Evaluation of Industrial and Thermal Properties of Mangrove Tree (*Rhizophora racemosa*) Tannin on Variegated Wood Waste

Egwunatum, A.E., Ndulue, N.B., Onejeme, U. and Obasi, C.M.

Department of Forestry and Wildlife, Nnamdi Azikiwe University, Awka

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*CORRESPONDING AUTHOR

ae.egwunatum@unizik.edu.ng

ABSTRACT

Poor thermal capacity accompanied with deleterious fumes of nitrogen, sulphur and carbon oxides from sawmill wood wastes has led to its decreased utility as domestic energy alternative with consequent environmental implications during combustion at source. This study was undertaken to assess the effect of red mangrove tannin on the thermal capacity of wood waste as potential industrial material for other wood-based products. Tannin extracted from Rhizophora racemosa (red mangrove) bark with methanol (TBM) and water (TBW) as well as leaves with methanol-water (TLMW) were investigated for pH, specific gravity, viscosity, gelation time, total solid content, stain potential, flash point, cold and warm setting times. These were further employed to produce three (3) single-source tannin flaming balls – TBM, TBW and TLMW as well as composite-source types - TBM+TBW, TBM+TLMW and TBW+TLMW using wood-shavings and dust. Flaming balls were engaged to heat up distilled water for 3, 6, 9, 12 and 15 minutes while temperature attained were recorded respectively. Data collected were analysed using analysis of variance (ANOVA) and significant means separated with Duncan Multiple Range Test (DMRT) at 5% level of probability. The results showed that TBM had highest specific gravity (1.80g/cm^3), pH (7.60) and Viscosity (2.98poise) while the thermal capacity of the wood-waste was composite TBM+TLMW (100.5 ± 0.63^{o}C) >TBM+TBW> TBW+TLMW compared to sole TBM (90.8^{o}C) > TBW > TLMW > CTR (48.1^{o}C) flaming balls. Thus recommends the need of wood-wastes tannin flaming balls as improvement in the energy sector to combat global warming and mitigate climate change in low-income conurbations.

INTRODUCTION

Forest conservation efforts have been significantly threatened by the poor extraction and conversion processes of wood-based industries that has not only given birth to increased traffic in the forest for more exploitation but has also led to abounding generation of wastes to constitute serious environmental menace and pollution in towns and cities. An average of 20-40 tons of wood waste are generated on daily basis as saw dust, particles and chippings from bench mills located in tropical forest communities and towns (MOE, 2017; Babayemi and Dauda, 2010). These local conversion machines have been reported as major causes of waste generation compared to the high precision band-saw equipment with known potential for minimal waste.

However, some of these wood wastes have been engaged in open heating stoves for use in generating energy domestically for cooking (Dubinina *et al.,* 2016; Bourguignon, 2015). The associated gas fumes were reported as detrimental to human health and accounted for a good proportion of respiratory related diseases in the female gender known for preparation of family meals in developing countries (Rinne *et al*, 2006; Khushk, 2005). The poor and prolong heating time as a result of the huge volume required to produce essential heat energy produces large amount of carbon monoxide fumes which have altogether made these sawn wood by-product unappealing. The poor combustion potential of wood waste and dust may not be unconnected with the weak internal bond strength and linkages within the waste particles, particularly in the flakes. Hence at ignition, these often burn singularly as individual fire points with weakened internal bond strength as a result of the disintegration created by the impact of conversion equipment. These poor characteristics therefore result in huge quantities of wood waste employed as domestic heating materials in many rural and semi-urban areas where economic situation does not financially support capacity to acquire kerosene or methane cooking gas.

Consequently, these wastes are abandoned within saw/bench mill premises to initiate eutrophication and many other times burnt at different times of the year to produce varying but significantly offensive oxides of carbon, nitrogen, sulphur, methane and other greenhouse gases (GHGs) as contribution to micro environmental pollution and the global climate change crisis (European Commission, 2014; Khudyakova *et al.*, 2017). The impact of fuel-wood and its allied product on climate change are well documented as singular major contributor to over 30-45% to global warming particularly in developing countries as a result of over reliance on direct use domestically as energy material. Hence, the projected 3.4% increase of the approximately of the 2006 National Population figure connotes further degradation of remnant forest for fuel-wood extraction with commensurate increase in utilization of wood wastes of different origins for domestic energy generation. Therefore, the proper coordination of these wastes through efficient use approach in the light present global climate mitigation practice could go a long way in reducing it as a potential GHGs source.

Tannin have been reported as phenolic natural binders and may therefore induce multiple internal linkages in different grain directions within as well as among the respective particles to sufficiently provide the wood waste external boost unlike the loose individual particles (Basso *et al.*, 2015; Fiori *et al.*, 2013; Gunduz *et al.*, 2011). Hence, its use either exclusively or as combination with urea and phenol formaldehyde resins in the manufacture of interior and exterior wood-based panel products (Von Leyser *et al.*, 2012). This is because its basic characteristics were conformed to the BSI 2020 and ISO 2000 for industrial wood product manufacture. Furthermore, tannin in red mangrove trees species have been reported as the preference to many other wood species for its use in the commercial fish drying scheme because of the attractive colour flavonoids emitted from the wood under increasing thermal conditions (Egwunatum *et al.*, 2022; Nordhaus *et al.*, 2011). It is against this backdrop that tannin from the leaves and bark of red Mangrove (*Rhizophora racemosa*) was characteristically studied as potential industrial materials and source for the improvement of internal bond strength for different wood-wastes in view of efficient thermal qualities with reduced heating time and fume generation to combat global warming *viz-a-viz* climate change.

MATERIALS AND METHODS

Description of study area

The study materials of barks and leaves were collected from the mangrove forest in Koko, Warri North Local Government Area of Delta State, Nigeria. It lies between 6°00′N 5°28′E**.** Koko is the administrative headquarters for the Warri North Local Government Area. The mangrove forest which is particularly rich in *Rhizophora racemosa, R. mucronta* and variety of wildlife species covers an area of over 120 km^2 and provide shoreline protection for the coastal communities while providing valuable forest produce as ropes, fuel-wood, wildlife, timber, etc to sustain livelihood (Aroloye and Numbere, 2020; Mitra, 2020 ;Akanni, *et al*., 2018).

Methods of data collection

The bark was collected from the mid and upper part of the *Rhizophora racemosa* trees by slashing with cutlass and the leaves from the matured lower branches with higher photosynthetic capacity while inside a canoe. The sand was dug from the lower range stilt root region of the mangrove forest.

Experimental materials

The materials used during data collection include

Medium sized hot clay pot; Thermometer; Tannin extract; Variegated wood wastes (sawdust, wood shavings); Heating mantle; Magnetic stirrer; Mortar and pestle; Conical flask; Electric weighing balance; Beaker; Knife ; Water; Consumables as hand gloves, reagents, face shield, etc.

The tannin extraction, industrial characterization of tannin extracts, production of flaming balls and the determination of thermal capacity of the various types of tannin flaming balls were conducted in the Central Chemistry Laboratory of the Faculty of Science, Science Village, Nnamdi Azikiwe University, Awka.

Bark preparation

Fresh barks and leaves were harvested from standing *Rhizophora racemosa* forest in Koko. These were dried under the sun for seven (7) days in order to completely eliminate moisture present in the bark and leaves. Then mechanically grind to produce powder and then stored under room temperature before use in the laboratory.

Tannin extraction

Tannin was extracted from the powdered bark and leaf by method of maceration at 100°C for 130 mins with a solvent-to-bark ratio of 1:4 using methanol and water (50/50) in round bottom flask with a heating mantle as employed by Fuwape *et al.* (1999). These were stirred continuously using a magnetic stirrer until the ground powder samples dissolved in the solvent to allow for sufficient osmosis and diffusion processes.

The solutions were allowed to cool at room temperature for 12 hours after heating and then decanted by filtration into 500 ml beakers using Filter paper No 1 in a funnel. Filtrates were then concentrated for a period of 65 mins and the tannin was allowed to cool at a room temperature before decanted into sample bottles and then stored in refrigerator.

Production of flaming balls

Extracted tannin was used for production of flaming balls. Flaming ball is an improvised fuel source that comprised of sawdust and wood shavings incorporated with liquid tannin using sharp sand as a binder. These were moulded into round balls and then left to dry under the sun for two (2) days. Each flaming ball was constituted of 150 g of wood waste + 100 ml tannin + 25 ml silt-sand. Then, for the production of composite flaming balls, it constituted of 150 g of wood waste + 50 ml of individual composite tannin extract + 25 ml of mangrove silt-sand. These include TBM (Tannin bark extracted with methanol); TBW (Tannin bark extracted with water); TLMW (Tannin leaf extracted with methanol + water); and control (Wood-waste without Tannin).

Experiment with tannin flaming balls

An average of 10 flaming balls per tannin extract type was loaded in aluminium foiled clay-pot upon ignition to generate heat up of 250 ml of water in a beaker from beneath. The heat generated to raise the temperature of water by 1degree Celsius per second ($1^{o}C/s$) at 3, 6, 9, 12 and 15 minutes was estimated as the thermal capacity of tannin flaming balls type. Control treatment consists of wood wastes not impregnated with tannin.

Data analysis

Data collected were analysed using Analysis of Variance (ANOVA) and significant means separated using Duncan Multiple Range Test (DMRT) at 5% level of probability.

RESULTS

Characteristics of extracted tannin

The tannin extract types were compared to the related prescriptions index (RPI) in ISO 2000 for forest product extractives as shown in Table 1. The highest gelation time of 173 mins was recorded by TBW while the lowest time of 135 mins was recorded by TLMW. The TBM recorded a gelation time of 150mins. With respect to viscosity, the TBM record the highest value of 2.98 poise while the TLMW recorded a viscosity of 2.55poise. The least value of 1.86poise was recorded by the TBW. The hydrogen ion [H+] content also ranged as TBM > TBW > TLMW.

The specific gravity was highest for TBM that has a value of 1.80 g/cm^3 while the least (1.31 g/cm^3) was shown by TLMW. The TBW has a value of 1.64 g/cm^3. The total solid was highest for TBM (43.5%) while the least of 28.6% was recorded TLMW. The TBW has a value of 35.4% which also was with the range of ISO 2000 for bark extractives.

Table 1: Industrial characteristics of tannin extract

Tannin Properties	TBM	TBW	TLMW
Gelation time (min)	150.0	173.0	135.0
Viscosity (poise)	2.98	1.86	2.55
pH (H_2O)	7.60	7.20	7.10
Specific gravity (g/cm^3)	1.80	1.64	1.31
Total Solid (%)	43.50	35.40	28.60
Flash point (C)	102.0	180.0	136.0
Stain potential	High	Low	High
Cold setting (min)	30.50	54.30	48.30
Warm setting (min)	90.00	68.00	33.00

Effect of single-source tannin on heating time

The effect of different tannin flaming balls in heating time are shown in Table 2. With respect to 3 min intervals, there were significance difference in the various temperature and heat produced by the different tannin flaming balls ($p < 0.05$). At 180 sec. the highest temperature (30.5ºC) was produced by TBM while the lowest was produced by the control (CTR) at 18.3ºC and there was significance difference. Then, at 360 sec. heating time, the highest temperature was also produced by TBM at 43.6ºC while the lowest temperature was produced by the CTR at 24.5ºC and there was significance difference among them, with regards to the 540 sec. There was significance difference between the heat and temperature produced with TBW flaming balls having the highest temperature of 50.7ºC and also the lowest temperature was produced by the CTR at 26.3ºC, meanwhile at 720 sec; TBW flaming balls also produced the highest temperature of 60.5ºC while TBM and TLMW recorded 50.4ºC and 38.5ºC respectively. The lowest temperature was recorded by the CTR at a temperature of 35.8ºC and there was significance difference.

At the final stage of 900 sec. heating time, there was significance difference in the temperature attained by the various tannin flaming balls. However, there was no significant difference between TBM and TBW flaming balls at temperature of 90.8ºC and 90.3ºC respectively. There was significant difference between TBW, TLMW and the CTR flaming balls.

Table 2: Effect of single source Tannin flaming balls in heating time

		Temp (ºC)		
Time (s)	TBM	TBW	TLMW	CTR (NT)
180.00	30.5^{a}	28.3^{b}	20.8^{c}	18.3^{d}
360.00	43.6^{a}	30.3^{b}	25.3^{c}	24.5^{c}
540.00	48.8^{b}	50.7^{a}	30.3^{c}	26.3^{d}
720.00	50.4^{b}	60.5^{a}	38.5^{c}	35.8^{d}
900.00	90.8^{a}	90.3^{b}	52.4^{c}	48.1^{d}

Mean in the same row with same superscript are not significantly different ($p < 0.05$). Legend: TBM = Tannin bark extracted with methanol; TBW = Tannin bark extracted with water; TLMW = Tannin leaf extracted with methanol + water; CTR (NT) = Wood waste without Tannin (Control)

Effect composite-source tannin flaming balls on heating time

Table 3 showed the effect of combined tannin flaming balls on heating time with respect to 3 min interval heating time. There were significant differences among the various combinations with the TBM + TLMW showing the highest temperature (53.4 ± 0.43ºC) at 3 mins heating time. There was no significant difference between TBM + TBW and TBW + TLMW. There was significance difference among the heating temperature attained, also with TBM + TLMW producing the highest temperature 63.5 ºC at 6 mins. At 9 mins., highest temperature was attained by TBM + TLMW and this also differ significantly from the other combinations (TBM + TBW and TBW + TLMW).

The TBM + TLMW at 12 min recorded the highest temperature of 83.4ºC and was significantly different from TBM + TBW and TBW + TLMW with temperature of 75.3ºC and 58.8ºC respectively. At 15 mins heating time, the highest temperature of 100.5ºC was produced by the TBM + TLMW while TBM + TBW recorded a temperature of 98.1ºC which was also significantly different from TBW + TLMW with a temperature of 67.3ºC.

Table 3: Effect of combined tannin flaming balls on heating time

		Temp (ºC)	
Time (m)	TBM + TBW	TBW + TLMW	TBM + TLMW
3.00	38.5 ± 0.13^{bc}	39.5 ± 0.17^{b}	53.4 ± 0.43^{a}
6.00	48.3 ± 0.34^{b}	41.3 ± 0.29^{c}	63.5 ± 0.56^{a}
9.00	60.1 ± 0.48^{b}	48.8 ± 0.33^{c}	78.1 ± 0.58^{a}
12.00	75.3 ± 0.55^{b}	58.8 ± 0.46^{c}	83.4 ± 0.63^{a}
15.00	98.1 ± 0.73^{b}	67.3 ± 0.49^{c}	100.5 ± 0.63^{a}

Mean ±standard error in the same row with same superscript are not significantly different ($p > 0.05$). Legend: TBM = Tannin bark extracted with methanol; TBW = Tannin bark extracted with water; TLMW = Tannin leaf extracted with methanol + water.

DISCUSSION

Using the ISO and BSI 2000, the gelation time of all the extracted tannin types were with standard specifications except TBW which was above the range of 120 – 160 mins. Apart from the TBW, the TBM and TLMW recorded when they were in consonance with the IS0 2000 range of 2.00-3.00 poise. In line with the ISO 2000, these were all above the standard value, (> 7.00), which in the neutral pH value at a temperature of 24.5˚C. Apart from TLMW with value of 1.31 g/cm^3, the other tannin extract was with the value of ISO 2000 that ranges from 1.50 – 1.90 g/cm^3. The results revealed that the resultant effect of each tannin extract obtained from Mangrove tree parts using different solvents had impact on the thermal properties and heating times investigated with the flaming balls produced with wood wastes. These flaming balls were of much better thermal capacity compared to raw wood waste as shown in the control without tannin

The TBM-flaming balls had a higher differential temperature (30.5ºC at 180 sec.) because it may have generated the greater amount of heat compared to the control with more or less a bulk and higher pore space materials that were not bonded to produce steady heating process (Bello and Adegbulugbe, 2010). The increase in heating time with the tannin flaming ball of TBM had the highest temperature (43.6ºC) compared to the control which produced the lowest temperature (24.5ºC) probably due to the faster combustion of wood.

The TBW-flaming balls at an increased time of 540 sec. produced the highest temperature of 50.7°C and control possessed the least temperature of 26.3°C. This is majorly because of the presence of a phenolic compound in the flaming ball serving as an adhesive hence improving its thermal capacity agrees with the findings of De Ramos *et al*, (2019) on the flammability qualities of phenolic materials of natural origin. The heating time was increased to 720 sec, the best performing flaming ball at this stage was TBW attaining a temperature of 60.5ºC with the least performing flaming ball being control possessing a temperature of 35.8 ºC. This may be due to the passage of conventional airflow within the loosely packed materials. At 900 sec., the most suitable flaming at this time was TBM it attained a temperature of 90.8ºC while control had the least temperature of 48.1ºC.

The TBM+TLMW combined tannin flaming ball warmed up water to attain the highest temperature among the different heating times to reach the boiling point of water in 15mins. Between TBW+TLMW and TBM+TLMW, the former seem to possess better thermal potential. The thermal potential was TBM+TLMW > TBW+T/W > TBW+TLMW flaming balls throughout the investigated heating period. This superior performance may not be unconnected with the capacity of methanol solvent to have extracted significant quantity as well as quality of tannin from the Mangrove bark compared to water, especially with the poor hydrogen ion content during the various stages of maceration in which osmotic potential occurs to create essential gradient for diffusion process to account for higher yield of tannin before a recourse to simultaneously osmosis-diffusion condition.

Although the TBM+TBW flaming balls performed appropriately, the quantity of tannin yield from the mangrove bark may have resulted in the better binding structure of the balls to enhance thermal properties for reduced heating time compared to the yield from the same weight of mangrove leaves. This is because most forest trees species have greater tannin yield as well as chemical quality from the barks compared to other parts the trees (Bianchi *et al*, 2014; Bianchi *et al*, 2016). The ash content of the various flaming balls varied significantly with the TBM+TLMW type producing the least while the TBW+TLMW the highest. This suggested vividly that the capacity of inherent tanning materials as flammable to induce higher combustion rate for heat generation.

The best performing flaming ball with respect to heating time and temperature was the composite flaming balls produced from tannin extracted with water and tannin extracted with methanol, while the least performance were flaming balls without tannin. Also according to Cesprini *et al.* (2020) organic materials with adhesive characteristics often negatively affects nitrogen oxides and other associate gases production during combustion and emissions. Hence, the flaming balls that have tannin adhesive and phenolic qualities are represent great potential as complimentary thermal product for the efficient and eco-friendly use of wood wastes in the face of global warming and greenhouse gases (GHG) for the mitigation as well as adaptation of rural populace to climate change crisis.

CONCLUSION AND RECOMMENDATION

The findings implicated wood wastes made into flaming balls from *Rhizophora racemosa* tannin bark and leaves extracted with methanol as practicable local products with higher thermal efficiencies for generating heat. Thus, significantly projects the enhanced utilitarian value of the abounding sawmill wood wastes as an abatement strategy for carbon and its associated fumes during source disposal by burning and thereby mitigating global warming and climate change. The study further recommends possible use of tannin extracts for forest floor litters in pursuit of better alternative to fuel-wood for reduced deforestation and degradation.

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