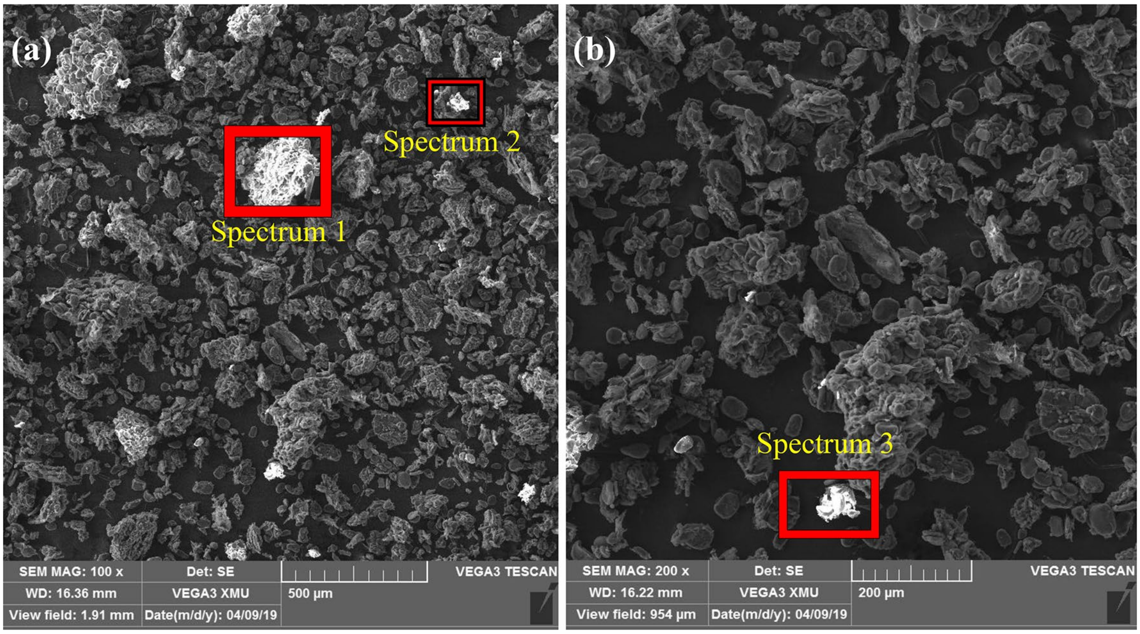

Fig. 4 **a**, **b** SEM images of UM-WP at 100× and 200×, respectively

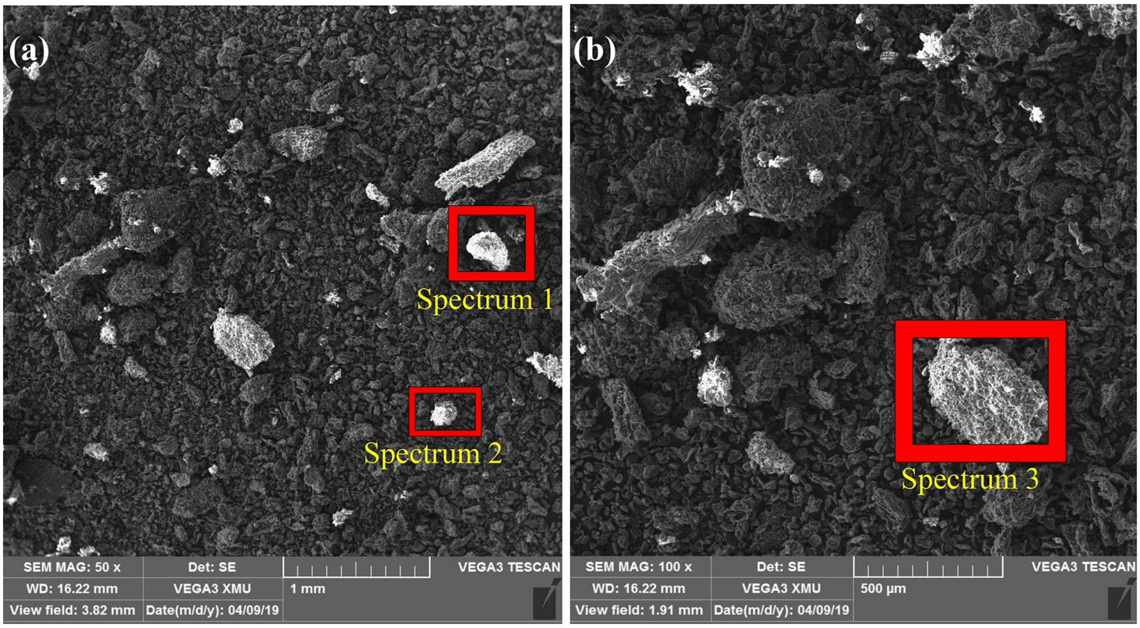

Fig. 5 **a**, **b** SEM images of UN-WP at 100× and 400×, respectively

SEM analysis of UM-WP and UN-WP

Figures 4a, b and 5a, b show the results of the morphological analysis of the UM-WP and UN-WP samples using SEM (sieved fraction of 200 µm, 500 µm and 1 mm). The morphologies of the samples were very similar. The micrographs revealed that the UM-WP and UN-WP have large and irregular particles and starch granules with high cellulose content, which are due to the increases in restrictions on molecular motion [19, 20]. These results might cause the oxygen to easily disperse inside the particles during combustion because the combustion reactivity of a biomass directly relates to the char morphology formed [7]. During carbonization of UM-WP and UN-WP, high fluidity and bubbles were produced due to the release of a large amount of volatile matter and which form a porous structure, which flows through the fluid mass and produces a non-homogeneous vacuolated structure [21, 22].

EDXS analysis of UM-WP and UN-WP

In the study, the EDXS was used to determine the elemental composition and to provide a structural idea of the biomass sample as illustrated in Figs. 6a–c and 7a–c. White spots appear in the sample which are elements. White spots are observed during SEM which was indicated in the form of spectrums as illustrated in Figs. 4a, b and 5a, b. These are elements from different categories as analyzed using EDXS.

The elements identified were potassium (K), magnesium (Mg), phosphorus (P), oxygen (O), carbon (C), nitrogen (N), sulfur (S), chlorine (Cl), silicon (Si), and cobalt (Co) (as

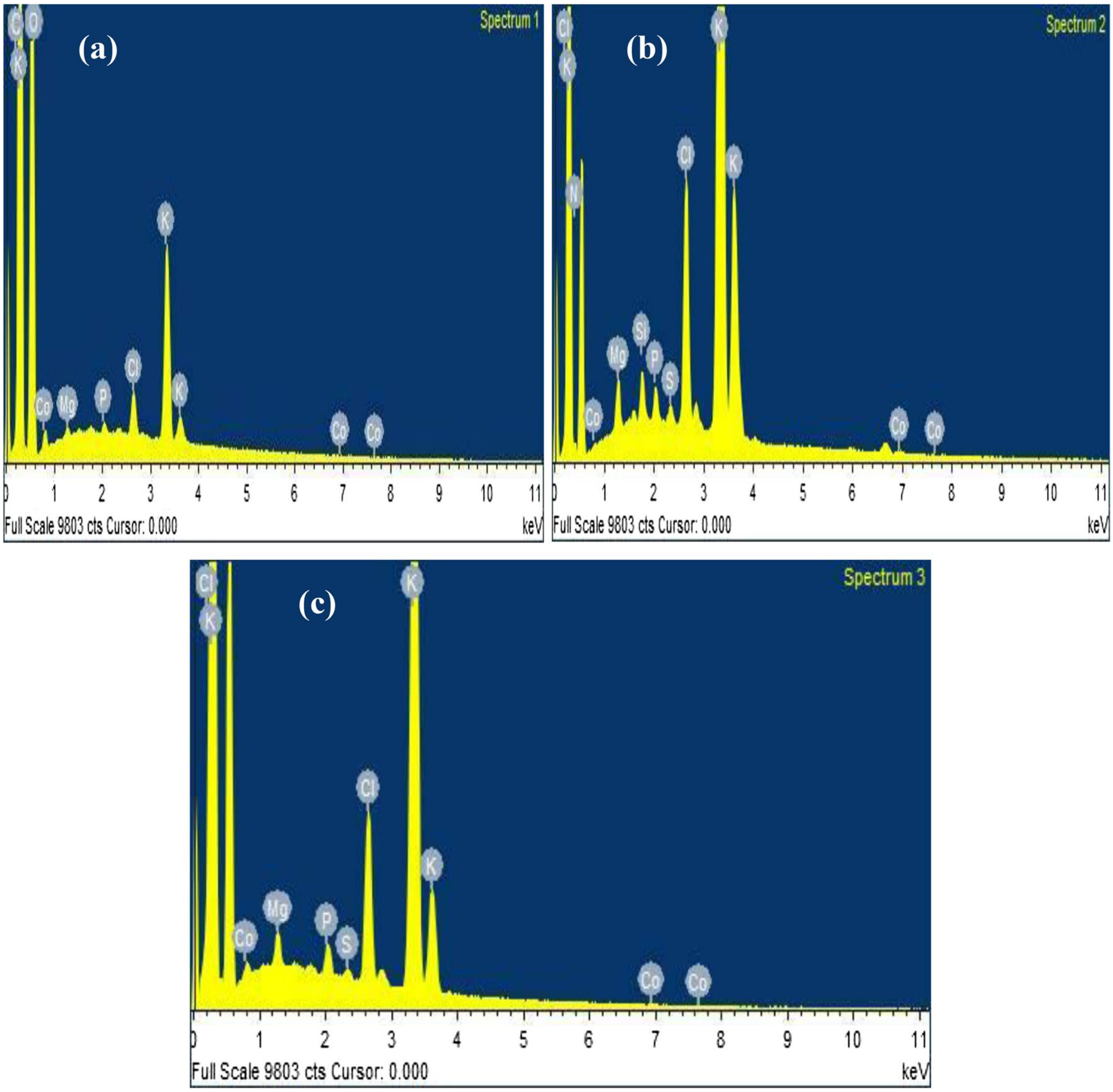

Fig. 6 **a**, **b**, and **c** EDXS spectrums of UM-WP at different points

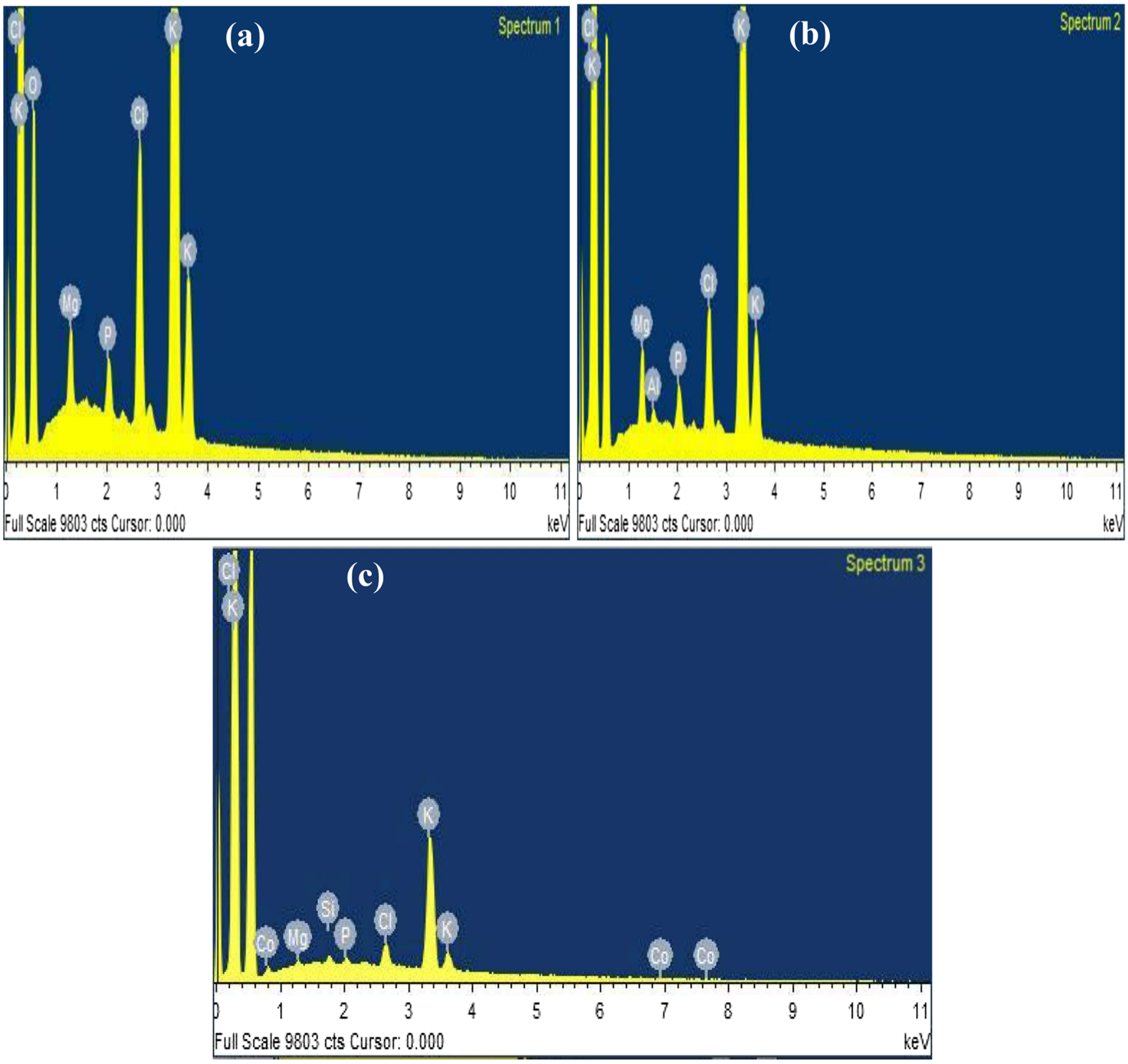

Fig. 7 **a**, **b**, and **c** EDXS spectrums of UN-WP at different points

shown in Table 2). Among these, the percentage of Mg, K and P decreased with an increase in C and O after pretreatment [7]. Besides, the percentage of O was found to be less compared to that of C. This trend is due to the fact that carbon forms the structural unit of cellulose and hemicelluloses. During combustion of biomass, the final solid phase is the most essential stage to the problem of alkali metals. The elements such as Cl, Si, S, Mg facilitates the mobility of several chemical species, particularly K, O and Fe, which is confirmed by KCl in deposits adherent [23], SiO_2, FeS_2, MgO, shows in Table 2 elemental compositions of UM-WP and UN-WP using EDXS. This biomass might grow an interest in the preparation of SiO_2, FeS_2, and MgO particles for a variety of applications, where the purity of materials is one of the most essential key parameters. Pure SiO_2 particles with crystalline phase can be used as the material source in photovoltaic [24], humidity sensors, film substrates and ceramics [25]. Pyrite (FeS_2) is a promising photoelectric material for solar energy conversion and storage [26].

Conclusion

This research presents new biomass accessible in Uganda for future bioenergy production. The HHV was found to be 15.52 MJ-kg^{-1} and 15.49 MJ-kg^{-1} for UM-WP and UN-WP, respectively. As compared to pretreated biomass, it was found that the smaller particle sizes had only minor intra-particle gradients and the bigger particle sizes had more of a linear pattern variation. The micrographs showed irregular particles and starch granules with high cellulose content which might enable the oxygen inside the particles to disperse more easily during combustion. The amount of O was found to be less compared to C in

Table 2 Elemental compositions of UM-WP and UN-WP as analyzed using EDXS

Sample	Element	Elemental compositions		
		(wt. %)		
		Spectrum 1	Spectrum 2	Spectrum 3
UM-WP	C	17.17	*	*
	O	16.38	*	*
	K	61.01	65.87	80.08
	N	*	23.36	*
	Cl	4.29	6.65	13.73
	Mg	2.49	1.23	2.54
	P	3.07	0.89	2.43
	Si	*	1.01	*
	S	*	0.43	0.88
	Co	-0.41	0.57	0.34
UN-WP	C	*	*	*
	O	49.34	*	*
	K	39.94	81.22	81.09
	N	*	*	*
	Cl	7.33	9.58	10.43
	Mg	1.98	5.40	2.34
	P	1.41	3.14	*
	Si	*		2.52
	Al	*	0.65	*
	Co	*		0.92

*Not detected

UM-WP. This trend is due to the fact that carbon forms the structural unit of cellulose and hemicelluloses. It is suggested that this exploration shows that UM-WP and UN-WP can be added to the biomass database as alternative energy sources, and material source for photovoltaic.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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