Synthesis of Furfural from the Shea-Nut Waste Cake and Furfurylation of Wood Flakes and Wood Cellulose

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Abstract: **The shea-nut cake is a by-product of the shea-nut obtained after processing of the shea butter oil. Locals consider this a waste product and it is discarded into the environment or nearby river, which add to the pollution of the water system due to the presence of it residual oils. The shea-nut cake has found little and/ or no useful applications in most places globally. In some places it is incinerated in the open, which contributes to atmospheric pollution. It has found few applications as component of livestock feeds. Being a renewable material, it is imperative to find new and useful applications due to its relative abundance and workability. Furfural was synthesized by mineral acid hydrolysis using H_2SO_4 and HCl by dilute acid concentrations, catalyzed by $CaCl_2$. The synthesized furfural was used in the form of its furan alcohol to modified wood cellulose /wood flakes by impregnation of the substrates. The products were characterized using FT-IR and NMR. The success of furfural synthesis from Shea-nut cake was revealed by the FT-IR bands at 3652-3108, 3090, 2922, 1840, 1722, 1617, 1613, 1585-1502 and 1461-1423, 2113, 2120 cm^{-1} for –COH, C-H, -C=C-C=O, C=O and C-O; the yield obtained was in the range of 73-80 %; physical parameters such as: density, boiling point, solubility in water and refractive index were similar to standard reports; and Furfurylation of cellulose was evidenced by the presence of absorption peaks of the furfural skeleton and the reduction in the –OH bands of cellulose.**

Keywords: **Synthesis, Shea-nut waste, Furfural, cellulose, Furfurylation**

I. INTRODUCTION

The consumption of Shea products (kernel, butter and oil) is increasing, especially in their production zone due to the high cost of imported oils (Honfo *et al.,* 2011; Victor, 2015). It is locally abundant in the middle-belt areas (Benue, Kwara and Niger States and Abuja - Federal Capital Territory) of Nigeria, where it is found growing as a wild tree (Olerede and Longe, 1999). Shea is an important income earning activity for many rural women and in international market, it is highly demanded due to its richness in food nutrients and other fatty spread (Victor, 2015; Patrick and Kenan, 2017). The fruits of the Shea tree consist of a green fleshy mesocarp which has high nutritional value and contains between 0.7 to 1.3 grams of protein and 41.2 gram of carbohydrate (Bernice, 2011; Victor, 2015). Shea kernel is a rich source of fat (Abdul-Mumeen *et al.,* 2013; Adetuyi and Dairo, 2015). It contains a fleshy pulp which is sweet and perfumed when matured. It can be eaten raw when allowed to over-ripe. Fruit contains 1-2 large shining brown seeds. The kernel is whitish and rich in fats (45-55%) from which is produced Shea butter (Ani *et al*., 2012; Adetuyi and Dairo, 2015; Patrick and Kenan, 2017). The Shea tree has enormous economic importance ranging from consumption of the caterpillar by the Koro (Mijili) in Niger State and Tivs in Benue State. The caterpillar got from the Shea butter tree, known in Koro and Tiv languages as "UGBILI and IGYU" is specially prepared with sauce and serves as a special delicacy and is found marketed along the streets (Ani *et al*., 2012; Victor, 2015). The Shea kernels are high in oils and have long been collected and processed by women in rural communities, where they provide a useful source of fat in their diets. The kernels are processed into Shea butter and pressed cake. The tree gains important as an economic tree crop because of the heavy demand for its butter both locally and internationally (Abdul-Muneen *et al*., 2013; Victor, 2015). The commercialization of Shea products represents an important source of income for different individuals (Victor *et al.,* 2015). It has found industrial significance as a biomaterial for renewable energy in countries such as France, Great Britain, Netherlands, Denmark, North America and Japan, who are the main importers of Shea (Carette *et al*., 2009). In 2003, the European Union accepted Shea butter as one of the six vegetable fats to serve as a Cocoa Butter Equivalent (CBE) (Victor, 2015). Shea pulp contains ascorbic acid (196 mg/100 g), iron (2 mg/100 g) and calcium (36.4 mg/100 g). It is a rich source of sugars, proteins, calcium and potassium (Olerede and Longe, 1999; Patrick and Kenan, 2017). The Shea plant (*Vitellaria),* belonging to the family Sapotaceae and species *paradoxa* consists of sub-species *paradoxa* and *nilotica* which are widely distributed in the Savannah zone of Nigeria. Furfural is produced from agricultural waste biomass that contain pentosans, which are aldose sugars, composed of small rings formed from short five-member chains, that constitute a class of complex carbohydrates, present in cellulose of many woody plants such as corn cobs, sugar cane bagasse, rice and oat hulls etc. (Brady *et al.,* 2009; Ong and Sashikala, 2007). Furfural has been produced from Pisthachio green hulls as agricultural residues (Masoud and Mohamma, 2009). These authors reported about 17 % furfural yield, which made the pisthachio green hull a potential source for furfural

production. The objective of the study was to find and alternative useful applications of the cake as a source for furfural production and applications.

II. EXPERIMENTAL WORK

A. Materials and Methods

All the chemicals used were of analytical grade and were used without further purification and these include; Sodium chloride ($CaCl_2$), Tetraoxosulphate (Vi) acid (H_2SO_4), Hydrochloric acid (HCl), Alpha naphthol and Ethanol.

B. Sample Collection and Preparation

Shea-nut cake was obtained from Doko in Lavun Local Government Area of Niger State. Samples collected were air-dried and stored in polyethylene bags to avoid contamination by other chemicals in the Laboratory. Samples were ground into fine powdered particles and collected and stored in polyethylene bags. These samples were used for the synthesis of furfural according to Yan et a., (2014).

C. Reagent Preparation

Sulphuric acid (H_2SO_4), 2 $moldm^{-3}$ and Molisch's Reagent were prepared according to standard methods.

D. Furfural Production from Shea-nut Cake

The fine powdered Shea-nut cake, 23 g was weighed and transferred into 500 cm^3 round bottom flask and thereafter, 500 cm^3 of 2M H_2SO_4 was added followed by the addition of 125 cm^3 of 3 $moldm^{-3}$ HCl/10 mL of $CaCl_2$ to the mixture. The resultant mixture was heated and allowed to boil for 3 h. The distillate was collected in a stoppered reagent bottle.

E. Tests for Furfural using the Molisch's Test

2 cm^3 of the distillate from the furfural produced was measured and transferred into a test tube. 2 drops of the Molisch's reagent were then added into it and was swilled thoroughly. The test tube was inclined and 5 cm^3 of concentrated H_2SO_4 acid was added to the mixture in the test tube. The formation of purple colour at the interface between the acid and the extract is a positive test for the presence of furfural.

III. RESULTS AND DISCUSSION

A. The Physicochemical Parameter of Synthesized Furfural

The physical appearance and odour of the synthesized furfural from Shea-nut cake were similar to the findings by Grazielle *et al.,* (2016) on the production and catalytic hydrogenation of furfural; Yan and Arias, (2013) on the production of furfural from biomass. The values for the density of the synthesized furfural were 1.160 and 1.159 g/cm^3, similar to the values obtained by Grazielle *et al.,* (2016); Sashikala and Ong, (2007) on furfural from rice husk; Ong and Sashikala, (2007) on identification of furfural from pentosane rice husk. The values for the boiling point were in agreement with the values documented by Yan et al., (Grazielle et al., 2016). The solubility index values of the synthesized furfural were similar to the findings by Grazielle *et al.,* (2016). The yield of furfural obtained with the two mineral acids hydrolysis were 73.13 % and 80.12 % respectively. It is evidenced from the relative appearance and the physicochemical parameter of the synthesized furfural that the synthesis of furfural from Shea-nut cake was successful based on other literature reports as well as properties of furfural produced by the chemical industries. It worthy of note to say that Shea-nut cake is a good raw material for the production of furfural and other furfural derivatives.

Table 1: Property of furfural produced from Shea nut cake

Property	Shea-nut cake-H_2SO_4-Furfural	Shea-nut cake-HCl-Furfural
Physical appearance	Colourless	Colourless
Odour	Almond smell	Almond smell
Mass (g)	22.62	25.10
Volume (cm^3)	14.50	15.90
Density (g/cm^3)	1.160	1.159
Boiling Point (^oC)	162.5	161.9
Solubility in Ethanol	Soluble	Soluble
Solubility in water	Slightly soluble (8.1 %)	Slightly soluble (8.1%)
Refractive Index	1.515	1.524
Acidity	0.0092	0.0079
Yield (%)	73.13	80.12

B. FTIR spectra are good evaluation tools for the characterization of functional groups

From the (*Tables 2*) furfural obtained for the 3 and 6h hydrolysis showed absorption Peaks around 3652-3108 cm^{-1}, due to C-H of the COH aldehyde functional group. The band at 3090 and 2922 cm-1 have been assigned to the aldehydic C-H stretching vibration. Peak absorption around 1613-1617 are due to C=O of the carbonyl whereas the absorption band which occurred around 1585-1505 and 1174 are assignable to the presence of –C=C- and O-C=O. These absorptions have been reported by Sashikala and Ong, (2007) on furfural form rice straw; Wankasi and Naidoo, (2012) on furfural obtained from the epicarp of wild mango respectively. The Furfurylation of wood cellulose (*Table 3 and 4*) for 1 and 2h duration yielded furfurylated products which were studied using FT-IR. Results indicate reductions in the absorption band of the cellulose –OHs, measured at 3332 cm^{-1} and 3324 cm^{-1} for the 1 and 2 h Furfurylation time. Many changes in the functional groups of the substrates were not expected, since Furfurylation of cellulose is filling/impregnation mechanisms. Thus, bands related to those of furfural were detected. FT-IR revealed the presence of strong absorption band at 1840 cm-1 and 1722 cm-1 in the modified wood cellulose confirming the presence of aldehydes and ketone

carbonyl (C=O) absorption *(Tables 5 and 6).* The absorption due to the glycosidic group was found around 1159-1107 cm^{-1}. The reduction in the –OH absorption was observed in the furfurylated samples as revealed by the FT-IR analysis, which was good evidence of the success of modification. Absorption peaks which provided evidence for the successful synthesis and modification were observed around 3652-3108, 3090, 2922, 1840, 1722, 1617, 1613, 1585-1502 and 1461-1423, 2113, 2120 cm^{-1} for –COH, C-H, -C=C-C=0, C=O and C-O respectively. The proton NMR (1H NMR) chemical shift (*Appendix)* revealed the four 1H environments and their interaction with each other. The aldehydic proton which appeared downfield due to the C=O functional group approximately around 9.67 ppm while the protons on carbon 2, 3 and 4 exhibited splitting due to the closeness of their environment. The proton on carbon 2 was split by the one on carbon 3, thus, two chemical shift values were recorded at 2.67 and 2.66 ppm as doublet respectively. The proton on carbon 3 occurred as a quadruplet due to splitting by the one on carbon 2 and carbon 4. This proton had chemical shift values in the range of 6.574-6.580 ppm. The proton on carbon 4, which is further from carbon 2 appeared as a triplet also due to splitting.

Table 2: FT-IR Peak Assignment for the Furfural Synthesized for 3 and 6h Hydrolysis

Hydrolysis Time (h)	Absorption Peak (cm^{-1})	Functional group
3	3652-3306	C-OH Bond stretching vibration
	3090-2922	C-H vibration of the aldehydes
	2120	C=C stretching
	1613	C=O ketone
6	3347-3108	O-H Bond stretching vibration
	2340	C-H Bending vibration
	2113	C=C Stretching
	1617	C=O ketone
	1585-1505	C=C stretching of the furan ring
	1438-1442	C-O Stretching of aldehyde
	1341	C-H Bending vibration
	1174	O-C=O stretching

C. *Application of the synthesized furfural for the Modification of Wood Flakes*

To find useful applications for the furfural synthesized from shea-nut waste cake, wood flakes/wood dust was treated using the synthesized furfural for protection of wood against degrading bacteria and insects. FT-IR was used to characterize the modified wood flakes *(Tables 3 and 4)* and wood cellulose *(Tables 5 and 6).*

Table 3: FTIR Peak Assignment for the 1h Furfurylation of Wood Flakes

Sample	Absorption band	Functional group
Wood Flakes	3324	O-H Bond stretching vibration
	2899	C-H bending vibration
	2117	C=C stretching in conjugated ketones
	1581-1502	C=C stretching in conjugated ketones
	1461-1423	C-O stretching in cellulose
	1364-1319	C-H bending vibration
	1226	CH_2 wagging in cellulose

Table 4: FTIR Peak Assignment for the 2h Furfurylation of Wood Flakes

Sample	Absorption band	Functional group
Wood Flakes	3332	O-H Bond stretching vibration
	2896	C-H bending vibration
	2109	C=C stretching in conjugated ketones
	1551-1505	C=C stretching in conjugated ketones
	1364-1319	C-O stretching in cellulose
	1461-1423	C-H bending vibration
	1226	CH_2 wagging in cellulose

Table 5: FTIR Peak Assignment for the 2h Furfurylation of Wood Cellulose

Sample	Adsorption Band	Functional group
Wood Cellulose	3336	O-H Bond stretching vibration
	2892	C-H bending vibration
	2102	C=C stretching in conjugated ketones
	1840	C=O due to CHO and RC=O-R
	1423	C-O stretching in cellulose
	1312	C-H bending vibration
	1200	CH_2 wagging in cellulose

Table 6: FTIR Peak Assignment for the 1h Furfurylation Wood Cellulose

Sample	Absorption band	Functional group
Wood Cellulose	3332	O-H Bond Stretching Vibration
	2892	C-H bending vibration
	2363	C=C stretching in conjugated
	2079	C=O in aromatic ring of syringyl in lignin
	1722	C=O due to modification
	1315	C-H bending vibration
	1159-1107	C-O-C cellulose back bone

IV. CONCLUSION

Furfurals have been synthesized from Shea nut cake while modification was successful using the synthesized furfural as evidenced by the FT-IR analysis of both furfural and furfurylated samples. Significant band absorptions are; 3652-3108, 3090, 2922, 1840, 1722, 1617, 1613, 1585-1502 and 1461-1423, 2113, 2120 cm^{-1} for –COH, C-H, -C=C-C=0, C=O and C-O respectively. 1H NMR chemical shifts revealed the presence of H-C=C-H and C-OH proton environments, confirming the structure of furfural. Yield of furfural obtained was 80.12 and 73.13 % respectively.

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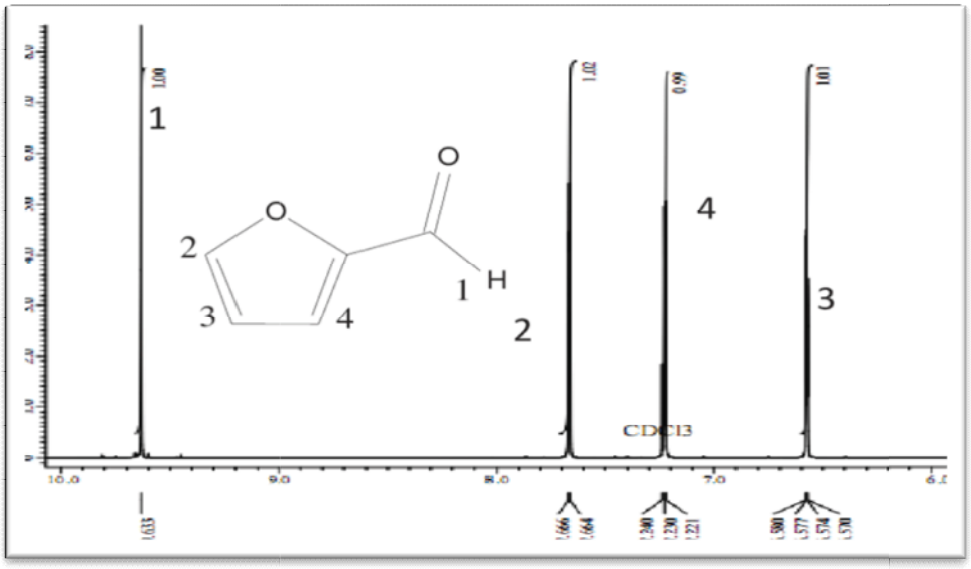
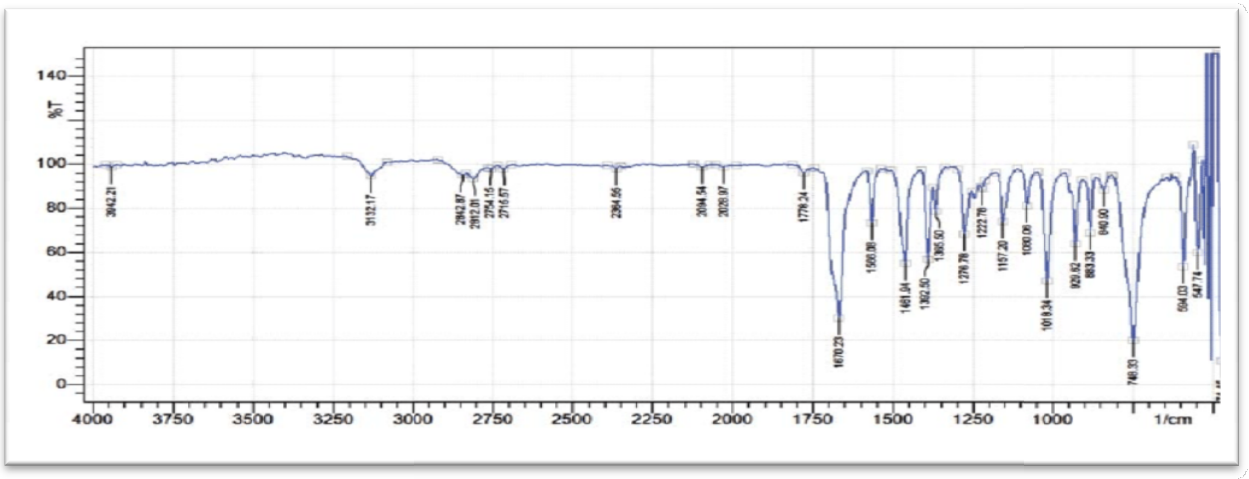


Appendix II: ^{1}H NMR Spectrum of Synthesized Furfural from Shea-nut Cake



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