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EFFECT OF ACIDITY ON FURFURAL PRODUCED FROM RICE HUSK AND GROUNDNUT SHELL

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ABSTRACT

This research work aimed to produce furfural from Rice husk and Groundnut shell and compare the effect of acid concentration on the yield of furfural produced which are lignocellulosic biomass consisting of pentosan which undergoes acid hydrolysis to yield furfural. The effect of acid concentration on the yield was investigated. The optimum furfural yield obtained was 9.48% and 36.78% for Groundnut-shell and Rice Husk respectively at 7.5% acid concentration. Thus it is concluded that the most favorable Sulphuric acid concentration for furfural yield is 7.5%, and that Rice husk shows a high optimum increase in % furfural yield than Groundnut-shell. Also the furfural obtained was characterized using FTIR and GC-MS spectroscopic techniques. The IR spectrum observed exhibited a very strong absorption at 1669 cm^{-1} indicating the presence of the conjugated carbonyl (C=O) group. The presence of the aldehyde was proven by two peaks at 3134 cm^{-1} and 2812 cm^{-1}. Also the result of the Gas chromatography-Mass spectrophotometer was in agreement with the target molecule (Furfural) for which the observed molecular weight and the empirical formula was 96.05 g/mole and $C_5H_4O_2$ respectively.

Keywords: Furfural, rice husk, Groundnut shell, FTIR,

INTRODUCTION

Concern over the growing demand of energy globally and the challenges associated with fossil fuels have triggered a renewed interest in producing fuels from renewable biomass as alternative to solve the economic and environmental issues posed by the fossil fuels demand. Renewable biomass resources have the potential to serve as a sustainable supply of fuels and chemical intermediates (Ragauskas *et al.*, 2006). The challenge for the effective utilization of these sustainable resources is to develop cost-effective processing methods to transform highly functionalized carbohydrate moieties into value-added chemicals (Chheda *et al.*, 2007). Agricultural and agro-industrial residues are potential carbohydrate sources for production of chemicals. Corn cob, rice husk, groundnut shell, saw dust, sugar cane bagasse, etc, are lignocellulosic materials that are biodegradable agricultural and industrial wastes. Lignocellulosic materials have a great industrial potential since they are available in large quantities worldwide, cheap and renewable resources. Lignocellulosic materials are mainly composed of three compounds (lignin, cellulose and hemi-cellulose) (Zeitsch, 2000).

Furfural produced from biomass is a promising material for the synthesis of alkanes, which are the basic components of fuels (Dumesic *et al.*, 2005). Furfural has been used in oil refineries, as well as in the plastics, food, pharmaceutical and agricultural industries (Dias *et al.*, 2006). Furfural is a heterocyclic aldehyde, with the chemical formula $C_5H_4O_2$ obtained from hydrolysis and dehydration of lignocellulosic biomass. Furfural was first isolated in 1821 by the German chemist Johann Wolfgang Dobereiner (1832), who produced a small sample as a by-product of formic acid synthesis. At the time formic acid was formed by the distillation of dead "ants", and Dobereiner's "ant" bodies probably contained some plant matter (Anthonia and Philip, 2015). Also in 1840, the Scottish chemist John Stenhouse found that the same chemical could be produced by distilling a wide variety of crop materials including corn, oats, bran, and sawdust with aqueous sulfuric acid, having an empirical formula of $C_5H_4O_2$ (Anthonia and Philip, 2015).

Furfural, one of the important industrial chemicals, can be produced extensively from lignocellulosic biomass such as rice husk, groundnut shell, corn cobs, sawdust, sugar cane bagasse, etc (Brady *et al.*, 2000). In theory, any material containing pentosans can be used for the production of furfural. Technically, furfural is produced by acid hydrolysis of the pentosans in woody biomass as shown in the figure below (Dalin Yebo Trading, 2004):

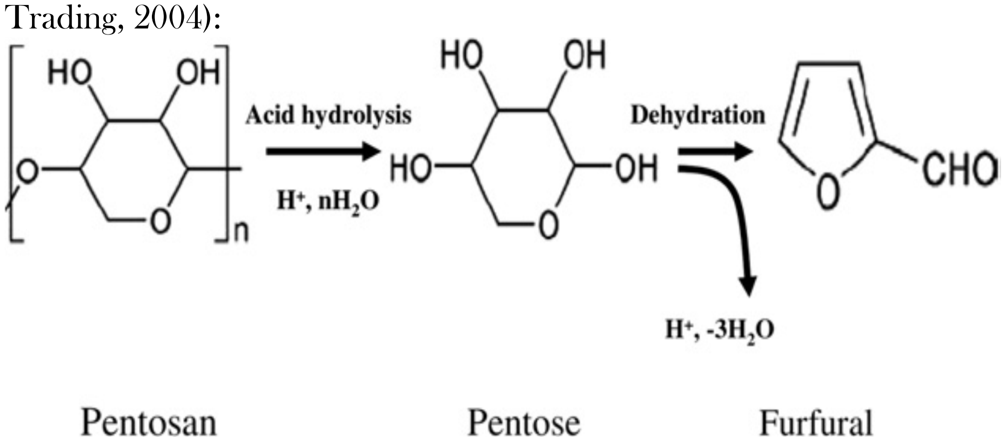

Figure 1: Acid Catalyzed production of furfural from biomass

The aim of this research work is to compare the effect of acid concentration on the yield of furfural produced from rice husk and groundnut shell. The objectives of the study were listed below:

i. To produce furfural from Rice husk and groundnut-shell.
ii. To compare the effect of acid concentration on the yield of furfural in both samples.
iii. To characterize the furfural produced using FTIR and GC-MS spectroscopic techniques.

MATERIALS AND METHODS

Dry sample of rice husk was collected from kalambaina Rice mill,sokoto and groundnut-shell was collected from Sanyinna town, Sokoto State. The materials used for the analysis include convectional laboratory glass wares and bench reagents. In addition to reagents and apparatus listed in Table 1 and Table 2.

Table 1: List of Chemical Reagents used.

Reagents	% Purity	manufacturer
Sulfuric acid (H_2SO_4)	98	sigma-Aldrich
Sodium Sulphate (Na_2SO_4)	99	May and Bayers
Dichloromethane (CH_2Cl_2)		BDH chemicals
Sodium chloride (NaCl)	99	Sigma –Aldrich

Table 2: List of Apparatus Used.

Apparatus	Model	Manufacturer
Rotary evaporator	SB-1100	Shanghai Eyela co.ltd
FTIR	MB 3000	ABB-analyser
GC-MS	QP2010PLUS	Shimadzu, Japan

RESULTS AND DISCUSSION

Results obtained from the analysis are shown in Tables 3 and 4 as well as in Figure .1, 2, 3,4,5 and 6 respectively

Table 3.1: Percentage furfural yield for Groundnut-shell

Concentration (%) H_2SO_4	% Yield
5.0	6.30
7.5	9.48
10	6.00

Table 3.2: Percentage furfural yield for Rice Husk

Concentration (%) H_2SO_4	% Yield
5.0	34.00
7.5	36.78
10	24.06

Table 1 and 2 shows % yield of furfural produced from groundnut shell and rice husk at % concentration sulphuric acid (5.0,7.5,10) for ground shell at these concentration the % yield is 6.30,9.48 and 6.00, respectively. While for rice husk % yield of furfural are 34.00, 36.78 and 24.06 respectively. As shown in the above table, the % yield increases with increasing concentration (at 7.5% acidic concentration). These values agree quite closely with the observation of O'Neil *et al* (2009). Also as observed, the increase in % furfural yield at 7.5% concentration for rice husk (36.78%) was quite higher than the observed % furfural yield for Groundnut-shell (9.48).

However as observed, both the % furfural yields for the rice husk and Groundnut-shell decreases with further increase in acidic concentration (at 10% acidic concentration). This could be attributed to condensation reaction (cross and self-polymerization) that occurs during the acid catalyzed conversion process (O'Neil *et al.,* 2009). From these observations therefore, the optimum acidic concentration for furfural percentage yield is 7.5%.

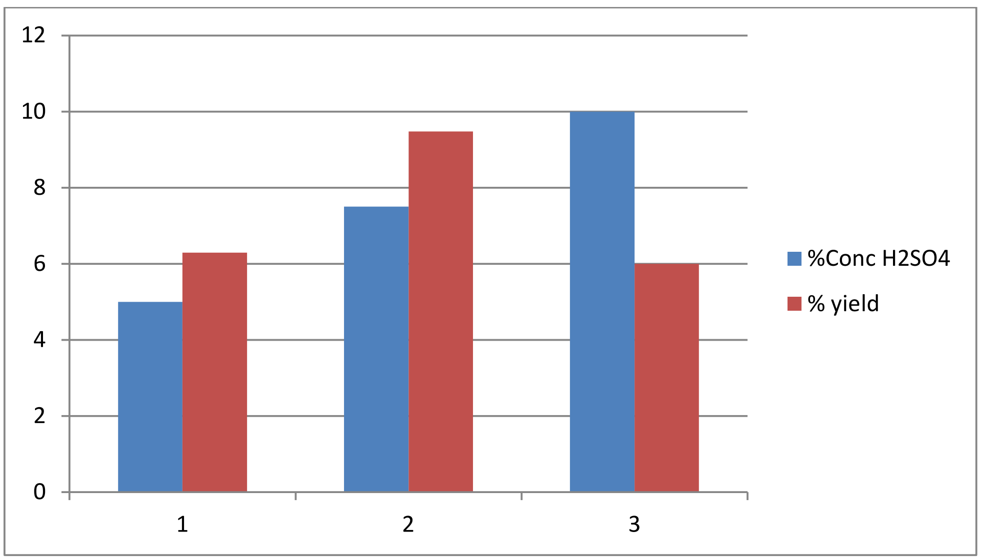

Figure 1: Effect of acidity on yield furfural produce from groundnut shell

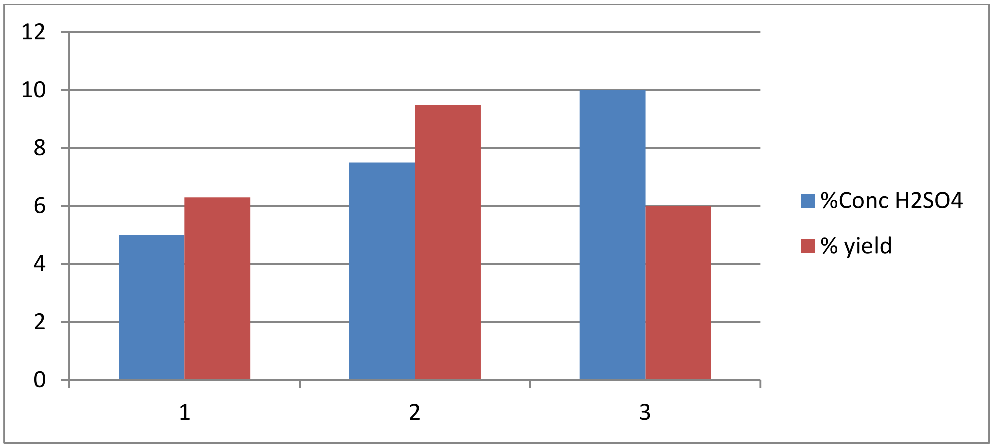

Figure 1: effect of acidity on yield of Furfural Produced from Rice Husk

FTIR Analysis of the Furfural Produced

The result of the FTIR analysis of the furfural produced from Rice husk and Groundnut-shell was described by the FTIR spectrums Figure.1 and Figure .2 respectively.

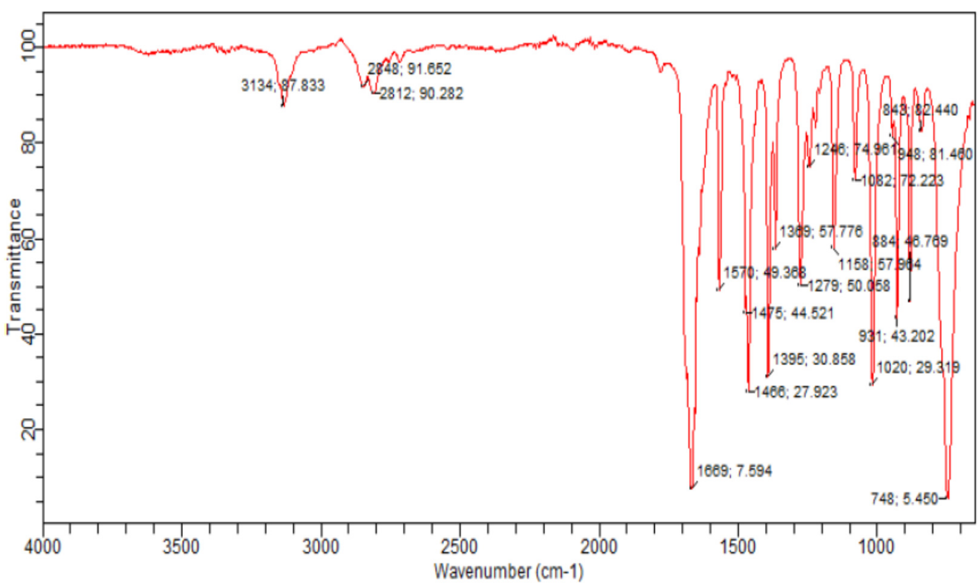

Figure 3: FTIR spectrum for furfural from Rice husk.

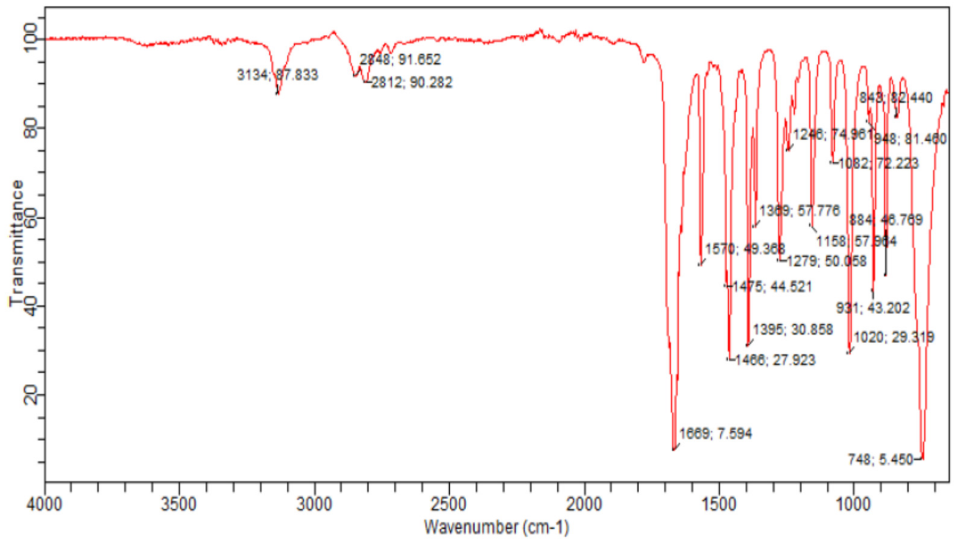

Figure 4: FTIR spectrum for furfural from Groundnut-shell

The IR spectrum for both the Rice husk and Groundnut-shell shows a very strong absorption at 1669 cm^{-1}. These absorptions were comparable with absorption of a significant functional group, which is the conjugated carbonyl (C=O) stretching that occurs at 1870-1610 cm^{-1}, in which for aldehyde, such absorption is between 1740-1720 cm^{-1}. And although the observed frequency was lower than usual, it is partly due to the internal hydrogen bonding that occurs in conjugated aldehydes. Also, though this absorption may appear for ketonic group, the absence of peak at 1725 cm^{-1} indicates strongly the presence of aldehyde and not ketonic group. Furthermore, the spectrum shows a pair of peaks at 3134 cm^{-1} and 2812 cm^{-1} with moderate to weak stretching respectively, which confirms the presence of an aldehydic group.

In addition, the FTIR spectrums obtained was quite comparable with the furfural FTIR spectrum published by NIST (2004), in which the finger print region in the observed IR spectrum of the furfural agrees very closely to the standard furfural IR spectrum published by NIST (2004).

Gas Chromatography-Mass Spectrophotometer Analysis of the Furfural Produced

The Gas chromatography-Mass spectrophotometer analysis of the furfural produced from Rice husk and Groundnut-shell are shown in Figure 5 and 6 respectively.

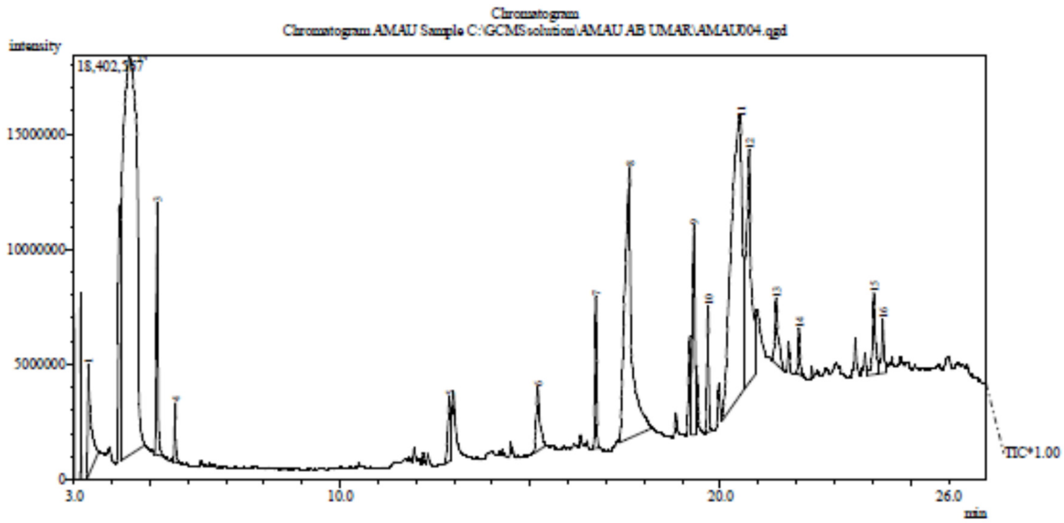

Figure 5: GC-MS spectrum for furfural from Rice Husk

AMAU AB UMAR [SAMPLE- GSE]

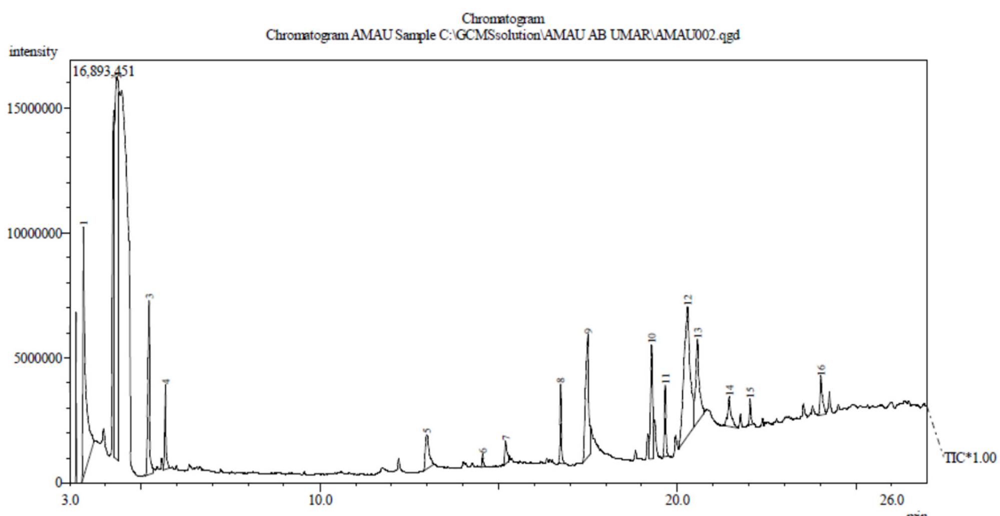

Figure 6: GC-MS spectrum for furfural from Groundnut-shell.

The GC-MS spectrum for the produced furfural shown in figure 5 and 6 indicates 16 absorption peaks each. The mass spectra indicate that Peak one (1) of each of the spectrum corresponds to furfural with percentage (%) peak area of 3.54%. This implies that the compound produced is furfural mixed with other compounds. The furfural produced has molecular weight and molecular formula of 96.05g/mole and $C_5H_4O_2$ respectively.

CONCLUSION

The Fourier Transformed Infrared spectroscopy (FTIR) and Gas Chromatography-Mass Spectrophotometer (GC-MS) agrees very closely to the target compound thus confirms the presence of furfural. Also the optimum acidic concentration for furfural percentage yield is 7.5%. However as observed, though the % furfural yield of both the rice husk and groundnut-shell increases significantly at 7.5% acid concentration, the observed increase in % furfural yield for Rice husk was quite higher than the observed increase of % furfural yield for Groundnut-shell. As such, it is concluded that the most favorable Sulphuric acid concentration for furfural yield is 7.5%, and that Rice husk shows a high optimum increase in % furfural yield than Groundnut-shell.

RECOMMENDATIONS

The observed decrease in furfural yield at much higher concentrations indicates that further research and development should be carried out to improve the production of high quality and quantity of furfural from rice husk and groundnut shell. Also, variables such as time, temperature and others should be optimized in detail so as to discover and develop the best optimum points for higher %furfural yield production. Furthermore, government should invest wisely in the production of value added products from the lignocellulosic biomass, since these lignocellulosic materials are renewable and largely abundant in this country.

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