PRINT ISSN 1119-8362
Electronic ISSN 2659-1502

Full-text Available Online at
https://www.ajol.info/index.php/jasem
http://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 27 (3) 579-583 March 2023

Optimization of Furfural Production from Corncobs using p-Toluene Sulphonic Acid

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ABSTRACT: Furfural is a promising renewable platform compound derived from lignocellulosic biomass that can be further converted to bio-based industrial chemicals. About 90% of what is used in Nigeria is imported, translating to hundreds of millions of Dollars in foreign exchange. Hence, this research aim was to optimize the production process of furfural from corncobs, a lignocellulosic biomass using a three steps methods which includes; pretreatment of raw materials, acid hydrolysis and distillation according to standard methods. The corncobs were grind to powdered form and then hydrolysed in a stirred reactor using p-toluene sulphonic acid (p-TsOH) by varying parameters which includes; temperature (60, 65 and 70 ºC), reaction time (1, 2 and 3hrs) and concentration (30 ml, 40 ml and 50 ml). Analysis using FTIR was conducted to identify the functional group present in the furfural produced. The results showed yield of furfural increased from 23.66 % to 28 %, and the highest yield of furfural production was obtained using 50 ml p-TsOH at 70 ºC for 3 h.

DOI: **https://dx.doi.org/10.4314/jasem.v27i3.23**

Cite this paper as: AWE, F. E; OKUNOLA, O. J; IBRAHIM, Z. H; SULE, M (2023). Optimization of Furfural Production from Corncobs using p-Toluene Sulphonic Acid. *J. Appl. Sci. Environ. Manage.* 27 (3) 579-583

Dates: Received: 18 February 2023; Revised: 21 March 2023; Accepted: 24 March 2023
Published: 31 March 2023

Keywords: Furfural; Corncorb; Optimization; Analysis

Our planet is confronted by the multiple challenge of the reduction of fossil resources based on the price of fossil-fuel based materials and the increase of greenhouse gas emissions (Harmaajärvi *et al*., 2004; Okunola *et al*., 2013; Delbecq *et al*., 2018) as well as increasing societal demand for industrial ecology aimed at disconnecting growth of production of goods and wealth from environmental impacts of all sorts and associated concepts. Over the years, replacement of non-renewable fossil feedstock with renewable biomass feedstock for the efficient production of industrial chemicals is a great challenge in the area of green chemistry (Ezeanyanaso *et al*. 2013). About 300-700 Ktons of furfural is produced annually worldwide and 72.6% of total market volume in 2013 was produced in China (Kumar, 2015). This value represents more than half of the global capacity. Most (90%) of what is used in Nigeria is imported, translating to hundreds of millions of Dollars in foreign exchange. With the current implementation of the National Economic Reconstruction and Growth Plan (NERGP) and challenges posed by COVID-19, the need to produce industrial chemicals locally is urgent. In addition, because of concerns of climate change the race for producing these chemicals from natural biological and renewable sources instead of synthetic ones is on. Production of furfural locally using renewable biobased feedstock will also address Goal 9 of Sustainable Development Goals (SDGs), namely promotion of sustainable and inclusive industrialization and foster innovation. Furfural is a promising renewable platform compound derived from lignocellulosic biomass that can be further converted to biofuels and biochemicals. The highly fractionalized molecular structure of furfural makes it a desired raw material for the measurable production

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of value-added chemicals containing oxygen atoms (Li *et al*., 2016). Lately, studies focusing on the conversion of xylans to bioenergy, chemicals and biomaterials have received a lot of attention in the context of biorefineries. Among the products which can be obtained from pentoses, there is furfural, which is a promising alternative, since it is a versatile compound that can be used in the synthesis of several important chemicals, such as furan and furfuryl alcohol, and it is vastly used in several applications in refining oil, plastics production, pharmaceutical and agrochemical industries (Wang *et al*., 2015; Machado *et al*., 2016). Furfural production process is affected by several factors including catalyst concentration, reaction temperature, pressure, time, agitation, liquid and solid ratio, and size of raw material. (Sangarunlert *et al.,* 2007). Furfural production has become a case study in Nigeria. Research has shown scanty production in Nigeria and therefore leading to this important additive. Furfural has been tagged as an expensive additive. Hence, the objective of this work is to optimize the production process of furfural from corncobs, a lignocellulosic biomass using a three-step techniques.

MATERIAL AND METHODS

Sample collection and preparation: The corncobs were collected from a nearby maize plantation in Dutsin-Ma town, Katsina State. The collected corncobs were washed carefully with distilled water and allowed to dry at room temperature for twenty days to ensure adequate removal of moisture from the sample. The dried corncobs were later subjected to a size reduction process by pounding with a wooden mortal to powdered form with a maximum particle size 150 mesh (Widyastuti and Istiqomah, 2015). The powder was then dried in an oven at 60^{o} C for 6 hours to ensure adequate removal of moisture to 8% dry weight of the sample before commencing treatment (Widyastuti and Istiqomah, 2015).

Optimization of furfural using hydrolysis method: Powdered corncobs of 3g were hydrolyzed with 0.2 M p-Toluene Sulphonic acid. The reactions were carried out in a stirred refluxed reactor equipped with a thermometer and a condenser. The optimization process of furfural production was carried out according to modified method Widyastuti and Istiqomah (2015) and Ji *et al*. (2017) at varying temperature, reaction time, and volume of 0.2 M p-Toluene Sulphonic acid (p-TsOH) as shown in Table 1. The reactions were carried out normal atmospheric pressure.

Separation of furfural from the hydrolyzed sample: The hydrolysate was filtrated using a filter paper and an equivalent amount of toluene solution was added to the filtrate in ratio of 1:1 (Widyastuti and Istiqomah, 2015). Separation of air-furfural-toluene was conducted by decantation for 10 hours which resulted in the furfural-toluene at the upper layer. Then $MgCl_2$ was used in place of NaCl obtained in Widyastuti and Istiqomah (2015). Then, 0.1M – 0.8 M $MgCl_2$ was added to the furfural-toluene mixture to promote furfural formation and thereby increased furfural yield. The furfural-toluene mixture was distilled at 110 ^{o} C.

Table 1: Varied parameters for furfural production

Temperature (^{o} C)	Time (hours)	Mass of powder corncobs (g)	p-Toluene sulphonic acid(ml)
60	1	3	30
	2	3	30
	3	3	30
65	1	3	40
	2	3	40
	3	3	40
70	1	3	50
	2	3	50
	3	3	50

Determination of furfural yield: The furfural yield was determined according to Zeitsch (2000). This was done by taking ratio of furfural residue (g) obtained and dividing it with the mass of sample powder (gram) used for the production process and multiplying the result by 100 so as to present the obtained result in percentage.

$$\frac{\text{Furfural residue (gram)}}{\text{Mass of sample powder (gram)}} X\ 100$$

Analysis of the product using FT-IR: The furfural sample produced was analyzed quantitatively using Fourier Transform Infrared Spectroscopy (FTIR) to check for the functional group of the sample as well as to know the Wavelength and also the Transmittance. Each sample was prepared for analysis by carefully cleaning the machine and checking if the sample that will be analyzed is solid or liquid. The analysis was done by cleaning the surface of the diamond crystal plate to avoid any form of contamination. Then the liquid sample was placed carefully using a dropper into the diamond crystal plate. The FTIR spectrometer generated a graph in the form of absorbance spectra, which shows the unique chemical bonds and the molecular structure of the sample material.

RESULTS AND DISCUSSION

Yield of products from the optimized parameters: The yields of furfural from corncob hydrolysis at varied conditions are shown in Table 2.

Effect of reaction temperature on furfural formation: As shown in Table 2, there was a sharp increase in the yield of furfural as the temperature rise at the beginning and the maximum furfural yield of 28.0% was accounted for at 70^{0}C. Similar results were also reported by Du *et al*. (2015) at 200 ^{0}C.

Effect of time on furfural formation: The timing of 1 to 3 hours was employed while keeping other conditions constant. As shown in Table 2, there were high yields in furfural production as the time increases. The maximum furfural yield was achieved at 70^{o}C for 3hours.

Table 2: Yield of Furfural from Experiments

Temperature (^{0}C)	Time (hours)	Mass of sample powder(gram)	p-TsOH (ml)	Furfural residue (gram)	Yield (%)
60	1	3	30	0.71	23.66
	2	3	30	0.73	24.33
	3	3	30	0.75	25.00
65	1	3	40	0.73	24.33
	2	3	40	0.78	26.00
	3	3	40	0.76	25.33
70	1	3	50	0.77	25.66
	2	3	50	0.81	27.00
	3	3	50	0.85	28.00

Table 3a: FT-IR results of the product at 30 ml PTsOH

Acid Catalyst PTsOH (ml)	$MgCl_2$ (M)	Time (Hour)	Wave Number (cm^{-1})	Compound Class and Functional Group
30	0.2	1	3335 2117 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		2	3335 2102 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		3	3331 1279 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
	0.4	1	3335 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		2	3331 2121 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		3	3335 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
	0.6	1	3335 2110 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		2	3335 2102 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		3	3331 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
	0.8	1	3335 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		2	3335 2110 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		3	3335 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene

Effect of p-SOH on furfural formation: To study the effect of acid catalyst on corncobs, the experiment was done by varying the volume of acid catalyst used.

The highest furfural yield of 28 % was obtained from 50ml p-SOH at 70^{o}C in 3 hours as shown in Table 2.

Effect of toluene on furfural formation: Toluene is as an important organic solvent in the production of furfural as it serves as extracting agent. After refluxing corncob with the acid catalyst and filtration was carried out, toluene was added to the filtrate thereby forming two layers (furfural-toluene). Sahu and Dhepe (2012) reported that toluene was the preferred solvent as an extracting agent, this was also evident in this study. The extraction of furfural into the organic layer was to retard further secondary reactions because the catalyst p-TsOH only exists in the aqueous layer, hence halting the further reaction process (Widyastuti and Istiqomah, 2015).

Table 3b: FT-IR results of the product 40 ml PTsOH

Acid Catalyst PTsOH (ml)	$MgCl_2$ (M)	Time (Hour)	Wave Number (cm^{-1})	Compound Class and Functional Group
40	0.2	1	3286 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		2	3316 2113 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		3	3335 2117 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
	0.4	1	3331 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		2	3335 2217 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		3	3320 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
	0.6	1	3331 2091 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		2	3335 1640 2113	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		3	3335 2095 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
	0.8	1	3324 1640 2095	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		2	3331 2106 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		3	3335 2117 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene

Table 3c: FT-IR results of the product 50 ml PTsOH

Acid Catalyst PTsOH (ml)	$MgCl_2$ (M)	Time (Hour)	Wave Number (cm^{-1})	Compound Class and Functional Group
50	0.2	1	3335 2113 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		2	3335 1640 2106	O-H Stretching (Alcohol) C=C Stretching conjugated alkene Alkyne
		3	3335 2121 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
	0.4	1	3335 1640 2110	O-H Stretching (Alcohol) C=C Stretching conjugated Alkene Alkyne
		2	3331 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		3	3335 2110 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
	0.6	1	3335 2117 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		2	3331 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		3	3331 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
	0.8	1	3335 2213 1640	O-H Stretching (Alcohol) Alkyne C=C Stretching conjugated alkene
		2	3331 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene
		3	3335 1640	O-H Stretching (Alcohol) C=C Stretching conjugated alkene

Effect of $MgCl_2$ on furfural formation: $MgCl_2$ is used as a promoter of furfural yield in furfural production. Therefore, various concentration of $MgCl_2$ ranging from 0.2 M to 0.8 M. The result shows the yield of furfural using 50 ml PTSA at 70^{o}C at 3hours using 0.8 M of $MgCl_2$. The high yield at 0.8 M could be attributed to the salting out effect of $MgCl_2$, which decrease the solubility of furfural in water, forcing the furfural to transfer to the organic phase (Marcotullio and de Jong, 2011; Du *et al*., 2015).

FTIR Analysis: As shown in Tables 3a, 3b and 3c, the functional groups OH stretching (alcohol), conjugated Alkene in the products is indicative of presence of furfural.

Conclusion: Furfural was synthesized from corncobs which contains pentose up to 32%. At higher reaction temperature and longer reaction time, rate of hydrolysis reaction was getting more rapid. The result showed the highest yield was 28% which was obtained from hydrolysis using 50ml PTSA at 70^{o}C for 3 hours and using 0.8 M $MgCl_2$ which serves as a promoter in furfural formation. The FTIR confirmed the furfural compound and other impurities. It is therefore recommended that corn cobs should not be disposed since it has a good potential in the production of furfural.

Acknowledgment: The research team wishes to express their gratitude to the Institution Based Research (IBR) TETFUND for the grant given to enable the completion of this research work. Appreciations also goes to the Nigerian Defence Academy for giving us the opportunity in executing this project.

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