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Proximate and Ultimate Analyses of Bagasse, Sorghum and Millet Straws as Precursors for Active Carbons

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Abstract: This study reports the proximate and ultimate characteristics of bagasse, sorghum and millet straws in relation to their suitability for producing highly porous carbon. The results of ad hoc samples indicated, that particle size has a decisive influence on the proximate characteristics of bagasse, sorghum and millet straws. The effects of particle size on weight loss characteristics; rates of dehydration and de-volatilization of the carbon precursors were used to assess particle sizes that may be appropriate for carbonization. Particle sizes of 425-1180 μm are thus, suggested to be the most desirable, for the production of good quality porous carbon. This range of particles of bagasse, sorghum and millet straws were associated with diminishing ash contents. However, the optimum particle size of the cellulosic materials that is expected to yield highly porous carbon with minimum ash contents is 1180 μm.

Key words: Sorghum, millet, bagasse, straws, porous carbon, carbonization

INTRODUCTION

Proximate and ultimate analyses are used to determine the characteristics of carbonaceous materials that may be used as precursor for active carbons (Minkova *et al*., 2000; Minkova *et al*., 2001; Garcia-Perez *et al*., 2002; Hayashi *et al*., 2002; Barkauskas *et al*., 2004). Proximate characteristics include contents of moisture, volatile materials, ashes and fixed carbon. Ultimate analysis describes the elemental composition, such as content of carbon, hydrogen, oxygen, nitrogen and metals. Adsorption characteristics of activated carbon from cellulosic wastes are affected by the type of carbon, which is governed by the source of the raw materials and preparation procedures (Zanzi, 2000). Different raw materials and manufacturing processes produce activated carbon of different physio-chemical properties, thereby resulting in different adsorption characteristics (Hayashi *et al*., 2000; Yun *et al*., 2002; Zanzi, 2000; Minkova *et al*., 2001; Lua *et al*., 2004). During carbonization, elements such as hydrogen and oxygen or oxides are eliminated from the cellulosic structure of the carbon precursors to produce char at 250°C and 1 atmosphere (Zanzi, 2000).

$$(C_6H_{10}O_5)_n+O_2 \xrightarrow{\text{Heat}} \underset{\text{(Char carbon)}}{C_n}+nCO+nCO_2+nH_2O$$

High moisture content may catalyse the decomposition of the char carbon, thereby resulting in very low yield of the carbon, as shown by the following equations.

$$\begin{aligned} H_2O &+ C \rightarrow H_2 + CO \\ 2\,H_2O &+ C \rightarrow 2H_2 + CO_2 \\ CO_2 &+ C \rightarrow 2CO \\ 2H_2 &+ C \rightarrow CH_4 \text{ (Zanzi, 2000)} \end{aligned}$$

A non-stoichiometric formation of char carbon, volatile by-products and tar from carbonization of cellulosic materials below 250°C, at atmospheric pressure, could be represented as:

$$(C_6H_{10}O_5)_n+O_2 \xrightarrow{\text{Heat}} \underset{\text{(Char C)}}{C_n}+\underset{\substack{\text{low B.P}\\\text{Hydrocarbon}}}{(CH)n}+nCH_3COOH+nCH_3COCH_3+$$

nCH_3OH + Tar + other products (Gimba, 2001)

The ash content of a sample is the inorganic residue remaining after the organic matter has been burnt away. The ash obtained which is usually small and made up of alkali (Na, K), alkaline earth (Mg, Ca) and other elements including heavy metals, is not necessarily of exactly the same composition as the mineral matter present in the

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original sample as there may be losses due to volatilization or interactions between resulting constituents such as the volatiles and char. High ash content, which suggests high inorganic constituents, may also suggest heterogeneous distribution of pores in the final carbon. The porosity development during preparation of porous carbons is greatly influenced by several factors, such as the nature of the precursor including amount of inorganic components (Kyotani, 2000; Yun *et al.*, 2001, 2002; Oh and Park, 2002). The inorganic components are considered to prevent porosity evolution by blocking pore entrances during the activation process (Yun *et al.*, 2002). The ash content should be very low, to yield a final product which is mainly carbonaceous in nature. The volatile matter consists of a complex mixture of gaseous and liquid products resulting from the thermal decomposition of the precursor. The fixed carbon content indicates the proportion of solid carbon in the final product of carbonization. Large volatile matter and fixed carbon contents are therefore essential for producing highly porous materials. Heavy metal content of precursors should be low as the complete removal from the final carbon is only seldom, if ever accomplished, because the salts of the metals are strongly held by carbon and only a small portion is released with each extraction (washing) with acid. Heavy metals must thus be taken into account for an approach to the environmental issues raised by the process.

This study, therefore reports the proximate and ultimate characteristics of bagasse, sorghum and millet straws in relation to their suitability for producing highly porous carbon.

MATERIALS AND METHODS

Ad hoc samples of dry straws of sorghum and millet were collected from Rigasa farm center (non industrial area) in Kaduna State (Nigeria), in March 2006, after harvest. Sugarcanes were obtained from the same area and processed to bagasse. Cellulose absorbs large quantities of water and takes time to dry (Tutor, 2007). The straws and bagasse were therefore air-dried for 3 months on plastic mesh, to ensure adequate drying for easy milling and avoid the loss of carbon residue due to oven-drying (Gimba, 2001). The straws were cut into pieces of approximately 3 cm to obtain the samples for the analysis. The bagasse and chopped straw samples were milled with Christy and Morns miller at the National Animal Production Research Institute (NAPRI), Zaria. The milled bagasse and straw samples were sieved into the different particle sizes (100, 125, 180, 250, 300, 355, 425, 850, 1180, 1680 and 2300 μm) with the various Endecotts Laboratory test sieves on Omron No. 17748 (manual timer) sieve shaker. The sieved samples were packed into polythene bags and labeled accordingly.

Proximate analysis of the samples were carried out using standard protocols described in official methods of analysis by AOAC (1990). Nitrogen was determined by the Kjeldahl method (Christian, 2004). Sulphur in the bagasse, sorghum and millet straws was determined by turbidimetry as described for plants by Rowell (1994); 0.5 g of the sample was placed in a porcelain crucible and heated in a furnace at 600°C. The ash was extracted with 0.1 mol dm^{-3} HCl. 5 cm^3 of the digest was placed in 25 cm^3 volumetric flask and gelatin $BaCl_2$ mixture was added. The absorbance of the resulting mixture was read on WPA S100 Unicam Spectrophotometer at 480 nm. The amount of sulphur was estimated from standard calibration curve. The dichromate method for the determination of oxidisable organic carbon as described by Rowell (1994) was adopted, to determine carbon in the bagasse, sorghum and millet straws. 0.0125 g of the sample was weighed into 250 cm^3 conical flask. 5 cm^3 of 1 mol dm^{-3} $K_2Cr_2O_7$ and 100 cm^3 of concentrated H_2SO_4 were added. The mixture was allowed to digest for 30 min on bench top. 100 cm^3 deionised water followed by 5 drops of 1,10-phenanthroline were added and the mixture was titrated with 0.5 mol dm^{-3} ferrous ammonium sulphate to a red end point. A blank was similarly prepared and titrated without the sample.

$$C\,(\%) = \frac{0.003 \times \text{T-b} \;\times 100 \times 0.5 \times 1.33}{\text{Weight of sample}}$$

where:
T = Titrant
b = Blank

For the heavy metal analysis, 1 g of each of the milled bagasse, sorghum and millet straw samples were treated with 45 cm^3 concentrated HNO_3 and 15 cm^3 concentrated H_2SO_4. The mixtures were heated at 165°C to evaporate most of the acids. 15 cm^3 H_2O_2 was added to complete the oxidation and clear the residual colour of the digests. The mixtures were filtered with Whatman paper No. 541 into 100 cm^3 volumetric flasks and diluted to the mark on the flask, with de-ionised water. The filtrates were kept in plastic containers for Atomic Absorption Spectrometric analysis (AAS) using Unicam SOLAAR32 AA Atomic Absorption Spectrometer.

RESULTS AND DISCUSSION

The particle size has shown a decisive influence on the proximate characteristics of bagasse, sorghum and millet straws. There was an initial fluctuation in moisture

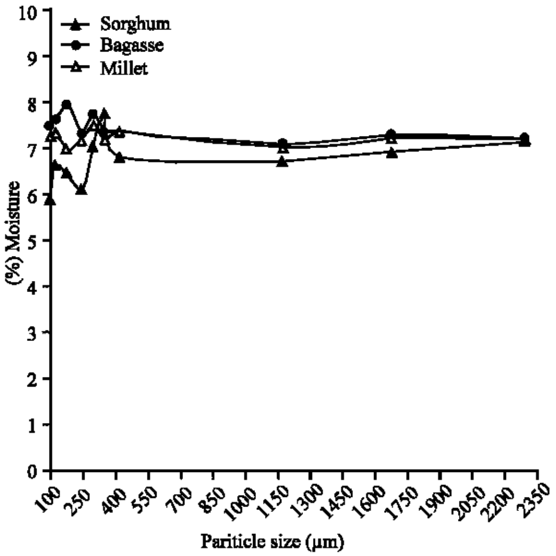

Fig. 1: Effects of particle size on moisture contents of bagasse, sorghum and millet straws

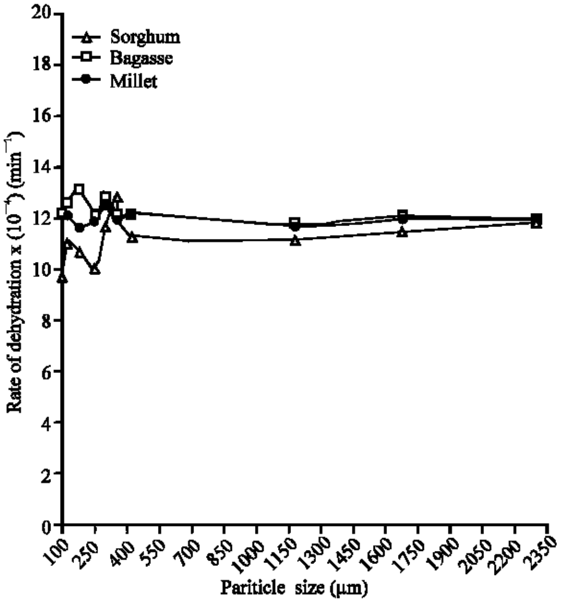

Fig. 2: Effects of particle size on rates of dehydration of bagasse, sorghum and millet straws

contents of the three cellulosic carbon precursors with particle sizes of 100-355 μm (Fig. 1). Greater particle sizes up to 2300 μm did not show any appreciable variation in the moisture contents of bagasse or sorghum and millet straws. However, bagasse and millet straws appeared to have more moisture than sorghum straws. The mean moisture content of bagasse varied from 7.07±0.15 to 7.90±0.10%. However, mean total moisture was found to be 7.41±0.25%, but the mean moisture content of sorghum straw ranged from 5.87±0.15 to 7.73±1.17% with a mean total moisture of 6.73±0.53%. The mean total moisture in the millet straw was 7.21±0.15%, but, the mean moisture for the different particles of millet, ranged from 6.97±0.25 to 7.50±0.36%. A correlation appeared to exist between moisture contents and rates of dehydration of bagasse, sorghum and millet straws (Fig. 1 and 2). From Fig. 2, it is clear that dehydration of bagasse, sorghum and millet straws may be non-uniform with particle sizes of 100-355 μm. This could give rise to a dehydrate product that may be essentially dehydrated at some parts, most likely the external parts and partially or non-dehydrated at other parts. This initial tendency of the cellulosic fine particles to increase and decrease moisture contents when heated, may be linked to possible shrinkage of the matrices with formation of a solid mass, which may be having a higher density (Gimba, 2001). This is consistent with dehydration of cellulose to stable anhydro cellulose, reported by Zanzi (2000).

Particle sizes of 100-355 μm are therefore, likely to yield low char carbon when carbonized as the remaining moisture may only favour the conversion of carbon to CO or CO_2. The consequence is a low yield of active carbon following pyrolysis of the straws or bagasse. It is also likely that higher particle sizes greater than 355 μm may permit uniform dehydration. The mean total rates of dehydration per minute were $(12.34\pm0.42)\times10^{-4}$, $(11.22\pm0.90)\times10^{-4}$ and $(12.01\pm0.25)\times10^{-4}$ for bagasse, sorghum and millet straws, respectively. Influence of fine particle sizes (100-355 μm) on the quality and extent of de-volatilisation of bagasse, sorghum and millet straws is also evident from Fig. 3. Only particle sizes above 355 μm for bagasse, sorghum and millet straws have been found to de-volatilise uniformly. The weight loss characteristics of the cellulosic materials are related to their volatile matter. Sorghum straw had the highest mean total volatile matter (66.65±3.07%). Millet straw and bagasse had 64.52±1.18 and 65.88±2.15%, respectively. Figure 4 shows the rates of de volatilisation of bagasse, sorghum and millet straws were non-uniform with particle sizes of 100-355 μm. This may be due to those small particles, containing large domains, rich in inorganics/volatile materials which may tend to form intermediate solids that require slightly higher heat than that, required by the original matrix, which may be made heterogeneous in particle sizes by the new intermediate solids. The observation is also supported by the fact that heat flux and heating rate are higher in small particles than in large particles and this may reduce the active carbon yield (Zanzi, 2000). With particle sizes greater than 355 μm, sorghum and millet straws showed a steady weight loss

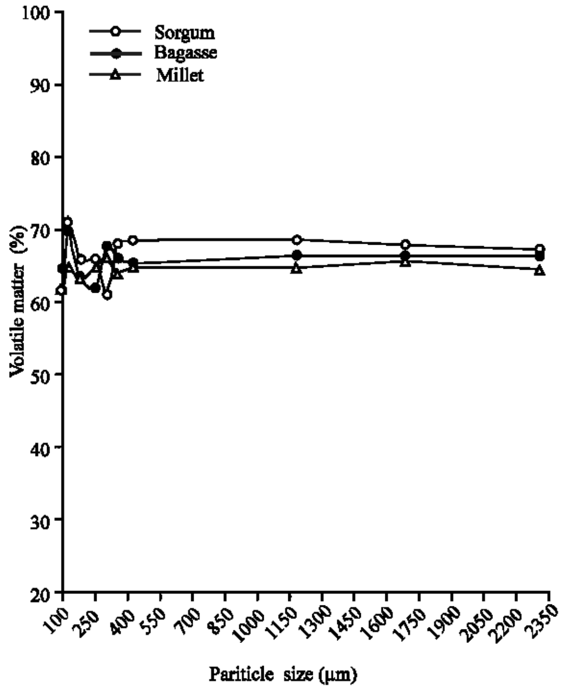

Fig. 3: Effects of particle size on volatile matter of bagasse, sorghum and millet straws

rate up to a particle size of 1180 µm and beyond this particle size, indicated a decline in mean weight loss rates with millet straws presenting an upset at 1680 µm. This may be due to those initial tendencies of particles with large domains, rich in volatile matter. Bagasse particles greater than 425 µm showed a sharp increase in mean weight loss rate up to a particle size of 1180 µm and then, a steady loss in weight. The mean total weight loss rates per minute were 0.094±0.003, 0.095±0.0044 and 0.092±0.002 for bagasse, sorghum and millet straws, respectively.

The gradual decrease in the rates of weight loss of sorghum and millet straw particles above 1680 µm may be associated with a gradual change in the mass of the carbonaceous materials as a result of slow de-volatilisation. Steady weight loss due to dehydration or de-volatilisation is a good characteristic of carbon precursors for highly porous active carbons with homogenous pore distribution. The bulk de-volatilisation collapses the void volume in the precursors to yield good quality active carbons (Gimba, 2001). The steady de-volatilisation and dehydration observed in this study are similar to those produced in active carbon production from bagasse and straws (Zanzi, 2000). However, particle sizes of 500-1180 µm did not show any indication of steady-state rate of weight loss from coconut shell (Gimba, 2001), but steady weight loss was observed with 1400 µm particle size, under conditions similar to those for

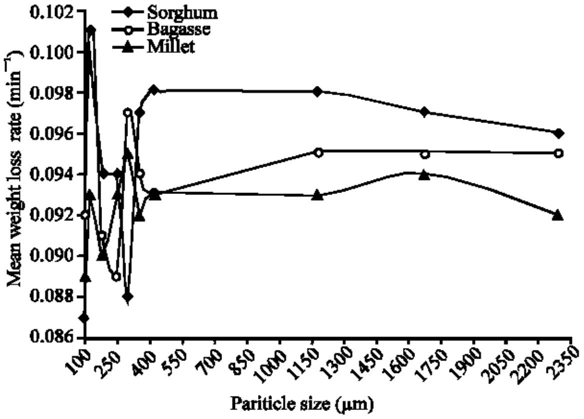

Fig. 4: Effects of particle size on weight loss characteristics of bagasse, sorghum and millet straws at high heat

de-volatilisation of bagasse and straws in this study. The difference in rates of de-volatilisation of coconut shell and the cellulosic materials study may be related to the variation in the proportions of cellulose, hemi-cellulose and lignin which are common constituents of agricultural residues such as coconut shell, bagasse and straws (Zanzi, 2000; Gimba, 2001). From Fig. 2 and 3, it is deduced, that the appropriate particle sizes of bagasse, sorghum and millet straws to be carbonized for porous carbons are greater than 425 µm. However the weight loss characteristics of these carbon precursors (Fig. 4) have shown that particle sizes of 425-1180 µm are the most desirable for carbonization to produce good quality porous carbon. These deductions have been complemented by the low ash contents of this range of particle sizes of the cellulosic materials (Fig. 5). The particle size of the cellulosic materials that is expected to yield highly porous carbon with minimum ash contents is 1180 µm.

The evaluation of the effect of particle size on the ash contents of bagasse, sorghum and millet straws showed, that the lower the particle size the higher the % ash content (Fig. 5). Although, % ash contents varied erratically for particle sizes below 425 µm, the high ash contents associated with the fine particle sizes show evidence of large % of inorganics, oxidisable and volatile materials (Fig. 3). Bagasse had the lowest ash content while millet straws burnt to produce the highest ash content. Bagasse and sorghum straws are thus suspected to be better suited for active carbon production.

The fixed carbon contents of bagasse, sorghum and millet straws were influenced by particle sizes of 100-355 µm (Fig. 6), but particle sizes greater than 425 µm did not indicate any strong influence on the tendencies of

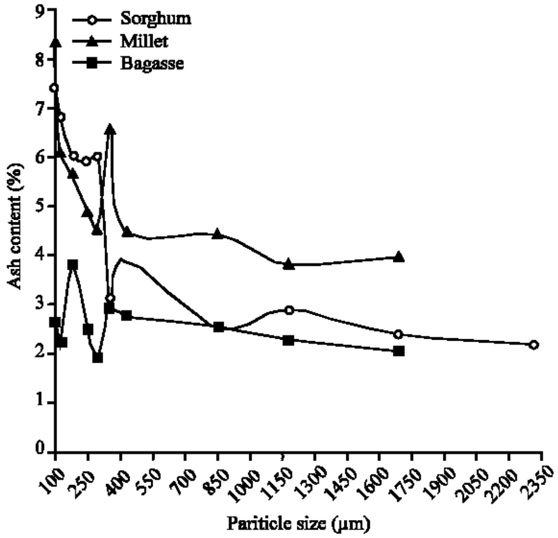

Fig. 5: Effects of particle size on ash contents of bagasse, sorghum straw and millet straw

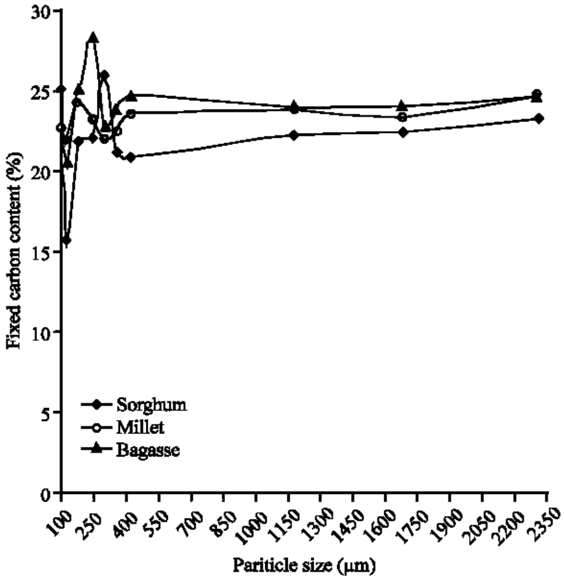

Fig. 6: Effects of particle size on fixed carbon contents of bagasse, sorghum and millet straw

the cellulosic materials to produce high solid contents following, carbonization. The low fixed carbon content obtained from particle sizes of 100-355 μm may be explained by the fact that the high ash content associated with fine particles enhances the conversion of biomass to gaseous products (Zanzi, 2000), thereby reducing the fixed carbon content. The mean fixed carbon contents of bagasse, sorghum and millet straws were 24.16±1.94, 23.02±0.93 and 21.93±2.74%, respectively, thus indicating the sequence bagasse > sorghum straw > millet straws, respectively. The yields of active carbon from the precursors are also expected to follow the same sequence (Minkova, 2001).

Table 1: Ultimate characteristics of bagasse, millet and sorghum straws

Samples	Nitrogen (N) (%)	Carbon (C) (%)	Sulphur (S)×10^{-4} (%)
Bagasse	0.33±0.03	67.31±0.38	71.77±0.75
Millet straw	0.33±0.02	85.80±0.28	228.90±0.80
Sorghum straw	0.25±0.01	81.47±0.40	96.19±0.35

Table 2: Heavy metal contents (mg dm^{-3}) of bagasse, millet and sorghum straws

Metals	Bagasse	Millet straw	Sorghum straw
Ag	ND	ND	ND
Cd	ND	ND	ND
Co	0.1210±0.0140	0.1412±0.0120	0.1684±0.0110
Cr	ND	ND	ND
Cu	0.4986±0.0010	0.1315±0.1140	0.1166±0.0450
Fe	4.8342±0.0120	1.1955±0.0110	0.1166±0.0450
Mn	0.1722±0.0150	0.0781±0.0190	0.2569±0.0100
Ni	ND	ND	ND
Pb	ND	ND	ND
Zn	0.4186±0.0000	0.4039±0.0140	0.4071±0.0090

ND: Not Detected

The levels of nitrogen were 0.33±0.03, 0.33±0.02 and 0.25±0.01 for bagasse, millet and sorghum straws, respectively (Table 1). The amounts of carbon were nearly same in millet (85.80±0.28%) and sorghum (81.47±0.40%) straws and higher than the carbon content in bagasse (67.31±0.38%). The sulphur contents were in the order, millet straw (228.90±0.80 %) > sorghum straw (96.19±0.35%) > bagasse (71.77±0.75%). The sums of N, C and S contents were used to indicate the levels of inorganic contents in bagasse, millet and sorghum straws. These values indicated that millet straw had the highest inorganic contents while bagasse had the least. The observations were consistent with the results for ash contents, which indicated the trend in ash contents as millet straw > sorghum straw > bagasse (Fig. 5).

Table 2 present the Ag, Cd, Cr, Ni and Pb were neither detected in bagasse nor millet and sorghum straws. The levels of Co were 0.1210±0.0140 mg dm^{-3} (bagasse), 0.1412±0.0120 mg dm^{-3} (millet straw) and 0.1684±0.0110 mg dm^{-3} (sorghum straw), respectively. The level of Cu in bagasse (0.4986±0.0010 mg dm^{-3}) was higher than the levels in either of millet (0.1315±0.1140 mg dm^{-3}) or sorghum (0.1166±0.0450 mg dm^{-3}) straws. Fe ranged from 0.1166±0.0450 mg dm^{-3} in sorghum straw to 4.8342±0.0120 mg dm^{-3} in bagasse. Mn was also detected in bagasse (0.1722±0.0150 mg dm^{-3}), millet (0.0781±0.0190 mg dm^{-3}) and sorghum (0.2569±0.0100 mg dm^{-3}) straws. The levels of zinc were approximately same in bagasse (0.4186±0.0000 mg dm^{-3}), millet (0.4039±0.0140 mg dm^{-3}) and sorghum (0.4071±0.0090 mg dm^{-3}) straws. The metal results thus suggest the need for heavy metal analysis of active carbons that may be produced from the bagasse and straw samples in other to monitor trace metal residues in the carbon. Washing of the resulting active carbon with hydrochloric acid and de-ionised water (Baquero *et al*., 2003) may adequately remove or reduce the heavy metals.

Previously, proximate and ultimate characteristics of carbon precursors were commonly, used to justify the characteristics of active carbons that are produced (Guo *et al*., 2000; Hayashi *et al*., 2000; Minkova *et al*., 2001; Garcia-Perez, 2002; Lua *et al*., 2004), but not as a necessary tool to select materials and conditions prior to carbonization. In most cases, this makes the investigation of new precursors for the production and studies of active carbons very tedious as wide range of particle sizes may have to be carbonized at different residence times to ascertain their suitability for highly porous carbon (Zanzi, 2000; Gimba, 2001; Garcia-Perez, 2002; Jaguaribe *et al*., 2005). This present study is therefore, a novel approach to the planning of active carbon production that considers a preliminary study to select materials and possibly conditions for active carbon production.

CONCLUSIONS

The results from ad hoc samples have shown that particle size has a decisive influence on the proximate characteristics of bagasse, sorghum and millet straws. Based on the weight loss characteristics; rates of dehydration and de-volatilisation of these cellulosic materials, particle sizes of 425-1180 μm, which were associated with diminishing ash contents, are therefore, suggested for the production of good quality porous carbon. However, the optimum particle size of the cellulosic materials that is expected to yield highly porous carbon with minimum ash contents is 1180 μm. Washing of the resulting active carbon with hydrochloric acid and de-ionised water to remove residual heavy metals, is also recommended. The production of active carbon from the cellulosic materials is currently being studied.

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REFERENCES

AOAC, 1990. Official Methods of Analysis by Association of Official Analytical Chemists. 15th Edn., Arlington, VA. ISBN 0-85226-141-1, pp: 331.

Barkauskas, J., S. Tautkus and A. Kareiva, 2004. Residual content of inorganic ions in activated carbons prepared from wood. J. Anal. Applied Pyrol., 71: 201-212.

Baquero, M.C., L. Giraldo, J.C. Moreno, F. Suarez-Garcia, A. Martinez-Alonso and J.M.D. Tascon, 2003. Activated carbons by pyrolysis of coffee bean husks in presence of phosphoric acid. J. Anal. Applied Pyroly., 70: 779-784.

Christian, G.D., 2004. Analytical Chemistry. 6th Edn., John Wiley and Sons Ltd., Singapore, pp: 287-289.

Garcia-Perez, M., A. Chaala and C. Roy, 2002. Vacuum pyrolysis of sugarcane bagasse. J. Anal. Applied Pyrol., 65: 111-136.

Gimba, C.E., 2001. Preparation and adsorption characteristics of activated carbon from coconut shell. Ph.D Thesis, Ahmadu Bello University, Zaria, Nigeria, pp: 45.

Guo, Y., K. Yu, Z. Wang and H. Xu, 2000. Effects of activation conditions on preparation of porous carbon from rice husk. Carbon, 41: 1645-1687.

Hayashi, J., A. Kazehaya, K. Muroyama and A.P. Watkinson, 2000. Preparation of activated carbon from lignin by chemical activation. Carbon, 38: 1873-1878.

Hayashi, J., T. Horikawa, I. Takeda, K. Muroyama and F.N. Ani, 2002. Preparing activated carbon from various nutshells by chemical activation with K_2CO_3. Carbon, 40: 2181-2186.

Jaguaribe, E.F., L.L. Medeiros, M.C.S. Barreto and L.P. Araujo, 2005. The performance of activated carbons from sugarcane bagasse, babassu and coconut shells in removing residual chlorine. Braz. J. Chem. Eng., 22: 1-11.

Kyotani, T., 2000. Control of pore structure in carbon. Carbon, 38: 269-286.

Lua, A.C., T. Yang and J. Guo, 2004. Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. J. Anal. Applied Pyrol., 72: 279-287.

Minkova, V., S.P. Marinov, R. Zanzi, E. Bjornbom, T. Budinova, M. Stefanova and L. Lakov, 2000. Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide. Fuel Proc. Technol., 62: 45-52.

Minkova, V., M. Razvigorova, E. Bjornbom, R. Zanzi, T. Budinova and N. Petrov, 2001. Effect of water vapour and biomass nature on the yield and quality of the pyrolysis products from biomass. Fuel Proc. Technol., 70: 53-61.

Oh, G.H. and C.R. Park, 2002. Preparation and characteristics of rice-straws-based porous carbons with high adsorption capacity. Fuels, 81: 327-336.

Rowell, L.D., 1994. Soil Science: Methods and Applications. Longman Group, Limited, United Kingdom pp: 48-49, 213-215.

Tutor, F., 2007. Thermal degradation of cellulose. http://www.fibersource.com/f-tutor/cellulose.htm.

Yun, C.H., Y.H. Park and C.R. Park, 2001. Effects of pre-carbonization on porosity development of activated carbons from rice straw. Carbon, 39: 559-567.

Yun, C.H., Y.H. Park, G.H. Oh and C.R. Park, 2002. Contribution of inorganic components in precursors to porosity evolution in biomass-based porous carbons. Carbon, 41: 2009-2012.

Zanzi, R., 2000. Pyrolysis of biomass. Rapid pyrolysis at high temperature. Slow pyrolysis for active carbon preparation. Ph.D Thesis, Royal Institute of Technology, Stockholm, Sweden, pp: 35.