FURFURAL PRODUCTION FROM RICE STRAW USING OXALIC ACID HYDROLYSIS & SULPHURIC ACID DEHYDRATION PRETREATMENT

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Summary

Rice straw is one of the abundant agriculture residues in India. Rice straw consists of cellulose, hemicellulose and lignin. Oxalic acid helps to remove hemicellulose from rice straw and does not affect lignin and cellulose. So the rice straw can be pre-treated by oxalic acid for production of furfural before using it for pulping process. Oxalic acid is dicarboxylic acid with two pKa, produces less toxic compounds than other strong acid pre-treatments such as hydrochloric acid or sulphuric acid. Xylan undergoes hydrolysis to form xylose when treated with oxalic acid. Response Surface Methodology was applied to optimize oxalic acid treatment of rice straw using 2^3 full factorial methods. After hydrolysis, hydrolysate is treated with sulphuric acid and sodium chloride to produce furfural. Optimum conditions for pre-treatment are 12g/l oxalic acid, 80℃ temperature and 35 minutes of reaction time. UV spectrophotometer was used to determine the xylose content. FTIR was used for characterization of hydrolysate and furfural. 1.91007 mg/g of xylose was produced which was treated with 9% (v/v) sulphuric acid.

Introduction

Rice straw is the vegetative part of rice plant which is considered as waste after harvesting the rice grain. After wheat and corn, rice is believed to be the third most important grain crop in the world. Global rice production in 2016 was estimated to be 751.9 million tonnes by Food and Agriculture Organization (FAO) of United Nations. In 2016, the annual production of rice was 163 million metric tonnes in India and 206 million metric tonnes in China [FAO, 2017]. The quality of rice varies from one region to other, as the quality depends on rainfall, quality of soil and local climate. In recent years, the bio-refinery approach for the production of fuels and chemicals is gaining more attraction with major advantages of complete utilization of biomass with zero waste generation. Moreover the processes will be economically more viable when it target low volume high value products in addition to high volume low value products. The utilization of the rice straw residue for fuel and chemicals would be very economical [Abraham et al., 2016]. Rice straw is seen as potential source for producing furfural. Hemicellulose from rice straw mostly consists of xylose which on dehydration using sulphuric acid gives furfural [Lin et al., 2013]. At present, China is leading in furfural production followed by South Africa and Dominican Republic. Furfural is widely used as an important chemical raw material for pesticides, pharmaceuticals, food additives, and so on. It can also be used as a raw material for refined petroleum, oil, and solvents for various industrial applications [Yan et al., 2014].

Literature Review

Hydrolysis of biomass provides a cellulose-rich solid fraction which has potential for conversion into pulp or cellulosic ethanol, while the liquid fraction which is rich in hemicellulose sugars, can be converted into furfural. The availability of the cellulose fraction for further conversion into pulp or ethanol gives the hydrolysis process a major advantage over the conventional batch process used in industry [Mandalika and Runge, 2012]. Scale-up study of oxalic acid pre-treatment of agricultural lignocellulosic biomass for the production of bio-ethanol has been done by researchers [Lee et al., 2011]. Fractionation of hemicelluloses and lignin from rice straw by combining auto hydrolysis and optimized mild organosolv delignification has been studied [Rodriguez et al., 2008]. Oxalic acid modifies the cell wall structure and hydrolyzes hemicellulose to pentose and hexose sugars [Li et al., 2011]. Fractional separation and structural features of hemicellulose from sweet sorghum leaves and bioconversion of hemicelluloses have been done by researchers' earlier [Peng et al., 2012]. Review study of structural analysis for lignin characteristics in biomass straw has shown different aspects of its utilization in production of various composites and new products [Ghaffar et al., 2013].

Response surface method (RSM) is a suitable optimization technique which consists of a group of mathematical and statistical techniques to build empirical model. RSM has been employed to optimization of pre-treatment conditions. Response surface optimization of oxalic acid pre-treatment of yellow poplar based on full factorial design for production of glucose and xylose has been studied. Xylose and glucose are converted to ethanol by fermentation, however during pre-treatment inhibitors such as furfural and levulinic acids are formed at extreme condition. RSM helps to find the right conditions for pre-treatment [Moniz et al., 2015].

Furfural production using continuous feeding process has been discussed. This is named as Westpro modified Chinese Huaxia Furfural Technology. It uses fixed-bed reactors and continuous dynamic refining. A continuous dynamic azeotropic distillation is used. Current world production of furfural is about 250,000 t/a, at a stable price of $1,000/t. Most furfural plants are located close to available raw materials and dictated by the availability in harvesting season of agricultural products. So most plants operate for 7-8 month schedule only [Win, 2005].

In north India, large quantity of rice straw is available which is burnt due to not finding proper use. Rice straw is inferior to wheat straw for being used as a cellulosic raw material for paper and paper board making industries due to high silica content. So the pre-treatment process for production of furfural will boost the industrial utilization by improving profit. The treated rice straw has good potential for production of rice straw fibers using catalyzed acetic acid pulping which have been studied and the fibers are suitable for manufacturing of paper and fiber composites [Sinha, 2011; Sinha et al., 2011; Sinha et al., 2010].

Isolation and characterization of cellulose from sugarcane bagasse has been done. A study on polymer degradation and stability has been done [Sun et al., 2004]. Hydrolysis of lignocellulosic materials for ethanol production is famous topic of research for utilization of agro residues like rice straw [Sun et al., 2002].

Experiment

Oxalic acid is a dicarboxylic acid which has been used here for pre-treatment, as it is selective for hemicellulose and mild compared to sulphuric acid. Rice straw was cut in 2 inch then 15 g of it was put in digester. 75 ml Oxalic acid of different concentrations from 0.3% to 1.5% were added and they were mixed properly. After this heat is added and this cooking of rice straw is considered as the actual reaction time and heat supply is stopped. The cooked material was filter and filtrate was kept in a beaker. The solid residue was shifted in digester. Hot water about 150 ml is added to the digester to remove the sugar properly and heated at 110 ^{o}C for 10 min it is then filter and filtrate is added to the first filtrate . Then again hot water is added to solid residue so that residue sugar could be removed and it is heated at 70 ^{o}C for 20 min and filtered. The time of cooking the rice straw as well as temperature has been varied. Oxalic acid hydrolyzes xylan present in hemicellulose of rice straw into pentose and hexose.

Conversion of xylose into furfural using sulphuric acid and NaCl

Hydrolysate obtained from pre-treatment is mixed with different concentrations of sulphuric acid along with NaCl salt. Concentration varied from 6, 9, 12, 15 and18 %(v/v). The distillation still is heated; distillate is condensed and collected in a beaker. Operating conditions were 115 ^{o}C and atmospheric pressure. Sulphuric acid dehydrates pentoses present in hydrolysate and converts then to furfural. As furfural is miscible in water, distillate collected is mixture of water and furfural. To separate furfural and water, chloroform is used for extraction. Aqueous and organic phases containing furfural are separated using separation funnel. Chloroform is evaporated at temperature less than 40 ^{o}C leaving furfural. The yield of furfural is measured using following equation.

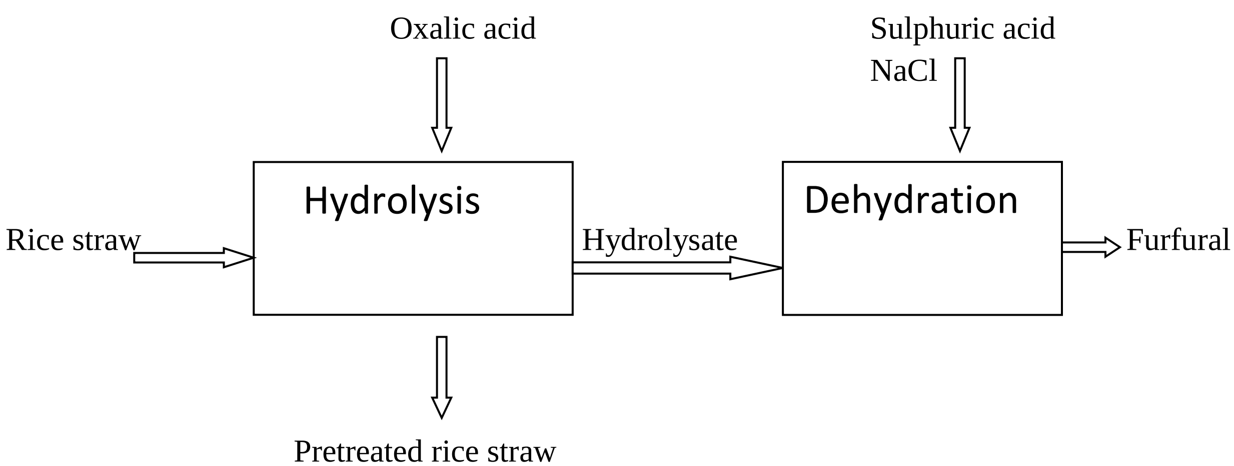

Fig. 1: Two-stage furfural production process

$$\text{yield of fufural} = \frac{\text{quantity of fufural produced}}{\text{quatity of rice straw}}$$

$$\text{yield of furfural} = \frac{\text{Moles of furfural produecd}}{\text{Moles of xylose in hydrolysate}}$$

Based on quantity of rice straw

$$\text{yield of fufural} = \frac{\text{quantity of fufural produced}}{\text{quatity of rice straw}}$$

Response surface methodology (RSM)

Stat Ease Inc. design expert version 10 has been used for optimization of xylose. Central Composite design was opted to investigate the factors affecting composition rice straw and hydrolysate after pre-treatment. The factors affecting statistical analysis are oxalic acid concentration, temperature and reaction time that were determined from fundamental experiments. Fundamental experiments were performed to determine the range of each of these factors to use in statistical model. There are six central points, six axial points and 2^3 factorial points thus the total number of runs is 20. The pre-treatment conditions range for concentration (A) is 6-12 % oxalic acid, temperature (B) is 80-100 ^oC and time (C) is 5-40 min.

Table 1: Design of experiment (full factorial) using response surface methodology

Std	Run	Factor 1 A: oxalic acid concentration (g/l)	Factor 2 B: temp (^0C)	Factor 3 C: time (min)	Response 1 xylose (mg/g)
1	12	6	80	10	1.1455
2	4	12	80	10	1.51828
3	1	6	100	10	1.78424
4	16	12	100	10	1.18868
5	9	6	80	35	1.25578
6	2	12	80	35	1.79223
7	3	6	100	35	1.80402
8	10	12	100	35	1.12842
9	20	3.95	90	22.5	1.20779
10	8	14.05	90	22.5	1.23923
11	15	9	73.18	22.5	1.49939
12	7	9	106.82	22.5	1.15283
13	18	9	90	1.48	0.88965
14	14	9	90	43.52	2.09994
15	6	9	90	22.5	2.04368
16	17	9	90	22.5	2.04809
17	11	9	90	22.5	2.05637
18	19	9	90	22.5	2.03615
19	5	9	90	22.5	2.04958
20	13	9	90	22.5	1.99909

Results and Discussion

Analysis of rice straw is given is the table 2.

Table 2: Analysis of rice straw in %

Ash	17.67
Moisture	8.58
Hot water solubility	22.22
Solvent Extractives	18.97
α -Cellulose	30.02
Holocellulose	54.92
Pentosans	18.72
Klason lignin	9.7

Pentosan in rice straw is 18.72% which is hydrolyzed to xylose. In the work done by Sashikala et al. (2009), sulphuric acid was used for hydrolysis of rice straw as well as dehydration of xylose. They used a single stage process and distillate containing water furfural mixture was separated using chloroform.

Reaction for hydrolysis of xylan

Inside the digester, oxalic acid attacks hemicellulose at intermediate positions along its long backbone which releases oligomers made up of many sugar molecules that can be successively broken down to shorter chained oligomers before single sugar molecules are formed ***(Wyman et al., 2005).***

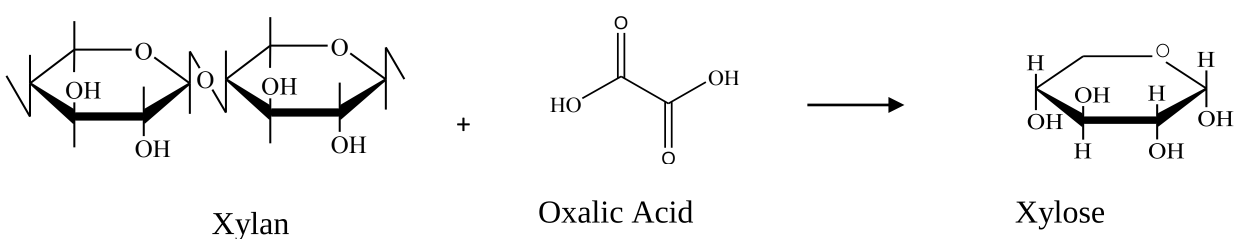

Fig. 2: Hydrolysis of xylan

Xylose dehydration

Xylose in presence of sulphuric acid and sodium chloride undergoes dehydration to form furfural. NaCl is used as catalyst to enhance the reaction. Excess NaCl is used to prevent solubilization of furfural.

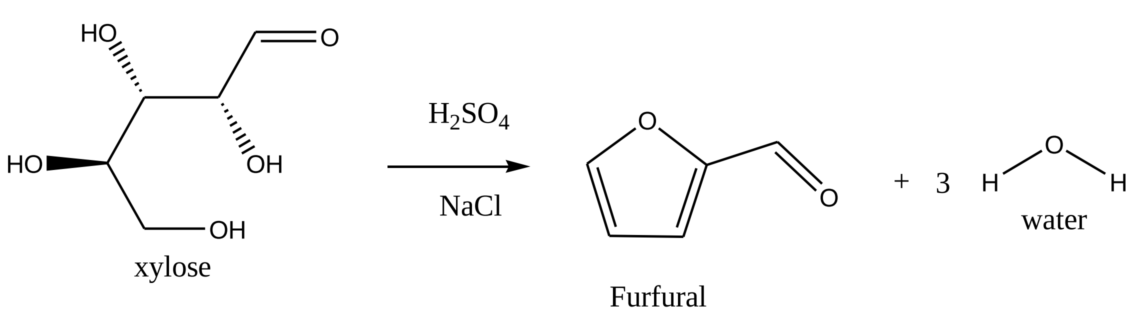

Fig. 3: Dehydration of xylose

The hydrolysis of xylan was optimized using Response Surface Methodology.

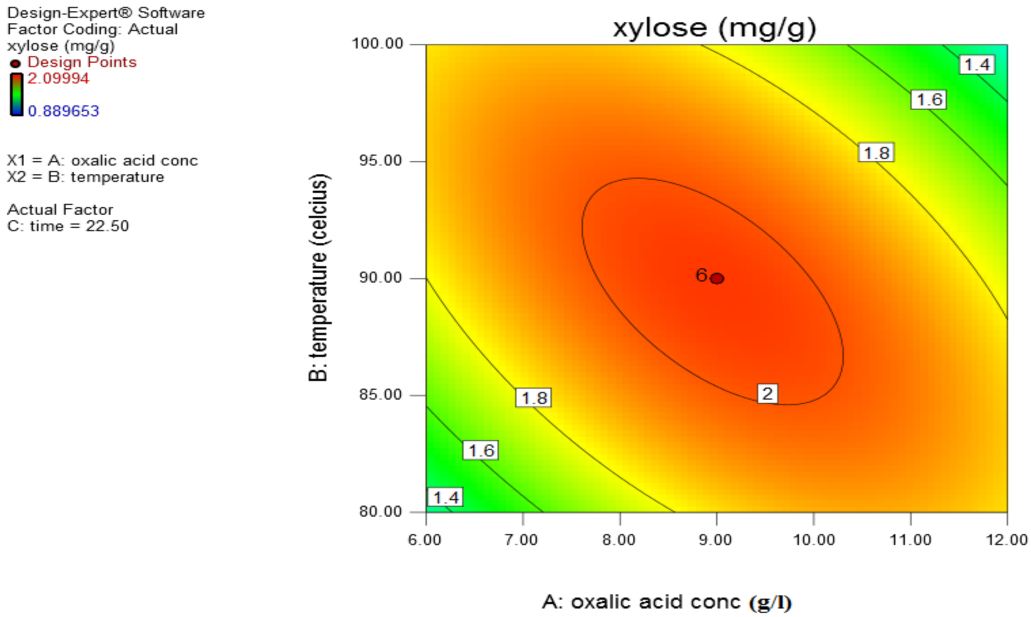

Fig. 4: Effects of oxalic acid concentration and temperature on xylose concentration (in hydrolysate)

Three dimensional plots showed the predicted peak of xylose concentration in hydrolysate at the optimum conditions. The behavior of the system was explained by the following second-degree polynomial equation:

$$R= 2.03-0.023A-0.029B+0.17C-0.27AB+ 0.010AC-0.053BC-0.26A^2-0.22B^2 -0.16C^3$$

The coefficient of variation (CV) is the degree of precision with which experiments are similar. In the current study, a CV of 13.63% was obtained. The CV is a function of the standard deviation 0.22 and standardizes the scale of data. A low value of CV is indication of high reliability and reproducibility of the design. Value of R^2 is 0.8539; value of Adjusted R^2 is 0.7224 and Predicted R^2 -0.1087. The high value of R^2 indicates higher reliability regarding the relationship between the observed experimental data and designed predictions.

Xylose is produced on hydrolysis of xylan present in hemicellulose by oxalic acid. The above graph shows the relation of xylose with temperature and acid concentration. It can be seen that the optimum value is off centered. Keeping in mind the relative weight of responses, optimum value of each response has been obtained. The centered value of xylose 2.04368 mg/g is obtained at 9% oxalic acid concentration, 22.50 minutes reaction time and 90°C temperature. This value is obtained at Std# 15 and run # 6. Run# 14, treatment at 90 °C with 9% oxalic acid for 43.52 min, gave maximum xylose 2.09994, and the least xylose was gives by run#18 0.88965.

Determination of furfural

After hydrolysis of rice straw with oxalic acid, hydrolysate was mixed with sulphuric acid and NaCl to form furfural dehydrating xylose

Using aniline acetate test, presence of furfural was confirmed as it gives pink colour after reaction. Quantification was done using UV spectrophotometer by taking filtrate in cuvette and observing absorbance at 267nm wavelength.

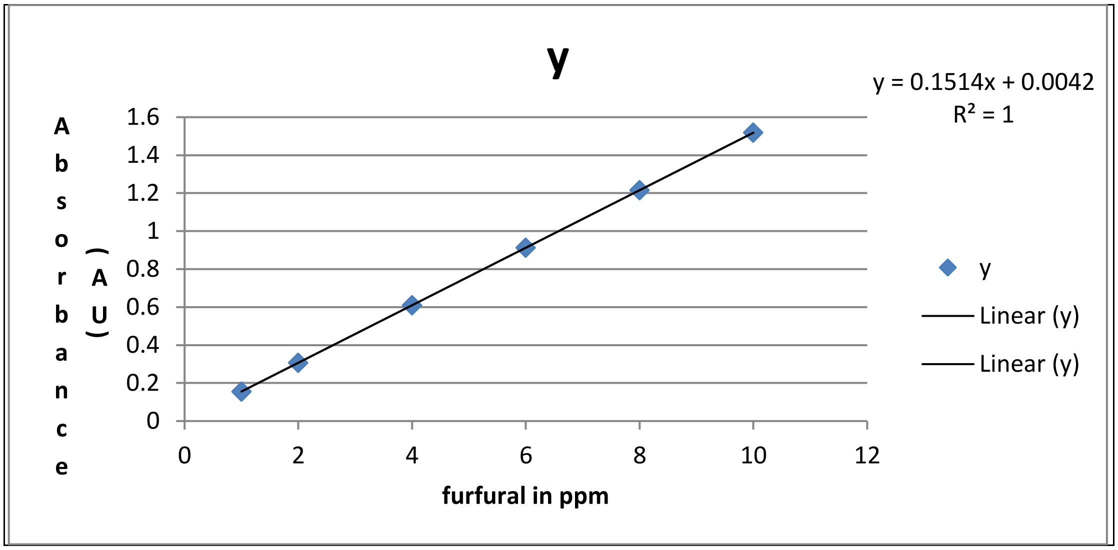

Fig. 5: Calibration graph for furfural

The slope of calibration curve is 0.151 and constant is 0.004 this graph is used to find value of furfural. The absorbance was 1.682 from graph it is found at 11.081 ppm. After calculation, it was found that total furfural obtained per mole of xylose was 0.16584 and the 0.14175 mg/ g of rice straw.

Table 3: Yield of furfural at different concentrations of sulphuric acid

%Volume of sulphuric acid added to total volume of mixture	Yield of furfural based on moles of xylose in hydrolysate
6	0.1536
9	0.16976
12	0.16584
15	0.1582
18	0.1432

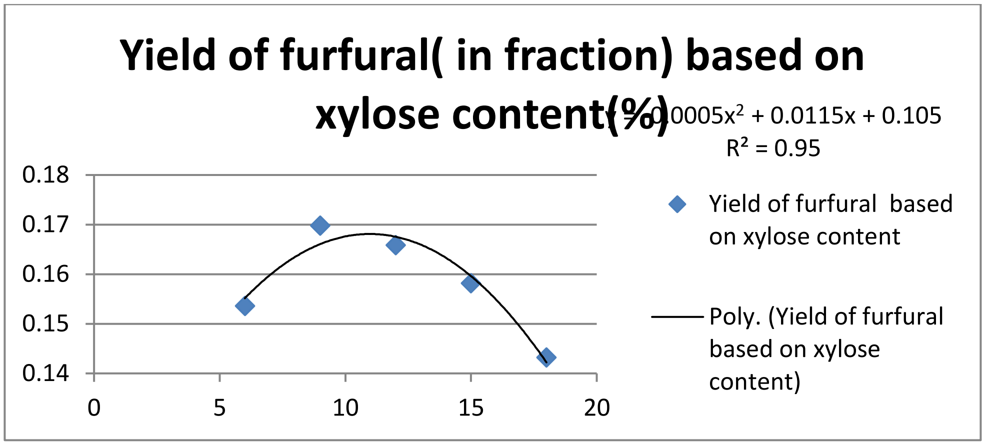

Fig. 6: Yield of furfural based on xylose

From the graph, it is clear that optimum xylose is obtained when sulphuric acid added is 9% of the total volume of hydrolysate. When less sulphuric acid is added, dehydration reaction is low. When more sulphuric acid is added, furfural undergoes further degradation forming humus. This value is high compared to single stage sulphuric acid treatment of rice straw to form furfural.

Analysis of hydrolysate and furfural

Presence of furfural in distillate can be confirmed by aniline acetate test. Aniline acetate gives pink colour when mixed with furfural solution. Aniline acetate was prepared by mixing water, aniline and acetic acid in 1:1:1 ratio. Then 5ml of distillate was mixed with 5 ml of prepared acetic acetate. FTIR(Bruker Tensor) was used with Spectral Range 4000 to 400 cm^{-1}, with standard KBr beam splitter and resolution of 1 cm^{-1}. Interferometer used is RockSolid™ type having permanent aligned system with high stability and has scanning speed in the range of 2.2 to 20 kHz. It has DigiTect™ detector system and size of spectrometer is 66.5cm*43.4cm*28.1cm. The standard sample cell in the FTIR is of attenuated total reflectance (ATR) type equipped with a ZnSe single crystal. Furfural dissolved in carbon tetrachloride was studied here using ethanol as cleaning agent.

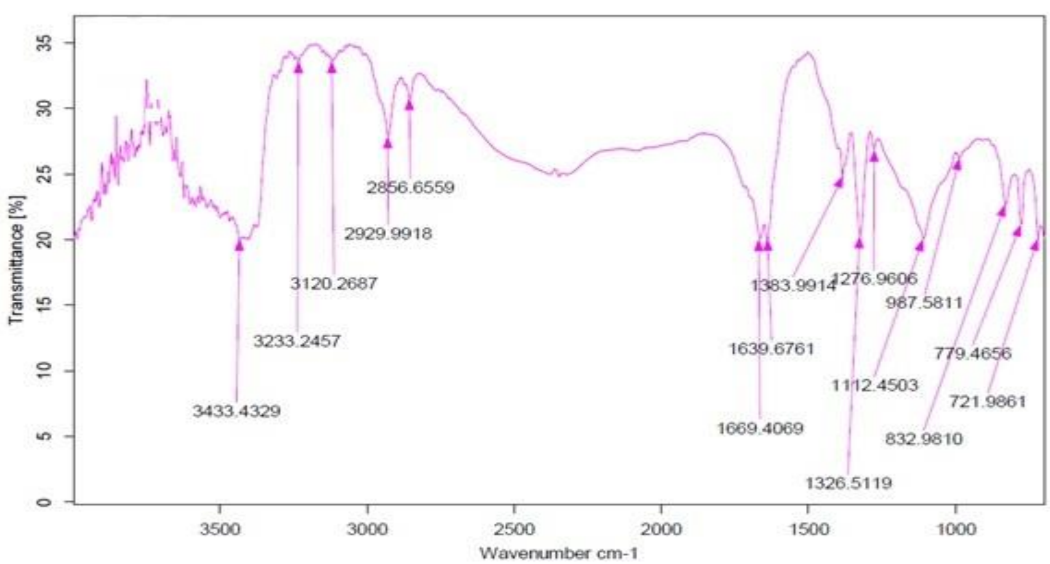

Fig. 7: Infrared spectrum of hydrolysate

Absorption bands at 3433.4329 $cm^{-1}$and 3233.2457 cm^{-1} are assigned to O-H stretching vibration which was attributed by the presence of lignin. Absorption band at 3120.2687 cm^{-1} is due to unsaturated C=C-H present in hemicellulose. Bands at 2929.9918 cm-1 and 2856.6559 cm-1 are assigned to methyl stretches, which are due to syringyl lignin. Absorption band at 1639.6761cm^{-1} is assigned to conjugated ketone which confirms presence of lignin. While absorption bands at 721.9861 cm^{-1}, 779.4656 cm^{-1}, 832.9810 cm^{-1}, 987.5811 cm^{-1} and 1112.4503 cm^{-1} indicated the presence of hemicellulose fraction. Absorption band at 1383.9914 cm^{-1} and 1326.5114 cm^{-1} are assigned to C-H vibration carbohydrates in hemicellulose fraction.

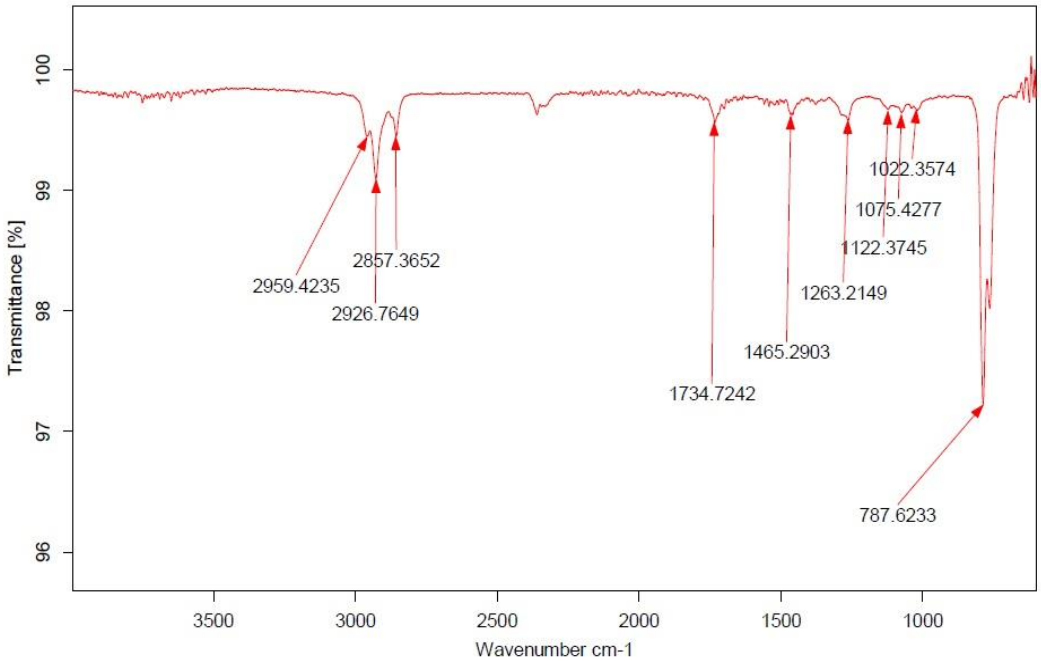

Fig. 8: Infrared spectrum of furfural

Presence of band at 1734.7242 cm^{-1} suggested that aldehydic group was present, absorption band at 1263.21149 cm^{-1} indicated aryl-O stretch. Absorption band at 1465.2903 cm^{-1} confirmed aromatic ring stucture while 1122.3745 cm^{-1}, 1075.4277 cm^{-1} and 1022.3574 cm^{-1} showed aromatic C-H plane bend. The data was compared to Spectral Database for organic compound SDBS and confirmed prsence of furfural. (National Institute of Advanced Industrial Science and Technology; SDBSWeb : http://sdbs.db.aist.go.jp).

CONCLUSIONS

1) After obtaining optimized parameters, experiments were performed to compare the results. The experimental value of xylose was 1.8002 mg/g which was less than predicted by software.
2) Using RSM Stat Ease Inc design expert version 10, optimum conditions were found to be 1.2% oxalic acid concentration, 80^{o}C temperature and 35 minutes of reaction time.
3) Conversion of xylose to furfural using sulphuric acid was done at 9% (v/v) sulphuric acid concentration. In 2 stage process, amount of sulphuric acid used was less compared to single stage process. But 20% (v/v) of sulphuric acid was used for hydrolysis and dehydration both.

4) Pre-treatment helped to extract pentosans present in rice straw which otherwise was dissolved in residual liquor during pulping. Predicted value of xylose at optimum condition was 1.91007 mg/l and actual value was 1.8 mg/l
5) The yield of furfural was 16.97% on molar basis (moles of furfural formed from moles of xylose present in hydrolysate).

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