

Identification of furfural synthesized from pentosan in rice husk (Pengenalpastian furfural yang disintesis daripada pentosan di dalam sekam padi)

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Key words: furfural, rice husk, infrared (IR), gas chromatography with mass spectrophotometer (GC-MS)

Abstract

Synthesis of furfural from pentosan in rice husk was carried out in an attempt to produce value-added products from rice husk which is commonly burnt around rice mills of Malaysia. This process involved the conversion of the pentosan fraction in rice husk into pentose, which was then cyclodehydrated to furfural using dilute sulphuric acid. Yield of furfural obtained was 15 g/kg of dry husk. Furfural obtained was characterised using infra-red analysis (IR), gas chromatography (GC) and gas chromatography with mass spectrophotometer (GC-MS). IR spectrum exhibited a very strong absorption at $1,714.46\text{ cm}^{-1}$, indicating the presence of the conjugated carbonyl (C=O) group. The presence of the aldehyde was proven by two peaks attained at $3,019.55\text{ cm}^{-1}$ and $2,881.87\text{ cm}^{-1}$. 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. Furfural obtained was in liquid form, with a molecular weight of 96.2 g/mole and the formula of $\text{C}_5\text{H}_4\text{O}_2$.

Introduction

As a major by-product of the rice milling industry, rice husk is produced in large quantities annually. The estimated annual rice husk production in the world is 100 million tonnes, 90% of which are generated in developing countries (FAO 1996). In Malaysia, the annual production was estimated at 0.47 million tonnes in 2000, approximately 22% of rice production (Mazlina 2005). In years to come, the production of rice husk is expected to increase as the country attempts to increase the yield of rice to 10 t/ha. Depending on the size and location of rice mills, most of them face rice husk disposal problem. Attempts have been made to utilize rice husk in various ways. Ash from burnt rice

husk is used in a limited way for recycling to the field. In only a few cases, the husk is used as fuel. Composting was found to take a long time. Open burning of husks is rather common, although recently it has become increasingly difficult due to greater restrictions imposed by federal and local authorities.

Houston (1972) described rice husk as having four structural layers, namely: a) an outer epidermis coated with a thick cuticle of highly silicified sinuous cells among which surface hairs are found; b) sclerenchyma of hypoderm fibres with a thick and lignified silicified wall; c) spongy parenchyma cells elongated with rather wavy outline and short or quadrilateral, and d) inner epidermis generally of

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isodiametric cells. Rice husk has high content of inorganic compounds which is approximately 20% of the dry weight. Of this, 94% is silica and 6% is mineral salts such as potassium oxide, calcium oxide, and others. Rice husk does not decompose easily as it is very resistant to bacterial decomposition due to high content of silica, although it must be admitted that aerobic composting remains the cheapest way of stabilizing such by-products in a developing country.

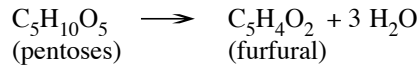
The major components of rice husk are hemicellulose (19%) and cellulose (40%), silica (17%) and lignin (16%) (Gravitis and Suzuki 1999). Rice husk contains about 120 g pentosan per kilogramme of dry husk, suggesting that it could be used to synthesize furfural, an aldehyde of pyromucic acid. Furfural is widely used in industries as a base material for synthesizing 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. The worldwide market for furfural is about 300,000 tonnes per year, with a current market price of about US\$1,800 per tonne. This paper reports an attempt to identify furfural synthesized from local rice husk.

Materials and methods

Principle of synthesis

Furfural can be produced from lignocellulosic biomass by dehydrating pentoses which are found in hemicelluloses of agricultural waste. The pentosan fraction of lignocelluloses is converted into monosaccharide by acid hydrolysis. Then further dehydration reactions of pentoses yield furfural. Pentosan ($C_5H_8O_4$)_n fraction in the rice husk is converted into pentose ($C_5H_{10}O_5$)_n which is then cyclodehydrated to furfural ($C_5H_4O_2$) using dehydration method. Dilute sulphuric acid is used for this purpose (Antal et al. 1991). Reaction time was 300 min at a temperature of about 225 °C. Furfural formed is recovered using distillation and separation. Formation of furfural is illustrated in the chemical mechanism shown in *Figure 1*.

The stoichiometric equation for this reaction is as below:



Rice husk sampling

Rice husk was collected from Tanjung Karang, Selangor. It was dried under the sun, packed and stored in sacks in a dry place.

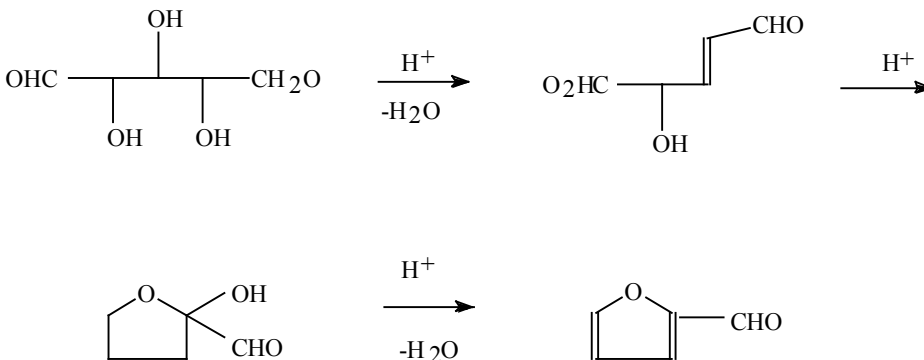


Figure 1. Formation of furfural from pentose

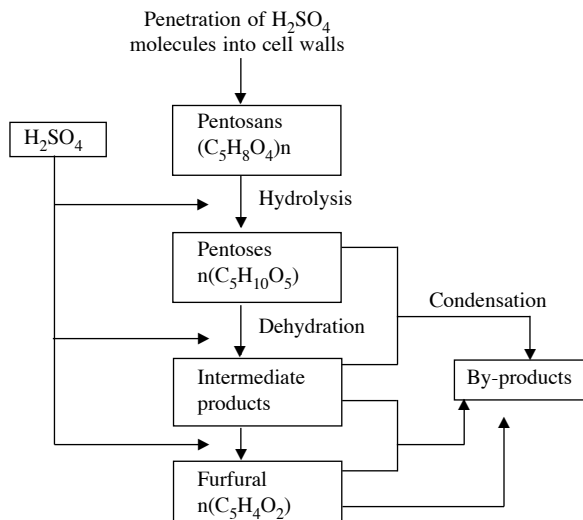


Figure 2. Flow diagram of furfural formation in the presence of dilute sulphuric acid

Synthesis procedure

About 1.1 kg of dried rice husk 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. About 4.17 litres of 10% sulphuric acid (H_2SO_4) was added into the round-bottomed flask. The flask was connected to an upright column and water condenser. Distillation process was carried out for approximately 7 h. A simplified flow diagram is shown in *Figure 2*.

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 was distilled earlier to ensure dryness and purity.

Identification

Furfural synthesized was identified using spectroscopic techniques of Fourier Transform Infra-red (FTIR) and gas chromatography with mass spectrophotometer (GC-MS). Horizontal attenuated total reflectance (HATR) method

using zinc selenide crystal with density of 5.27 g/cm³ was carried out in FTIR analyser (Perkim Elmer Spectrum RX 1 System). 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 was used as the carrier gas.

GC-MS 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 and infra red identification of furfural was carried out by comparing with the mass spectral library of National Institute of Standards and Technology (NIST 2005). This GC analysis

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

Biomass	Potential yield ^a	Reported yield ^b
Sugar cane bagasse	170	80–110
Corn cob	220	100–120
Corn stalk	165	–
Sunflower hull	160	–
Wood	150–170	40–80
Olive stone	–	40–95*
Rice husk	120	50–70
		15 (this study)

Source: ^aMontane et al. (2002); ^bWin (2005)

*High temperature tubular reactor

method is a modified method from GC-MS analysis on tobacco (Cai et al. 2002).

Results and discussion

Table 1 shows the yield of furfural from rice husk relative to its potential yield as well as the yields from other biomass. The yield of 15 g/kg (15 kg/t) of husk was much lower than that from corn cob and other biomass. Assuming that the price of furfural is US\$1,800/t, then one tonne of local dry husk would produce only about RM100 worth of furfural. Unless the yield could be increased very much, its potential for commercial production appears to be rather bleak. It was originally hoped that an attempt at 'bio-refinery' (Gravitis and Suzuki 1999) might prove beneficial from both the socio-economic and environmental view points, considering that they are renewable resources that are currently burnt. It is noted that attempts to recover other secondary by-products were not made in the initial experiment. These might offset the low economic viability due to low yield of furfural obtainable. In the case of furfural production from corn cobs, typical by-products obtainable are methyl alcohol (0.15–0.175 kg/kg of furfural), acetone (0.15–0.175 kg/kg of furfural) and acetic acid (0.45–0.8 kg/kg of furfural) (Win 2005).

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). The yield is also affected by acid concentration, reaction time, acid-to-lignocellulosic mass ratio and temperature of synthesis, since such factors affect the amount of sugars to be recovered from the raw materials (Pessoa et al. 1996). Potential yields of furfural in kg/t of dry biomass are 220, 170, 165, 160 and 120 for corn cobs, bagasses, cornstalks, sunflower hulls and rice hulls respectively (Montane et al. 2002). These potential yields are based on recovery of pentosan present in each raw material. In industrial scale plants, yields of furfural are typically 45–50% of the potential yields. However, yields of about 70% of the potential yield have been achieved using plug flow reactors operated at high temperature of about 250 °C (Brennan et al. 1986; Abatzoglou et al. 1990).

Losses due to secondary reactions of degradation and condensation might have occurred (Montane et al. 2002). Attention would have to be paid to the maximum generation of pentoses with minimal loss of cellulose in the production process. The contents of silica and lignin in rice husk might demand a higher temperature of greater than 160 °C using dilute acid (Ye Sun and Cheng 2002). The decomposition products of lignin are phenolic compounds (Aguilar et al. 2002). The formation of acid-soluble lignin also results in an impurity that needs to be removed from furfural products (Lavarack et al. 2002). While special processes such as the use of supercritical carbon dioxide may increase furfural yield to 80% (Sako et al. 1992), such an attempt would have to take into consideration the cost of production versus the product price obtainable.

Another factor worthy of consideration is the type of acid used. Basta and Houssni (2003) found that the hemicellulose of corn cobs was more easily hydrolysed if HCl was used instead of H₂SO₄. However, in the case of bagasse, HCl is less active than H₂SO₄ in degrading xylose (Lavarack et al.

2002). Clearly, the results are dependent on raw material type as well as operating conditions. According to Neureiter et al. (2002), acid concentration is the most important parameter affecting sugar yield, while temperature has the highest impact on sugar degradation products. Nominal temperatures are around 220–240 °C (Montane et al. 2002).

The furfural obtained was in the 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 and induces tears in the eyes. Both liquid and vapour are highly flammable.

The residual solid left after chemical reaction was made up of lignin and depolymerised cellulose. Theoretically, the residue left could be dried and then burnt in a boiler that could provide heat to maintain the desired temperature of the operation should the project prove viable to run. On the other hand, it could be explored as a future product to be incorporated into the soil, if residual furfural is present, since furfural acts as a fungicide and nematicide for plants (Bauske et al 1994; Zeitsch 2000). Combination of furfural with urea may yield a slow-release fertilizer, with both fungicidal

as well as nematicidal effects (Martinez-Garcia et al. 2004).

The IR spectrum (*Figure 3*) shows a very strong absorption at 1,714.46 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 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, ester and aldehyde groups. The absence of peak at 1,725 cm^{-1} indicates strongly the presence of aldehyde and not the ketone group (Silverstein et al. 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 ester group, when a double bond is adjacent to the -O-, a strong C=C peak would be observed in the 1,685 cm^{-1} to 1,660 cm^{-1} region.

The presence of the aldehyde group was proven with the existence of two peaks gained at 3,019.55 cm^{-1} and 2,881.87 cm^{-1} . These absorptions show a moderate intense stretching of aldehyde C-H which

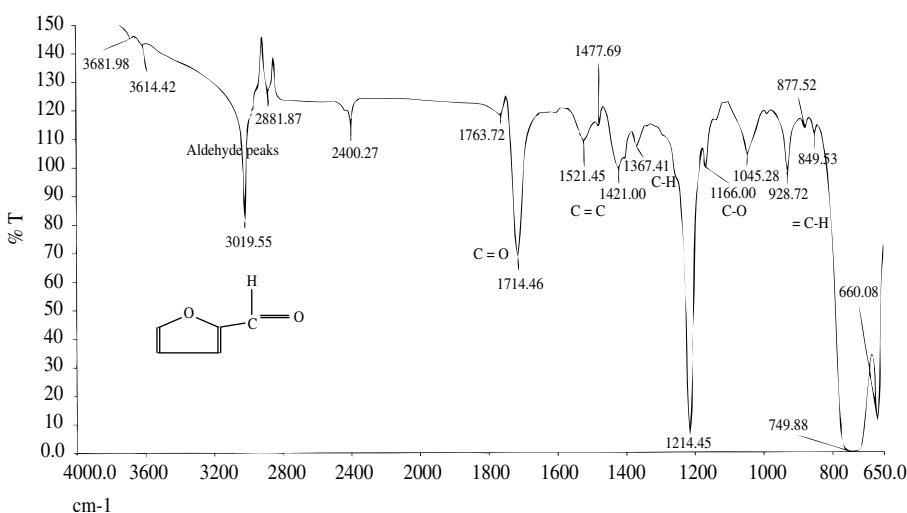


Figure 3. Infrared spectrum of furfural

Identification of furfural

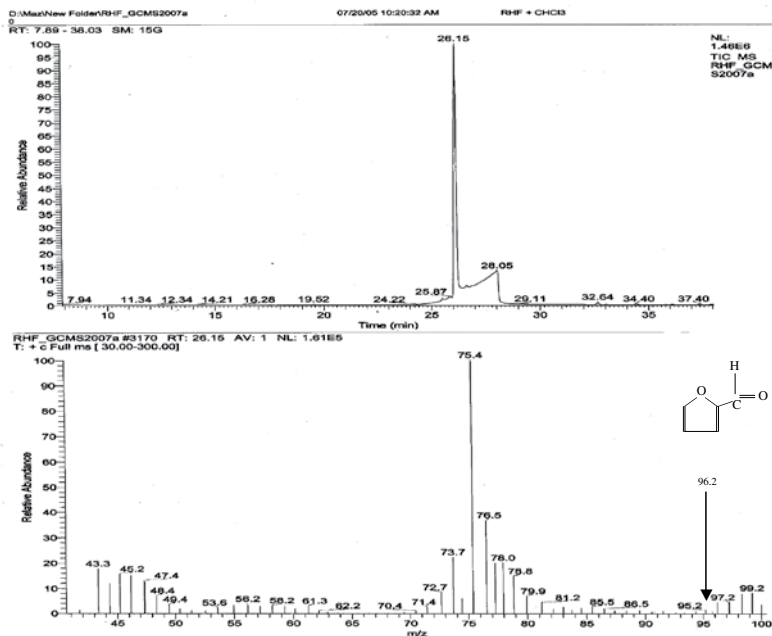


Figure 4. GCMS spectrum of furfural



Figure 5. Formation of carbonium

is attributable to Fermi resonance between the fundamental aldehydic C-H stretching and the first overtone of the aldehydic C-H bending vibration. It appears at $1,367.41\text{ cm}^{-1}$ in the spectrum. These bands are frequently observed for aldehyde group. Strong peaks indicated from $1,521.45\text{ cm}^{-1}$ to $1,421\text{ cm}^{-1}$ are inactive of stretching of C=C from aromatic ring. Aromatic =C-H bending out of plane peaks was observed from 928.72 cm^{-1} to 849.53 cm^{-1} . Two strong peaks at $1,166\text{ cm}^{-1}$ and $1,214.45\text{ cm}^{-1}$ 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 4. Furfural has a retention time of 26.15 min with relative abundance of 100%.

The spectrum showed a molecular ion peak at $m/z\ 96.2$ which correlates to a molecular formula of furfural ($\text{C}_5\text{H}_4\text{O}_2$). A peak at $m/z\ 95.2$ ($\text{M}-1$)⁺ was obtained due to the loss of hydrogen to form a carbonium ion (Figure 5). An electron was given away by the aldehyde carbon to hydrogen to form this fragmentation since a more stable cation can be formed. Due to the formation of hydrocarbon pattern, peak at $m/z\ 75.2$ became dominant compared with ($\text{M}-1$)⁺.

Table 2. Characteristics of furfural

Formula	$\text{C}_5\text{H}_4\text{O}_2$
Molecular weight	96.2 g/mole
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 induces tears in eyes

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 synthesised from rice husk by acid hydrolysis method albeit its low yield of 15 g/kg of dry rice husk. Its functional groups and molecular weight were identified using IR and GC-MS equipment. It has a formula of $C_5H_4O_2$ and a molecular weight of 96.2 g/mole. 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.

Acknowledgement

The authors would like to thank Mr Soo Siew Peng and Mr S. Poovan for their technical support. This study was funded by IRPA (Research Grant No. 01-03-03-0171-EA001).

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Abstrak

Untuk menghasilkan produk bertambah nilai bagi sekam padi yang telah menjadi punca pencemaran alam sekitar di kawasan kilang beras disebabkan oleh pembakaran secara terbuka, satu kajian sintesis furfural daripada sekam padi telah dijalankan di makmal. Penghasilan furfural berdasarkan penukaran bahagian pentosan di dalam sekam kepada pentose, yang kemudiannya ditukarkan kepada furfural dengan asid sulfurik. Kadar penghasilan furfural yang didapati ialah 15 g/kg sekam kering. Pengenalpastian furfural telah dilaksanakan dengan analisis infrared, kromatografi gas and juga kromatografi gas-MS. Spectrum IR yang terdapat menunjukkan satu penyerapan yang kuat pada $1,714.46\text{ cm}^{-1}$, yang memberi makna bahawa terdapat karbonil berkonjugat (C=O). Dua puncak pada $3,019.55\text{ cm}^{-1}$ dan $2,881.87\text{ cm}^{-1}$ menunjukkan adanya kumpulan aldehid. Furfural yang terdapat 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. Furfural yang terhasil berbentuk cecair, dan mempunyai berat molekul 96.2 g/mol serta formula kima $\text{C}_5\text{H}_4\text{O}_2$.