IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 13, Issue 3 Ser. II (March. 2020), PP 36-41
www.iosrjournals.org

Production of Nanocellulose – Based Gel Fuel for Domestic Heating Using Pride of Barbados Pods (POBPS) and Corn Cobs (CC) Agro Wastes

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Abstract: *Nanocellulose material was extracted from Pride of Barbados pods and Corn cobs agro waste materials and used as a gelling agent in the production of gel fuel. The gelling capacity, quantity and physicochemical properties of the nano material was determined using X-ray diffraction (XRD) and X – ray fluorescence (XRF). Ultraviolet and Visible Absorption Spectroscopy (UV-Vis) was used to determine the nano particle size nature of the cellulose while Fourier Transform Infrared Spectroscopy(FTIR) was used to ascertain the degree of purity of extracted Nanocellulose material that is devoid of contaminants like lignin, hemicellulose and other extractive. The Scanning Electron Microscope (SEM) was used to visualize the surface morphology. SEM images show that both Agrowaste contained abundance and long fibers. The use of the Nanocellulose from agro wastes in gelling the fuel will further reduce the overall cost of producing the fuel which will be providing an economically cheaper alternative heating material to fossil kerosene.The absence of characteristic peaks at wavelength of 1734 and 1509 cm*^{1} *for lignin, hemicellulose indicates the effective extraction of those contaminants from the agro waste material.*

Keywords: *Pride of Barbados pods, Corn cobs, Agrowaste, fuel gel, Nanocellulose, Domestic heating*

Date of Submission: 12-03-2020 Date of Acceptance: 27-03-2020

I. Introduction

Domestic energy use generally refers to the energy used in a household, and the supply depends on factors such as the standard of living in the country, climate, the type of residence, age of the occupants and literacy level [1,2,3,4]. Energy for domestic purposes is determined by two major factors: availability and affordability. This implies that energy must be readily available and the price must be within the reach of the people especially the poor. Making energy available to all and sundry in a particular society is a measure of level of economic development of that particular society. For example, in advanced economies like UK, USA and France, majority of their population have access to cheap and affordable energy supply because they are technologically advanced. The necessary energy infrastructures are available while the costs of energy are affordable by the majority of the people.

Energy is a basic necessity of life for meeting domestic, social and industrial needs [5]. Adequate and regular energy supply for industrial and domestic purposes are prerequisites for keeping socio-economic life moving. Energy is required at all times for meeting various purposes especially at the household levels. Life becomes difficult and meaningless without the availability of adequate and regular energy supply.

The reverse is however the case with people living in low income country like Nigeria, where the purchasing power of large proportion of the populace is low while necessary energy infrastructure are not in place. Thus, majority of the people do not have access to energy sources of their choice. In addition, there is lack of adequate energy infrastructure and adequate energy supply. This further compounds the problems of energy availability. Overall, most of the developing nations do not have access to cheap, reliable and environmentally friendly energy sources.

Huge amounts of agricultural wastes are produced in many countries of the world. However, only a fraction of these materials are reused [5]. These agricultural wastes which are biomass related materials can serve as source of domestic energy. Most developing countries use biomass energy for cooking. Report from different research groups indicates that the potential of biomass energy in Nigeria is very high [6,7,8]. The use of biomass related materials for domestic energy use in Nigeria due to unavailability and high cost of modern energy services has been reported by various authors [9,10,11,12,13,14].

The advantages of biomass energy if used in a sustainable manner, forms a reasonable part of the carbon cycle through arboricultural management or coppicing. Unsustainable use of biomass has antecedent problems hence harnessing biomass energy need to be done in a sustainable manner in order to reap its immense benefits. Majority of Nigerians do not have access to energy sources of their choice due to unavailability and high cost of energy supply. Overall, most Nigerians especially those in less economically developed states like Nasarawa Satate do not have access to cheap, reliable and environmental friendly energy sources, thus there is over dependence on the use of wood, charcoal, crop residues and untreated coal for cooking which has serious negative consequences on both people and environment. This is because fuel wood, charcoal, agricultural residues, animal dung and saw dust all produce high emissions of carbon monoxide, hydrocarbons and particulate matter which are agents of air pollution and global warming. Hence, there is need for scientific investigation into production of bio-friendly, efficient, available and affordable heating fuel.

II. Materials and Methods

Sample Collection

Pride of Barbados Pods (POBPs) and Corn Cobs (CC) were the agro– wastes selected for this study. POBPs were collected from the premises of Nasarawa State Polytechnic Lafia while CC were collected from local farms at Lafia. The samples were air dried, cut, and grinded and sieved to the desired size [15].

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Preparation of White Liquor

Five hundred and ninety five (595) g of sodium hydroxide (NaOH), 17.5 g of sodium sulphite (Na_2SO_3), 35 g of sodium sulphate (Na_2SO_4), and 87.5 g of sodium carbonate (Na_2CO_3) was weighed into a plastic water bath containing 5.250 L of water. The mixture was stirred continuously until the chemicals completely dissolved in the water. Then, 175 g of sodium sulphide (Na_2S) was weighed into the mixture and stirred to dissolve completely and give a solution referred to as white liquor **(Plate 1.1) [15]**.

Extraction of Nanocellulose

A 700 g of the cut sample was weighed into a stainless steel pressure pot **(Plate 1.2)** and 4900 mL of the white liquor was measured into the stainless steel pressure pot. The pressure pot with its content was covered and heated until the sample was completely pulped. During the heating process, the content (sample) of the pressure pot was checked intermittently to know when the sample was completely pulped **(Plate 2.1)**. POBPs and CC were pulped for 9.5 and 3 hours respectively [15].

Plate 1.1: White Liquor Stirred and White Liquor is being Poured

Plate 1.2: Sample inside the Pressure Pot

Plate 2.1: Pulped Agro – waste Still inside Black Liquor

Plate 2.2: Washing of Pulped Sample to Remove the Black Liquor

After the pulping, the black liquor was decanted off from the sample. The sample was thoroughly washed with borehole water to remove the black liquor **(Plate 2.2)**.

In a 2 L reagent bottle, the pulped sample was completely immersed in 0.5 M sulphuric acid (H_2SO_4) until the sulphuric acid is about 2 cm above the sample. The reagent bottle and its content was kept for 24 hours and then washed thoroughly with borehole water. After thoroughly washed, the sample was sieved with a cloth sieve to remove excess water.

The hydrolysed sample was ground with borehole water using a grinding engine **(Plate 3)**. The sample was ground repeatedly till fine granules were obtained. After grinding, water was removed from the sample using a cloth sieve. The sample was then air dried for 24 hours before being oven dried at 50 ^{O}C. The dried sample was ground to a powder with mortar and sieved to a desired size using cloth sieve. The sieved sample was stored in a clean container for laboratory analysis and compounding of gel fuel.

Plate 3: Grinding the washed hydrolyzed pulped sample

III. Results and Discussion

Fourier Transform Infra – Red (FTIR) Spectra Analysis

The translucent sample disk used in the FTIR spectra analysis was prepared by encapsulating 30 mg of finely ground sample in 300 mg of KBr. The FTIR spectra was recorded using Shimadzu – 8400S Fourier Transform Infrared Spectrometer (FT – IR) over the spectra range of 4000 – 500 cm^{-1}with a resolution of 4 cm^{-1}. This was carried out at the National Research Institute for Chemical Technology (NARICT) Zaria.

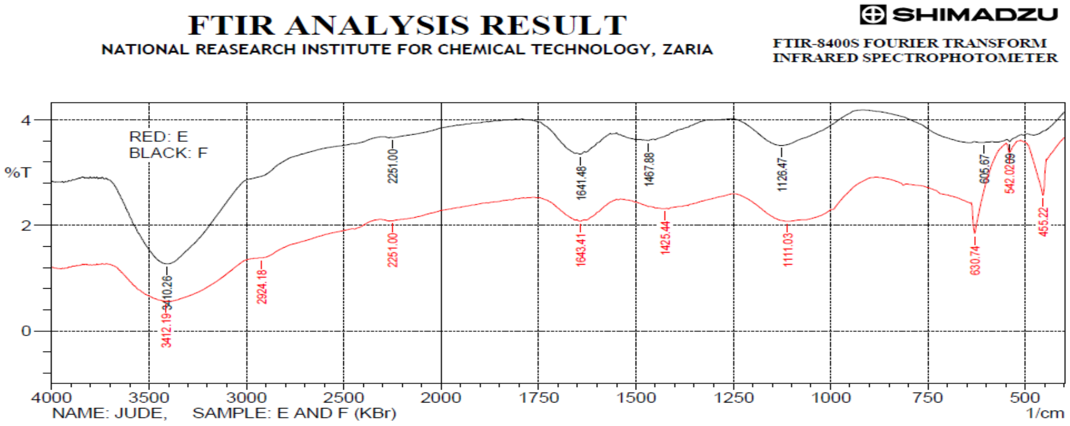


Figure 1: FTIR Spectra for Raw [Red (E) Spectra] and Nanocellulose [Black (F) Spectra] POBPs

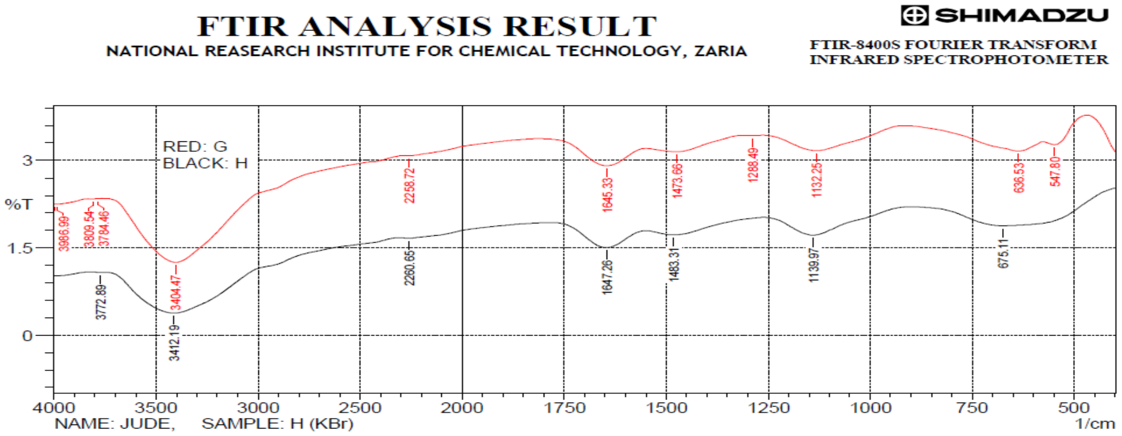


Figure 2: FTIR Spectra for Raw [Red (G) Spectra] and Nanocellulose [Black (H) Spectra] Corn Cobs **(CC)**

Fourier transform infrared (FT-IR) spectroscopic analysis was used to study the surface chemistry of the raw and Nanocellulose POBPs and CC. It can be seen from Figures 1 and 2 that FT-IR spectra of the Raw and Nanocellulose for each have different frequencies. These Figures show that there was a significant change in structure upon pulping and hydrolysis processes. The high intensity and sharp peaks observed in the samples, may be due to the high crystalline nature of the products.

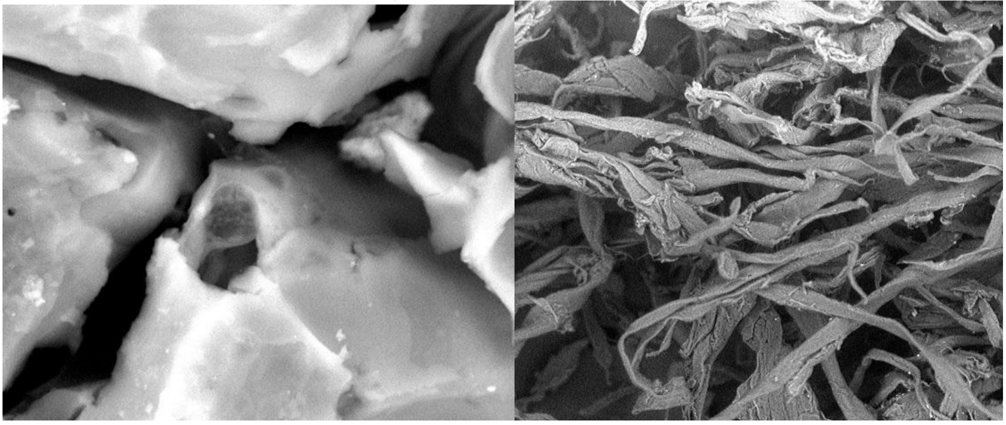
Table 1: FT-IR adsorption band for the nanocellulose

S/N O	Group frequencies (cm^{-1})	Observed frequencies (um)				Functional Group
		POBPs RAW	POBPs Nano	CC Raw	CC Nano	
1.	750-350	416.64; 514.05; 616.28; 720.44	432.07; 529.48; 651.96; 732.97	429.18; 600.85; 683.79; 745.51	585.42; 685.75	C-H
2.	1250-750	914.29; 1007.84; 1166.97	848.71; 1073.42; 1167.94	839.06; 919.11; 1057.03; 1158.29	758.05; 901.75; 1076.32; 1187.23.	C-O Stretch; CH_3 Symmetric deformation; N-O
3.	1750-1250	1369.50;1449.55; 1588.43	1256.67; 1383.97; 1608.69; 1692.59	1293.31; 1384.94; 1452.45;1594.22	1267.27; 1357.93; 1654.98	N-N bend; C≡C Stretch; C=C Stretch
4.	2500-1750	2270.29	1876.80	1784.21; 1880.66; 1970.35; 2265.47; 2389.88	1892.23; 2469.93	N=N=N, Anti Symmetric Stretch; C≡N; -PH; C≡N
5.	3500-2500	3421.83	2513.33; 3047.63; 3238.59; 3366.86; 3442.09	2809.41; 3109.35; 3457.52	3357.72	O-H Broad; O-H Stretch; -NH Stretch; ≡CH-H Stretch
6.	4500-3500	3997.60	4132.63	3687.05; 3774.82		O-H Broad; O-H Stretch; -NH Stretch; ≡CH-H Stretch

The FTIR spectra (Fig. 1) of the POBPs and CC (Fig.2) for both Raw and Nanocellulose showed broad bands at a range of 3446-3281 cm^{-1} corresponding to -OH and –COOH stretching vibrational frequencies. However, the disappearance of these bands in the Nanocellulose (POBPs (D) and CC (F)) is due to the fact that the organic functional groups existing in these agro wastes are transformed into carbon phases with highly-porous structural properties leaving behind carbon. It was also observed that all the samples had group frequencies of 350-750 with functional groups of C-H; group frequencies of 750-1250 with functional groups of C-O stretch, $-CH_2$ symmetric deformation, N-N; group frequencies of 1250-1750 with functional group N-N bend, C≡C stretch, C=C stretch; group frequencies of 1750-2500. Raw POBPs had no frequency but the other samples had with functional groups of N=N=N anti symmetric stretch, C≡N, PH, C≡N; group frequencies of

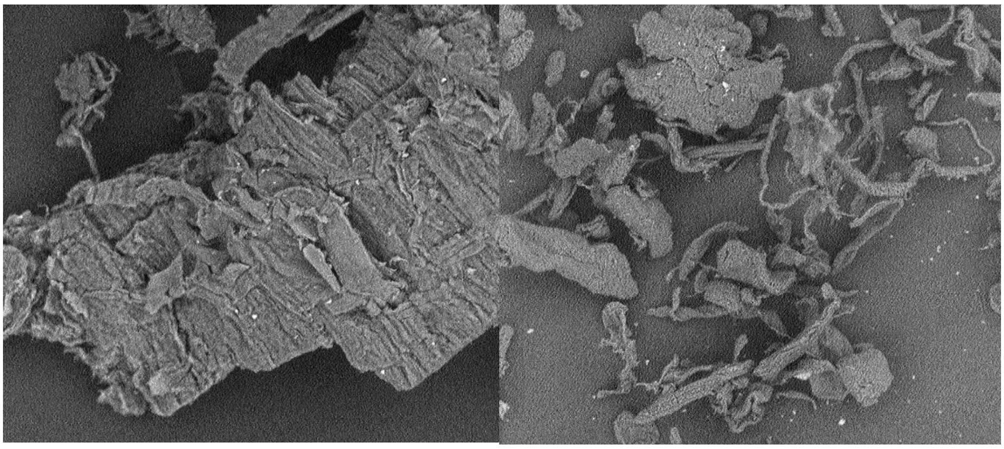
2500-3500, O-H broad, O-N stretch, NH stretch, and ≡CH-H stretch. None of the samples had frequencies of 3500-4500 with functional groups of O-H broad, O-H stretch, -NH stretch, or ≡CH-H stretch

Scanning Electron Microscope (SEM) Analysis



(a) (b)

Plate 4: (a) SEM Micrographs for Raw and (b) Nanocellulose POBPs



(a) (b)

Plate 5: (a) SEM Micrographs for Raw and (b) Nanocellulose Corn Cobs

The SEM images were used to investigate the surface morphologies of the Raw and Nanocellulose. The materials displayed uniform (homogeneous) structure (Plates 4 and 5). The micrograph of the Raw POBPs (Plate 4 (a))shows solid surface with tiny interspaced structures. Nanocellulose POBPs micrograph Plate 4 (b) has rod-like crystal shaped surfaces which might have resulted from reduced contact area.

The micrograph of Raw CC(Plate 5(a)) also composed of rough, solid surface interspaced structures. The micrograph of Nanocellulose CC (Plate 5 (b)) also has strand-like shaped surfaces with interspace which might have resulted from the pulping and hydrolysis processes. It is evident that upon pulping and hydrolysis the structure of POBPs and CC has changed.

Plate 4 (b) and 5 (b) showed strand-like micrograms which are as a result of pulping and hydrolysis processes which will aid and enhance burning.

Table 1: Viscosity, Heat of Combustion and Burning Duration of the Produced Gel Fuels

Fuel	Viscosity in Centipoise (Cp)	Burning Duration of 100 mL Gel Fuel (min)	Heat of Combustion Based On Material Burnt (KJ/mol)
Ethanol	1095.0± 5.0	15.0	1300.0
Gel Ethanol	25,000± 13.0	34.0	1508.0
NC – POBPs Gel Ethanol	32,600± 25.0	47.0	2416.0
NC – CC Gel Ethanol	36,800± 10.0	61.0	1905.0

A Comparisim of Viscosity, Heat of Combustion and Burning Duration of the Produced Gel with Ethanol and Gel Ethanol

The Viscosity in Centipoise (Cp) for Ethanol, Gel Ethanol, NC-POBPs and NC-CC were 1095.0± 5.0, 25,000± 13.0, 32,600± 25.0, and 36,800± 10.0 respectively. The burning duration of 100 mL gel fuel was 15 mins, 34 mins, 47 mins and 61 mins for Ethanol, Gel Ethanol, NC-POBPs and NC-CC respectively. The produced gel fuel gave favourable burning duration. The Heat of Combustion Based on Material Burnt (KJ/mol) for Ethanol, Gel Ethanol, NC-POBPs and NC-CC were 1300.0, 1508.0, 2416.0 and 1905.0 respectively.The high viscosity at low Nanocellulose concentrations makes Nanocellulose very interesting. (VTT Technical Research Centre of Finland, 2010).

IV. Conclusion

Pride of Barbados Pods (POBPs) and Corn Cobs (CC) agro wastes are found abundantly in Nigeria and all over the world. The production of Nanocellulose was possible with these agro wastes. The use of the techno-economic method to obtain the pulp which gave rise to the Nano cellulose from the POBPs and CC to gel the 'green fuel' further reduces the overall economic utility of the fuel, imparting an economically cheaper alternative heating material for domestic use. The Nanocellulose gave a gel on addition of a very little quantity. It also enhanced the thermal quality (heat of combustion) this process makes the local production economically feasible for both rural and urban dwellers. The use of Nanocellulose from POBPs and CC agro wastes in gelling the fuel enhances the economic utility potential of producing fuel imparting an economically cheaper alternative heating material to fossil kerosene.

Acknowledgements

The authors are most grateful to the Vice Chancellor, University Management, TETFUND and Council, for the sponsorship and approval of this research work.

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Onwuka J.C,etal. "Production of Nanocellulose – Based Gel Fuel for Domestic Heating Using Pride of Barbados Pods (POBPS) and Corn Cobs (CC) Agro Wastes." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 13(3), (2020): pp 36-41.