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Original Article

Suitability of Sudanese pearl millet stalks *Pennisetum glaucum (L.)* for alkaline pulping with additives

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Abstract

Pennisetum glaucum pearl millet as whole stalks and core were examined for suitability in the production of pulp and paper. Fiber dimensions, morphological, and chemical characteristics are reported. The pulping trials with soda-AQ, ASAM, and soda as reference were carried out. ASAM pulping gave good results in yield, degree of delignification, and mechanical properties. The best screened yield, lowest kappa number, highest brightness, and viscosity were obtained by ASAM cooking. Soda-AQ gave pulps with good screened yield, kappa number, and viscosity compared with soda cooking. The separation of bark and core is not recommended.

Keywords: *Pennisetum glaucum* stalks, fiber dimensions, chemical composition, alkaline pulping

1. Introduction

Pearl millet (*Pennisetum glaucum* L.) is a low priced food grain crop that belongs to the Poaceae family which is drought- and high-temperature tolerant. The distribution area of pearl millet in the West and Central Africa harbors a wide range of climatic and environmental conditions (Chaudhari *et al.*, 2018; Jaiswal *et al.*, 2018; Rajaram *et al.*, 2013; Stich *et al.*, 2010).

The stems of pearl millet are cut into small pieces to improve their digestibility and they are used to improve livestock diet and the stalks are used to prevent soil erosion (Lamers, 1993; Michels, Sivakumar, & Allison, 1995; Rebafka, Hebel, Bationo, & Stahr, 1994). Millet is the main food for the western Sudanese people in several types of food dishes such as Balila (whole cooked grain), non-fermented whole millet flour to make acida (stiff porridge) and madidat atroon (thin porridge with natron), fermented dough to make kisra (unleavened bread), nasha (thin porridge), and Marisa (opaque beer) and the extracted starch is known as Jir or Geeria (Abdelsamad, Ahmed, Ahmed, El Tinay, & Ibrahim, 2009; Ayanwale, Adekunle, & Akinola, 2013; Babiker, Khai, & Tahir, 2014; Issa *et al*., 2018).

The application of millet stalks in pulp and paper manufacturing can be more beneficial because they are abundant, inexpensive, and can provide economic and environmental benefits (Dulermo, *et al.*, 2016; Elzaki, Khider, & Omer 2012). Harinarayana *et al*. (2005) found that the millet stalks were rich in cellulose content (39.4%), hemicellulose (23.9%), and relatively low in lignin (12.8%), thus representing a promising feedstock (Saeed, Liu, Lucian, & Chen, 2017).

The soda process is an alternative method for producing sulfur-free pulp. However, using a high alkali charge associated with high temperature damages the soda pulp viscosity and the quality and paper strength as well. Pulping additives can be used to improve these parameters

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(Almeida & Gomide, 2015). The chemical materials that make up the alkaline sulfite-anthraquinone-methanol (ASAM) process are sodium sulfite, sodium hydroxide (NaOH), anthraquinone (AQ), and methanol. These materials play a unique role in pulping because, sodium sulfite and NaOH are the major ingredients of the alkaline sulfite process while AQ and methanol act as catalysts to enhance the chemical penetration delignification of the lignocellulose biomass (Paridah *et al.*, 2018).

The soda process is an alternative method for producing sulfur-free pulp. The objective of the current work was to investigate the suitability of pulping of pearl millet stalks with NaOH (soda lye), soda-AQ, and alkaline sulphite–AQ with the addition of methanol in the ASAM process.

2. Materials and Methods

Millet stalks were collected according to TAPPI 2002, from a farmer in the Alfasher locality of North Darfur State, Sudan. It is subtropical area characterized by low soil fertility and limited moisture content where annual rainfall ranges 200–800 mm and the average total area annually cultivated is approximately 2.5 million ha. However, millet stalks are used as feed for animals and used mostly as building material or fuel (Abuelgasim, 2011) The height of the collected plant stalks ranged 0.5–4 m and were cultivated in the autumn of 2017. Twenty kilograms of stalks were collected by hand, packaged in bags, and transported to Khartoum (National Centre for Research) by bus. The air dried samples of core and whole millet were manually separated and chopped into 3–5 cm lengths. Fiber dimension evaluations were done after maceration with a mixture of 30% hydrogen peroxide and acetic acid (1:1) and were carried out microscopically at 300x and 400x magnifications after staining with aqueous safranin using an Aus Jena microscope equipped with a Laboval 4-Carl Zeiss trinocular head with micrometer resolution (Horn, 1978; Kirci, 2006). About 100 fibers were measured and the standard deviation was calculated for each fiber dimension. Representative sample of a portion prepared chips for pulping trails was ground in a star mill and the 40X60 mesh fraction was used for chemical analysis according to TAPPI standards (2002) & Obolens kaya, Tshegolov, Akim, Kossoviz, and Emelyannova (1965). The raw materials were characterized chemically in accordance with applicable TAPPI standards for different components, namely preparation for chemical analysis (TAPPI 264 cm-97), sampling and testing for moisture (TAPPI 210 cm-93), lignin (TAPPI-222), alpha cellulose (TAPPI 203OS-61), hot water soluble (TAPPI T-207), Pentosans (TAPPI 223-cm-01) solvent extraction of wood (TAPPI 204), and ash (TAPPI 212). The experiments were repeated three times and the mean was calculated for each chemical analysis.

Pulping was carried out in 7l electrically heated digesters with forced liquor circulation. Three different alkaline pulping processes with and without additives were used: soda-AQ (Holton 1977; Khider, Omer, & Taha, 2012; Khristova, Gabir, Bentcheva, & Khider, 1998), and alkaline sulphite-AQ methanol (ASAM) (Kordsachia, Wandianger, & Patt, 1992) with soda cooking as the reference according to the cooking conditions (Table 1). The pulp was then beaten in a Valley beater according to TAPPI 200-sp-01 freeness of pulp (Canadian standard method TAPPI 227om-99), Kappa number (TAPPI 236om-99), viscosity (TAPPI 230om-99), physical testing of pulp sheets (TAPPI 220-sp-01). Conditioning of testing atmosphere (TAPPI 402-sp-98), burst strength (TAPPI 403om-97) and tensile (TAPP-404-cm-92).

3. Results and Discussion

The millet bark average length (0.52 mm) was in the range of short fiber tropical hardwoods while the core portions were shorter (0.39 mm) (Table 2). The quite wide core and bark fibers (27.2 and 28.3 µm, respectively) had medium thick walls (4.9 and 5.1 µm, respectively) with more or less the same lumen width (17.4 and 18.2 µm, respectively). This was reflected in the same morphological indices, indicating their ability to collapse easily and to form good fiber-to-fiber bonding which is important for paper strength. The Runkel index for both fiber types was less than 1.0 which indicated they were suitable for papermaking. The flexibility index was 63.9 and 64.3 (2nd category of the Istas classification 1965) which is positively correlated to the tensile strength and burst factor. Although there is still controversy in accepting the morphological data in predicating the properties of pulp the multi-regression technique seems undoubtedly valuable in showing which morphological characters are important in the pulp properties (Dinwoodie, 1965). Since the bark and core of the millet stalk had the same morphological indices, there was no need to separate the fibers, which is also more attractive and economical.

The ash contents of the core and whole millet stalks were rather high (4.8% and 5.6%, respectively) but typical for tropical non-woody plants (Table 3). The silica content was high in both raw materials which is usual for such agricultural

Table 1. Pulping conditions of millet stalks.

Cooking conditions	Soda	Soda-AQ	ASAM
Active alkali charge as Na_2O %	15.4	13.4	12.9
NaOH: Na_2SO_3 ratio	-	-	70:30
Anthraquinone, %	0	0.1	0.1
Methanol added as % to white liquor	0	0	15
Liquor to millet ratio,	4	4	4
Maximum temperature, °C	160	160	165
Time to maximum temperature, min	60	60	65
Time at maximum temperature, min	90	90	90

Abbreviations: Na_2O, sodium oxide; NaOH, sodium hydroxide; Na_2SO_3, sodium sulfite.

Table 2. Fiber dimensions and morphological indices of millet stalks.

Fiber dimensions	Measured value of bark	SD	Measured value of core	±SD
Fiber length, mm	0.52	0.8	0.39	0.7
Fiber width, µm	28.3	0.8	27.2	0.6
Lumen width, µm	18.2	0.9	17.4	0.9
Wall thickness, µm	5.1	N.A	4.9	N.A
Morphological indices	-	-	-	-
Runkel index	0.56	-	0.56	-
Wall fraction	36	-	36	-
Flexibility coefficient, %	64.3	-	63.9	-
Rigidity coefficient, %	18.02	-	18.01	-
Felting power (slenderness)	18.4	-	14.3	-

Abbreviations: SD, standard deviation
**N.A= not available

Table 3. Chemical components with bark and without bark of millet stalks.

Chemical composition, %	Whole millet	Core
Ash	5.6	4.8
Total silica	3.6	3.9
Solubility in		
Hot water	7.4	6.2
Cold water	7.6	6.9
Alcohol (Ethanol)	2.7	2.6
Ethanol: cyclohexane (1:2)	0.7	0.8
1% NaOH	37.1	31.2
Kurschner-Hoffer cellulose	47.4	45.1
Alfa-cellulose	42.2	40.4
Holocellulose	64.3	62.0
Pentosans	17.0	16.2
Lignin	21.1	22.3
Total extractives	8.1	7.3
Cellulose to lignin ratio	2.25	2.02

residues. The lignin was rather low predicting low to moderate chemical consumption. However, the hot water, cold water, 1% NaOH soluble, and total extractives were rather high, while cyclohexane, alcohol, and ethanol soluble extractives were low to moderate which suggested low to moderate chemical consumption (Table 3). The cellulose (Kushner-Hoffer) was 45.1% and 47.4% for core and whole millet stalks, respectively, which meant good pulp yields. The presence of water-soluble hemicelluloses in pulp fibers increases their swelling tendency and water absorption during beating, thus the fiber-to fiber bonding improves, which leads to further considerable increase in most properties, especially the tensile strength, these reflected by good pentosan and holocellulose contents for both raw materials (Khristova, Bentcheva, & Karar, 1998; Khristova, Bentcheva, & Khider, 1998). Cellulose-to-lignin ratio was higher than 2 and predicted normal pulping with the alkaline methods.

AQ is a powerful redox-catalyst in alkaline pulping especially when agricultural residues are cooked (Shakhes, Zeinaly, Marandi, & Saghafi, 2011). The results of alkaline sulfite and AQ with methanol (ASAM [MS5 and MS6]), and soda with (MS3 and MS4) and without (MS1 and MS2) the addition of AQ are shown in Table 4. The use of a higher temperature in ASAM pulping (165 °C) compared with soda-AQ and soda cooking (160 °C) was because of the methanol in ASAM cooking. The use of 0.1% AQ substantially enhanced the delignification in both processes due to the stabilizing effect of AQ on the carbohydrates (Table 1). It also gave higher screened yields at lower active alkali (12.9–13.4%), and better viscosities than the soda pulping with 15.4% active alkali charge. With 12.9% active alkali charge, ASAM (MS5 whole millet) gave pulp with good screened yield and initial ISO brightness but with a higher Kappa number and higher viscosity compared to soda-AQ pulps (MS3 and MS4) (Table 1). According to Gierer (1982), the intermediate formation of quinonemethide is preceded by cleavage of β-ether aryl-ether bonds. Subsequently, sulfonation occurs at the electrophilic β-carbon, followed by a sulfolytic cleavage of β-aryl ether bonds. The most distinctive advantage of ASAM cooking compared to soda-AQ cooking was the much higher initial ISO brightness of pulps and the more intensive delignification at higher total yield. The viscosity values indicated that cellulose degradation had the lowest MS5 (ASAM whole millet) and the highest cellulose degradation occurred during ASAM cooking of core (MS6) could be attributed to weakening of the fiber of core because it's chemical constituents, especially carbohydrates (Table 4) compared to whole millet pulps. However, the overall evaluation of pulping results showed the cooking of millet stalks as a whole will give better yields, kappa numbers, and viscosities. Therefore, it is economically beneficial to reduce the separation cost during the cooking pretreatment of millet.

Table 4. Pulping results of millet stalks.

Pulping process cooking code	Soda whole millet MS1	Core MS2	Soda-AQ whole millet MS3	Core MS4	ASAM whole millet MS5	Core MS6
Total yield,%	34.7	42.7	37.3	45.4	47.3	48.2
Screened yield,%	33.6	42.1	35.2	43.9	47.2	47.3
Reject, %	1.1	0.6	2.1	1.5	0.1	0.9
Kappa number	26.1	27.5	22.4	21.9	24.1	20.5
Viscosity, ml g^{-1}	545	525	552	533	563	520
ISO brightness,%	21	23	23	22	40	42

Abbrevistions: AQ, anthraquinone; ASAM, alkaline sulfite-anthraquinone-methanol; MS, millet stalks.

The pulp properties for soda and ASAM for both core and whole millet are reflected in Figures 1–5. The superiority of ASAM pulps was obvious compared to soda pulps in weight (Figure 1), grammage (Figure 2), and thickness (Figure 3). The ASAM bark had very thick pulps due to the fact that ASAM cooking of millet stalks bark had more inter-fiber bonding and therefore a more condensed and compact sheet. On the other hand, the tensile strength of soda pulps was higher than the ASAM (Figure 4) pulps which was supported further by the high viscosity and the same pattern for burst (Figure 5) when comparing the different properties versus beating time. It was also found that the pulp properties of bamboo subjected to the ASAM pulping process were significantly affected by the cooking conditions (P≤0.05) (Paridah, *et al.* 2018). The pulp at 18% NaOH and 90 min cooking time gave low pulp yield and tear index of 41.24% and 18.64 mN.m²/g, respectively. The pulp made with 16% NaOH and 90 min cooking time presented the best properties, pulp yield, Kappa number, tensile strength, tear and burst indices with values of 49.06%, 14.2, 20.86 Nm/g, 22 mN.m²/g, and 10.05 kPa.m²/g, respectively (Paridah, *et al.* 2018). The overall strength properties of whole and core pulps indicated no need to separate the fiber core from the bark as it seemed more or less similar in morphological and chemical properties.

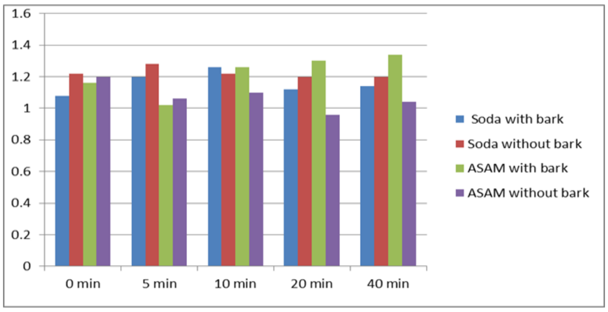

Figure 1. Histogram average weight (grams) vs beating time, min for soda and ASAM pulps.

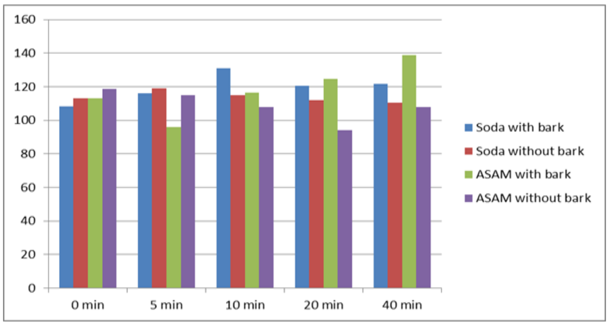

Figure 2. Histogram of grammage (g/m²) vs beating time, min for soda and ASAM pulps.

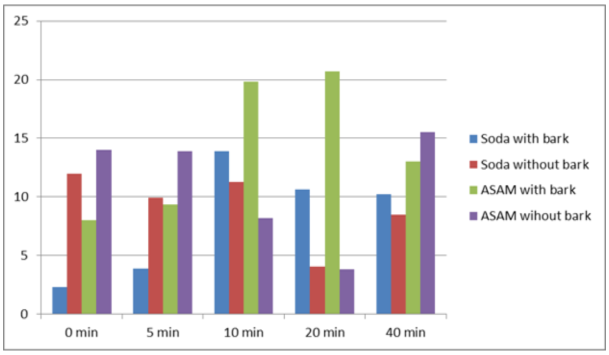

Figure 3. Histogram of thickness (μm) vs beating time (min) for soda and ASAM pulps.

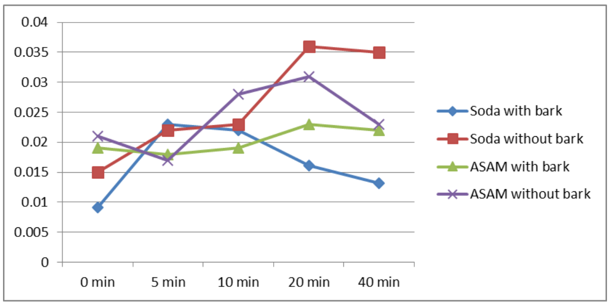

Figure 4. Tensile index (Nm/g) vs beating time (min) for soda and ASAM pulps.

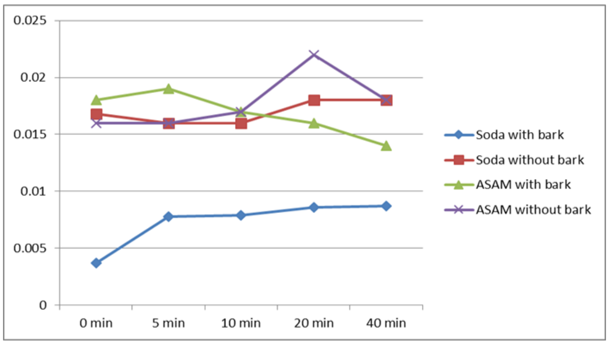

Figure 5. Burst index (k Pa m²/g) vs beating time (min) for soda and ASAM pulps.

Figure 6. Digester and instruments used for cooking and chemical characterization.

4. Conclusions

The fiber characteristics and morphological indices of the pearl millet stalks were typical of non-woody plants and agricultural residues. The wide fiber lumen diameters with high flexibility coefficient and favorable Runkel ratio indicated good paper properties of the corresponding pulps. The chemical composition of millet stalks showed resemblance to the tropical species. However, ash content, high silica, good carbohydrates, and cellulose/lignin ratio were favorable for alkaline pulping with acceptable charge and pulp yields as would be expected. Pulping with ASAM, and soda with and without AQ as reference, confirmed the beneficial effect of AQ-addition, especially a dose of 0.1% AQ. The use of whole millet stalks without separation of core and bark gives pulps with good quality. It seems possible to avoid the high cost of separation, which would represent a problem for industrialization of this agricultural residue.

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