EFFECT OF TEMPERATURE AND CATALYST ON THE PRODUCTION OF FURFURAL FROM FLUTED PUMPKIN FRUIT (*Telfairia Occidentalis*) WASTE

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ABSTRACT

Complete utilization of agricultural waste in the production of organic chemicals such as furfural was studied. Furfural was obtained from fluted pumpkin fruit (Telfairia occidentalis) pulp which is an agricultural waste. The method of production was a simple dilute acid hydrolysis. Parameters such as temperature, catalyst, resident time, acid and acid concentration were varied to determine the condition for best yield. The physico-chemical properties of the furfural obtained was determined using standard analytical methods and the results were compared to commercial Furfural. From the results, furfural yield of 21.86% W/V was obtained from fluted pumpkin fruit pulp under optimized condition of 180°C, 1 M H_2SO_4, W/V ratio of 5:100, 10g of KCr_2O_7 catalyst and a residence time of 2 hours. The product compared favourably with commercial furfural. This proves that agricultural wastes such as fluted pumpkin fruit pulp can be useful in the production of organic chemicals such as furfural. This calls for the need to engage agricultural wastes in the production of useful chemicals as agro-wastes are promising alternatives to fossil fuels.

INTRODUCTION

Agricultural residues are created in large quantities from cocoa, plantain, banana, palm bunches, pumpkin fruit, etc. and there is inappropriate dumping and burning of these residues leading to the release of probable harmful volatile compounds into the environment (Kuponiyi and Amuda, 2013). During the processing season, vegetable wastes are generated in huge quantities but are not consumed at the same pace so they become readily available and thus, surplus quantities of these are discharged which can cause environmental pollution. These wastes usually contain high levels of organic matter, nutrients, moisture and sometimes salts and are not suitable for disposal in municipal landfills because of their physical, chemical and biological properties.

A great portion of worldwide energy carriers and material products come from fossil fuel refinery. Due to the price increase of fossil resources, their uncertain availability and environmental concerns, the feasibility of oil exploitation is foreseen to decrease in the near future. Consequently, alternative solutions able to mitigate climate change and reduce the consumption of fossil fuels are currently being promoted (Cherubini, 2010). The replacement of oil with biomass as raw material for fuel and chemical production is an interesting option.

Exploiting biomass as an alternative to petrochemicals for the production of commodity plastics is vitally important in building a sustainable society.

Fluted pumpkin fruit pulp (*Telfairia occidentalis*) is a member of the cucurbitacase family. Fluted pumpkin is a dioecious and perennial plant that is characterised by greenish leafy vegetables and fleshy fluted gourds with hard edible seeds. When cultivated, the plant develops tendrils that usually creeps and spreads on the surface of the ground if left unattended to and coil through stakes. Characterised by broad leaves, the fluted pumpkin leaves are locally referred to as “ugu” (Igbo) or “ikong ubong” (Ibibio) and is used for cooking soups, stews, yam and vegetable sauces and even for medicinal purposes.

Figure 1: Fluted pumpkin fruit pulp (FPFP)

The seeds are also edible. However, they are to be properly cooked before consumption. The cooked fluted pumpkin seeds can be dipped in palm oil or local sauces before eating and can be used for making soaps. Fluted pumpkin seeds are an excellent source of protein and oil and thus, are highly beneficial to human health. Interestingly, the seeds can last for months or up to a year in the gourd if left uncut and whole (Nyong, Ita, Ita, and Idim, 2021). There has been an overwhelming increase in the consumption of fluted pumpkin leaves and seeds over the past years due to all the nutritive benefits obtainable from them. The most used part of the plant includes the leaves, shoots and seeds. The fruit pulp (figure 1) is not edible and is regarded as a waste.

Furfural (figure 2) is a heterocyclic aldehyde. It can be produced from materials containing pentosans (Zeitsch, 2002) and lignocellulosic feedstock (Lange, Heide, Buijtenen and Price, 2012). Furfural is the only compound of the furan series that can be directly obtained from biomass at industrial scale (Marcotullio, 2011). Furfural production is generally carried out by hydrolysis of pentosans into monomeric pentoses and their subsequent acid-catalyzed dehydration into furfural. It is also obtained from xylose via dehydration. Furfural has various interesting properties, for example; it thermosets easily, it has physical strength and exhibits resistance to corrosion. It is a raw material for the production of various furan-based chemicals and solvents such as; methyl furan, furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydrofuran, furoic acid, etc.

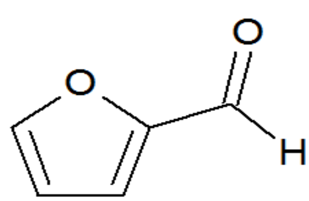

Figure 2: Structure for furfural

Furfural is among the several products that can be obtained from biopolymeric wastes. Due to the presence of an aldehyde group and a conjugated system of double bonds, furfural can undergo several reactions, allowing the production of a range of value-added products (Machado, Leon, Santos, Lourega, Dullius, Elizabeth and Eichler, 2016). Although pentosans are present in virtually all plant materials as constituents of hemicelluloses, their concentration varies depending upon the type of hemicellulose (Marcotullio, 2011).

Furfural may be obtained by the acid catalysed dehydration of 5-carbon sugars called pentose (Adams and Voorhees, 1921). These sugars may be obtained from hemicelluloses present in biopolymers thus, furfural may be considered a green chemical. The chemistry of reaction is as shown below:

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + H_2O$$

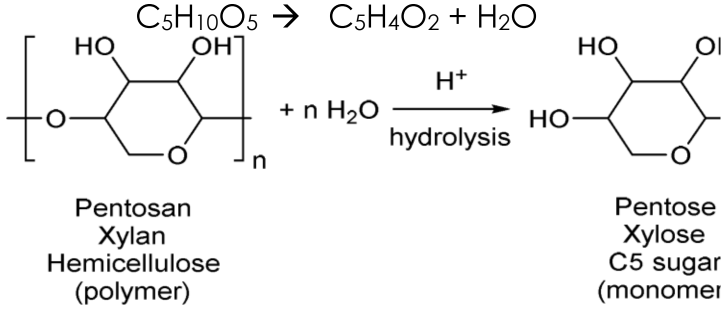

Figure 2: Preparation of furfural

Furfural is commercially produced from biomass in a batch or continuous process using mineral acids as catalysts. Aiming to optimize furfural production processes, several studies have been done involving the use of new types of catalysts in monophasic and biphasic reaction systems. One of the possible catalysts is metallic chloride, which has shown improvement in the rate of furfural yield (Wang *et al.* 2015).

Acid hydrolysis has been investigated as a possible process for treating biopolymeric materials such as wood chips (Silva, 1996), sugar beet pulp (Chamy, Illanes, Aroca and Nunes, 1994) and wheat straw (Fanta, Abbott, Herman, Burr and Doane, 1984).

In general, acid treatment is effective in solubilizing the hemicellulosic component of biomass. Proper combinations of pH, temperature and reaction time can result in high yields of sugars, primarily xylose (Seema *et al,* 2005).

MATERIALS AND METHOD

Sample Collection and Treatment

Fluted pumpkin fruit (*Telfairia occidentalis* fruit) was collected from a dumpsite at Akpan Andem Market, Uyo, Akwa Ibom State. The samples were washed, ground, sundried, ground to powder and stored in an airtight container prior to analysis.

The dried sample (10 g) was introduced into a flat bottom flask containing 100 ml of 1M aqueous HCl and 10 g of $CaCl_2$, shaken and placed in a distillation apparatus. Distillation was observed for 2 hours at 100°C. The distillate was set to flow into a conical flask containing 20 ml chloroform to aid the formation of two layers with the aqueous layer at the top and the chloroform-furfural layer at the bottom of the flask. The chloroform-furfural layer was collected and subjected to rotary evaporation at 14mmHg to remove the chloroform until a clear yellowish liquid was obtained. This procedure was repeated with 0.5, 2 and 5 M HCl and H_2SO_4, respectively. The temperature, catalyst as well as reaction time was also varied to determine the best condition for optimal yield.

Percentage yield: The percentage yield was calculated using equation

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \text{ X } 100$$

Where theoretical yield = the theoretical yield is the maximum amount of product a chemical reaction could create based on chemical equations. Actual yield = is the amount of the product obtained after experiment.

IR Spectroscopic Analysis: A drop of the produced chemicals was placed between two polished flat sodium chloride plates, mounted on the FTIR Spectrophotometer and scanned.

Furfural Estimation in Hydrolysate: Exactly 25 ml of the hydrolysate and 200 ml of 2 M HCl was measured into a conical flask containing 20 ml of 0.05M $KBrO_3$ solution and allowed to stand for 5 minutes. 10 ml of KI was then added and the liberated iodine was titrated against 0.1 M sodium thiosulphate solution. The titre values were used to calculate the actual yield of furfural using equation.

$$\text{Concentration of furfural} = \frac{\text{a X v X } 0.0024}{\text{n} - \text{g}}$$

Where a = volume of thiosulphate used in titration (ml); v = total volume of the hydrolysate that was obtained in the hydrolysis (ml); n = volume of the hydrolysate which was taken for analysis (ml); g = dry mass of the sample which was taken for analysis (5 g); 0.0024 = mass of furfural which corresponds to 1 ml of sodium thiosulphate solution (constant).

RESULTS AND DISCUSSION

Percentage Yield of Furfural obtained from Acid Hydrolysis of fluted pumpkin fruit pulp (FPFP): The efficiency of thermochemical conversion process depends on the operating conditions including residence time, temperature, substrate concentration, catalyst type and catalyst concentration (Peterson *et al.* 2009). The % yield of furfural is presented in Table 1. Results revealed that different acids (HCl and H_2SO_4) did not affect the production of furfural. However, furfural yield increased on addition of salts and there was a slight increase in furfural yield when dilute H_2SO_4 and 10 g of KCr_2O_7 was used as the reaction medium compared to other catalysts.

When 2 M H_2SO_4 was used in the hydrolysis, the maximum yield of furfural reached 5.24%, this shows that FPFP is a good source of pentosan as compared to literature. When compared to other agricultural wastes, the furfural yield obtained from acid hydrolysis of FPFP was higher than 3.34% reported by Mansilla *et al.* (1998) for rice hull at 125°C for 30 minutes.

Table 1: Percentage Yield of Furfural Using Different Acids/Catalysts at Different Concentrations

	Furfural Yield (%)				
Acid used	**Without catalyst**	**$CaCl_2$**	**$KMnO_7$**	**$FeCl_2$**	**KCr_2O_7**
0.5 M HCl	2.07	4.74	8.84	12.10	18.83
1 M HCl	3.14	5.23	9.60	13.00	20.13

2 M HCl	4.53	7.20	9.05	13.98	21.39
5 M HCl	3.17	9.46	9.80	13.80	18.93
0.5 M H_2SO_4	2.69	6.64	9.37	13.37	20.39
1 M H_2SO_4	3.78	7.18	10.10	15.32	21.47
2 M H_2SO_4	5.24	7.50	10.64	15.61	21.86
5 M H_2SO_4	3.79	7.13	10.46	14.33	19.41

Liquid / Solid ratio100 ml /5 g; Temperature: 180°C; Reaction time: 120 Minutes; Catalyst: 10 g

The liquid /solid (L/S) ratio had been recognized as an important factor in furfural yield at low acid concentration (Mital, 1977). The variation of L/S ratio (13 – 50 m/g) at 2 M H_2SO_4; 100°C and 120 minutes showed that the L/S ratio of 20 ml/g gave the high furfural yield of 5.24%. This agrees with the findings of Li *et al.* (2014). According to them, L/S ratio has a great impact on hemicelluloses hydrolysis rate. When L/S ratio is increased, the rate of hydrolysis also increases. In their study, L/S ratio was varied from 6 ml/g to 14 ml/g which led to increased rate of hydrolysis from 67.16% to 83.39%.

The highest yield of furfural obtained in this study was 21.86% on the basis of the sample weight at 108°C using 2 M H_2SO_4, 10 g KCr_2O_7, L/S ratio of 20 ml/g for 120 minutes. These results are comparable with 35.8% furfural yield from hydrolysis of oil palm frond at 260°C using ethanol and formic acid reported by Mohamed *et al.*

Effect of Temperature on Furfural Yield: Furfural yields obtained at different temperatures is presented in Figure 3. Five temperatures; 100, 120, 150, 180 and 200°C were used at L/S ratio of 20 mg/g, 5 g of $CaCl_2$ and a residence time of 2 hours. Results revealed that the percentage yield of furfural from fluted pumpkin fruit pulp (FPFP) increased with increasing temperature. At a temperature of 180°C, 5.23% yield of furfural was obtained.

This agrees with the findings of Chen, Qin and Yu (2015), who reported high yield of furfural (31.00%) from rice straw at 160°C. Yemis and Mazzaa (2011) obtained similar result in their study. Here, the best furfural yield of 5.23% was observed at 180°C for 120 minutes.

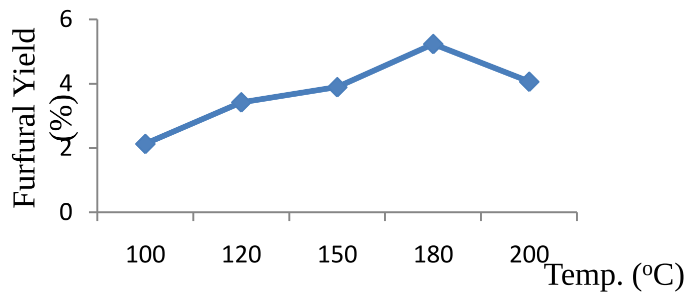

Figure 3: Effect of temperature on furfural yield

The reaction temperature is the most important influence on all thermo chemical conversion processes. According to Dias *et al* (2010), the conversion of plant biomass to furfural is strongly influenced by temperature. Low reaction time and higher reaction temperature produced a higher furfural yield from FPFP. Yadav *et al.* (2017) obtained a similar result on the hydrolysis of peapod waste. Furfural yield of 40.60% was obtained using 6% H_3PO_4 at 160°C. The reduction in furfural yield despite higher temperature can be attributed to the cross –linking and self-polymerization taking place simultaneously in the reaction (Yemis *et al.,* 2011). Cross polymerization between furfural and the intermediates produced from xylose – to –furfural results in furfural decrease at higher temperatures above 180°C (Mohamed *et al.,* 2015).

Effect of Catalyst and Catalyst Concentration on Yield of Furfural: The result of effect of catalyst on furfural yield is presented in Figure 4 and 5. The catalysts used in this study were calcium chloride ($CaCl_2$); ferric chloride ($FeCl_3$); potassium permanganate ($KMnO_4$) and potassium dichromate (KCr_2O_7). During the study, concentration of acid, temperature and duration of biomass treatment were kept constant at 1 M H_2SO_4, 180°C and 120 minutes respectively.

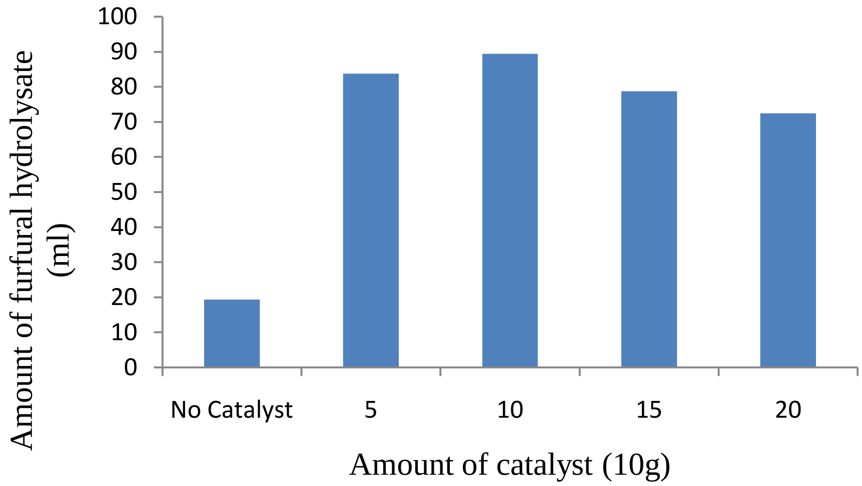

Figure 4: Effect of catalyst amount on the production of furfural from TOF and LAF

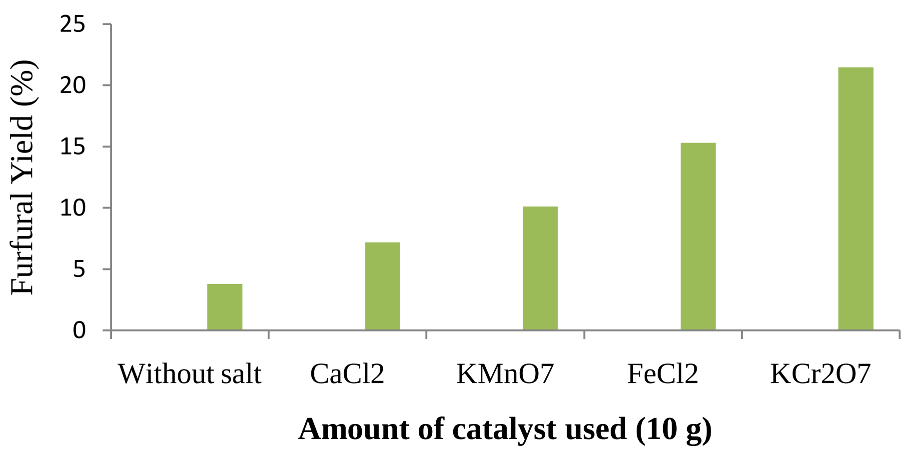

Figure 5: Effect of catalyst type on the production of furfural from fluted pumpkin fruit pulp.

Catalyst is one of the chief parameters in furfural production process as it speeds up the rate of the reaction. In this study, the effect of catalyst as well as the amount of catalyst used on the FPFP furfural production process was studied over a wide range of concentrations (5g to 20g). The catalysts used in this study were calcium chloride ($CaCl_2$); ferric chloride ($FeCl_3$); potassium permanganate ($KMnO_4$) and potassium dichromate (KCr_2O_7). Three constant parameters of the hydrolysis process; concentration of acid, temperature and duration of biomass treatment were 1 M H_2SO_4, 180°C and 120 minutes respectively.

As demonstrated by our results, the addition of salt to the hydrolysis increased the amount of hydrolysate obtained from 19.37 ml to 83.80 ml when 5g of the salt was used. Increase in the amount of $CaCl_2$ from 5 g to 10 g gave an increase in the amount of hydrolysate obtained. Further increase in the amount of the catalyst resulted to a decrease in the amount of hydrolysate (Figure 4). The highest amount of the hydrolysate was obtained using 10 g of $CaCl_2$.

The effect of the catalyst is to increase the net rate of furfural formation without significantly altering the maximum yield. Smuk and Zoch (2009) concluded that furfural yield is dependent upon the amount of xylose decomposed in acidified solutions containing metallic catalysts. They argued that this observation is apparently valid for temperatures as high as 240^{o}C and all salt concentrations up to saturation. The presence of the catalyst accelerates the rate of furfural production and has no adverse effects on yield.

The highest amount of hydrolysate was obtained with KCr_2O_7 (Figure 5). Metallic salts have been reported as enhancers in the production of furfural. Among the most common catalysts employed are TiO_2, $ZnCl_2$, $AlCl_3$, etc. (Mansilla *et al.,* 1987). They may act as lewis acids promoting the reaction or may stabilize intermediates in the hydrolysis of pentosans.

In this work, different metallic oxides and chlorides were used to evaluate their effect on furfural yield. Results proved that all the salts used in this study improved furfural yield. The results obtained here agree with the findings of Zhang *et al.* (2012) who reported on the use of several metal chlorides for the dehydration of glucose. They reported that $CrCl_2$ was an efficient catalyst, yielding up to 70% furfural in 3 hours. Several explanations for high furfural yields achieved using chlorides has been put forward, such as the low concentration of water present in the reaction medium, decreasing the activation barrier for the furfural formation and the formation of complexes between the sugar and metal chlorides (Zhou and Zhang, 1985). The salt has a positive effect on enhancing the rate of formation of furfural (Gebre, Fisha, Kindeya and Gebremichal, 2015).

Similarly, Mao, Zhang, Gao and Li (2013) reported on the digestion of corn cobs using both acetic acid and $FeCl_3.6H_2O$ solid catalyst in a semi-batch reactor system. Notably, a 73% furfural yield was achieved. In an effort to find more environmentally friendly alternatives to mineral acid catalysts, the application of solid metal chloride catalysts has shown promise. Halide ions, especially Cl^-, appear to promote enolization and improve the selectivity and yield of furfural from xylose (Marcotullio and De-jong, 2011).

FTIR Spectra of Furfural obtained from fluted pumpkin fruit pulp (FPFP): The FTIR spectra of furfural produced from FPFP hydrolysate is presented in Figure 6. The spectra showed well defined peaks at 3019, 2811, 1367, 1521, 1768, 1714, 1214 and 1045cm^{-1}.

The presence of furfural was proven in fluted pumpkin fruit pulp hydrolysate by FTIR spectra (Figure 6). The spectrum showed a very strong absorption at 1714.46 cm-1. This absorption indicates a conjugated carbonyl (C=O). The absorption wave number is slightly lower than usual due to internal hydrogen bonding which occurs in conjugated unsaturated aldehydes. But this peak can appear for chemical compounds like carboxylic acid (COOH), ketone, ester and aldehyde groups. The absence of peak at 1763.72 cm^{-1} indicated the presence of aldehyde and not the ketone group

(Sashikala and Ong, 2009). Furthermore, no broad peaks were observed at the area of 3400 to 2400 cm^{-1} which belongs to the hydroxyl (OH). This confirms the absence of carboxylic acid group.

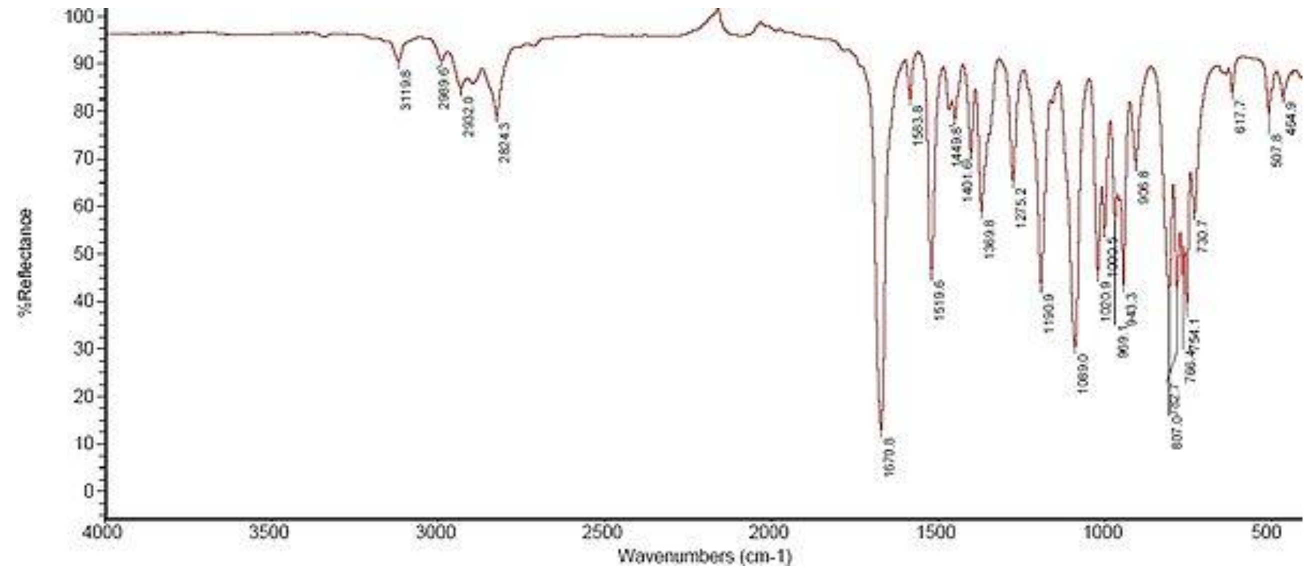

Figure 6: FTIR spectrum of furfural from fluted pumpkim fruit pulp

Furthermore, the presence of the aldehyde was proven with the existence of two peaks gained at 3019.55 cm^{-1} and 2811.71 cm^{-1}. These absorptions show a moderate intense stretching of aldehydic C-H bond attributed to Fermi resonance between the fundamental aldehydic C-H stretching and the first overtone of the aldehydic C-H bending vibration. It appears at 1367.41 cm^{-1} in the spectrum. These bands are frequently observed for aldehyde group. However strong peaks from 1521.45 cm^{-1} to 1421 cm^{-1} are the stretching of C=C from aromatic ring. Aromatic =C-H bending out of plane peaks were observed from 928.72 cm^{-1} to 849.53 cm^{-1}. Two strong peaks at 1045.28 cm^{-1} and 1214.45 cm^{-1} indicated the C-O stretching vibration.

CONCLUSION

The objective of this research was to produce furfural from fluted pumpkin fruit pulp (*Telfairia occidentalis)* fruit. Results of the analysis revealed that dilute acids when combined with metallic salts enhanced the formation of furfural resulting in high yield. However, furfural yield could be improved by changing the reaction conditions such as temperature, residence time, amount of catalyst, type of catalyst, solid/liquid ratio, type of acid and concentration of acid. From this study, the optimal reaction conditions were; temperature of 180°C, 1 M H_2SO_4, liquid /solid ratio of 100:5, 10 g of KCr_2O_7 catalyst and a residence time of 2 hours. Under optimized reaction conditions, 30.03% was obtained from sponge gourd and 21.86% from fluted pumpkin fruit.

Biopolymers are promising alternatives to fossil fuels. The utilization of agricultural residues and wastes for furfural production is a cost effective and environmentally friendly approach for sustainable development.

REFERENCES

Adams, R. and Voorhees, V. (1921). Furfural. Cells, 1, 280 – 282.

Chamy, R., Illanes, A., Aroca, G. and Nunes, I. (1994). Acid Hydrolysis of Sugar beet pulp as pretreatment for fermentation. *Bioresource Technology,* 50, 149 – 159.

Cherubini, F. (2010). The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy conversion and management,* 51 (7): 1412 – 1421.

Dias, A. S., Lima, S., Carriazo, D., Rives, V., Pillinger, M. and Valente, A. A. (2010). Exfoliated titanate, niobate and titanoniobate nanosheets as solid acid catalysts for the liquid-phase dehydration of d-xylose into furfural. *Journal of Catalysis,* 244, 230–237.

Fanta, G. F., Abbott, T. P., Herman, A. I., Burr, R. C. and Doane, W. M. (1984). Hydrolysis of wheat straw hemicellulose with trifluoroacetic acid: Fermentation of xylose with *Pachysolen tannophilus*. *Biotechnology Bioengineering,* 26, 1122 – 1128.

Gebre, H., Fisha, K, Kindeya, T. and Gebremichal, T. (2015). Synthesis of furfural from bagasse. *International Letters of Chemistry, Physics and Astronomy,* 57, 72 – 84.

Kuponiyi, T. I. and Amuda, O. S. (2013). Evaluation of the production of oxalic acid from some solid industrial wastes in Nigeria. *International Journal of Basic and Applied Science,* 2 (1): 91 – 97.

Mansilla, H., Baeza, J., Urzúa, S., Maturana, G., Villaseñor, J. and Duran, N. (1998). Acid-catalysed hydrolysis of rice hull: Evaluation of furfural production. *Bioresource Technology,* 66, 189-193.

Marchado, G., Loen, S., Santos, F., Lourega, R., Dullius, R., Elizabete, M. M. and Eichler, P. (2016). Literature review on furfural production from lignocellulosic bioimass. *Natural Resources,* 7, 115 – 129.

Marcotullio, G. (2011). The chemistry and technology of furfural production in modern lignicellulose feedstock biorefineries. Published Ph.D. Thesis, Delft University of Technology, Italy. P. 27.

Marcotullio, G. and De-Jong, W. (2011). Furfural formation from d-xylose: the use of different halides in dilute aqueous acidic solutions allows for exceptionally high yields. *Carborhydrate Research*, 346, 1291 – 1293.

Mital, K. V. (1977). *Optimization methods.* New Delhi Wiley Eastern Ltd. Pp 23-26.

Nyong, B. E., Ita, O. O., Ita, P. O. and Idim, V. D. (2021). Utilization of Sponge Gourd (*Luffa Acutangula*) as a Starting Material in the Production of Bioethanol. *Research in Material Sciences,* 1: 23 – 28.

Peterson, A., Hohmann, L., Huang, L., Kim, B., Eng, J. K. and Martin, D. B. (2009). Analysis of RP-HPLC loading conditions for maximizing peptide identifications in shotgun proteomics. *Journal of Proteome Resources,* 8 (8):4161- 4168.

Seema, J., Patel, R., Onkarappak, T. and Snobia, S. (2007). Bioethanol production from fungi pretreated wheat and rice straw. *International Journal of Microbiology,* 4, 1 – 7.

Silva, J. B. A. (1996). Utilization of the hydrolysate of *eucalyptus* hemicellulose for production of microbial protein. *Biological Technology,* 38, 147 – 153.

Wang, W., Ren, J., Li, H., Deng, A. and Sun, R. (2015). Direct transformation of Xylan-type Hemicelluloses to Furfural via $SnCl_4$ catalysts in aqueous and biphasic systems. *Bioresource Technology,* 181, 188 – 194.

Yadav, S. P., Ghosh, U. K. and Ray, A. R. (2017). Kinetic studies on *Pisum sativum* waste (Peapod) hydrolysis to Furfural. *Biotechnology resources,* 12 (2): 2326 – 2338.

Yemis, O. and Mazza, G. (2011). Acid – catalyzed conversion of Xylose, Xylan and Straw into Furfural by microwave - assisted reaction. *Bioresource Technology,* 102, 7371 – 7378.

Zeitsch, K. J. (2002). The Chemistry of Furfural and its Many By-products. Accessed online on 29th August, 2021 via www.sigmaaldrich.com.

Zhang, Y., Xu, Y. H., Yi, H. Y. and Gong, J. M. (2012). Vacuolar membrane transporters OsVIT1 and OsVIT2 modulate iron translocation between flag leaves and seeds in rice. *Plant Journal,* 72 (3):400-410.