Isolation and Evaluation of Horse Grass Fiber (*Andropogon tectorum*) for Lignin Production

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Abstract

The aim of this study is to Isolate and purify lignin from non-wood cellulosic biomass (Horse grass fiber) by methanol/water pulping method. The Horse grass fiber was pulped by varying the time of cooking 30, 60, 90, and 120min with 1:3 methanol/water at 105^{0}C. Isolated lignin was purified to remove impurities and characterized by Fourier transform infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA) analysis to compare thermal properties and chemical composition. It was found that lignin obtained from methanol as a solvent mixed with water 1:3, at 105°C for 1h provided the highest yield of the same sources, most thermally stable and purity. With the above characteristics it is concluded that horse grass is another good sources of lignin production.

Key words*- FTIR, HCl, Horse grass, Lignin, Methanol, TGA, XRD.*

1.0 INTRODUCTION

Horse grass (*Andropogon tectorum*) is widely available in Nigeria, which occupied more than 10 thousand hectares from each state across Nigeria [1]. Lignin is aromatic, a binding agent and not a constitutional defined compound coniferous wood source or from non-woody sources like bamboo, raffia palm, bagasse, straw and grasses. These structural differences between carbohydrate and lignin of lignocellulosic biomass serve as criterion for their separation. [2]. Lignin is the most abundant aromatic organic compound on earth. It is generally accepted that lignin binds together the holocellulose components of lignocellulosic biomass and is capable of been dissolve away from them because it is thermoplastic, this process is facilitated by the presence of chemicals (inorganic or organic) [3]. Lignin is considered as an inegral part of the wood and is highly valued in service. Lignin contents in different woods range between 25-35% in softwoods and 18-25% in hardwoods while, non-wood fibers contain between 5-23% lignin [4]. The black liquor after pulping usually containing dissolve chemicals and lignin derivatives, which was widely regarded as waste products, which usually discharged as waste products or burnt off for energy recovery purpose [5]. Lignin-derived compounds have some application as alternative to fossil fuels. The phenolic ring inside lignin has been proved to be effective precursor adhesive resin in particle boards [6, 7]. Because of its importance in pulp and papermaking, several advances have been made towards its removal during pulping processes. It is only in pulping and bleaching that lignin is more or less released in degraded and altered form [8]. Some of these include the use of 75% sulphuric acid (Klasson lignin method), the use of solvents like sodium hydroxide or in conjunction with sodium sulphide (sodium lignin method) and recently, the organosolv pulping process represents an alternative to traditional pulping methods, such as alkaline kraft and acidic sulfite chemical pulping [9]. The ease of delignification of the material during the chemical pulping process can be estimated from lignin content [10]. Kraft method, cellulolythic enzyme method, technical isolation method, klason method and organosolv method had been applied in the isolation of lignin component from black liquor. From the above methods, organosolv method have shown considerable better solubility and thermal stability [3, 11]. Many analytical methods have been used to investigate the interactions between the molecules and characterized the functional group present in lignin [12, 13]. The aim of this work is to use methanol/water for extraction of lignin from horse grass, document the properties of lignin obtained and compared compare them to other non-wood sources.

2.0 Materials and methods

Materials

Fresh samples of Horse grasses *(Andropogon tectorum)* were collected from Adekunle Ajasin University Boys hostel at Ikare Akoko, Ondo State, Nigeria. Horse grass was air dried; the air dried samples was chopped into 2-4cm was selected as raw material in this study. All chemicals used were of analytical grade.

2.1 Methanol-Water Treatment

The chopped raw materials (20 g) were placed in an Erlenmeyer flask of 1L capacity and mixed with the required amount of Methanol/water. A mixture of organic solvent (Methanol/water mixture 1:3 by volume) was added to the biomass in the flask at a fiber to liquor ratio 1:8. Then it was cooked in autoclave at 105^{0}C for 30min, 60min, 90 min and 120min. After each cooking time, flask and its content was allowed to cool to ambient temperature. Fibers were filtered in a Buchner funnel and washed with 25% Methanol/water mixture followed by hot distilled water.

2.2 Isolation and purification of lignin

After cooking, waste liquor was separated from the pulp by filtration. The methanol-water lignin in the solution from black liquor was precipitated by addition of 20% HCl to pH$_2$ and then filtered and the precipitates was filtered in a buchner funnel. Finally, the precipitate lignin was washed with distilled water and vacuum dried P_2O_5.

2.3 Characterization

2..3.1 Fourier Transform Infrared (FTIR) spectroscopy

FT-IR was used to determine the chemical structure of obtained lignin. The measurement of the resulting lignin was taking using Shimadzu FTIR 8400s equipped with MIRacle™ ATR. It was scan in the range from 4000-500 cm^{-1} with resolution of 4cm^{-1}.

2.3.2 Thermogravimetric analysis (TGA)

TGA curves were obtained by the use of a thermogravimetric instrument. Thermal behavior of the preparations was obtained by recording the TGA curves in the range 25 to 900^{0}C under conditions of nitrogen atmosphere using weighed samples in the range 10 to 15mg, at 20^{0}C min^{-1}

3.0 Results and Discussion

3.1 Lignin yield

Lignin contents in different woods range between 25-35% in softwoods and 18-25% in hardwoods while, non-wood fibers contain between 5-23% lignin [4]. Lignin is considered as an integral part of the wood and is highly valued in service. It is only in pulping and bleaching that lignin is more or less released in degraded and altered form [8]. Because of its importance in pulp and papermaking, several advances have been made towards its removal during pulping processes. Some of these include the use of 75% sulphuric acid (Klasson lignin method), the use of solvents like sodium hydroxide or in conjunction with sodium sulphide (sodium lignin method) and Now adays, the organosolv pulping process represents an alternative to traditional pulping methods, such as alkaline kraft and acidic sulfite chemical pulping [9]. The ease of delignification of the material during the chemical pulping process can be estimated from lignin content [10]. Lignin yield was calculated by comparing the amount of lignin precipitated with 20% HCl from the black liquor after removal of organic solvents with the total amount of purified lignin present in the horse grass.

Fig. 1: The yield of lignin obtained from methanol-water extraction

Time (min)	30	60	90	120
% lignin yields	51.08	68.30	66.10	66.35

The results from Table1, showed the experimental results, that methanol-water treatment of horse grass with 1:3 methanol-water for 30min cooking time released 51% lignin, 60 min cooking time released 68%, 90 min cooking time released 66% and 120min cooking time released 66% of lignin. The maximum lignin yield was obtained by use of methanol-water at 1:3 for 1h.

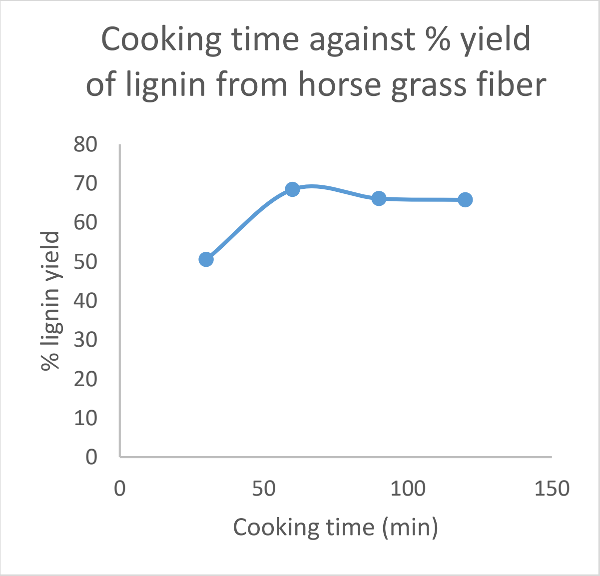

Fig. 2: shown the results of cooking time against the percentage yield of lignin from horse grass fiber

It was showed from fig2, that increased in residence time has no effect on the lignin yield after 60 min cooking time. It can be seen from fig2 that there was significant change in extraction yields of lignin for 30min and 60min, but there is decline in lignin yield with 90 min without any differences in 120 min yield. Obviously, between the extraction times 30 and 60min extraction yields of lignin were increased from 51% to 68%, respectively. Approximately all of the total lignin were separated during the methanol-water extraction at 60min duration. This implied that methanol-water extraction time is a main parameter affecting the lignin yields under the conditions used, this is in agreement with [14]. The lignin yield results were higher than the value of lignin isolated from wheat straw using hydrothermally pretreated method and also higher than ionoSolv pretreatments of Miscanthus and pine yield as reported [15, 16]. The results were comparable with lignin isolated for Poplar wood chips and also comparable to the lignin yields of acetone–IL pretreatments Miscanthus and pine as reported [11, 15]. The result also shown that the residence time play significant role in lignin removal from horse grass, this may be attributed to the more biomass sample is dissolved with subsequent precipitation in solvent [15, 17].

3.2 Fourier Transform Infrared (FTIR) spectroscopy

The results of the lignin analysis using FT-IR, for sample of 30min, 60min, 90min and 120min is presented in fig3, the FTIR spectra of the lignin isolated from horse grass with different time interval were similar, with only slight different from methanol/water at 105^0C for 60 min. This similarity can be attributed to fact that the lignin isolated were from same sources, the slight difference noticed in spectrum from methanol/water at 105^0C for 60 min, at the 2900-2800 cm^{-1} region can be attributed to its high methyl (−CH3) and methylene (−CH2) groups, to other time interval (Satoru and Hikaru, 2015). The purpose of the functional group analysis is to know the functional groups present in lignin from the isolated lignin products used. The bands at 2800 cm^{-1} correspond to methyl (−CH3) and methylene (−CH2) groups. The phenolic OH groups in lignin at band 1367 cm^{-1}, are produced during chemical process when β-O-4 linkages are cleaved and generate non-etherified hydroxyls [12]

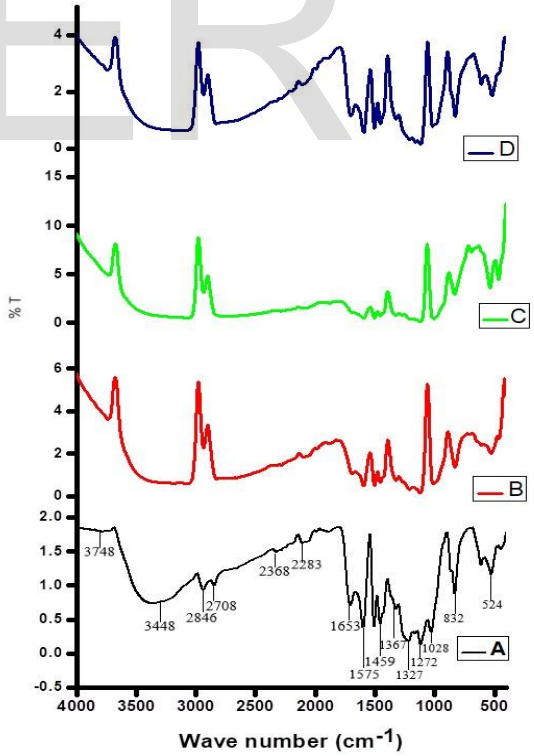

Fig.3: FTIR spectra of horse grass lignin powders (wavelength 4000 to 500 cm^{-1}). (A), Methanol/water for 60 min (B), Methanol/water for 90min (C), Methanol/water for 120min and (D), Methanol/water for 30min

High intensity of this band in 60 min spectrum shows that large portion of phenolic OH group is generated (due to less β-O-4 linkage cleavage), while the low intensity of this band in (30, 90 and 120min) spectrum shows that small portion of phenolic OH group is generated (due to less β-O-4 linkage cleavage). The absorption band range 1028 cm^{-1} show high intensity in the lignin isolated from horse grass spectra (30, 60, 90 and 120min) from fig3, above is assigned to deformation vibration of C−H bonds in the guaiacyl ring and also assigned to C-O bonds in both syringyl and guaiacyl according to [14]. Bands at 1327 cm^{-1} were attributed to syringyl with C-O stretching [18]. The presence of absorption bands at wave numbers with a strong intensity of about 1272 cm^{-1} in the horse grass lignin suggests the presence of guaiacyl which are the units in lignin constituents in non-wood lignin [19]. The lignin from Methanol/water for 60 min was the best and most purely isolated.

3.3 Thermogravimetric analysis (TGA)

Fig4 illustrates the thermograms of lignin obtained with 1:3 methanol-water from extraction time of 30min, 60min, 90min, and 120min. Fig4 shows the TGA curves for pyrolysis of the horse grass lignin studied. As shown in the thermogravimetric curve, the thermal degradation of both lignin proceeded over a wide temperature range from approximately 180 °C to 900 °C. This can be attributed to the fact that lignin contains many aromatic rings with various branches with different activities of its chemical bonds and functional groups [16, 20]. In the first degradation stage between 30-100 °C the weight loss was less than 7% and can be mainly attributed to the loss of moisture mainly water present in the samples [14]. After the first weight loss, the degradation process is slower between 110-180 °C and the main degradation process for both lignin occurs at around 180 °C, for horse grass a plateau can be seen in this temperature range.

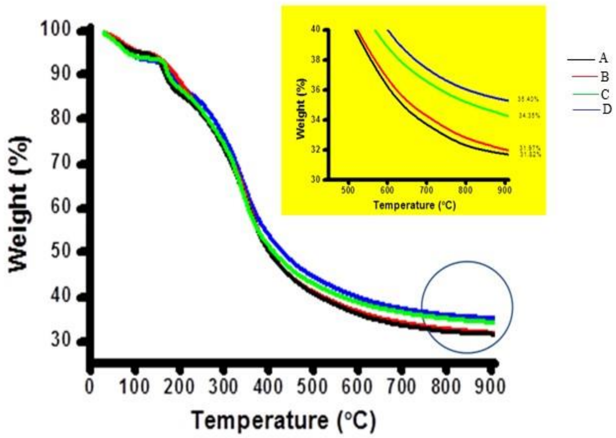

Fig. 4: TGA curve of horse grass lignin powders (temperature 0 to 900^{0}C). (A): Methanol/water for 60 min; (B), Methanol/water for 90min (C), Methanol/water for 120min and (D), Methanol/water for 30min.

The second stage of decomposition, which happened to be the main lignin degradation process occurs between 180-500 °C; as shown in figure3 showed a remarkable drop in weight of the sample due to rapid thermal decomposition of inter-unit linkages, releasing monomeric phenols into the vapor phase [21, 22]. The third stage, after 500^{0}C, the weight loss is less important than the second period due to the steady decomposition of some aromatic rings in lignin [23, 24]. The degradation of lignin from methanol/water for 60 min was faster than the others shown as it inserts at the top of figure3. The maximum thermal degradation rate of (30, 60, 90 and 120min) lignin occurred at 343, 352, 347 and 344^{0}C, respectively. The lignin obtained from methanol/water for 60 min required higher temperature of (510^{0}C) to reach complete degradation, the high thermal stability may due to formation more condensed polymeric structures in its composition, at 800°C almost 50% of all lignin samples still remain non volatilized due to the formation of highly condensed aromatic structures according to [22].

4.0 Conclusion

Lignin extracted with Methanol-water (1:3) at boiling temperature (105^{0}C) for 60 min produced highest yields of organosolv lignin (68%). The FTIR spectra shows the homogeneity in the chemical structure of extracted lignin samples with treatments of organic solvents. In addition, the difference in residence time of isolating the lignin samples from same sources was seen to affect the thermal properties. In overall, lignin extracted with residence time 60 min possess the highest thermal stability; crystallinity and is the most purer sample. These characteristics demonstrate the suitability of horse grass for lignin production.

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