

Synthesis, identification and evaluation of furfural from rice straw (Sintesis, pengenalanpastian dan penilaian furfural daripada jerami padi)

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Key words: furfural, rice straw, FTIR, GCMS

Abstract

Synthesis of furfural from rice straw was carried out under mild conditions in an attempt to create value-added products from rice straw, which has become a seasonal source of air pollution in granary areas of Malaysia due to open burning. It was based on the conversion of the pentosan fraction in rice straw into pentose, which was then cyclodehydrated to furfural using dilute sulphuric acid. Furfural obtained was characterised using infrared analysis (IR), gas chromatography (GC) and gas chromatography with mass spectrophotometer (GCMS). IR spectrum exhibited a very strong absorption indicating the presence of the conjugated carbonyl (C=O) group. Results obtained from GC and GCMS also identified the presence of furfural with a probability of 98.4%. A molecular ion peak at m/z 96.03 was obtained, which correlates to a molecular formula of furfural, namely $C_5H_4O_2$. The product was colourless but turned yellowish and then dark brown upon exposure to air and light. It had a smell resembling that of bitter almond and its vapour was irritable to skin and eyes. The yield of furfural synthesised is affected by the concentration of acid and the catalyst.

Introduction

Rice straw is one of the main cereal straws that is produced in large amount annually. Yearly, two million tonnes of straw is produced in 350,000 ha of paddy field in Malaysia (MADA). As the country attempts to increase the yield of rice to 10 t/ha, the production of rice straw is expected to increase correspondingly. Indirectly, this will also raise the amount of carbon dioxide if the rice straw is to be burnt.

Air quality in many places in Malaysia especially in the northern region deteriorates during harvesting season. This is due to the open burning of rice straw at the paddy field as it is the common, cheapest and fastest method used by farmers to dispose it. Rice straw takes long time to be decomposed on

the field as it is very resistant to bacterial decomposition. Burning rice straw generates air pollutants, including carbon monoxide (CO), hydrocarbons, nitrogen oxides (NO_x), sulfur dioxide (SO₂) and production of polynuclear aromatic hydrocarbons in both gas and particulate forms, many of which are carcinogenic. For every tonne of rice straw, the amount of carbon dioxide emitted is 893.9 kg. Therefore, from MADA area alone, about 1,787, 800 tonnes of carbon dioxide is being released by 2 million tonnes of rice straw.

At harvest, the moisture content of straw is usually more than 60%. However in dry weather, straw can quickly dry down to its equilibrium moisture content of around 10–12%. Due to its high ash and

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low protein content, rice straw does not decompose as readily as straws from other grain crops such as wheat or barley. The main carbohydrate components of rice straw are hemicellulose, cellulose and lignin of the cell wall. Generally, straw contains 90% of cell wall, 3% of silica and 7% of extractives (Goldboard Dev. Corp. 2004).

The extraction of chemicals from rice straws could be an option to create high-value product from this renewable biomass. Furfural is one of them. It is an aldehyde of pyromucic acid. The worldwide market for furfural is about 300,000 tonnes per year. The current market price is US\$1700 per tonne. Furfural is widely used in industries as a base material for synthesizing a family of derived solvents like furfuryl alcohol and tetrahydrofuran and in production of resins for moulded plastic and metal coatings. Furthermore it plays a big role in the manufacture of insecticide as well.

Recently, furfural has been used in the food industry for flavouring purpose. This paper reports the characteristics of furfural and the effects of acid concentrations and catalyst on the production of furfural from local rice straw. It is sometimes called “green chemistry” (Lancaster 2004) in the sense that production of a chemical is achieved with a biomass.

Materials and methods

Rice straw sampling

Rice straw was collected from Tanjung Karang, Selangor. It was dried well under the sun. The size of the rice straw was reduced by using a shredder. It was later packed and stored in sacks in a dry place.

Extraction method

Two different stages were involved in the synthesis of furfural. Firstly, 50 g of rice straw was autoclaved at various concentrations of sulphuric acid at 1.5 atm for 30 min. Secondly, 50 g of rice straw and 0.5 g of sodium chloride were mixed and autoclaved at various concentrations of sulphuric acid at 1.5 atm for 30 min.

The above process was carried out in three replicates.

Separation procedure

Distillate collected from the distillation process was subjected to partitioning using chloroform in separation funnel. Aqueous and non-aqueous layers were obtained. Furfural was isolated from the non-aqueous solution using rotary evaporator with temperature not exceeding 40 °C. The chloroform (CHCl₃) used in this experiment was distilled earlier to ensure dryness and purity.

Identification

Furfural extracted was identified using spectroscopic techniques of Fourier Transform Infrared (FTIR) and gas chromatography with mass spectrophotometer (GCMS). Infrared analysis was performed with Perkim Elmer Spectrum RX 1 FTIR System. Horizontal attenuated total reflectance (HATR) method using zinc selenide crystal with density of 5.27g/cm³ was carried out in FTIR machine. Transmission rate used was at 17000–650 cm⁻¹ and refraction index at 1000 was at 2.4 cm⁻¹. Acetone was used as cleaning and diluting agent.

Capillary GC analysis was performed with a Hewlett-Packard 5927A quadrupole mass spectrometer fitted with HP 5890 gas chromatograph. AJ & W Scientific Durabond DB 35 (30 m x 0.25 mm I.D.) fused silica column with 0.25 µm film thickness was used. Helium gas was used as the carrier gas at flow rate.

GCMS was operated at 200 °C in the electron impact mode of 70 eV with the electron multiplier voltage at ~2000 eV. The injection port was maintained at 300 °C and sample was injected with split less mode followed by purge at 1 min after the injection. The column temperature was held at 45 °C for 10 min to 180 °C at ramping rate of 3.5 °C/min. The final temperature was held for 30 min.

Scanning was done from m/z 30 to 300 in one scan. The mass spectral identification of furfural was carried out by comparing with the mass spectral library of National Institute of Standards and Technology (NIST). This GC analysis method is a modified method from GCMS analysis on tobacco (Cai et al. 2002).

Results and discussion

Samples were autoclaved in mild conditions. Pentose was released from the lignocellulosic of rice straw and dehydration of pentose occurred. The pentosan fraction of lignocellulosic is converted into monosaccharides by acid hydrolysis. Then further dehydration reactions of pentoses yielded furfural. Pentosan fraction in the rice straw was converted into pentose which was then cyclodehydrated to furfural using dehydration method. Dilute sulphuric acid was used for this purpose (Antal et al. 1991).

Furfural formed was recovered using distillation and separation. The furfural

obtained was in a liquid form, practically colourless at first but turned yellowish and then dark brown when exposed to light and air (Table 1). Its smell resembled that of bitter almond. Its vapour irritates the eyes and causes tearing. Both liquid and vapour are highly flammable. It also causes allergic skin reaction.

The IR spectrum (Figure 1) shows a very strong absorption at 1714.46 cm^{-1} . This absorption shows a very significant functional group which is the 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} indicates strongly the presence of aldehyde and not the ketone group (Silverstein and Webster 1998). Furthermore, no broad peaks were observed at the area of $3400\text{ to }2400\text{ cm}^{-1}$ which belongs to the hydroxyl (OH). This confirms the absence

Table 1. Characteristics of furfural

Formula	$\text{C}_5\text{H}_4\text{O}_2$
Molecular weight	96.03
Form	Liquid (Flammable: flash point $60\text{ }^\circ\text{C}$)
Smell	Bitter almond smell
Colour	Colourless, but turns to dark brown upon exposure to light and air
Exposure	Can be absorbed through skin with possible systemic effects; vapour causes tearing in eyes

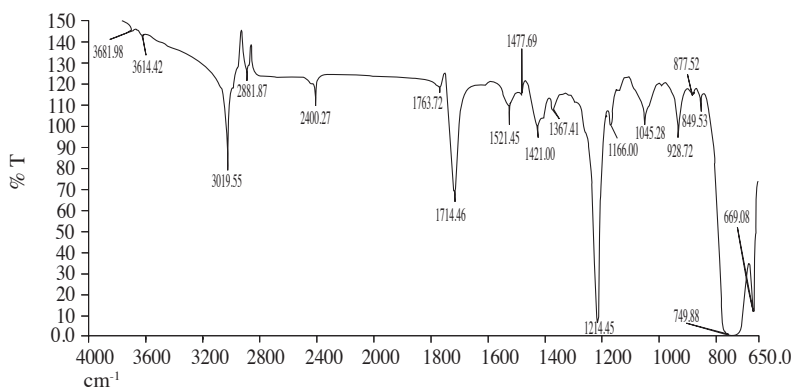


Figure 1. Infrared spectrum of furfural

Synthesis of furfural from rice straw

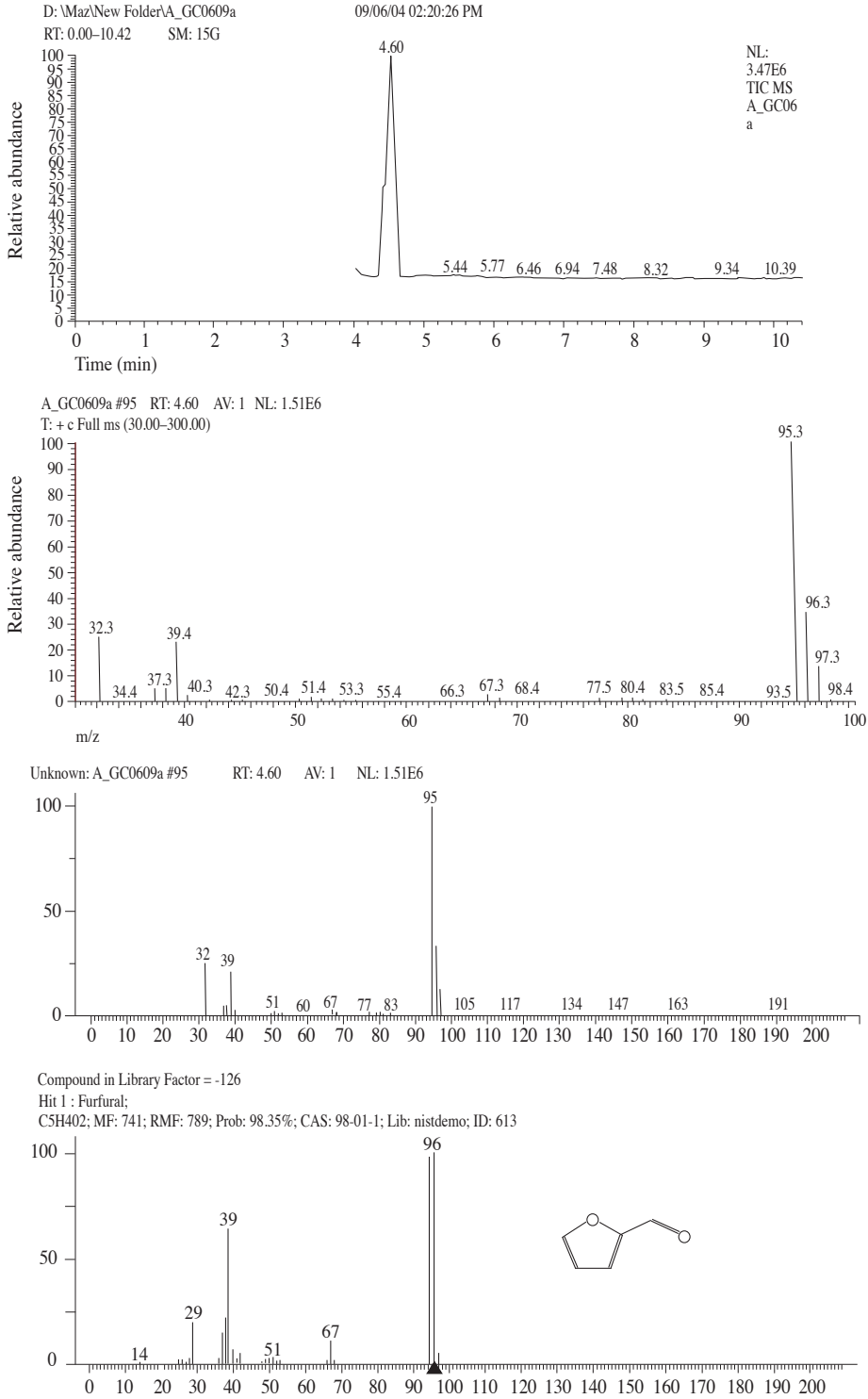


Figure 2. GCMS spectrum of furfural

of carboxylic acid group. If the sample belongs to the ester group, when a double bond is adjacent to the -O-, a strong C=C peak would be observed in the 1685 cm^{-1} to 1660 cm^{-1} region.

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 which attributes 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 indicated 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. This IR spectrum was also compared with the furfural IR spectrum published by NIST (2004) and it suits that spectrum very well.

Results obtained from GC and GCMS are shown in *Figure 2*. Furfural has a retention time of 4.60 min with relative abundance of 100%. Sample is proven as furfural after comparing the data obtained with the NIST library in the GCMS machine with a probability of 98.35%.

The spectrum showed a molecular ion peak at m/z 96.03 which correlates to a molecular formula of furfural ($\text{C}_5\text{H}_4\text{O}_2$). A peak at m/z 95.3 ($\text{M}-1$)⁺ was obtained due to the loss of hydrogen to form a carbonium ion. Electron was given away by the aldehyde carbon to hydrogen to form this fragmentation because it can form a more stable cation. This fragmentation peak matches that of the mass spectrum proposed by NIST (2004). The probable fragmentation pattern is shown in *Figure 3*.

The yield of furfural is dependent on the percentage of pentosan in agricultural residues. Furfural is the principal

decomposition product of pentoses (Belitz and Grosch 1999). Rice straw contains 563.1 kg/tonne of total sugar, of which 65.29% and 34.7% are of 6-C and 5-C sugars, respectively. Its lignin content is about 17% (Roberto et al. 2003; Energenetics 2004).

The yield could also be affected by acid concentration and extraction temperature. Thus there could be room for improving the yield by manipulating these factors in future work. The comparatively low yield could be due to other secondary reactions taking place simultaneously, although in the extraction process only the hydrolysis and dehydration steps are important. The hydrolysis reaction is about 50 times faster than the dehydration reaction (Gravitis et al. 2004). Thus, the later reaction becomes the limiting step.

Researchers should pay attention to the maximum generation of pentoses with minimal loss of cellulose in the extraction process. While special processes such as the use supercritical carbon dioxide may increase furfural yield to 80% (Sako et al. 1992), future work would have to take into consideration the production cost versus the product price obtainable. However, considering there are renewable resources which are being burnt, a bio-refinery or "green chemistry" attempt might prove beneficial from both the socio-economic and environmental view points. The maximum yield of furfural gained was 0.034 g/kg at 20% concentration of sulphuric acid and 0.057 g/kg at 20% concentration of sulphuric acid with catalyst (*Tables 2 and 3*). These yields were lower than those reported in literature review, and this could be due to the mild conditions such as low pressure and short reaction time.

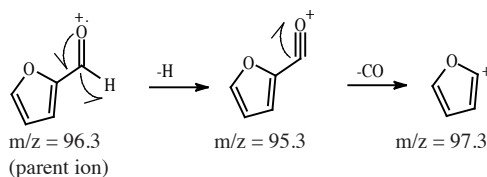


Figure 3. Furfural mass spectrum fragmentation

Table 2. Yields of furfural obtained at various concentrations of sulphuric acid (g/kg)

Concentration of sulphuric acid (%)	Yield of furfural obtained (g/kg)
1	0.0036
5	0.012
10	0.023
15	0.033
20	0.034
25	0.030
30	0.024

Table 3. Effect of sodium chloride on furfural production

Concentration of sulphuric acid (%)	Yield of furfural obtained (g/kg)
1	0.0044
5	0.003
10	0.037
15	0.053
20	0.057
25	0.044
30	0.038

Conclusion

Furfural has been successfully synthesised from rice straw under mild condition, but produced very low yield conversion of sugar. Two parameters that influenced the yield of furfural obtained were identified as acid concentration and the presence of catalyst. The maximum yield of furfural synthesised was at 20% concentration of sulphuric acid with the presence of sodium chloride as the enhancer in the synthesis. The functional groups and molecular weight of furfural were identified accurately using IR and GCMS equipments. It has a formula of $C_5H_4O_2$ and a molecular weight of 96.03. It is in a flammable liquid form, which smells like bitter almond. It is colourless but turns yellowish and then brown upon exposure to light and air.

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Abstrak

Kajian sintesis furfural daripada jerami padi telah dijalankan di makmal untuk menghasilkan produk tambah nilai bagi jerami padi yang menjadi punca pencemaran alam sekitar di kawasan padi disebabkan oleh pembakaran terbuka. Penghasilan furfural berdasarkan penukaran bahagian pentosan di dalam jerami kepada pentose yang kemudiannya ditukarkan kepada furfural dengan asid sulfurik. Pengenalpastian furfural telah dilaksanakan dengan analisis inframerah, kromatografi gas (GC) dan kromatografi jisim (GCMS). Spektrum IR menunjukkan penyerapan yang kuat dan ini menunjukkan kehadiran karbonil tertasrif (C=O). Keputusan yang diperoleh daripada GC dan GCMS mengesahkan kehadiran furfural dengan kebarangkalian 98.4%. Satu puncak ion molekul pada m/z 96.03 yang mengkorelasikan formula molekul furfural yang bersamaan dengan $C_5H_4O_2$ diperoleh. Furfural tidak berwarna tetapi menjadi kuning dan kemudian perang apabila terdedah kepada cahaya dan udara. Baunya seperti badam pahit dan wapnya rensa di mata dan kulit. Daripada kajian didapati bahawa kadar penghasilan furfural dipengaruhi oleh kepekatan asid dan kehadiran mangkin ketika sintesis.