African Journal of Agricultural Research Vol. 7(40), pp. 5518-5524, 23 October, 2012
Available online at http://www.academicjournals.org/AJAR
DOI: 10.5897/AJAR12.1136
ISSN 1991-637X ©2012 Academic Journals

Full Length Research Paper

Correlates of the yield of chemical pulp, lignin and the extractive materials of tropical hardwoods

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Accepted 2 October, 2012

The aim of this investigation is to correlate the percentage yields of pulp of twenty tropical hardwood species with their lignin and extractive contents. The hardwoods studied include Abura (*Hallea ciliata*), Afara (*Terminalia superba*), Agba (*Entada gigas*), Akomu (*Pycnanthus angolensis*), Akun (*Uapaca guineensis*), Eki-Eki (*Lophira alata*), Erimado *(Ricindendron heudelotii*), Erun-obo (*Erythropleum suaveolens*), Iroko (*Milicia exelsa*), Itako (*Strombosia pustulata),* Itara (*Sacoglottis gabonensis*), Mahogany (*Khaya ivorensis*), Masonia (*Masonia altissima*), Obeche (*Triplochiton scleroxylon*), Odoko (*Ipomoea asarifolia*), Ofun (*Avicennia germinans*), Okilolo (*Symphona globulifera*), Opepe (*Nauclea diderrichii*), Oporoporo (*Pterygota macrocarpa*) and Some (*Ceiba pentadra*). Hardwood species such as *H. ciliata*, *T. superba* and *S. globulifera* that gave pulp yield of 50% were found to have the lowest lignin contents in the range of 19.0 to 28.4% and extractives contents of 4.8 to 6.0%. The results obtained showed that there is significant negative correlation ($p < 0.01$ and $r = -0.84$) between the percentage pulp yield and the lignin contents as well as between percentage pulp yield and contents of extractive materials ($p < 0.01$, $r = -0.811$). However, a significant positive correlation ($p < 0.01$, $r = 0.649$) between the percentage lignin contents and the extractive components of the wood samples was observed. The chemical integrity of the pulp, lignin and extractive contents of the wood samples was confirmed by infra-red (i.r.) spectroscopic studies.

Key words: Tropical hardwood species, pulp yield, lignin content, extractives.

INTRODUCTION

Wood is a complex of natural organic polymer substances that include cellulose, hemicelluloses and lignin. Cellulose is a structural polysaccharide and consists of long chains of D-glucose units linked by β-1, 4 glycosidic bonds. Hemicelluloses are built up from a relatively limited number of sugar residues that include D-xylose, D-mannose, D-glucose, D-galactose, L-arabinose, 4-O methyl-D-glucuronic acid, D-galacturonic acid, D-glucuronic acid and to a lesser extent, L-rhamnose, L-fructose and various O-methylated neutral sugars (Sjostrom, 1993). Lignin is made up of three primary precursors which include trans-coniferyl, trans-sinapyl and trans-*p*-coumaryl alcohols (Argyropoulos et al., 2002; Froass et al., 1996). Lack of enzymic control during lignin polymerization results in an almost random series of bonding and a very complex structure (Jung and Fahey, 1983). The existence of strong carbon-carbon (C-C) and ether (C-O-C) linkages in the lignin affects its susceptibility to chemical disruption (Karhunen et al., 1999). The non-structural components of wood include extractives which consist of triglycerides, fatty acids, waxes, fatty alcohols, sterols and steryl esters (Fengel and Wegener, 1989; USDA, 1999). The various polymer substances present in wood are not uniformly distributed within the cell wall and their concentrations change from one morphological region to the other (Saka, 2001).

Various studies have shown that the chemical composition of hardwoods of temperate zones is different from those of tropical regions (Hon and Shiraishi, 2001). In many cases, the latter contain higher percentages of extraneous substances and lignin. This fact is not

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unconnected with the difficulty encountered in pulping of most tropical hardwoods (Sykes and Prentice, 1996; Poke and Raymond, 2006).

Studies on hardwoods from the temperate zone are well documented in literature (Foster et al., 1996; Kreyling, 2010; Pijut et al., 2011) but very little information exist on wood species from the tropical forest of Africa and its sub-region, despite the quantum of foreign exchange earnings and the increasing potential for wealth creation obtainable from this sector (Odeyemi, 1986). Few West African hardwood species have been studied (Lai and Iwamida, 1993) and sufficient details about the levels and composition of lignin and extraneous materials contents of these hardwoods have received little attention. This formed the basis for the present studies in the determination of amount of lignin, extraneous materials and the pulp yield obtainable from twenty tropical hardwood species sourced from Nigeria.

MATERIALS AND METHODS

Wood samples

The tropical hardwood species chosen for this study are Abura (*Hallea ciliata*), Afara (*Terminalia superba*), Agba (*Entada gigas*), Akomu (*Pycnanthus angolensis*), Akun (*Uapaca guineensis*), Eki-Eki (*Lophira alata*), Erimado *(Ricindendron Heuotii*), Erun-obo (*Erythropleum suaveolens*), Iroko (*Milicia exelsa*), Itako (*Strombosia pustulata*), Itara (*Sacoglottis gabonensis*), Mahogany (*Khaya ivorensis*), Masonia (*Masonia altissima*), Obeche (*Triplochiton scleroxylon*), Odoko (*Ipomoea. asarifolia*), Ofun (*Avicennia germinans*), Okilolo (*Symphona globulifera*), Opepe (*Nauclea diderrichii*), Oporoporo (*Pterygota macrocarpa*) and Some (*Ceiba pentadra*). The species were chosen based on their availability in the region of study. The samples were obtained from Forestry Research Institute of Nigerian (FRIN) between August and November, 2006.

Pulping process

The Kraft process was employed in the pulping investigations using 2 kg each of the wood sample in sawdust form in a stainless steel rotary digester. The white liquor was made of 28.5% sulphidity, 21.5% effective alkali and 24.5% active alkali. Cooking was carried out for 1 h and 45 min in a batch process at 170°C, pressure of 2 bars, with liquor to wood ratio of 4:1 according to the method earlier reported (Odeyemi,1986). At the end of each cook, the contents of the digester were discharged into a bowl followed by sequential washing of the pulp with deionized water and air-dried to obtain the wood pulp.

Determination of extractives

The extractive contents of the wood samples were determined using soxhlet extractor in accordance with standard Tappi T204 om-88 test method (TAPPI, 1988). A solvent mixture consisting of benzene and ethanol (2:1 v/v) was used in the extraction of the extraneous materials. 1g of air-dried wood sample from each of the hardwoods investigated was placed in a 28 × 100 mm thimble obtained from Toyo Roshi Kaisha, Ltd. Japan. The extraction thimble containing the specimen was then placed in the soxhlet apparatus and extracted with 200 cm^3 ethanol-benzene mixture for 4 to 6 h. The solvent obtained at the end of each extraction process was evaporated at reduced pressure to obtain the extractive content of the wood sample. The weight of the dried extract was expressed as a percentage of the moisture-free sample.

Determination of lignin

The lignin contents of the wood samples were determined on the extractive free wood. A weighed amount of the wood sample (1.00 g) was placed in a 50 cm^3 beaker containing 15 cm^3 of 72% H_2SO_4 and allowed to stand at 25°C for 2 h. The contents of the beaker were later transferred into a 1 L Erlenmeyer flask and the volume adjusted to 575 cm^3 with distilled water and thereafter refluxed for 4 h in a round-bottomed flask. The mixture was allowed to cool down to room temperature and filtered through a previously weighed Gooch crucible of porosity 4. The residue was washed with distilled water before drying to a constant weight at 105°C in an oven. The lignin content was expressed as a percentage of the extracted oven-dried wood. All determinations were carried out in triplicates and the mean values of pulp, lignin and extractive contents of each wood sample recorded. The infra-red analysis of the pulp, lignin and the extractive components of the tropical hardwoods was carried out on a Perkin-Elmer spectrometer FT- IR 2000 model in a KBr beam splitter and DTG detector in the region 4000 to 400 cm^{-1}. They were run as mulls in Nujol in KBr windows.

Statistical analysis

Pearson's correlation and regression analyses were used to test for significant correlation and relationship between the investigated parameters at 0.01 levels. The analysis was performed using computer soft ware SPSS 10.0 for windows.

RESULTS AND DISCUSSION

The results showing the mean percentage yield of pulp, lignin, extractive materials and moisture content of the twenty tropical hard wood species selected for this study are shown in Table 1. The results showed that five samples, namely Akun (*U. guineensis*), Eki-Eki (*L. alata*), Iroko (*M. exelsa*), Masonia (*M. altissima*) and Ofun (*A. germinans*) gave the lowest yield of pulp and were in the range of 35.0 to 39.0%. A moderate yield of pulp (40.0 to 43.3%) were observed for Agba (*E. gigas*), Mahogany (*K. ivorensis*), Itako (*S. pustulata*) and Itara (*S. gabonensis*) while relatively high yield (45.0-50.0 %) of pulp were observed for eleven samples namely Abura (*H. ciliata*), Afara (*T. superba*), Akomu (*P. angolensis*), Erimado (*R. heudelotii*), Erun obo (*E. Suaveolens*), Obeche (*T. scleroxylon*), Odoko (*I. asarifolia*), Okilolo (*S. globulifera*), Opepe (*N. diderrichii*), Oporoporo (*P. macrocarpa*) and Some (*C. Pentadra*).

The lignin contents of the wood samples were in the range 19.00 to 34.40%. Three wood samples, namely Abura (*H. ciliata*), Afara (*T. superba*) and Okilolo (*S. globulifera*) had relatively low contents of lignin which were observed to range between 19.00 to 21.50%. Lignin contents in the range of 28.35 to 29.30% were observed for Akomu (*P. angolensis*), Erimado *(R. heudelotii*), Erun-obo (*E. Suaveolens*), Obeche (*T. scleroxylon*), Opepe (*N.*

Table 1. The mean percentage yield of pulp, lignin and extractive contents of tropical hardwood samples.

S/N	Common names (Yoruba)	Botanical names	Mean % yield of pulp (at 28.55% sulphidity)	Mean % lignus content (klason lignin)	Mean % extractive content (benzene ethanol extract)
1	Abura	*H. ciliata*	50.00 ± 1.00 ^{E}	19.00 ± 1.00^{A}	6.00 ± 0.26^{B}
2	Afara	*T. superba*	50.00 ± 1.00 ^{E}	20.10 ± 0.95^{A}	5.33 ± 0.76^{B}
3	Agba	*E. gigas*	43.33 ± 8.39^{C}	32.30 ± 1.25^{C}	7.17 ± 0.90^{C}
4	Akomu	*P. angolensis*	49.00 ± 1.00^{E}	28.35 ± 0.44^{b}	5.00 ± 0.50^{B}
5	Akun	*U. guineensis*	38.33 ± 2.52^{B}	34.40 ± 0.66^{D}	11.87 ± 0.86^{D}
6	Araba	*C. pentadra*	49.00 ± 2.00 ^{E}	28.44 ± 0.51^{B}	4.80 ± 0.26^{A}
7	Eki-Eki	*L. alata*	38.00 ± 1.00^{B}	33.47 ± 0.55^{C}	11.23 ± 0.31^{D}
8	Erimado	*R. heudelotii*	46.00 ± 1.00^{D}	29.00 ± 0.87^{B}	4.80 ± 0.26^{A}
9	Erun-obo	*E. suaveolens*	47.00 ± 3.00^{D}	29.33 ± 0.76^{B}	4.60 ± 0.52^{A}
10	Iroko	*M. exelsa*	35.00 ± 1.00^{A}	35.17 ± 1.26^{D}	10.57 ± 0.61^{D}
11	Itako	*S. pustulata*	40.00 ± 1.00^{B}	32.10 ± 1.05^{C}	7.33 ± 0.90^{C}
12	Itara	*S. gabonensis*	40.00 ± 1.00^{B}	30.10 ± 0.90^{B}	5.33 ± 0.76^{B}
13	Mahogany	*K. ivorensis*	40.00 ± 2.00^{B}	31.40 ± 1.25^{C}	7.47 ± 0.76^{C}
14	Masonia	*M. altissima*	39.00 ± 1.73^{B}	33.40 ± 0.79^{C}	8.10 ± 0.95^{C}
15	Obeche	*T. scleroxylon*	49.00 ± 2.00 ^{E}	28.57 ± 0.86^{B}	5.57 ± 0.71^{B}
16	Odoko	*I. ascarifolia*	45.00 ± 2.00^{D}	30.07 ± 0.90^{B}	6.07 ± 0.32^{B}
17	Ofun	*A. germinans*	38.00 ± 2.65^{B}	34.17 ± 1.04^{D}	11.50 ± 0.50^{D}
18	Okilolo	*S. globulifera*	50 ± 2.00 ^{E}	28.44 ± 0.51^{B}	4.80 ± 0.26^{A}
19	Opepe	*N. diderrichii*	48.00 ± 2.00^{D}	29.07 ± 0.81^{B}	6.06 ± 0.21^{B}
20	Oporoporo	*P. macrocarpa*	46.00 ± 3.61^{D}	29.00 ± 0.67^{B}	4.57 ± 0.51^{A}

Means with different letters in a column are significantly different in the Duncan's multiple range test at p = 0.05.

diderrichii), Oporoporo (*P. macrocarpa*) and Some (*C. Pentadra*). The remaining ten wood samples namely Agba (*E. gigas*), Akun (*U. guineensis*), Eki-Eki (*L. alata*), Iroko (*M. exelsa*), Itako (*S. pustulata*), Itara (*S. gabonensis*), Masonia (*M. altissima*), Mahogany (*K. ivorensis*), Odoko (*I. asarifolia*) and Ofun (*A. germinans)* were observed to have relatively high lignin contents of 30.10 to 34.40%.

Results of the extractive contents for the twenty wood species investigated showed that five samples namely Erimado *(R. heudelotii*), Erun-obo (*E. Suaveolens)*, Okilolo (*S. globulifera*), Oporoporo (*P. macrocarpa*) and Some (*C. Pentadra*) gave the lowest contents of extractives in the range of 4.50 to 4.80%. Moderate values of extractive contents in the range of 5.00 to 7.50% were obtained for Abura (*H. ciliata*), Agba (*E. gigas*), Afara (*T. superba*), Akomu (*P. angolensis*), Itako (*S. pustulata*), Itara (*S. gabonensis*), Mahogany (*K. ivorensis*), Obeche (*T. scleroxylon*), Odoko (*I. asarifolia*), and Opepe (*N. diderrichii),* while the highest extractive contents in the range of 8.10 to 11.90% were obtained for Akun (*U. guineensis*), Eki-Eki (*L. alata*), Iroko (*M. exelsa*) Masonia (*M. altissima*) and Ofun (*A. germinans*).

The extractive contents of wood depend on the species as well as the area where the wood is grown (Freire et al., 2006). The amount and composition of wood extractives are important parameters in the wood processing for pulp and paper production (Back and Allen, 2000; Hillman, 2002). Lipophilic extractives have been reported to give rise to pitch deposits that lead to the formation of dark spots on bleached pulp and paper (Freire et al., 2002; Manji et al., 2005). High contents of extractives will require high levels of bleaching chemicals during pulp and paper production which ultimately lead to increased operating cost and increase in incidences of quality defects in the final product (Del Rio et al., 2000; Neto et al., 2004). Thus, wood samples that are high in extractives such as Akun (*U. guineensis*), Eki-Eki (*L. alata*), Iroko (*M. exelsa*) an Okun (*A. germinans*), may not be good materials for pulp and paper production. The values of the lignin and extractive contents obtained in this study for tropical hardwood samples such as Akun (*U. guineensis*), Eki-Eki (*L. alata*), Iroko (*M. exelsa*) and Ofun (*A. germinans*) were observed to be higher than the values reported for hardwood samples such as Aspen (*Populus grandidentata*), Beech (*Fagus grandifolia*), Birch (*Betula populifolia*) and Marple (*Acer nigrum*) from the temperate zones (Browning, 1963; Fengel et al., 1989; Scheer and Morrell, 1998).

There was a fair correlation between the mean percentage pulp yield and the lignin content of the wood samples as shown in Figure 1. Iroko (*M. exelsa*) that gave the lowest pulp yield was observed to have the highest lignin content and Abura (*H. ciliata*) the sample

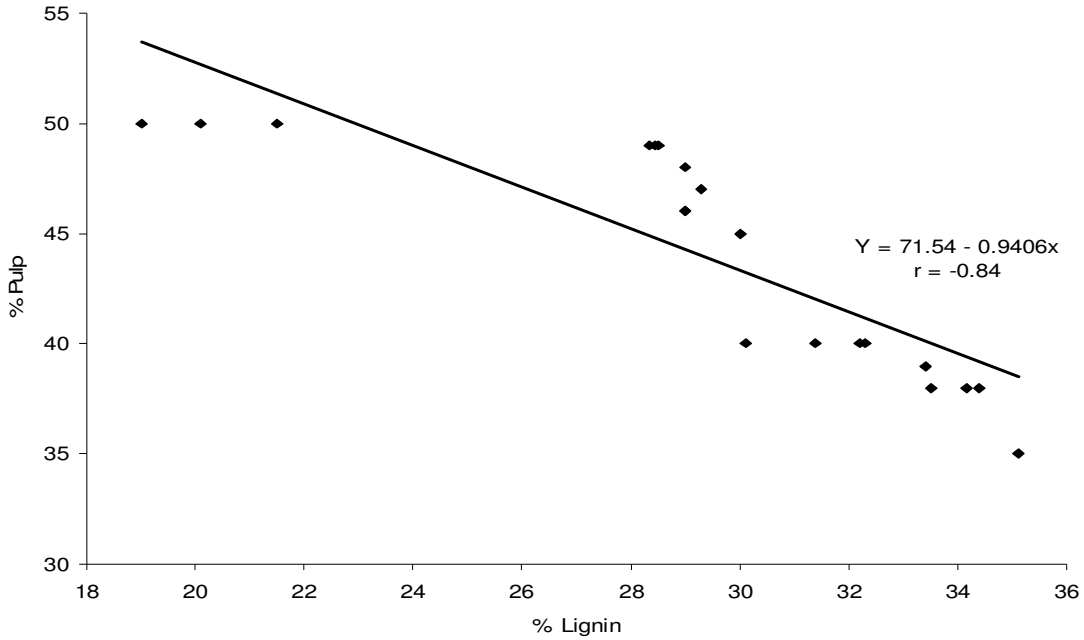

Figure 1. The correlation between % pulp yield and the % lignin contents of the wood samples.

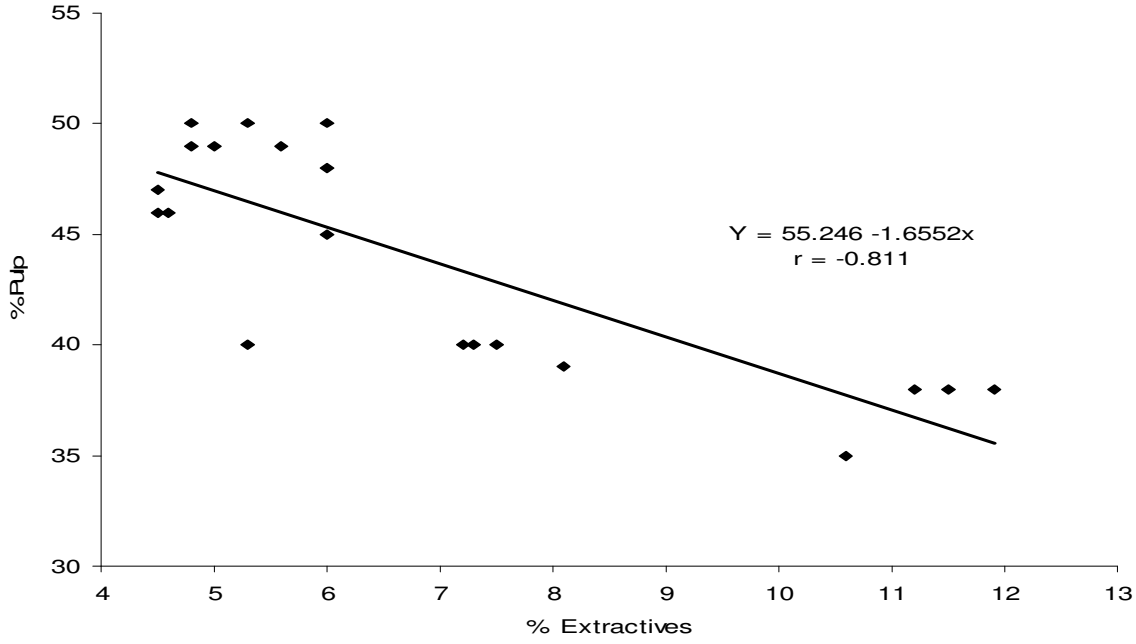

Figure 2. The correlation between % pulp yield and % extractive contents of the hardwood samples.

with the lowest lignin content was one of the samples that gave the highest yield of pulp. However, the percentage pulp yield did not correlate well with the extractive contents of the wood shown in Figure 2. Statistical analysis of the results using Pearson's correlation test showed a negative significant correlation between the mean percentage pulp yield and the lignin content, $r = -0.84$ ($p < 0.01$), as well as between mean percentage pulp yield and extractives, $r = -0.811$ ($p < 0.01$). There was, however, a positive correlation, $r = 0.649$ ($p < 0.01$), between the % lignin content and the extractive component of the wood samples studied as shown in

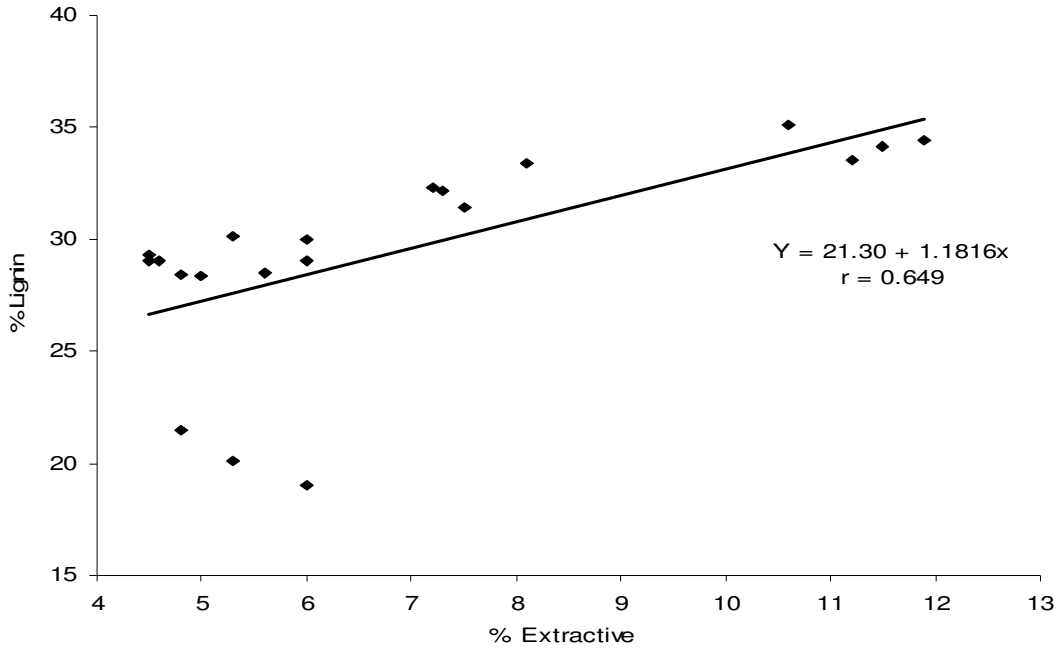

Figure 3. The correlation between % lignin and % extractive contents of hardwood samples.

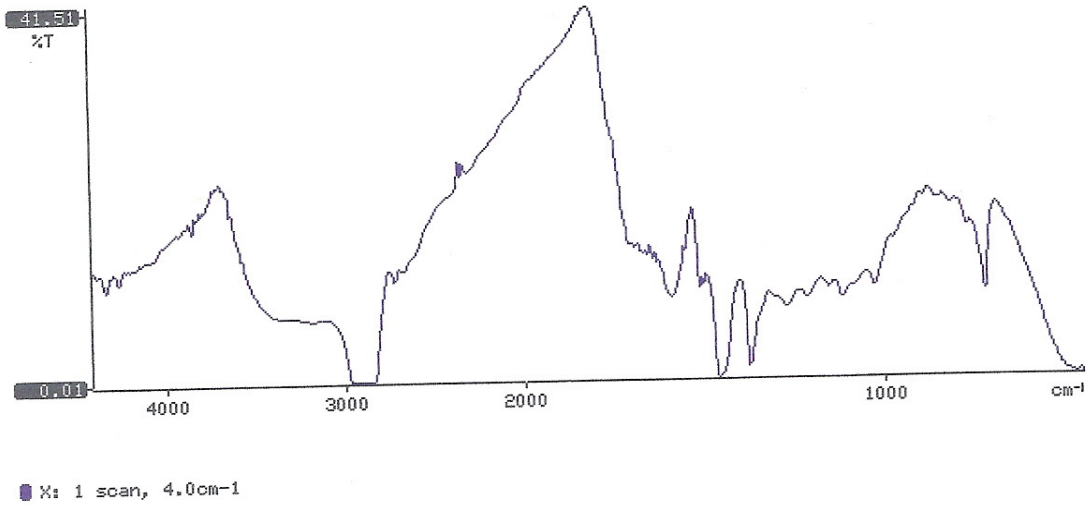

Figure 4. The i.r. spectra of lignin obtained from *T. superba*.

Figure 3. The Pearson's correlation is used to find a correlation between at least two continuous variables. The value for a Pearson's can fall between 0.00 (no correlation) and 1.00 (perfect correlation). P< 0.01 is the probability that the Pearson's correlation between % pulp yield and the lignin content; % pulp yield and extractives and the % lignin and extractives contents of the wood samples studied is less than 0.01.

The chemical integrity of the pulp, lignin and extractive components of the wood samples was confirmed from infra-red (i.r) spectroscopic studies shown in Figures 4 and 5 for lignin and extractives respectively. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. The i.r studies carried out on the pulp showed that the OH absorption occurred between 3150 and 3400 cm^{-1} while the C-C bonds were observed in the region of 550 to 1300 cm^{-1}. These absorptions are typical of the OH and C-C bonds found in cellulose (Ndukwe et al., 2009).

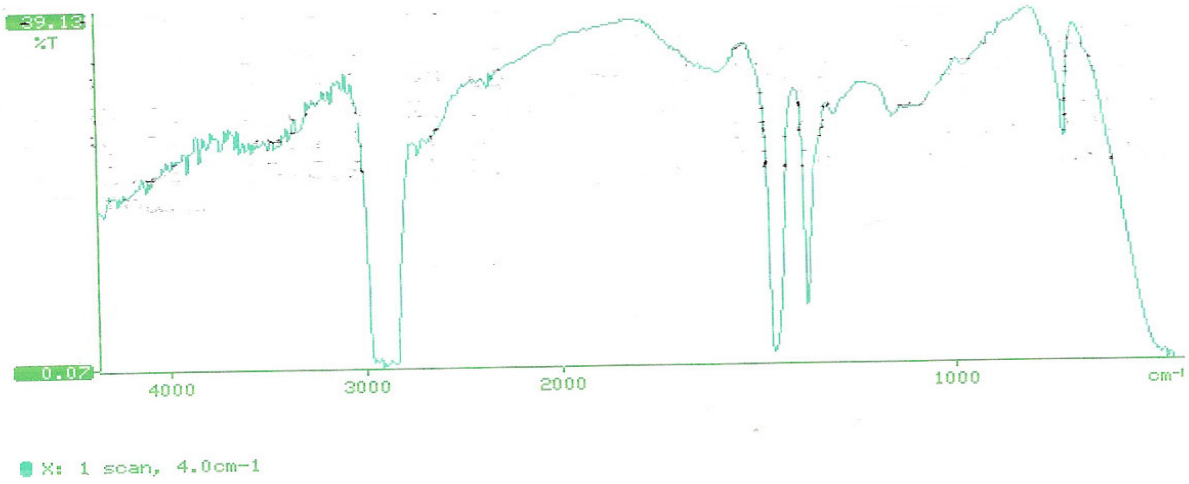

Figure 5. The i.r. spectra of extractives obtained from *T. superba*.

The absorption band at 1500 to 1510 cm^{-1} in Figure 4 is assigned to aromatic vibrations found in lignin, while the region ranging from 1485 to 1495 cm^{-1} is associated with the phenyl propane units, a major constituent of lignin molecule. The phenolic hydroxyl group is observed at 1340 to 1380 cm^{-1}. These groups play important role in the chemistry of lignin. In Figure 5 while the absorption at 500 to 700 cm^{-1} and 1300 to 1500 cm^{-1} are characteristics of alkaloids, phenols and triglycerides that are present in wood extractives (Fengel and Wegener, 1989; Malan et al., 1996).

Conclusion

The results obtained from this study showed that many of the tropical hardwood samples investigated such as *A. germinans*, *U. guineensis*, *M. altissima*, *L. alata* and *M. exelsa* have high contents of lignin and extractive materials and will not be suitable for pulp and paper production.

ACKNOWLEDGEMENTS

Our profound gratitude goes to Professor S.O. Odeyemi for the interest shown in the study. We also appreciate the assistance of Mr E. A. Mgbachiuzo and Dr C. C. Igwe of Chemical and Fibre Technology Department, Federal Institute of Industrial Research of Nigeria (FIIRO).

REFERENCES

Argyropoulos DS, Jurasek L, Kristofova L, Xia Z, Sun Y, Palus E (2002). Abundance and reactivity of dibenzodioxocins in softwood lignin. J. Agric. Food Chem. 50(4):658-666.

Back EL, Allen LH (2000). Pitch Control, Wood Resin and Deresination. Tappi Press Atlanta Georgia. pp. 151-184.

Browning BL (1963). The chemistry of wood pulp. Interscience Publishers, New York, London. pp. 104-183.

Del Rio JC, Romero J, Gutierrez A (2000). Analysis of pitch deposits produced in kraft pulp mills using a totally free chlorine free bleaching sequence. J. Chromatogr. A. 874(2):235-245.

Fengel D, Wegener G (1989). Wood Chemistry, Ultrastructure and Reactions. Waiter De Gruyter Inc. Berlin. pp. 90-108.

Foster DR, Orwig DA, McLachian JS (1996). Ecological and Conservation Insights from reconstructive studies of temperate old growth forests. Tree 11(10):419-424.

Freire CSR, Silvestre AJD, Pereira CCL, Neto CP, Cavaleiro JAS (2002). New lipophilic components of pitch deposits from an Eucalyptus globules ECF bleached Kraft Pulp Mill. J. Wood Chem. Technol. 22(1):55-66.

Freire CSR, Pinto PCR, Santiago AS, Silvestre AJD, Evtuguin DV, Neto CP (2006). Comparative study of lipophilic extractives of hardwoods and corresponding ECF bleached Pulps. BioResources 1(1):3-11.

Froass P M, Ragauskas AJ, Jiang J (1996). Chemical structure of residual lignin from kraft pulp. J. Wood Chem. Technol. 16(4):347-365.

Hillman DC (2002). Single Species Pulping. The World's Preferred Market Pulps. Solutions. pp. 27-28.

Hon DNS, Shiraishi N (2001). Cellulosic Chemistry 2nd Edition. Marcel Dekker Inc New York. pp. 443-501.

Jung HJ, Fahey GC Jr (1983). Interactions among phenolic monomers and *in-vitro*fermentation. J. Dairy Sci. 66:1255.

Karhunen P, Mikkola J, Pajunen A, Brunow G (1999). The behavior of dibenzodioxocin structures during alkaline pulping processes. Nordic Pulp Paper Res. J. 14 (2):123-128.

Kreyling J (2010). Winter climate change: a critical factor for temperate vegetation performance. Ecology 91(7):1939-1948

Lai YZ and Iwamida T (1993).“Effect of Chemical Treatments on Ultra-high yield Pulping (1), Fiber Separation”. Wood Sci. Technol. 27(3):195-203.

Malan E, Swinny E, Ferreira D, Stemberg P (1996). The Structure and Synthesis of a 7,8,4-Trihydroxyflavan-Epioritin Dimer from Acacia Caffra. Phytochemistry 44(3):529-531.

Manji A, Salgar S, Constant J, Silva DJS, Almeida JM (2005). Uma nova alternative para eliminar o talco e reduzir pitch e extractives na producao de cellulose. O Papel, Maio. pp. 82-87.

Ndukwe NA, Jenmi FO, Okiei WO, Alo BI (2009). Comparative study of percentage yield of pulp from tropical hardwood samples. Afr. J. Environ. Sci. Technol. 3(1):21-25.

Neto CP, Silvestre AJD, Evtuguin DV, Freire CSR, Pinto PCR, Santiago AS (2004). Bulk and Surface Composition of ECF bleached hardwood Kraft Pulp Fibres. Nord Pulp Paper Res. J. 19(4):513-520.

Odeyemi SO (1986). Comparative Kraft Cooks of Some Tropical Woods

from Nigeria. Finska Kemist. Medd. 75:2.
Pijut PM, Lawson SS, Michler CH (2011). Biotechnological efforts for preserving and enhancing temperate hardwood tree biodiversity, health, and productivity. *In Vitro* Cell. Dev. Biol. Plant. 47:123-147.
Poke FS, Raymond CA (2006). Predicting Extractives, Lignin andCellulose Contents Using Near Infrared Spectroscopy on Solid Wood in Eucalyptus globules. Wood Chem. Technol. 26:187-199.
Saka S (2001). Chemical Composition of Wood and Distribution. In: Wood and Cellulosic Chemistry, 2nd edition and expanded. Hon DNS and Shiraishi N (eds.). Marcel Dekker Inc., New York. pp. 51-81.
Scheer TC, Morrell JJ (1998). Natural durability of Wood. A worldwide checklist of species. Forest Research Oregon State University Research Contribution 22, Cor Vallis, Oregon. p. 58.
Sjöström E (1993). Wood Chemistry: Fundamentals and Application. Academic Press. Orlando. p. 293.
Sykes MT, Prentice IC (1996). Climate change, tree species distribution and forest dynamics: A case study in the mixed conifer/ northern hardwoods zone of northern Europe. Climatic Change 34:161-177.
TAPPI (1988). Solvent Extractives of Wood and Pulp. T 204 om-88. Standard Methods of the Technical Association of the Pulp and Paper Industry, New York, USA.
USDA (1999). Wood Handbook. Wood as an Engineering material. Forest Product Laboratory General Technical Report EPL-GTR-113. Forest Products Society, Madison, Wisconsin.