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Review Article

QUANTITATIVE SYNTHESIS OF FURFURAL FROM WASTE MATERIAL RICE HUSK – A REVIEW

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ABSTRACT

Furfural is a naturally occurring substance found in food and beverages (e.g., fruits and vegetables). The International Programme on Chemical Safety (IPCS 2000) has reported that furfural is also formed during the thermal decomposition of carbohydrates[1]. Furfural is formed when carbohydrates (or any substance that contains GLUCOSE) are heated and undergo acid hydrolysis. During last century, furfural has been used for fragrance industry, pharmaceutical, agriculture, and in leather manufacture because of its active aldehyde group. Purpose of this research is to find out the methods to separate furfural from rice husk economically and profitably. The experiment was performed by hydrolysis of rice husk with various acids like HCl, H_2SO_4 of different concentration in the presence if oxidizing agent and glucose. From the practical study of furfural formation it is found that H_2SO_4 and lactose is more effective because it gives higher yield as compare to other acids.

Keywords: Rice Husk, Furfural, Acid Hydrolysis, Oxidizing Agent, 1N Sulfuric Acid.

INTRODUCTION

Every year rice millers worldwide generate more than 100 million tons of rice husks. Rice husk has very low food value and has a very low nutritional value and as they take very long to decompose are not appropriate for composting or manure[1,2]. Therefore the 100 million tons of rice husk produced globally begins to impact the environment if not disposed of properly[3]. Being fibrous it can prove to be fatal for the cattle feeding. Use of rice husk or rice husk ash in land filling is also an environmentally hazardous way of disposing waste. There are so many reasons associated with rice husk for not being utilized effectively[2] like,

1) Lack awareness of its potential to a farmers and industry persons

2) Insufficient information about proper use

3) socio-economic problems

4) Penetration of technology

5) Lack of interest

6) Inefficiency of information transfer, etc.

Figure 1: Rice Husk

The following table 1 from Hwang and Chandra's article "The Use of Rice Husk Ash in Concrete"[4] shows the amount of rice cultivated and the significant amount of rice husk accumulated across the world. About 20% of a dried rice paddy is made up of the rice husks. The current world production of rice paddy is around 500 million tons and hence 100 million tons of rice husks are produced[5]. China and India are the top producers of rice paddy, but most all other countries referenced in this table are in South-East and East Asia.

Table 1: Amount of Rice Cultivated and the Significant Amount of Rice Husk Accumulated Across the World[5]

S. No	Country	Rice paddy	Rice husk
1	Bangladesh	27	5.4
2	Brazil	9	1.8
3	Burma	13	2.6
4	China	180	36.00
5	India	110	22.0
6	Indonesia	45	9.0
7	Japan	13	2.6
8	Korea	9	1.8
9	Philippines	9	1.8
10	Taiwan	14	2.8
11	Thailand	20	4.0
12	US	7	1.4
13	Vietnam	18	3.6
14	Other	26	5.2
Total		500	100

Associated with utilization of this solid waste needs to be worked out not only from the quality point of view but quantitatively as well, because quantity of rice husk produced is very large[2]. The most promising and profitable use of this biomass is its use for the electrical energy generation[2]. The use of rice husk for electricity generation in efficient manner is likely to transform this agricultural by product or waste into a valuable fuel for industries and thus might help in boosting the farm economy and rural development.

Gasification of rice husks at paddy mills combines the benefits of reasonably efficient delivery of energy with a reasonably high carbon char and ash mixture[6]. Biomass gasification has been developed in developing and industrializing countries with companies such as Ankur Scientific Energy Technologies Pvt. Ltd. (based in India) manufacturing a range of gasifiers from a few kW to hundreds of kW capacity[7]. (www.ankurscientific.com/). Ankur has sold over 1000 gasification units, predominantly in South Asia, but also in to Africa, Europe, South America and South East Asia. The char from such gasifies is sometimes used as a fuel, where the calorific value is sufficiently high (e.g. >15 MJkg^{-1}). Where rice husks are used, however, the high silica content limits the Calorific value of the rice husk char (e.g. total calorie 8.5 MJ kg^{-1})[8], hence it has less value as a charcoal-type fuel and the rice husk char can become a waste disposal or pollution problem. In these circumstances, it may make sense to regard the rice husk char as a form of bio char and to apply to agricultural soils to enhance crop yield sands oil 'health'. This was the motivation behind the BIOCHAR M project (Biochar for Carbon Reduction, Sustainable Agriculture and Soil Management), supported by the Asia Pacific Network on Global Change (APN) and by the UK Biochar Research Centre[9].

Rice Husk is also use in the steel, cement and refractory bricks industry[3]. The reasons behind the use of rice husk in the construction industry are its high availability, low bulk density (90-150kg/m^3), toughness, abrasive in nature, resistance to weathering and unique composition. The main components in rice husk are silica, cellulose and lignin. The composition of rice husk as a percentage of weight is shown in Table 2[10].

Table 2: Composition of Rice Husk[10]

S. No	Component In Rice Husk	Percentage (%)
1	SiO_2	18.80 – 22.30
2	Lignin	9 – 20
3	Cellulose	28 – 38
4	Protein	1.90 – 3.0
5	Fat	0.30 – 0.80
6	Other nutrients	9.30 – 9.50

Spectral analysis-chemical composition of the inorganic part from different parts of rice husk is shown in Tab. 3. Silica was present all over the rice husk but is concentrated in protuberances and in hairs (trichomes) on the outer epidermis, Fig. 2b, and also in the inner epidermis, Fig. 2a. The inorganic impurities were mostly concentrated in the inner epidermis of the rice husk, Tab. 3. Upon heating to 600°C the non treated rice husk yielded ashes grey in color with considerable amount of black particles. An increased concentration of inorganic impurities, especially potassium oxide was noticed. The potassium must be accelerating the carbon fixation in rice husk ash[11].

Table 3: Spectral Analysis-Chemical Composition from Different Parts of Rice Husk[12]

Spectral analysis	SiO_2	K_2O	MgO	SO_3
Spectar-01	84.12	7.33	4.00	4.56
Specter-02 (hairs)	99.68	0.32	-----	-----
Specter-03	100.00	-----	-----	-----

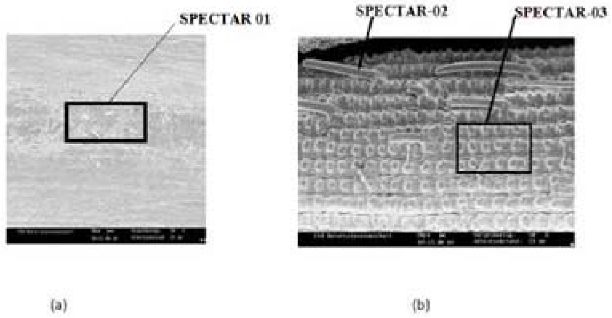

Figure 2: SEM Micrographs of the: A) Inner Epidermis of Rice Husk (X50), B) Outer Epidermis of the Rice Husk (X50)[12]

Burning rice husk as fuel to generate energy resulted in a waste product, namely rice husk ash. Rice husk ash is a by-product from the burning of rice husk. Disposal of this rice husk ash is an important issue in these countries which cultivate large quantities of rice[3]. The landfill of waste rice husk ash is a problem of environmental effects because these waste ashes are not used in any work. Therefore, a large number of researchers have been directed toward the utilization of waste materials. Nowadays, waste materials or pozzolans from industrial and agricultural by-products such as fly ash and rice husk ash are receiving more attention since their uses generally improve the properties of the blended cement concrete, the cost, and the reduction of negative environmental effects[13].

Rice husk ash is rich in silica (92-97%) and can be an economically viable raw material for production of silica gel and powders[14]. SiO_2 Nanowires were synthesized by thermal evaporation of rice husk ash and charcoal with the ratio of 1:2 by weight heated at a temperature of 1,350°C in atmosphere of nitrogen for 1 hour[15].

Rice husk is an attractive abundant source for active silica production[16-17]. Silica with 98.4 % purity was obtained by pretreatment with hydrochloric acid at 90±5°C and combustion at 600°C. This silica remained in amorphous form and possessed specific surface area of ~ 300 m^2/g. It is constituted by particles with indefinite geometry and expressed relief. The particle size ranged from 2 to 8 mm. An agglomerated silica powder with specific surface area of ~180m^2/g was obtained by mechanical activation wet milling for 3h. The agglomerates size ranged from 10-30 µm, and they were constituted by primary particles of ~20 nm.[18]

Rice husk is extremely prevalent in East and South-East Asia because of the rice production in this area. The rich land and tropical climate make for perfect conditions to cultivate rice and is taken advantage by these Asian countries. The husk of the rice is removed in the farming process before it is sold and consumed. It has been found beneficial to burn this rice husk in kilns to make various things[5].

Besides this rice husk are also used in the synthesis of furfural. Furfural (2-furaldehyde, fural, 2-furancarboxaldehyde, furfuraldehyde) with a molecular formula C_4H_3OCHO is a white liquid when freshly distilled and is best purified by distillation under reduced pressure (B.P. 54°-55°C/17mmHg)[19]. Furfural was first discovered by Dobreiner in 1832 and during the next 90 years, there was still no commercial production of furfural. It was not until 1922, the first drum of furfural was produced by the Quaker Oats Company for the production of phenolic resins[20].

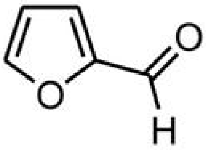

Figure 3: Furfural

Furfural has a high order of thermal stability in the absence of oxygen at temperatures above 230°C and a high selectivity property, these properties are attributed to the high solvent power in the treatment of oils and kerosene as well as lubricating oils and for those components of petroleum which are relatively unstable to oxygen and other undesirable materials including colored bodies[20]. It is also being used to increase the stability, remove sulfur, and produce high quality diesel fuel oils and burning oils. However, its application in the extraction of low boiling points gas oils and kerosene makes the recovery of furfural less simple due to the small difference and overlapping of boiling points. Its high density and low surface tension permits rapid phase separation and has sufficient volatility to permit ready recovery from lubricating oils. Furthermore, it does not react chemically with the oil components and under certain conditions of use it has a high degree of stability and industrially nontoxic[10]. The boiling point of furfural (161.5°C / 760 mmHg) is below the boiling point ranges of the lubricating oil and gas oil fractions (> 375°C/ 760 mmHg) and that makes the recovery of the furfural relatively simple.

Table 4: General Properties of Furfural[21]

Molecular Weight	96.1
Freezing Point (°C)	-36.5
Boiling Point (°C)	161.7
Density at 25°C	1.16
Viscosity at 25°C	1.5
Critical Pressure (psi)	798.2
Critical Temperature (°C)	397.4
Heat of Combustion at 25°C (kcal/gm.mole)	-560.3
Heat of Formation (liquid at 25°C) (kcal/gm.mole)	-49.2
Heat of Fusion (kcal/gm.mole)	3.43
Heat of Vaporization at 433.8°K (kcal/gm.mole)	9.22

About 74% of the world's furfural production capacity is located in China, as of January 1, 2008. Other important countries with furfural production include the Dominican Republic and South Africa. Together, these three countries account for about 90% of worldwide installed furfural production capacity[21] (see figure 4). However, recently there is an increasing awareness in the most of the countries towards producing furfural and other furanic compounds from biomass as a result of an increase in oil prices and the potential of these compounds to produce value added chemicals.

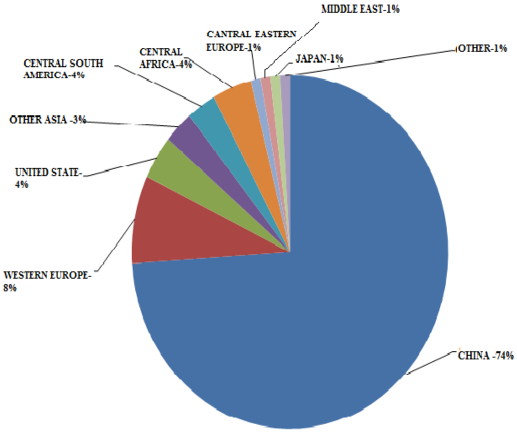

Figure 4: World Consumption of Furfural In 2007

Economic Considerations

Economic evaluation of a typical 1500 metric-ton/year furfural plant Furfural produced at 1500 MT/Yr with the market price of $ 1700/ton but selling at $900/ton yields $1350, 000.[22]

Industrially, furfural is produced in a single step operation by treating the raw material in dilute sulfuric acid and is recovered by steam distillation. Dahlgren[23] reported that lactose containing material is found to produce high yield of furfural. The yield of furfural may be due to the formation of a carboxyl group. This in turn splits off carbon dioxide to form furfural. A mild oxidizing agent can be used to improve the" furfural yield and this includes aqueous bromine, aqueous hydrogen peroxide, dilute nitric acid and per acids (peracitic acid and perbenzoic acid). Rice husk consist of lignin and cellulose as their main component hence we can separate furfural from rice husk economically and profitably.

There are two ways of producing furfural through biomass, that is, one-step method and two-step method, which depend on whether the reaction of furfural production is in the same container. In the one-step method, reaction of hydrolyze and dehydrate of pentose are completed in the same hydrolyze boiler. Be different from it, hydrolyze and dehydrate of pentose are separated in the two-step method at different temperature. Many researchers have investigated the technique of furfural synthesis[24-28]. Because of the conditions operations and side reaction, the practical output of furfural is usually a little far from theoretic[29-30].

An advanced technique of furfural production from rice husk was investigated in this work. The better output of furfural was reached by 8%, which was 30% of the theoretic.

METHODS

Five hundred grams of dried rice husks (dried in the oven temperature of 210°C for 48 hours) ground into minute particles of size 0.5 mm to1 mm, added into the different concentration of acid[12], and 500 g (6.84 mole) NaCl were introduced into a 5L three-neck round bottom flask. A 30 cm Friedrichs column and a condenser were attached and the reaction mixture was heated and stirred with a mechanical stirrer. The mixtures were heated with a thermostatically controlled oil bath at 150°C-170°C, reflux-cooled for 2h, then circumfluence distilled for 4h. The distillate was set to flow into an extraction flask containing 500 ml chloroform. Two layers were formed the aqueous layer at the top and the chloroform- furfural containing layer at the bottom of the flask. The top aqueous layer was charged into the reaction flask by a return tube connected to one of the neck. The bottom chloroform-furfural layer was replaced with fresh chloroform every 1 hour interval for a period of 5 hours[31]. The chloroform-furfural layer was subjected to the rotary evaporator (14 mmHg) to remove the chloroform, and a clear yellowish liquid furfural remained[26]. The hydrolysis of rice husks is performed with different concentrations of acid, with the method described above.

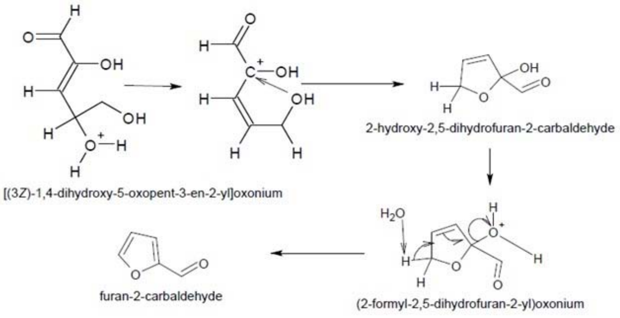

Figure 5: Proposed Mechanism for the Formation of Furfural Process[32]

Major Factors Affecting Furfural Yield

Yield-loss reactions occur while the furfural is in the liquid phase, by polymerization and by reaction with the precursor pentose, leading to low final furfural yield[26]. Condensation reactions between furfural and intermediates of the xylose-to-furfural conversion give rise to species such as furfural pentose and difurfural xylose[33]**.** Concomitantly, resinification, which is the combination of multiple furfural molecules to give intermediates, could also take place (see, Figure 6).

- The loss by condensation is much greater than the loss by resinification[34], and
- The loss of furfural via both these processes diminishes strongly with increasing temperature due to the so-called "entropy effect": increasing temperature creates an environment that propagates the disintegration of molecules, which in turn inhibits the buildup of larger molecules.

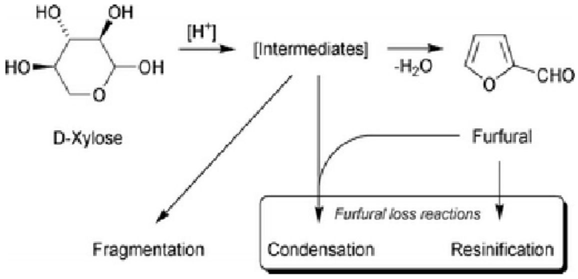

Figure 6: Scheme of the Possible Reactions in the Xylose-To-Furfural Process[35]

The hydrolysis of rice husks was carried out using Hydrochloric acid (HCl) and Sulfuric acid (H_2SO_4) of different concentrations using above method the result obtained is as given below

1) The hydrolysis of rice husks with aqueous HCl[36]

The hydrolysis of rice husks with aqueous HCl was also performed with different concentrations of acid, with the method described above. Table 5 is a tabulation of the experimental results.

Table 5: Hydrolysis of rice husks with Different Concentration HCl[36]

Different concentration of HCL used	Weight of furfural obtain	% Weight of furfural obtain
0.5 M	25.52	5.10%
1M	28.92	5.78%
1.5M	29.31	5.86%
2M	26.86	5.37%
2.5M	25.44	5.08%
3M	15.10	3.02%

2) The hydrolysis of rice husks with aqueous H_2SO_4[36]

The hydrolysis process was done with H_2SO_4 in the presence and absence of 20 percent (150 ml) hydrogen peroxide (H_2O_2) oxidizing agent. The procedure of the experiments is similar to the hydrolysis process with HCl. The results obtained are tabulated in Table 6.

Table 6: Hydrolysis of Rice Husks with Different Concentration of H_2SO_4 Used

Different concentration of H_2SO_4 used	Weight of furfural obtain	% Weight of furfural obtain
0.5 M	37.48	7.49%
1M	38.66	7.73%
1.5M	36.55	7.31%
2M	31.92	6.38%
2.5M	28.95	5.79%
3M	20.32	4.06%

The hydrolysis of rice husks was carried out using hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) of different concentrations. Results indicate that the, there was a slight increase in the furfural production when sulfuric acid of 1M concentration was used. The results indicate that with HCl, furfural was seen to produce even after 8 hours of hydrolysis while it took less than 5 hours when H_2SO_4 was used. Furthermore, the rate of furfural production was seen to increase when 1M H_2SO_4 was used as compared to 1M HCl. And it is found that furfural was still being produced after 5 hours of hydrolysis with 1M HCl. However, when 1M H_2SO_4 was used (table 7) the second hour shows a high yield of furfural and the production proceeds in less than 5 hours. Thus in the hydrolysis process, a shorter reaction time is achieved with H_2SO_4 as catalyst[36].

Table 7: Product Yield Furfural Conditions

Hydrolysis 1m H_2so_4	Product Yield Furfural Conditions	
	Grams	Percent Weight
With lactose	25.3gm	8.63%
With lactose and H_2O_2	16.63gm	5.43%
With H_2O_2	21.95gm	7.40%
With bromine water	20.60gm	6.86%
With lactose and bromine water	17.80gm	5.93%

The hydrolysis processes were also done with 1M H_2SO_4 in the presence of H_2O_2 and bromine water, a mild oxidizing agent and lactose. However, there was an increase in the yield of furfural when lactose was added to the reaction mixture.

CONCLUSION

This study revealed that Furfural is a utility chemical. The manufacture is simple, the raw material is agriculture waste Rice Husk, the capital is reasonable and within reach of many small communities. Acid hydrolysis of rice husk with 1 N H_2SO_4 gives the furfural in large quantity which will be used for many purposes. Rice husk is utilized where it is produced on small scales in brick kilns as a fuel. Despite having so many well established uses of rice husk. This will further increase the financial benefits and will help us to improve farm economy indirectly. This Competitive environment for the Rice Husk will helpful to fetch more prices of the rice husk for farmers.

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