PRELIMINARY INVESTIGATION INTO THE SYNTHESIS OF FURFURAL FROM SUGARCANE BAGASSE

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Abstract: This work studied furfural production via acid hydrolysis using two different bagasse (waste product from the sugar industry) samples. Analysis of the bagasse samples indicated that they contained 33% hemicellulose. Acids used in furfural synthesis were hydrochloric acid, sulphuric acid and ethanoic acid with sodium chloride as a promoter. The physicochemical properties, UV scan and IR scan of the distillates confirmed that the product were furfural. The yields of furfural were typically low (4.53 – 4.98%) and was found to be largely independent of bagasse and acid types (with average value of 4.713% and standard deviation of 0.176). FTIR analysis of the distillate samples shows the presence of aldehyde functional group due to the strong peaks between the range of 1640 and 1710 cm^{-1}. Furthermore, the ultra-violet scanning of the distillate samples shows that the presence of strong absorbance at the ultra-violet region of between 200 nm and 300 nm, which indicated the presence of aldehyde functional group.

Keywords: Ethanoic acid, furfural, hydrochloric acid, hydrolysis, sugarcane, yield

Introduction

The conversion of lignocellulosic biomass to liquid fuels has attracted renewed attention in recent years due to its environmental, economic, and strategic advantages. An increasing effort has been devoted to find paths to utilize biomass as feedstock for the production of organic chemicals because of its abundance, renewability and worldwide distribution. Furfural is an important chemical in the synthesis of chemicals and fuels from renewable sources (Agirrezabal-Telleria *et al*., 2014). Researches into furfural from biomass has been gaining interest (from corn-corbs, rice hulls, bagasse (Saad *et al*, 1978; Vittaya, 2008), from palm fruit fibre (Odozi *et al.*, 1985), from garbage (Win, 2005), from raphia hookeri (Wankasi and Tarawou, 2011), from pawpaw and pineapple peels (Wankasi *et al*, 2011), from Banana and plantain peels (Wankasi and Yabefa, 2011) and from wild mango fruit (Wankasi and Naidoo, 2012). It is also a versatile chemical that acts as a starting material for a large family of other chemicals and polymer products. Furfural is a basic chemical which can be utilized in a variety of industries such as chemical industry, refining oil industry, food industry and agricultural industry (Ong and Sashikala, 2007). It is a versatile and renewable chemical with wide industrial applications both as a solvent and as a building block for the synthesis of various other chemicals such as furfuryl alcohol, agrochemicals, pharmaceuticals, fragrances, and other 5-membered oxygen-containing heterocycles like furan and tetrahydrofuran (Xuejun, 2011).

Bagasse is the fibrous residue from sugarcane, after the cane had been harvested and crushed to extract the juice (Guilherme *et al.,* 2015). Bagasse is described as a waste product from the sugar industry, which is usually used as energy source in factories. However, the amount of bagasse left is still high enough for more value-added products for example furfural (Hayelom *et al*., 2015). Furfural can be produced by acid catalyzed hydrolysis of agricultural by-products containing hemi-cellulose or pentosan. Pentosan is one of the important fibre components of the non-starch polysaccharides called hemi-cellulose. Hemi-cellulose can be any of several hetero-polymers present in almost all cell walls (Wankasi *et al*., 2011).

Besides that, the yield of solid biomass hydrolysis is very low because of mass transfer limitations. Available studies about furfural production from aqueous hemicelluloses solutions are sparse, necessitating more studies to prove the viability of using this material for furfural production (Liu *et al.,* 2009). The aim of this research work was to produce furfural from bagasse which was obtained from locally grown sugar cane crop and to compare the yields when two different inorganic acids (hydrochloric acid and sulphuric acid) are used as well as a weak organic acid (ethanoic acid).

Materials and Methods

The sugarcane crop which were labelled samples *A* and *B* were obtained from a sugarcane plantation in Zaria. The bagasse samples **A** and **B** were identified to be *Saccharum bengalense* (Voucher number: 1086) and *Saccharum officinarum* (Voucher number: 900111), respectively. The sugarcane samples were then shredded into bagasse after the cane juice had been removed, after which they were sun dried for 14 days and finely ground using a hammer mill and thenstored (in plastic bottles at room temperature) separately. The prepared samples were analyzed for density, moisture content, ash contents, lignin, cellulose and hemicellulose contents after the sun drying period of 14 days (Omoniyi and Olorunisola, 2014).

Furfural production was carried out using a batch reactor and a distillation system, while the acid hydrolysis of the bagasse samples took place in the batch reactor. The bagasse samples **A** and **B** were dried in an oven at 200°C for 48 h, grounded and sieved to 1000 µm mesh size. Aqueous hydrochloric acid (300 ml of 1M), 30 g of sodium chloride and 30 g of bagasse sample, **A** was introduced into a 500 ml 3-necked round bottom flask, to which a stirrer was attached. A Vigreux column and a condenser were attached to the 3-necked round bottom flask, and the reaction mixture was heated and stirred mechanically. The effluent from the batch reactor experienced rapid distillation at 104°C, then the aqueous distillate mixture was collected over chloroform in a separating funnel and two distinct layers were formed which are, the furfural-chloroform layer as well as the aqueous layer (Wankasi and Naidoo, 2012).

After 2 h of distillation (after which there was no increase in the furfural-chloroform layer), the furfural-chloroform layer was decanted, then poured into a conical flask. The decanted furfural-chloroform mixture was subjected to a rotary evaporation at a temperature of 100°C for 30 min to

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remove the chloroform away from the mixture and leave furfural as the residue and then the sample was measured in a measuring cylinder. The furfural left in the flask was then measured and labelled F1 (Ambalkar and Talib, 2012). The above procedure were repeated for samples **A** and **B** using the same amount of 1M sulphuric acid, and 2M ethanoic acid in turns, and the resulting samples were labelled accordingly (F2, F3, F4, F5, and F6). All reagents were of AnalaR grade and were obtained from BDH Chemicals. The produced furfural was then characterized in terms of the density, boiling point, pH, FTIR Spectroscopy (*Thermo Scientific-Nicolet iS10*) and UV Spectroscopy (Shimadzu UV-VIS Spectrophotometer, *Model: UV- 2550*).

Results and Discussion

The bulk densities, moisture contents, ash contents as well as average crude fibre analysis are presented in Table 1. The moisture content and ash content shown in Table 1 are similar to those reported by literature of 7.5% and 3.3% respectively (Omoniyi and Olorunisola, 2014). Guilherme *et al.* (2015) reported an ash content of 8.8± 0.02% in bagasse, suggesting that origin may affect ash content. The crude fibre analysis of both bagasse samples shown in Table 1 for cellulose, hemicellulose and lignin were also found to be typical of literature values: Omoniyi and Olorunisola (2014) reported compositions of cellulose (43.2%), hemi-cellulose (31.5%) and lignin (22.0%). Guilherme *et al.* (2015) reported Cellulose composition of 38.59 ± 3.45%. Hemicelluloses, which are the main feedstock for furfural production, are the second polysaccharide mostabundant in nature, composing around 20% - 35% of lignocellulosic biomass (Machado *et al.,* 2016). However, the bulk density shown in Table 1 is slightly lower than those reported by Omoniyi and Olorunisola (2014) of between $0.32 – 0.28$ g/cm^3.

Table 1: Composition of some physicochemical properties of bagasse samples

Parameters	Sample A	Sample B
Bulk density, g/cm^3	0.160	0.168
Moisture content, %	6.83	8.65
Ash content, %	3.85	3.50
Cellulose, %	33.58	34.06
Hemicellulose, %	32.84	32.91
Lignin, %	29.73	29.53

Table 2: Yield of furfural from bagasse samples A and B

Substrate	ID	Hydrolysis Acid	Volume of Distillate (ml)	% Yield (g/g)
A	F1	1M HCl	3.4	4.53
	F2	1M H$_2$SO$_4$	3.4	4.60
	F3	2M ethanoic acid	3.2	4.83
B	F4	1M HCl	3.6	4.98
	F5	1M H$_2$SO$_4$	3.4	4.77
	F6	2M ethanoic acid	3.4	4.57

Yield of furfural

The quantity of distillate from the various runs is presented in Table 2. Yield was computed as:

$$Yield(\%) = \frac{\text{mass of furfural produced}}{\text{mass of bagasse used}} \, x \, 100 \dots \dots (1)$$

The yields of furfural from the various runs as shown in Table 2 were found to be identical with an average value of 4.713% and standard deviation of 0.176. The yield values were found to be low but not uncommon for

furfural processes: 4%–12% (Win, 2005; Dashtban *et al.,* 2012).

Physicochemical properties of distillate samples
The physicochemical properties of the distillate samples from the acid hydrolysis of the bagasse samples **A** and **B** as well as the percentage yield (on weight basis) is presented in the Table 3. The boiling points and density of all furfural samples as shown in Table 3 were similar to reported literature values of 161.8^{o}C (at 1 atm) and 1.1598 g/cm^3 (at 20°C), respectively (Dean, 1999; Wankasi and Naidoo, 2012).

Table 3: The physicochemical properties and the percentage yield of the distillate samples

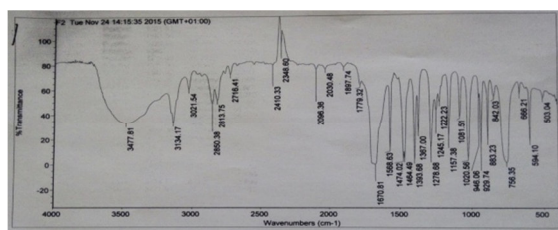| Samples	pH	Density (g/cm^3)	Boiling Point (^{o}C)
F1	3.8	1.18	161
F2	4.6	1.19	161
F3	3.1	1.25	165
F4	4.5	1.12	160
F5	3.6	1.19	163
F6	3.8	1.19	162

FTIR analysis

Wankasi and Naidoo (2012) noted that carbonyl compounds are those that contain the C=O functional group. In aldehydes, this group is at the end of a carbon chain, whereas in ketones it's in the middle of the chain. As a result, the carbon in the C=O bond of aldehydes is also bonded to another carbon and a hydrogen, whereas the same carbon in a ketone is bonded to two other carbons. Aldehydes show a strong, prominent, stake-shaped band around 1640 - 1710 cm^{-1}. Aldehydes and ketones have strong bands which is due to the highly polar C=O bond. Because of its position, shape, and size, it is hard to miss. Because aldehydes also contain a C-H bond to the *sp*2 carbon of the C=O bond, they also show a pair of medium strength bands positioned about 2700 and 2800 cm^{-1}. These bands are missing in the spectrum of a ketone because the *sp*2 carbon of the ketone lacks the C-H bond (Stuart, 2004).

The FTIR results of the distillate sample F1, F2, F3, F4, F5 and F6 are presented as Figs. 1 – 6 and that of a commercial furfural (Qualikems, Analytical Reagent) as Fig. 7, for comparison.
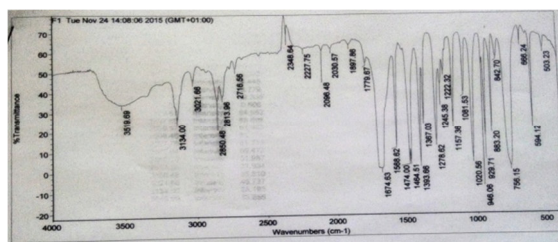
Fig 1: Infra-red scan of the distillate sample F1

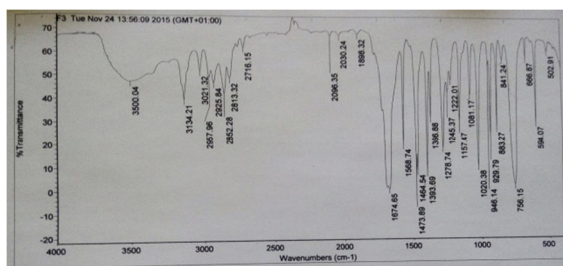**Fig 2:** Infra-red scan of the distillate sample F2

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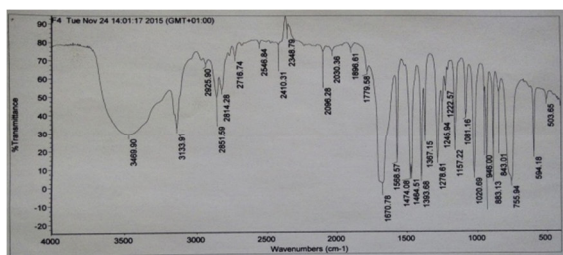**Fig. 3:** Infra-red scan of the distillate sample F3

Fig 4: Infra-red scan of the distillate sample F4

The infra-red spectrum in Fig. 1 shows that the sample distillate F1 has a strong band at the wavelength of 1674.63 cm^{-1} and a medium band at 2850.48 cm^{-1} which indicates presence of the aldehyde functional group .In the infra-red scan of distillate, sample F2 indicated in Fig. 2 shows that there is a strong band at 1670.81 cm^{-1}, also the presence of medium peak at 2850.38 cm^{-1} shows that the aldehyde functional group which characterizes furfural is present. At wavelength band of 1674.65 cm^{-1} and 2852.28 cm^{-1}, there is a strong and medium band, respectively; indicating the presence of the aldehyde functional group in the sample distillate F3. In Fig 4, the sample F4 has a low percentage transmittance (that is a strong band) at the wavelength of 1670.78 cm^{-1} which shows the presence of an aldehyde group in the sample. The presence of aldehyde is evident in the sample F5 as shown in Fig. 5 as a result of the strong band at 1667 cm^{-1} wavelength band and a medium band at 2851 cm^{-1}. In the Fig. 6 the aldehyde group is the dominant functional group in the sample F6, because the strongest band can be seen at 1670.91 cm^{-1} and a medium band also exist at 2851.19 cm^{-1} wave length. In the Fig. 7 the strongest band can be seen at 1674.49 cm^{-1} and a medium band also exist at 2852.19 cm^{-1} wavelength which indicates the strong presence of aldehyde functional group. This verifies that all the distillate samples, F1, F2, F3, F4, F5 and F6 exhibit same characteristics as the commercial furfural.
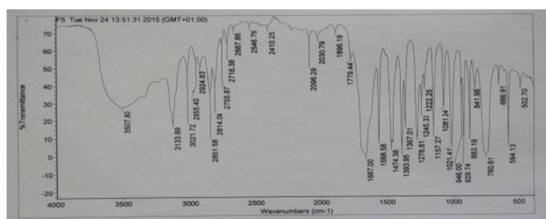

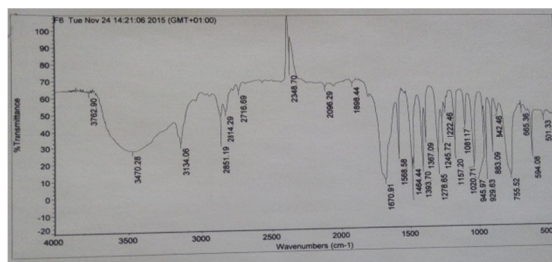**Fig. 5:** Infra-red scan of the distillate sample F5

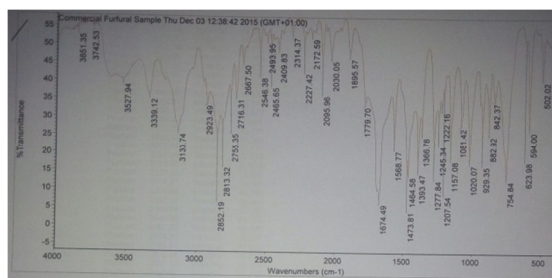**Fig. 6:** Infra-red scan of the distillate sample F6

Fig. 7: Infra-red scan of commercial furfural sample

Results of the UV scanning of distillate samples
The UV scan for the prepared samples are shown in Fig. 8 – 13. The carbonyl groups of saturated aldehydes and ketones gave a strong absorption band in the ultraviolet region between 270-300 nm, which shifts to longer wavelengths (300-350 nm) when the carbonyl group is conjugated with a double bond (Wankasi *et al*., 2011). As the degree of conjugation increases, the absorption will shift to longer wavelength. Generally, each additional double bond increases or gives rise to longer wavelength. Each additional conjugated double bond increases the wavelength of absorption band to about 300 nm (Kamalu and Ogbome, 2008)
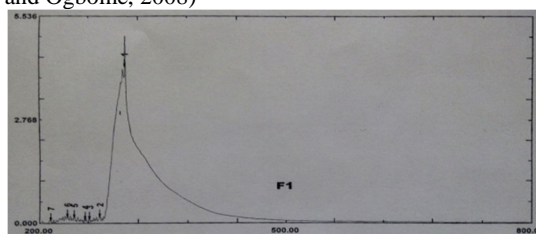

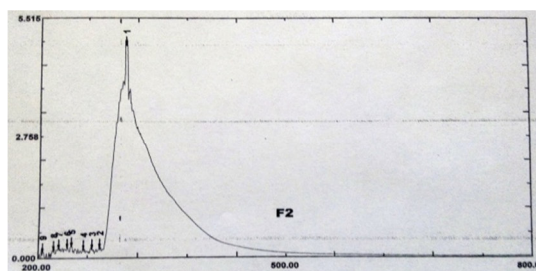**Fig. 8:** Ultra-violet scan of the distillate sample F1

Fig 9: Ultra-violet scan of the distillate sample F2

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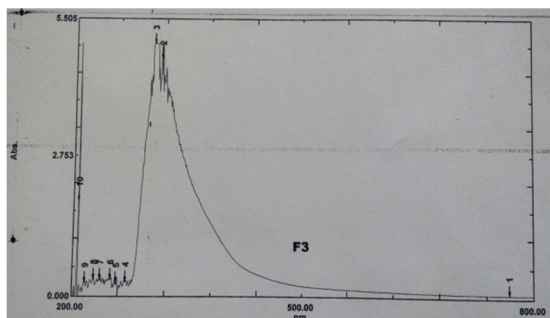
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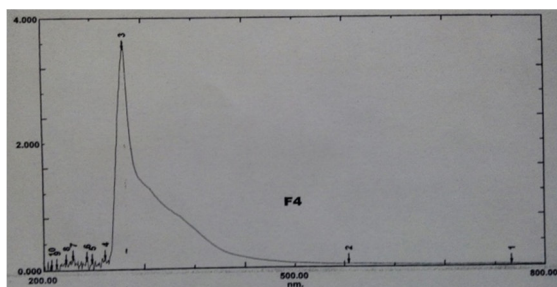**Fig. 10:** Ultra-violet scan of the distillate sample F3

Fig. 11: Ultra-violet scan of the distillate sample F4

Figure 8 shows there is a strong absorption at the ultra-violet region of 280 nm, which shows the presence of the carbonyl group in sample F1. In Fig. 9, at about 290 nm region the sample F2 shows a strong absorbance, which indicates the presence of the aldehyde functional group. In Fig. 10, it can be observed that the sample F3 distillate shows a strong peak at the band of about 280 nm. Fig. 11 indicates distillate sample F4 showing the presence of an aldehyde functional group as result of the sharp absorbance at 270 nm band. There exists a strong absorbance at the ultra-violet region of about 300 nm, which indicates the presence of aldehyde functional group in F5. Distillate sample F6 in Figure 13 shows strong absorbance in the ultra-violet region of 200 nm – 230 nm and a medium absorbance at the ultra-violet region of 270 nm, which indicates presence of aldehyde group. Forfurfural ($C_5H_4O_2$) certification, fractionation of distillate and further characterization of synthesized sample is recommended.
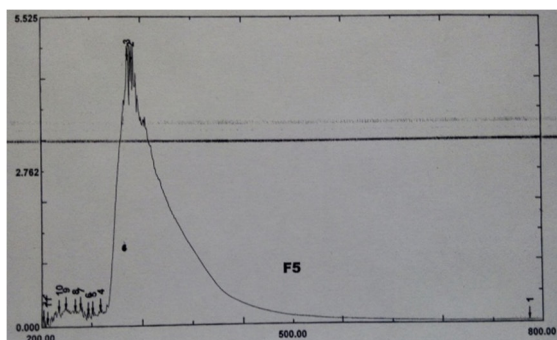

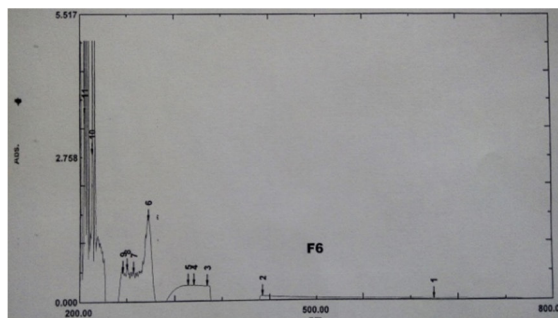**Fig. 12:** Ultra-violet scan of the distillate sample F5

Fig. 13: Ultra-violet scan of the distillate sample F6

Conclusion
From the crude fibre analysis carried out for the both bagasse samples, it was observed that the both samples had similar hemicellulose contentsand furfural yield: average values of 32.875% and 4.742%, respectively. The type of hydrolyzing acid (hydrochloric acid, sulphuric acid or ethanoic acid) also did appear to have an effect on the furfural yield. The densities and boiling points of the distillate samples were found to be similar to those reported for furfural. FTIR analysis of the distillate samples confirmed the presence of aldehyde functional groups as indicated by the strong band between the range of 1640 and 1710 cm^{-1}, and medium bands in the region of 2840 and 2860 cm^{-1}.The ultra-violet scan also showed a presence of strong absorbance at the ultra-violet region between 200 nm and 300 nm, this indicates the presence of aldehyde functional group in the distillate samples, which further confirms that the distillate samples are furfural.

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