

PRODUCTION OF FURFURAL FROM OIL PALM FIBRES

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ABSTRACT

Furfural is a chemical compound produced by biomass rich in pentoses content in the hemicellulose as raw material, in a reaction catalysed in presence of strong acids. This study determines the process parameters for converting xylan, extracted from oil palm empty fruit bunches (OPEFB), into furfural using a two-step process, namely acid hydrolysis, followed by dehydration. Xylan was first extracted from OPEFB using direct alkaline extraction method. The resulting xylan was then treated with a known concentration of sulphuric acid (H_2SO_4) (ranging from 11%-15% v/v) with reaction time (ranging from 30-150 min), with or without presence of sodium chloride (NaCl) as co-catalyst to produce xylose. After dehydration process, xylose was converted into furfural with parameters as in dehydration process. Furfural was characterised using Fourier transform infrared (FTIR) and Proton nuclear magnetic resonance (1H -NMR). FTIR spectrum exhibited a very strong absorption at 1706 cm^{-1} , indicating the presence of the conjugated carbonyl (C=O) group. The highest yield of furfural produced was 9.01% after treatment with 15% H_2SO_4 using NaCl as catalyst for 90 min. However, pentosans only contribute a portion of the total composition of lignocellulose, compared to cellulose which is the largest fraction of lignocellulosic biomass. Therefore, the furfural should be extracted using an integrated value economy method.

Keywords: dilute acid hydrolysis, empty fruit bunch fibre, furfural.

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INTRODUCTION

Furfural or 2-furaldehyde and its derivatives are considered as a versatile precursor to obtain a wide range of chemicals for various applications (Kamm *et al.*, 2006; Alonso-Fagundes *et al.*, 2012; Sadaba *et al.*, 2011; Mansilla *et al.*, 1998). The furfuryl alcohol produced from hydrogenation of furfural has been used as additive or solvent in the production of resins with different characteristics in chemical industry (Merlo *et al.*, 2009; Vazquez *et al.*, 2007; Mansilla *et al.*, 1998). One of the common and important usage of furfural in gas oil, diesel fuel and petroleum refining industry is as selective solvent for separating saturated and unsaturated compounds (Mansilla *et*

al., 1998). In addition, furfural along with its sister molecule, hydroxymethyl furfural (HMF) can serve as a building block for other potential transportation fuels, including dimethylfuran and ethyl levulinate. These fuels could replace furan from petroleum based maleic anhydride (Shen *et al.*, 2018).

Furfural is produced by acid hydrolysis process and dehydration of pentoses containing (mainly xylose) in lignocellulosic materials. Figure 1 shows simplified reaction scheme for conversion of lignocellulosic biomass into furfural. Several researchers investigated the production of furfural by hydrolysis of lignocellulosic waste materials in dilute acid, such as hydrochloric acid (Herrera *et al.*, 2004; 2003; Lavarack *et al.*, 2002) nitric acid (Rodriguez-Chong *et al.*, 2004), sulphuric acid (H_2SO_4) (Yat *et al.*, 2008; Rahman *et al.*, 2006; Aguilar *et al.*, 2002; Montane *et al.*, 2002) and phosphoric acid (Lenihan *et al.*, 2010; Vazquez *et al.*, 2007; Gamez *et*

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al., 2006). The advantage of acid hydrolysis is that the rate of acid hydrolysis is faster than enzyme hydrolysis but glucose also degrades rapidly under acidic conditions (Cheung and Anderson, 1996).

Acid hydrolysis employs usually H_2SO_4 and hydrochloric acid at concentrations of 1%-15% using moderate temperature (in the range of 100°C -150°C) (Wingren *et al.*, 2003). Dilute acid hydrolysis is generally more desirable compared to concentrated acid because of its lower cost. It also allows the high degradation of lignocellulosic biomass under relatively low reaction temperatures. The H_2SO_4 and hydrochloric acids are the most commonly used catalysts for hydrolysis of lignocellulosic biomass.

The formation of furfural from pentosan can be understood in terms of hydrolysis of pentosan (xylan), followed by dehydration of pentose (xylose). Introduction of water molecule in hydrolysis process is to break the glycosidic bond to form xylose or arabinose, and later in dehydration process, three water molecules are then released from the respective sugars to form furfural. *Figure 2* shows

acid hydrolysis and dehydration process of xylose for furfural production.

Several mechanisms have been proposed for furfural formation from xylan. Nimlos *et al.* (2006) favoured closed-chain formation of a dehydrofuranose intermediate by ring contraction of the O2-protonated pyranose (*Figure 3*) in the presence of strong acid such as H_2SO_4 .

Furfural can be extracted from lignocellulosic materials, including plant fibre, such as eucalyptus (García-Domínguez *et al.*, 2013), olive tree (Romero *et al.*, 2010), agriculture waste such as rice husks (Suxia *et al.*, 2012), corn cobs (Sánchez *et al.*, 2013), sorghum straw (Vazquez *et al.*, 2007), sugar cane bagasse (Gamez *et al.*, 2006), wheat straw (Yemis and Mazza, 2011) rice straw (Lin *et al.*, 2013) and non-wood fibre such as date palm tree (Bamufleh *et al.*, 2013). For non-wood, the study on the conversion of oil palm fibre into furfural was limited. About 17.34% furfural was produced from oil palm mesocarp fibre when it was subjected to 15% H_2SO_4 (Riansa-Ngawong and Prasertsan, 2011).

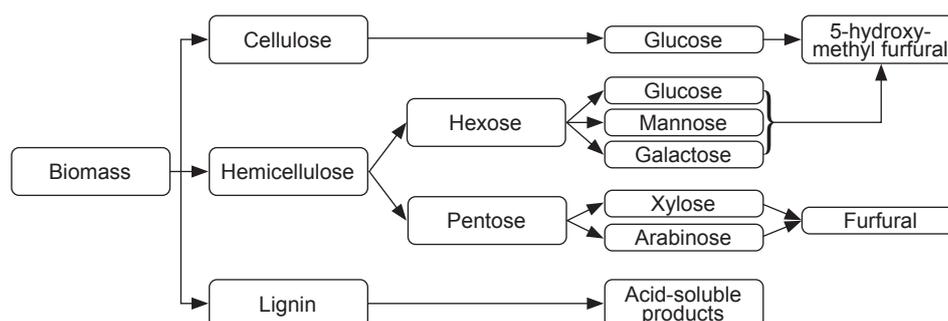
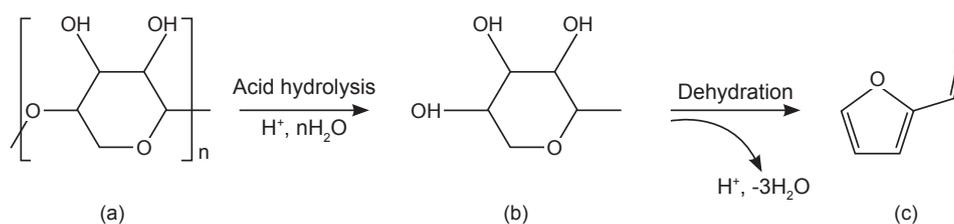


Figure 1. Simplified reaction scheme for conversion of lignocellulosic biomass to furfural.



Source: Riansa-Ngawong and Prasertsan (2011).

Figure 2. (a) Hydrolysis of pentosan (b) followed by dehydration of pentose, (c) to form furfural.

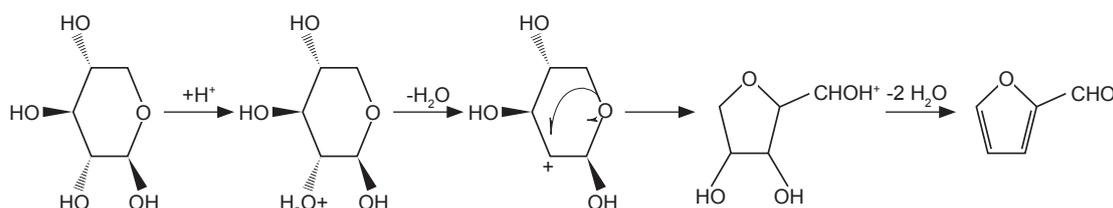


Figure 3. Proposed closed-chain mechanism for furfural formation from xylose.

It is estimated about one third of total pentosans (raw material) can be converted into furfural by existing production processes (Mansilla *et al.*, 1998). In theory, any material containing a large amount of pentose (five carbon) sugars arabinose and xylose can serve as raw material for furfural production. Table 1 outlines the approximate pentosan content of several plants and agricultural residues potentially suitable for furfural production.

In Malaysia, from 17.16 t ha⁻¹ of oil palm fresh fruit bunches produced in 2018, the oil palm industry generates 20%-22% oil palm empty fruit bunches (OPEFB) (Kushairi *et al.*, 2019). The OPEFB biomass with cellulose, hemicelluloses and lignin is estimated to contain about 23%-26% xylan, a sugar polymer made of pentose sugar, xylose (Rahman *et al.*, 2006). Studies available on furfural production from oil palm tree wastes are scarce, relatively old and limited in scope (Rahman *et al.*, 2006; Riansa-Ngawong and Prasertan 2010; 2011; Loi *et al.*, 2011).

The aim of this work is to investigate the production of furfural from OPEFB using H₂SO₄ as catalyst for the process and sodium chloride (NaCl) will be introduced as a co-catalyst or promoter. The effect of acid concentration and reaction time will be investigated and the optimum condition to maximise furfural yield will be determined.

TABLE 1. PENTOSAN CONTENT OF PLANTS AND AGRICULTURAL RESIDUES

Plant material	Pentosan content (%)
Corn cobs	35
Almond husks	30
Rye straw	30
Oat hulls	29
Cottonseed hulls	28
Barley straw	25
Birchwood residues after felling	25
Sugarcane bagasse	25
Sunflower husks	25
Wheat straw	24
Flax shives	23
Hazelnut shells	23
Birchwood logs	22
Eucalyptus wood	20
Rice hulls	17
Maple wood	16
Pinewood	8
Peanut shells	3

Source: O'Brien (2006).

METHODOLOGY

Materials

Shredded OPEFB fibres were collected from the Palm Oil Milling Technology Centre (POMTEC), located in Labu, Negeri Sembilan, Malaysia. After drying, OPEFB fibres were kept in a plastic bag and stored at room temperature. All chemicals used were analytical grade and used without further purification. Xylan from beech wood and 2-furfuraldehyde (furfural) standard reference materials were purchased from Sigma-Aldrich.

Method

OPEFB pretreatment and xylan extraction. Pretreatments of OPEFB fibres were carried out according to ASTM D 1104-56 (1978). Dry EFB-fibre was initially treated by soaking in 24% solution sodium chlorite (NaClO₂) in the ratio of 1:10 (w/v) and (ml) 0.01% acetic acid solution, at 70°C for 1 hr. The solid residues were then washed with hot water followed by acetone, to remove water. The treated OPEFB fibres was then dried in an electric oven at 105°C for 3 hr.

The treated OPEFB fibres were then soaked in 3M sodium hydroxide (NaOH) at ratio of 1:10 (w/v) for 4 hr. The solid residue material was then separated from the solution by vacuum filtration. The filtrate was collected and neutralised with 50% acetic acid (v/v). Cold isopropanol was then slowly mixed into the filtrate admixture resulting in a colloidal suspension. After being left overnight, the suspension was then separated into two heterogenous layers containing xylan solid. After filtration, the xylan was washed with 100 ml distilled water and dried in an electric oven at 60 ± 5°C for 6 hr. The yield (%) of xylan was measured as dry weight basis and calculated using the following Equation (1):

$$\text{Yield (\%)} = \frac{\text{Weight of dried xylan}}{\text{Weight of dried OPEFB}} \times 100 \quad (1)$$

Conversion of xylan into furfural. Furfural was converted from xylan using a modified steam distillation method (Sashikala and Ong, 2007). About 1 g dry xylan was placed into a 250 ml round bottomed flask with 100 ml of dilute H₂SO₄. The mixture was constantly stirred and heated at 175°C. The vapour produced was condensed and collected in a receiving flask. The distillation process ran for 30-150 min.

Characterisation of xylan and furfural. The extracted xylan was characterised using Fourier transform infrared (FTIR) spectroscopic technique. Furfural was also characterised using FTIR and Proton nuclear

magnetic resonance ($^1\text{H-NMR}$). FTIR analysis was performed by Perkin Elmer TG-IR Hyphenation System and $^1\text{H-NMR}$ spectra were obtained using JEOL ECZ 600R/S1 spectrometer. The $^1\text{H-NMR}$ spectra were measured at 600.17 MHz in deuterium oxide (D_2O).

Amount of furfural in distillate was determined by Ultraviolet visible (UV-Vis) spectroscopy, as furfural has a strong absorption in ultra violet at wavelength of 276 nm (Zhang *et al.*, 2017). The concentration of furfural can be calculated from the calibration graph of commercial furfural. The calibration graph of commercial furfural was obtained based on absorption spectrum of a set of different concentrations at 276 nm. The UV-Vis spectroscopy was carried out using a Thermo Scientific Genesys 10S UV-Vis (Figure 4).

RESULTS AND DISCUSSION

Characterisation of Xylan by FTIR Spectroscopy

The xylan yield was about 22%-25% per kg of EFB-fibre processed. From FTIR spectroscopy analysis, spectrum of xylan from EFB was found to be comparable to that of standard commercial xylan (Sigma).

The FTIR spectrum of xylan from OPEFB within the region of $650\text{-}4000\text{ cm}^{-1}$ is shown in Figure 5. The region of between $850\text{-}1200\text{ cm}^{-1}$ is typical for hemicellulose. This indicates that the alkaline extraction did not change the macromolecular structure of xylan. The absence of absorption band at 1710 cm^{-1} which is the finger-print peak for carboxyl groups in lignin, showed that the extracted xylan was pure and clean from lignin residue (Herrera *et al.*, 2003).

Absorption band at 1037 cm^{-1} was due to the C-O-C stretching glycosidic linkages in xylan. The broad absorption band at 3400 and 2400 cm^{-1} were due to the stretching vibrations of OH and C-H respectively. The C-H bending vibration showed

absorption bands at 1555 and 1406 cm^{-1} while the OH bending vibration showed absorption bands at 1344 cm^{-1} .

Characterisation of Furfural by FTIR Spectroscopy

The furfural obtained was in liquid form. It was colourless initially but turned yellowish to dark brown when exposed to light and air. Its scent resembled that of bitter almond. Its vapour irritates the eyes. Figure 6 shows an overlay FTIR spectra of xylan and furfural from OPEFB.

The FTIR spectrum of furfural showed a very strong absorption at 1706 cm^{-1} . This absorption indicates a very significant functional group in furfural which is the conjugated carbonyl ($\text{C}=\text{O}$) (Sashikala and Ong, 2007). The absorption wave number was slightly lower than usual, which is around $1740\text{-}1720\text{ cm}^{-1}$, due to internal hydrogen bonding that occurs in conjugated unsaturated aldehydes. However, this peak can be attributed to chemical compounds such as carboxylic acid (COOH), ketone, ester and aldehyde groups. The absence of peak at 1725 cm^{-1} strongly indicates the presence of aldehyde and not ketone group. Furthermore, no broad peak is observed between $3400\text{-}2400\text{ cm}^{-1}$ of hydroxyl (OH), as in xylan FTIR spectrum. This confirmed the absence of carboxylic acid group. The presence of aldehyde was proven with the existence of two peaks at 2841 cm^{-1} and 2816 cm^{-1} respectively. These absorptions showed moderate intense stretching of aldehydic C-H, attributed to the resonance between stretching and bending vibration of aldehydic C-H, which appeared at 1389 cm^{-1} in the spectrum. These bands were observed in aldehyde group.

Strong peaks between $1565\text{-}1466\text{ cm}^{-1}$ represent stretching of $\text{C}=\text{C}$ from aromatic ring. Aromatic $=\text{C-H}$ bending out of plane peaks were observed from $929\text{-}881\text{ cm}^{-1}$. Two strong peaks at 1016 cm^{-1} and 1077 cm^{-1} indicated the C-O stretching vibration. This FTIR spectrum was comparable to commercial furfural standard reference material FTIR spectrum.

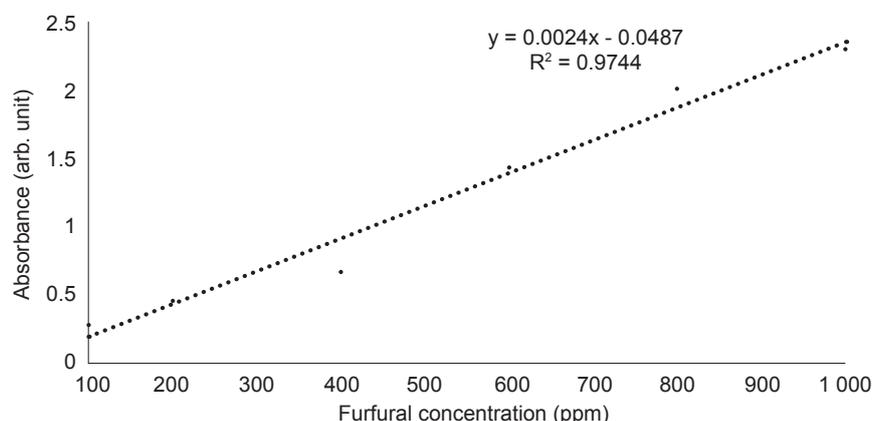


Figure 4. Calibration graph of standard commercial furfural in distilled water at different concentration.

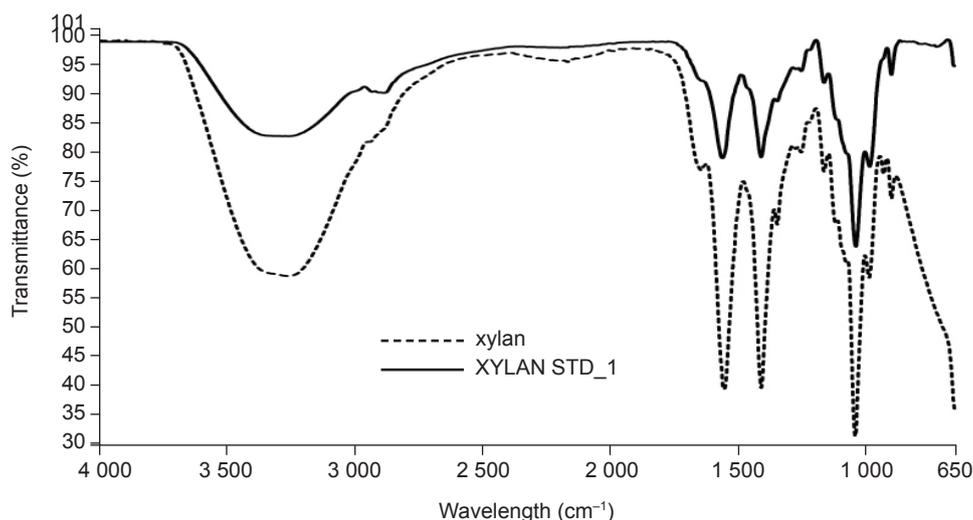


Figure 5. An overlay Fourier transform infrared (FTIR) spectrum of xylan from oil palm empty fruit bunches (OPEFB) and standard commercial xylan from beech wood (Sigma).

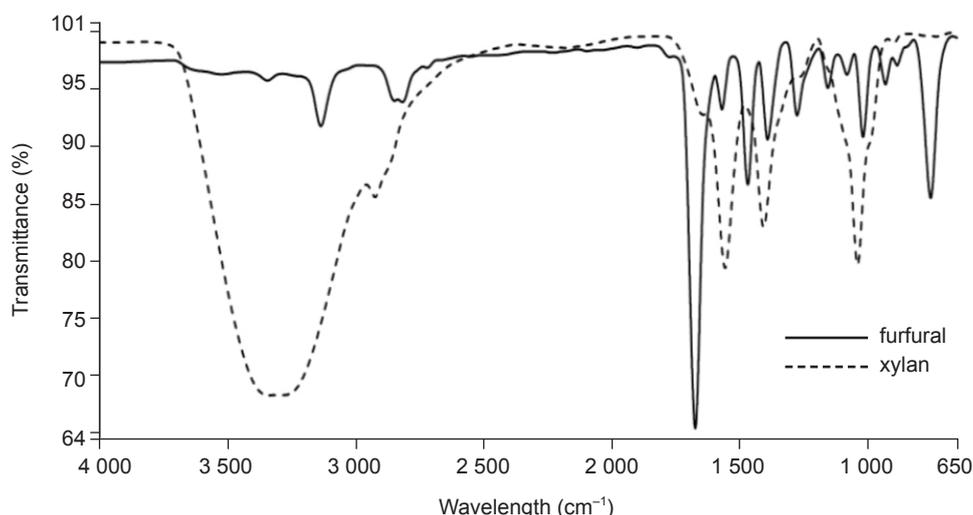


Figure 6. An overlay Fourier transform infrared (FTIR) spectrum of xylan and furfural from oil palm empty fruit bunches (OPEFB).

Characterisation of Furfural by $^1\text{H-NMR}$ Spectroscopy

The $^1\text{H-NMR}$ spectrum of furfural is shown in Figure 7. In this spectrum, both the individual groups and their component lines are well separated and thus the formal analysis is quite straight forward. The spectrum was separated by the coupling of the aldehyde proton to one of the ring protons. The aldehyde proton signal appears in normal low-field signal at δ 9.298 (1H) similar as reported by other researchers at δ 9.63-9.67 (Ismiyarto *et al.*, 2017; Bhaumik and Dhepe 2014).

The ring protons appeared as the three groups signal in region 6.56-7.72 ppm (3H) due to the asymmetric ring structures. On the basis of the chemical shift data, the low field signal would be

expected to be that of proton 4. Further, spin-spin coupling constants are known to be very insensitive to substitution. For example, Richards and Schaeffer (1958) have shown that the coupling constant in a series of para-substituted benzenes vary by less than 10% over a whole range of substituent groups. This again supports the assignment of the low field signal in furfural to proton 4 at δ 7.72 (1H). However, the spin-spin coupling between the aldehyde proton and the proton giving the low field signal would normally be expected to be between the aldehyde proton and the nearest neighbouring proton in the ring. On this basis, the low field signal in region 7.38-7.39 ppm would be assigned to proton 2. The chemical shift data as proton 2 and proton 4 in furfural would be expected to be at lower field than hydrogen 3 due to the influence of the electronegative aldehyde group.

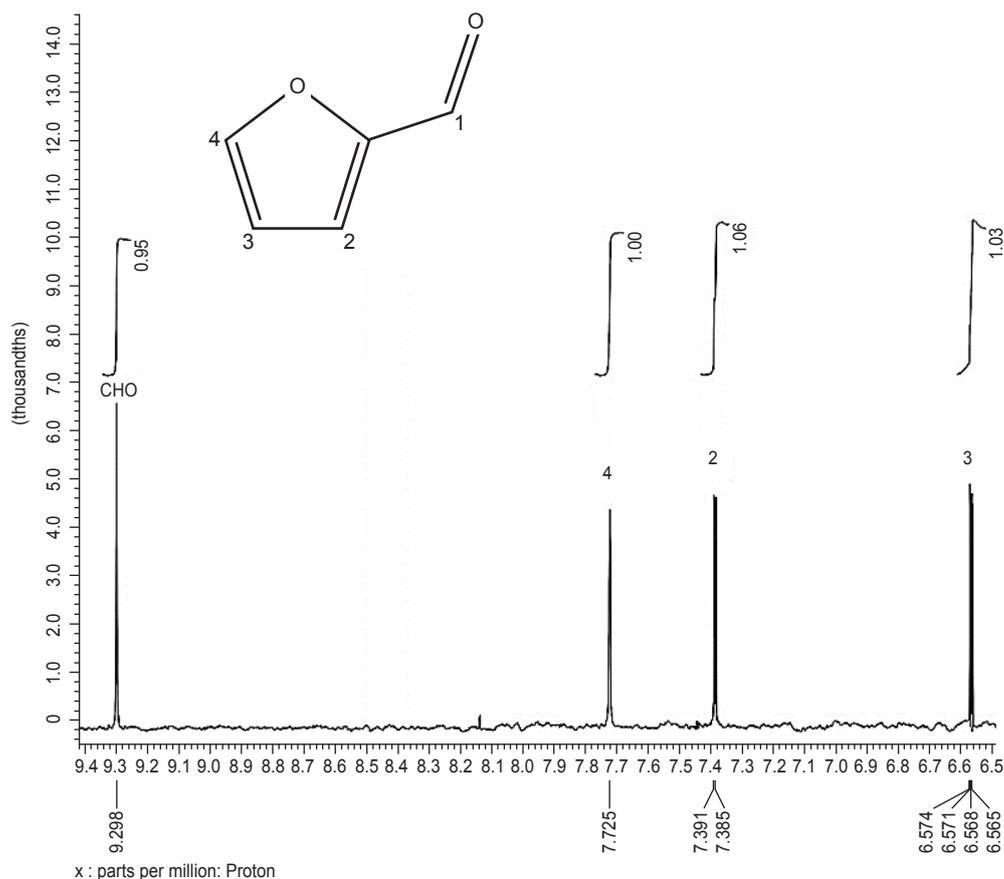


Figure 7. The Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectrum of furfural dissolved in deuterium oxide (D_2O).

Production of Furfural from Xylan

Hydrolysis using dilute acid is very complex, mainly because the substrate was in solid phase while the acid catalyst was in liquid phase. Results showed that the reaction parameters that influence yield of furfural production are acid concentrations, reaction time and presence of NaCl as promoter (Table 2). Furfural yield increased with increasing reaction time (up to 120 min) (Figures 8a and 8b) and H_2SO_4 concentration (up to 15% v/v) (Figures 8a and 8b).

The highest amount of furfural production was achieved at 90 min reaction time in H_2SO_4 with or without the presence of NaCl. The amount of furfural produced were lowest at 30 min reaction time while the yield of furfural continued to increase until 90 min. From 90-120 min reaction times, yield of furfural produced were high, ranging from 2.99%-9.01%. Beyond 120 min, the furfural's yield started to decrease due to degradation to acetic acid. Gupta *et al.* (2009) and Mansilla *et al.* (1998) reported that the highest concentration of acid for steam distillation was performed with 15% H_2SO_4 as the increment to 20% did not appear to increase furfural yield. Any further increase in acid concentration caused the increase in

inhibitor release, resulting in a decrease of furfural concentration in distillate.

Furfural yields were increased with addition of NaCl into reaction with H_2SO_4 compared to without NaCl (Figure 8). The highest yield of furfural produced in the presence of NaCl was 9.01% which was achieved in 15% H_2SO_4 and 90 min reaction time (Figure 8b). Meanwhile the highest yield of furfural produced without NaCl was about 6.63% in 15% H_2SO_4 and 120 min reaction time (Figure 8a). It was found that NaCl and H_2SO_4 , which produces an inorganic salt NaHSO_4 greatly improved the yield of furfural (0.8%-2.38%) compared to reaction with only H_2SO_4 . Similar finding was reported by Yazdizadeh *et al.*, (2016), whereby addition of NaCl into the reaction increased the yield of furfural by 1%-5%.

Furfural yield in this article was lower than a reported yield from oil palm pressed fibre of 17.34% (Riansa-Ngawong and Prasertsan, 2011). This is because only pentosans (xylose and arabinose) contribute a portion of the total composition of lignocellulose to the furfural production, compared to cellulose which is the largest fraction of lignocellulosic biomass. Therefore, the integrated strategies need to be introduced or the sole production of furfural from these residues would be wasteful, inefficient and uneconomic.

TABLE 2. AMOUNT OF FURFURAL PRODUCED IN DIFFERENT ACID CONCENTRATIONS AND WITH DIFFERENT REACTION TIMES

Acid concentration (H ₂ SO ₄)	Reaction time (min)	Without NaCl			With presence NaCl		
		Amount of furfural (%)					
		11%	13%	15%	11%	13%	15%
	30	0.42	0.87	3.27	3.28	6.83	7.80
	60	1.11	2.31	5.36	3.37	7.03	8.03
	90	2.80	5.83	6.07	3.70	7.70	9.01
	120	3.12	6.49	6.63	3.92	8.17	6.67
	150	2.72	5.67	4.70	2.88	5.99	5.52

Note: H₂SO₄ - sulphuric acid; NaCl - sodium chloride.

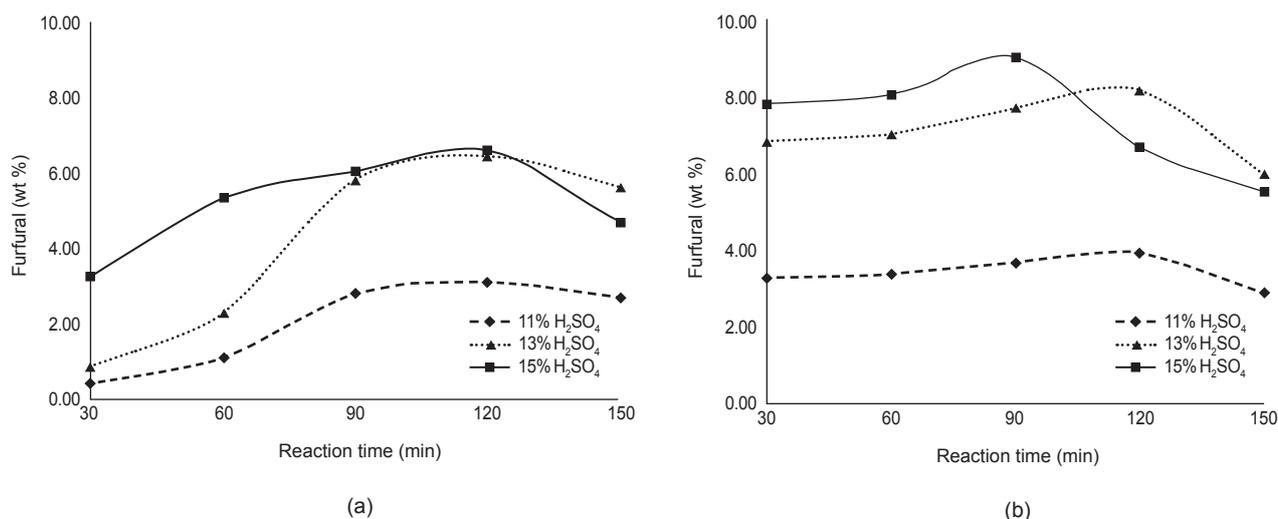


Figure 8. (a) Amount of furfural produced without sodium chloride (NaCl), and (b) with presence of NaCl at different reaction time in different sulphuric acid (H₂SO₄) concentration.

CONCLUSION

Furfural was successfully extracted from OPEFB by two-step process consisted of acid hydrolysis, followed by dehydration with highest yield of 0.90 ± 0.002 g litre⁻¹ of dry OPEFB. Xylan was extracted from OPEFB was used as substrate for furfural production. The xylan and furfural extracted were analysed using FTIR spectroscopy for structural confirmations and found to be comparable to commercial standard. The highest yield of furfural produced was 9.01% which achieved at 90 min reaction time in 15% H₂SO₄ in the presence of NaCl. To be economically visible, the production of furfural should be intergrated with cellulose extraction as pentoses (xylose) is just a minor portion of OPEFB chemical composition.

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