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THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL INVESTIGATION OF RICE HUSK CELLULOSE

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ABSTRACT

A Cellulose isolation from rice husk waste was achieved through subjecting the bulk waste to a sequence of chemical processes and treatment. The rice husk cellulose was characterized using FTIR and thermal analysis. Investigation of the thermal decomposition of the cellulose sample was carried out using the technique of thermogravimetry (TGA) and differential thermal analysis (DTA). The FTIR chart displayed characteristic peaks typical of cellulose moiety at 3386, 2899, 1632, 1318 and 1159 cm^{-1} . The TGA curve showed the decomposition pattern of the cellulose with the onset temperature at around 275 °C and decomposition continuing up to 380 °C. The DTA showed inflection point determined by extrapolation at 380 °C. The range of thermal stability of this moiety provides requisite information for the choice of reaction procedure for the modification/functionalization of the cellulose.

Keywords: Cellulose, Thermogravimetric analysis, Differential thermal analysis, Rice husk, Agro-waste

INTRODUCTION

With the world cellulose consumption at about 95.6 million tons in 2015 and global demand expected to reach USD 36,968.8 million by 2020 (Researchandmarket, 2016), Nigeria with her enormous bioresource potential is placed at advantage to be a major player in this economic fortune of the cellulose market. However, at the moment, neither Nigeria nor any country in sub Sahara Africa is found on the map of world cellulose producers (Durbak, 1993). This is at a time the world is discouraging wood and other economic plants as bioresources. Cellulose is an organic substance abundant in plants with wide range of applications. Cellulose can be converted to several derivatives which result in increased application (Mench, *et al.*, 1966; Heck, *et al.*, 2004; Heinze & Petzold-Welcke, 2012). There are several known sources from which cellulose have been derived, these include wood (Kenyazera *et al.*, 2008), cotton (Frick Jr & Robert, 1982), sugarcane bagasse (Sun, *et al.*, 2004; Abdel-Halim, 2014; Li & Ge, 2012; Liu, *et al.*, 2007), rice straw (Das, *et al.*, 2014; Kalita, *et al.*, 2015), corn straw (Ping, *et al.*, 2013; Kumar, *et al.*, 2014), soyabean husk (Uesu, *et al.*, 2000), non-edible fruit and seed (Meireles, *et al.*, 2012; Achor, *et al.*, 2014), banana stem (Omotosho & Ogunsile, 2009) and etcetra Auyo and Kafin Hausa communities in the Hadeija Emirate council of Jigawa state are

major rice and sugarcane producers and qualifies Jigawa as a top rice producing state in Nigeria(Olawale, 2018). This partly account for the launch of the Dangote outgrower scheme by the Dangote Food Limited in conjunction with the Jigawa state government's Responsible Agricultural Investment (RAI) in the area. The scheme is expected to start with 20,000 hectre of rice cultivation to be expanded to 800,000 hectares over three years years(Committee, CDF II Technical, 2016; Dangote, 2016).

Today, the Danmodi Rice milling factory is unarguably the biggest producer of processed rice grain in this 'rice belt' within Jigawa state and arguably one of the biggest in Northern Nigeria. Information obtained locally at the factory in Kafin Hausa, reveals that rice husk (RH) has a wide application in agriculture, where it served both as manure and animal feedstock. A mixture of finely divided rice husk and dried fish serve as poultry feed. It is used as bed layer as elevation for storing bagged rice, millet, corn, and other agricultural products because it can not be attacked by termite and other harmful insects. Rice husk is also used in heating and in local construction, RH mixed with clay soil is used in the building of mud houses.

These local applications of RH in Kaffin Hausa and environ have been replicated elsewhere and this have served as a driving force behind several scientific investigations globally.

The research findings of the constituents of RH which is mainly cellulose and silicate material (Stefani, *et al.*, 2015), has helped to justify the various roles played by RH in agriculture, construction, energy, etcetra. Lignin and cellulose have for instance been found to have a significant biological role in the nutritive value of animal feeds (Crampton & Maynard, 1937). Cellulose therefore serve as a substance with potential application in the food, pharmaceutical, energy, construction, and especially have the great advantage of generating several other chemical feedstock with source from agrowaste. Isolation of RH cellulose for organic, inorganic and organometallic derivatization and nanonization of cellulose as well as their applications in energy; such as biofuel, fine chemical feedstock, drug delivery, water purification, catalysis, oil spill and general environmental remediation and etcetra are all current trends in the exploitation of cellulose from agricultural waste (Keshawy, *et al.*, 2013; Hubbe, *et al.*, 2012; Filho, *et al.*, 2015; Saliba, *et al.*, 2000; Kamel, *et al.*, 2008).

A great chunk of RH is treated as waste and with Government effort toward self sufficiency in rice production, we expect a larger volume of this waste in the very near future. In several ways this waste is harmful to the environment. Proper handling of rice husk waste can yield cellulose, lignin and other products that are of immense benefit (Ramiah, 1970; Stefani, *et al.*, 2015). The main interest of this work is the derivatization of inorganic/organometallic cellulose which can have useful application in phase transfer catalysis and biological chemistry as drug carriers. However, the current work is aimed at isolating cellulose from rice husk obtained from Danmodi Factory, characterise the cellulose using FTIR, thermogravimetry and differential thermal analysis.

MATERIAL AND METHODS

Reagents and solvents – potassium hydroxide, hydrochloric acid, and sodium metabisulfite were all analytical reagent grade, sodium hypochlorite was obtained as Jik (3.5 % m/v sodium hypochlorite) by Reckit Benckiser (Nig) Ltd.

Thermal analysis – thermogravimetric analysis and differential thermal analysis was carried out using Perkin Elmer, TGA 4000 thermogravimetric analyzer. 20 mg of cellulose sample was heated from 30 °C to 950 °C under nitrogen flow at 10 °C/min.

FTIR spectra was recorded using a Agilent Cary 630 FTIR spectrometer. The spectrum was collected from 4000 – 650 cm^{-1} at a resolution of 8 cm^{-1} with an accumulation of 10 scans.

Preparation of crude sample

RH was obtained as bulk waste from Danmodi Factory, the RH was washed thoroughly under running tap water with continuous stirring. After washing, the RH was air dried. The dry material was milled. The powder was passed through 100 mesh size sieve and stored in plastic containers.

Extraction of Cellulose

20 g of RH powder in 250 mL of 3 % (w/v) of KOH was stirred and left to boil for 30 minutes with continuous stirring. The mixture was then left to stand overnight then filtered and the residue was washed twice with distilled water and 100 mL 10 % (v/v) HCl was added. The organic part retained in the residue which contain cellulose was treated with sodium hypochlorite 0.7 % (w/v) at a ratio of 1:50 g solid /mL liquor at pH 4 and kept boiling for 2 h. the solid was further treated with 5 % (w/v) sodium bisulphite solution at room temperature for 1 h using a solid to liquor ratio of 1 g/50 ug and then washed with distilled water and dried at 80 °C in the oven. It was then treated with 17.5 % (w/v) of NaOH solution at room temperature for 8 h using a solid to liquor ratio of 1 g/50 mL, washed and dried at 80 °C (Stefani, *et al.*, 2015; Brendel, *et al.*, 2000).

RESULTS AND DISCUSSION

FTIR Analysis

A white insoluble dissolving pulp was obtained. The alpha cellulose displayed characteristic vibrational absorbance at 3386, 2899, 1638, 1318, and 1159 as shown in the spectrum of the RH cellulose in figure 1, the bands are generally associated with cellulose moiety and is very useful in cellulose identification (Sun, *et al.*, 2004).

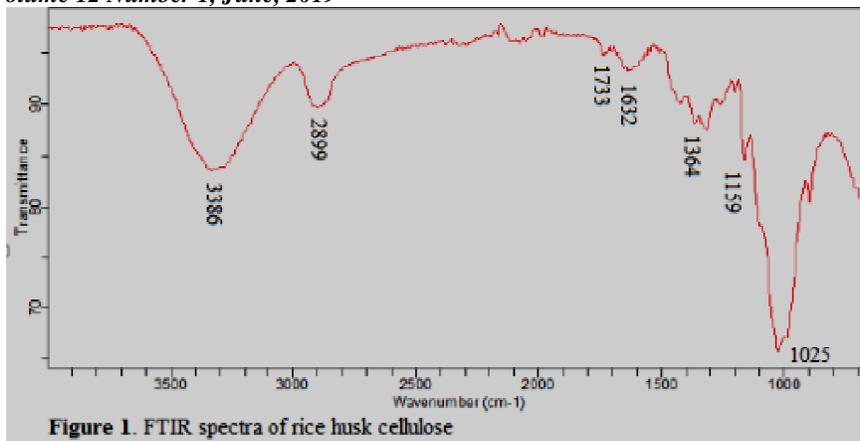


Figure 1. FTIR spectra of rice husk cellulose

The peak observed at 1632 cm⁻¹ is assigned to OH bending vibration of absorbed water, this is typical of cellulose. The hydroxyl and C-H of methylene group stretching vibrations are displayed at 3386 cm⁻¹ and 2899 cm⁻¹ respectively. The peak at 1364 cm⁻¹ is assigned to the asymmetric vibration of the methylene group. The peak at 1733 cm⁻¹ corresponding to vibrations of acetyl and uronic ester groups is identified as hemicellulose band. The presence of this band indicates that the procedure for the cellulose isolation did not effectively eliminate hemicellulose. However, the absence of absorption bands from 1500 – 1595 cm⁻¹ in the spectra indicate the successful dewaxing process, assuring total removal of lignin.

Thermal Analysis

The thermal analysis was carried out using a TGA 400 thermogravimetric analyzer. The TGA/DTA analyzer can be conveniently used for the investigation of the thermal behavior of cellulose. RHC has been reported to show major thermal decomposition peak of the cellulose at around 362 °C (Stefani, et al., 2015), just as native sugarcane bagasse cellulose is reported to start thermal decomposition at 245 °C at 50 % weight loss with the major decomposition at 339°C (Liu, et al., 2007). The extrapolated onset temperature (T₀) for the TGA curve of the RHC for the current work is 270 °C as displayed in figure 2.

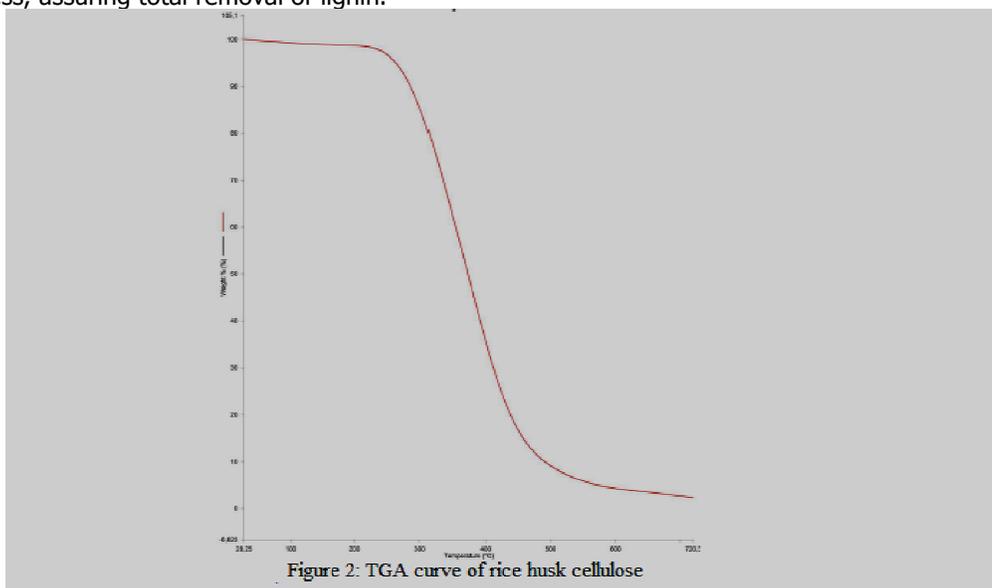


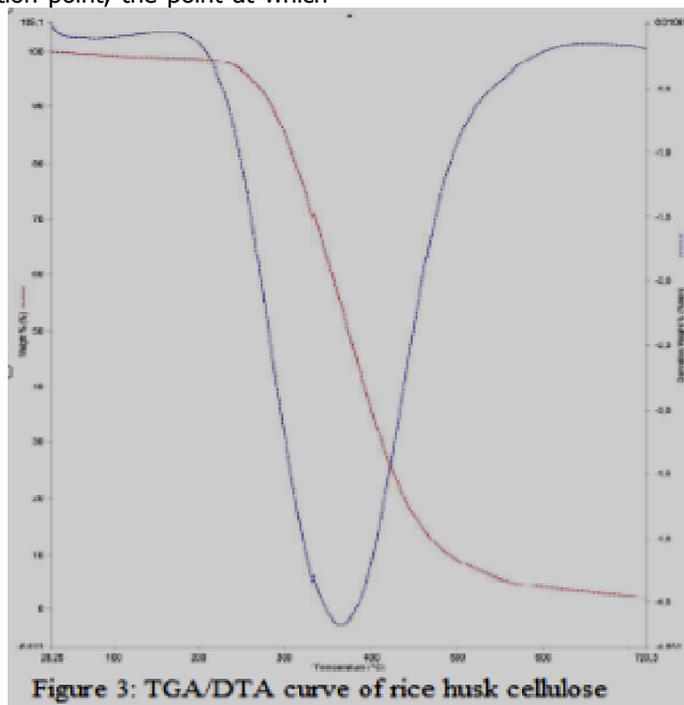
Figure 2: TGA curve of rice husk cellulose

It can be observed that there is a significant mass loss at around 275 °C with mass percent of 92 % reaching around 380 °C at 54 % weight loss. The extrapolated onset temperature is reproducible and specified to be used by the ASTM
The DTA/TGA curve of the RHC (figure 3), shows a weight loss around 100 °C

corresponding to vaporization of absorbed water which could not be given off completely on drying (Ramiah, 1970), it further displayed a deep endotherm around 380 °C corresponding to the rapid mass loss, as in the TGA curve ascribed to the decomposition of the cellulose polymer.

This is the first derivative peak temperature (T_p) calculated during the thermal analysis, it indicates the inflection point, the point at which

the greatest rate of change on the weight loss curve in figure 3 occurred.



This observation is in agreement with earlier report that cellulose decomposition usually start at around 275 °C and continue up to 380 °C (Stefani, *et al.*, 2015). The complete decomposition at below 400 °C, further prove the complete delignification process as lignin decomposition would have tailed up to around 550 °C. The exclusion of air in the analysis guaranteed a non-oxidative atmosphere which would have given rise to pyrolysis products and hence generate a complicated thermogram useful only for reaction studies (Akita & Kase, 1967).

CONCLUSION

Cellulose modification before now is largely via grafting/copolymerization without necessarily dissolving the solid or making use of the expensive ionic liquid (Marsh, *et al.*, 2009) or other environmentally unfriendly solvents such as pyridine (Malm, *et al.*, 1957). More recently, cellulose dissolution have been achieved by the use of aqueous mixture of alkali hydroxide and urea (Gu, *et al.*, 2007; Isogai & Atalla, 1998). Synthetic functionalization of cellulose and cellulose derivatives through this environmentally friendly route require a good knowledge of the thermal property of the cellulose material to help in

making the correct choice of reaction protocol. This is quite necessary since unnecessary heating can easily destroy the chemical nature of cellulose; and possibly jeopardising the dream of making cellulose material a material of choice for deriving fine chemicals. With the detailed information now available on the thermal behaviour of cellulose derived from rice husk waste in Kafin Hausa, Nigeria, further efforts can now be made at solubilizing the moiety and making useful derivatives out of it.

Though not fully characterized, the high yield of inorganic silicate product separated during this isolation is a pointer to the danger rice husk waste might portend to agricultural practices in this community. However the positive implication explains why the waste is useful in fortifying clay soil for local building construction purposes.

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