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Evaluation of physicochemical properties and soda pulping of *Nypa fruticans* frond and petiole

Aniekan E. Akpakpan[1,*], Ukana D. Akpabio[2] and Ime B.Obot[2]

[1]Department of Chemistry, University of Ibadan, Ibadan, Oyo State, Nigeria.

[2]Department of Chemistry, University of Uyo, Akwa Ibom State, Nigeria.

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ABSTRACT

The physicochemical parameters of the *Nypa fruticans* (Nypa palm) frond and petiole have been determined. The fibre dimensions determined were: fibre length, fibre diameter, cell wall thickness, lumen diameter, slenderness ratio, flexibility ratio and Runkel ratio. Chemical composition determined were lignin contents, cellulose contents and the ash contents. Soluble contents were also determined. Petiole contained more water soluble than the frond but the frond contained more 1% NaOH soluble. The solubles in 1:2 ethanol-benzene were of the same order for both samples. Soda pulps were produced at the pulping temperature of 120^{o}C using 8% and 12% NaOH as cooking liquors at the pulping time of 30 and 60min. The pulps obtained were characterized by determining the pulp yield and residual Klason lignin. Pulp yield and residual Klason lignin decreased with increase in the concentration of the pulping liquor and the cooking time. These results obtained indicate that *Nypa fruticans* frond and petiole left as waste in Nigeria can be exploited for the production of commercial pulps for several industrial applications.

Introduction

The search for local sources of fibrous raw material in Nigeria has long history. During 1960 to 1964, plants such as *Gmelina arborea*, and various species of eucalyptus and pines (*Pinus caribeae and pinus merkusii*) were identified as sources of raw materials for pulp and paper making. Eucalyptus was eliminated because of high cost of establishing the species in the plantation and it susceptible to termite attack [1].

At present, the main source of raw material for the paper industry in Nigeria is *Gmelina arborea*. It produces short fibre pulps which when used alone produces paper with poor strength properties hence, the long fibres are imported at extra high cost for blending with the short fibre pulp in order to produce acceptable paper [2]. As a result, intensive research on various other plants including kenaf, hemp, raphia palm, banana and plantain pseudo-stem were identified as sources of fibres of medium to long fibre length [2]. Pulps can also be obtained from stem, root and leaves of some agricultural residue [3]

Nypa fruticans also known as Nypa palm are mangrove palms, and renewable agro-waste [4]. Its can serve as alternative source of fibres for pulp production. *Nypa fruticans* (family: *Arecaceae*) has a fairly wide distribution in India, Myanmar, Thailand, Malaysia, Indonesia, Borneo, Philippines, Ryukyu Islands, New Guinea, the Solomon Islands and northern Australia [5]. The family Arecaceae (Palmae) is one of the largest monocotyledonous families, comprising over 200 genera and totalling about 2,600 species [6]. *Nypa fruticans* was introduced to West Africa at two main locations in Nigeria. In 1906, seeds from the Botanic Gardens of Singapore were used to establish a trial plantation in Old Calabar in Cross River State, from where a subsequent plantation was initiated in Oron in Akwa Ibom State in 1912 to check erosion in these coastal areas. In 1946, a further 6000 seeds originating from Malaysia were planted throughout the brackish swamps of the Niger Delta [7]. It is from these two single points of entry that the species has today colonized large areas of coastline throughout West Africa [8]. The plant which was brought primarily to check erosion in the coastal town of these regions is now becoming invasive and has spread east ward through the Rivers, Bayelsa and Delta State reaching the coast of Ondo State. Nypa palm is no longer checking erosion along the coast, after about one hundred years of existence in Nigeria. Now the story of Nypa palm has change, rather the palm is threatening Nigerian extensive natural mangrove vegetation causing reduction in fish, poor navigation, ecological degradation and loss of biodiversity [9].

Environmental impact assessments carried out for the oil industry observed that Nypa has invaded the mangrove areas of the Niger Delta especially around the Bonny and Imo Rivers and is causing long-term ecological damage [10]. Mangroves in areas adjacent to petrochemical installations are frequently in poor condition. Wherever mangrove cover is poor and the ground is bare Nypa can rapidly invade, out-competing native mangrove species and causing permanent displacement. The study concluded that ″Nypa is extending its range within the Niger mangrove system and has the potential to become a substantial problem" [10].

In Nigeria, Nypa palm as a whole has no significant commercial value. Presently, a large quantity of seeds and leaves are not utilized and they constitute nuisance by blocking estuaries and other coastal water ways. There are moves now to replace this palm with traditional mangroves if they cannot be utilized industrially. Hence there is need to investigate the suitability of *Nypa fruticans* as a non-wood fibrous raw material for pulp production for the preparation of cellulose derivatives and paper making.

Tele:

E-mail addresses: anieswill@yahoo.com

Thus, the aim of this work is to investigate the fibre properties and chemical composition of *Nypa fruticans* frond and petiole in order to evaluate its suitability or otherwise as the fibrous raw materials for pulp production in Nigeria.

Materials and Methods

The raw materials used in this research work were *Nypa fruticans* fronds and petioles. They were collected at Oron Beach in Oron Local Government Area of Akwa Ibom State. The samples were dried in air to reduce moisture. It was then cut into chips of about 2cm by 2cm. The pith of the frond was removed because the pith consist of non-fibrous materials and causes serious problems such as increasing chemical consumption in pulping and bleaching and drainage problem in paper making [11]. Moisture contents of the air dried chips were determined to know the weight of the dry matter. Part of the chips were ground and used for chemical analysis, while the remaining chips where used for pulping experiment.

Specific Gravity

Specific gravity signifies the density, workability or the strength properties of the pulping raw material. The specific gravity was determined using representative samples. The moisture content of the air dried sample chips were determined in order to permit description of the specific gravity on the basis of dry mater. This was determined in accordance with ASTM standard procedure designated D 2395-89 method B [12].

Fibre Dimensions and Morphological Indices of *Nypa fruticans*

Fibre dimensions of *Nypa fruticans* were determined by cutting the samples into thin strip/filaments using razor blade. The filaments were soaked in a glass bottle containing 50ml of 80% acetic acid and 50ml of 30% hydrogen peroxide for one week. It was later put in the oven for 48h with sequential shaking in mechanical shaker until the samples were completely defiberized. The reaction liquor was diluted and the fibres obtained were screened and wash with distilled water to neutral pH. The fibres were mounted on the slide and the fibre length, fibre diameter, lumen width, and cell wall thickness of each sample were measured under the digital camera microscope, Model XSZ, 2003, at Forest Research Institute (FRIN) Ibadan, Oyo State.

The following morphological indices were determined from these measurements:

$$\text{Runkel Ratio} = \frac{2 \text{ X Cell Wall Thickness}}{\text{Lumen Diameter}}$$

$$\text{Slenderness Ratio} = \frac{\text{Fibre Lenght}}{\text{Fibre Diameter}}$$

$$\text{Flexibility Coefficient} = \frac{\text{Lumen Width}}{\text{Fibre Diameter}}$$

Chemical Characterisation

The chemical characteristics of Nypa fruticans were determined in accordance with TAPPI standard designated as follows:

Solubility in hot and cold water – T207 cm99 [13], Solubility in 1% NaOH – T212 om 02 [14], Solubility in ethanol/benzene – T204 cm 97 [15], Lignin content -T222 om 98 [16]. Ash content- T 211 om-02 [17]. Cellulose content was determined using Kurschner-Hoffer cellulose method [18].

Pulping Experiments

Pulping experiments were carried out separately on the chips of *Nypa fruticans* frond and petiole using 8% and 12% sodium hydroxide (NaOH) solution. The pulping was done in the laboratory digester at 120^{o}C for 30 and 60min. respectively. The pulps obtained were washed thoroughly with tap water and the pulp yield was determined gravimetrically after drying to constant weight in the oven at 105^{o}C.

Kappa number of the pulp was determined in accordance with TAPPI standard designated T236 om-99 [19], while residual Klason lignin was calculated from kappa number according to the following relation:

% Residual Klason Lignin (RKL) = Kappa number x 0.13 [19].

Results and Discussions

Specific Gravity

The result of specific gravity determinations were 0.62 and 0.77 for *Nypa fruticans* frond and petiole respectively. These values fell within the range of 0.3- 0.8 reported for bamboo elsewhere [20]. Petiole showed higher specific gravity than the frond which means that petiole is denser than the frond.

Fibre Dimensions and Morphological Indices of *Nypa fruticans*

The results of the fibre dimensions and morphological indices of *Nypa fruticans* frond and petiole are presented in Table 2. The average fibre length of *Nypa fruticans* frond was 1.59 mm, which was higher than that of hardwood and lower than that of softwood. The fibre length of the petiole was 1.06 mm; this was shorter than that of the hardwood and softwood [21]. However, the fibre lengths of both samples are longer than that of cotton stalks (0.6-0.8 mm), kenaf core fibre (0.6 mm) Papyrus (1.0 mm), and maize (0.75mm) [22], but shorter than that of bamboo (2.7 mm), jute (2.5 mm) and sisal (3.0 mm) [23]. Moreover, the fibre length of the frond is comparable with that of the bagasse, reeds and wheat straw [23]. Pulping raw material with short fibre lengths are less suitable for paper making than the long-fibre [24 - 26].

The fibre width of *Nypa fruticans* frond and petiole was very short about 12µm, which was lower than those of wood and other common non-woods fibres (approximately 32.0 – 43.0µm and 18.0 – 30.0µm for softwood and hardwoods, respectively) [27]. The fibre width of *Nypa fruticans* was comparable to that of wheat (13µm) and rice straw (11µm) [23].

The cell wall thickness is one of the significant fibre dimensions that determine the choice of a fibrous raw material for pulp and paper production. The value obtains for *Nypa fruticans* frond and the petiole were 2.96µm and 3.37µm respectively. Lumen diameter was 5.79µm and 4.96µm respectively. The values obtained for fibre length, width, cell wall thickness and lumen width are lower than that of *Bambusa vulgaris* [28]. Lumen size and cell wall thickness affect the rigidity and strength of papers made from fibre. Large fibre with thin walls were found to collapse into ribbons which being flexible could pack closely and contact each other over extensive areas. Therefore, they form non- porous sheets of tightly bonded fibres that have good strength [11]. On the other hand, fibres with thick walls cannot collapse and are less flexible. They form bulkier more open sheets with less bonded contact and lower burst and tensile strength. Tearing strength however depends on other factors in addition to bonding, and sheet of thick- walled fibres may be stronger in tear than one of thin fibres [29].

The physical properties of a paper sheet are closely related to morphological properties of the raw material [30]. Fibre morphological indices determined include: Runkel ratio, slenderness ratio and flexibility ratio. The value of Runkel ratio obtained for *Nypa fruticans* frond and petiole fibres were 1.02

and 1.36, slenderness ratio was 136.0 and 90.56 while flexibility ratio was 49.46 and 43.39 respectively.

It is stated that if slenderness ratio of a fibrous material is lower than 70, it is invaluable for quality pulp and paper production [30, 31]. The slenderness ratio of *Nypa fruticans* frond and petiole was very high as compared to other non-wood fibres [32]. This indicates high rate of tear resistance. However, some authors have a different opinion, because not only strength properties depend on slenderness ratio, but also cell wall thickness [33]. High Runkel ratio fibres (that is fibres with relatively thick walls, such as those in summerwood) are stiffer, less flexible and form bulkier paper of low bonding area than low Runkel ratio fibres, this effect is related to the degree of the fibre collapse during paper drying, a phenomenon affected by the cell-wall thickness and the degree of refining that the fibres undergo prior to papermaking. Casey [11] concluded that fibres with ratio less than or equal to one are very good for paper making. However, the pulps obtained from *Nypa fruticans* frond and petiole will give stiffer, less flexible and bulkier paper since its Runkel ratio is greater than one. Hence Nypa palm pulps may be suitable for producing paper boards.

The higher the value of the flexibility coefficient, the greater the suppleness of the fibres and the well–bonded the sheet formed. Although pulp mechanical strength also depends on other processing variables such as pulping conditions, bleaching and beating, etc.

Chemical Characterization of *Nypa fruticans*

The results of the chemical composition and soluble contents of *Nypa fruticans* are presented in Table 1. These include solubility in cold water, hot water, 1% sodium hydroxide and ethanol-benzene (1:2 %v/v). The Chemical parameters determined were, ash content, cellulose, and acid insoluble lignin (Klason lignin).

The values of the cold water soluble were 8.12% and 22.36% and hot water soluble were 11.17% and 22.61% for the frond and petiole respectively. The value obtained for the frond was within the range for those reported for some non-woods, while that obtained for petiole was higher [34]. This implies that petiole contain more tannins, gums, sugar, colouring matter, and starch, than the frond.

1% Sodium Hydroxide solubility is used to determine the degree of fungus decay that can taken place in a given wood or non- wood sample. The value obtained for the frond and petiole were 32.16% and 6.09% respectively. The value obtained for petiole was very low compared to those obtained for some non-woods raw materials reported elsewhere [34]. However, that of the frond was within the range. This is an indication that *Nypa fruticans* frond will undergo fungus degradation at the higher rate than the petiole. This is due to high pith contents in the frond. Hence it cannot be kept for longer time before pulping.

Ethanol-Benzene Solubility indicates the measure of the waxes, fats, resins, oils, and tannins and certain ether-insoluble components. The value obtained were 2.38% and 2.51% for the frond and petiole respectively. These values are within the range of those reported elsewhere for some non-wood pulping raw materials [34].

The Klason lignin contents (acid insoluble lignin) of *Nypa fruticans* were 19.85% for the frond and 21.15% for the petiole respectively. The lignin contents were within the range of those reported for some non-wood species. However, the value was slightly higher than the value of 18.1 % reported for the *Nypa frticans* frond (golpata frond) [35]. This may be due to the level of maturity of the plant. However, the results obtained here indicated that the lignin contents of *Nypa fruticans* frond and petiole are low. This low lignin content is an indication of easy delignification, and low chemical consumption. However it is expected that petiole will consume more cooking liquor than the frond in order to achieved good delignification.

The cellulose content of *Nypa fruticans* frond and petiole were 48.22% and 37.56% respectively. High cellulose content is desirable for higher pulp yield. *Nypa fruticans* frond gives higher cellulose content. Hence it is expected that frond will give higher pulp yield than the petiole.

The result of the ash contents of *Nypa fruticans* were 4.06 % for the frond and 3.01 % for the petiole. The ash content obtained fell within the range of those obtained for some non-wood species especially wheat straw [34]. Higher ash contents are undesirable for pulping because it gives problems during recovery of the cooking liquor (evaporation, combustion and lime mub reburing) and operational problems in material handling, pulp washing as the trace elements interfere with the bleaching agents example H_2O_2.

Pulping Experiments

The results of the pulp yield, kappa number and residual Klason lignin of *Nypa fruticans* pulps are presented in Table 3. At both soda concentrations and time, *Nypa fruticans* frond gave higher pulp yield. This is due to the high cellulose contents in the sample. It was observed that the higher the concentration of the pulping liquor, the lower the pulp yield; and the lower the concentration, the higher the pulp yield. This is because higher concentration of the cooking liquor, results in high rate of delignification and degradation of carbohydrate which in turn result in the lower pulp yield [36].

Cooking time also influence the pulp yield of *Nypa fruticans.* Longer cooking time results in lower pulp yield while shorter cooking time results in higher pulp yield. This is because high rate of cellulose degradation occurs at longer pulping time.

Cooking variables such as soda concentration and cooking time also influence residual Klason lignin of *Nypa fruticans* pulps. At higher concentration of the soda liquor with longer pulping time, lower residual Klason lignin was obtained for both frond and petiole. This is because high rate of delignification occurs at these conditions.

Conclusion

The results of this work showed that pulp with good yield can be obtained from *Nypa fruticans,* frond and petiole which are presently environmental waste in Nigeria. The results of chemical composition indicate their suitability as a pulping raw material. This is as a result of high cellulose content and lower lignin content of the raw material. Soluble contents are also within the acceptable range for non-wood pulping raw materials. Pulp was produced from the petiole and the depithed frond of *Nypa fruticans* under soda pulping process. Higher pulp yield was obtained at lower concentration of the pulping liquor and shorter pulping time. Also lower residual lignin was obtained at maximun pulping conditions, i.e, concentration (12 % NaOH) and time 60min. The values of fibre dimensions and morphological indices of *Nypa fruticans* frond and petiole lie between that of hardwood and softwood. From these parameters, the Nypa fibres may be stronger than the hardwood fibre. Hence the pulp obtained can be mixed with long fibres from softwood to produce paper with good strength properties, and it can also be use in the preparation of cellulose derivatives.

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Table 1: Physicochemical Characterization of *Nypa fruticans*

	Frond	Petiole
Solubility in cold water (%)	8.12	22.36
Solubility in hot water (%)	11.17	22.61
Solubility in 1% NaOH (%)	32.16	6.09
Solubility in ethanol-benzene (%)	2.38	2.51
Specific gravity	0.62	0.77
Lignin (%)	19.85	21.15
Cellulose (%)	48.22	37.56
Ash (%)	4.06	3.01

Table 2: Fibre Dimensions and Morphological Indices of *Nypa fruticans*

	Frond	Petiole
Fibre length (mm)	1.59	1.06
Fibre diameter(μm)	12	12
Cell wall thickness (μm)	2.96	3.37
Lumen diameter (μm)	5.79	4.96
Slenderness ratio	136.00	90.56
Flexibility ratio	49.46	43.39
Runkel ratio	1.02	1.36

Table 3: Pulp Yield, Kappa Number and Residual Lignin of *Nypa fruticans* Pulps (pulping temp. 120^{o}C)

Samples	Time to temp. (Min.)	Time at temp. (Min.)	Liquor (NaOH) Concentration (%)	Pulp Yield (%)	Kappa Number	Residual Lignin (%)
Frond	22	30	8	53.48	41.0	5.3
	24	60	8	52.82	31.8	5.0
	22	30	12	49.56	37.7	4.9
	24	60	12	48.91	35.2	4.6
Petiole	22	30	8	46.85	35.7	5.6
	24	60	8	45.43	35.6	4.6
	22	30	12	44.02	35.7	4.6
	24	60	12	40.22	35.2	4.6