American-Eurasian Journal of Scientific Research 9 (3): 45-50, 2014
ISSN 1818-6785

DOI: 10.5829/idosi.aejsr.2014.9.3.853

Surface Chemistry and Thermogravimetric Analysis of Some Timbers in South Eastern Nigeria

[1]*Nkechi H. Okoye,* [1]*Augustine N. Eboatu,* [2]*James S. Fabiyi,*
[3]*Prisca I.Udeozo,* [1]*Rosemary U. Arinze and* [1]*Stanley C. Odinma*

[1]Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria
[2]Department of Forest Products and Wood Science, Virginia Tech., Blacksburg, VA, 25061, USA
[3]Department of Chemical Sciences, Tansian University, Umunya, Anambra State, Nigeria

Abstract: Wood is a natural renewable polymeric composite made up of cellulose, hemicelluloses, lignin and extractives. Surface characterization of eight timbers collected from South Eastern Nigeria was performed using Fourier Transform Infrared spectroscopy (FTIR) and thermal degradation pattern was determined by Thermogravimetric analysis (TGA). The infrared bands of the selected wood species with their peak assignments and structural polymers show that the positions of most bands and their intensities in the fingerprint region are similar. Qualitatively, these timbers yielded thermogravimetric responses that are also similar. Results suggest that *Erythrophleum suaveolens* and *Nauclea latifolia* would be better lignocellulose substitute resins, as they present higher amounts of lignin and higher thermal decomposition temperature.

Key words: Thermogravimetric, thermal degradation, timbers and surface chemistry.

INTRODUCTION

Timber is man's most important natural and endlessly renewable source of energy with a complex chemical structure made up of cellulose (40-50%) and hemicelluloses (15-25%) impregnated with lignin (15-30%) and extractives [1]. Cellulose is responsible for strength in wood fiber because of its high degree of polymerization and crystallinity while hemicelluloses act as matrix for the cellulose and as link between the fibrous cellulose and amorphous lignin [2]. Lignin acts as a cementing material for wood fibers while extractives enhance natural durability and reduces moisture sorption of wood. Lignin in softwood is essentially characterized by guaiacyl (Trans-coniferyl alcohol) nuclei whereas both guaiacyl and syringyl (Synapyl alcohol) nuclei are characteristic of hardwoods. These chemical components behave differently when subjected to thermal treatment.

Surface properties of wood can be divided into two major groups: physical and chemical properties. Physical properties include morphology, roughness, smoothness, specific surface area and permeability. Chemical properties include elemental and molecular, or functional group composition. Methods for characterizing surface properties of wood may be divided into three broad categories: microscopic, spectroscopic and thermodynamic. Microscopic methods provide information about surface morphology; spectroscopic methods provide information about surface chemistry and thermodynamic methods provide information about the surface energy [3]. The use of Fourier transform infrared (FTIR) spectroscopy has been reported for surface chemical characterization and qualitative estimation of the lignin and carbohydrate contents in wood, various lignocellulosics and wood plastic composites [4- 7]. This technique has advantage over conventional chemical analysis methods (Chemical extraction techniques) because it is very fast, requires less specimen preparation and does not result in a concomitant degradation of natural polymers.

Thermogravimetric analysis (TGA) is a technique in which a change in the weight of a substance is recorded as a function of time and temperature in air or in an inert atmosphere [8-10]. In isothermal thermogravimetry, the

---

Corresponding Author: Nkechi H. Okoye, Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria.

change in weight is recorded as a function of time as temperature remains constant while in dynamic or non isothermal thermogravimetry, it is recorded as a function of both temperature and time as the temperature is raised at a given heating rate. With the use of a derivative computer, the rate of weight loss as a function of time and temperature can be determined [11]. TGA has been used to predict the composition of cellulose and lignin in wood / cellulose-lignin mixtures using the Pyrolytic Unit Thermographs (PUTs) [12]. The main use of this technique has been to study the thermal decomposition of polymeric materials and to accumulate kinetic information about such decomposition. Other applications include the examination of adsorptive surfaces, the examination of water of crystallization, the identification and comparison of varnishes and other surface coatings in forensic analysis, the determination of the age of art treasures such as paintings, the examination of drug stability and the rate of degradation of drugs when exposed to air and the characterization of polymers [13,14].

Wood has been proposed as an ideal material for what could be a future 'ligno-chemical' industry in providing new lignin-glue applications, recyclable food packaging, rubber tire replacement application, bacterial medical agents and high strength fabrics or composites [15,16]. Based on these facts, it is very important to have well documented information on the surface chemistry and thermal stability of different wood species as this information is not available in literature for most Nigerian timbers. Hence this study was aimed at investigating the surface chemical and thermal characterization of some selected timbers in South Eastern Nigeria.

MATERIALS AND METHODS

Sample Collection and Preparation: From a collection of over fifty tropical timbers of South Eastern Nigeria whose flammability properties were studied elsewhere [17], eight were selected for further characterization. They are: *Erythrophleum suaveolens, Triplochyton scleroxylon, Daniella oliveri, Albizie ferruginea. Tetrapleura tetraptera, Vitex doniana, Ficus platyphylla* and *Nauclea latifolia.* These species are among the most commonly used timbers in Nigeria and were obtained from local sawmills at Anambra and Enugu States.

Surface Chemical Characterization: Specimens for the surface chemical analysis were obtained from each of the eight wood species and ground into fine powder. Spectra were measured directly from wood powder (1% w/w basis) thoroughly dispersed in KBr (99% w/w basis). Spectra were recorded at room temperature using a Thermo Scientific Nicolet 8700 spectrometer equipped with a DTGS detector. Each spectrum was taken as an average of 64 scans at a resolution of 4 cm-1. A separate background spectrum was collected and automatically subtracted from the raw spectrum for each specimen.

Thermogravimetric Analysis: This was conducted using a TA Q500 Thermogravimetric analyzer. Samples of 6-8 mg were randomly excised using razor blade. Test specimens were obtained from 5 mm depth from the surface of wood, to avoid the possible migrated extractives at the machined surface. The specimens were conditioned at 12% moisture content prior to analysis. Two specimens per wood species were analyzed at a heating rate of 10°C/min from room temperature to 900°C in a nitrogen atmosphere (Flow rate 60 mL/min). The weight change was recorded as a function of temperature. Derivative peak temperature was taken as the maximum temperature acquired from the differentiation of the weight change as a function of temperature.

RESULTS AND DISCUSSIONS

Surface Chemistry: The infrared bands of the selected wood species with their peak assignments and structural polymers are respectively presented in Figure 1 and Table 1. The positions of most bands and their intensities in the fingerprint region are similar while some are slightly different for the wood species investigated.

In all the wood species, there is a broad band at 3337-3343 cm^{-1} assigned to O-H groups due to the combination of cellulose, hemicelluloses and lignin [7]. The position of the *O*-acetyl-4-*O*-methylglucurono-xylan peak at 1737 cm^{-1} is the same for *Triplochyton sclerochyton*, *Erythrophleum suaveolens*, *Nauclea latifolia*, *Vitex doniana*, *Ficus platyphylla* and *Albizie ferruginea* while the wave number slightly shifted to 1731 cm^{-1} for *Daniella oliveri* and *Tetrapluera tetraptera*. *Daniella oliveri*, *Erythrophleum suaveolens*, *Nauclea latifolia* and *Vitex doniana* have the same but lowest concentration of *O*-acetyl-4-*O*-methylglucurono-xylan (Judging from the absorbance) among all the wood species. *Tetrapluera tetraptera* has the highest concentration among them all; *Ficus platyphylla* and *Albizie ferruginea* contained the same amount of *O*-acetyl-4-*O*-methylglucurono-xylan. Such differences were also observed for different Nigerian wood species by Fabiyi *et al.* [16].

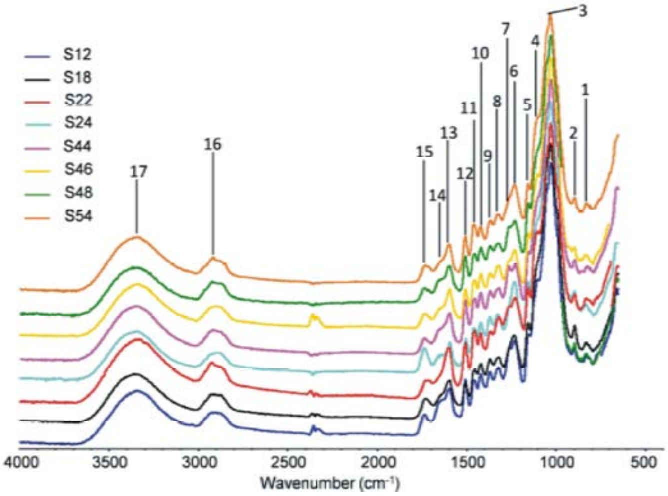

Fig. 1: Infrared spectra of different wood species. Each spectrum is an average of spectra from two specimens per wood species. Peak position and assignment as well as structural polymer for each peak are presented in Table 1.

Table 1: Infrared bands observed in some selected wood species

S/N	Position (cm^{-1})	Peak assignment	Structural polymer
1	830	CH out of plane associated with the syringyl nuclei	Lignin (Syringyl)
2	897	C1-H deformation of glucose ring	Cellulose
3	1031	C–O stretch	Cellulose and hemicellulose
4	1100	Aromatic skeletal and C–O stretch	Polysaccharides and Lignin
5	1157	C–O–C vibration	Cellulose and hemicellulose
6	1232	C–O of syringyl ring	Lignin
7	1261	C–O of guaiacyl ring	Lignin
8	1325	C_1–O vibration	Syringyl
9	1367	C–H deformation	Cellulose and hemicellulose
10	1422	C-H in-plane deformation with aromatic ring stretching	Lignin
11	1461	CH deformation, asymmetry in CH_3 and CH_2	Cellulose
12	1507	aromatic skeletal vibration (C=C), guaiacyl>5	Lignin
13	1596	aromatic skeletal vibration (C=C), guaiacyl>5	Lignin
14	1641	aromatic skeletal vibration (C=C)	Tannin
15	1736	Conjugated C=O	Xylan in hemicelluloses
16	2909	C-H stretching	
17	3342	OH stretching from cellulose	Cellulose

Table 2: Ratios of the peak absorbance of lignin to carbohydrate associated bands

Wood species	A_{1507}/A_{1032}	A_{1507}/A_{1157}	A_{1507}/A_{1736}	S/G (A_{1232}/A_{1262})
Triplochytons clerochyton	0.23	0.58	2.14	1.08
Daniella oliveri,	0.14	0.40	1.67	1.15
Erythrophleum suaveolens,	0.22	0.52	2.76	1.08
Tetraplueratetraptera,	0.14	0.41	1.23	1.32
Nauclea latifolia,	0.21	0.56	2.68	1.01
Vitex doniana,	0.17	0.46	2.10	1.13
Ficus platyphylla,	0.21	0.53	2.17	1.07
Albizie ferruginea,	0.20	0.52	2.07	1.14

The lignin content of these wood species is evident at the wave number 1507cm^{-1} for all the investigated wood except the *Tetrapluera tetraptera* with 1502cm^{-1} and *Vitex doniana* with 1504cm^{-1} (Figure 1). Generally, an increase in the amount of syringyl units in lignin tends to shift the aromatic ring maximum toward lower wave numbers [6]. This suggests that *Tetrapluera tetraptera* has the highest amount of syringyl units compared to guaiacyl which is in agreement with ratio of syringyl to guaiacyl (Table 1).

Table 3: TG / DTG results of the tree species under nitrogen gas atmosphere

TG/DTG	Triplochyton scleroxylon	Daniella olieveria	Erythrophleum suaveolens	Tetrapluera tetraptera	Nauclea latifolia	Vitex doniana	Ficus platyphylla	Albizie ferruginea
1^{st} peak								
Onset Temperature	30°C	31°C	28°C	30°C	29°C	26°C	31°C	31°C
Peak Temperature	61°C	61°C	57°C	55°C	57°C	58°C	60°C	61°C
Final Temperature	119°C	119°C	116°C	115°C	117°C	118°C	119°C	119°C
%Weight loss	3.40	3.66	4.56	2.84	4.5	3.87	3.43	3.43
2^{nd} peak								
Onset Temperature	201°C	200°C	206°C	210°C	201°C	198°C	198°C	200°C
Peak Temperature	364°C	339°C	326°C	260°C	246°C	275°C	375°C	337°C
Final Temperature	426°C	340°C	360°C	367°C	249°C	276°C	429°C	339°C
%Weight loss	62.69	18.99	21.81	32.63	0.51	4.93	60.45	22.19
3^{rd} peak								
Onset Temperature		340°C	360°C	367°C	249°C	276°C		339°C
Peak Temperature		395°C	399°C	392°C	388°C	367°C		383°C
Final Temperature		433°C	438°C	440°C	436°C	416°C		429°C
%Weight loss		51.10	38.28	41.60	61.18	55.88		37.05
Residue sample mass (% Char)	27.4	21.2	29.3	18.9	27.9	23.9	23.8	29.8

Table 4: Result of oven dry density, flame propagation rate and peak temperatures of some timber species [17]

Botanic name	Sample Code	Oven dry density (g/cm^3)	Ignition time(s)	Flame duration(s)	After-glow time (s)	Flame propagation rate (cm/s)	Peak temperature (°C)	Residue (% Char) % Char
Triplochyton scleroxylon	S12	0.380	2.70	127.7	204.6	0.37	364	27.4
Tetrapleura tetraptera	S24	0.467	4.00	493.5	73.0	0.10	392	18.9
Vitex doniana	S46	0.554	2.30	138.3	242.0	0.34	367	23.9
Daniella oliveri	S18	0.598	3.30	176.9	307.0	0.27	395	21.2
Nauclea latifolia	S44	0.627	5.30	329.3	301.6	0.14	388	27.9
Ficus platyphylla	S48	0.664	5.30	302.3	476.3	0.16	375	23.8
Albizie ferruginea	S54	0.687	5.00	506.7	386.8	0.09	383	29.8
Erythrophleum suaveolens	S22	1.069	4.00	376.0	12.0	0.13	399	29.3

From the ratios of the absorbance of the lignin band at 1507cm^{-1} and polysaccharides peaks at 1032 cm^{-1} due to C-O stretch, 1157 cm^{-1} due to C–O–C vibration for holocellulose (cellulose and hemicelluloses) and 1736 cm^{-1} for acetyl groups in hardwood xylan (Table 1), *Daniella oliveri* and *Tetrapluera tetraptera* contain the lowest proportion of lignin to polysaccharides while *Triplochyton sclerochyton*, *Erythrophleum suaveolens*, *Nauclea latifolia*, *Ficus platyphylla* and *Albizie ferruginea* had the highest proportion. The ratio of lignin to xylan is significantly high for *Erythrophleum suaveolens* and *Nauclea latifolia* while significantly low for *Tetrapluera tetraptera*. These give an indication that lignin content of *Erythrophleum suaveolens* and *Nauclea latifolia* is of higher proportion than other wood species. Another important difference between these wood species can be observed in the guaiacyl to syringyl ratio. Syringyl/guaiacyl ratio for *Nauclea latifolia* is the lowest among all the wood species investigated. This is in agreement with previous study which reported that different hardwoods have their S/G ratio around 1 [17]. In our case, it ranges between 1.01 and 1.32.

Thermogravimetric Analysis: The summary of the onset, peak and final temperatures of the wood decomposition stages under nitrogen gas are depicted in Table 3.

From Table 3, it is observed that the thermal decomposition of all the selected timbers was in three thermogravmetric steps, except for *Triplochyton scleroxylon*, *Nauclea latifolia* and *Ficus platyphylla* where the last two stages were merged or indistinguishable. The first region, 30 - 119°C, shows a peak temperature at approximately 60°C which is due to the evaporation of the free or bonded water and gaseous inclusions. The three major constituents of wood i.e. cellulose, hemicelluloses and lignin, in the lingo cellulosic materials become active and decompose thermo-chemically between 150 and 500°C. The observed peaks on the DTG thermograms between 250 and 320°C are due to the superposition of the lignin and the hemicelluloses degradations while the temperatures higher than 320°C depict the overlap of cellulose decomposition with that of lignin and stabilizing around 438°C. In this second region, 198 – 438°C, formation of volatile and combustible compounds and high loss of weight take place. It is observed that the bulk of the weight losses (> 55%) take place during the second stage of the second step, i.e. between 300 and 400°C except for *Albizie ferruginea* having a value less than 45%.

Thermal decomposition in nitrogen inhibits oxidation of the samples during the actual test and explains the high peak temperatures (364 - 399°C), which contradict the findings of Momoh *et al*. [9] on wood degraded in the air (345 -350°C). This accounts for the high percentage of residual char (18.9 – 27.9%). Char is a concentration of the carbon skeletal remnants of the pyrolysed molecules following degradation. However, between 400 and 550°C an insignificant loss in weight also occurs. The low after-glow time for *Erythrophleum suaveolens* [17] may account for the corresponding high peak temperature of 399°C. Qualitatively, all the eight timbers yielded thermogravimetric responses that are similar. The degradation process of these tropical timbers can be summarized thus: After the evaporation of the free water, the degradation of the main constituents of the wood begins at 120°C and presents two or three stages in general [10]. The lignin content, being more stable, contributes more to char formation than does cellulose and hemicelluloses. Increased char formation reduces flammable gas formation and helps insulate wood from further thermal degradation, as is observed with *Erythrophleum suaveolens* and *Albizie ferruginea*.

It was also observed (Table 4) that there was a somewhat direct correlation with ignition time and flame duration while an inverse relationship existed with after-glow time and flame propagation rate [17].

CONCLUSIONS AND RECOMMENDATIONS

This study investigated the surface chemistry and thermal degradation pattern of eight Nigerian timbers and the following conclusions could be drawn:

The ratio of lignin to xylan is significantly high for *Erythrophleum suaveolens* and *Nauclea latifolia* while significantly low for *Tetrapluera tetraptera*. These give an indication lignin content of *Erythrophleum suaveolens* and *Nauclea latifolia* is of higher proportion than other wood species.

The syringyl/guaiacyl ratio for *Nauclea latifolia* is the lowest while *Tetrapluera tetraptera* has the highest among all the wood species investigated in this study.

The thermal decomposition of all the selected timbers was in three thermogravmetric steps, except for *Triplochyton schleroxylon* and *Ficus platyphylla* where the last two stages are merged or indistinguishable. Qualitatively, all the eight timbers yielded thermogravimetric responses that are similar.

The bulk of the weight losses (> 55%) take place during the second stage of the second step, i.e. between 300 and 400°C, except for *Albizie ferruginea* having a value less than 45%.

It is also concluded that there is a somewhat direct correlation between peak temperature of degradation, ignition time and flame duration while an inverse relationship exists with after-glow time and flame propagation rate.

Both structural and thermal characteristics suggest that *Erythrophleum suaveolens* and *Nauclea latifolia* would be better lignocellulose substitute resins, as they present higher amounts of lignin and higher thermal decomposition temperature.

REFERENCES

1. Beall, F.C. and H.W. Eickner, 1970. Thermal Degradation of Wood Components: A Review of the Literature, USDA Forest Service Research Paper FPL, pp: 130.
2. Winandy, J.E. and R.M. Rowell, 1984. The chemistry of wood strength, in: R.M. Rowell (Ed.), The Chemistry of Solid Wood, ACS Publication, Washington DC., pp: 211-255.
3. Tshabalala, M.A., 2005. Surface Characterization, Chapter 8 In Handbook Of Wood Chemistry and Wood Composites, CRC Press, pp: 25.
4. Pandey, K.K. and K.S. Theagarjan, 1997. Analysis of Wood Surface and Ground Wood by Diffuse Reflectance (Drift) and Photoacoustic (Pas) Fourier Transform Infrared Spectroscopy, HolzRohWerkst., 55: 383-390.
5. Fabiyi, J.S. and A.G. McDonald, 2011. Physical Morphology and Quantitative Characterization of Chemical Changes of Weathered PVC/Pine Composites, J. Polym. Environ., 18: 57-64.
6. Faix, O., 1991. Classification of lignins from different botanical origins by FT-IR spectroscopy, Holzforschung, 45(Suppl): 21-27.
7. Faix, O., 1992. Fourier Transform Infrared Spectroscopy, In: S.Y. Lin, C.W. Dence (Eds.), Methods in Lignin Chemistry, Springer-Verlag, Berlin, pp: 83-132.
8. Eboatu, A.N. and A.M. Altine, 1991. Studies on the Thermal Characteristics of Some Tropical Wood. Nigerian Journal of Renewable Energy, 12: 49-53.
9. Momoh, M., A.N. Eboatu, E.G. Kolawole and A.R. Horrocks, 1996a. Thermogravimetric Studies of the Pyrolytic Behaviour in Air of Selected Tropical Timbers. Fire and Materials, 20: 173-181.
10. LeVan, S.L., 1989. Thermal Degradation In: Schniewind, Amo P., Ed. Concise Encyclopedia of Wood and Wood-Based Materials, 1: 271-273.

11. Singh, K., M. Risse, K.C. Das and J. Worley, 2007. Determination of Composition of Cellulose and Lignin Using Thermogravimetric Analysis (TGA), 15th North American Waste To Energy Conference, May 21-23, 2007,Miami, Florida, USA. NAWTEC15-3222, pp: 219-226.
12. Sichina, W.J., 2000. Characterization of Polymers using TGA, Thermal Analysis Application note, PETech 78: 1-5. <http://depts.washington.edu/mseuser/Equipment/RefNotes/TGA.notes.pdf accessed on 25/8/2010>.
13. Gasparovic, L., Z. Kerenova and L. Jelemensky, 2009. Kinetic Study of Woodchips Decomposition by TGA.Proceedings of 36thInernational Conference of Slovak Society of Chemical Engineering, SSCHE, May 25-29, 2009, Slovakia.http://kchbi.chtf.stuba.sk /cevoze/doc/kinetic study of wood chips decomposition by TGA.pdf accessed on, 02-04-2011.
14. Pettersen, R.C., 1984. The Chemical Composition of Wood, In: R.M. Rowell, (ed.). The Chemistry of Solid Wood, Advances in Chemistry Series 207, ACS Publication, Washington DC., pp: 57-126.
15. Okoye, N.H., 2012. Flammability Characteristics And Thermal Degradation Of Some Nigerian Timbers. Ph.D Thesis NnamdiAzikiwe University Awka, Nigeria.
16. Fabiyi, J.S., J.A. Fuwape and B. Olufemi, 2011. SurfaceChemistry and Thermo-Mechanical Analysis of Some Nigerian Wood Species. Thermochimica Acta, 524: 80-87.
17. Momoh, M., A.R. Horrocks, A.N. Eboatu and E.G. Kolawole, 1996b. Flammability of Tropical Woods 1- Investigation of the Burning Parameters. Polymer Degradation and Stability, 48: 403-411.