



Effect of alkaline pretreatment on the thermal behavior and chemical properties of rice husk varieties in relation to activated carbon production

E. Menya^{1,2} · P. W. Olupot¹ · H. Storz³ · M. Lubwama¹ · Y. Kiros⁴ · M. J. John⁵

Received: 2 January 2019 / Accepted: 2 July 2019 / Published online: 19 July 2019
© Akadémiai Kiadó, Budapest, Hungary 2019

Abstract

Thermal behavior and chemical properties of selected raw and NaOH-pretreated rice husk varieties were investigated. NaOH-pretreatment process involved soaking 5 g rice husk samples in 40 mL of 2%w/v NaOH, shaking (400 rpm) and heating (50 °C) for 3 h. NaOH-pretreated samples were water-washed, oven-dried, and milled for use in the determination of their thermal behavior and surface functional groups. Alkaline wash-water was also analyzed for sugar components. Thermal decomposition temperatures, degradation rates, and the subsequent mass losses varied from one rice husk variety to another. These thermal properties increased after NaOH-pretreatment of the rice husk varieties, reducing their char yields (17.1–20.4% db). These changes mainly had to do with the lignin, hemicellulose, and ash removal from the rice husk varieties, as confirmed by their FTIR analysis, as well as by the sugar composition analysis of their alkaline wash-water. Consequently, the FTIR spectra differed between the raw and NaOH-pretreated rice husk varieties.

Keywords Rice husk varieties · NaOH-pretreatment · Thermal behavior · Surface functional groups · Sugar composition

Introduction

Rice husk is one of the lignocellulosic biomasses, with promising prospects for utilization as activated carbon precursor. This is due to its suited physicochemical properties, abundant availability, low cost, as well as due to its renewability compared to the conventional precursors [1]. However, its unusually high ash content (13–32% db) [2]

obstructs pore formation, lowering the adsorption capacity of the resulting rice husk activated carbon [3]. Besides, during chemical activation, silica (SiO_2), which accounts for a significant fraction of the rice husk ash (80–90 wt%), reacts with the activating agent, reducing the activating agent to carbon ratio. Consequently, activation only occurs on the exterior surface of the rice husk, reducing pore formation in the resulting activated carbon [4, 5]. For these reasons, the high ash content of rice husk is preferably lowered prior to activation [6]. Alkaline pretreatment using sodium hydroxide (NaOH) is one of the most commonly preferred methods, due to its relatively lower cost, higher effectiveness, need for shorter reaction times, as well as due to its need for relatively lower pretreatment temperatures, making the pretreatment process less energy intensive, as compared to the other pretreatment options [7].

During NaOH-pretreatment, SiO_2 in the ash reacts with NaOH, forming water-soluble sodium silicate (NaSiO_3), which is subsequently removed from the rice husks via the water-washing stage. Our previous study on the alkaline pretreatment of rice husk varieties in Uganda revealed that a NaOH concentration of 2–4%w/v sufficiently reduces the ash content by as much as 74–93%, depending on the rice

✉ E. Menya
emenya@cedat.mak.ac.ug

¹ Department of Mechanical Engineering, College of Engineering, Design, Art and Technology, Makerere University, P.O. Box 7062, Kampala, Uganda

² Department of Biosystems Engineering, Gulu University, P.O. Box 166, Gulu, Uganda

³ Thuenen Institute of Agricultural Technology, Bundesallee 47, 38116 Brunswick, Germany

⁴ Department of Chemical Engineering, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden

⁵ Polymer and Composite Unit, Council for Scientific and Industrial Research, Port Elizabeth 6000, South Africa

husk variety [2]. However, besides ash removal, many other changes in the rice husks occur during NaOH-pretreatment, which may influence the distribution and quality of products resulting from the pyrolysis and/or gasification processes, typical of the activation process. For instance, NaOH-pretreatment disrupts the cell walls of the rice husk, (1) by partly dissolving the lignin, hemicellulose, and silica, (2) by hydrolyzing uronic and acetic esters, (3) by decreasing the degree of polymerization and crystallinity, and (4) by swelling of the cellulose, which consequently increases the internal surface area of the lignocellulosic biomass [8]. NaOH-pretreatment of the rice husks has also been reported to increase their moisture retention [9]. Many other changes in the rice husks have been widely reported in the literature [10–12]. Similar findings have also been reported in the NaOH-pretreatment of other biomass, such as sugarcane bagasse [13] and sorghum [14]. In a study by Sambusiti et al. [14] about the effect of alkaline pretreatment on the structure, as well as on the chemical composition of sorghum, it was revealed that the extent of changes may differ, depending on the sorghum variety. Consequently, different extents of thermal behavior and products distribution may be expected from the thermal decomposition of the different NaOH-pretreated sorghum varieties. Despite these positive findings, studies on how the thermal behavior and the chemical properties differ among the raw and the alkaline-pretreated rice husk varieties are still very limited. This study therefore aimed at investigating the effect of NaOH-pretreatment on the thermal behavior and chemical properties of the rice husk varieties in Uganda in relation to activated carbon. More specifically, the thermal behavior and the surface functional groups of the rice husk varieties were determined via thermogravimetric analysis (TGA) as well as via the Fourier transform infrared (FTIR) spectroscopy, respectively. On the other hand, the sugar components in the alkaline wash-water were detected via the high-performance liquid chromatography (HPLC). Knowledge of the thermal behavior and the chemical properties of the raw and the NaOH-pretreated rice husk varieties is vital for understanding the behavior of their lignocellulosic components when thermally decomposed at different temperatures. Moreover, with such information, the most suitable temperature for activation of each of the rice husk varieties can be obtained.

Materials and methods

Sample collection

Thirteen rice varieties dominantly grown in four agro-ecological zones of Uganda were obtained from Zonal

Agricultural Research and Development Institutes (ZAR-DIs) and from selected rice irrigation schemes (Table 1). Rice agronomists were involved, to identify each of the rice varieties, thus obtaining pure samples for the study. Each of the rice varieties was then identically milled to obtain rice husk samples for the study.

Sample preparation and pretreatment

Samples from each rice husk variety were prepared via two routes, to provide for the raw samples, as well as for the NaOH-pretreated samples (see Fig. 1). The former involved milling each of the as-received rice husk varieties to fractions of particle size 250 μm , and subsequently employing them in the determination of their respective thermal behavior, as well as their respective surface functional groups. Milling of the samples was preferred to obtain homogeneous samples that could give good reproducible results. The other preparation route was limited to rice husk varieties with relatively lower ash content (R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , and R_{11}) and presumably the more promising activated carbon precursors. The samples of these selected rice husk varieties were initially washed with distilled water to remove any contaminants present in them, followed by oven drying at 105 $^{\circ}\text{C}$ for 12 h. Each of the oven-dried samples was then NaOH-pretreated by soaking 5 g sample in 40 mL of 2.0%w/v NaOH, followed by mixing (400 rpm) and heating (50 $^{\circ}\text{C}$), for 3 h in a thermo shaker and allowing the samples to stand for 12 h. Each of the pretreated rice husk samples together with their alkaline wash-water was transferred to a chromatographic column, with a filter at its bottom, as well as a top cover with a flexible hose, connected to the water tap. The alkaline wash-water intended for sugar composition analysis was then collected via the filter of the chromatographic column, prior to rinsing of the NaOH-pretreated rice husks with distilled water. Each of the thoroughly rinsed NaOH-pretreated rice husk varieties was then oven-dried at 105 $^{\circ}\text{C}$ for 12 h, followed by milling to fractions of particle size 250 μm . These were subsequently employed in the determination of thermal behavior and surface functional groups.

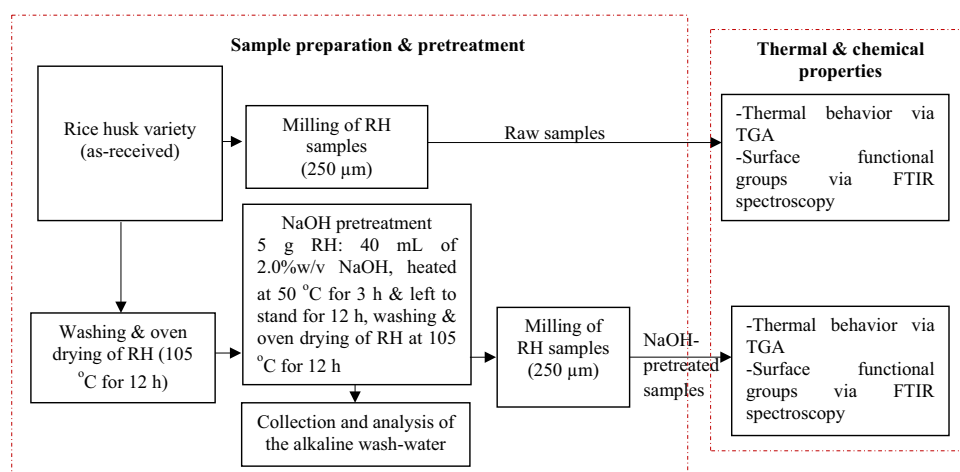
Thermal behavior

The raw and NaOH-pretreated samples from each rice husk variety were subjected to TGA in a nitrogen (N_2) atmosphere. This involved heating about 10–15 mg rice husk sample in a thermal analyzer (TA instruments Q500), from 25 to 800 $^{\circ}\text{C}$, at a heating rate of 20 $^{\circ}\text{C min}^{-1}$, under N_2 gas flow (50 mL min^{-1}). Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of percent weight loss (mass%) versus temperature ($^{\circ}\text{C}$) and percent

Table 1 Paddy rice varieties obtained from each of the selected agro-ecological zones, and irrigation schemes of Uganda

Rice variety	Sample code	Lowland/upland*	Geographical location
NERICA 1	R_1	Upland	Bulindi ZARDI
NERICA 1	R_2	Upland	Buginyanya ZARDI
NERICA 4	R_3	Upland	Bulindi ZARDI
NERICA 4	R_4	Upland	Buginyanya ZARDI
NERICA 4	R_5	Upland	Ngetta ZARDI
NERICA 10	R_6	Upland	Bulindi ZARDI
NERICA 10	R_7	Upland	Ngetta ZARDI
Wita-9	R_8	Lowland	Buginyanya ZARDI
Wita-9	R_9	Lowland	Kibimba irrigation scheme
Pusa	R_{10}	Lowland	Kibimba irrigation scheme
K-85	R_{11}	Lowland	Doho irrigation scheme
K-98	R_{12}	Lowland	Doho irrigation scheme
Super	R_{13}	Lowland	National Crops Resources Research Institute

(1) NERICA is New Rice for Africa; (2) *lowland rice is normally grown in flooded areas, while upland rice is grown on dry land

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

rate of weight loss ($\text{mass}\% \text{ min}^{-1}$) versus temperature ($^{\circ}\text{C}$), respectively, were generated using thermal analysis (TA) universal software. From the TG/DTG curves, important information about the raw and the NaOH-pretreated rice husk varieties was carefully obtained. Such information included mass losses that occurred in the different temperature zones, onset and offset temperatures, maximum thermal degradation rates, as well as information about the lower and higher peak temperatures. The onset and offset temperatures refer to the temperatures at which devolatilization of the biomass can be considered to start and complete, respectively [15]. These were determined by drawing tangents to the respective TG curves, with the onset temperature being the temperature corresponding to the intersection of the first and second tangents on the TG curve. On the other hand, the offset temperature was obtained as the temperature corresponding to the intersection of the second and third tangents on the TG curve. The

maximum thermal degradation rates of the rice husk varieties were obtained from their respective DTG curves. The temperature corresponding to the maximum thermal degradation rate was subsequently obtained as the higher peak temperature.

Surface functional groups and sugar composition

Surface functional groups present on the surface of each of the selected raw and NaOH-pretreated rice husk varieties were obtained by FTIR spectroscopy. This involved clamping each of the milled rice husk samples on the probe and the respective spectra subsequently obtained by scanning in the range of $4000\text{--}400 \text{ cm}^{-1}$. The background scan was obtained using a diamond crystal for each experimental condition. The sugar components in the alkaline wash-water were determined by HPLC. However, prior to HPLC analysis, the alkaline wash-water was neutralized,

where a clear supernatant thus obtained, was centrifuged, as well as filtrated by a syringe filter.

Results and discussion

Thermal behavior of raw rice husks

The thermal behavior of the raw rice husk varieties as determined by TGA is depicted in the TG/DTG curves (Fig. 2). These curves indicate that thermal decomposition of the raw rice husk varieties occurred in three temperature zones, typical of lignocellulosic biomass [16, 17]. The first zone commenced from room temperature to about 105 °C, where 5–7% of the total mass was lost, depending on the rice husk variety. This mass loss may be attributed to the evaporation of the physically adsorbed water from the rice husk biomass. Moreover, depending on the rice husk variety, this zone further extended to about 289–311 °C, but with very slight mass losses, which could be attributed to the loss of light volatiles from the rice husk materials [18]. This slight mass loss also suggests that the organic

constituents in the rice husk varieties were still thermally stable within this temperature zone.

In the second temperature zone, major thermal decomposition started at temperatures ranging from 289 to 311 °C and completed at 363–392 °C, with major mass losses of 43–55 mass%, depending on the rice husk variety (see Table 2). The decomposition temperatures obtained in this study are close to/or within the range of 300–450 °C, reported for major decomposition of agricultural residues [19]. The mass losses within this temperature zone were mainly due to the decomposition of the cellulose and hemicellulose fractions, and to a lesser extent due to the lignin decomposition, which were consequently lost from the rice husks as volatiles [20]. A significant body of research indicates that hemicellulose decomposes within the temperature range of 100–380 °C, cellulose 250–380 °C, while lignin decomposes over a wide temperature range of 180–900 °C [21]. Moreover, since the cellulose, hemicellulose, and lignin contents varied from one rice husk variety to another [2], then the noticeable variations in mass loss among the rice husk varieties were expected. From the DTG curves, the maximum thermal decomposition of hemicellulose is depicted by the low-temperature shoulder peaks around 312–336 °C, while the maximum thermal decomposition of cellulose is depicted by the higher temperature peaks around 334–363 °C, depending on the rice husk variety. These temperature ranges are comparable to those reported in the previous studies [10, 16]. However, the temperature ranges were quite different from those reported by Arora et al. [22]. This is possibly due to differences in the chemical composition of the rice husks employed in the different studies. The lower decomposition temperature range of hemicellulose is due to the presence of acetyl groups in its amorphous and random structure with many branched units that are less thermally stable [23]. On the other hand, the higher decomposition temperature of cellulose is due to its partly crystalline structure made of ordered microfibrils, which make it more thermally stable than hemicellulose [24].

Unlike the other rice husk varieties, the low-temperature shoulders were not obvious for rice husk varieties; R_1 , R_6 , and R_8 (Fig. 2b). Some researchers have linked this tendency to the low hemicellulose content of a given biomass [25]. However, this assertion could not be proven here, since R_1 , R_6 , and R_8 exhibited relatively higher hemicellulose contents, as compared to some of the rice husk varieties whose low-temperature shoulders were obvious [2]. The most probable explanation could be that the hemicellulose's low-temperature shoulder peak got overlapped with that of cellulose [26]. Shen et al. [25] attribute this overlap to the possibly high content of the less reactive components, such as glucomannan and arabinogalactan in the hemicellulose, which consequently postpone its thermal

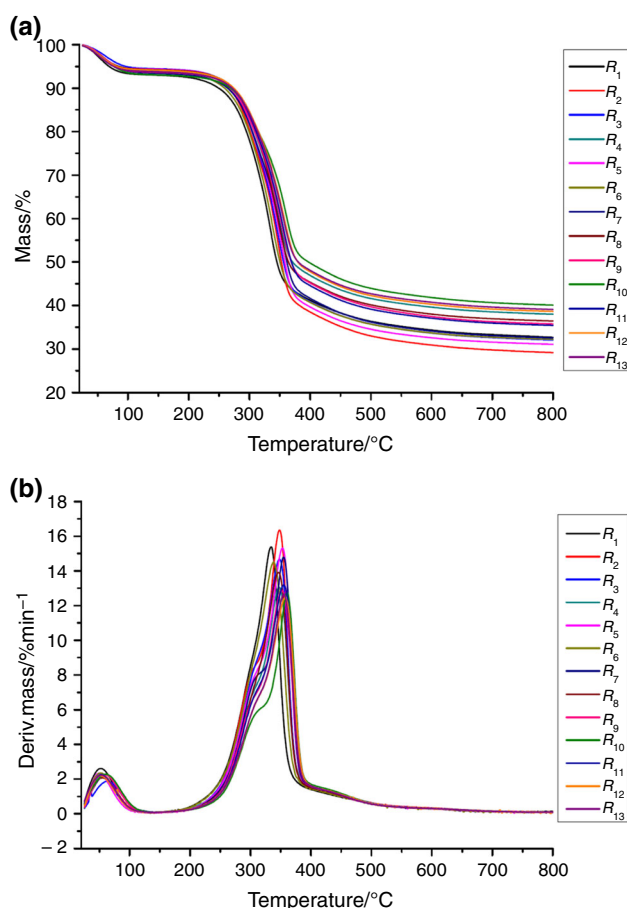


Fig. 2 TG curves for the raw rice husk varieties (a), and DTG curves for the raw rice husk varieties (b)

Table 2 Important results of the TGA obtained from the TG/DTG curves

Rice husk variety	Results of the TGA obtained from the TG/DTG curves of the raw rice husk varieties							Results of the TGA obtained from the TG/DTG curves of the NaOH-pretreated rice husk varieties						
	$T_{\text{onset}}-T_{\text{offset}}/^{\circ}\text{C}$	$M_{\text{loss},2}/\text{mass}\%$	$T_{\text{hem}}/^{\circ}\text{C}$	$\text{DTG}_{\text{peak temp}}/^{\circ}\text{C}$	$R_{\text{peak temp}}/\% \text{min}^{-1}$	$M_{\text{loss},3}/\text{mass}\%$	Residual weight at 800 $^{\circ}\text{C}/\% \text{ db}$	$T_{\text{onset}}-T_{\text{offset}}/^{\circ}\text{C}$	$M_{\text{loss},2}/\text{mass}\%$	$T_{\text{hem}}/^{\circ}\text{C}$	$\text{DTG}_{\text{peak temp}}/^{\circ}\text{C}$	$R_{\text{peak temp}}/\% \text{min}^{-1}$	$M_{\text{loss},3}/\text{mass}\%$	Residual weight at 800 $^{\circ}\text{C}/\% \text{ db}$
R_1	289.1–363.7	52.1	*	334.1	15.4	11.4	36.5	315.2–380.1	70.4	322.8	357.7	23.5	10.9	18.7
R_2	297.6–374.8	58.7	312.4	347.1	16.7	10.8	30.5	315.9–381.1	68.9	321.8	358.7	22.1	11.7	19.4
R_3	295.9–377.7	55.3	312.4	347.9	14.7	10.0	34.7	310.2–377.8	69.5	*	355.8	21.8	11.0	19.5
R_4	296.3–379.5	48.7	313.3	347.1	13.1	9.9	41.4	313.6–379.8	68.5	319.9	357.7	22.2	11.1	20.4
R_5	300.4–380.9	57.2	317.1	353.0	15.3	9.1	33.7	309.3–381.2	72.2	322.8	354.0	20.5	10.7	17.1
R_6	290.0–371.6	54.6	*	338.2	14.5	10.8	34.6	315.7–380.6	70.0	322.8	358.7	23.0	10.9	19.1
R_7	302.8–382.9	54.5	324.4	354.7	14.8	9.7	35.8	314.8–380.0	70.7	324.7	357.7	21.9	10.7	18.6
R_8	298.1–378.0	50.7	*	346.7	13.9	9.8	39.5	315.2–385.8	70.6	323.7	362.5	20.4	10.4	19.0
R_9	299.2–386.1	50.8	315.1	352.6	12.9	10.0	39.2	313.6–384.8	70.6	327.5	362.5	21.8	10.8	18.6
R_{10}	310.4–391.9	46.7	335.7	362.3	12.8	10.0	43.3	–	–	–	–	–	–	–
R_{11}	301.4–387.3	52.3	319.4	354.7	13.2	9.2	38.5	316.9–387.7	72.1	326.5	364.4	21.8	10.3	17.6
R_{12}	303.0–388.9	48.7	329.1	357.8	12.4	9.4	41.9	–	–	–	–	–	–	–
R_{13}	305.0–389.2	48.0	330.3	357.5	12.7	9.6	42.4	–	–	–	–	–	–	–

(1) $T_{\text{onset}}-T_{\text{offset}}$ is the temperature range corresponding to the second temperature zone, where major thermal decomposition occurred, (2) T_{onset} and T_{offset} are the temperatures at which devolatilization of the rice husk was considered to start and complete, respectively, (3) $M_{\text{loss},2}$ is the mass loss in the second temperature zone, (4) T_{hem} is the lower peak temperature at which maximum thermal degradation of the hemicellulose occurred, (5) $\text{DTG}_{\text{peak temp}}$ is the higher peak temperature at which maximum thermal degradation of the cellulose occurred, (6) $R_{\text{peak temp}}$ is the maximum thermal degradation rate corresponding to the DTG peak temperature, (7) $M_{\text{loss},3}$ is the mass loss in the third temperature zone, and (8) *implies the low-temperature shoulder of the rice husk variety was not obvious

decomposition, coinciding with that of cellulose. Similar tendencies were observed in the thermal decomposition of perennial grass [20] and natural fibers [27].

The peak position and height of the DTG evolution profiles within the second temperature zone also varied among rice husk varieties (Fig. 2b). These variations mainly have to do with differences in the physicochemical properties of the rice husk varieties, which consequently influenced their reactivity. According to Vamvuka et al. [28], the peak height is directly proportional to reactivity, while the temperature corresponding to the peak height is inversely proportional to reactivity. Therefore, based on this, R_2 was presumably the most reactive, followed by R_1 , R_5 , R_7 , R_3 , R_6 , R_8 , R_4 , R_{11} , R_9 , R_{12} , and lastly R_{13} . However, the differences in peak heights among some rice husk varieties were considerably small, suggesting that they possibly exhibited similar reactivity. For instance, (1) R_1 and R_5 , (2) R_7 , R_3 , R_6 , and R_8 , (3) R_4 , R_{11} , and R_9 , and (4) R_{12} , R_{13} , and R_{13} . It can also be noticeably seen from Table 2 that the more reactive rice husk varieties, and in particular the NERICA rice husk varieties, not only exhibited higher thermal degradation rates, but also experienced greater mass losses, as compared to the other rice husk varieties. This is due to their relatively higher volatile matter contents than the other rice husk varieties, as reported in our previous study [2]. Similar tendencies were observed between eucalyptus wood and corn residues, where the latter exhibited a higher volatile matter content, than the former [29]. McNamee et al. [30] also found the untreated eucalyptus more reactive than its torrefied counterparts, due to its relatively higher volatile matter content. Moreover, since the mass losses are directly linked to internal porosity development [2], then NERICA rice husk varieties could result in activated carbon with relatively good adsorptive properties, once activated. However, due to greater devolatilization, NERICA rice husk varieties resulted in relatively lower char yields, as compared to the other rice husk varieties. This could make their pyrolysis process less economically viable, since higher char yields are most desired in char production and consequently in the production of activated carbon.

In the third temperature zone, thermal degradation started at temperatures ranging from 363 to 392 °C and completed at 800 °C, with mass losses of 9.05–11.42% db, depending on the rice husk variety. On the DTG curve, this zone is represented by a flat trailing section, which is attributed to the slow decomposition of lignin over a wide temperature range [31]. This thermal behavior of lignin is due to its structure, consisting of a complex network of cross-linked aromatic molecules that are difficult to decompose and consequently its high thermal stability. Aside from lignin decomposition, mass loss in this zone could also be due to further decomposition of carbon

residues formerly produced at the lower decomposition temperatures [32]. The residual mass at 800 °C was considered to be char, with yields ranging from 30.5 to 43.3% db obtained, depending on the rice husk variety (Table 2). However, some rice husk varieties exhibited relatively similar char yields, suggesting similarity in their chemical composition. For instance, (1) R_1 , R_3 , R_5 , R_6 , and R_7 , (2) R_8 , R_9 , and R_{11} , and (3) R_4 , R_{10} , R_{12} , and R_{13} . On the TG curve, the curves of these rice husk varieties are noticeably seen overlapping. On the other hand, the differences in char yields among some of the rice husk varieties may be attributed to differences in their lignin content, the main constituent for char formation, as well as due to differences in their ash content [2].

Thermal behavior of NaOH-pretreated rice husks

The thermal behavior of the selected NaOH-pretreated rice husk varieties as determined by TGA is depicted in the TG/DTG curves (Fig. 3). From these curves, it can noticeably be seen that thermal decomposition of the pretreated rice husk varieties also occurred in three temperature zones,

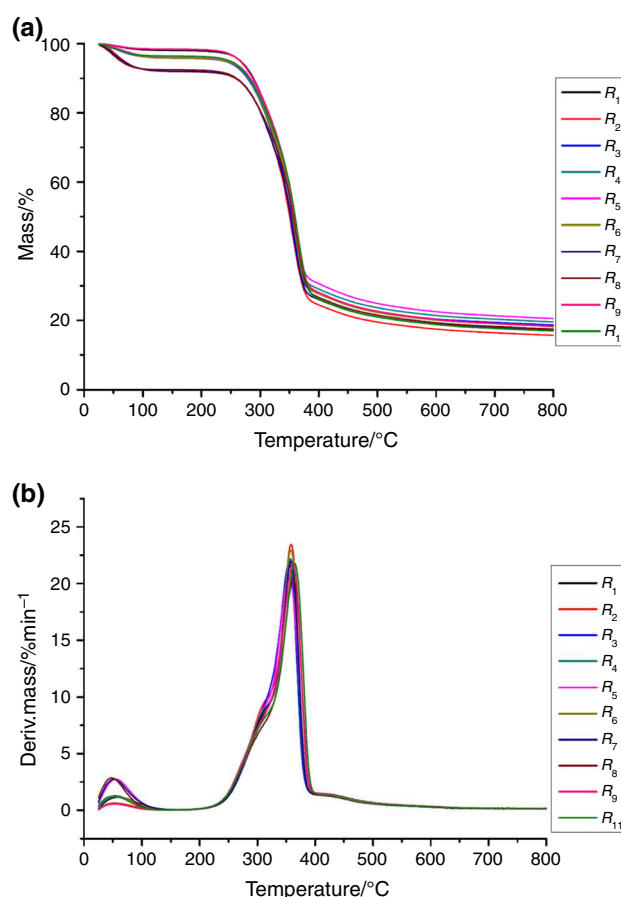


Fig. 3 TG curves for the NaOH-pretreated rice husk varieties (a), and DTG curves for the NaOH-pretreated rice husk varieties (b)

suggesting the presence of chemical components similar to those of the raw rice husk varieties. Major mass losses (66–73% db) occurred in the second temperature zone, which commenced from about 309–317 °C until temperatures of about 377–388 °C, depending on the rice husk variety. Compared to the raw rice husk varieties, NaOH-pretreated rice husk varieties exhibited higher onset decomposition temperatures, higher peak temperatures, higher maximum thermal degradation rates, as well as greater mass losses. Consequently, NaOH-pretreated rice husk varieties were more thermally stable, but with relatively lower char yields, as compared to the raw rice husk varieties (see Table 2). Similar observations were made in the thermal decomposition of poplar wood [33], wheat straw [34], and oil palm empty fruit bunches [35]. Moreover, the extent of the changes slightly varied from one rice husk variety to another, suggesting slight differences in their chemical compositions after NaOH-pretreatment. These changes mainly have to do with ash removal from the rice husk varieties. More specifically, the greater mass losses and, consequently, the lower char yields are presumably because the inorganic constituents in the ash that would otherwise suppress the release of volatiles and, consequently, promote the charring reactions that were no longer present/or possibly reduced after NaOH-pretreatment of the rice husk varieties [33, 36]. The shift to slightly higher thermal decomposition temperatures suggests that some catalytic species in the ash were possibly removed/or reduced, upon NaOH-pretreatment and water-washing of the rice husk varieties. The extent of ash removal from selected rice husk varieties was reported in our previous study [2].

Besides ash removal, the distinctive thermal behavior between the raw and NaOH-pretreated rice husk varieties may also be attributed to differences in their lignocellulosic composition. Though not quantified in this study, the lignin and hemicellulose contents of the rice husk varieties were presumably reduced after NaOH-pretreatment, while at the same time, their cellulose contents were increased [36]. This tendency was visibly confirmed on the DTG curves (Fig. 3), where the lower temperature shoulder peaks appeared less pronounced, and the high temperature peaks shifted to relatively greater heights, while the flat trailing section shifted to the lower end of the TG/DTG plot. These distinct peaks and section are typical of the hemicellulose, cellulose, and lignin thermal decomposition, respectively, as earlier discussed. Because of the increased cellulose concentration, the increase in decomposition temperatures of the rice husk varieties after NaOH-pretreatment was expected, since cellulose is more thermally stable than lignin and hemicellulose [11, 12, 37]. On the other hand, the presumed reductions in lignin and hemicellulose contents of the rice husk varieties after NaOH-pretreatment

could have also accounted for their relatively lower char yields, since less char could only be formed from the remaining lignocellulosic components. Although the relatively lower char yields could make the pyrolysis process, and consequently the activation process less economically viable, this could be compensated for, with the enhanced specific surface area of the resulting activated carbon, which is a requisite in many applications, including adsorption and in the preparation of electrodes [38, 39]. The enhanced specific surface area is due to the ash removal from the rice husks, which otherwise blocks porosity formation, reducing the internal surface area of the produced activated carbon.

In the third temperature zone, thermal degradation commenced at temperatures ranging from 377 to 388 °C up to 800 °C, with mass losses of about 9.70–11.70% db, depending on the rice husk variety. This zone is attributed to the lignin thermal decomposition, suggesting that the rice husk varieties still contained lignin, even after NaOH-pretreatment. This is desired in activated carbon production, since the remaining lignin contributes to char formation, which could increase the carbon yield, once the char is activated. The char yields obtained from the pyrolysis of NaOH-pretreated rice husk varieties did not vary widely (Table 2), suggesting that the wide differences in char yields obtained from pyrolysis of the raw rice husk varieties may be largely attributed to their relatively large differences in ash contents.

Surface functional groups

FTIR spectroscopy was employed to determine the surface functional groups of selected rice husk varieties, before and after NaOH-pretreatment. From Fig. 4, it can noticeably be seen that the FTIR spectra of the raw rice husk varieties followed a similar trend/shape, suggesting the presence of similar surface functional groups. However, upon NaOH-pretreatment, the peak positions and/or intensities corresponding to lignin, cellulose, hemicellulose, and silica slightly changed, suggesting slight structural changes in the NaOH-pretreated rice husk varieties. For instance, the prominent bands around $3345\text{--}3312\text{ cm}^{-1}$ presumably attributed to the stretching of the hydrogen bonded –OH groups in the cellulose [40] intensified after NaOH-pretreatment of the rice husk varieties: R_2 , R_3 , R_5 , and R_{11} . This is possibly due to the increased exposure of cellulose, following the partial removal of hemicellulose [41]. On the contrary, the intensity of this band slightly decreased after NaOH-pretreatment of the rice husk varieties; R_1 , R_6 , R_8 , and R_9 , suggesting rupture of the hydrogen bonds of cellulose. Similar tendencies were observed in the alkaline pretreatment of wheat straw [42], rice straw [43], and corn stover [44]. The intensity of the bands around

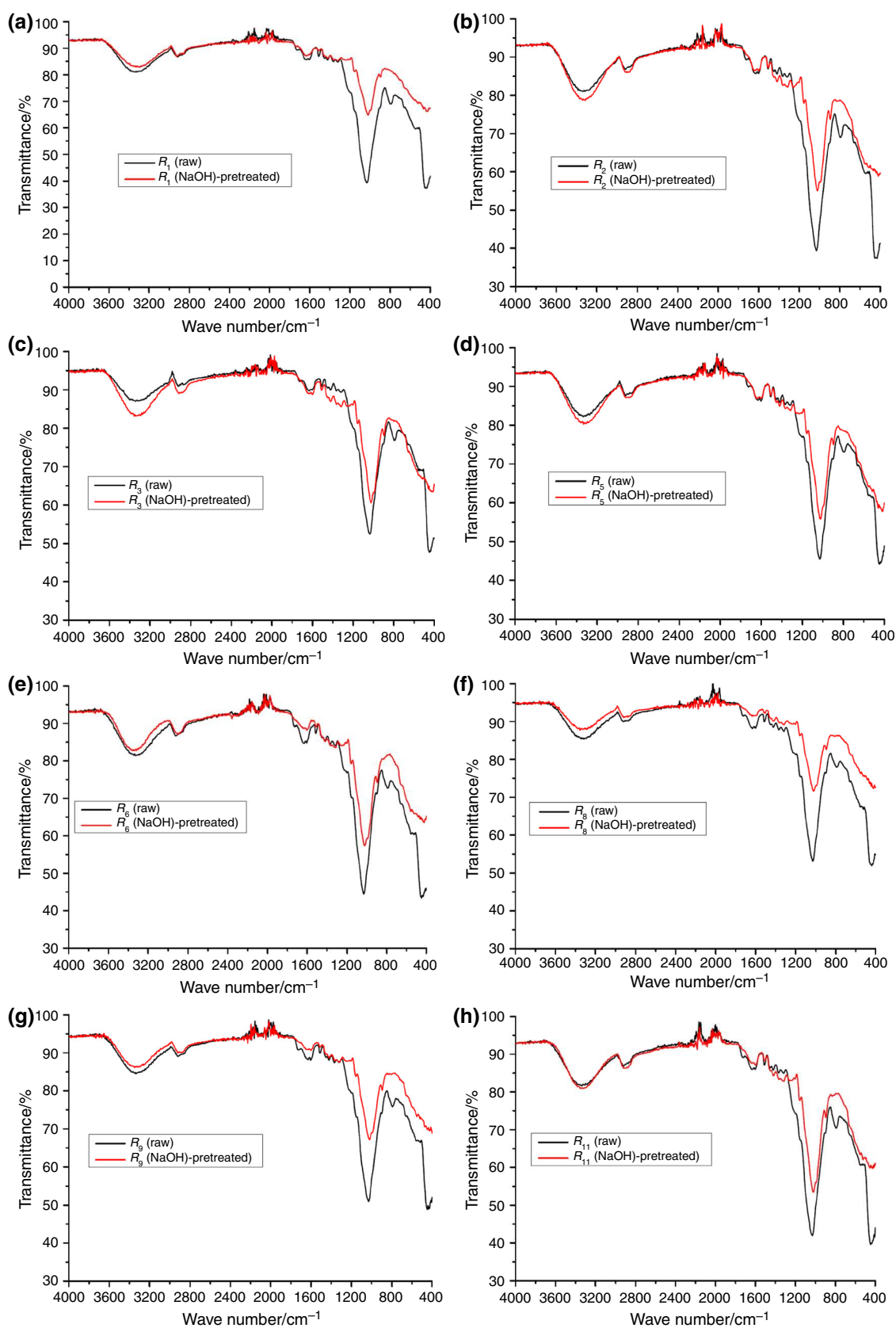


Fig. 4 FTIR spectra for the raw and NaOH-pretreated rice husk variety, R_1 (a), R_2 (b), R_3 (c), R_5 (d), R_6 (e), R_8 (f), R_9 (g), and R_{11} (h)

2854–2927 cm^{-1} presumably attributed to the stretching vibration of the aliphatic $-\text{CH}$ and $-\text{CH}_3$ and did not noticeably change after NaOH-pretreatment of the rice husk varieties: R_1 , R_5 , R_6 , R_8 , R_9 , and R_{11} , suggesting that the methyl and methylene portions of their cellulose were possibly not ruptured. Assignment of surface functional groups to the many overlapping bands around 2325–1879 cm^{-1} could not be unambiguously done.

The slight shoulders around 1728–1717 cm^{-1} that attributed to the stretching vibration of the carbonyl ($\text{C}=\text{O}$) group in the hemicellulose and/or lignin [6, 45] were noticeably reduced, suggesting chemical changes in the hemicellulose and/or lignin [46]. More specifically, the ester bonds between the lignin and hemicellulose were possibly broken, thus releasing part of the lignin and/or hemicellulose from the polysaccharide network [7]. The bands around 1644–1506 and 1368–1318 cm^{-1} attributed to $\text{C}=\text{C}$ stretching vibrations [47], as well as to the aromatic $-\text{OH}$ group [48], respectively, also decreased slightly after NaOH-pretreatment, suggesting that lignin was partially removed from the rice husk varieties. This is advantageous, since lignin is much desired in char formation, for reasons already cited in “[Thermal behavior of NaOH-pretreated rice husks](#)” section. The bands around 1454–1450 cm^{-1} presumably attributed to the CH_2 bending of cellulose, slightly reduced after NaOH-pretreatment, suggesting a slight reduction in the crystalline structure of the cellulose [48]. The bands around 1206–1154 and 902–895 cm^{-1} attributed to the $\text{C}-\text{O}$ stretching vibration and $\text{C}-\text{H}$ deformation of cellulose [49], respectively, slightly increased after NaOH-pretreatment, presumably because of the increased exposure of cellulose [50]. Lastly, the bands around 1036–1022, 794–780, 567–517, and 449–433 cm^{-1} may have to do with the presence of silica, and thus a reduction in the band intensities after NaOH-pretreatment suggests silica removal from the rice husk varieties [51–53]. This is also advantageous, since activated carbons of relatively higher specific surface area may be obtained, once the desilicated rice husks are activated.

Sugar composition in the alkaline wash-water

Alkaline wash-water was analyzed for sugar components, to further evaluate the severity of the NaOH-pretreatment process on the chemical structure of the rice husk varieties. From Table 3, it can noticeably be seen that sucrose, glucose, arabinose, rhamnose, and mannose were the sugar components in the alkaline wash-water, suggesting that part of the structural carbohydrates in the rice husk varieties was degraded upon NaOH-pretreatment. These results confirm our findings obtained from the FTIR spectroscopy, in “[Thermal behavior of NaOH-pretreated rice husks](#)” section. Although the loss of the sugar components via the

Table 3 Sugar composition of the alkaline wash-water

Sugar type	Concentration/g L^{-1}
Sucrose	0.2364 ± 0.0021
Glucose	0.0414 ± 0.0005
Arabinose	0.0153 ± 0.0001
Rhamnose	0.0067 ± 0.0000
Mannose	0.0052 ± 0.0001
Total	0.3051 ± 0.0021

alkaline wash-water may consequently lead to relatively lower carbon yields, these could be compensated for, with the enhanced specific surface area of the resulting activated carbon.

Conclusions

The effect of NaOH-pretreatment on the thermal and chemical properties of rice husk varieties in Uganda was investigated. Thermal decomposition temperatures, degradation rates, and the subsequent mass losses varied from one rice husk variety to another. These thermal properties increased after NaOH-pretreatment of the rice husk varieties, reducing their char yields. These changes mainly had to do with the lignin, hemicellulose, and ash removal from the rice husk varieties, as confirmed by their FTIR analysis, as well as by the sugar composition analysis of their alkaline wash-water. Consequently, the FTIR spectra differed between the raw and NaOH-pretreated rice husk varieties.

Acknowledgements The authors gratefully acknowledge funding from the Volkswagen Foundation under its “Postdoctoral Fellowships programme for African Researchers in the Engineering Sciences (Grant 90014).” Technical support from Ms. Evgenia Tryastina and Mr. Laslo Eidt at the Thuenen Institute of Agricultural Technology, Braunschweig is also gratefully acknowledged.

Compliance with ethical standards

Conflict of interest There is no conflict of interest among the authors.

References

1. González-García P. Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications. *Renew Sustain Energy Rev.* 2018;82:1393–414.
2. Menya E, Olupot PW, Storz H, Lubwama M, Kiros Y. 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. *Waste Manag.* 2018;81:104–16.
3. Menya E, Olupot PW, Storz H, Lubwama M, Kiros Y. Production and performance of activated carbon from rice husks for removal of natural organic matter from water: a review. *Chem Eng Res Des.* 2018;129:271–96.
 4. Liou TH, Wu SJ. Characteristics of microporous/mesoporous carbons prepared from rice husk under base- and acid-treated conditions. *J Hazard Mater.* 2009;171:693–703.
 5. Menya E, Olupot PW, Storz H, Lubwama M, Kiros Y, John MJ. Optimization of pyrolysis conditions for char production from rice husks and its characterization as a precursor for production of activated carbon. *Biomass Convers Biorefinery* 2019. <https://doi.org/10.1007/s13399-019-00399-0>.
 6. Deiana C, Granados D, Venturini R, Amaya A, Sergio M, Tancredi N. Activated carbons obtained from rice husk: influence of leaching on textural parameters. *Ind Eng Chem Res.* 2008;47:4754–7.
 7. Ahmadi F, Zamiri MJ, Khorvash M, Ziaee E, Polikarpov I. Pretreatment of sugarcane bagasse with a combination of sodium hydroxide and lime for improving the ruminal degradability: optimization of process parameters using response surface methodology. *J Appl Anim Res.* 2016;44:287–96.
 8. Garcia-Torreiro M, Pallín MÁ, López-Abelairas M, Lu-Chau TA, Lema JM. Alkali treatment of fungal pretreated wheat straw for bioethanol production. *Bioethanol.* 2016;2:32–43.
 9. Bazargan A, Gebreegziabher T, Hui C-W, McKay G. The effect of alkali treatment on rice husk moisture content and drying kinetics. *Biomass Bioenergy.* 2014;70:468–75.
 10. Ahiduzzaman M, Islam AKMS. Thermo-gravimetric and kinetic analysis of different varieties of rice husk. *Procedia Eng.* 2015;105:646–51.
 11. Carmona VB, Oliveira RM, Silva WTL, Mattoso LHC, Marconcini JM. Nanosilica from rice husk: extraction and characterization. *Ind Crops Prod.* 2013;43:291–6.
 12. Fauziah S, Draman S, Daik R, Latif FA, El-sheikh SM. Characterization and thermal decomposition kinetics of Kapok (*Ceiba pentandra* L.)—based cellulose. *BioResources.* 2014;9:8–23.
 13. Cruz G, Santiago PA, Braz CEM, Selegim P, Crnkovic PM. Investigation into the physical–chemical properties of chemically pretreated sugarcane bagasse. *J Therm Anal Calorim.* 2018;132:1039–53.
 14. Sambusiti C, Ficari E, Malpei F, Steyer JP, Carrère H. Effect of sodium hydroxide pretreatment on physical, chemical characteristics and methane production of five varieties of sorghum. *Energy.* 2013;55:449–56.
 15. Biagini E, Fantei A, Tognotti L. Effect of the heating rate on the devolatilization of biomass residues. *Thermochim Acta.* 2008;472:55–63.
 16. El-Sayed SA, Mostafa ME. Kinetic parameters determination of biomass pyrolysis fuels using TGA and DTA techniques. *Waste Biomass Valoriz.* 2015;6:401–15.
 17. Lemos MS, Yokoyama L, Viana MM, Dweck J. A study of coke and char formation during pyrolysis of rice husk. *J Therm Anal Calorim.* 2019. <https://doi.org/10.1007/s10973-019-08196-7>.
 18. Zhang S, Dong Q, Zhang L, Xiong Y. Effects of water washing and torrefaction on the pyrolysis behavior and kinetics of rice husk through TGA and Py-GC/MS. *Bioresour Technol.* 2016;199:352–61.
 19. Biswas B, Pandey N, Bisht Y, Singh R, Kumar J, Bhaskar T. Pyrolysis of agricultural biomass residues: comparative study of corn cob, wheat straw, rice straw and rice husk. *Bioresour Technol.* 2017;237:57–63.
 20. Saikia R, Baruah B, Kalita D, Pant KK, Gogoi N, Katak R. Pyrolysis and kinetic analyses of a perennial grass (*Saccharum ravennae* L.) from north-east India: optimization through response surface methodology and product characterization. *Bioresour Technol.* 2018;253:304–14.
 21. Zhang J, Zhang X, Li C, Zhang W, Zhang J, Zhang R, Yuan Q, Liu G, Cheng G. A comparative study of enzymatic hydrolysis and thermal degradation of corn stover: understanding biomass pretreatment. *RSC Adv.* 2015;5:36999–7005.
 22. Arora S, Kumar M, Dubey G. Thermal decomposition kinetics of rice husk: activation energy with dynamic thermogravimetric analysis. *J Energy Inst.* 2009;82:138–43.
 23. Quan C, Gao N, Song Q. Pyrolysis of biomass components in a TGA and a fixed-bed reactor: thermochemical behaviors, kinetics, and product characterization. *J Anal Appl Pyrolysis.* 2016;121:84–92.
 24. Wang P, Zhang J, Shao Q, Wang G. Physicochemical properties evolution of chars from palm kernel shell pyrolysis. *J Therm Anal Calorim.* 2018;133:1271–80.
 25. Shen DK, Gu S, Luo KH, Bridgwater AV, Fang MX. Kinetic study on thermal decomposition of woods in oxidative environment. *Fuel.* 2009;88:1024–30.
 26. Wei J, Meyer C. Degradation of natural fiber in ternary blended cement composites containing metakaolin and montmorillonite. *Corros Sci.* 2017;120:42–60.
 27. Yao F, Wu Q, Lei Y, Guo W, Xu Y. Thermal decomposition kinetics of natural fibers: activation energy with dynamic thermogravimetric analysis. *Polym Degrad Stab.* 2008;93:90–8.
 28. Vamvuka D, Kakaras E, Kastanaki E, Grammelis P. Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite. In: *Fuel*, 2003. p. 1949–60.
 29. Onsree T, Tippayawong N, Zheng A, Li H. Pyrolysis behavior and kinetics of corn residue pellets and eucalyptus wood chips in a macro thermogravimetric analyzer. *Case Stud Therm Eng.* 2018;12:546–56.
 30. McNamee P, Darvell LI, Jones JM, Williams A. The combustion characteristics of high-heating-rate chars from untreated and torrefied biomass fuels. *Biomass Bioenergy.* 2015;82:63–72.
 31. Wang T, Yin J, Liu Y, Lu Q, Zheng Z. Effects of chemical inhomogeneity on pyrolysis behaviors of corn stalk fractions. *Fuel.* 2014;129:111–5.
 32. Luo Q, Peng H, Zhou M, Lin D, Ruan R, Wan Y, Zhang J, Liu Y. Alkali extraction and physicochemical characterization of hemi-celluloses from young bamboo (*phyllostachys pubescens mazel*). *BioResources.* 2012;7:5817–28.
 33. Eom IY, Kim JY, Kim TS, Lee SM, Choi D, Choi IG, Choi JW. Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass. *Bioresour Technol.* 2012;104:687–94.
 34. Trubetskaya A, Jensen PA, Jensen AD, Steibel M, Spliethoff H, Glarborg P. Influence of fast pyrolysis conditions on yield and structural transformation of biomass chars. *Fuel Process Technol.* 2015;140:205–14.
 35. Shariff A, Aziz NSM, Abdullah N. Slow pyrolysis of oil palm empty fruit bunches for biochar production and characterization. *J Phys Sci.* 2014;25:97–112.
 36. Ndazi BS, Nyahumwa C, Tesha J. Chemical and thermal stability of rice husks against alkali treatment. *BioResources.* 2008;3:1267–77.
 37. Gu S, Zhou J, Luo Z, Wang Q, Shi Z. Kinetic study on the preparation of silica from rice husk under various pretreatments. *J Therm Anal Calorim.* 2015;119:2159–69.
 38. Kizito S, Wu S, Kipkemai Kirui W, Lei M, Lu Q, Bah H, Dong R. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry. *Sci Total Environ.* 2005;505:102–12.
 39. Zhang W, Lin N, Liu D, Xu J, Sha J, Yin J, Tan X, Yang H, Lu H, Lin H. Direct carbonization of rice husk to prepare porous carbon for supercapacitor applications. *Energy.* 2017;128:618–25.

40. Zulkiple N, Maskat MY, Hassan O. Pretreatment of oil palm empty fruit fiber (OPEFB) with aqueous ammonia for high production of sugar. *Procedia Chem.* 2016;18:155–61.
41. Subhedar PB, Gogate PR. Alkaline and ultrasound assisted alkaline pretreatment for intensification of delignification process from sustainable raw-material. *Ultrason Sonochem.* 2014;21:216–25.
42. Asghar U, Irfan M, Iram M, Huma Z, Nelofer R, Nadeem M, Syed Q. Effect of alkaline pretreatment on delignification of wheat straw. *Nat Prod Res.* 2015;29:125–31.
43. He Y, Pang Y, Liu Y, Li X, Wang K. Physicochemical characterization of rice straw pretreated with sodium hydroxide in the solid state for enhancing biogas production. *Energy Fuels.* 2008;22:2775–81.
44. Kumar R, Mago G, Balan V, Wyman CE. Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies. *Bioresour Technol.* 2009;100:3948–62.
45. Lim WC, Srinivasakannan C, Al Shoaibi A. Cleaner production of porous carbon from palm shells through recovery and reuse of phosphoric acid. *J Clean Prod.* 2014;102:501–11.
46. Chandel AK, Antunes FFA, Anjos V, Bell MJV, Rodrigues LN, Singh OV, Rosa CA, Pagnocca FC, da Silva SS. Ultra-structural mapping of sugarcane bagasse after oxalic acid fiber expansion (OAFEX) and ethanol production by *Candida shehatae* and *Saccharomyces cerevisiae*. *Biotechnol Biofuels.* 2013;6:4.
47. Abnisa F, Wan Daud WMA, Sahu JN. Optimization and characterization studies on bio-oil production from palm shell by pyrolysis using response surface methodology. *Biomass Bioenergy.* 2011;35:3604–16.
48. Barlianti V, Dahnum D, Hendarsyah H, Abimanyu H. Effect of alkaline pretreatment on properties of lignocellulosic oil palm waste. *Procedia Chem.* 2015;16:195–201.
49. Liou TH. Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation. *Chem Eng J.* 2010;158:129–42.
50. Zhu Z, Rezende CA, Simister R, McQueen-Mason SJ, Macquarrie DJ, Polikarpov I, Gomez LD. Efficient sugar production from sugarcane bagasse by microwave assisted acid and alkali pretreatment. *Biomass Bioenergy.* 2016;93:269–78.
51. Bakar RA, Yahya R, Gan SN. Production of high purity amorphous silica from rice husk. *Procedia Chem.* 2016;19:189–95.
52. Luo J, Zhou Y, Milner ST, Pantano CG, Kim SH. Molecular dynamics study of correlations between IR peak position and bond parameters of silica and silicate glasses: effects of temperature and stress. *J Am Ceram Soc.* 2018;101:178–88.
53. Mathur L, Saddam Hossain SK, Majhi MR, Roy PK. Synthesis of nano-crystalline forsterite (Mg_2SiO_4) powder from biomass rice husk silica by solid-state route. *Bol la Soc Esp Ceram y Vidr.* 2018;57:112–8.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.