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Article

Preparation of Pulp and Cellulose Acetate from Nypa Palm Leaves

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Abstract: Soda pulp and sulphate (kraft) pulp were prepared from Nypa palm leaves while cellulose triacetate and diacetate were prepared from the resultant pulps by acetylation with acetic acid anhydride in the presence of sulphuric acid (as a catalyst). For pulp preparation, the leaves were separated into raffia (surface film), lamina and midrib. The soda (sodium hydroxide) pulp yield was 33.22% for raffia, 17.13% for lamina and 34.22% for midrib with an average of 28.21% while kraft (sodium hydroxide and sodium sulphide) pulp yield was 40.24% for raffia, 15.6% for lamina and 47.75% for midrib with an average of 34. 56%, which showed that kraft pulp yield was higher than the soda pulp yield. The average yields based of cellulose diacetate were 51.0% and 57.1% and cellulose triacetate 117.47% and 122.23% for the soda and kraft pulp, respectively. The infrared spectra of the acetate showed marked absorption at 1735 – 1750 cm^{-1} due to the presence of the acetyl group. The Nypa palm leaves which presently are not used for any industrial purpose, but are nuisance to the environment, can be used in making pulp which in turn serves as input for the preparation of cellulosic plastics (cellulose acetates).

Keywords: Nypa palm leaves; raffia; lamina; midribs; pulp; cellulose acetates.

1. Introduction

Progress of civilization from the most primitive stage to the present highly developed technological era is linked with man's dependence on wood and other forest products (Eboatu and Alhaji, 2002). Production of paper, plastic films, household and industrial heating material are

examples of typical applications of wood and forest products. Cellulose obtained from wood is used for production of cellulose derivatives for example, cellulose acetate, cellulose nitrate, carboxymethyl cellulose, regenerated cellulose and other applications (Casey, 1980).

Cellulose being rigid, highly crystalline, and insoluble in common organic solvents is an ideal structural engineering material (Mathur and Mathur, 2001). Cellulose is a polydisperse, linear, syndiotactic polymer. Its basic monomeric unit is D-glucose (anhydroglucose unit), which links successively through a β-configuration between carbon 1 and carbon 4 of adjacent units to form a long chain 1,4 glucans (Mathur and Mathur, 2001). Two glucose molecules react to form a cellobiose which is the basic chemical unit of a cellulose molecule. The pyranose rings are in the 4C1 conformation, which means that $-CH_2OH$ and –OH groups as well as glycosidic bonds are all equatorial with respect to the mean planes of the rings. The hydroxyl groups at both ends of the cellulose chain show different behavior. The C-1 end has reducing properties, while the glucose end group with a free C-4 hydroxyl group is non-reducing (Casey, 1980). The multiple hydroxy groups of cellulose in cellulosic materials (agro-waste) can be partially or wholly modified by reacting with various chemicals to produce a wide range of end products referred to as 'cellulose derivatives'. These derivatives such as cellulose nitrates, acetates, xanthates, ethers, rayon and cellophanes have far reached industrial applications (Obot et al., 2008).

Cellulose acetates (CA) are important esters of cellulose, which are obtained by reaction of cellulose with acetic acid anhydride in the presence of sulphuric acid. The most common form of cellulose acetate fiber has an acetate group on approximately 2–2.5 degree of substitution of every three hydroxyls. This cellulose diacetate is known as secondary acetate, or simply as ''acetate''. The solubility of cellulose acetate depends among other things on the degree of substitution (DS). CA with DS of 2 – 2.5 is soluble in the solvent such as acetone, dioxane and methyl acetate. Higher acetylated types are soluble in dichloromethane (Fischer, 2008). CA can be produce from wood and non-wood materials.

Nypa palm (*Nypa fruticans*) leaves are forest products and renewable agro-waste (Ojebo, 2002). It can be exploited for the preparation of cellulose acetate. In Nigeria, the Nypa palm as a whole has no significant commercial value but has threatened the Nigeria coastal vegetation destroying mangroves and causing reduction in fish growth and catch, poor navigation, ecological degradation and loss of biodiversity (Ojebo, 2002). This invasion is fast spreading westwards along the coast of Nigeria. Research works, are therefore conducted to determine the possible uses of the Nypa palm products in order to use the agro-waste (Nypa leaves) as industrial input to enhance the development of our local economy. Locally, the kernels are only used in making beads, and the leaves for making arrows, brooms, mats and for thatch roof tops. Presently, a large quantity of the leaves and seeds are

not utilized and they constitute nuisance to the environment by blocking estuaries and other coastal water ways. There are moves now to replace these palms with the traditional mangroves if there are no industrial uses of Nypa palm products.

However, chemical studies (Maim, 1962; White and Brown, 1989) have shown that such leaves contain a large quantity of cellulosic fibres which normally when pulped, yield pulp which can be used industrially in paper making and in the production of cellulose plastics such as cellulose acetate. Cellulose acetate finds numerous applications in forming transparent sheets, cigarette filters, textiles, toys, photographic materials and electrical insulators (Amin and Shahjahan, 1999). Therefore, utilizing Nypa palm leaves in pulp and paper production as well as in the production of cellulose plastics will promote economic growth in the locality where the plant grows.

2. Materials and Methods

2.1. Sample Collection and Preparation

The raw materials were the leaves of Nypa palm collected at Oron beach near Oron Museum in Oron Local Government Area of Akwa Ibom State, Nigeria. The leaves were separated into the raffia by peeling with a sharp knife from the upper surface of the young leaves, the midribs (petioles) were separated from the centre and the edge of each leaf and the lamina which consists of the leaves veins and sheet. The samples were cut into chips and the moisture contents were determined before pulping.

2.2. Methods

The methods used in most part of the work were in accordance with those specified by the Technical Association of Pulp and Paper Industries (TAPPI) of the U.S.A, while in few cases the methods were modified or developed depending on the availability of equipment.

2.3. Preparation of Cellulose Acetate

2.3.1. Preparation of Cellulose triacetate

A 35 mL of acetic acid was added to 2.0 g of the bleached pulp contained in a 250 mL beaker and covered with a watch glass. The system was placed in a water bath in a fume cupboard and maintained at 50 - 55 °C for 30 min with frequent stirring.

An acetylating mixture consisting of 10 mL of acetic acid anhydride and 0.4 mL of concentrated sulphuric acid was added to the reaction mixture keeping the temperature below 60 °C. The reaction mixture was then kept in a water-bath for one hour at 50 – 55 °C with occasional stirring until a clear solution was obtained.

The mixture was then divided into two equal parts. The first portion was used in preparing cellulose triacetate by carefully pouring into a large volume of water (500 mL) with stirring. Cellulose triacetate was formed as precipitate. The precipitate was filtered with Buckner funnel, and washed to neutrality and dried in air.

2.3.2. Preparation of Cellulose Diacetate

To the second portion of the mixture, 12.0 mL of acetic acid and 3.5 mL of water were added with vigorous stirring to avoid precipitation, and it was allowed to stand for 1 h at 50 – 55 °C. The mixture was poured into a large volume of water, and precipitate was formed. It was filtered through Buckner funnel, and washed to neutrality and dried in air. The oven dried weight of the acetate per initial weight of the pulp expressed as a percentage gives the acetate yield.

2.4. Physical Characterization of Nypa Palm Leaves.

2.4.1. Characterization of the Cellulose Acetate

(i) Solubility test: Solubility test of the product was conducted in acetone, chloroform, and a mixture of chloroform and methanol (9: 1, v/v).

(ii) Determination of IR absorption spectra of samples: A 0.1 g of each of the samples-cellulose triacetate and cellulose diacetate were weighed and ground into a mull with nujol. The IR spectra of the samples were run and the carboxyl functional group of the product (ester) was determined.

2.4.2. Fibre Dimensions

A 1 g of each of the samples was digested separately in a solution mixture of hydrogen peroxide and acetic acid in a ratio 1: 1, and kept in an oven at 60 °C for 24 h, after which they were removed, disintegrated and washed. The bleached fibres obtained, were mounted on a slide and the length, width, and cell-wall thickness were measured with a microscope fitted with a calibrated eyepiece at X 10 magnification for each of the samples, twenty measurements were taken (TAPPI standard T233 os-82). Runkel ratio was determined using the formula below:

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

2.4.3. Determination of Basic Density Moisture Content of Green Samples

These were determined in accordance with TAPPI standard designated as T258 os-89.

2.5. Chemical Characterization of Nypa Palm Leaves

The chemical characteristics of Nypa palm leaves were determined in accordance with TAPPI standard methods designated as follows: solubility in hot and cold water - T207 cm 99; alkaline solubility - T212 om 02; solubility in ethanol-benzene - T204, cm 97; lignin content - T222 om 98; ash content - T211 os 80.

2.6. Pulping Experiment

The samples raffia, lamina and midrib were cut separately into small chips of about 2 cm by 2 cm, then washed, air-dried and kept for pulping studies.

2.6.1. Preparation of Cooking Liquor

The pulping processes employed in this research were the soda pulping method and sulphide (kraft) pulping method. For the soda process, 18% NaOH was used. For the sulphide process, the cooking chemicals were sodium hydroxide and sodium sulphide. The liquor was prepared by dissolving 37.0 g of NaOH and 7.2 g of Na_2S in a beaker. The sulphidity ratio was kept at 16%. The solution was quantitatively transferred to a 1000 mL volumetric flask and made up to mark with deionised water.

2.6.2. Impregnation and Cooking

To 50.0 g of each of the samples, 200 mL of the freshly prepared liquors were added separately to completely submerge the samples. The mixtures were allowed to stand for 30 min while warming on a hot plate to enhance uniform soaking. Thereafter the mixture was cooked for 2 h at 100 °C at one atmospheric pressure with occasional addition of cooking liquor (50 mL each) to the system for five times. The mixture was filtered off, and mildly beaten in a mortar for complete defiberization, and then washed with water.

2.6.3. Bleaching Process

The bleaching solution was the commercial parazole bleaching solution branded "Jik" consisting 3.5% w/v sodium hypochlorite. A 500 mL of the parazole was added to each of the digested samples in 500 mL beaker, boiled for one hour, and removed from the source of heat and allowed to bleach for 24 h. The resultant mixture was beaten, and washed till the filtrate became neutral to litmus paper.

Another bleaching was done with 100 mL of parazole and 50 mL of distilled water for one hour, until the sample became properly bleached. The final mixture was washed to completely remove

the bleaching agent. The samples were dried at 80 ± 5 °C in the oven for 2 h. A dry cellulose pulp was obtained for each of the samples.

Pulp yield and Moisture content of each pulp from midrib, lamina and raffia were determined gravimetrically.

3. Results and Discussion

3.1. Physical Characteristics of Nypa Palm Leaves.

Physical characteristics of Nypa palm leaves are shown in Table 1.

Table 1. Physical characteristics of Nypa palm leaves

Physical characteristics	Sample			Average
	Raffia	Lamina	Midrib	
Basic density (g/cm^3)	-	0.165 ± 0.005	0.293 ± 0.008	0.229 ± 0.009
Fibre length (mm)	1.20 ± 0.07	1.30 ± 0.07	1.30 ± 0.01	1.27 ± 0.10
Fibre width (mm)	0.011 ± 0.009	0.012 ± 0.0007	0.016 ± 0.0005	0.013 ± 0.0004
Fibre cell-wall thickness (mm)	0.0008 ± 0.0004	0.0007 ± 0.0004	0.0009 ± 0.0001	0.0008 ± 0.0002
Runkel ratio	0.17	0.13	0.13	0.14
Moisture content (%)	81.25 ± 0.25	84.5 ± 0.25	84.73 ± 0.16	83.49 ± 0.47

Note: Each value represents the mean ± standard error for triplicate determination.

3.1.1. Basic Density

The basic density is defined as the weight of oven-dried sample per green volume. As indicated in Table 1, the midrib has a higher basic density of 0.293 ± 0.008 g/cm^3 while the lamina has a basic density of 0.165 ± 0.00 g/cm^3 and an average of 0.229 ± 0.009 g/cm^3 corresponding to 15% of their volume occupied by wood substance. This value is comparable to that of bamboo which is 0.4 g/cm^3 (Rydholm, 1965). Akpabio and Enoh (1999) reported an average of 0.34 g/cm^3 for the stem and root of *Pandanus candelabrum* plant. The density of wood substance is about 1.53 g/cm^3 and shows variation with age, species, type of growth or chemical composition and these variations are frequent both within a stand and within one single trunk.

Commercial pulp woods have densities in the range 0.3 - 0.6 g/cm^3 that is 20 - 40% of their volume occupied by wood substance (Casey, 1980; Rydholm, 1965). Apart from the density of the actual wood substance which is of industrial interest, determination of basic

density is important as the cost of transportation per unit volume of the raw material depends on it.

3.1.2. Fibre Dimensions

The result of the fibre dimensions measured with a microscope fitted with a calibrated eyepiece at X 10 magnification showed that the midribs of *Nypa fruticans* leaves have an average fibre length of 1.30 ± 0.01 mm, lamina 1.30 ± 0.07 mm and raffia 1.20 ±.07mm giving an average fibre length 1.27 ± 0.10 mm. The width measurements were given as 0.011 ± 0.0007 mm, 0.012 ± 0.0007 mm and 0.016 ± 0.0005 mm for raffia, lamina and midribs, respectively. These results as shown in Table 1 are based on the average of twenty readings from each of the stock. With the fibre length of 1.27 ±0.10 mm, the fibres are termed short fibres. This value is comparable to the fibre length of some commercially non-wood plants such as esparto 1.1 mm, red gum 1.6 mm, rice straw 1.5 mm and cornstalks 1.5 mm (Casey, 1980). Bamboo fibres are particularly long with an average fibre length of 2.7 mm. Some commercial pulpwood woods also show similar fibre lengths, such as *Swietenia macrophylla* (1.042 mm), *Octo tea rodiaei* (1.04 mm) and *Diospyros* sp (Ebony) (1.05 mm) (Rydholm, 1965).

The result of the cell-wall thickness gave 0.0008 ± 0.0004 mm, 0.0007 ± 0.0002 mm and 0.0009 ± 0.0001 mm for raffia, lamina and midrib of *Nypa fruticans* leaves, respectively. The average cell-wall thickness and width measurements were gotten as 0.0008 ± 0.0012 mm and 0.013 ± 0.0004 mm, respectively, with an average Runkel ratio of 0.143 ± 0.013 as shown in Table 1. These values are comparable to those of some commercial non-woody pulps like rice straw and esparto whose cell-wall thickness are 0.009 mm for the two plants and width 0.010 mm and 0.014 mm, respectively. For commercial pulp like *Eucalyptus saligna* (Sydney blue gum) average cell-wall thickness of 0.0014 mm and width of 0.013 mm have been reported (Rydholm, 1965).

The value of the fibre length obtained is comparable with those of the bagasse, reeds and wheat straw reported by Atchison (1993). Fibre length, width, cell-wall thickness and the cell-wall fraction (Runkel ratio) aids in determination of the flexibility or stiffness of the fibres and hence their bonding characteristic as well as other paper properties. Generally, short fibres do not give very strong paper but the slenderness of the Nypa palm leaves fibres with relatively low cell-wall thickness would make then a preferred raw material for fine papers where formation opacity and smoothness are essential properties.

3.1.3. Moisture Content

The moisture content has an important bearing on the deterioration of samples of wood during

storage (Akpabio and Enoh, 1999). Besides, industrially, moisture content of pulping materials is important. Best pulping control can be achieved only if the accurate moisture content of wood/material is known because moisture content helps in determining accurate liquor – to – wood ratios which are usually constant in different pulping system (Casey, 1980). As indicated in Table 1, the moisture content of the midrib, lamina and raffia of Nypa palm leaves were 84.73 ± 0.16%, 84.50 ± 0.000% and 81.25 ± 0.25% respectively, giving an average of 83.49 ± 0.41% which is comparable to the moisture content (80%) of the leaves of *Pandanus canderabrum* (Akpabio and Enoh, 1999).

3.2. Chemical Characteristics of Nypa palm Leaves

Chemical characteristics of Nypa palm leaves are shown in Table 2.

Table 2. Chemical characteristics of Nypa palm leaves

Chemical Characteristics	**Sample**		
	Raffia (%)	**Lamina (%)**	**Midrib (%)**
Ash content	1.20 ± 0.00	1.53 ± 0.025	1.88 ± 0.013
Ethanol-benzene	2.08 ± 0.06	2.50 ± 0.10	3.89 ± 0.010
Acid – insoluble lignin	10.73 ± 0.03	18.50 ± 0.00	19.95 ± 0.05
1% NaOH solution	10.23 ± 0.03	29.00 ± 0.00	20.00 ± 0.00
18% NaOH solution	19.38 ± 0.13	35.83 ± 0.03	28.83 ± 0.03
Cold water soluble	6.35 ± 0.64	13.70 ± 0.00	3.80 ± 0.05
Hot water soluble	11.10 ± 0.00	15.08 ± 0.02	12.21 ± 0.14

3.2.1. Ash Content

The ash content of wood or non-wood plant is an indication of the amount of inorganic substances present in the plant. The inorganic substances have physiological functions in the plant and contain mainly silica, alkaline, and alkaline earth oxides and carbonates (Rydholm, 1965). Table 2 indicates that the ash content is highest in the midrib with 1.88 ± 0.13%, followed by that of lamina with 1.53 ± 0.025% and raffia as 1.2 ± 0.00 %. These give an average ash content of 1.53 ± 0.03%. This value is comparable to the ash content of non-wood plants such as bamboo with 1.2%, wheat straw 1.8% and cornstalk 1.2% (Casey, 1980).

3.2.2. Organic Soluble (ethanol-benzene)

Table 2 also presents the value of ethanol-benzene (1:2 v/v) soluble as 2.08 ± 0.06% for raffia, 2.50 ± 0.10% for lamina and 3.89 ± 0.010% for midrib, giving an average of 2.82 ± 0.15%. This value is comparable to those of rice straw which is 2.19%, kenaf 2.2%, bagasse 3.2% and bamboo 3.1% (Casey, 1980). Knowledge of the values of these extracts allows for control of harmful deposits on the machinery during industrial or large scale pulping.

3.2.3. Acid - Insoluble Lignin

This is the insoluble lignin obtained after the dissolution of the carbohydrates in the samples in 72% H_2SO_4. The carbohydrates dissolve and leave a dark brown condensed material (acid - insoluble lignin). The average content for the samples was 16.39 ± 0.06% while the lignin contents of 10.73 ± 0.025%, 18.50 ± 0.00% and 19.95 ± 0.05% were obtained for raffia, lamina and midrib, respectively, as shown in Table 2. The high value of the midrib is due to the fact that the midrib structure is more condensed than those of the lamina and raffia, hence, more lignin is used in binding the cellulosic fibres. This value could be compared to those of some non-wood plants like bamboo whose lignin content is 23.0%, rye 17.8%, oaths 17.5% and barley 16.6% (Rydholm, 1965).

3.2.4. Alkali Soluble

These are mainly lower molecular mass carbohydrates consisting of oligomers of hemicelluloses and degraded cellulose in the samples (Casey, 1980). For 1% NaOH soluble, an average value of 17.74 ± 0.03% was obtained for the samples. The individual values as shown in Table 2 were 10.23 ± 0.03, 29.0 ± 0.00% and 20.00 ± 0.00% for raffia, lamina and midrib, respectively. At a higher concentration of the alkali (18% NaOH), higher values were obtained. The average value obtained was 28.01 ± 0.13%, the value obtained for raffia was 19.38 ± 0.13%, 35.83 ± 0.03% was obtained for lamina while 28.83 ± 0.03% was obtained for the midribs. These values are shown in Table 2. The order of soluble in the two concentration of NaOH solution is in the following increasing lamina > midrib > raffia. Normally in wood 18% NaOH solution is used for extraction of hemicelluloses therefore the soluble in these substances should be mainly hemicelluloses, however since lamina had the highest soluble in both solutions, the NaOH solution must have dissolved chlorophyll in addition to the hemicelluloses in the lamina as this green coloring matter is present in green leaves.

3.2.5. Solubility in Cold and Hot Water

The cold water soluble is mostly polar molecules consisting of extraneous components

such as tannins, gums, sugars and coloring matter present in the sample (Pinder, 1960). The cold water soluble has average value of 7.95 ± 0.4%. The value for raffia is 5.35 ± 0.64%, 13.70 ± 0.00% for lamina and 3.80 ± 0.05% for midribs.

Hot water removes starches in addition to the extraneous components that could be removed by cold water (Sadov *et al*., 1978). The Nypa palm leaves show an average value of 12.82 ± 0.09% for hot water soluble. The values obtained as shown in Table 2 are 11.10 ± 0.00%, 15.08 ± 0.08% and 12.28 ± 0.03% for raffia, lamina and midribs, respectively. These values are comparable to those of some non-wood plants reported by Hurter (1988). Wood plants generally have a lower percentage of hot water soluble in the range of 1.5 – 7.5% (Sadov *et al*., 1978). This high hot water soluble content of *Nypa fruticans* like the other non-woody plants indicates a higher degree of accessibility of cell-wall components to pulping liquors than those of woods.

3.3. Pulping and Preparation of Cellulose Acetate

The structures of cellulose acetate are shown in Figure 1. The processes used for the pulping of Nypa palm leaves were soda process and the kraft process, and the results are shown in Figures 2 & 3. Cooking of the samples with steel vessel with their appropriate liquor led to the production of the pulp. For the soda process, cooking time was 2 h using 18% NaOH as the cooking liquor. In the kraft process, the same cooking time was also employed. With the sulphidity kept at 16%, there was the characteristic odor of hydrogen sulphide while the cooking continued because of the dissociation of NaHS into Na^+ and HS^- ions. The HS^- ion in the presence of water gives the following corresponding reaction of hydrolysis:

$$HS^- + H_2O \rightleftharpoons H_2S + OH^-.$$

Generally, it should be noted that the hydroxide is capable of opening the alkyl aryl ether bonds of lignin, which withstand most other pulping liquors and the lignin degradation products thus formed are soluble in alkaline medium while the sulphide also accelerates lignin dissolution, it also facilitates cleavage of the alkyl aryl ether bonds of lignin (Casey, 1980).

3.3.1. Moisture Content of Pulp

Determination of moisture content of pulp is important as pulps with high moisture content are easily degraded. The moisture content of the Nypa palm pulp from soda process are 15.15 ± 0.1%, 15.05 ± 0 .05% and 15.00 ± 0.00% for raffia, lamina and midrib, respectively, giving an average of 15.07 ± 0.11%. For the kraft process, an average value of 12.24 ± 0.06% was obtained with the midrib pulp 12.30 ± 0.05, lamina 12.23 ± 0.03% and 12.20 ± 0.00% for raffia. These values are shown in Table 3. According to Lauren (1996), air dry pulp contains

about 10 - 15% moisture, hence the values for moisture content of Nypa palm pulp are within the expected range.

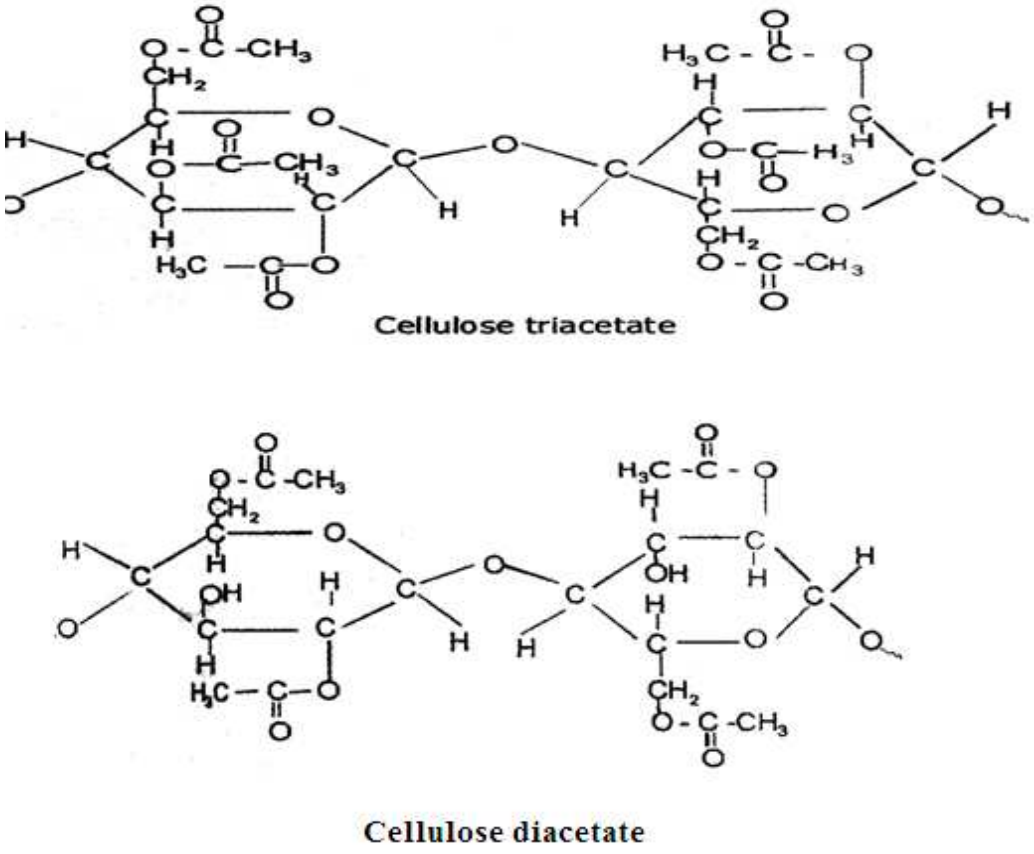

Figure 1. Structures of cellulose acetate (Smith and Block, 1982).

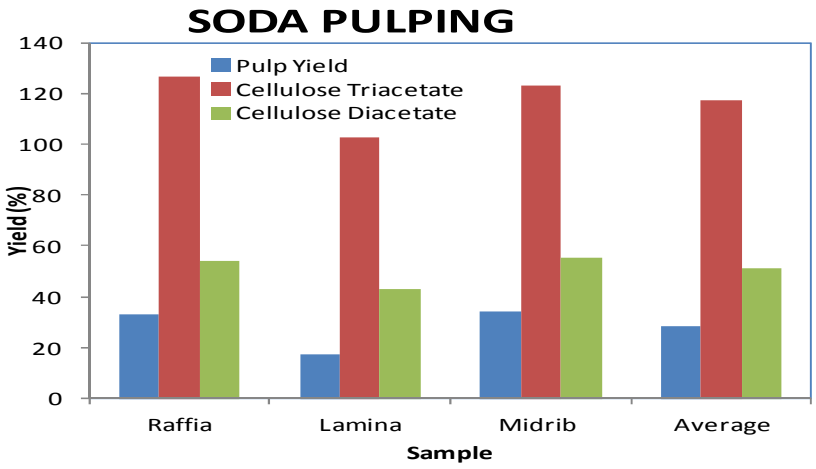

Figure 2. Pulp yield and acetate yield of each sample under soda pulping process

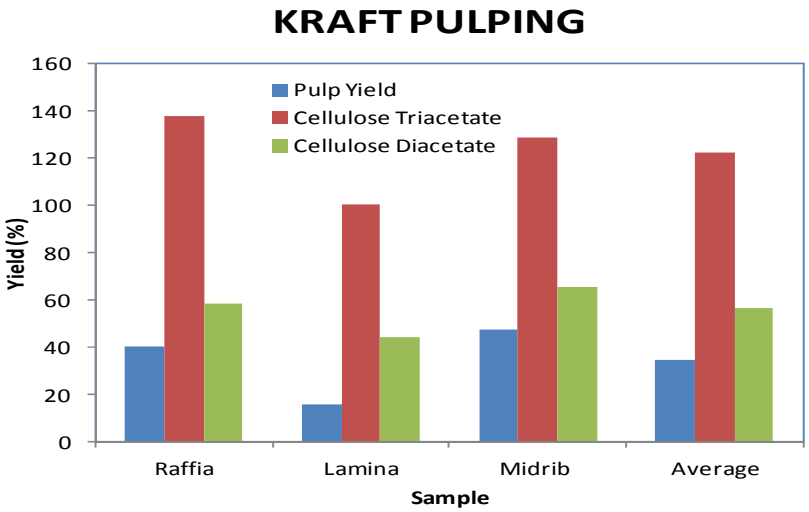

Figure 3. Pulp yield and acetate yield of each sample under kraft pulping process.

Table 3. Moisture content and pulp yield, triacetate and diacetate yield

Sample	Soda Process				Kraft Process			
	Moisture Content %	Pulp Yield %	Cellulose Triacetate %	Cellulose Diacetate %	Moisture Content %	Pulp Yield %	Cellulose Triacetate %	Cellulose Diacetate %
Raffia	15.15 ± 0.1	33.22	126.80	54.30	12.20 ± 0.00	40.24	137.70	58.70
Lamina	10.50 ± 0.05	17.13	102.60	43.20	12.23 ± 0.03	15.69	100.50	44.50
Midrib	15.00 ± 0.00	34.28	123.00	55.50	12.30 ± 0.05	47.75	128.80	65.80
Average	15.07 ± 0.11	28.21	117.47	51.00	12.24 ± 0.06	34.56	122.33	56.33

3.3.2. Pulp Yield

At the end of the cooking, yields of 33.22%, 17.13% and 34.28% were obtained for the raffia, lamina and midrib respectively for the soda process. Also, 40.24%, 15.69% and 47.75% were obtained for the raffia, lamina and midrib respectively for the kraft process. Table 3 indicates that the lamina has the lowest pulp yield in the two methods while the midrib has the highest pulp yield. This implies that the midribs are made-up of more cellulose fibres than the raffia and lamina. The average pulp yield of the Nypa palm leaves for the two cooking process were gotten as 28.21% for soda process and 34.56% for kraft process. The kraft process being an improvement of the soda process gave a better yield. This pulp yield is comparable to the pulp

yield of jute stick of Bangladesh origin, a non-wood plant whose values range between 40 – 43.50% (Amin and Shahjahan, 1999).

3.3.3. Yield of Cellulose Triacetate and Diacetate

The yields of cellulose acetate samples were estimated on the air-dry weight basis for the pulp. The yield ranged from 102.60 - 125. 80% for triacetate and 43.20 - 55.50 % for diacetate, based on the air-dry weight of the pulp made from soda process. The average yields of cellulose triacetate and diacetate are 117.47% and 57.00%, respectively. For the kraft process, the yield ranged from 100.50 - 137.70% for triacetate and 44.20 - 15.10% for diacetate with the average of 122.33% and 56.33% for cellulose triacetate and diacetate, respectively. The results were compared with the percentage cellulose acetate obtained for jute sticks of different cultivars - a non-wood plant, whose values were between 112.80 - 134.11% for cellulose triacetate and 43.50 - 63.74% for cellulose diacetate (Krishnan and Sarkar, 1984). These values are very high compared to the values obtained for other non-woods reported by Obot *et al.* (2007). The raffia and midrib therefore appears to be more significant in the production of pulp and cellulose acetate based on the results in Table 3 because they gave a higher pulp yield than the lamina.

3.3.4. Characterisation of the Cellulose Acetate

(i) Solubility test: The solubility test for both the triacetate and diacetate as shown in Table 4 indicates that the triacetate was soluble in chloroform and mixture of chloroform and methanol (9:1, v/v) but insoluble in acetone and vice versa for the diacetate. Cellulose diacetate is the one in which chemical modification converts about 80% of the hydroxyl (-OH) groups on the cellulose to acetate ($-OCOCH_3$) groups and in cellulose triacetate about 92% of the hydroxyl groups are converted to acetate (Smith and Block, 1982). Cellulose diacetate dissolves in acetone which is completely miscible with water, and cellulose triacetate dissolves in chloroform which is partially miscible in water but miscible in ethanol (Finar, 1981).

Table 4. Solubility test of cellulose di- and tri- acetate

Solvent	Cellulose triacetate	Cellulose diacetate
Acetone	Insoluble	Soluble
Chloroform	Soluble	Insoluble
Chloroform and methanol (9:1, v/v)	Soluble	Insoluble

(ii) Infrared (IR) spectroscopic analysis: The IR spectra of the samples of cellulose triacetate and cellulose diacetate showed a marked absorption at 1735 – 1750 cm^{-1} indicating the presence of carboxylate group (-O-C-) of the acetate present in the samples (Table 5). This absorption band was however not present in that of the cellulose, implying that the absorbance at 1735-1750 cm^{-1} is due to the presence of the acetyl group. In the spectra of the samples, the carboxylate absorption band of the cellulose triacetate was more prominent than that of the cellulose diacetate. A measurement of the length of absorption of acetyl functional group in both samples gives the length of 6.50 cm and 4.30 cm in cellulose triacetate and cellulose diacetate, respectively. This gives an approximate ratio of 3:2 cellulose triacetate to cellulose diacetate. It implies that in any anhydro-glucose repeating unit where acetylation takes place, three hydroxyl groups have been substituted with three acetyl groups in the triacetate whereas in the diacetate only two hydroxyl groups have been substituted by acetyl groups.

Table 5. Assignments of the FTIR spectral peaks cellulose, cellulose di- and triacetate

Sample	Wave Length (cm^{-1})	vibration	Functional group
Cellulose	3500	O-H stretch	Hydroxyl
	3450	O-H stretch	Hydroxyl
	2900	C-H stretch	Alkane
	1600	C=C	Alkene
	1200	C-H	Alcoholic, ester
	785	C-H	Week bending vibration
Cellulose Diacetate	3450	O-H	Hydroxyl
	3300	O-H stretch (H-bonded)	Hydroxyl
	2920	C-H stretch	Alkane
	2850	C-H stretch	Alkane
	1750	C=O	Carbonyl (Ester)
	1730	C=O	Carbonyl (Ester)
	1470	C-H bend	Alkane
	1450	C-H bending	Alkane
	1375	C-H bending	Alkane
	1070	C-O stretch	Alcohol and ester
	3400	O-H stretch (H-bonded)	Secondary OH
Cellulose Triacetate	3400	Free O-H	Primary O-H
	2920	C-H stretch	Alkane
	2850	C-C strre	Alkane
	1730	C=O stretch	Carbonyl (ester)
	1470	C-H bending	Alkane

1230	C-O stretch	Carbonyl or hydroxyl

4. Conclusion

In the course of this work, preparation of pulp from *Nypa fruticans* (Nypa palm) leaves has been achieved. Presently, these leaves are waste materials blocking river estuaries and other water ways because they are not easily biodegraded. However, this study has shown that they can be used as industrial raw materials for the commercial production of pulp, and cellulose plastics (cellulose acetates). Since kraft pulping process produced high yield pulp, kraft pulp mills can be established near the coastal area where the plants are abundant. Therefore, the present plan for destruction of these Nypa palms because of lack of the application of its products should be discouraged, and Nypa palm plantations opened up near the coastal zone for easy access to the leaves and other products for industrial application.

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