A Review on “Production of Furfural from Biomass”

Mr. Ashish Baldania[1], Prof. (Dr.) Bhalchandra Vibhute[2], Prof. (Dr.) Sachin Parikh[3]

[1]Research Scholar, R.K. University, Rajkot (Gujarat-India)
[2] Phd.Guide, Assoicate Professor, R.K. University, Rajkot (Gujarat-India)
[3] Phd.Co- Guide, Professor, L.D. Engineering College, Ahmedabad (Gujarat-India)

Abstract - In the current search for renewable energy sources, residual biomass has been highlighted as a potential source of chemical compounds that are currently obtained from petroleum. Among the derivatives obtained from this furfural is considered key part in this process as they are key compounds in the fine chemical industry. This study aims use of the pinewood and corncorb for the synthesis of furfural. The physical pre-treatment of biomass can be carried out followed by acid hydrolysis. For the synthesis of the furanic compounds, different concentration of Dilute Acid can be used. The products obtained in each step can be analyzed by GC - MS. The best yield of product can be obtained in case of corbcorb for specific concentration of dilute acid. [1], [2], [24], [29]

Index Terms— Furfural, Pine Wood, Corb Corb, GC- MS, Batch Reactor, Salt, Dilute Acid, Concentration.

◆

1 INTRODUCTION

FURFURAL, identified as one of the top 30 platform chemicals derived from biomass, as an important fuel precursor and can be converted to hydrocarbon fuels and fuel intermediates. With current global production greater than 200,000 tonnes annually it is currently a high-value commercial commodity chemical, produced primarily from agricultural wastes such as oat hulls, corn cobs, and sugar cane bagasse and wood. Industrial processes for furfural production were developed as early as 1921 when the Quaker Oats batch process was developed to produce furfural from oat hulls. [2], [3], [4], [5]

Since then, many alternative batch and continuous processes have been developed with most of the batch operations primarily using sulfuric acid as a homogeneous acid catalyst and temperatures ranging between 160 and 200 °C.6 High operating costs and low energy efficiency coupled with low furfural yield, on the order of less than 50%, resulted in the closure of batch process based plants in 1990s. Another significant industrial continuous process for furfural production was developed by Quaker Oats, which operated for 40 years in Belle Glade, Florida, until 1997. [1], [31], [32]

The continuous process utilized a traditional horizontal screw-style reactor, similar to the 1-ton per day horizontal reactor system (Metso, Norcross, GA) used at National Renewable Energy Laboratory (NREL) for dilute acid pretreatment. A slightly improved furfural yield (55%) was obtained in the continuous process developed by Quaker Oats using a residence time of 1 h. While this process was technically successful, the plant ultimately shut down due to the high maintenance cost of the continuous reactor system. Improving furfural yield beyond 55% in industrial production has been the subject of much research over the last 100 years. [3], [4], [5], [6], [18]

This is a difficult task because furfural, once produced, rapidly degrades through resinification and condensation reactions. Furfural resinification is a reaction in which furfural reacts with itself, while condensation reactions occur when furfural reacts with xylose or one of the intermediates of xylose-to-furfural conversion to form furfural pentose or difurfural pentose. The loss of furfural by condensation is significantly greater than the loss by resinification. Much research has been conducted in recent decades to try to minimize degradation and improve furfural yield. [2], [30], [31]

As a lignocellulosic waste material ie Corb Corb and Wood was hydrolyzed with acid to yield chemical ie furfural. 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. [3], [4], [17]

It is usually produced from agricultural wastes containing pentosan as the main component, notably corn cob, rice straw, bagasse and rice hull4 .In the past ten years. 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. [6], [16] 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. 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. [7], [9], [10], [14]

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. [8], [9], [11], [15]

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. [3], [5], [7], [25]

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-products8 .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 (H2SO4), 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. [8], [9]

2. MATERIALS & EXPERIMENTAL METHODS

Materials

Specific amount of Corb corb or Pine wood collected from a Loacal Area. 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. [19], [20]

Experimental Methods

This study is carried out in a batch reactor system. The apparatus is consisted of six main parts:3L capacity three-neck round bottom flask as batch reactor , 30 cm 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 are introduced into a 3L three-neck round bottom flask. A column and a condenser are attached and the reaction mixture is heated and stirred with a mechanical stirrer. Steam distillation is observed after 15 minutes at the distilling temperature of 107°C. The distillate is set to flow into an extraction flask containing 250 ml chloroform. Two layers are formed with the aqueous layer at the top and the chloroformfurfural containing layer at the bottom of the flask. [12], [13], [20], [21], [30]

Separation and identification of furfural

The chloroform-furfural layer is subjected to extraction to remove the chloroform, and a clear yellowish liquid (F-l) remained. Product of F-l is analyzed by GCMS and is determined as furfural. [12], [20], [21]

1. Effect of Type of Acid

The effect of type of acid on the yield of furfural can be studied. The different types of acid used such as HCl and H2SO4 can be used in this method. Sulfuric acid shows more yield of furfural than hydrochloric acid as per literature survey. [22], [23], [26]

2. Effect of Concentration of acid

The effect of Concentration of acid on yield of furfural is studied. The different concentrations of acid can be used such as (0.5 M, 1 M & 1.5 M). We can see the effect on yield of furfural. [3], [20],

The acid hydrolysis of corb corb or pine wood can be carried out using hydrochloric acid (HC1) and sulfuric acid (H2SO4) of different concentrations. Literaturre shows a slight increase in the furfural production when sulfuric acid of 1M concentration is used as comparre to HCL. [21], [28]

3. 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 Corb Corb or Pine Wood which can be confirmed by the various tests. In a view of environmental and economic aspects, production of furfural from biomass may provide cost-effective alternative to commercial furfural in many applications. [27], [29], [30]

REFERENCES

1. Cai, C. M.; Zhang, T.; Kumar, R.; Wyman, C. E. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. J. Chem. Technol. Biotechnol. 2014, 89 (1), 2− 10
2. (3) Climent, M. J.; Corma, A.; Iborra, S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. Green Chem. 2014, 16 (2), 516−547.
3. Lange, J. P.; van der Heide, E.; van Buijtenen, J.; Price, R. Furfural□a promising platform for lignocellulosic biofuels. ChemSusChem 2012, 5 (1), 150−166.
4. Dutta, S.; De, S.; Saha, B.; Alam, M. I. Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels. Catal. Sci. Technol. 2012, 2 (10), 2025−2036.
5. Zeitsch, K. J. The Chemistry and Technology of Furfural and its Many By-Products. Elsevier Science: Amsterdam, The Netherlands, 2000.
6. Karinen, R.; Vilonen, K.; Niemela, M. Biorefining: heteroge- □ neously catalyzed reactions of carbohydrates for the production of furfural and hydroxymethylfurfural. ChemSusChem 2011, 4 (8), 1002− 1016.
7. Dashtban, M.; Gilbert, A.; Fatehi, P. Production of furfural: overview and challenges. J. Sci. Technol. Forest Prod. Process 2012, 2 (4), 44−53.
8. Humbird, D.; Davis, R.; Tao, L.; Kinchin, C.; Hsu, D.; Aden, A.; Schoen, P.; Lukas, J.; Olthof, B.; Worley, M. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover; No. NREL/TP-5100-47764; National Renewable Energy Laboratory (NREL): Golden, CO, 2011.
9. Hurd, C. D.; Isenhour, L. L. Pentose reactions. I. Furfural formation. J. Am. Chem. Soc. 1932, 54 (1), 317−330.
10. Dunlop, A. Furfural formation and behavior. Ind. Eng. Chem. 1948, 40 (2), 204−209
11. Fulmer, E. I.; Christensen, L.; Hixon, R.; Foster, R. The Production of Furfural from Xylose Solutions by Means of Hydrochloric Acid−Sodium Chloride Systems. J. Phys. Chem. 1936, 40 (1), 133−141.
12. Brownlee, H. J.; Miner, C. S. Industrial development of furfural. Ind. Eng. Chem. 1948, 40 (2), 201−204.
13. Gu¨ rbü z, E. I.; Gallo, J. M. R.; Alonso, D. M.; Wettstein, S. G.; Lim, W. Y.; Dumesic, J. A. Conversion of Hemicellulose into Furfural Using Solid Acid Catalysts in γ-Valerolactone. Angew. Chem., Int. Ed. 2013, 52 (4), 1270−1274
14. Choudhary, V.; Pinar, A. B.; Sandler, S. I.; Vlachos, D. G.; Lobo, R. F. Xylose isomerization to xylulose and its dehydration to furfural in aqueous media. ACS Catal. 2011, 1 (12), 1724−1728.
15. Amiri, H.; Karimi, K.; Roodpeyma, S. Production of furans from rice straw by single-phase and biphasic systems. Carbohydr. Res. 2010, 345 (15), 2133−2138
16. Bhaumik, P.; Deepa, A.; Kane, T.; Dhepe, P. L. Value addition to lignocellulosics and biomass-derived sugars: An insight into solid acid-based catalytic methods. J. Chem. Sci. 2014, 126 (2), 373−385
17. Luo, Y.; Hu, L.; Tong, D.; Hu, C. Selective dissociation and conversion of hemicellulose in Phyllostachys heterocycla cv. var. pubescens to value-added monomers via solvent-thermal methods promoted by AlCl3. RSC Adv. 2014, 4 (46), 24194−24206.
18. Yang, Y.; Hu, C. W.; Abu-Omar, M. M. Synthesis of furfural from xylose, xylan, and biomass using AlCl3 · 6H2O in biphasic media via xylose isomerization to xylulose. ChemSusChem 2012, 5 (2), 405− 410
19. Yang, W.; Li, P.; Bo, D.; Chang, H.; Wang, X.; Zhu, T. Optimization of furfural production from d-xylose with formic acid as catalyst in a reactive extraction system. Bioresour. Technol. 2013, 133, 361−369.
20. Yang, W.; Li, P.; Bo, D.; Chang, H. The optimization of formic acid hydrolysis of xylose in furfural production. Carbohydr. Res. 2012, 357, 53−61.
21. Chheda, J. N.; Roman-Leshkov, □ Y.; Dumesic, J. A. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomassderived mono-and poly-saccharides. Green Chem. 2007, 9 (4), 342− 350.
22. Zhang, T.; Kumar, R.; Wyman, C. E. Enhanced yields of furfural and other products by simultaneous solvent extraction during thermochemical treatment of cellulosic biomass. RSC Adv. 2013, 3 (25), 9809−9819.
23. Cai, C. M.; Zhang, T.; Kumar, R.; Wyman, C. E. THF cosolvent enhances hydrocarbon fuel precursor yields from lignocellulosic biomass. Green Chem. 2013, 15 (11), 3140−3145.
24. Zeitsch, K. J. Process for the Manufacture of Furfural. U.S. Patent 6,743,928, Jun 1, 2004.
25. Molina, M. C.; Mariscal, R.; Ojeda, M.; Granados, M. L. Cyclopentyl methyl ether: A green co-solvent for the selective dehydration of lignocellulosic pentoses to furfural. Bioresour. Technol. 2012, 126, 321−327.
26. Kim, E. S.; Liu, S.; Abu-Omar, M. M.; Mosier, N. S. Selective conversion of biomass hemicellulose to furfural using maleic acid with microwave heating. Energy Fuels 2012, 26 (2), 1298−1304.
27. Gu¨ rbü z, E. I.; Wettstein, S. G.; Dumesic, J. A. Conversion of hemicellulose to furfural and levulinic acid using biphasic reactors with alkylphenol solvents. ChemSusChem 2012, 5 (2), 383−387.
28. Xing, R.; Qi, W.; Huber, G. W. Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries. Energy Environ. Sci. 2011, 4 (6), 2193−2205.
29. Weingarten, R.; Cho, J.; Conner, W. C., Jr.; Huber, G. W. Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. Green Chem. 2010, 12 (8), 1423− 1429.
30. Lessard, J.; Morin, J.-F.; Wehrung, J.-F.; Magnin, D.; Chornet, E. High yield conversion of residual pentoses into furfural via zeolite catalysis and catalytic hydrogenation of furfural to 2-methylfuran. Top. Catal. 2010, 53 (15−18), 1231−1234.
31. Shekiro, J., III; Kuhn, E. M.; Nagle, N.; Tucker, M.; Elander, R.; Schell, D. Characterization of pilot-scale dilute acid pretreatment performance using deacetylated corn stover. Biotechnol. Biofuels 2014, 7, 23.
32. Root, D. F.; Saeman, J. F.; Harris, J. F.; Neill, W. K. Kinetics of the acid-catalyzed conversion of xylose to furfural. Forest Prod. J. 1959, 9, 158−165.