



Characterization and alkaline pretreatment of rice husk varieties in Uganda for potential utilization as precursors in the production of activated carbon and other value-added products

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ABSTRACT

In this study, 13 rice husk (RH) varieties from 4 agro-ecological zones in Uganda were characterized, NaOH-pretreated, and evaluated for their potential utilization as precursors for production of bio-oil, ash, char, and activated carbon for selected applications. RH varieties were characterized through particle size analysis, bulk density, proximate and ultimate analyses, specific surface area, pore volume, as well as lignocellulosic and inorganic compositions. Selected RH varieties were subsequently pretreated at NaOH concentrations of 1–4% w/v, using pretreatment ratios of 5 g RH: 40 mL NaOH. Properties varied among RH varieties, suiting them as feedstocks for different applications. Upland rice husk varieties are more suited precursors for production of bio-oil, and activated carbon due to their relatively lower ash content, higher specific surface area, as well as higher volatile matter and fixed carbon contents. Upland rice husks could as well be employed in the preparation of electrodes for electrochemical devices, due to their relatively higher specific surface area. A high ash content (21–32% dry basis) of lowland rice husks presents good prospects for their calcination, since larger amounts of rice husk ash could be obtained, and employed in different applications. Lowland rice husk varieties could also be more suited precursors for production of char for soil amendment, due to their relatively higher ash content, which subsequently increases their char yields. However, alkaline pretreatment of rice husks using 2–4% w/v NaOH can reduce the ash content by as much as 74–93%, depending on the rice husk variety, which paves way for utilizing rice husks with a high ash content in different applications. Aside from ash reduction, the enhanced specific surface area (1.2–1.7 m² g⁻¹), volatile matter (68–79%db) and fixed carbon (19–24%db) contents of NaOH-pretreated rice husks suggests they are more suited feedstocks than when employed in their raw form, for production of bio-oil, as well as activated carbon.

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1. Introduction

About 22 countries in Africa have developed ambitious National Rice Development Strategies (NRDS), aimed at doubling their total annual rice production from 14 million tons in 2008 to 28 million tons by the end of 2018 (Demont, 2013). Uganda is one of the 22 countries, and its NRDS seeks to more than triple its paddy production from about 177,800 Mt in 2008 to 680,000 Mt by the end of 2018 (MAAIF, 2009). Although the increase in paddy production

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could improve food security, the subsequent increase in rice husks generated from the milling process is of major environmental concern, if not properly managed. With about 20% of the total paddy weight constituting rice husks (Jung et al., 2013), the total annual generation of rice husks in Uganda is projected to be 136,000 Mt by the end of 2018. This more than triples the rice husk generation of 44,000 Mt in 2016 (Olupot et al., 2016), suggesting a potential increase in the burden associated with rice husk disposal. Presently, rice husk is one of the least utilized agricultural residues in Uganda and many other developing countries (Quispe et al., 2017), due to limitations in traditional methods to convert rice husks into useful products. For instance, disposal of rice husk via composting is constrained by the low nitrogen content of rice husk (Ji-lu, 2007), coupled with its high cellulose and lignin contents,

which consequently lower its biodegradability (Genevini et al., 1997). Rice husk is also unfit for animal feed, and cannot be used in feed production because of its low nutritional properties and a high silica content (Moraes et al., 2014). Consequently, these limitations compel rice millers to opt for alternative disposal options, such as open dumping or merely burning in open air, causing numerous environmental problems (Olupot et al., 2016). However, concerted research efforts are being made to find ways of disposing of rice husks in a sustainable manner, including energy recovery via direct combustion (Quispe et al., 2017), pyrolysis (Zheng et al., 2006), gasification (Olupot et al., 2016), and liquefaction (Huang et al., 2013a,b). Rice husk could also be utilized as feedstock for production of rice husk ash, which has potential applications as a filler material in thermoplastics (Chaudhary et al., 2002), construction material to produce concrete (Padhi et al., 2018), and as an adsorbent for pollutants removal from water and wastewater (Shen et al., 2014). Moreover, once extracted from the rice husk ash, silica (SiO_2) could be converted to silicon for use as an anode material for high-capacity lithium-ion batteries (Jung et al., 2013). Silica could also be employed to manufacture zeolite, which has numerous applications as a catalyst, ion exchanger, or as an adsorbent (Mohamed et al., 2015; Shen et al., 2014; Sivakumar, 2015). Other possibilities to utilize rice husks include production of biocomposites as building materials (Choi et al., 2006), biochar as a soil amendment (Gamage et al., 2016), filler in composites (Santhiago et al., 2018), catalyst (Liu et al., 2015), and as an adsorbent (Lee et al., 2018). On the other hand, activated carbon resulting from the activation of rice husks could be employed as an adsorbent, as well as an active material in the preparation of electrodes for high-performance supercapacitors, and lithium-ion batteries (Ahiduzzaman and Sadrul Islam, 2016; Zhang et al., 2017). Research on these possibilities has been on the increase lately, not only due to the need to sustainably dispose of rice husks, but also to supplement efforts geared to finding low-cost, as well as sustainable alternative precursors for production of value-added, eco-friendly products. This could save developing countries costs that would otherwise be spent on the importation of fossil-derived products. For instance, by opting to produce low-cost activated carbons from rice husks, Uganda could reduce its annual budget of US \$ 160,107, spent on the importation of commercial activated carbons (Mundi, 2018).

Depending on the intended application, different properties are considered important in the selection of rice husks as suitable precursors. For instance, in the production of activated carbon, a high carbon content, low level of ash, high thermal stability, small pore diameters, high porosity, as well as a high specific surface area are some of the properties of rice husks considered important (Kalderis et al., 2008; Yeganeh et al., 2006). These influence the activation efficiency, and consequently the adsorptive properties of the resultant activated carbon (Tan et al., 2017). These same properties could be considered important, in the selection of feedstocks for preparation of electrodes for electrochemical devices, since activated carbons usually employed as the active materials, also demand a high specific surface area and porosity (Mirzaeian et al., 2017). In the production of char for soil amendment, suitable feedstocks may exhibit a high fixed carbon content, as well as low volatile matter and moisture contents. On the other hand, if the intention is to employ rice husks as feedstocks for biofuel production, then the properties of important consideration may include; a higher heating value, high bulk density, as well as a low moisture, high volatile matter, high fixed carbon, low ash, high hydrogen, low nitrogen, and low sulphur contents (Olupot et al., 2016).

Although rice husks have been shown to exhibit some of the above mentioned properties expected of suitable feedstocks for different applications, the properties vary widely with rice variety, geographical location, climate, soil chemistry, and type of fertilizer

employed in paddy growth (Benassi et al., 2015; Deiana et al., 2008). Consequently, different qualities of value-added products can be obtained from rice husks, even when prepared under similar conditions (Kumagai et al., 2009). Compared to feedstocks such as coconut shells, sugarcane bagasse, and hardwood, rice husks are unusually high in ash content, for which 76–99% of the total weight is silica (SiO_2) (Menya et al., 2018). Aside from paving way for utilization of rice husk ash as a source of silica for various silicon-based products, the high ash content of rice husks could also be a huge hindrance to the successful utilization of rice husks in some applications. For instance, activated carbons with relatively lower specific surface areas may be obtained when rice husks with a high ash content are activated (Menya et al., 2018; Yun et al., 2003). The ash obstructs pore development, which consequently leads to activated carbon with low adsorption capacity. Besides, during chemical activation, the activating agent is consumed when it reacts with silica (SiO_2) in the rice husk ash, reducing the activating agent/carbon ratio. Consequently, activation occurs only at the exterior of the rice husk, which decreases pore formation, and subsequently lowers the surface area of activated carbon (Liou and Wu, 2009). A high ash content also hinders the successful utilization of rice husks as feedstocks for biofuel production, by not only lowering the higher heating value of rice husks (Bazargan et al., 2014), but also by causing agglomeration, and fouling in components of thermochemical conversion systems (Van Hunget al., 2018). In such applications, the high ash content of rice husks should be lowered to suit them as potential feedstocks (Deiana et al., 2008). Previous studies have revealed that NaOH-pretreatment can potentially lower the ash content in rice husks by over 92%wt, depending on the alkaline concentration, pretreatment ratio, soaking time, process temperature, and effectiveness of the water-washing stage (Hsieh et al., 2009; Usmani et al., 1994). The removal of SiO_2 from rice husks by NaOH-pretreatment is due to formation of water-soluble sodium silicate (Na_2SiO_3), when SiO_2 reacts with NaOH. Na_2SiO_3 is subsequently removed from rice husks via the water-washing stage (Liou and Wu, 2009).

Unlike elsewhere in the developing countries where rice is majorly grown, few studies have been conducted to tailor the different rice husk varieties in Uganda to specific applications. This study therefore aims at the characterization of non-treated and NaOH-pretreated rice husk varieties in Uganda, hitherto not evaluated for potential utilization as precursors in the production of bio-oil, ash, char as a soil amendment, and activated carbon as an adsorbent, as well as an active material in the preparation of electrodes for electrochemical devices. Characterization of the rice husk varieties involved determination of particle size, bulk density, proximate and ultimate properties, surface area, pore volume, as well as lignocellulosic and inorganic compositions. On the other hand, NaOH-pretreatment studies were conducted to establish the NaOH-concentration, which results in significant ash removal from the rice husk varieties. Pretreated rice husk varieties were subsequently characterized to determine the effect of NaOH pretreatment on their volatile matter and fixed carbon contents, specific surface area, total pore volume, as well as their char yields resulting from pyrolysis.

2. Materials and methods

2.1. Sample collection

About 60 kg of each of the thirteen paddy rice varieties dominantly grown in four selected agro-ecological zones of Uganda were obtained from Zonal Agricultural Research and Development Institutes (ZARDIs), and from selected rice irrigation schemes.

To ensure that pure samples were obtained for this study, rice agronomists were involved to identify the paddy rice varieties. To obtain rice husks, each of the paddy rice varieties, dried to moisture content of 13–14% wet basis (wb), were identically milled using the milltop rice milling machine (model SB-10) at Uganda's Agricultural Engineering and Appropriate Technology Research Centre (AEATREC), Namalere.

Table 1 shows the different rice husk varieties, their corresponding assigned codes, fertilizer type(s) applied during rice paddy growth, planting and harvesting periods, soil type, irrigation information, geographical origins, and global position systems (GPS) coordinates.

2.2. Experimental layout

The experimental layout followed throughout this study is schematically shown in Fig. 1. Section A of the layout shows the different activities that were undertaken to prepare and pretreat each of the rice husk varieties. Section B indicates the different characterization studies that were conducted on the rice husk varieties. Section C indicates the parameters that were determined to assess the effect of NaOH pretreatment on the selected rice husk varieties. A detailed description of the methods employed in sample preparation, pretreatment and characterization is highlighted in the sections that follow.

2.3. Sample preparation and pretreatment

Samples from each rice husk variety, and on as-received basis, were employed to determine the respective particle sizes, and bulk densities (Fig. 1). Other samples from each rice husk variety were prepared via two routes. The first route involved milling each of the as-received rice husk varieties to fractions of particle size

250 μm , and subsequently employing them in the characterization studies. Milling of the samples prior to their characterization was preferred, to obtain homogeneous samples that could give good reproducible results. The other preparation route involved obtaining samples of the as-received rice husk varieties, particularly those with the lowest (R_2), medium (R_1) and highest (R_{13}) ash contents, and subsequently employing them in the NaOH-pretreatment studies. These were initially washed with distilled water to remove any contaminants present in them, followed by oven drying at 105 °C for 12 h. Each of the oven dried samples were then alkaline pretreated by soaking 5 g of each of the selected rice husk varieties in 40 mL of 1.0, 2.0, and 4.0% w/v NaOH, followed by mixing and heating at 400 rpm and 50 °C, respectively, in a thermo shaker (model: HLC MHR 23) for 3 h, and allowing the samples to stand for 12 h. The alkaline pretreated rice husk samples were then transferred to a chromatographic column, with a filter at its bottom, as well as a top cover with a flexible hose, which was connected to the water tap. The pretreated samples were then thoroughly rinsed with running distilled water from the tap, until a neutral pH was obtained, followed by oven drying of the samples at 105 °C for 12 h. The alkaline pretreated rice husk samples were milled to fractions of particle size 250 μm , and subsequently employed to determine the proximate properties, char yield, as well as the specific surface area and pore volume.

2.4. Measurement of physical properties

2.4.1. Particle size

The particle size distribution of each raw rice husk variety on as-received basis was determined using standard mesh sizes arranged in the order of 2.80, 2.50, 2.00, 1.60, 1.25 mm, and lastly a pan at the bottom which collected the rice husk samples that passed through the last sieve. About 250 g of samples from each

Table 1
Paddy rice varieties obtained from each of the selected ZARDIs and rice irrigation schemes in Uganda.

Rice variety/ assigned code	Upland/ lowland*	Fertilizer(s) applied	Planting period	Harvesting period	Soil type	Irrigated/ rainfed	Geographical origin	GPS coordinates
NERICA 1 (R_1)	Upland	Diammonium phosphate (DAP) and urea	August–September	November–December	Ferritic and generally acidic (Hoima District Local Government, 2015)	Rain-fed	Bulindi ZARDI	1°29'54.92"N and 31°29'50.38"E
NERICA 1 (R_2)	Upland	DAP and urea	August–September	November–December	Sandy loam	Rain-fed	Buginyanya ZARDI	0°26'18.29"N and 33°28'58.33"E
NERICA 4 (R_3)	Upland	DAP and urea	August–September	November–December	Ferritic and generally acidic (Hoima District Local Government, 2015)	Rain-fed	Bulindi ZARDI	1°29'54.92"N and 31°29'50.38"E
NERICA 4 (R_4)	Upland	DAP and urea	August–September	November–December	Sandy loam	Rain-fed	Buginyanya ZARDI	0°26'18.29"N and 33°28'58.33"E
NERICA 4 (R_5)	Upland	DAP and urea	August–September	November–December	Sandy loam to sandy clay (Khaki, 2014)	Rain-fed	Ngetta ZARDI	2°17'28.10"N and 32°55'41.80"E
NERICA 10 (R_6)	Upland	DAP and urea	August–September	November–December	Ferritic and generally acidic (Hoima District Local Government, 2015)	Rain-fed	Bulindi ZARDI	1°29'54.92"N and 31°29'50.38"E
NERICA 10 (R_7)	Upland	DAP and urea	August–September	November–December	Sandy loam to sandy clay (Khaki, 2014)	Rain-fed	Ngetta ZARDI	2°17'28.10"N and 32°55'41.80"E
Wita-9 (R_8)	Lowland	DAP and urea	August–September	November–December	Sandy loam	Flood irrigation	Buginyanya ZARDI	0°26'18.29"N and 33°28'58.33"E
Wita-9 (R_9)	Lowland	–	–	–	Plinth soils (Bugiri District Local Government, 2004)	Flood irrigation	Kibimba irrigation scheme	0°32'06.91" N and 33°52'31.09"E
Pusa (R_{10})	Lowland	–	–	–	Plinth soils (Bugiri District Local Government, 2004)	Flood irrigation	Kibimba irrigation scheme	0°32'06.91" N and 33°52'31.09"E
K-85 (R_{11})	Lowland	DAP and urea	August–September	November–December	Clay (Oonyu, 2011)	Flood irrigation	Doho irrigation scheme	34° 02'E and 0° 50'N
K-98 (R_{12})	Lowland	DAP, and urea	August–September	November–December	Clay (Oonyu, 2011)	Flood irrigation	Doho irrigation scheme	34° 02'E and 0° 50'N
Super (R_{13})	Lowland	DAP and urea	August–September	November–December	Clay loam (Lamo et al., 2007)	Flood irrigation	Namulonge, National Crops Resources Research Institute	0°31'43.37"N and 32°36'44.44"E

Note: (1) *Lowland paddy rice is normally grown in flooded areas, while upland paddy rice is grown on dry land.
(2) NERICA is New Rice for Africa.

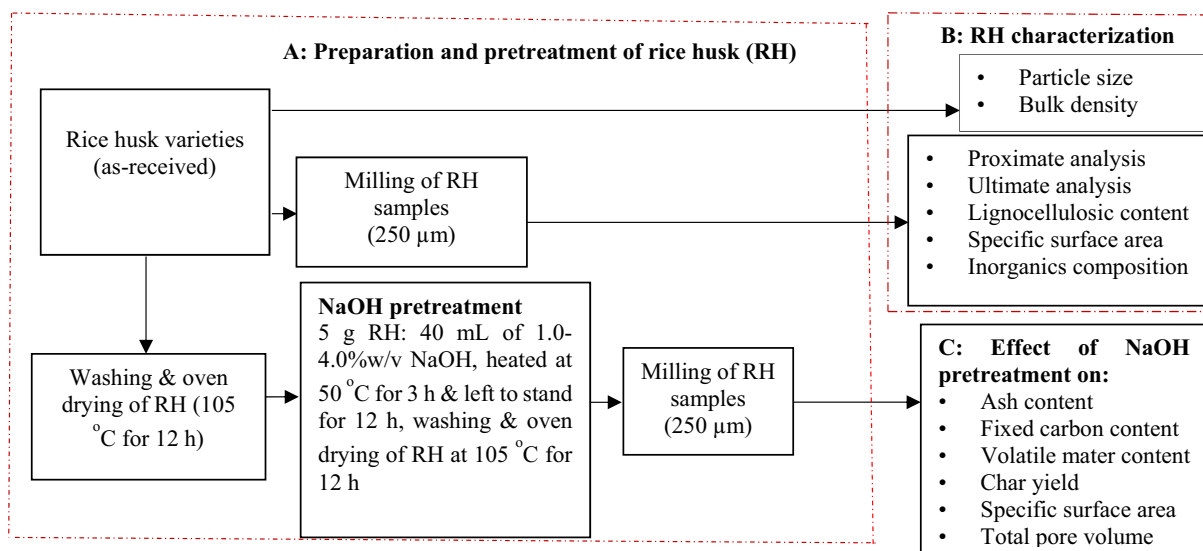


Fig. 1. Experimental layout of the procedures, followed throughout this study.

rice husk variety were randomly selected, placed in the first sieve, and covered with the sieve lid. The sieves were then mounted on a vibratory sieve shaker of series AS 200, Retsch, and operated at amplitude of 1.07 mm g^{-1} , for a sieving time of 10 min. The rice husk sample fractions collected in each sieve were then weighed, and the respective masses expressed as a percentage of the total sample weight.

2.4.2. Bulk density

The bulk density of each rice husk variety was determined according to the American Society for Testing and Materials (ASTM) E873–82 (2013). A cylindrical container of mass, 16.08 g and volume, 200 cm^3 (diameter 5.80 cm, height 7.57 cm), was used. The container was loosely filled with rice husks, and then dropped five times on a hard flat surface, allowing the rice husks to settle. More rice husks were added after settling, to fill the container. Finally, the container filled with the sample was weighed, and the bulk density of each rice husk variety determined as the ratio of mass of sample to the volume of the cylindrical container according to Eq. (1).

$$\text{Bulk density, } \rho_b \left(\text{kg m}^{-3} \right) = \frac{(W_2 - W_1)}{V} \quad (1)$$

where ρ_b is the bulk density of the sample (kgm^{-3}), W_2 is the weight of the container and sample (kg), W_1 is the weight of the container (kg), and V is the volume of the cylindrical container (m^3).

2.5. Proximate analysis and char yield

The method described by Omar et al. (2011) was followed to determine the proximate composition of the rice husk varieties. The method involves determining the moisture content, volatile matter, fixed carbon and ash content of the rice husk varieties using a thermogravimetric analyzer. About 10–15 mg sample of each rice husk variety (size $250 \mu\text{m}$) was placed in a platinum crucible, and heated in the furnace of the thermogravimetric analyzer (TA instruments Q500), from ambient temperature to $600 \text{ }^\circ\text{C}$ at a ramping rate of $20 \text{ }^\circ\text{C min}^{-1}$ under nitrogen flow of 60 mL min^{-1} . At the same ramping rate, heating was continued up to $900 \text{ }^\circ\text{C}$ but under air flow to allow for char oxidation. This temperature was held constant for 3 min until there was no further change in mass of the remaining residue. The moisture content, volatile matter, fixed carbon, and ash content of each rice husk variety were

then read off from the respective thermogravimetric curves of percent weight loss versus temperature, generated using the universal analysis software. Moisture content was obtained as weight loss due to dehydration of rice husks from room temperature to temperatures ranging from 105 to $120 \text{ }^\circ\text{C}$. Volatile matter content was obtained as weight loss due to thermal degradation between 120 and $600 \text{ }^\circ\text{C}$. Fixed carbon content was obtained as the weight loss due to combustion of the remaining organic material at temperatures ranging from 600 to $900 \text{ }^\circ\text{C}$. Char yields of the different rice husk varieties were determined from their respective thermogravimetric (TG) curves, as the ratio of dry sample weight after pyrolysis to the weight of the dry raw sample (Lua et al., 2004). The remaining residue after combustion of the organic material represented the ash content.

2.6. Ultimate analysis

The ultimate analysis on each of the rice husk varieties was carried out to determine the elemental composition, including carbon (C), hydrogen (H), sulphur (S), nitrogen (N), and oxygen (O). The C, H and S were determined using an ELTRA CHS analyzer. On the other hand, nitrogen content in the rice husks was determined separately using the Kjeldahl method (AACC International, 2000). This is based on the conversion of the fuel bound nitrogen to ammonia (NH_3), which is subsequently separated by distillation and determined by titration using HCl solution and methyl red as indicator. The oxygen content in the rice husks was determined by difference.

2.7. Lignocellulosic composition

Lignin, hemicellulose and cellulose contents of the rice husk varieties were analyzed via neutral detergent fibre (NDF), acid detergent fibre (ADF) and acid detergent lignin (ADL), according to methods described by van Soest et al. (1991). Hemicellulose content was obtained by subtracting ADF from the NDF value, while the cellulose content was obtained by subtracting ADL value from the ADF value (Carrier et al., 2011).

2.8. Specific surface area and pore volume

The total specific surface areas ($a_{s,BET}$) of the rice husk varieties were determined by an automatic adsorption instrument

(BELSORP-mini, BEL JAPAN, INC) using liquid nitrogen at 77 K, based on the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938). More specifically, multi-points of up to 5 were considered in the determination of $a_{s,BET}$. However, prior to measurement, about 100–120 mg of the sample was pretreated, first by oven drying overnight at 105 °C and later degassing under vacuum in the sorption analyzer at 105 °C under N_2 atmosphere for 3 h to remove the remaining moisture and/or gases on the sample surface. The total pore volume, V_T , was evaluated from the N_2 adsorption data as liquid volume of adsorbate adsorbed at a relative pressure (P/P_0) of 0.99.

2.9. Metal composition analysis

In this study, K, Al, Ca, Mg, Na, P, Fe, Mn, and Zn contents of the selected rice husk varieties were determined by means of the inductively coupled plasma optical emission spectroscopy (ICP-OES) technique. The method described by Kleinebecker et al. (2013) was followed to determine concentrations of the inorganics in the selected rice husk varieties. This involved weighing 300 mg of each of the milled rice husk samples into Teflon digestion tubes, followed by addition of 6 mL of 65% HNO_3 and 4 mL of 30% H_2O_2 , to extract the ion-exchangeable metal species from the rice husk sample, while maintaining the sample structure. The well-mixed sample was then digested by refluxing in a microwave oven (model: CEM Mars Express) at 190 °C for 15 min. The digested samples were transferred to 50 mL centrifuge tubes and centrifuged (model: Rotofix 32 A) at 4000 rpm for 20 min. The samples were then left to stand overnight. 1 mL of each sample was transferred into ICP autosampler tubes and diluted using ICP millipore water to a final volume of 12 mL prior to analysis using ICP-AES. The different concentrations of inorganics in the digest were then determined according to Eq. (2).

$$\text{Concentration (dry weight)} \text{ (mg g}^{-1}\text{)} = \frac{(C \times V)}{(W \times S)} \quad (2)$$

where C is concentration (mg L^{-1}), V is final volume in liters after sample filtration, W is weight of wet sample (kg), and S is percentage of solids.

3. Results and discussions

3.1. Particle size distribution

The experimental results of the particle size distribution of the raw rice husk varieties (on as-received-basis) are presented in Table 2. The results indicate that the particle sizes predominantly range from 1.30 to 2.50 mm and less than 2.0 mm for upland (R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and R_7) and lowland (R_8 , R_9 , R_{10} , R_{11} , R_{12} and R_{13}) rice husk varieties, respectively. The obtained particle sizes are within/or close to the ranges of 2–3 mm and 1.70–2.40 mm reported by Fang et al. (2004) and Mansaray and Ghaly (1997) for rice husks from China and Sierra Leone, respectively. A wider particle size distribution, which is typical of the raw rice husk varieties employed in this study, is advantageous for the densification

(pelleting or briquetting) process. This is because the smaller particles are able to rearrange and fill in the void space of larger particles producing denser and durable pellets or briquettes (Mani et al., 2004). The resulting pellets or briquettes could then be employed as precursors in the production of activated carbon, giving it mechanical strength sufficient to withstand abrasion and attrition. This is especially important, if the resulting activated carbon is to be employed as a partial or full replacement of the sand filtration medium in water treatment (Schendel et al., 2009).

The particle size of the rice husk varieties may also influence the char yield upon pyrolysis of the rice husks, since larger particles offer higher resistance to the escape of primary pyrolysis products, which are later thermally cracked in the secondary reactions, forming more char (Basu, 2010; Mansaray and Ghaly, 1997). For this reason, pyrolysis of raw upland rice husk varieties could result in higher char yields than the raw lowland rice husk varieties due to their relatively larger particle sizes. Char yield is of primary interest, for instance, if the char produced will be employed either as a fuel, soil amendment, adsorbent, or as activated carbon precursor (Tripathi et al., 2016). In the latter option, the char formed is activated in the presence of either suitable oxidising gases (Álvarez et al., 2015) or alkaline metallic oxides (Somasundaram et al., 2013). However, for purposes of producing activated carbon with enhanced pore development, activation of biomass is still better with smaller particles, since the volatiles escape easily from smaller biomass particles.

3.2. Bulk density and moisture content

3.2.1. Bulk density

The results in Table 3 indicate that the bulk density of upland rice husk varieties is typically lower than that of lowland rice husk varieties, with values ranging from 81 to 108 kg m^{-3} and 111 to 135 kg m^{-3} , respectively. The lower bulk density of upland rice husk varieties may be attributed to their relatively larger particle sizes (Table 2), which increase the pore space between the particles, and consequently decreasing the bulk density (Chevanan et al., 2010). The bulk densities obtained in this study lie within the ranges reported in the literature (Mansaray and Ghaly, 1997; Olupot et al., 2016). However, the low bulk density of rice husk is problematic due to challenges associated with its handling, transportation, storage, and utilization in its original form. The latter could lead to increased reaction rates and reduced residence time in the reactor, resulting in a lower conversion efficiency (Mansaray and Ghaly, 1997). Besides, some applications that require activated carbon with high mechanical strength to withstand abrasion and attrition during backwashing, may not be suitably obtained from rice husk due to its low bulk density (Pendyal, 1999). A possible intervention to these challenges is to densify rice husks or its char using suitable binders to form either pellets or briquettes.

3.2.2. Moisture content

The moisture content of the rice husk varieties range from 6.0 to 7.7 %wt (Table 3). This compares well with the moisture contents

Table 2
Particle size distribution of the rice husk varieties.

Particle size (mm)	Proportion of particle sizes (%wt)												
	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	R_{13}
<1.3	10.0	14.5	3.7	8.2	10.7	7.4	13.8	16.5	11.3	20.1	20.0	24.8	25.3
1.3–1.6	13.9	15.8	10.6	16.5	13.6	16.8	11.8	26.8	16.9	21.0	17.9	26.6	18.4
1.6–2.0	44.7	35.0	46.2	52.7	46.2	43.5	30.1	47.7	53.4	50.8	52.1	40.0	41.9
2.0–2.5	29.1	32.3	37.5	20.7	28.0	31.3	43.1	8.2	18.0	7.6	9.4	7.8	13.0
>2.5	2.3	2.3	2.0	1.7	1.5	0.8	1.2	0.8	0.4	0.4	0.6	0.7	1.4

Table 3
Bulk density, moisture content, proximate, ultimate and lignocellulosic properties of rice husk varieties in Uganda.

Rice variety	Mean bulk density (kg m ⁻³)	Mean moisture content (%wt)	Ultimate analysis (%daf)				Proximate analysis (%db)				Char yield (%db)	Char yield (%daf)	VM and FC content of 2%w/v NaOH pretreated rice husks	Lignocellulosic composition (%daf)				
			C				Ash							VM	FC	Lignin	Hemicellulose	Cellulose
			H	S	N	O	FC	VM										
R ₁	102.25 ± 1.67	6.90 ± 0.24	34.05 ± 0.31	5.87 ± 0.22	0.21 ± 0.01	0.82 ± 0.06	59.05 ± 0.96	17.57 ± 0.42	19.90 ± 0.15	62.53 ± 0.18	37.47 ± 0.22	24.14 ± 0.34	76.45 ± 1.12	20.72 ± 1.33	12.08 ± 0.11	26.78 ± 0.89	32.88 ± 0.12	
R ₂	95.75 ± 0.74	6.69 ± 0.30	37.30 ± 0.14	6.30 ± 0.15	0.23 ± 0.01	0.81 ± 0.05	55.36 ± 0.79	13.80 ± 0.16	19.14 ± 0.27	67.06 ± 0.25	32.94 ± 0.06	22.20 ± 0.12	78.68 ± 1.09	19.64 ± 0.80	13.35 ± 0.14	22.60 ± 0.91	38.79 ± 0.86	
R ₃	99.35 ± 1.19	7.22 ± 0.13	35.60 ± 0.53	6.10 ± 0.15	0.20 ± 0.01	0.70 ± 0.00	57.40 ± 0.45	16.98 ± 0.09	19.01 ± 0.13	64.01 ± 0.47	35.99 ± 0.28	22.90 ± 0.36	-	-	15.19 ± 0.09	26.15 ± 0.01	31.31 ± 0.50	
R ₄	107.72 ± 1.68	6.13 ± 0.88	35.70 ± 0.15	5.90 ± 0.01	0.08 ± 0.01	0.70 ± 0.00	57.62 ± 0.28	24.40 ± 0.79	17.34 ± 0.70	58.26 ± 0.28	41.74 ± 0.48	22.94 ± 0.33	-	-	12.62 ± 0.54	17.04 ± 0.90	31.66 ± 0.85	
R ₅	105.98 ± 3.74	7.39 ± 0.20	33.86 ± 0.59	5.82 ± 0.04	0.21 ± 0.01	0.81 ± 0.01	59.30 ± 0.48	18.94 ± 0.41	18.25 ± 0.07	62.81 ± 0.33	37.19 ± 0.51	22.51 ± 0.43	-	-	13.65 ± 0.00	20.72 ± 0.57	36.23 ± 0.66	
R ₆	81.32 ± 0.73	6.82 ± 0.85	34.87 ± 1.20	5.92 ± 0.09	0.22 ± 0.00	0.93 ± 0.00	58.06 ± 0.30	18.78 ± 0.26	19.78 ± 0.67	61.44 ± 0.27	38.56 ± 0.13	24.35 ± 0.41	-	-	12.13 ± 0.31	23.50 ± 0.81	32.83 ± 0.83	
R ₇	102.85 ± 1.21	7.34 ± 0.21	35.61 ± 0.43	6.05 ± 0.07	0.07 ± 0.02	0.81 ± 0.08	57.46 ± 0.01	18.33 ± 0.82	18.68 ± 0.35	62.99 ± 0.94	37.01 ± 0.49	22.86 ± 0.61	-	-	12.90 ± 0.53	24.83 ± 0.25	32.59 ± 0.71	
R ₈	111.62 ± 1.69	7.06 ± 0.86	36.95 ± 0.45	5.87 ± 0.11	0.20 ± 0.00	0.69 ± 0.00	56.29 ± 0.69	21.10 ± 0.67	18.48 ± 0.31	60.42 ± 0.28	39.58 ± 0.98	23.42 ± 0.39	-	-	12.58 ± 0.22	25.16 ± 0.39	32.37 ± 0.06	
R ₉	116.50 ± 0.99	6.01 ± 0.69	36.66 ± 0.14	6.06 ± 0.09	0.06 ± 0.01	0.58 ± 0.04	56.64 ± 0.19	21.59 ± 0.69	19.28 ± 0.04	59.13 ± 0.13	40.87 ± 1.65	24.59 ± 0.08	-	-	18.30 ± 0.09	19.85 ± 0.75	33.84 ± 0.33	
R ₁₀	124.82 ± 1.89	7.35 ± 0.96	30.67 ± 0.75	4.90 ± 0.07	0.05 ± 0.00	0.58 ± 0.02	63.80 ± 0.03	28.58 ± 0.35	15.69 ± 0.74	55.73 ± 0.85	44.27 ± 0.37	21.97 ± 0.38	-	-	10.39 ± 0.15	17.90 ± 0.48	31.46 ± 0.26	
R ₁₁	120.93 ± 2.28	7.69 ± 0.98	36.82 ± 0.35	6.19 ± 0.08	0.22 ± 0.00	0.46 ± 0.00	56.31 ± 0.73	22.36 ± 0.06	17.87 ± 0.60	59.76 ± 0.30	40.23 ± 0.54	23.02 ± 0.22	-	-	12.00 ± 0.04	17.66 ± 0.90	40.94 ± 0.92	
R ₁₂	134.27 ± 2.70	7.50 ± 0.57	33.01 ± 0.24	5.34 ± 0.10	0.09 ± 0.02	0.82 ± 0.03	60.74 ± 0.01	27.34 ± 0.69	15.90 ± 0.07	56.76 ± 0.52	43.24 ± 0.21	21.88 ± 0.16	-	-	15.87 ± 0.70	22.23 ± 0.11	32.36 ± 0.44	
R ₁₃	113.80 ± 2.81	7.18 ± 0.31	31.95 ± 0.15	5.86 ± 0.06	0.05 ± 0.00	0.45 ± 0.01	61.69 ± 0.06	31.15 ± 0.11	15.30 ± 0.28	53.55 ± 0.32	46.45 ± 0.17	22.22 ± 0.21	68.78 ± 1.86	23.33 ± 0.08	10.00 ± 0.05	18.19 ± 0.65	34.25 ± 0.23	

Note: FC is fixed carbon; VM is volatile matter; %daf is %dry-ash-free basis; db is dry basis.

of rice husks successfully activated elsewhere (Kaldaris et al., 2008; Liou and Wu, 2009; Liu et al., 2016). The amount of moisture in the rice husks may influence the char yield, which is of primary interest for economic feasibility of the pyrolysis process, and consequently the activation process. According to Wang and Cheng (2014), biomass should have moisture content below 10 %wt prior to pyrolysis. Otherwise, pyrolysis of biomass with a higher moisture content results in a low char yield (Tripathi et al., 2016), coupled with high yields of condensable products, such as pyrolytic oil or tar (Demirbas, 2004a). Based on this, all the rice husk varieties were well suited for pyrolysis to produce char, which could subsequently be activated by employing suitable activating agents such as carbon dioxide, steam, air or their mixtures via physical activation or by employing either NaOH or KOH via chemical activation. Pyrolysis of rice husks with low moisture contents has several other benefits including, (i) possibility to minimize the need for extra heat energy to vaporize the moisture in the rice husks, (ii) possibility to minimize the formation of tar, which would otherwise reduce char formation, and (iii) possibility to lower the time required to attain the final pyrolysis temperature, making the pyrolysis process more economically viable (Tripathi et al., 2016). Previous studies have also indicated that moisture content increases dry grinding energy requirements, as well as affects final particle size distribution of biomass, with dry feeds having more fine particles (Mani et al., 2004; Williams et al., 2016). Moreover, pyrolysis of the more finely ground particles results into increased reaction rates and decreased residence times in the reactor, leading to low thermochemical conversion efficiencies (Williams et al., 2016). However, for purposes of producing activated carbon with a high specific surface area and a more developed micropore volume, biomass with smaller particle sizes is preferred for activation (Bagheri and Abedi, 2009). Aside from pyrolysis, the rice husk varieties could also be employed in combustion systems, since their moisture contents are less than 50 %wb (McKendry, 2002).

3.3. Proximate, ultimate and lignocellulosic composition

The results of the proximate, ultimate and fibre analyses of the raw rice husk varieties on dry basis are shown in Table 3.

3.3.1. Proximate analysis

The volatile matter, fixed carbon and ash content of the rice husk varieties ranged from 53.55 to 67.06%db, 15.30 to 19.90%db, and 13.80 to 31.15%db, respectively as shown in Table 3. These results compare well with the proximate composition of rice husks successfully activated in the previous studies (Álvarez et al., 2015; Kumagai et al., 2007). With such composition, these authors were able to obtain activated carbon from rice husks with specific surface area as high as 176–2841 m² g⁻¹, depending on the extent of pretreatment and process conditions. In particular, upland rice husk varieties (R₁, R₂, R₃, R₅, R₆ and R₇) that exhibited relatively lower ash content, as well as higher volatile matter and fixed carbon contents could result in activated carbons with a much more enhanced surface area than the other rice husk varieties. Moreover, since activated carbon with a relatively high specific surface area is desired in the preparation of electrodes for electrochemical devices such as supercapacitors (Mirzaeian et al., 2017), then upland rice husk varieties could also be the most suitable precursors for such an application. During pyrolysis, volatile matter is released, which leads to the development of internal porosity of char by opening of previously blocked pores, creating new pores, and/or enlargement of existing pores. However, increased devolatilization of the biomass leads to low char yields (Lua et al., 2004). On the other hand, the enhancement in surface area of activated carbon from precursors with low ash content may be attributed to; (i) the increased ratio of activating agent to carbon resulting from the

reduced consumption of the chemical activating agent, and (ii) the minimized extent of pore obstruction by inorganics, which otherwise lead to activated carbon with low adsorption capacity, and low mechanical strength (Yeganeh et al., 2006). The low ash content in upland rice husk varieties could also imply that low pre-treatment costs would be incurred, since low concentrations of the alkaline (e.g. NaOH, KOH), and/or acid (e.g. HCl, HNO₃), would be needed to lower their ash content to desired levels. The low ash content in these rice husk varieties is indeed expected since the soil with rainwater; the only water source for upland rice, lacks enough silicon element. On the other hand, the lowland rice husk varieties, which are normally irrigated, obtain considerable amounts of silicon from the typically less-weathered soils and silicon rich groundwater used to flood the crop (Winslow, 1995), thus the high ash content in the lowland rice husk varieties.

Although not desired in the production of activated carbon, the high ash content of lowland rice husk varieties presents good prospects for their calcination, since relatively larger amounts of rice husk ash (predominantly silica) could be obtained, and subsequently employed for various industrial applications, as highlighted in Section 1. However, each of the potential industrial applications demands specific properties of the rice husk ash. For instance, a high purity level of rice husk ash is required if it is to be employed in the synthesis of advanced materials, high reactivity with cement if rice husk ash is to be employed in construction materials, appropriate grain size if rice husk ash is to be employed as loading agent in polymer production, and a high surface area and porosity if adsorption and catalytic properties are demanded for Chandrasekhar et al. (2005). These properties can be attained by judicious selection of appropriate combustion technology and conditions (Fernandes et al., 2016). Based on ash content, the order of suitability of the rice husk varieties as feedstocks for ash (or silica) production is as follows; $R_{13} > R_{10} > R_{12} > R_4 > R_{11} > R_9 > R_8 > R_5 > R_6 > R_7 > R_1 > R_3 > R_2$.

The relatively higher volatile matter content of upland rice husk varieties suggests promising prospects for pyrolyzing rice husks, where the released volatiles could serve as raw materials to produce synthesis gas, while at the same time, the produced char could serve as catalyst for catalytic reforming of the volatiles (Li et al., 2017). On the other hand, since the results of the proximate composition of the rice husk varieties compare well with those of rice husks successfully pyrolyzed elsewhere, for bio-oil production (Abu Bakar and Titiloye, 2013; Balasundram et al., 2018; Huang et al., 2013a,b), then the rice husk varieties in this study could also be employed for bio-oil production. Though not investigated in this present study, pyrolysis of upland rice husk varieties could result into higher bio-oil yields than the lowland rice husk varieties, due to their relatively higher volatile matter content. During pyrolysis, the volatiles produced are condensed to bio-oil; a valuable low-cost renewable liquid fuel, as well as a potential feedstock for producing some renewable chemicals (Balasundram et al., 2018).

3.3.2. Ultimate analysis

The carbon, hydrogen, oxygen, nitrogen and sulphur contents of the rice husk varieties ranged from 30.67 to 37.30%db, 4.90 to 6.30%db, 55.36 to 63.80%db, 0.45 to 0.93%db, and 0.05 to 0.23%db respectively (Table 3). The ultimate composition of the rice husk varieties is close to that of rice husks activated elsewhere (Álvarez et al., 2015; Kumagai et al., 2007; Liu et al., 2016). In the selection of activated carbon precursors, biomass with a comparatively higher carbon content is most desired (Menéndez-Díaz and Martín-Gullón, 2006). Based on this, the order of suitability of the rice husk varieties is as follows; $R_2 > R_8 > R_{11} > R_9 > R_4 > R_7 > R_3 > R_6 > R_1 > R_5 > R_{12} > R_{13} > R_{10}$. This same order could still apply if the produced activated carbon is to be employed as the

active material in the preparation of electrodes for electrochemical devices, such as supercapacitors. This is because a higher carbon content of rice husks could translate to a higher carbon yield, as well as a higher specific surface area of activated carbon, which are desired in the preparation of electrodes for electrochemical devices. On the other hand, the relatively high oxygen content in the rice husk varieties, implies a higher reactivity during pyrolysis, which consequently lowers the final product yields and quality (Tripathi et al., 2016). It is also worth noting that all the rice husk varieties in this study could be suited for chemical activation, since their hydrogen and oxygen contents are greater than 5% and 25% respectively (Louis, 1975). At such concentrations, a considerable amount of activation can be realized, making chemical activation commercially useful.

The results of the elemental composition of rice husk varieties compare with those of rice husks successfully pyrolyzed for soil amendment (Mohan et al., 2018), as well as bio-oil production (Abu Bakar and Titiloye, 2013), suggesting that the rice husk varieties could be employed for such applications. By applying char to the soil, the soil's organic carbon levels could increase, while at the same time returning most nutrients harvested with the rice husks back to the soil (Kongthod et al., 2015). Moreover, once applied to the soil, carbon mitigation could be achieved, since the char remains stable in the soil, achieving longer term carbon sequestration (Munda et al., 2018). In bio-oil production, suitable feedstocks need to have a low oxygen content, as well as high carbon and hydrogen contents (Balasundram et al., 2018). Based on this, R_2 could be the most promising feedstock for bio-oil production. However, because of the relatively high oxygen content of the rice husk varieties, low quality bio-oils could be expected (Vasilkovová et al., 2014).

The low nitrogen and sulphur contents in the rice husk varieties, compared to precursors like petroleum coke (Wu et al., 2005), and pomegranate seeds (Uçar et al., 2009) are of environmental benefit, since upon thermochemical treatment of rice husks, a minimal risk of NO_x and SO_x emissions could be expected (Tripathi et al., 2016).

3.3.3. Lignocellulosic composition

The lignin, hemicellulose and cellulose contents of the rice husk varieties ranged from 10.00 to 18.30%daf, 17.04 to 26.78%daf, and 31.31 to 40.94%daf respectively (Table 3). The lignin content obtained in this study is close/or within the range 10.58–13.47% daf reported by Olupot et al. (2016) for selected upland rice husk varieties in Uganda, but lower than the range 24.95–31.41% reported by Mansaray and Ghaly (1997) for rice husks from Sierra Leone. Hemicellulose and cellulose contents of the rice husk varieties were also close/or within the ranges reported by Olupot et al. (2016). These lignocellulosic fractions influence the product yield of pyrolysis (Tripathi et al., 2016). For instance, lignin contributes a higher proportion of carbon content in the activated carbon compared to cellulose, due to its high aromatic content, as well as its complex polymer structure. The low carbon yield resulting from the thermal decomposition of cellulose is due to the fact that significant amount of carbon is lost from the glucose derivatives due to volatilization. Therefore, based on the lignin content, the order of suitability of the rice husk varieties as activated carbon precursors is as follows; $R_9 > R_{12} > R_3 > R_5 > R_2 > R_7 > R_4 > R_8 > R_6 > R_1 > R_{11} > R_{10} > R_{13}$. This same order could apply if carbon-based materials are to be prepared from the lignin fractions of the rice husk varieties, for application as electrode materials for supercapacitors, and lithium-ion batteries. A significant body of research reveals that carbonization of lignin under carefully controlled conditions could result in nanoporous carbon, suitable as electrode material (Liu et al., 2017; Santhiago et al., 2018).

Based on the lignocellulosic fractions, the suitability of rice husk varieties as feedstocks for bio-oil production is as follows; $R_2 > R_1 > R_{11} > R_8 > R_7 > R_5 > R_3 > R_6 > R_{12} > R_9 > R_{13} > R_4 > R_{10}$. This is based on the fact that, bio-oil from the pyrolysis of lignocellulosic biomass is largely contributed by its cellulose and hemicellulose fractions, as compared to the lignin fraction. Cellulose and hemicellulose fractions are mainly made of carbohydrates, which are less thermally stable than the polyaromatic hydrocarbons and complex organic compounds present in lignin. Consequently, the hemicellulose, and cellulose fractions decompose more easily, resulting in higher bio-oil yields (Muley et al., 2016; Wang and Cheng, 2014). However, to maximize bio-oil yield, a low temperature, high heating rate, as well as short gas residence time, are required during pyrolysis of biomass (Demirbas, 2004b).

3.4. Char yield of the raw rice husk varieties

On dry basis, char yields obtained from the pyrolysis of rice husk varieties ranged from 32 to 47%db, which compare well with char yields reported in literature (Table 4). In the order of increasing char yields, the rice husk varieties could be ranked as; $R_{13} > R_{10} > R_{12} > R_4 > R_{19} > R_{11} > R_8 > R_6 > R_1 > R_5 > R_7 > R_3 > R_2$, suggesting that pyrolysis of lowland rice husk varieties results in higher char yields than upland rice husk varieties. However, when computed on dry ash-free basis (Table 3), the variation in char yields among the rice husk varieties was relatively small, suggesting that their wide variation in char yields could be largely due to differences in their ash contents. Therefore, in char applications where ash is not much desired, alkaline pretreatment paves way for utilization of rice husks with high ash contents. However, alkaline pretreatment of rice husks could increase the cost of char production, since water, heat energy, alkaline and/or acid are among the consumables during the pretreatment process. Production of activated carbon is one of the numerous char applications, where a high level of ash is not much desired, for reasons already cited in Section 3.3.1. In such applications, expression of char yield on dry ash-free basis is usually preferred to avoid a positive bias in the yield, in case of using biomass samples with a high ash content. On the other hand, expression of char yield on dry basis is preferred in applications, where ash (or minerals) in the char are also of significant importance. Such char applications are mostly

limited to soil conditioning, where soil fertility, and subsequently crop growth is improved. More specifically, the presence of mineral nutrients (Ca, Mg, K, Si and P) in the char may allow the char to act as a direct source of mineral nutrients, promoting plant growth (Xu et al., 2017). On the other hand, the release of anions such as OH^- , CO_3^{2-} , PO_4^{3-} and SO_4^{2-} from the minerals in the char to the soil, could immobilize the heavy metals in soil, by forming metal precipitates, and subsequently reducing their availability to plants (Al-Wabel et al., 2015). However, if heavy metals within the ash fraction of the resulting char occur in relatively high concentrations, then char application as a soil amendment could contribute to a heavy metal loading in soils they are applied to, raising health and environmental concerns (Beesley et al., 2015).

3.5. Effect of alkaline pretreatment

3.5.1. Ash content

As can be seen from Fig. 2, the ash content of the rice husk varieties decreased with increasing NaOH concentration. At a NaOH concentration of 2–4%w/v, the ash content was reduced by 74–93%, depending on the rice husk variety (Table 4). This reduction allows the rice husk varieties to attain ash content levels that are close to or less than 5%db, which is typical of activated carbon precursors (Arena et al., 2016; Hidayu et al., 2013; Kalderis et al., 2008; Kumar and Jena, 2016), as well as biomass fuels with relatively low ash content (FAO, 1986). Moreover, the remaining ash in the rice husks could have a catalytic effect on the pyrolysis reactions, leading to increased char yields (Brownsort, 2009). Once the resulting char is upgraded to activated carbon, a reasonably small amount of ash could be desired in the activated carbon, depending on its intended application. For instance, the presence of metallic impurities in activated carbon has been reported to enhance its adsorption capacity for humic and fulvic acids in water (Daifullah et al., 2004). Presence of minerals in the activated carbon could also play an important role in applications, where activated carbon is to be employed as a precursor for electrodes of fuel cells and supercapacitors, or as photoactive components (Xu et al., 2017; Yuan et al., 2013). Consequently, ash removal from rice husks should be limited to acceptable levels, depending on the target application.

Table 4

Comparison of rice husk char yields, pretreatment conditions and extent of ash removal obtained in this study with literature values.

Biomass type	Initial ash content (%db) pyrolysis temperature (°C)		Pretreatment conditions				Highest ash removal		Reference
			NaOH conc (%w/v)	Pretreatment ratio (g RH: mL NaOH)	Heating temperature (°C)	Heating period (h)	NaOH conc (%w/v)	Ash removal (%)	
Rice husk	13–32	600	32–47	–	–	–	–	–	This study
Rice husk	8.93	600	31.70	–	–	–	–	–	Guerrero et al. (2008)
Rice husk	10.95	700	38.22	–	–	–	–	–	Yavari et al. (2017)
Rice husk	–	400	48.60	–	–	–	–	–	Jindo et al. (2014)
Rice husk	–	500	42.40	–	–	–	–	–	Jindo et al. (2014)
Wood	0.20	600	24.40*	–	–	–	–	–	Ronsse et al. (2013)
Eucalyptus	0.98	600	24.00	–	–	–	–	–	Guerrero et al. (2008)
Rice husk	17.57 (R_1)	–	–	1.0–4.0	1:8	50	3 ^a	2.0	83.84 This study
Rice husk	13.80 (R_2)	–	–	1.0–4.0	1:8	50	3 ^a	2.0	89.91 This study
Rice husk	31.15 (R_{13})	–	–	1.0–4.0	1:8	50	3 ^a	2.0	74.67 This study
Rice husk	17.57 (R_1)	–	–	1.0–4.0	1:8	50	3 ^a	4.0	91.06 This study
Rice husk	13.80 (R_2)	–	–	1.0–4.0	1:8	50	3 ^a	4.0	92.88 This study
Rice husk	31.15 (R_{13})	–	–	1.0–4.0	1:8	50	3 ^a	4.0	84.94 This study
Rice husk	18.90	–	–	0.1–7.5	–	–	4	1.0	93.00 Usmani et al. (1994)
Rice husk	25.81	–	–	3.0	–	–	24 ^b	–	– Yalçın and Sevinç (2001)
Rice husk	22.80	–	–	0–2.0 ^c	1:5	50–85	1.0 ^c	92.10	Hsieh et al. (2009)
Rice husk	10.54	–	–	1.0 ^c	–	100	1.0 ^c	92.13	Liou and Wu (2009)

Note: (1) * implies char yield is expressed on dry ash-free basis; (2) ^a implies the sample was left to stand for 12 h after heating; (3) ^b implies the sample was pretreated at room temperature; (4) ^c implies the unit of NaOH concentration is molarity.

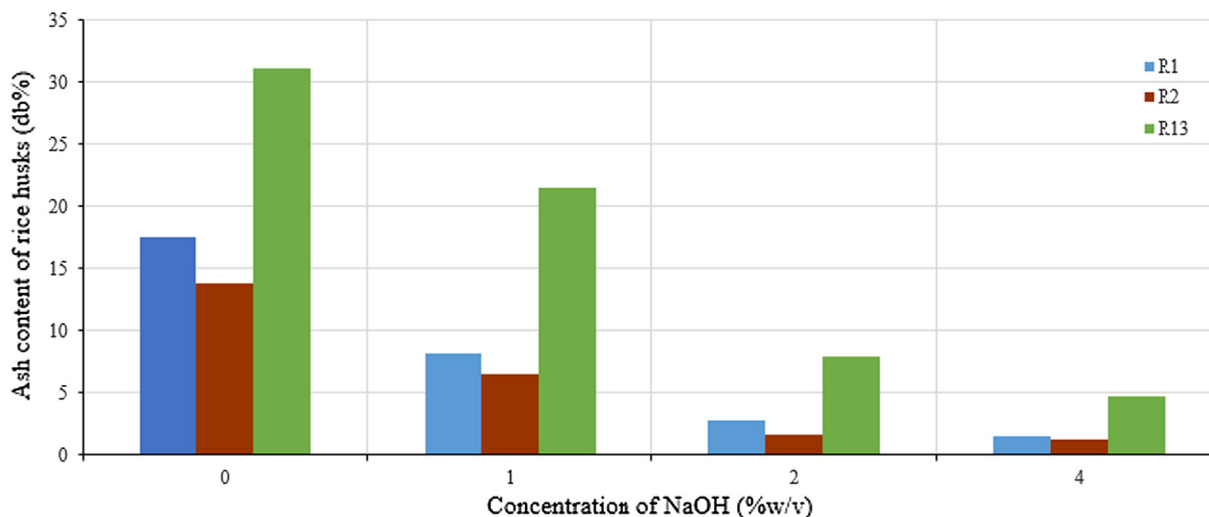


Fig. 2. Effect of NaOH pretreatment on ash content of selected rice husk varieties.

The extent of ash removal from the rice husk varieties is comparable to literature values (Table 4). The lowest ash removal of 74.67 and 84.94% from R₁₃ at NaOH concentrations of 2.0 and 4.0%w/v, respectively, may be attributed to its initially higher ash content, compared to the rest of the rice husk varieties. This has mainly to do with the particle size distribution, low specific area and low lignin content as discussed in the previous sections, as well as higher concentrations of some inorganics, such as Fe, Ca and Zn (see Table 7). A significant body of research links the reduction in ash content of rice husks to the activated carbon's enhanced porosity and surface area, which are essential properties for activated carbon to be employed as an adsorbent, catalyst support, and as an electrode material for electrochemical devices (Deng et al., 2016). Because of this, alkaline pretreated rice husks could be more preferred activated carbon precursors for such applications, than the raw rice husks. Though not investigated in this study, addition of suitable amounts of mineral acid to the aqueous solution of Na₂SiO₃, resulting from the water-washing of NaOH-pretreated rice husks, could aid the precipitation of silica from the aqueous solution, which could subsequently be employed in the synthesis of various advanced materials (Mohamed et al., 2015).

3.5.2. Volatile matter and fixed carbon contents

The volatile matter and fixed carbon contents of the selected rice husk varieties (R₁, R₂ and R₁₃) increased after NaOH-pretreatment (Table 3). This increase may be attributed to the reduction in ash content, which subsequently increased the relative proportions of volatile matter and fixed carbon contents of the rice husk varieties. A similar trend was observed by Sana et al. (2017). The increased volatile matter content suggests good prospects for utilizing the pretreated rice husk varieties as feedstocks for production of synthesis gas (Li et al., 2017), as well as bio-oil (Balasundram et al., 2018). Other important aspects concerning potential uses of rice husk varieties in Uganda, for energy applications were thoroughly discussed in our previous study (Olupot et al., 2016). On the other hand, the pretreated rice husk varieties could also be employed as feedstocks for preparing activated carbons with high surface areas, due to their higher volatile matter and fixed carbon contents, required of suitable activated carbon precursors (Dai et al., 2012).

3.5.3. Char yield

Char yield (%db) of the rice husk varieties decreased with increasing concentration of NaOH (Fig. 3). More specifically, at a

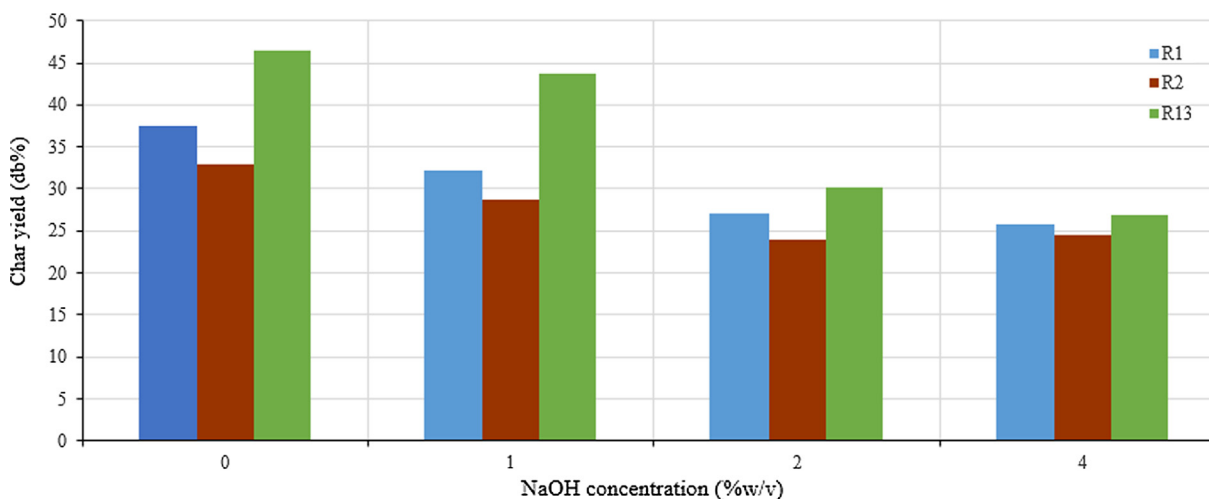


Fig. 3. Effect of NaOH-pretreatment of selected rice husk varieties on char yield (%db).

NaOH concentration of 2–4%w/v, the char yield ranged from 23 to 31%db, depending on the rice husk variety. This is expected due to the increased ash removal from rice husks with increasing NaOH concentration (Section 3.6). Besides ash removal, the decrease in char yield may also be attributed to the increased decomposition of lignin by NaOH, which otherwise contributes significantly to char formation (Ndazi et al., 2008; Yeganeh et al., 2006).

3.5.4. Specific surface area and total pore volume

Rice husk varieties with relatively low, medium, and high ash contents were considered for specific surface area, and pore volume determinations, to gain more insight into the effect of ash content on the two properties. The total specific surface area and total pore volume varied among rice husk varieties as indicated in Table 5. The low specific surface area of the rice husk varieties may be related to their inherently high ash content (Table 3), which allows the inorganics to fill or block some portions of the micropore volume (Yeganeh et al., 2006). Consequently, the raw rice husk variety R₂ with the lowest ash content (13.80%db) exhibited the highest specific surface area (1.5833 m² g⁻¹), while R₁₃ with the highest ash content (31.15%db) exhibited the lowest specific surface area (0.3017 m² g⁻¹). However, upon ash removal from the rice husks, the specific surface areas of the NaOH-pretreated rice husks slightly increased as indicated in Table 5. Indisputably, if activated under similar conditions, rice husk varieties with lower ash contents could result in activated carbons of higher specific surface areas, than those obtained from rice husks with higher ash contents (Menya et al., 2018). Therefore, based on total specific surface area, the order of suitability of the raw rice husk varieties as activated carbon precursors is as follows; R₂ > R₇ > R₅ > R₁ > R₆ > R₃ > R₁₃. Moreover, since a relatively high specific surface area of activated carbon is usually desired in the preparation of electrodes for electrochemical devices, such as supercapacitors, and lithium-ion batteries (Mirzaei et al., 2017; Wang et al., 2017), then this same order of suitability could still hold.

Both the total specific surface areas and total pore volumes obtained in this study compare well with the literature values, but with some few exceptions (Table 6), which could be attributed to differences in the physical and chemical properties of the biomass.

3.6. Metal composition

Generally, the concentration of metals varied among rice husk varieties, with potassium (K) being the most predominant, followed by iron (Fe), calcium (Ca) and magnesium (Mg) among others (Table 7). The predominant presence of K is expected, as it is often found in silica-based materials (Benassi et al., 2015). However, the concentration of the inorganics obtained in this study were lower than those reported by Wannapeera et al. (2008). This may be attributed to differences in type of fertilizer applied during

Table 6

Comparison of specific surface area and pore volume obtained in this study, with literature values.

Biomass type	Total specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Reference
Rice husk	0.30–1.60	0.024–0.047	This study
Rice husk	0.92	–	Hu et al. (2008)
Rice husk	1.45	0.005	Liou (2004)
Rice husk	5.72	–	Wannapeera et al. (2008)
Rice husk	7.14	0.005	Daffalla et al. (2013)

paddy rice cultivation, soil chemistry, geographical location and rice husk variety (Benassi et al., 2015; Deiana et al., 2008; Mansaray and Ghaly, 1997). While it is preferable to remove ash (which is predominantly silica) in the rice husks, suiting them as feedstocks for different applications, its removal could preferably be limited due to its beneficial role in some applications, as discussed in Section 3.5.1.

3.7. Conclusions

Rice husks from dominant rice varieties in Uganda were characterized and NaOH-pretreated, evaluating their potential utilization as precursors for production of bio-oil, ash, char as a soil amendment, and activated carbon as an adsorbent, as well as an active material in the preparation of electrodes for electrochemical devices. Properties varied among rice husk varieties, suiting them as feedstocks for different applications. Moreover, their order of suitability depended on the requisite properties for a given application. For instance, based on carbon content, which is a requisite for feedstocks to be employed as activated carbon precursors, the order of suitability of the rice husk varieties could be; R₂ > R₈ > R₁₁ > R₉ > R₄ > R₇ > R₃ > R₆ > R₁ > R₅ > R₁₂ > R₁₃ > R₁₀. Because of their relatively lower ash content, higher specific surface area, as well as higher volatile matter and fixed carbon contents, upland rice husk varieties are seemingly more suited precursors for production of bio-oil, and activated carbon, as compared to the lowland rice husk varieties. Moreover, since activated carbon with a relatively higher specific surface area is desired in the preparation of electrodes for electrochemical devices, then upland rice husk varieties could also be the most suitable precursors for this purpose. The high ash content of lowland rice husk varieties presents good prospects for their calcination, since relatively larger amounts of rice husk ash could be obtained, for employment in various industrial applications. Lowland rice husk varieties could also be more suited precursors for production of char for soil amendment, due to their relatively higher ash content, which subsequently increases their char yields, as compared to upland rice husk varieties. However, when computed on dry ash-free basis, the char yields obtained from pyrolysis of the different rice husk varieties varied from 21 to 25%daf, suggesting that the wide variation in

Table 5

Total specific surface areas and total pore volumes of selected raw and pretreated rice husk varieties.

Rice husk sample	Non-pretreated rice husks			Pretreated rice husks		
	Total specific surface area (m ² g ⁻¹)	Total pore volume (×10 ⁻² cm ³ g ⁻¹)	R ² -values	Total specific surface area (m ² g ⁻¹)	Total pore volume (×10 ⁻² cm ³ g ⁻¹)	R ² -values
R ₁	1.18	3.28	0.9997	1.23	8.83	0.9997
R ₂	1.58	2.49	0.9999	1.73	10.10	0.9996
R ₃	1.10	4.63	0.9996	–	–	–
R ₅	1.18	3.34	0.9998	–	–	–
R ₆	1.14	3.08	0.9997	–	–	–
R ₇	1.54	4.37	0.9997	–	–	–
R ₁₃	0.30	3.02	0.9999	–	–	–

Table 7

Inorganics composition of rice husk varieties.

Inorganics	Concentration in (mg g ⁻¹)												
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	R ₉	R ₁₀	R ₁₁	R ₁₂	R ₁₃
K	1.130	0.643	0.652	0.262	0.484	0.975	0.466	0.230	0.255	0.135	0.218	0.223	0.364
Fe	0.309	0.343	0.385	0.252	0.389	0.272	0.336	0.007	0.265	0.237	0.308	0.259	0.508
Ca	0.134	0.119	0.101	0.053	0.099	0.112	0.108	0.052	0.040	0.070	0.052	0.061	0.132
Mg	0.115	0.105	0.079	0.047	0.063	0.089	0.062	0.039	0.031	0.036	0.040	0.040	0.080
Al	0.026	0.017	0.022	0.011	0.011	0.037	0.015	0.027	0.005	0.007	0.010	0.014	0.019
Na	0.021	0.026	0.030	0.078	0.010	0.016	0.029	0.072	0.068	0.078	0.067	0.068	0.029
P	0.008	0.008	0.008	0.006	0.008	0.005	0.005	0.007	0.005	0.005	0.007	0.010	0.018
Mn	0.011	0.023	0.013	0.033	0.032	0.012	0.029	0.024	0.011	0.013	0.014	0.020	0.040
Zn	0.001	0.001	0.108	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.161

char yields of lowland and upland rice husk varieties could be largely due to differences in their ash contents. Alkaline pretreatment of rice husks using 2–4%w/v NaOH can reduce the ash content by as much as 74–93%, depending on the rice husk variety, which paves way for utilizing rice husks with a high ash content in different applications. Aside from ash reduction, the enhanced specific surface area, volatile matter and fixed carbon contents of NaOH-pretreated rice husks suggests they are more suited feedstocks than the raw rice husks, for production of bio-oil, as well as activated carbon.

Conflicts of interest

There is no conflict of interest among the authors.

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