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Synthesis and identification of furfural from rice straw

(Sintesis dan pengenalpastian furfural daripada jerami padi)

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Key words: furfural, rice straw, infra-red (IR), gas chromatography with mass spectrophotometer (GCMS)

Abstract

Laboratory-scale extraction of furfural from rice straw was carried out 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. The extraction was based on the conversion of the pentosan fraction in rice straw into pentose, which was then cyclodehydrated to furfural using dilute sulphuric acid. Yield of furfural obtained was 71 g/kg of dry straw. This yield was lower than a reported yield from corn cob (110 g/kg), but higher than that from bagasse (25 g/kg). The yield obtained was only 56.8% of the maximum theoretical yield. Furfural obtained was characterised using infra-red analysis (IR), gas chromatography (GC) and gas chromatography with mass spectrophotometer (GCMS). IR spectrum exhibited a very strong absorption at 1,706.02 cm^{-1}, indicating the presence of the conjugated carbonyl (C=O) group. The presence of the aldehyde was proven by two peaks attained at 3,004.26 cm^{-1} and 2,811.71 cm^{-1}. 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.

Introduction

Rice straw is one of the main cereal straw that is produced in large amount annually. In Malaysia, about 1.3 million tonnes of rice straw are produced yearly from 350,000 ha of paddy fields including 70,000 tonnes from MADA area alone. As the country attempts to increase the yield of rice to 10 t/ha, the production of rice straw is expected to increase correspondingly. Currently rice straw is mostly burnt by farmers as they could not find a way to dispose it. This causes undesirable incidents like haze and traffic accidents due to poor visibility. Efforts have been expended to try to utilise rice straw, but the value of these products has not been high enough to make it worthwhile for farmers to collect and transport straw.

At harvest, the moisture content of straw is usually more than 60% on a wet basis. However, in dry weather straw can quickly dry down to its equilibrium moisture content of around 10–12%. Rice straw has a high ash content and low protein content. As a result, rice straw does not decompose

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as readily as other straw from other grain crops such as wheat or barley. It is also very resistant to bacterial decomposition. 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 (GDC 2004).

The extraction of chemicals 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 for furfural is around US$1,700 per tonne. It is widely used in industries as a base material for synthesising a family of derived solvents like furfuryl alcohol and tetrahydrofuran and in the 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 too. This paper reports an attempt to extract and identify furfural obtained 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

Principle of extraction

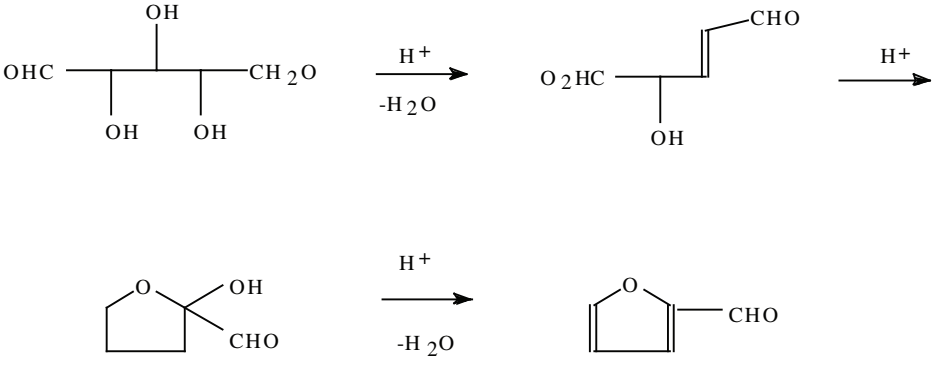
Furfural can be produced from lignocellulosic biomass by dehydrating pentoses which are found in hemicelluloses of agricultural waste. The pentosan fraction of lignocellulosic is converted into monosaccharides by acid hydrolysis. Then further dehydration reactions of pentoses yield furfural. Pentosan fraction in the rice straw is converted into pentose which is then cyclodehydrated to furfural using dehydration method. Dilute sulphuric acid is used for this purpose (Antal et al. 1991). Furfural formed is recovered using distillation and separation. Formation of furfural is illustrated in the chemical mechanism shown in *Figure 1*.

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 later reduced by using a shredder. It was packed and stored in sacks in a dry place.

Extraction method

The method used here is a method of furfural synthesis using corn cob (Adams and Voorhees 2004). About 1.1 kg of dried



The stoichiometric equation for this reaction is as below:

$$\underset{\text{(pentoses)}}{C_2H_{10}0_5} \longrightarrow \underset{\text{(furfural)}}{C_5H_40_2} + 3H_20$$

Figure 1. Formulation of furfural from pentose (Lancaster 2004)

rice straw and 1.67 kg of sodium chloride (NaCl) were mixed together in a big clean basin. Then the mixture was placed in a 10-litre round bottomed flask. A volume of 4.17 litres of 10% sulphuric acid (H_2SO_4) was added into the round bottomed flask. The round bottomed flask was connected to an upright column and water condenser. Distillation process was carried out for approximately 7 h. 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. Chloroform ($CHCl_3$) used in this experiment was distilled earlier to ensure dryness and purity.

Identification

Extracted furfural was identified using spectroscopic techniques of Fourier Transform Infra-red (FTIR) and gas chromatography with mass spectrophotometer (GCMS). Infra-red 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/cm^3 was carried out in FT-IR machine. Transmission rate used was at 17,000−650 cm^{-1} and refraction index at 1,000 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. J & 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.

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

Table 1 shows the yield of furfural obtained in this study, in comparison with the maximum theoretical yield and the yields from other biomass. The yield of 71 g/kg of straw was lower than that from corn cob, but higher than that from bagasse. Extrapolated, the yield would be 71 kg/t of dry straw. If the price of furfural is US$1,700/t, then

Table 1. Yields of furfural from biomass (g/kg)

Biomass	Potential yield	Yield obtained in this study	Reported yields
Rice straw	125	71	–
Bagasse	170		25[a]
Corn cobs	220		110[b]
Corn stalks	165		–
Sunflower hulls	160		–
Rice hulls	120		–

[a]Aquilar et al. (2002)
[b]Adams and Voorhees (2004)

one tonne of local dry straw would produce about RM458 worth of furfural. However, the cost of production details of its commercial viability need to be studied.

The yield of furfural is dependent on percentage of pentosan in agricultural residues. Furfural is the principal decomposition product of pentoses (Belitz and Grosch 1999). Rice straw contains some 563.1 kg/t of total sugar, of which 65.3% and 34.7% are of 6-C and 5-C sugars, respectively. Its lignin content is about 17% (Roberto et al. 2003; Ernegenetics 2004). The yield could also be affected by acid concentration and temperature of extraction. Thus, there could be room for improving the yield by manipulating these factors in future work, since the yield obtained now was only 56.8% of the maximum theoretical yield. Potential yields of furfural in kg/tonne of dry biomass are 220, 170, 165, 160 and 120 for corn cobs, bagasse, cornstalks, sunflower hulls and rice hulls respectively (Montane et al. 2002).

In industrial scale plants, yields of furfural are typically 45–50% of the potential yields. However, yields of about 70% have been achieved using plug flow reactors operated at high temperature of about 250 °C (Brennan et al. 1986; Abatzoglou et al. 1990). 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. Attention would have to be paid to the maximum generation of pentoses with minimal loss of cellulose in the extraction process. While special processes such as the use of supercritical carbon dioxide may increase furfural yield to 80% (Sako et al. 1992), future work would have to consider the production cost versus the product price obtainable. The potential yields of rice straw and rice hulls are lower that those listed in *Table 1*. However, considering that they are a renewable resource that are currently burnt, a bio-refinery or 'green chemistry' attempt might prove beneficial from both the socio-economic and environmental view points.

The furfural obtained was in liquid form. It was practically colourless at first but turned yellowish and then dark brown when exposed to light and air. 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 2)* shows a very strong absorption at 1,706.02 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 i.e. 1,740 cm^{-1} to 1,720 cm^{-1} due to internal hydrogen bonding which occurs in conjugated unsaturated aldehydes. But this peak can appear for chemical compounds like carboxylic acid (COOH), ketone, esther and aldehyde groups. The absence of peak at 1,725 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 3,400 to 2,400 cm^{-1} which belongs to the hydroxyl (OH). This confirms the absence of carboxylic acid group. If the sample belongs to the esther group, when a double bond is adjacent to the -O-, a strong C=C peak would be observed in the 1,685 to 1,660 cm^{-1} region.

Furthermore, the presence of the aldehyde proven with the existence of two peaks gained at 2,830 cm^{-1} and 2,811.71 cm^{-1}. These absorptions shows 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 1,393.87 cm^{-1} in the spectrum. These bands are frequently observed for aldehyde group.

However strong peaks indicated from 1,569.63 cm^{-1} to 1,420.58 cm^{-1} are stretching

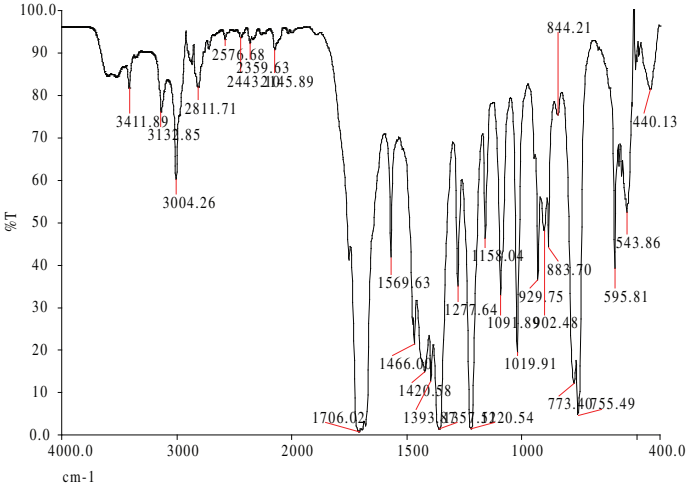


Figure 2. Infrared spectrum of furfural

Table 2. Characteristics of furfural

Formula	$C_5H_4O_2$
Molecular weight	96.03
Form	Liquid (Flammable: flash point 60 °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

of C=C from aromatic ring. Aromatic =C-H bending out of plane peaks were observed from 929.75 cm^{-1} to 883.7 cm^{-1}. Two strong peaks at 1,019.91 cm^{-1} and 1,220.54 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 GC-MS are shown in *Figure 3*. 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 GC-MS 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 ($C_5H_4O_2$). A peak at m/z 95.3 $(M-1)^+$ was obtained due to the loss of hydrogen to from 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 the NIST (2004). The characteristics of the furfural are summarised in *Table 2*.

Conclusion

Furfural has been successfully extracted from rice straw by acid hydrolysis method with the yield of 71 g/kg of dry rice straw. Its functional groups and molecular weight 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. The yield obtained was 56.8% of the maximum theoretical yield.

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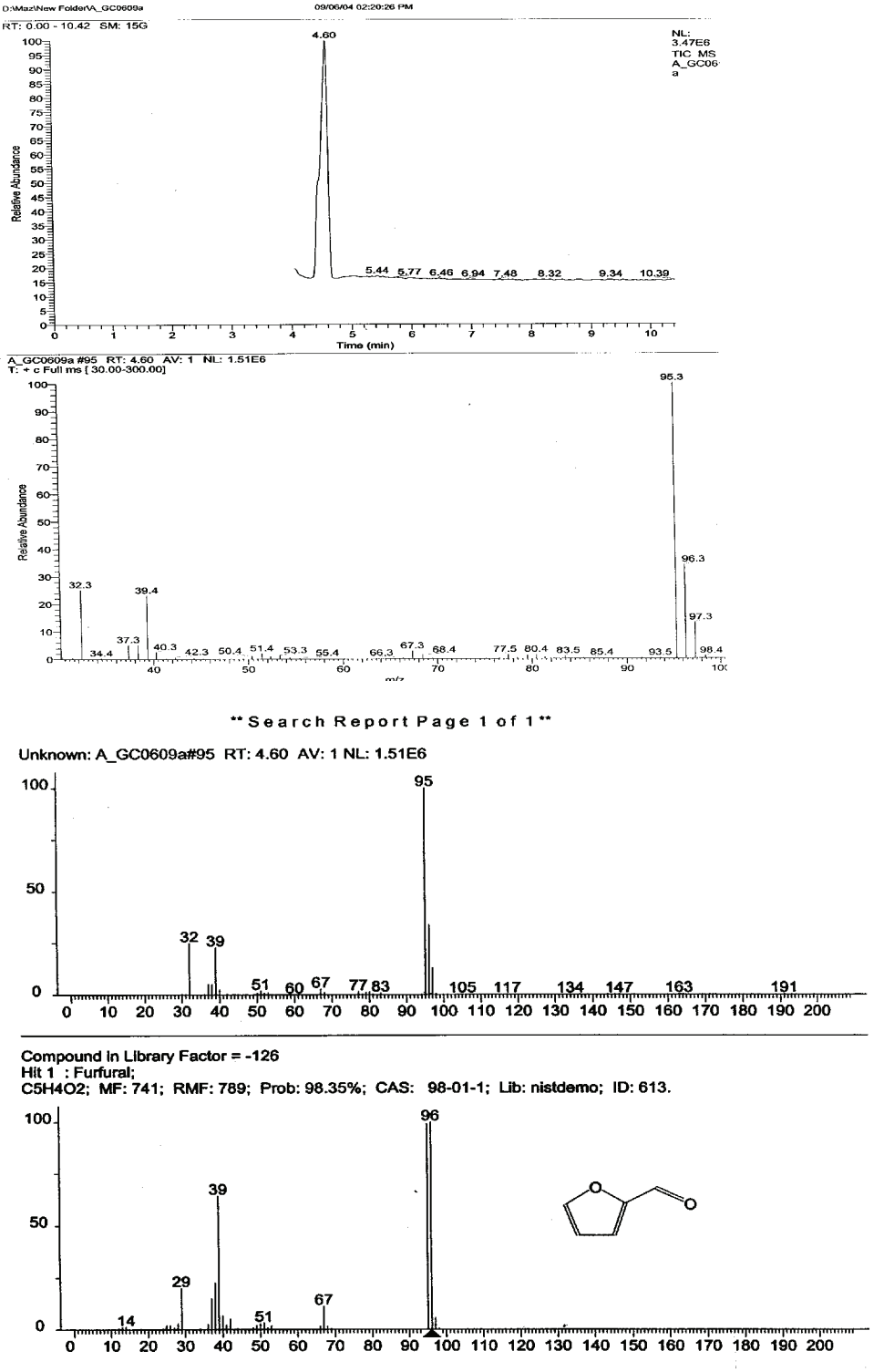

Figure 3. GCMS spectrum of furfural

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Abstrak

Kajian mensintesis furfural daripada jerami padi telah dijalankan di makmal untuk menghasilkan produk tambah nilai bagi jerami padi yang telah menjadi punca pencemaran alam sekitar di kawasan padi disebabkan oleh pembakaran secara terbuka. Penghasilan furfural berdasarkan penukaran bahagian pentosan di dalam jerami kepada pentose yang kemudiannya ditukarkan kepada furfural dengan asid sulfurik. Kadar penghasilan furfural yang didapati ialah 71 g/kg jerami kering. Hasil ini adalah kurang berbanding dengan hasil yang didapati daripada bahan buangan jagung (110 g/kg), tetapi lebih tinggi daripada hasil sumber bahan buangan tebu (125 g/kg). Kadar penghasilan furfural adalah sebanyak 56.8% daripada potensi penghasilan. Pengenalpastian furfural telah dilaksanakan dengan analisis inframerah, kromatografi gas (GC) dan kromatografi jisim (GCMS). Spektrum IR yang terdapat menunjukkan penyerapan yang kuat pada 1,706.02 cm^{-1}, yang menunjukkan kehadiran karbonil tertasrif (C=O). Dua puncak pada 2,830 cm^{-1} dan 2,811.71 cm^{-1} menunjukkan adanya kumpulan aldehid. 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 $C_5H_4O_2$. Furfural yang diperoleh tidak berwarna tetapi menjadi kuning dan kemudian perang apabila terdedah kepada cahaya dan udara. Baunya seperti badam pahit dan wapnya rengsa di mata dan kulit.

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