Supported by tetfund

PRELIMINARY STUDIES ON SELECTED CHEMICAL PROPERTIES, PULPING AND BLEACHING RESPONSE OF *Sterculia tragacantha* (LINDL) WOOD

M. A. Kolapo[1]*, A. O. Oluwadare[2] and S. R. Kolapo[2]
[1]Department of Forestry, Wildlife & Fisheries, Olabisi Onabanjo University, Ogun State, Nigeria
[2]Department of Forest Production & Products, University of Ibadan, Oyo State, Nigeria
*Corresponding author: abosede.kolapo@oouagoiwoye.edu.ng

Received: February 10, 2020 **Accepted:** April 03, 2020

Abstract: Production of quality paper entails both long and short fibre pulp wood. There is shortage of industrial hardwood with long fibres for pulp and paper production in Nigeria. A preliminary investigation into the pulping potentials of *Sterculia tragacantha* was carried out to determine its suitability for papermaking. A single tree of *Sterculia tragacantha* was selected (due to its rarity) from which billets were collected behind the Central Mosque, along the Faculty of Agriculture and Forestry in the University of Ibadan. These billets were converted to chips for easy chemical impregnation during pulping. The milled samples were collected for the determination of solubility, extractives and lignin contents using standard procedure. Pulping trials were then carried out by Kraft process at 100 and 110°C using chips from the top, middle and base of the tree. Pulp produced at 110°C was bleached using multistage hypochlorite sequence. Completely randomized design was used to investigate the influence of height along the tree axis on the chemical composition and pulp yield. The data obtained were subjected to ANOVA at $\alpha = 0.05$. Position along the tree axis significantly affected the ethanol-benzene extractive and lignin contents of *Sterculia tragacantha* wood while solubility and alpha cellulose contents showed no significant effect at $\alpha = 0.05$. The *Sterculia tragacantha* pulp was hard to bleach and required high chemical consumption to achieve remarkable brightness, though hypochlorite performed better than peroxide. The results of this research work showed that *S. tragacantha* may be suitable for pulp and papermaking. It is therefore recommended that further studies on paper making and strength properties be carried out that can encourage mass propagation of the species.

Keywords: Chemical composition, pulping, *Sterculia tragacantha*

Introduction

Pulpwood is used to describe all timber resources that are used to make wood pulp (Manthy *et al.*, 1973). Many softwood species such as spruce, pine, hemlock, fir and larch as well as hardwood species such as birch, eucalyptus, gmelina and Sterculia, to mention a few, have been used to produce wood pulp. All lignocellulosic materials used to make pulp have three main components (apart from water) which include cellulose, lignin and hemicellulose. The lignin is a three-dimensional polymer that binds the cellulose fibers together. Hence, pulping is necessary to break down the structure of the fibre source (chips, stems and other plant parts), into the constituent fibres.

Lignin and cellulose content of raw plant materials are major determinants of paper strength as the mechanical and tensile strengths of pulps are directly proportional to the cellulose content (Cave, 1966). The amount of lignin in a lignocellulose material affects the pulping time and chemical charge (Duncan, 1955). Meanwhile, the presence of lignin is undesirable as its removal leads to high energy and chemical consumption. Cellulose, a white fibrous and abundant constituent, has high affinity for water yet is insoluble in water and neutral organic solvents making it suitable for paper making (Dutt and Tyagi, 2011).

Wood fibre sources consist of 45% sawmill residue, 21% logs and chips, and 34% recycled paper (Bank of Canada, 2008; Sixta, 2006). About 93% of the global market pulp is made from chemical pulp (Market Pulp Association, 2007). Chemical pulp involves a combination of wood chips and cooking chemicals in digesters with heat application to break down cellulose binding lignin without any serious degradation of the cellulose fibres. When strength is needed in a pulp, then chemical pulping is the preferred process. Of all the chemical pulping process, Kraft process is the dominant method. Kraft pulps are known for high strength as well as excellent technological properties. The major disadvantages of complicated chemical recovery and bleachability have now been largely eliminated (El-Osta and Megahed, 1992). In order to remove or reduce color and residual lignin in the pulp, bleaching is carried out usually with lignin-attacking chemicals to increase the brightness of the pulp. Water is used to wash pulp during the bleaching but modern mills use oxygen in the first stage of bleaching (Bajpai, 2005a) as a way of avoiding chlorine chemicals.

In 2006, the global wood pulp production was about 160 million tonnes (Metso Corporation, 2006), it is not difficult to project the pulp demand by the year 2030 considering population and educational demands of the incoming generations. In the previous year, 63 million tons of market pulp (not made into paper in the same facility) was sold, with Canada being the largest source at 21 percent of the total, followed by the United States at 16 percent. Due to environmental concerns, non-wood pulps are being revisited in order to reduce pressure on the forests. Cotton, linen, hemp, jute among others are modern sources of fibres. Quality papers for certificates, passports and currency are made from 100% cotton and linen pulps (Bank of Canada 2008; Bureau of Engraving and Printing, 2017). As important and accessible as non-woods are for alternative pulp, processing them requires high energy needs (Stenius, 2000). Moreover, wood remains a renewable resource, producing about 90% of pulps from plantations or reforested areas (Martin, 2004) while non-wood fibre sources account for just 5-10% of global pulp production as a result of seasonal availability, chemical recovery, pulp brightness among other factors (Market Pulp Association, 2007; Manfred, 1994). Hence, it is important to focus research on lesser used hardwood species; such as *Sterculia tragacantha* used in this study.

Sterculia tragacantha tree is usually between 3 and 24 m tall; has a cylindrical bole and sometimes with fluted buttresses. Its bark is rough, grey or greyish brown, often deeply fissured with pale pink or pale orange slash, quickly becoming deep orange and exudate is clear. *Sterculia tragacantha* Lindl has a worldwide distribution but can be found abundantly intropical West Africa, Tanzania, Katanga, and Angola. It is widespread from Guinea to Cameroon, eastward to Sudan and Rwanda and south to the Democratic Republic of the Congo, Angola and Zambia. This research work was aimed at studying the pulping potentials of the fibres of *Sterculia tragacantha* Lindl.

Materials and Methods

Sample collection

The materials used for this study were collected from a natural stand (since there are no existing plantations of *Sterculia tragacantha*) in the University of Ibadan, Ibadan, Oyo State. It is located in Ibadan North Local Government Area of Oyo State. It is about 6 kilometers to the North of the city of Ibadan Metropolis at Longitude 3°54′ East and Latitude 7°26′ North and at a mean altitude of 27 m above sea level. The annual rainfall is approximately 1600 mm, most of which falls within the period of April-October giving a predominantly dry season from November to March. The land area of the University of Ibadan is over 1,032 hectares and the major road networks are lined with tree species.

Samples of the species were collected from sawn log at the base (1.9 m), middle (3.1 m) and the top (4.3 m). Milled samples were collected at each of these positions, labelled and kept for chemical composition tests. The remaining wood from each height were made into chips of 5 cm long for pulping experiment. The chemical constituents and solubility tests evaluated in triplicates are; extractive contents, lignin, cold water solubility and 1% sodium hydroxide content.

Determination of ethanol-benzene extractive content

The Ethanol-benzene extraction of the milled samples was determined using ASTM designation D1107-56. In this method, 5 g of milled sample of known moisture content was extracted in soxhlet apparatus with 200 cm^3 of ethanol-benzene for 8 hours in the ratio 1:2. After this, the sample was filtered by suction and extracted with 95% ethanol for 4 hours. The extracted sample was later washed free of the solvent with hot distilled water and later air-dried for three days and weighed. The extractive content was then calculated as follows:

$$\%\ Extractive = \frac{W_u - W_e}{W_u}\ x\ \frac{100}{1} \text{ .... (eqn. 1)}$$

Where: Wu = Weight of un-extracted sawdust (g); We = Weight of extracted sawdust (g)

Determination of lignin content

The lignin content was determined using ASTM designation D1106-56. In this method, 1 g oven dried weight of extractive free sawdust was digested with 15 cm^3 of 72% cold sulphuric acid for 2 h at room temperature. Thereafter, 475 cm^3 of distilled water was added. The content was then allowed to boil for 4 h with constant volume by addition of hot distilled water. The insoluble lignin formed was allowed to settle overnight, filtered and washed with hot distilled water until it became neutral to litmus. The sample was then oven dried at 85°C to constant weight. The percentage insoluble lignin was calculated as:

$$\%\ Lignin = \frac{WL}{Wo} x\ 100/1 \text{..................... (eqn. 2)}$$

Where: W_L= Weight of lignin (g); W_o= Oven dry weight of extractive free milled sample (g)

1% Sodium hydroxide solubility test

The solubility of the milled sample in hot dilute alkali solution was determined using ASTM designation D1109-56 in which 2 g of air dried moisture free milled sample was placed in 200 cm^3 beaker followed by the addition of 100 cm^3 1% NaOH. The beaker was then covered and placed in boiling water bath for 1 h. The content was stirred at 10, 15 and 25 min of the extraction period. After this, the content was filtered by suction on a tarred crucible and washed with 100 ml hot distilled water, 50 ml of 10% acetic acid and thoroughly with hot water in-turn. The crucible and the content were then dried in an oven at 100±2°C to constant weight. The result was then reported thus:

$$\%\ NaOH\ solubility = \frac{w_1 - w_2}{w_1}\ x\ \frac{100}{1} \text{ ...... (eqn. 3)}$$

Where: $w1$ = Weight of moisture free sample (g); $w2$ = Weight of dried sample after 1% NaOH extraction (g)

Cold water solubility test

Cold water solubility test is a measure of the sugar, gums, tannins and colouring matter in the milled sample of *Sterculia tragacantha*. The test was carried out based on ASTM designation D1110-56. One gram (1 g) of milled sample of known moisture content was placed in a 200 ml beaker and covered with 150 cm^3 of distilled water. The mixture was digested at a temperature of 27±2°C for 48 h with frequent stirring. The sample was then filtered by suction, washed with cold distilled water and placed on a tarred crucible of known weight. The crucible was dried with the sample in an oven at 100±2°C to constant weight. The result was reported as a percentage of matter soluble in cold water on the moisture free basis and calculated as follows:

$$\%\ Cold\ water\ solubility = \frac{w_1 - w_2}{w_1}\ x\ \frac{100}{1} \text{ ...... (eqn. 3)}$$

Where: $W1$ = Weight of moisture free milled sample (g); $W2$ = Weight of dried sample after extraction with cold water (g)

Pulping experiment

The Kraft process was the pulping method used for this research work. Time, temperature and concentration of the cooking liquor are the variables that were considered in comparing the yield and bleachability of the pulps obtained from each labelled sample.

Preparation of cooking liquor

The cooking liquor was prepared as follows:

20 g of Sodium hydroxide pellets was dissolved in 10 litres plastic container with 500 ml distilled water. 21 and 18 ml of this solution were poured each into a 500 ml standard flask and diluted with 100 ml of distilled water to make up the 21 and 18% as effective alkali of the stock solution needed. Also, sodium sulphide was dissolved using 500 ml distilled water in another 10 L plastic container. 25 ml of the solution was measured into a 500 ml standard flask and diluted with 100 ml distilled water to get the required 25% sulphidity. The Kraft cooking liquor was then prepared by mixing three parts by volume of sodium hydroxide with one part by volume of sodium sulphide. This gives a (3:1v/v) of white Kraft solution.

Pulping procedures

150 g composite chips from the base (heartwood and sapwood), middle and top were pulped in a 0.5 litre electrically heated auto-clave digester. The time, temperature and concentrations of the cooking liquor were varied in order to find the optimum pulping conditions. In order to have enough pulp for further studies, the combination of each cooking condition were replicated twice. A summary of the pulping variables used for the pulping method is in Table 1.

Table 1: Summary of the pulping variables used for the study

Cooking variables	Cooking conditions	
Number of cooks	2	2
NaOH Concentration (%)	21	18
Na_2S Concentration (%)	25	25
NaOH to Na_2S ratio	3:1	3:1
Liquor to chip ratio	3:1	3:1
Cooking temperature (°C)	100	110
Cooking time (minutes)	360	300

Statistical analysis

The data collected on 1% sodium hydroxide, cold water solubility, ethanol-benzene extractive and lignin contents were analysed using analysis of variance.

$$Y_{ij} = \mu + T_i + e_{ij}$$

Where: μ = Overall mean; T_i = effect of ith treatment; e_{ij}= random error term

Results and Discussion

Ethanol-benzene extractives (%)

The summary of the pulping variables used for the study is shown in Table 1. The average extractive content of *S. tragacantha* used for this study was 18.49% (Table 2). The trend showed an increase from the bark to the pith and a decrease from the base to the top (29.16% -14.66%) (Table 2) corroborating the submission that extractive content increases with maturity in trees as well as with position from sapwood to heartwood (Oluwadare, 1998; Sotannde, 2014; Rowell *et al*., 2000). The result presented in Table 3 showed that sampling heights had significant effect on the Ethanol-benzene extractive content of *Sterculia tragacantha*. This value is still closer to the 17 and 25% opined by Oluwadare (1998) for hardwoods and softwoods, respectively. Studies have shown that extractive content cause pitch deposits in pulp and paper production often leading to higher consumption of cooking chemicals, lower yields as well as increased defects in the end products (Marques *et al.*, 2010b).

Table 2: Effect of height on the percentage soluble extracts of *Sterculia tragacantha* wood

Sources	Ethanol-Benzene	1% NaOH	Cold Water	Lignin
Position				
Base Heartwood				
Minimum	32.60	22.93	3.25	19.11
Maximum	25.71	33.35	13.28	24.56
Mean	29.16_a	28.14_b	8.27_b	26.84_a
Base Sapwood				
Minimum	9.20	31.97	17.67	17.54
Maximum	12.12	39.95	25.08	19.62
Mean	10.66_b	35.66_a	21.38_a	18.58_b
Middle				
Minimum	20.42	33.63	5.36	18.73
Maximum	21.38	64.45	18.66	26.88
Mean	20.90_a	49.04_a	12.01_b	22.81_a
Top				
Minimum	12.67	34.03	29.63	11.92
Maximum	16.64	63.89	34.51	12.63
Mean	14.66_b	48.96_a	32.07_a	12.28_b

*Means of 3 replicate samples; Values with the same alphabet in each column are not significantly different at α=0.05 using LSD test

Lignin content (%)

The average lignin content obtained for *S. tragacantha* in this study was 19.27% (Table 2). The top of *S. tragacantha* tree used for this study had the lowest lignin content of 12.28% indicatingan increase from the top 12.28% to the base 26.84% and from the sapwood 18.58% to the heartwood 26.84%. There are significant differences in the lignin content for the various heights of the tree as simplified by Table 3. Meanwhile, the average lignin content of *S. tragacantha* was lower than 25-32% for softwoods but within range of 17-26% reported for hardwoods (Eroglu, 1998). This implied that mild pulping conditions, (higher temperature and chemical charges) is all that was needed to delignify the species to obtain pulp.

Sodium hydroxide (1%) solubility

The average sodium hydroxide soluble extract of *S. tragacantha* was 43.3% (Table 2). Meanwhile sodium hydroxide solubility decreases from the top to the base of the tree. This is an indication that the degradation of the wood due to fungal decay, heat and light is more likely to occur in young wood than matured wood.Variation in height on the tree had no significance on 1% sodium hydroxide soluble contents (Table 3).

However, the result from this study was similar to 37.78% in *Musa paradisiaca*, 42.29% in *Musa cavendish* (Omotoso and Ogunsile, 2009) but higher compared to 8-14% and 15-22% for softwoods and hardwoods respectively (As *et al*., 2002). This high value indicates higher degradation of cellulose from the top wood during pulping and bleaching which might affect the strength properties of the finished paper (Anderson, 1937).

Cold water solubility test

In this study, water solubility decreased from the top, 32.07%, to the base heartwood 8.28% (Table 2). However, there was no significant difference in the cold water solubility with height (Table 3). *S. tragacantha* exhibited a high content (32.07%) of dissolved substances in cold water compared to 5.20% in *Pterygotamacrocarpa* (Pawlicka and Waliszewska, 2011), 5.88% in *Pinusnigra* (Akgul and Tozluoglu, 2009) and 4.12% in *Maclurapomifera* (Mohamed *et al.*, 2013).

Table 3 Significance (P values) of variations in heights on the percentage soluble extracts in the *Sterculia tragacantha* milled sample

Source	Df	Ethanol-Benzene	1% NaOH	Cold Water	Lignin
Height	3	0.013	0.533	0.075	0.048
Error	4				

P values > 0.05 are not significant

Table 4: Effect of cooking variable on pulp yield and bleaching response of pulp to hydrogen peroxide and sodium hypochlorite

Source	Base heartwood		Base sapwood		Middle		Top	
Alkali charge (%)	21	18	21	18	21	18	21	18
Temperature (°C)	110	100	110	100	110	100	110	100
Time (minutes)	300	360	300	360	360	300	300	360
Average pulp yield(%)	43.4	35.2	45.4	31.9	50.6	32.5	48.6	42.1
Pulp yield after bleaching (per 100 g)								
Hydrogen peroxide	30	18	43	38	26	24	34	25
Sodium hypochlorite	70	60	75	70	64	69	65	76

Influence of cooking variables on Kraft pulping of Sterculia tragacantha

All the cooking variables investigated had remarkable effect on the yield of the Kraft pulp in one way or the other. The dominant factors affecting the yield were the cooking liquor and temperature. Table 4 showed that cooking with 21% white liquor concentration at 110℃ for five hours gave pulp yield as high as 42.48%. This can be summarized as the optimum condition. At a temperature above 110ºC, more than half of the chips of *S. tragacantha* were pulped. This trend can be attributed to the solving power of caustic soda which leads to the dissolution of lignin-carbohydrate complexes (Zhinam and Raimo, 2001). Further increase in the ratio of sodium hydroxide to sodium sulphide led to a substantially high pulp yield at constant temperature and time.

Bleaching properties of Sterculia tragacantha pulp

From Table 4, the Kraft pulp obtained using a combination of the optimum condition of 21% concentration; temperature of 110℃ for 5 h was used for the bleaching studies. Hydrogen peroxide was found to have a degrading effect on the pulp as is evident in Table 4. On the other hand, sodium hypochlorite gave better yield without degradation. Kraft pulps are generally known to be hard to bleach and *Sterculia tragacantha* pulp is no exception.

Conclusion

From the results of the research study, the following conclusions were drawn:

The chemical composition of *Sterculia tragacantha* does not vary significantly with height which translates to the possible combination of wood from every part of the tree together in a digester for cooking. However, the low percentage of lignin contents showed that under normal Kraft pulping condition, it may be possible to obtain high pulp yield of *S. tragacantha*. Also, the moderate percentage of soluble contents of the wood implied that the wood can stay long in storage provided proper storage conditions are put in place to ensure minimal degradation. The *Sterculia tragacantha* pulp was hard to bleach (typical of Kraft pulp) and required high chemical consumption to achieve remarkable brightness. Going from the above conclusion, *Sterculia tragacantha* may be suitable for pulp and paper making. It is therefore recommended that further studies be carried out using more of this species to validate its suitability in order to promote mass cultivation of the species.

Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

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