

Potentials of Industrial Utilization of Bark

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Abstract

Forests have provided mankind with strong basis for economic development for centuries. The last century witnessed unprecedented industrial evolution and expansion in the fields of wood engineering and utilization. However, the need to develop bioresources as substitutes to petrochemicals has necessitated gregarious research and development on conversion of wastes such as bark to industrial raw materials. Research and development have shown the potentials of wood bark for the production of adhesives and antimicrobials. Advances have also been made in the use of bark components for production of high value added environmental friendly products in pharmaceuticals, fungicides and plants protection. The use of bark tannins as adhesives in wood based panels is an expanding field that may eclipse the importance of petrochemicals in the nearest future in the wood industry. Advances in other fields are have also demonstrated that barks bioactive compounds can be used as intermediates which can be upgraded to specialty chemicals and compounds.

Keywords: bark, tannins, polyphenols, adhesives, bioresources and petrochemicals.

1.0 Introduction

Forests have provided mankind with important socio cultural and ecological values as well as strong basis for economic development for centuries. The last century witnessed unprecedented industrial evolution and expansion in many fields of wood processing and utilization. Improvements in saw milling equipment led to widespread use of head rigs and edgers as well as thin band saws and other products that opened up possibilities for timber engineering. Also, engineering designs provides for greater security against earthquakes, while advancement in log peeling equipment became the key to the growth of the plywood industry.

While the frontiers of knowledge in wood science and technology expanded considerably and promoted efficiency of forest industries over the years, the development and industrial utilization of bark has taken the back stage. Changing needs for products to meet the needs for daily living in the 21st Century will shape the uses of wood as they have in the past (Wegner et al, 2010). The changing need and uses of wood are driven by social, economic and environmental factors generally beyond the control of forest managers and policy makers (Wegner el, 2010). According to Wegner et al (2010), the driving forces are increasing world population, human needs for packaging furnishing, energy and shelter; the need to mitigate and adapt to climate change; increased competition for global markets; the need to adapt products and uses; shifting demographic patterns and the need to adapt to technological change. Other imperatives are requirements for a better standard of living and to shift the emphasis of desirable properties.

Although, wood technology has advanced considerable over the past century, the development and utilization of wood bark has not enjoyed such tremendous developments. However, the petroleum crises of the early 1970's, coupled with need for climate change mitigation globally, have led to renewed interest in bioresources as industrial raw materials. Also evidence of the unsustainability of large scale petrochemical use in the industry has become insurmountable (Hokkarien, 2012). This has also necessitated increased drive towards more sustainable environmental friendly substitutes. For instance, in laminate production, the use of urea formaldehyde (UF) and melamine formaldehyde resins as hot press adhesives have resulted in some laminates emitting small quantities of formaldehyde and volatile organic compounds (VOCs) (Wiglusz et al 2002; Kim et al, 2007). Many wooden flooring products containing formaldehyde based resins release formaldehyde vapors, thus causing consumers dissatisfaction and health related complaints (Kim, 2009). Various symptoms, among which are irritation of the eyes and upper respiratory tracts are attributable to emission of formaldehyde gases. Also, according to Kim (2009), formaldehyde has been found to produce nasal carcinomas in mice and rats after a prolonged exposure at 14.1 and 5.6mg/L level respectively. Thus, consumer products, especially construction materials are a major source of formaldehyde emission in the indoor environment (Kim et al, 2007; Brown, 1999).

The tree bark which is the term loosely applied to outermost covering of tree stems, is a complex of tissues located outside the vascular cambium and generally includes live and dead cells produced by the cambium. Currently, bark management is a serious residue problem facing the wood conversion industries (Harkin and

Rowe, 1971). The sheer volume of bark that wastes away annually makes the search for industrial outlet for bark a serious source of concern. Among other drivers of this initiative are air pollution regulation and high stumpage prices which is making maximum utilization of forest products a necessity.

At present, emphasis on bark utilization is premised on its chemical composition. The present direction of research and development is expected to create new industries that will boost global economy through conversion of invaluable wastes to valuable assets (Wegner, et al, 2012). This paper examines the properties of bark and their prospects as industrial raw materials. The primary objectives are to highlight the efforts being made to promote efficient industrial application of vast quantities of wood bark that wastes away annually. The prospects and challenges of developing bark for industrial use in Nigeria are also highlighted.

2.0 Bark structure

In order to understand the complexity of the situation, it is important that the structure of bark and its composition be highlighted. The bark comprises the outer part of woody stems and branches (USDA, 1971; Romero, 2012). It includes all plant tissues outside the cambium. More recently, bark is defined as the complex of tissues located outside the vascular cambium and generally includes both live and dead cells produced by the cambium (Romero, 2012). As a result, treating bark as a single entity can obscure important aspects of its biochemistry, physiology, ecology and evolutionary biology (Romero, 2012). Among its many ecological roles, bark covers and protects the vascular cambium of most trees. Inner bark is produced by the vascular cambium, but the protection function of bark as a whole is augmented by cell divisions in the cork cambium (the phellogen). The vascular cambium provides for girth increments in trees. Although the term bast is sometimes used as equivalent of bark or inner bark, it applies more correctly to the lignified fibres commonly found in many bark and other fibrous materials (Harkin and Rowe, 1971). These may account for 35-45% of some inner barks. Bark formation is initiated by the process of cell division in the cambium which produces xylem on the inner woody side and phloem on the exterior side. The phloem tissue contains phloem parenchyma, bast fibres, companion cells and very important sieve cells. The structure of the bark is further complicated by the presence of a second cambial layer within the bark called phellogen or cork cambium. Periderm is produced by this cambium and contributes appreciably to the structure of the outer bark. The innermost layer of the periderm is normally considered to be the boundary between inner and outer bark.

In general, the bark is a highly complex, heterogeneous material composed mainly of a thin, physiologically active inner layer whose principal functions are to protect the cambium and prevent loss of water. However, the structural characteristics of bark are influenced by the proportional representation and distribution of different tissues. For example, granular inner bark usually indicates presence of sclereids. Bark can also be brittle and crumbly due to inclusion of calcium oxalate crystals or stone cells. A more fibrous texture is found in the barks with abundant fibres and with periderms that separates easily. All these influence the industrial utilization potential of the bark.

3.0 Bark composition

Bark differs from all other plant parts in its development, anatomy and chemistry. Chemical compounds found in low concentrations in other plant parts are in some cases highly concentrated in the bark (Young, 1971). Some barks also contain novel substances (Romero, 2012). Vast differences in the nature and amounts of various chemical components and various extraneous materials contained within the bark can be found with even a single species, depending on age and growth site of the sampled tree and the fraction of bark examined (Langenheim, 2003).

Studies on bark chemistry and composition have suffered from two major setbacks. The first is that most investigators of bark chemistry do not specify the bark tissues from which the compounds are derived. As a result, accurate determination of the sites of production and storage of chemical compounds are not available at the level of inner or outer bark. In general however, mineral compounds are up to ten times more abundant in bark than in wood (Romero, 2012). Bark ash contents predominantly made up of calcium, silica and phosphorus have been reported by Jensen et al (1963). Bark extractives can be up to 20-40% of bark mass with most of the remaining components made up of suberin, lignin, lignans and phenolic acids along with non structural carbohydrates. Phenolic acids are mostly found in outer bark cells. Cellulose is the main carbohydrate found in barks. Other sugars present in low concentrations are galactose and mannose while starch is found only in inner bark (Romero, 2012).

Studies have shown different types of compounds extracted from the bark using different types of solvents. Some of these are shown in Table I. The cellulose and hemicelluloses in the fiber portions of bark are largely similar to the corresponding materials in wood. However, extractive-free bark consists of a mixture of true lignin and suberized phlobaphene (cork). Average figures delineating limits for the proximate composition of wood and bark are shown in Table 2. Table 2 also shows that the chemical composition of bark vary extensively than in wood. The high lignin content make it difficult to prepare holocellulose even from well-extracted bark (Harkin and Rowe, 1971). To get the rough estimate of a polysaccharide content of bark, it is best to extract the bark with solvents to remove extractives and then to hydrolyse the residue with acid and determine the monosaccharides formed by measuring their reducing power with copper salts, or as individual sugars using some chromatographic and colorimetric methods (Harkin and Rowe, 1971). Typical barks will produce hydrolysates containing about 60-70%, glucose, 5-15%, xylose, 5-10% arabinose, and 3-4% each of galactose and mannose.

Among bark extractives, polar materials (tannins, polyphenols, glycosides) are generally three to five times as abundant as nonpolar constituents (fats, waxes, terpenes, steroids, etc.). Although bark tissue carefully sectioned out of the bark does not normally contain more inorganic materials than wood, ordinary extractive-free bark is found to contain up to 20 percent ash. This is because wind-borne soil or sand particles are usually trapped in the rhytidome, raising the apparent ash content. Furthermore, bark from logs that are skidded may contain a lot of sand and grit embedded in the bark that can create impressions of high ash contents. According to Romero (2012), proteins and less frequently, single amino acids are stored in the inner bark of some species in concentrations that typically fluctuate seasonally. These substances are translocated from leaves to the bark of some species before leaf senescence. The bark protein increase resistance of some temperate tree species to frost (Siminovitch and Briggs, 1949) and chemical composition of the bark of some species vary as a function of ontogeny, history of disturbance, environmental conditions and the sampling height (Romero, 2012).

4.0 Bark generation and disposal problems

On the average, bark comprised of about 9 to 15% of a typical log by volume or slightly more (13 to 21%) on a dry weight basis (Young 1971; Chamberlain and Meyer 1950). The variation in the bark of five hardwood species growing in Nigeria is shown in Table 3. The table indicated that bark proportion vary considerable between tree species. The bark proportion varies from 7.82% in *Parkia fellicoida* to 13.6% in *Butyrospermum paradoxum*. The total annual production of bark is well above 20 million tons in the United States of America alone (Harkin and Rowe, 1971). In Nigeria bark is used to a lesser degree. The percentage of wood bark utilized is less than 0.05% of total production. Since a major cost of processing any natural material include the cost of collection and transportation, the cost of bark can be considered already paid when wood is harvested and transported to site. These make its industrial utilization increasingly attractive as a potential raw material. Enforcement and stricter environmental policies are also forcing industries to search for new materials that can substitute the current high embodied energy industrial materials. Thus, the environmental and disposal problems created by accumulation of considerable volumes of bark in the forest industry and the increasing scarcity of wood and fibre are forcing industrialists and foresters to consider the utilization of bark as a raw material for the production of higher value products (Kazemi et al, 2009). These developments have heightened research and development on wood bark utilization globally.

5.0 Traditional utilization of bark

Bark has a long history of utility ranging from the Indians' birch-bark canoes to the tapa cloth of South Pacific. Cork, fibre, tannins, dyes, gums, resins, latex materials, food stuffs, flavorings, fish, arrow prisons, antibiotics and medicines are all derived from the bark. Other traditional products obtained from the bark are flavors, cinnamon, anti-malaria drugs, etc, that are being used in rustic societies for health care delivery services.

Apart from the above, there has been several other low-grade utilisation of wood bark. One of the major areas of use is as fuel. This is promoted by the development of heavy duty presses (Trainor, 1968; Bush and Tribble, 1966), and improved multi-fire burners (Harkin and Rowe, 1971). The utilisation of bark for this is purpose is however constrained by its low calorific value. Bark is also used in charcoal production. Bark from mechanical debarkers and slabwood, high in bark content form an important raw material for charcoal production (Dargan and Smith, 1959; Jensen et al. 1963). However, charcoal from bark is more easily crumbled than wood charcoal and contain a higher percentage of fines (Harkin and Rowe, 1971). In addition, various researchers have investigated the use of bark as raw material in the production of wood-based panels such as particleboard,

hardboard and medium density fibre board (Kazemi et al, 2009). In most cases, the mechanical properties of the panels such as the modulus of elasticity, bending strength and internal bond decrease with increasing bark content. Furthermore, bark consists of a high amount of extractives which are principal physical and chemical contributors to surface inactivation and poor wettability by adhesives (Kiaiefarm, 2008).

Despite the above, bark finds one of its most attractive low-grade outlets as a soil conditioner or mulch (Harkin and Rowe, 1971). Bark, especially softwood bark is widely used in horticulture as primary component in most nursery and greenhouse substrates (Bush and Tribble, 1966). However, bark transportation is expensive, thus, limiting bark utilization to a reasonable radius from debarking plants. Among the advantages of bark utilization as mulch is the lower rate of decomposition when compared to wood (Alison, 1965). Hence, it lasts longer as mulch, and has lower nitrogen consumption when incorporated into the soil, thereby, resulting in less nitrogen starvation of crop plants (Harkin and Rowe, 1971).

6.0 Prospects for industrial utilization of bark.

More recently, research and development efforts are being initiated to focus on transforming bark biomass to higher value, eco-friendly industrial products with large market potentials. The major areas of focus are green adhesives and bark-based foams. These bioproducts can be used either as substitutes or replacement for petroleum-based products and help to mitigate climate change. In addition, innovative research in these areas has great potentials to improve forest, chemical and automotive industries operation as well as resulting in higher economic and environmental benefits (BBP, 2011).

Currently, the major focus of application of bark is in production of adhesives. Generally, the utilization of tannin from bark for adhesives production have been proposed by many authors from different countries (Long, 1991; Zhao et al, 1994; Lu et al, 1995; Vazquez et al, 1996; Yakazi, 1998; Ogama et al, 2000). Since the introduction of tannin as a substitute to phenol, in the production of adhesive resins, efforts have been made to improve tannin formaldehyde resin. Efforts by researchers have led to commercial production of resin of low viscosity and with reactivity that equals that of ureaformaldehyde resins. Tannin adhesive resins have been applied in the production of plywood and particleboard and used in gulam, finger, jointing and boat construction. The antimicrobial properties of condensed tannin also make their application in wood composite very attractive (Scalbert, 1991). Tannins are also used as substitute to synthetic resins as a result of their ability to precipitate in the presence of formaldehyde to form a polymer of rigid structure (Goncalves & Lelis, 2000). The reaction of tannins with formaldehyde represents the basis for its role as an adhesive forming polycondensates of high molecular weight (Roffael & Dix, 1994). The reaction of polyphenols with formaldehyde enables its use in the manufacture of wood panels under normal gluing and pressing conditions (Prasetya and Roffael, 1991). According to Cardoso et al (2011), *Pinus caribaea* and *Pinus oocarpa* have the potentials to supply tannins for wood gluing in Brazil.

The key factors for successful utilization of bark for adhesives are polyphenol compound known as tannins and its reactivity to conduct polymerization reaction toward formaldehyde or to form condensation products (Pizzi, 1980; Chen, 1991; Prasetya et al. 1991). However, the extract content of bark depends on wood species, tree ages and position in wood. Generally however, the extractive and tannin contents in bark are higher than those in wood (Fengel 1966, Prasetya 1989).

Cannas (2012) define tannin as any phenolic compound of high molecular weight containing sufficient hydroxyls and other suitable groups (carboxyls) to form effectively strong complexes with protein and other macromolecules under particular environment being studied. Tannin can complex with proteins, starch, cellulose and minerals. They belong to the phenolic class, a group of compounds that are formed via the shikimic acid pathway also known as phenylpropanoid pathway. Tannins have the capacity to transform animal skins and hides into leather. The process is achieved by associating the hydroxyl groups of tannins with the peptide bonds of amino acids present in animal protein, known as collagen (Hasalam, 1966). Besides the tanning action, tannin solutions have other uses among which are manufacturing of tiles and floors, drilling of oil wells, use as dispersants and flocculants amongst others (Poser & Gosman, 1990).

According to Pizzi (1983), the term ‘tannin’ has been frequently adopted to define two different groups of chemical compounds of phenolic nature: hydrolysable tannins and condensed tannins. Hydrolysable tannins can be considered as polyesters derived from glucose. These can be classified as gallotannins, which release gallic acid and its derivatives when subjected to acid hydrolysis and ellagitannins, which on hydrolysis release ellagic and valonic acids (Clifford & Scalbert, 2000). Condensed tannins consist of flavonoid units, known as flavan-3-ols (catechins) and flavan-3,4-diols (leucoantocyanidins) (Pizzi, 1983; Schofield et al., 2001). These prevent

various degrees of condensation and hydrolysis. They precipitate with formaldehyde and hydrochloric acid (Roffael & Dix, 1994). The condensed tannins are most commonly present as polymers, with an average degree of condensation ranging from 4 to 12 flavonoid units.

Tannins give plants their natural ability to defend themselves against their natural enemies. They are responsible for the astringency of many fruits and plants, due, in part, to the complexes formed between tannins and proteins. This forms the basis for some of their biological properties including the control of insects, fungi and bacteria (Scalbert, 1992; Luck et al., 1994; Aerts et al., 1999). Concerned with the action of hydrolysable tannins in herbivores, Guimarães-Beelen et al. (2006) opined that tannins may hamper digestive system of animals as a result of the complexes formed between tannins and proteins involved with the production of digestive enzymes.

Tannins ranged between 2 and 40% of the dry bark of many species (Hergert, 1989). Table 4 shows the acetone/water tannin extractive content of the bark of five wood species growing in Germany. From the table it can be observed that the extraction yield of tannins vary considerable from 6.5% in Eucalyptus to 30.1% in Aleppo pine. The total phenols also vary from 2% in Eucalyptus to 26% in spruce. Thus in order to develop industrial green wood based adhesives, tanning needs to be available in large quantities in tree species. High values may render the product economically viable for industrial utilization when the range of possible applications for tannins is considered. Tannins are most commonly obtained from the wood and bark of certain deciduous trees. They are commonly found in both gymnosperms and angiosperms. In angiosperms, tannins are more common in dicotyledons than monocotyledons. Examples of families of dicotyledons rich in tannins are shown in Table 5. Apart from those shown in Table 5, other important tannin containing plants are *Quercus species* (oak), *Betula sp* (birch), *Salix capera* (willow) *Pinus species* (Pine) and Sorghum species. The bark of *Picea abies* contain up to 15% tannin. Some mangrove species also possess values of up to 35%, and, in the case of the *Quebracho* tree (*Schinopsis balance* Engl.), the tannin content varies between 30 and 35% (Roffael & Dix, 1994).

In some species of pine, polyphenols may appear in the form of phlobaphens. In this form it is highly condensed and insoluble in water. In literature, there are reports indicating that the bark can also contain large amounts of non-phenolic compounds (Dix & Marutzky, 1982). According to Roux et al. (1975), when extracting the bark with weak alkaline solutions in the presence of sulfite and bisulfate, the pyran rings of polyphenols are partly cleaved with the formation and deposition of carboxylic groups and sulfonic acids.

Other uses of tannins are in preservative treatment of fishing nets, the dyestuff industry as cationic dyes (tannin dyes) and also in the production of inks (iron gallate ink). It is also used in the food industry to clarify wine, beer and fruit juices. Tannin is also a popular coagulant in the rubber industry and also used as astringents against diarrhea, as diuretics against stomach and duodenal tumors and as anti inflammatory, antiseptic and haemostatic pharmaceuticals. There has lately been a growing interest in bio adsorbents especially tannin bases adsorbent for removing low concentration of heavy metal ions from aqueous solutions.

More recently, a bark biorefinery project was initiated in Canada as a partnership between forest, chemical and automotive industries and the public sector with the aim of converting green bark into green value added products (BBP, 2011). Research team from the University of Toronto and Lakehead University received funds from the Ontario Ministry of Research and Innovation and equal amounts from the private sector and institutional support that amounted to \$5.26 for research on transforming bark into higher value eco friendly products with large market potentials along two industrial areas which include green adhesives and bark based foams. The project aim at using these products as replacements to petroleum based products for mitigating climate change.

Also ongoing research in Finland has led to identification of agricultural pest control that uses natural compounds from tree bark (Hokkarién, 2012). The control method is expected to change the behavior of the pests instead of killing them. The aim is to ensure that the pests are protected and natural population regulation processes are not disrupted. In addition, work on biotechnological enhancement of bark by specialist fungi appears promising in providing designer composts for several important applications including management and prevention of plant diseases in growth substrates, remediation of soils contaminated with organic and heavy metal pollutants, water retention capacity and slowing down of decomposition which will facilitate and accelerate restoration of vegetation in arid desert conditions (Hokkarién, 2012). Furthermore, the development of new microbial agents based on compounds isolated from birch, pines, spruces larches firs and aspen barks has been achieved. According to Hokkarién (2012), it is likely that the most promising medical applications of the wood bark containing compounds, or their semi synthetic derivatives and analogues will be in the field of antimicrobials. For example, the ForestSpeCs project in Finland has identified derivatives of birch bark terpene

called betulin as compounds that inhibit the growth of parasites that are causative of tropical disease leishmanises. Betulin has also shown promise in the areas of cosmetics as it is a large perfectly white extremely hydrophobic molecule (Hokkari, 2012). The superior antimicrobial activity of plants extracts were also reported by Alizadeh-Behbahani et al (2013). According to Alizadeh-Behbahani (2013), some plant extracts mostly phenolic and terpene compounds exhibit strong antifungal activity against undesirable fungi in foodstuffs during storage period.

7.0 Challenges and prospects for industrial utilization of bark in Nigeria

Currently, bark utilization in Nigeria is limited to mundane applications which include firing of boilers, domestic energy generation and grazing by herbivores. Presently, less than 0.05% of wood bark produced in the country is used. However, a number of ongoing research and development results have shown that polyphenolics can be produced from a number of tree species locally. For instance Nigeria has a vast mangrove forest that is mostly untapped. The mangrove swamps in Nigeria cover a total of 10,000 km² and extend from Badagry in the West to Calabar in the east. They form a 15km to 45km vegetation band along the coast. The mangrove forest constitutes one of the most fascinating resources in tropical Africa (Ajao and Dowe, 1997). It is characterized by three species of *Rhizophora*, namely, *R. harrisoni*, *R. mangle* and *R. racemosa* (Adegbehin, 1993). Two other less abundant mangroves *Avicenni germinans* and *Langucularia racemosa* as well as salt water fern, *Acrostitum aureum* are also present. Mangrove plant extracts have been used for centuries as popular cures for severe health disorders. Mangroves also provides non timber products such as tannins, fish poison and medicines (Bandaranayake, 2002).

As the mangrove trees are major sources of tannins, the potentials for industrial production of tannin in the country is high. Apart from the mangrove species, research and development have indicated that a number of other tree species also have economic quantities of tannin. In a study carried out by Taiwo and Ogunbodede, (1995), the bark of *Khaya ivorensis* and *Avicennea alba* growing in Nigeria were reported to contain 27% and 24% tannins respectively. The performance of the adhesives indicated that the tannins from *A. alba* could replace phenol in synthetic adhesives formulation. Further improvement was attained by incorporation of formaldehyde. Results indicated that the adhesives are best applied at 25°C for 5 minutes (Taiwo and Ogunbodede, 1995).

A number of problems may however constrain development of a viable bark industry in Nigeria. The most important of this is fund. Research and development in Nigeria is highly underfunded and most research personnel are forced by inadequate funding to concentrate on popular areas that may likely attract funding. Another important constraint that may confront industrial bark tannin processing is the few number of trees of the same species. that grows in the same environment in the tropical forests. This may create problems of getting adequate volume of bark from desirable species for industrial processing. To overcome this problem, it may be necessary that plantations of desired species are established for this purpose.

8.0 Conclusion

The climate change problem is a major driver pushing the frontiers of bioresources as industrial inputs forward. This has necessitated the need to find sustainable production systems based on renewable raw materials for use in various sectors of the economy. The forest industry produces huge amount of bark which wastes away. The need to find ways to add value to the rich natural sources of complex organic molecules available in the bark is now a global imperative. A number of research and development work are ongoing which aims at converting the worthless waste to valuable raw materials. A most important of this is the production of adhesives from bark tannin. The commercial uptake of this initiative will reduce dependence on synthetic adhesives. Efforts being made in other directions are also bearing fruits.

In Nigeria, the potential for industrial use of bark is high. Wood based panels production in the country rely solely on importation of adhesives. This is one of the major constraints militating against development of the subsector. For this initiative to work in Nigeria there is need for adequate support for research and development and formulation of policy that will promote industrial bark processing locally.

References

Adegbehin, O.J. (1993). Mangroves in Nigeria. Technical report of the project conservation and sustainable utilization of mangrove in Latin America and African regions. . International society of mangrove Ecosystems, Okinawa, Japan : 135-153

Aerts T.J. , Barry, T.N. and McNabb, W.C. (1999). Polyphenols and agriculture; beneficial effects of proanthocyanidins in forages. *Agriculture, Ecosystems and Environment*. 75:1-12.
[http://dx.doi.org/10.16/S0167.8809\(99\)00062-6](http://dx.doi.org/10.16/S0167.8809(99)00062-6).

Ajao, A.E and Dore, O.P.M. (1997). Conservation and Sustainable utilization of Mangrove forest in Nigeria. In: Kjerfve, B., Lacerda, L.D and Diop, E.H.S. (eds.) *Mangrove ecosystem studies in Latin America and Africa*, UNESCO, France, pp.307-315.

Alizadeh-Behbahani, BF. Tabatabaei-Yadzi, F. ,Shahidi, F. and Mohebbi, M. (2013). The antifungal effect of edible film (CMC) containing an aqueous and ethanolic mangrove plant extract on Citrus pathogens in vitro. *Scientific Journal of Agriculture* 2(1): 47-52.

Allison, F.E. (1965). Decomposition of wood and bark sawdusts in soil. Nitrogen requirement and effects on plants. *USDA Agr. Res. Serv. Tech. Bull. No. 1332*. 58pp

Bandaranayake, W.M. (2002). Bioactivities, bioactive compounds and chemical constituents of mangrove plants. *Wetlands ecology and Management*, 10,421-452.

BB (2011) Bark Bio-refinery Poster. <http://barkbiorefinery.com/about-us.html>

BBP Biofuels and Bioenergy Project (2011). *Natures Biorefineries. Unlocking the green energy potential of our forests*. <http://www.woodutilisation.org>

Bertaud, F., Tapin-lingua, S, Pizz, A. Navarrete, P., and Petit-conil, M.(2012). Characterisation of industrial barks for their tannin contents for further green wood based adhesive applications. *Intechfibres. Research in Fibres*. COST FP0901-20.08.2010-F. BERTAUD-1.

Brown, S.K. (1999). Occuring of volatile organic compounds in indoor air. In Salthammer, T. (ed). *Organic indoor air pollutants, Occurrence and Measurement*. Wiley-VCH, Weinheim, pp 71-184.

Bush, C.C. and Tribble, J.J. (1966). Simultaneous burning of bark and gas or oil. *Tappi* 46(6); 160A-163A.

Cannas, A. (2012). Plants poisonous to livestock. Cornell University Department of Animal Science. <http://www.ansci.cornell.edu/plants/toxicagents/tannin/html>.

Cardoso, M., Lelis, R.C.C., Couuto da Silva, B and Oliveira, G. (2011). Tannin extraction from the bark of *Pinus oocarpa* var *oocarpa* with sodium carbonate and sodium bisulfate. *Floresta e Ambiente* 18(1):1-8.

Chamberlain, E. B. and Meyer, H. A. (1950). Bark volume in cordwood. *Tappi* 33(11): 554-555.

Clifford, M.N. and Scalbert, A. (2002). Ellagitannins-nature, occurrence and dietary burden. *Journal of the Science and Food Agriculture*. 80:1118-1125.

Dargan, E.E. and Smith, W.R. (1959). Progress in charcoal production: continuous residue carbonization. *Forest Prod. J.* 9(12): 395-397.

Dix, B. Marutzky ,R. (1982). Untersuchungen zur Gewinnung von Polyphenole aus Nadelholzrinden. *Holz als Rohund Werkstoff* 41:45-50

Goncalves, C.A. (2000). Utilizacao do tanino de Madeira de mimosa *ceasalpiniaefolia* Bentham (Sabia) como material prima alternaiva para a producao de de adesivos (dissertacao). Seropendica, R.J. Universidade Federal Ruraldo Rio de Janeiro.

Guimaraes-Beeleen, P.M, Berchielli, T.T., Burddington, R. and Beelen, R. (2006). Efeito dos taninos conensados de forrageiras native do semi-arido nordestino sobre o crescimento e atividade celololitica de *Ruminococcus flavefaciens* FDI. *Arquivo Brasileiro de Medicina Veterinaria e Zootecnia* 68(5): 910-917.

Harkin, J.M and Rowe, J.W. (1969). Bark and its possible uses. *USDA Forest Service. Forest Products Laboratory Report FLP-091* 41pp.

- Hergert, H.L. (1989). Condensed tannins in adhesives: Introduction and historical perspectives. In Hemingway, R.W, Conner, A.A, Branham, S.J. Adhesives from renewable resources. Washington D.C: American Chemical Society pp. 155-171
- Hokkanen, H. (2012). The search for renewable raw materials. ForestSpecCs. 50 International Innovation. www.forestspeccs.eu/
- Jensen., W. Fremer, K.E, Sierila, P. and Wartiowaara, V. (1963). The chemistry of bark. In B.L. Browning (ed.) The Chemistry of Wood. Interscience Publishers, New York. Pp587-666.
- Kazemi, n Kiaefar and Tajvidi, M. (2009). Effect of bark flour content on hygroscopic characteristics of wood-polypropylene composites. Wood Science and Technol
- Kiaefarm, A. (2008). Effect of bark content on physical and mechanical properties of wood plastic composites. M.Sc Thesis. Tarbiat Modarres University.
- Kim, J.S, Eom, Y.G., Kim, S., and Kim, H.J. (2007a). Effects of natural resource based scavengers on adhesion properties of formaldehyde of engineered flooring. Journal of Adhesion Science and Technology 21(3-4):211-225.
- Langenheim, J.H. (2003). Plant resins: Chemistry, Evolution, Ecology and Ethnobotany. Timber Press, Portland, Oregon, 586 pp
- Long, R. (1991). Quebracho based polyphenols for use in wood panel adhesives system. Holz Roh-Werkstoff. 49; 485-487.
- Lu, Y. Shi, Q. and Gao, Z. (1995). Thermal analysis and application of larch tannin based adhesive for plywood and hardboard. Holz Roh-Werkstoff. 53; 205-208.
- Luck, G. Liao, H, Murray, N.J., Grimmer, H.R. Warminski,E.E and Williamson, M.P. (1994). Polyphenols, Astrigency and Proline rich Proteins. Phytochemistry. 37: 357-371.
- Ogawa, S. Susanti, CME and Yano, H (2000). Direct utilization of Acacia magnum as bark waterproof adhesives. Proc. 4th International Wood Science Symposium. 182-187.
- Ogunwusi, A.A. (2010). Strategies for Promoting Private Sector Investment in Plantation Establishment in Nigeria. *Nig. Jour. For.* 40 (1 & 2): 8-16.
- Ogunwusi, A.A. (2013). Heartwood, sapwood and bark proportions in five lesser used tropical hardwood species growing in Nigeria. *Journal of Biology, Agriculture and Healthcare* 3(1): 80-83.
- Posser, G.L. von and Gosmann, G. (1990). Acacia-Negra Ciencia Hoje 11(63): 68-70.
- Prasetya, B. and Roffel, E. Neuartige Charakterisierung von natulichen Polyphenolen hinsichtlich ihrer Vernetzbarkeit. Holz als Roh-und Werkstoff. 49:481-484.
- Prizzi, A. (1983). Wood adhesives. Chemistry and technology. New York: Marcell Dekker; 1983.
- Roffeal, E. and Dix, B. (1994). Tannine als Bindemittel fur Holzwerkstoffe. Holz-Zentralblatt 120(6): 90-93.
- Romero, C (2012). Bark ecology. Ecology. Info 34. <http://www.ecology.info/bark-ecology.htm>.
- Roux, D.G. Ferreira, D., Hundt, H.K.L. and Malan, E. (1975). Structure, stereochemistry, and reactivity of natural condensed tannins as basis for extended industrial application. Applied Polymer Symposium. 29;335-353.
- Scalbert, A.(1991). Ant imicrobial properties of tannins. Phytochem. 39: 3875-3883
- Schofield, P. , Mbugua, D.M, and Pell, A.N (2001). Analysis of condensed tannins. A review. Animal Feed Science and Technology. 19:21-40
- Sumin, S. (2009). Environment friendly adhesives for surface bonding of wood based flooring using natural tannin to reduce formaldehyde and TVOC emission. Bioresource Technology 100(2009): 744-748.

Taiwo, E.A. and Ogunmodede, R.A. (1995). Production of tannin adhesives from bark of Nigerian trees. *Wood Science and Technology* 29:103-108.

Trainor, J.W. (1968). Special boilers for waste fuels. *Power Eng.* 72(2): 42-44.

Vazquest, G. Antorrena, G., Gonzalez, J. and Alverrez, J.C. (1996). Tannin based adhesives for bonding high moisture Eucalyptus veneers: Influence of tannin extraction and press conditions. *Holz Roh-Werkstoff.* 54; 93-97.

Wagner, T., Skog, K.E, Ince, P.J. and Michler, C.J. (2009). Uses and Desirable properties of wood in the 21st Century. *Journal of Forestry.* June 2010: 165-173.

Wiglusz, R. Sitcho, E. Nikel, G. , Jarnuszkiewicz, I and Igielska, B. (2002). The effect of temperature on emission of formaldehyde and volatile compounds (VOCs) from laminate flooring. *Building and Environment* 37(1): 41-44.

Yakazi, Y., Morita, S. and Collins, P.J. (1998). Potential use of Acacia mangium bark for waterproof wood adhesives. The 4th Pacific Bio Rim Bio-Based Composites Symposium. Nov. 2-5, Bogor, Indonesia.

Young, H.E. (1971). Preliminary estimates of bark percentages and chemical elements in complete trees of eight species in Maine. *Forest Products Journal* 21:56-59.

Zhao, L., Cao, B. Wang, F. and Yazaki, Y. (1996). Chinese wattle tannin adhesive suitable for producing exterior grade plywood in China. *Holz Roh-Werkstoff.* 52; 113-118.

Table 1: Chemical substances removable by different solvents from tree bark

Solvent	Types of substance removed
Petroleum ether, benzene, chloroform	Terpenes and their derivatives, fats, waxes, free fatty acid wax ether, acids and alcohols, sterols, resins.
Alcohol, acetone, aqueous alcohol, aqueous acetone	Simple polyphenols and their glycosides, tannins, mono- and disaccharides (sugars).
Hot or cold water,	Disaccharides, starch, gums, pectins, tannins, mucilages.
Aqueous alkali	Phlobaphenes, phenolic acids, some bark lignin and Hemicelluloses, suberin fragments.
Acid hydrolysis	Simple sugars and uronic acids derived from holocellulose,

Source: Harkin and Rowe (1971)

Table 2: Proximate Composition of ask Free Wood and Bark (%)

Type of Chemical	Softwoods		Hardwoods	
	Wood	Bark	Wood	Bark
Lignin*(%)	25-30	40-55	18-25	40-50
Polysaccharides(%)*	66-72	30-48	74-80	32-45
Extractives(%)	2-9	2-25	2-5	5-10
Ash(%)	0.2-0.6	Up to 20	0.2-0.6	Up to 20

*Based on extractive-free materials.

Source: Harkin and Rowe (1971)

Table 3: Means, range and coefficient of variation of bark proportions of five hardwood species growing in Nigeria

Species	Statistical parameters	Bark (%)
<i>B. paradoxum</i>	Mean	13.6
	Range	10.38-16.10
	CV	16.4
<i>A. zygia</i>	Mean	10.77
	Range	8.60-12.50
	CV	15.6
<i>L. acida</i>	Mean	11.06
	Range	9.76-12.0
	CV	7.2
<i>P. felicoida</i>	Mean	7.82
	Range	3.84-10.38
	CV	28.90
<i>I. doka</i>	Mean	10.80
	Range	5.88-11.11
	CV	30.91

CV =Coefficient of Variation

Source : Ogunwusi (2013)

Table 4: Characteristics of acetone/water (70/30, v/v) extracts of five wood barks

Tree species bark (g/100 oven dry bark)	Extraction yield	Total phenols (UV 280nm) ¹	Phenolics (FC) ²	Condensed tannins ³
Spruce	26.6	26 ⁺ .1	4,7 ⁺ .1	11,0
Allepo pine	30.1	5 ⁺ .1*	7,5 ⁺ .1	16,6
Douglas fir	22.8	11 ⁺ .1	3,6 ⁺ .1	6,7
Maritime pine	10.2	3 ⁺ .1	0,8 ⁺ .1	1,2
Eucalyptus	6.5	2 ⁺ .1	0,2 ⁺ .1	0,2

¹eq. mimosa tannin ²eq. tannic acid, ³eq. catechine

* after 0.45um glass membrane filtration, Source: Bertaud et al (2010)

Table 5: Families of plant species known for tannins

Families	Species within families
Leguminosae	<i>Acacia species</i> (wattle) <i>Sesbania specie</i> <i>Lotus species</i>
Anacardiaceae	<i>Scinopsis balansae</i>
Combretaceae	<i>Myrobalan</i>
Rhizophoraceae	<i>Mangrove species</i>
Myrtaceae	<i>Eucalyptus species</i> <i>Mirtus specie</i>
Polinaceae	Canaigre

Source: Cannas (2012)

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