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Synthesis of Furfural from Lignocellulosic Biomass as Agricultural Residues: A Review

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ABSTRACT

Husk is the waste product of deseeded sunflower head as agro wastes. The annual production of Sunflower Husk in India is 1.8 million metric ton and this amount is predicted to increase in the future. The high fiber content and low protein and energy content of sunflower hulls reduce their nutritional value. So it is not used as animal feed. In last decades, corncobs used as the raw material for synthesis of furfural using acid hydrolysis method. Autoclave or pressure digester is used as batch rector for synthesis of furfural from corncobs. The presence of mild oxidizing agents seems not to affect the yield of furfural but the presence of catalyst affect the yield of furfural. This study is performed by experimentally using a tubing-bomb reactor system by using olive stones as feed. The maximum furfural yield obtained is 50% to 65%. The supercritical carbon dioxide Extraction experiment showed that increasing temperature, pressure, CO_2 flow rate and sulfuric acid concentration and decreasing ratio of liquid to solid would improve furfural yield. This study suggested that the furfural production by acid hydrolysis of sorghum straw with phosphoric acid at 134^0C giving furfural yield 0.1336 g furfural/g initial dry matter. Sugar cane bagasse by steam explosion method in a stainless steel reactor produces xylose which is then converted into furfural. This experimental study has give idea about the yields of furfural which depend on pentoses content in pistachio green hulls (PGH). One of the approaches is the conversion of rice husk to furfural, as an intermediate product in synthesizing chemical products such as nylons, lubricants and solvents, adhesives, medicines, and plastics. This study revealed a good yield of the furfural from rice husk which have been confirmed by the various tests including infrared spectrophotometric scans.

Key words: Sunflower Husk, Furfural, acid hydrolysis, Biomass

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I. Introduction

Husk is the waste product of deseeded sunflower head as agro wastes which is generated as agriculture as well as edible oil refinery. The annual production of Sunflower Husk in India is 1.8 million metric ton and this amount is predicted to increase in the future. The northern part of the state of Karnataka, India is a semi arid tropical region, well known for the production of pulses and oil seeds (sunflower)[1].It has been reported that because of their high content of reducing sugars, it is possible to produce furfural and ethyl alcohol from sunflower hulls. As a lignocellulosic waste material ie sunflower hulls was hydrolyzed with acid to yield chemical ie furfural[2].The hull which is byproduct of oil extraction, contain 22–28% of the total weight of oilseed sunflower and may be removed before or immediately following oil extraction or may remain in the meal. Sunflower hulls contain: 4% crude protein; 5% lipid material, including wax, hydrocarbons, fatty acids, sterols, and triterpenic alcohols; 50% carbohydrates, principally cellulose and lignin; 26% reducing sugars, of which the majority is xylose; and 2% ash . The high fiber content and low protein and energy content of sunflower hulls reduce their nutritional value[3].The interest for producing chemicals from renewable resources has increased in the last decade which having direct impact on increasing prices of fossil fuels. Biomass residues available from agricultural and forest processing constitute a potential source for production of chemicals such as ethanol, reducing sugars and furfural by using enzyme or acid-catalyzed hydrolysis. Furfural is a basic chemical which can be utilized in a variety of industries such as chemical industry, refining oil industry, food industry and agricultural industry. It is usually produced from agricultural wastes containing pentosan as the main component, notably corn cob, rice straw, bagasse and rice hull[4].In the past ten years, on an average 0.52 tons/ha of pulses and 0.79

tons/ha of oil seeds are being produced every year, generating 3.1 tons/ha of husk of pulses and 14.3 tons/ha deseeded sunflower head as agro wastes annually. Husk of pulses is partly used as cattle feed and deseeded dried sunflower husk is burnt to produce ash which use as fertilizer. Ash is important challenges in waste management[1].Furfural (FF) is a solvent produced from plant pentosans (xylan, arabinan and polyuronids), the complex carbohydrates contained in the cellulose of plant tissues. The product has attracted some interest because it helps in the converting the relatively abundant supplies of lignocelluloses feedstocks into ethanol and higher-valued co-product chemicals[19]. The World market for furfural is currently 200,000 to 210,000 tpa, which includes 120,000 to 130,000 tpa for use to make furfuryl alcohol. Currently there are four important and potentially significant applications of product furfural in the industry such as agrochemicals, clean Fuels/Bio-fuels, timber treatment and PLA performance plastics[5].About 60 pounds of furfural was produced during the year 1920-21, using a small digester with dil sulfuric acid and the cobs themselves. Interest in the possibilities of furfural utilization has gain attention of several researchers for manufacturers as a cooperative research[6-8].In 1921, F.A. Forge[6] utilized corncobs as the raw material for synthesis of furfural using acid hydrolysis method. The corncobs were heated with dil hydrochloric acid at temperature of 180 -185 ^{0}C in an autoclave for 45 min. The yield of furfural was obtained approximate 7.75%.After that in 1924, researchers utilized corncobs and oat hull as the raw material for synthesis of furfural using acid hydrolysis method. The corncob was heated with dil hydrochloric acid at temperature of 180^{0}C in an pressure digester for 30 min. The yield of furfural obtained was 1-1.5 % and adhesive was 40-45%[7].This paper gave the idea about the production of furfural from corncobs. The unit consists of a pressure digester unit and a continuous column still. The cobs are digested with water and high-pressure steam, the vapors being condensed to form a dilute furfural solution. Optimum operating conditions are: Pressure, 130 to 135 pounds (180° C); ratio of water to cobs, 4:1; digestion period, 2 hours.

The furfural yield obtained is 6 % of the weight of cobs used. The chemicals formed during this process acetic acid, acetaldehyde, and methanol are by-products[8].After 1990 onwards, the various researcher described the process of hydrolysis of rice husks, wood and some edible plants species with different concentration of hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), and in the presence of lactose, some metallic oxides as catalyst and mild oxidizing agents. A gas chromatography (GC), HPLC and a UV visible spectrophotometer are used to confirm the presence of furfural. The presence of mild oxidizing agents seems not to affect the yield of furfural but the presence of catalyst affect the yield of furfural[9-12].

Daniel Montane & their co-worker [13]performed the experiment on olive stones, which in Spain are an abundant lignocellulosic residue derived from the production of olive oil . They focused on the acid hydrolysis of dilute sulfuric acid (0.05 to 0:250 mol l^{-1}), at high temperature (220–240^{O}C), and short reaction times. This experimental study was performed by using a tubing-bomb reactor system. They obtained maximum furfural yields ranging from 50% to 65% of the potential depending on acid concentration and temperature.H.K. Ong and M. Sashikala[14] reported method of Synthesis of furfural from pentosan by using rice husk as raw material. This process involved the conversion of the pentosan fraction in rice husk into pentose, which was then cyclodehydrated to furfural using dilute sulfuric acid. Yield of furfural obtained by this process was 15 g/kg of dry husk. The characterization of furfural is done by using infra-red analysis (IR), gas chromatography (GC) and gas chromatography with mass spectrophotometer (GC-MS). Wirungrong Sangarunlert and co-workers[15] developed a new method (supercritical carbon dioxide Extraction) to study the effect of furfural production from rice husk by acid hydrolysis accompanying supercritical CO_2 (SC-CO_2) extraction. The process variables were temperature range of 373-453 K, pressure 9.1-18.2MPa, CO_2 flow rate 8.3×10^{-5} to 1.7×10^{-4} kg/s (5-10 g/min), sulfuric acid concentration 1 to 7 (%wt) and ratio of liquid to solid (L/S) 5 : 1 to 15 : 1 (vol/wt). The experimental result showed that increasing temperature, pressure, CO_2 flow rate and sulfuric acid concentration but decreasing ratio of liquid to solid would improve furfural yield. Manuel Vazquez & their co-worker[16] performed the experiment on Sorghum straw is a waste raw material. The main application is its use as raw material for xylose production. This work gives the idea about the furfural production by acid hydrolysis of sorghum straw with phosphoric acid at 134^{0}C. Several concentrations of H_3PO_4 in the range 2–6% and reaction time (range 0–300 min) were evaluated. Optimal conditions for furfural production by acid hydrolysis were 6% H_3PO_4 at 134^{0}C for 300 min. The furfural yield of the process was 0.1336 g furfural/g initial dry matter was obtained.

Vittaya Punsuvon and co-workerss[17] synthesized furfural and α-cellulose pulp from Sugar cane bagasse by steam explosion method. The components of bagasse were fractionated after steam explosion. Bagasse undergoes several pretreatment at various temperatures condition. The water liquor was evaporated and further hydrolyzed and dehydrated with diluted H_2SO_4 in a stainless steel reactor to produce furfural. The result shows that the optimal pretreatment of steam explosion for 4 min at 218°C leads to the yield of α-cellulose pulp at 193-201 $g\cdot kg^{-1}$ of the original bagasse, and that furfural can be produced from xylose present in the liquor.Masoud Kazemi and their co-workers [18]used pistachio green hulls (PGH) as raw material which was obtained from Pistachio vera as agricultural residues for furfural production. In this method, the factors affecting on acid-hydrolysis of PGH are reaction temperature (from 425 to 545 K), sulfuric acid concentration (from 0.5 to 4.0 mol/l) and reaction times (from30 to 600 s) have been investigated. The reaction yields have been obtained on the basis of lignocellulose, pentoses and furfural.All the above cited references and researchers used the conventional techniques for synthesis of the furfural from various biomass. The research done by Khudzir Ismail and Abdul Rahim Atan gives an overview of production of furfural from rice husk by a novel and green approach to reduce the energy consumed and the waste generated in the production process, which can be an important contribution to the large scale production of furfural[9].Environmental and economic aspects of conversion of rice husk into furfural were also discussed.

Ii. Experimental

1. Materials

3 kg of rice husk collected from a rice-mill in central Saudi Arabia. It was dried in the oven temperature of 200°C for 48 hours. It was ground and sieved to a maximum size of 1mm and the sieved material was stored in the autodesiccator. The chemical composition was determined according to standard methods for analyzing wood and related materials are hemicellulose (19%) and cellulose (40%), silica (17%) and lignin (16%) . Rice husk contains about 120 g pentosan per kilogram of dry husk. The amount of pentosan was estimated from TAPPI T 223 cm-84[9-15].

2. Experimental Procedure

This study was carried out in a batch reactor system shown in Fig. 1. The apparatus was consisted of six main parts:3L capacity three-neck round bottom flask as batch reactor , 30 cm Vigreux column and a condenser, a mechanical stirrer , extraction flask and device to measure temperature. The chemicals such as 1M aqueous HCl (1. 50 liter) and 400 g (6.84 mole) NaCl were introduced into a 3L three-neck round bottom flask. A Vigreux column and a condenser were attached and the reaction mixture was heated and stirred with a mechanical stirrer. Steam distillation was observed after 15 minutes at the distilling temperature of 107°C. The distillate was set to flow into an extraction flask containing 250 ml chloroform. Two layers were formed with the aqueous layer at the top and the chloroform-furfural containing layer at the bottom of the flask. Formation of furfural is illustrated in the chemical mechanism shown in *Figure 1*. The stoichiometric equation for this reaction is as below[9].

$$C_5H_8O_4)n + nH_2O \rightarrow nC_5H_{10}O_5$$

Pentosans *Pentoses*

$$nC_5H_{10}O_5 \rightarrow nC_5H_4O_2 + 3\ nH_2O$$

Pentoses *Furfural*

3. Separation and identification of furfural

The chloroform-furfural layer was subjected to the rotary evaporator (14 mmHg) to remove the chloroform, and a clear yellowish liquid (F-l) remained. Product of F-l was analyzed by FTIR and GCMS and was determined as furfural. FTIR ie Fourier Transform Infrared Spectrometer (Perkin Elmer Co., USA).Transmission rate used was at 17,000–650 cm-1.

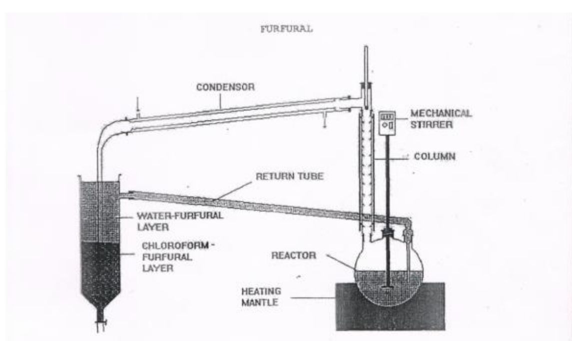


FIGURE 1: SETUP FOR THE PREPARATION OF FURFURAL

Iii. Results and Discussion

1. Effect of Type of Acid

The effect of type of acid on the yield of furfural was studied. The different types of acid used such as HCl and H_2SO_4 were used in this method. Sulfuric acid shows more yield of furfural than hydrochloric acid.

2. Effect of Concentration of acid

The effect of Concentration of acid on yield of furfural was studied. The different concentrations of acid were used such as (1 M, 2 M & 3 M). We see the effect on yield of furfural.

Table no.1 Hydrolysis of rice husks with hydrochloric acid.

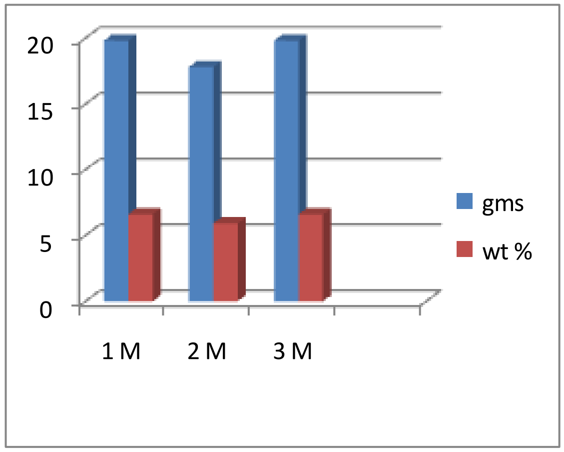
Furfural Yield	**Acid Concentration of HCl**		
F	**1 M**	**2M**	**3M**
gms	19.80	17.80	19.80
Wt %	6.60	5.90	6.60

Table no.2 - Hydrolysis of rice husks with sulfuric acid.

Furfural Yield	**Acid Concentration of H_2SO_4**		
F	**1 M**	**1M with H_2O_2**	**3M**
gms	22.40	22.20	15.80
Wt %	7.47	7.47	5.26

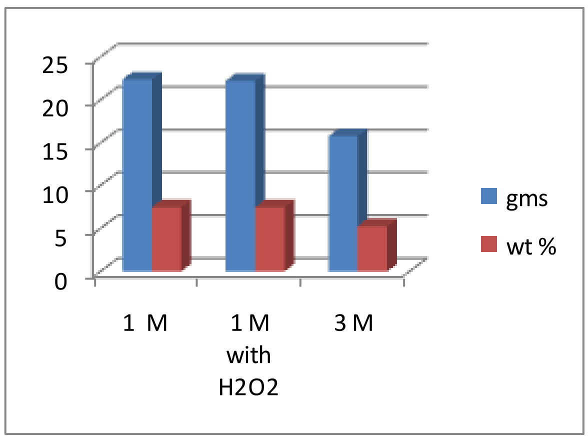
Table no.3 - Hydrolysis of rice husks with sulfuric acid in the presence of lactose and a mild oxidizing agent.

Hydrolysis 1 M H_2so_4	**Product Yield (F-L)Conditions Grams**	**Weight Percent**
With lactose	25.3	8.63
With lactose and H_2O_2	16.63	5.43
With H_2O_2	21.95	7.40
With bromine water	20.60	6.86
With lactose &bromine water	17.80	5.93



⟹ Acid Concentration

Fig 2- Effect of HCl Acid Concentration on Yield of Furfural

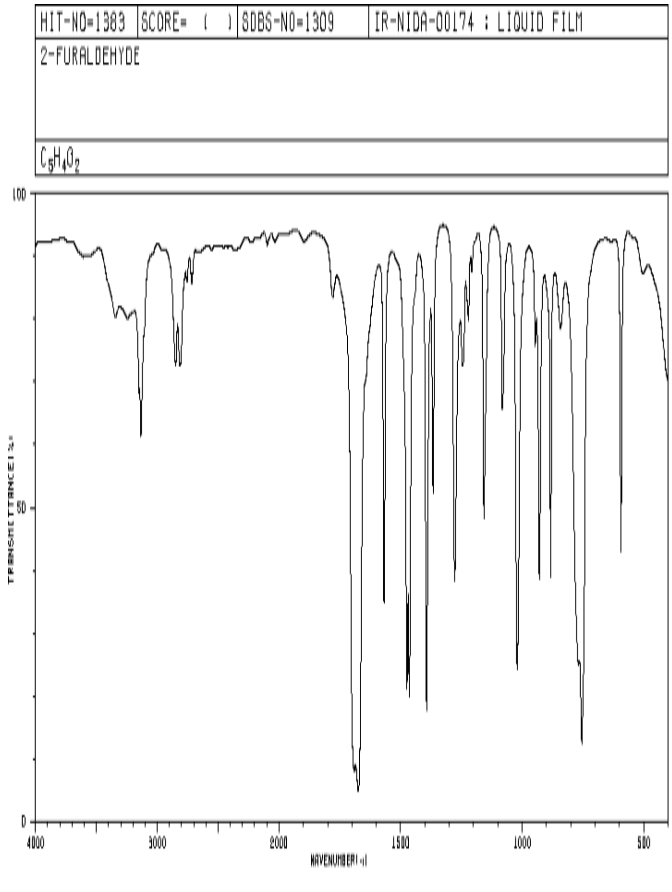


⟹ Acid Concentration

Fig 3- Effect of H_2SO_4 Acid Concentration on Yield of Furfural

The acid hydrolysis of rice husks was carried out using hydrochloric acid (HC1) and sulfuric acid (H_2SO_4) of different concentrations. Results from Figures 2 and 3 indicate that the weight percent of crude furfural is not much affected when the two types of acid were used. However, there was a slight increase in the furfural production when sulfuric acid of 1M concentration was used. The hydrolysis processes were also done with 1M H_2SO_4 in the presence of H_2O_2 and bromine water, a mild oxidising agent and lactose. The results show that H_2O_2 and bromine water did not affect the yield of furfural (Figure 4). However, there was an increase in the yield of furfural when lactose was added to the reaction mixture. This phenomenon is still under investigation[9].

The IR spectrum *(Figure 4)* 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 absence of peak at 1,725 cm-1 indicates strongly the presence of aldehyde and not the ketone group. 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. The spectrum showed a molecular ion peak at m/z 96.2 which correlates to a molecular formula of furfural ($C_5H_4O_2$)[14-20].



3342	77	1779	81	1367	60	1020	28	594	42
3149	66	1691	7	1278	37	947	72	503	84
3134	58	1674	4	1246	70	930	37		
2849	70	1569	34	1222	77	883	37		
2811	70	1474	20	1208	84	843	74		
2756	84	1464	19	1157	46	769	24		
2716	81	1394	17	1082	64	756	12		

Fig. 4- IR spectra of furfural from Spectral Database for Organic Compounds SDBS

IV. CONCLUSION

Many new developments will takes place in acid hydrolysis process and use of furfural for many applications such as for synthesizing a family of derived solvents like furfuryl alcohol and tetrahydrofuran and in the production of resins for molded 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 flavoring purpose too. Many of the researchers are worked on acid hydrolysis of rice hull, Lignocellulogic waste and Sorghum straw by using different metallic catalysts. This study revealed a good yield of the furfural from rice husk which have been confirmed by the various tests including infrared spectrophotometric scans. In a view of environmental and economic aspects, production of furfural from biomass may provide cost-effective alternative to commercial furfural in many applications.

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