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EVALUATION OF COMPOSITIONAL PROPERTIES OF SOME PLANT WASTES FOR INDUSTRIAL APPLICATIONS

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ABSTRACT

Compositional determination of some waste lignocellulosic plant materials were examined for their industrial potential. The results revealed that holocellulose contents ranged from 67.40 % for *Ananas comosus* to 73. 40 % for *Musa sapientum*, alpha-cellulose varied from 50.00 % for *Ananas comosus* 55. 83 % *Musa sapientum, Musa sapientum* had the highest hemicellulose content of 18. 07 % while *Pennisetum purpureum* had the lowest value of 16. 60 %. The total lignin content ranged from 22.98 % to 28.15 %, pentosan content showed that Musa species highest values (*Musa sapientum* 43. 73 % and *Musa paradisiaca* 41.93 %),while *Chromolaena odorata* had the lowest value of 21.07 %. The silica content ranged from 2. 43 % to 2.83 %, ash varied from 5.87 % to 9.1 %, cold water solubility was from 17.00 % to 30.33 %, hot-water solubility was from 18.67 % to 36.33 % and the moisture content was from 6.95 % to 9.90 %. In the face of dwindling and unstable supply of petroleum, the cellulose and hemicellulose could be utilized for biofuel production, while the lignin is vital for various industrial applications.

Keywords: plant-waste, alpha-cellulose, hemicellulose, pentosan, lignin

INTRODUCTION

The ever increasing world population has its attendant problem such as growing demand for energy, which is required to meet human social and economic development. World energy sources are from coal, oil and gas, all these have contributed to increase in carbon dioxide emissions, thus causing global warming (Himmel et al., 2007; Li et al., 2008). Also, the non-biodegradability of petroleum-based products and World regulations to protect the environment, have all triggered strong search for alternatives, that are renewable and available all year round that could replace petroleum based raw materials. According to Dee and Alexis (2011), about 54 % of the annual consumption of oil in the US, could be generated from lignocellulosic biomass and all things being equal, 20 % of the nation's transportation fuel market would be biomass-based by 2030.

Cellulose can be converted to glucose and this sugar can be fermented to produce ethanol or butanol for blending with current transportation fuels (Dee and Alexis, 2011). Chemical functionalization of cellulose can increase the usefulness of cellulose by altering its properties. For example, the worldwide annual production of cellulose ethers is estimated to be over 300,000 metric ton (Schweizer and Sorg, 1995). They exhibit useful properties of thickening, thermal gelation, surfactancy, film formation, and adhesion. Furthermore they are kinetically and thermodynamically more stable and appear easy to prepare and characterize. These characteristics earn them applications in areas such as pharmacy, cosmetics, food, oil drilling, paper, paint, textiles, construction, and adhesives (Davidson, 1980; Whistler and BeMiller, 1973; Nicholson and Meritt, 1985).

Hemicellulose is relatively amorphous and is readily converted to yield fermentable sugars (Niu, 2003; Lee et al. 2009). These can be used directly in polymeric form for novel industrial applications such as biopolymers (Waleed and Ulrike, 2008), hydrogels (Gabrielii, 2000), or thermoplastic xylan derivatives and chemicals such as succinic, levulinic, glucaric, aspartic, sorbitol, xylitol and glycerol (Waleed and Ulrike, 2008; Sun, 2002; Riansa-Ngawong, 2011).

Pentosan is one of the important components of lignocellulose materials and this can be converted to furfural, which as well can be converted to biofuels. The value chains of furanic biofuels are realized in terms of conversion of furfural to different components like example 2-methylfuran, 2-methyltetrahydrofuran amongst others (Dutta, 2012).

Lignin can be processed and utilized for value-added products such as aromatics or valuable phenolic by-products, carbon fiber, activated carbon filters, adhesives, monomeric units for polyurethane, polyesters, bioplastics, and bio-oils, non-viscous organic liquids suitable for blending with conventional fossil fuels (Bonini et al., 2005; Kleinert and Barth, 2008; Thielemans et al., 2002; Xu et al., 2006). Lignin can also be used as a dispersant agent for pesticides, emulsifiers, ion-exchange resins, water treatment agent, pesticide surfactants, heavy metal sequestrant, binders, animal foods, grinding aids, electrolytic refining, and tanning agents, (Hu, 2002; Baker et al., 2007; Ferhan, 2013; Sarkar and Adhikari, 2004).

Chromolaena odorata, Tithonia diversifolia and Pennisetum purpureum are all noxious fast growing aggressive weed plants, often considered a menace due to the danger they pose to crops and forage species as well as their fast rate of invading cleared forest (Sonke, 1997; Ayeni et al. 1997; Ambika and Jayachandra, 2002; Nick and Emmanuel, 2000). Large tons of stalks and pseudo-stems of banana and plantain, and pineapple leaf fiber, (*Ananas comosus)* are generated after harvest. These constitute an environmental menace, when they decay or are burnt (Heslop-Harrison and Schwarzacher, 2007; Ahmed, 2004).

In general, disposing or finding proper utilization for these plant materials is a major problem. Thus, the objective of this study is to determine the chemical composition of these waste plant materials, in order to present them for suitable industrial utilization.

MATERIALS AND METHOD

Plant materials used are pineapple (*Ananas comosus*) leaves, banana (*Musa sapientum*) and plantain *(Musa paradisiaca)* inflorescence flower stems. *Siam weed (Chromolaena odorata)* plant, sunflower (*Tithonia diversifolia)* and elephant grass (*Pennisetum purpureum*) stalks. All the samples were authenticated at the Department of Crop, Soil and Pest Management, Federal University of Technology Akure, Ondo State, Nigeria. All samples were cleaned to remove dust, sand, dirt and contaminations. They were cut into chips of about 2-4 cm, and sun-dried. The samples were milled stored separately in labeled polyethylene bags for subsequent experiment.

All the material were analyzed for ash content (T221om-93), silica content (T244om-93) ,one percent sodium hydroxide solubility (T212om-98), ethanol- benzene extractives (T204om-97), acid-insoluble lignin (Klason Lignin) (T222om-98), acid-soluble lignin (UM250), preparation of extractive free sample (ASTM D1105-56), holocellulose (ASTM D 1104-56), alpha-cellulose (ASTM D1103-60), pentosans (Al-Showiman, 1998) and Hemicellulose content (%) = holocellulose – alpha-cellulose)

RESULTS AND DISCUSSION

The result of the compositional properties of the six plant materials used in the study are presented in the Table below.

Ash content

The ash content which represent the inorganic substances such as silicates, sulfates, carbonates, or metal ions (Rydholm, 1965), ranges from 5.87 % - 9.1 %. The highest ash content was found in *A. comosus* (9.1 %) and *M. sapientum* had the lowest value (5.87 %). All these were within the range values expected of non-wood fiber. All these values were less than 16.6 % reported for rice straw (Tutus et al., 2004), 4.5 % - 9.0 % for wheat and 6.0% to 8.0 % for Esparto (Finell, 2003). Also, 6.9 %, 3.44 % and 11.8 % are reported respectively for mid-rib, pseudostem and stalk of *M. paradisiaca* (Ogunsile et al., 2006). Eroglu et al. (1992) reported 8.0 % for *T. diversifolia* stalk. Though, the ash contents recorded in this study are within the range expected of non-woody plant. There would be need for pre-hydrolysis of the plant materials to reduce the ash before pulping. This is necessary to reduce the interference of the inorganic elements with the bleaching chemical such as H_2O_2 which could lead to decomposition of the chemical (water and oxygen) thus causing chemical wastes.

Table: Compositional Properties of the Raw Material

Parameter (%)	*Chromoleana odorata*	*Musa sapientum*	*Pennisetum purpureum*	*Anana comosus*	*Musa paradisiaca*	*Tithonia diversifolia*
Ash	$6.37^{c} \pm 0.06$	$5.87^{a} \pm 0.06$	$8.87^{e} \pm 0.15$	$9.1^{f} \pm 0.10$	$6.1^{b} \pm 0.10$	$6.9^{d} \pm 0.10$
Silica	$2.43^{a} \pm 0.06$	$2.37^{a} \pm 0.06$	$2.43^{a} \pm 0.15$	$2.83^{c} \pm 0.06$	$2.47^{a} \pm 0.06$	$2.63^{b} \pm 0.06$
Pentosan	$21.07^{b} \pm 0.06$	$43.73^{f} \pm 0.12$	$17.61^{a} \pm 0.06$	$24.38^{c} \pm 0.12$	$41.93^{e} \pm 0.06$	$34.60^{d} \pm 0.12$
Ethanol-benzene	$2.03^{b} \pm 0.06$	$3.58^{f} \pm 0.03$	$2.05^{c} \pm 0.05$	$1.88^{a} \pm 0.03$	$3.40^{e} \pm 0.00$	$2.50^{d} \pm 0.00$
Acid-soluble lignin	$20.22^{a} \pm 1.00$	$22.00^{b,c} \pm 1.00$	$24.00^{d,e} \pm 1.00$	$25.00^{e} \pm 1.00$	$21.00^{a,b} \pm 1.00$	$22.97^{c,d} \pm 1.00$
Acid-insoluble lignin	$2.76^{c} \pm 0.10$	$2.32^{a} \pm 0.16$	$2.79^{c} \pm 0.90$	$3.15^{d} \pm 0.11$	$2.95^{c} \pm 0.35$	$2.51^{b} \pm 0.05$
1%soda solubility	$30.08^{d} \pm 0.38$	$26.00^{c} \pm 0.05$	$34.02^{e} \pm 0.03$	$43.67^{f} \pm 0.29$	$25.47^{b} \pm 0.03$	$23.98^{a} \pm 0.03$
Holocellulose	$70.60^{d} \pm 0.20$	$73.40^{a} \pm 0.20$	$69.60^{e} \pm 0.20$	$67.40^{f} \pm 0.20$	$72.60^{b} \pm 0.20$	$71.60^{c} \pm 0.20$
Alpha cellulose	$53.83^{b,c} \pm 0.29$	$55.33^{a} \pm 0.29$	$53.00^{c} \pm 0.50$	$50.00^{d} \pm 0.87$	$55.00^{a,b} \pm 0.90$	$54.00^{b,c} \pm 0.86$
Hemicellulose	$16.67^{a,b} \pm 0.35$	$18.07^{b} \pm 0.35$	$16.60^{a} \pm 0.70$	$17.40^{b,c} \pm 0.40$	$17.60^{b,c} \pm 0.11$	$16.90^{b,c} \pm 0.15$

Values are means of three replicate ± standard deviation. Row means followed by different letters are significantly different at $P < 0.05$.

Silica

The result of the silica content showed that *A. comosus* had the highest value of 2.83% and *M. sapientum* with least value of 2.37%. The highest content of silica in *A. comosus* could be as a result of plant's biological transport system, which allows easy movement of silicic acid to the plant fiber, because of its closeness to the ground (Lanning et al., 1958; Rafi and Epstein, 1999; Epstein, 1999). The result obtained was comparable with that of other authors for example, Bagasse had 2.10 % and Bamboo, 1.40 % (Tyagi et al., 2003). Katri (2001) reports 9-14% for rice straw, barley 3-6%, rye 0.5-4%, sisal less than 1 %, bagasse 0.7-3 % and bamboo 1.5- 3%. The differences in the silica contents between plant materials could be related to photosynthetic mechanism and the amount of water being transpired by the plant (Black, 1971). The silica contents recorded for the plant materials in this study are within the range of those of non-woody plants. Therefore, the reported results indicate the suitability of these plant materials for pulp and paper, and cellulose isolation for industrial usages. This is because the problem caused by extremely alkali soluble silica in inhibiting proper chemical recovery process after pulping would be prevented.

Ethanol-benzene solubility

The results of the ethanol-benzene solubility range from 1.88 % to 3.58 %. The ethanol-benzene solubility is a measure of waxes, fats, resins, oils, tannins, gums and other soluble materials in plant matter. The result showed that the *Musa* species has high ethanol-benzene content with *M. sapientum* having 3.58 %, followed by 3.40 % of *M. paradisiaca* and *A. comosus* having the lowest value of 1.88 %. The ethanol-benzene content of plant material could be affected by seasoning and drying method (T204om-97). The results obtained in this work are low compared to that reported for some other non-woody plants; Ates et al. (2008), reports 3.76 % for *P. elongota*, Eroglu et al. (1992) has 7.0 % for *T. diversifolia*, 9.5% for corn stalk (Usta et al. 1990), while 8.2 % and 12.8 % are reported for mid-rib and pseudostem of M. *paradisiaca* (Ogunsile et al., 2006). Kamoga et al. (2013), reported silica values ranging from 5.14 % to 17.36 % while working on some grasses and leaves. Meanwhile the obtained results in this study were higher than 3.0 % for cotton stalk (Kirci et al. 1998) and 2.3 % for stalk of *M. paradisiaca* (Ogunsile et al., 2006). From the pulp, paper and cellulose utilization point of view, all the plant materials in this study would be good and preferable materials for industrial products, cellulose and pulp utilization for food packaging products, because their low ethanol- benzene extractive contents would not allow the taste and odour that high extractive material will impact on food stuff.

1% Sodium hydroxide

One percent NaOH (1% NaOH) extractive indicates the amount of low-molecular–weight carbohydrates consisting mainly of hemicelloses and degraded cellulose. It indicates the degree of fungus decay or degradations by heat, light and oxidation (Sharma et al., 2011). The results varied from 23.98 % (*Tithonia diversifolia*) - 43.67 % (*Anana comosus*). Also, the high 1 % NaOH value of *Anana comosus* might be due to the fact that the plant leaves are very close to the ground allowing microbe activity even before harvesting. The moderate to high value of 1% NaOH extractives indicates that the raw material needs proper drying and good storage conditions to prevent fungus decay or degradation by heat and light after harvesting. Agarwal et al. (2011), reports that plant materials with 1 % NaOH solubility of 29.5 % would produce good fiber material for pulp and paper production. This means *Musa sapientum, Musa paradisiaca, Chromolaena odorata and Tithonia diversifolia* would be suitable for pulp and paper. The NaOH extractives results in this study are within the range of values reported for most non-wood materials like *H. Cannabinus* (25.8 %), *chenopodium album* (30.00 %) (Dutt et al., 2012), lemon grass 30.64 % (Harjeet and Dharm, 2013), sunflower 50.00 % (Lopez et al., 2005) cotton stalks 39.60 % (Kamoga et al., 2013) and tobacco stalk 42.00 % (Shakhes et al., 2011) and lower than that of wood like *eucalyptus grandis* 17.9 % (Shakhes et al., 2011) and *Pinus nigra arnold ssp* 13.0 % (Kamoga et al., 2013).

Pentosan

The pentosan results showed that all the plant materials in this study would be good sources of industrial chemicals via pentosan and furfural routes. The pentosan results revealed that *M. sapientum* has the highest pentosan content 43.73 %, followed by *Musa paradisiaca* (41.93 %), *T. diversifolia (* 34.60 %), *A. comosus* (24.38%), *C. odorata (*21.07%) and *P. purpureum* (17.61%). The high pentosan content of *Musa* species could be as a result of their being fruit-bearing plants with high carbohydrate content, which could be converted to pentosan. The pentosan reported here was within the range reported by other scientists. Finell (2003) has reported 23-28 % for rice, wheat 26-32 %, sugar cane 27-32 % and 15-26 %. Likewise, Tyagi et al. (2003), reported 23.90 %for *Eulaliopsis*, 23.86 % for Bagasse and 18.30 % for Bamboo. Also, hemicellulose which pentosan reflects has been known to contribute to the strength of paper pulp (Agnihotri et al., 2010). Therefore, high pentosan contents of all the plant materials used in this study would be suitable for pulp and paper production.

Lignin

It is observed that the acid soluble-lignin content of the plant materials varies from 20.22 % (*C. odorata)* -25.00 % (*A. comosus),* while the acid insoluble-lignin varies from 2. 51 % (*T. diversfolia)* - 3.15 % (*A. comosus).* The combined total lignin content ranges from 22.98 % (*C. odorata) to* 28.15 % (*A. comosus).* All the obtained lignin contents are within the satisfactory level (< 30 %) (Kamoga et al., 2013). The significance of this is that these plant materials in practice, would need milder pulping conditions (lower temperature and chemical charges, mild pulping liquor) to reach a satisfactory kappa number with appropriate tensile,burst and tear strength, and minimal carbohydrate loss (cellulose and hemicelluloses). This low lignin content would also assist in quick bleachability of the materials with less chemicals and good brightness. The lignin values obtained in this work were in the range of values that had been reported for non-woody plants, 20.5% is reported for *P. elongota* (Ates et al., 2008), Eucalyptus 23.30% (Ayata, 2008), bamboo 24.5% (Deniz and Ates, 2002), coniferous 25-32% (Eroglu, 1998), bagasse 23-32 % (Rowel, 1997). Furthermore, these plants materials may be a source for lignin that could be utilized for industrial purposes, since most have above 25.00 % lignin.

Holocellulose

The hollocellulose represents the total content of carbohydrate materials and high holocellulose content is desirable for pulp and paper and other allied industries, because it correlates with a higher pulp yield. The result revealed that Musa species had the first and second highest values; *M. sapientum* (73.43 %) and *M. paradisiaca* (72.60 %), followed by *T. diversifolia* (71.60 %), then *C. odorata* (70.60 %), after that *P. purpurem* (69.60 %) and lastly *A. comosus* (67.40 %). On the average, the holocellulose obtained in this research work was comparable to those of other researchers Ates et al. (2008) have reported 75.74 % for *P. elongota*, 70.50 % for bamboo (Deiz and Ates, 2002), rye straw 74.1 % (Usta and Eroglu, 1987), *T. diversifolia* stalk 77.6% (Kirci et al., 1998), 67.6 % for tobacco stalk (Usta et al., 1990) and Mokhtar et al. (2005) reports 75.20 % for pineapple leave. The total carbohydrate content obtained from this study is an indication that the plant materials fibers would be able to withstand processing condition, have good physical properties if used for paper (Crowell and Burnett, 1967). The results of holocellulose contents are also an indication of the industrial potential of the plant materials as good sources of industrial chemicals.

Alpha cellulose

The alpha-cellulose content in *M. sapientum* (55.33 %) is higher than *M. paradisiaca T. diversifolia*, *C. odorata,* P. *purpurem,* and *A. comosus* (55.00 %, 54.00 %, 53.83 %, 53.00 %, and 50.00 % respectively). The high content of alpha-cellulose in the *Musa* species could be attributed to the fact that the inflorescene flower stems from where the cellulose was extracted acts as seed/fruit carrier. This has the need for strong fibre for it to be able to carry the banana and plantain seed until maturity, thereby the need to store up more cellulose. According to the rating system designated by Nieschlag et al. (1960) plant materials with equal or higher than 34 % α-cellulose content were characterized as promising raw material for pulp and paper manufacture from a chemical composition view. According to this categorization, all the studied plant materials are promising sources of alpha-cellulose. Literature has shown that the result obtained for alpha-cellulose for the various plant materials in this work were in the range as expected for non-woody plants. Mokhtar et al. (2005) in their research work reported 57.20 % alpha-cellulose for pineapple leaves as against the 50.00 % reported in this work. While Ogunsile et al. (2006), reported 53.07 %, 48.01 % and 40.80 % respectively for mid-rib, pseudostem and stalk of *Musa paradisiaca*. Our research work reported 55.00 % for *Musa paradisiaca* inflorescene stalk and 55.33 % for *Musa sapientum* inflorescene stalk. Eroglu et al. (1992), reports 37.4 % for *Tithonia diversifolia* stalk, Gumuskaya and Usta, (2006) reports 63.77 % for Hemp, and Eucalyptus has 50.17 % (Ayata, 2008). The high cellulose content inherent in these plants are essential for chemical functionalization of cellulose, pulp and paper production, biotransformation and chemical transformation into biofuels and value-added bio-based products.

Hemicellulose

The hemicellulose content varied from 16.60 % (*Pennisetum purpurem*) - 18.07 % (*Musa sapientum)*. These hemicelluloses are worth exploiting and can be used directly in polymeric form for novel industrial applications such as biopolymers (Ebringerova, et al., 1994), hydrogels (Gabrielii et al., 2000), or thermoplastic xylan derivatives (Jain et al., 2000) or, once hydrolyzed, they can serve as a source of sugars for fermentation to fuels, such as ethanol, or chemicals, such as 1,2,4-butane-triol, a less hazardous alternative to nitroglycerine (Niu et al., 2003).

CONCLUSION

The compositional analysis of the various waste plant materials showed that they would be good sources of cellulose. The cellulose would be suitable for producing paper of various grades and cellulose functionalization in producing various cellulose derivatives. The high hollocellulose content is an indication that industrial chemicals and fuel could be produced using those materials, while the high pentosan content is a pointer that furfural which could serve as chemical precursor for different industrial useful chemicals, is abundantly available in those materials. Lignin can be extracted from these plant materials for adhesive, fuel, and other lignin based chemical production. . These materials are considered as waste and are not beneficially utilized but end up being burnt, but their compositional analysis could provide channels for their proper utilization.

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